INTEGRATED PRESSURE-DEPENDENCE IN AUTOMATED MECHANISM GENERATION: A NEW TOOL FOR BUILDING GAS-PHASE KINETIC MODELS

by

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ABSTRACT

A host of vital, current, and developing technologies, such as pyrolysis, thermal cracking, partial oxidation, and high-efficiency combustion engines, involve complex, gas-phase chemical mechanisms with hundreds of species and thousands of reactions. Building complete, explicit chemical models by-hand for these systems is exceedingly difficult. The bias and intuition of the developers figure strongly in the resultant mechanism, causing important but unanticipated pathways to be ignored, and useless pathways to be included. Thus many chemists and engineers have tried artificial intelligence software tools, or "automated mechanism generators", to build large chemical mechanisms systematically. These tools employ graph-theory algebra, and "rate rules" – estimates of rate constants for classes of reactions – to construct automatically all the possibly important reactions and species for a given set of conditions.

All of these tools have been severely hampered by their inability to capture the effects of pressure-dependence and falloff – even though these effects are important in almost every gas-phase system of interest to engineers and designers. Pressure-dependent reactions cannot be included using simple rate rules. Until now they presented an unresolved quandary for automated mechanism generators.

This work presents the first automated method for including pressure-dependent reactions generally and systematically, on-the-fly, in computerized mechanism generation. The approach includes in the mechanism only those pressure-dependent pathways important for the conditions of interest, but can find any potentially important pressure-dependent reaction. It works by building partial pressure-dependent reaction networks, step-by-step, in harmony with a rate-based termination criteria which rationally controls overall mechanism size. It uses a fast, approximate method, the Quantum-Rice-Ramsperger-Kassel/Modified-Strong-Collision (QRRK/MSC), to predict rate constants $k(T,P)$ employing only high-pressure-limit rate rules, pressure-dependent network structure, and heat capacity estimates. The error incurred by screening the pressure-dependent networks to include only important sections is small and bounded.

Successful applications to various systems, including reactions through cycloalkyl intermediates, are presented. Application of this tool to methane pyrolysis revealed a new, unexpected mechanism. It explained the decades-old mystery of methane autocatalysis at low conversion, a phenomenon which had defied all "by-hand" attempts at mechanism development. Such work hints at the predictive power inherent in the next generation of automated mechanism builders.
DEDICATION

This work is dedicated to my parents, Frank and Frances Matheu, and the family they built for Peter, Emily, Amanda, and me. Upon their deep-rooted and careful foundation this small stone rests. It is also dedicated to the memory of my grandparents, Michael and Ann Matheu.

QUID EST VERITAS?
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CHAPTER 1: INTRODUCTION
1 Motivation

1.1 The Challenge of Large Gas-Phase Kinetic Models

Many important gas-phase or heterogeneous industrial processes (combustion, partial oxidation, cracking, pyrolysis, auto-ignition) and natural processes (e.g. volatile organics oxidation) evolve through complex, nonlinear chemistry. In these systems, hundreds of species may participate in thousands of reactions, and the relative importance of many species and reactions will change dramatically with temperature and pressure. Detailed chemical kinetic mechanisms, which approach the size and complexity of the real systems' chemistry, are increasingly required in order to understand and design such processes.

But constructing such large kinetic models, even when restricted to the gas phase, is very difficult. When researchers are building a mechanism with thousands of reactions and hundreds of species, it becomes easy for them to miss critical pathways, as has happened with the methane pyrolysis studies in the late 1980s [1;2]. Furthermore, even when a large kinetic model is accurate for one regime of parameter space, changes in conditions can mean the modelers must update – or add – reactions and species. It is not always clear what should be added. Surprisingly, very few large kinetic models are truly constructed systematically. Most of those in popular use have been developed entirely by hand, from sets of smaller mechanisms (e.g. the Lawrence Livermore n-heptane mechanism [3]), and have been tested against a limited set of experimental data. The final shape of the typical kinetic model thus, unavoidably, reflects the intuition and bias of the developers.

1.2 Automated Mechanism Generation

These challenges to building gas-phase kinetic models have prompted the development of an astonishing array of computer algorithms for automatically constructing large chemical kinetic mechanisms\(^1\) [4-46] (a review and a more complete

\(^1\) Most of these tools are no longer active; a few are proprietary. It is likely that all of them have failed to overcome some of the fundamental limitations discussed in this work, when they are applied to gas-phase mechanisms.
list of references on automated mechanism generation may be found in Tomlin [47]). Ideally, an “automated mechanism generator” will systematically build the correct mechanism for the specified conditions, without bias, and with the ability to discover previously unknown reaction routes.

Most mechanism generation tools work by iteratively applying a set of reaction “families” to a set of initial chemical species. The reaction families are broadly defined classes of reactions (for example, H abstractions, radical recombinations, and so forth) that are translated into computer code, so that the computer will explore every possible instance of each family among a given set of species. The families thus define the set of possible reaction types. Each application of the reaction families generates a set of reactions and a set of new species, to which the reaction families are applied again. Rate constants must be assigned to each reaction discovered; these usually come from a combination of rate rules (estimates of Arrhenius parameters for a particular class of reactions) and thermochemical estimates, or from literature values where they are available. In this way a mechanism generator can build a model “from scratch”, which, theoretically, explores all the possibilities for reaction pathways, given a set of starting species and a set of possible reaction types.

All of these tools are plagued by combinatorial mechanism growth, as depicted in Figure 1-1. The figure illustrates the first stages of generation for a tool building an ethane pyrolysis mechanism. Instructed to start with ethane, the computer will examine the molecule (typically represented by a graph-theoretical construction) for all possible reactions the ethane molecule can undergo. It finds that the carbon-carbon and carbon-hydrogen bonds can dissociate, and it generates the products: methyl radical, ethyl radical, and H atom. At this stage, the “pool” of reactants now has four elements.
Figure 1-1. The combinatorial growth of a reaction mechanism. When the computer blindly applies even a very limited set of reaction families to a single starting species (ethane in this case), the number of reactions and species grows very rapidly to infinity. Most of these reactions will not be needed for a practical mechanism.

Next, the computer tool iterates “all possible reactions” among these four species. If we have employed only the reaction families for H abstraction, dissociation, recombination, radical addition to a double bond, disproportionation, and beta-scission, it will construct the following reactions:

\[
\begin{align*}
H + C_2H_6 &\rightarrow H_2 + C_2H_5 \\
H + C_2H_5 &\rightarrow C_3H_6 \\
H + C_2H_4 &\rightarrow H_2 + C_2H_4 \\
H + CH_3 &\rightarrow CH_4 \\
H + H &\rightarrow H_2 \\
CH_3 + C_2H_6 &\rightarrow CH_4 + C_2H_5 \\
CH_3 + C_2H_5 &\rightarrow CH_4 + C_2H_4 \\
CH_3 + C_2H_3 &\rightarrow C_3H_4 \\
CH_3 + CH_3 &\rightarrow C_3H_6 \\
C_2H_5 + C_2H_6 &\rightarrow C_4H_{10} \\
C_2H_5 + C_2H_5 &\rightarrow C_2H_4 + C_2H_6
\end{align*}
\]

After this step, it now has a pool of 8 reactants and a mechanism which includes 13 reactions (those above plus the dissociations of ethane). Most of the tools cited above will continue in this way, building a rapidly-expanding list of reactions and species until computer memory is filled, or the user intervenes. Automated growth of the mechanism is combinatorial and unmanageable, and somewhat arbitrary decisions must be made to truncate mechanism expansion; e.g., rank-based termination [9] or careful family selection with limited iteration steps and complicated user intervention (possibly [21] and works cited therein).

Even with arbitrary truncation, the great majority of reactions found in this way will not be important under the conditions of interest. In light of this problem, the elementary-step approach above is sometimes abandoned for an automated, lumped generation procedure, which has proved quite successful for some industrial processes.
(see [48], or especially, Quann and Jaffe [49]). But the lumped approach cannot build a model composed only of elementary steps, and thus lacks the explanatory power and flexibility such models have.

1.3 Rate-Based Control of Mechanism Growth

To address the problem of catastrophic mechanism expansion, Susnow et al. developed a natural, flux-based rule to limit mechanism growth and produce a useful chemical model [11]. In their approach the kinetic significance of each candidate species is determined via integration of the ordinary differential equations (ODE’s) representing the system at a given set of conditions. Only those species whose production rate exceeds a threshold criteria:

$$\frac{d[X](t)}{dt} > f_{\text{min}} R_{\text{char}}(t)$$

(1-1)

are included. In (1-1), $f_{\text{min}}$ represents a user-defined relative tolerance (typically 0.1-1.0%) and $R_{\text{char}}$ is a characteristic rate for the system (e.g. the sum of production fluxes for all species included in the system, or the flux of a set of primary reactants). This technique provides a physically-based and bounded method for truncating the growth of computer generated mechanisms.

Dr. Jeffrey Grenda of ExxonMobil added to and refined the work of Susnow and coworkers, developing the ExxonMobil Mechanism Generator, or XMG [50;51]. XMG uses rate rules, a library of high-pressure limit rate constants, a thermodynamic data library, and a group additivity approach for the estimation of thermodynamically reversible rate constants; this allows integration of the ODE’s at the specified conditions. Sensitivity or uncertainty analyses may then identify a set of critical rate constants which need more careful treatment. XMG represented the state-of-the-art in automated mechanism generation at the start of this work.

1.4 The Challenge of Pressure-Dependence

The XMG approach works well in the high-pressure limit, where all of the important rate coefficients are not strongly dependent on the pressure. Neither XMG nor any other mechanism generation tool, however, can include pressure-dependent pathways.
in a general and flexible fashion. At best, pressure-dependence can only be included for a small set of well-known, small-molecule reactions.

This is a severe limitation of mechanism generators, since pressure-dependent pathways may account for as many as half the reactions in some pyrolysis and combustion systems [52], and contrary to popular belief, pressure-dependent behavior is not confined to small species (see, for example, Wong [53], or Richter [54]). Pressure-dependent pathways cannot be ignored if one wants to generate useful chemical kinetic models for a great many gas-phase processes. Figure 1-2 highlights this fact for the case of methane pyrolysis.

![CH₄ Pyrolysis: 1038 K, 0.58 atm](Image)

**Figure 1-2.** Automatically-generated mechanisms for methane pyrolysis with and without proper treatment of pressure-dependence. The dashed-line prediction for ethane concentration represents a mechanism in which all reactions are treated as being in the high-pressure-limit. The solid line is a result from Chapter 7, in which pressure-dependent reactions are treated generally for the same conditions. The solid line is much closer to the data, as Chapter 7 shows – proper treatment of pressure-dependence is essential for many gas-phase mechanisms.

Pressure-dependent reactions are broadly neglected for a number of reasons. First, recall that rate rules are a necessity for any automated approach, as illustrated in Figure 1-3. In most cases, when a new reaction is discovered, a rate constant will not be available from the literature. The computer will resort to a rate rule, which is typically a
set of high-pressure-limit, modified Arrhenius parameters for a given reaction sub-family. All elementary steps which fit the rule will be assigned those rate parameters; as Figure 1-3 shows, while the reaction families are broad, the rate rules can be highly differentiated. In general, one tries to develop a set of high-pressure rate rules which are at least accurate to within a factor of 10 [55].

For each reaction discovered:

Is k in library? yes

no

Use Rate Rule for this family:

\[ A, n, E_a : k = A T^n e^{-E_a/RT} \]

**Example**

For reaction:

Use rate rule "1-4 H-Shift Primary → Tertiary" (R. Sumathi, MIT):

\[ A^* = 7.8 \times 10^{13} \text{ cm}^3/\text{mol}\cdot\text{s}; n = -0.12, E_{a^*} = 18.3 \text{kcal/mol} \]

**Figure 1-3.** Rate rules in mechanism generation. Usually the generator will need to use a “rate rule” for the rate constant when it finds a new reaction. These rate rules are often highly differentiated, as shown for the H-shift example. The particular reaction is 4-methyl-1-pentyl radical isomerizing via intra-radical H-abstraction to 2-methyl-2-pentyl. An automated builder will assign it the rule used for all 1,4 H-shifts that start with a primary alkyl radical, and end with a tertiary alkyl radical.

It is impossible to write down a rate rule for a pressure-dependent reaction. This is because pressure-dependent reactions exist as part of an isomer and channel network, and some knowledge of this network is required to predict rate constants such as \( k(T, P)_{A+B\rightarrow C} \). For example, an activated species such as \( C^* \) (the "*" indicates non-Boltzmann or chemical activation) forming from the collision of \( A + B \) may be quenched via collisions with the bath gas to thermalized \( C \). But \( C^* \) may also isomerize to other species, dissociate to reactants, or dissociate to products through various channels, at rates which are dependent on pressure and temperature.

Second, these pressure-dependent networks can involve very large numbers of wells (isomers) and product channels. For example, the full system resulting from the addition of H atom to methylcyclohexene has over 200 potential isomers and many more
product channels. Any attempt to include all possible pressure-dependent reactions will flood the mechanism with many useless and unimportant pathways. Only those components of the network necessary for the conditions of interest should be included, but it is not obvious which channels and isomers will be important under what conditions.

Third, the common method for predicting $k(T,P)$ employs a high-level, user-intensive approach, requiring detailed ab initio calculations on several stable species, products and transition states, as well as detailed and careful analyses of complicated contributions (such as hindered rotations) to the densities of states. In particular, Rice-Ramsperger-Kassel-Marcus (RRKM)/master equation approaches are often used to evaluate $k(T,P)$ where pre-calculated values or literature rates are not available. But performing the required ab initio calculations of the species, transition states, and potential surfaces for every pressure-dependent network in a pyrolysis or combustion system is not feasible. Indeed, just one pressure-dependent system, treated in this way, may be the subject of an extended computational investigation (e.g. vinyl + O$_2$ by Mebel and coworkers [56]); a large chemical mechanism may have well over one hundred such networks. Automation of a detailed RRKM/master equation or similar approach is, at best, far in the future.

1.5 Including Pressure-Dependence in Automated Mechanism Generation

An approximate, general and fast approach for including pressure-dependence in kinetic mechanisms is thus needed. This approach must provide $k(T,P)$ estimates for systems where the size of the full pressure-dependent network is arbitrarily large, literature $k(T,P)$ are not available, and ab initio calculations of transition states are not practical. It must be simple and reliable enough for use in mechanism generation computer tools. We have built just such an approach.

This thesis develops an automated mechanism generator with integrated pressure-dependence. It is, to our knowledge, the first mechanism generator to include pressure-dependence in a flexible, systematic, and general manner. As such, this work enables computerized mechanism generation to build models for a host of cases which were not previously accessible. As a demonstration case, we have used the approach to uncover
new and previously unconsidered pathways in methane pyrolysis, pathways which can explain that system’s experimentally observed autocatalytic behavior.

2 Thesis Overview by Chapter

This section presents a broad outline of the work, with a synopsis of each chapter. Section 3 (Background: A Detailed Review of XMG) explains the ExxonMobil mechanism generator in enough detail that the integrated pressure-dependence approach of Chapter 6 may be properly understood.

2.1 Chapter 2: OH + NO₂

This work began with a detailed study of rate prediction a priori for the OH + NO₂ \rightarrow HONO₂, HOONO system, in Chapter 2. This study was the author’s “warm-up” project, undertaken to learn the physical chemistry behind unimolecular and chemically-activated reactions and to gain experience in building and running codes to produce \( k(T,P) \) estimates. The OH + NO₂ system is of great importance to atmospheric chemistry modellers, and our work was able to demonstrate a few important points about the reaction system.

First, we were able to bound the rate constant to HONO₂ from first principles, with no manipulated or adjusted parameters, using an inverse-Laplace transform approach combined with a master-equation treatment of collisional deactivation. The work pointed out that an improved treatment of the adiabatic rotational mode (the J-mode) was the best way to improve a priori rate constant predictions for this system. After our work, Troe performed an advanced calculation which focused in part on the J-mode [57].

Second, our work suggested that the reaction OH + NO₂ \rightarrow HOONO was a strong possibility. We stated that the results of certain high-pressure, high NO₂-concentration experiments to measure the high-pressure limit of HONO₂ formation likely were convolved by peroxynitrous acid formation, though HOONO had not yet been observed in the gas phase. HOONO has now been observed experimentally in the gas phase, concurrent with HONO₂ formation [58], in general agreement with our prediction. The more detailed theoretical/fitting work of Troe, which followed our work, broadly agrees with our more primitive calculation: Troe suggests that under atmospheric
conditions, the yield of HOONO will be near 2%, but will be much larger (~20%) near 100 bar (where many experiments were conducted) [57]. The OH + NO₂ chapter was published as [59].

2.2 Chapter 3: Predicting Pressure-Dependent Reaction Rates

Estimating the pressure-dependent rate constants \( k(T,P) \) on-line during mechanism generation is a serious problem, even when one knows the full pressure-dependent network. Transition-state frequencies and geometries are not usually available to a mechanism generator; furthermore, the preferred time-dependent master-equation approaches are far too time-consuming and require too much user involvement to be left to an automated approach. Thus we choose CHEMDIS, a publicly-available Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) code [60] to predict \( k(T,P) \), given the connectivity and structure of a pressure-dependent network. We must use this code in combination with THERFIT [61], which supplies models of the densities-of-states for each network species to CHEMDIS.

The key advantage of the CHEMDIS/THERFIT approach is it requires only: 1) high-pressure-limit modified Arrhenius forms (with physically meaningful values of \( E_a \)) for each pathway in the network, and 2) heat capacity estimates for each isomer. Both sets of information are readily available within our mechanism generation tool; the modified Arrhenius forms from rate rules, and the heat capacities from group additivity methods. Neither transition state frequencies and geometries, nor individual isomer frequencies and rotational modes, are required. Chapter 3 describes our adaptation of CHEMDIS and THERFIT to automated mechanism generation.

Of all the aspects of this thesis, it is the choice of QRRK/MSC for \( k(T,P) \) which the wider chemistry community finds most troublesome, despite a considerable body of practical evidence that QRRK/MSC “works” in most cases. Chapter 3 reviews the errors and assumptions embedded in the CHEMDIS/THERFIT approach, and defends our choice of this general scheme for estimating \( k(T,P) \). It closes with recommendations for improving the approach, without requiring more information than is currently available within a mechanism generator.
2.3 Chapter 4: Screening Pressure-Dependent Reaction Networks

Chapter 4 details our work in developing a screening algorithm which would reliably truncate pressure-dependent reaction networks. As noted above, a full pressure-dependent network can have on the order of 100 isomers or more, and hundreds of separate product channels. Because a pressure-dependent network is made up of elementary steps, a mechanism generator, left on its own, will explore the whole network, potentially flooding the overall chemical mechanism with hundreds of unneeded pressure-dependent reactions. Chapter 4 explains the algorithm we developed to build a pressure-dependent network only as far as conditions required. A feature of the approach is that it bounds the error incurred when using only a small fraction of the full pressure-dependent network to predict \( k(T,P) \). Chapter 4 was published as [62].

2.4 Chapter 5: Building Pressure-Dependent Reactions From Scratch

Once the screening algorithm and a fast CHEMDIS were in place, it was time to test the approach “in the wild”, with rate rules, group additivity thermodynamics, and so forth. Chapter 5 describes the work in this area. Grenda adapted XMG so that it could explore a single pressure-dependent network to its full extent, simultaneously doing all the work necessary to build a CHEMDIS input file. After extensive debugging and modification of the proprietary XMG code, we applied the screening algorithm of Chapter 4 to these full, “from scratch” networks for the case of H atom addition to a series of cycloalkenes. The results were compared the data from the well-defined experiments of Stein and Rabinovitch [63].

The work demonstrated that integrated pressure-dependence, on-the-fly, from high-pressure-limit rate rules and group additivity inputs, would give reasonable results for \( k(T,P) \). The test cases of Chapter 5 suggest our approach, when integrated in XMG, would yield pressure-dependent rate predictions accurate to within a factor of 10, the same accuracy expected of the rate rules. Furthermore, the results of Chapter 5 reinforced the idea that in general, automated mechanism generation must be an iterative process, in which a generation “run” is followed by sensitivity, rate-of-production, and flux analyses to add important literature values to the data libraries. The generator should then be run again with new data, and the process repeated, until the researcher can be
confident that the important steps are well-estimated. Finally, Chapter 5 examines the deficiencies and error cancellation issues embedded in a QRRK/MSC approach. This work will soon be published [55].

2.5 Chapter 6: Integrated Pressure-Dependence

Chapter 6 describes how the screening and exploration approach of Chapters 4 and 5 was integrated with the XMG code. Key parts of the old XMG algorithm were removed or heavily modified, but in general, development of the computer code employed a modular approach. The result of Chapter 6 is a mechanism generator with fully integrated pressure dependence, using a combined exploration and screening approach, called "XMG-PDep". Chapter 6 provides enough detail that a programmer can reproduce our integrated exploration algorithm with pressure-dependence.

2.6 Chapter 7: Integrated Pressure-Dependence: Application to Methane Pyrolysis

Low-temperature methane pyrolysis has proven surprisingly difficult for chemical kinetic models to explain. At temperatures near 1000 K and pressures near 0.1-1 atm, neat methane pyrolysis will be autocatalytic at strikingly low conversions of substrate. Early methane mechanisms could not explain this behavior because they lacked the correct reactions and species, as shown by Dean [64], whose work appeared to resolve the mystery of the autocatalytic upturn.

However, recent experimental and computational results have revised the thermochemical data for key species in the Dean mechanism, especially cyclopentadienyl radical. The early QRRK/MSC code of Dean [65] has also been supplanted with a newer, more accurate version (CHEMDIS). Use of the new thermodynamic parameters, and to a lesser extent, the new QRRK/MSC code, renders the Dean mechanism unable to explain low-temperature methane pyrolysis.

Chapter 7 explores our application of mechanism generation with true pressure-dependence, XMG-PDep, to low-temperature methane pyrolysis. We find new pathways, previously unconsidered, which can explain autocatalysis in methane pyrolysis quite well. While "proof" of a chemical mechanism is never possible, our tool provides strong
evidence that particular gas-phase reactions, not considered by any other researcher in this context, provide the radical chain-branching to explain the autocatalytic upturn.

2.7 Chapter 8: Conclusions and Recommendations

Chapter 8 sums up the significant results of this work. Based on what was learned in the previous chapters, Chapter 8 recommends future directions for integrated pressure-dependence in mechanism generation. First, deficiencies in the approximate QRRK/MSC approach need to be examined more closely. Possible remedies include an inverse-Laplace transform approach and a fast master-equation approach (slow and very complicated approaches, not amenable to automation, currently dominate the field). Chapter 8 reviews some ways to accomplish this task, along with methods for addressing possible issues with the integrated approach.

Second, the approach of this thesis needs to be sensibly integrated with the range-analysis work of Song [66], since presently it can only generate a mechanism for a single temperature and pressure, for a batch reactor configuration, with a fixed set of starting concentrations. An outline for how to do this is provided.

Third, key deficiencies of the NetGen/XMG mechanism generation code structure need to be remedied. The hard-coded approach to reaction families makes working with this tool extremely difficult, and a great many new reaction families need to be added. Diradicals and resonance-stabilized radicals need to be treated properly, which will mean revision of the traditional graph-theory representation. NetGen and XMG allow only one reactor-model paradigm, the isobaric, isothermal batch reactor, and other models need to be explored. Finally, and most mysteriously, the rate-based philosophy itself may need re-examination, on the grounds that it may not always capture key autocatalytic pathways. Chapter 8 briefly explores ways of addressing all these challenges.

3 Background: A Detailed Review of XMG

The following section provides a detailed review of the ExxonMobil mechanism generator, XMG, so that the work of Chapters 5-7 may be properly understood. It describes XMG as it existed at the start of the work in Chapter 5. The author is greatly indebted to Jeffrey M. Grenda for supplying this software under the terms of the ExxonMobil Confidentiality Agreement, and for his invaluable assistance in working
with the code. Proprietary components of XMG are not discussed below, nor in other parts of this thesis.

Dr. Jeffrey M. Grenda, of ExxonMobil Research and Engineering, developed XMG as a proprietary mechanism generation code for ExxonMobil. XMG is a major revision of the NetGen software of Broadbelt and coworkers [7-11] and retains most of its essential features as published by Susnow et al [11]. These essential features are required for any elementary-step-based mechanism generator, and include: 1. A method for representing and uniquely identifying molecules in computer memory objects 2. An algorithm for allowing these molecules to react in defined ways 3. Methods to compute thermodynamic properties and estimate rate constants for reactions which the generator discovers but which do not appear in data libraries. 4. Bookkeeping methods to ensure reactions are not duplicated and can be output in a format that is easy to understand and use – this component may seem trivial but is in fact quite difficult and quite important. In the following text, italics will refer to computer data objects, and boldface will refer to specific modules, functions, or scripts.

3.1 Representing Molecules and Reactions

3.1.1 Adjacency Lists and Graph Theory

XMG employs graph-theory based adjacency lists to store molecules, in a data structure called the ChemGraph, as described by Broadbelt [7-9]. This system is reviewed very briefly below; the Broadbelt papers cited above provide a more complete explanation. An example of an adjacency list for cyclohexene is shown below:
// CY(C*CCCCC)
16
0 0 C : {1,2}, {5,1}, {6,1};
1 0 C : {0,2}, {2,1}, {7,1};
2 0 C : {1,1}, {3,1}, {8,1}, {9,1};
3 0 C : {2,1}, {4,1}, {10,1}, {11,1};
4 0 C : {3,1}, {5,1}, {12,1}, {13,1};
5 0 C : {4,1}, {0,1}, {14,1}, {15,1};
6 0 H : {0,1};
7 0 H : {1,1};
8 0 H : {2,1};
9 0 H : {2,1};
10 0 H : {3,1};
11 0 H : {3,1};
12 0 H : {4,1};
13 0 H : {4,1};
14 0 H : {5,1};
15 0 H : {5,1};

Figure 1-4. Adjacency list representation of cyclohexene.

In the adjacency list, each line represents an atom. The first number in the line indicates
the atom number, followed by the a character for the atom type. Each bracketed pair
indicates a bond of the atom: the first integer of the pair is the number of the other atom
of the bond, and the second integer is the bond type (1 = single, 2 = double, 3 = triple).
Thus, in Figure 1-4, atom 1, a carbon, is bonded to atom 0 by a double bond, atom 2 by a
single bond, and atom 7 by a single bond.

From this list a unique, undirected graph of nodes and edges can be constructed
which represents the molecule, with each atom as a node, and each bond an edge. The
adjacency list itself is not a unique representation, however. XMG thus utilizes a
canonicalization algorithm from the graph-theory literature, called the Biconnected
Components algorithm. This algorithm builds a unique character string from the
adjacency list. New molecules, when they are discovered, can be compared with current
molecules lexicographically using these "canonical strings". In this way XMG decides
whether the molecule is "new" or whether it has seen it before.

Radicals are represented by a specified radical center, as shown for ethyl radical
below. This approach will fail to represent resonantly-stabilized radicals properly,
because there is more than one formal structure for these cases, and the formal structures
will have different canonical strings. Note also that cis and trans isomers, and stereochemical features, are not captured by the adjacency list format.

```
// C2H5
7
0 0 C : {1,1}, {2,1}, {3,1}, {4,1};
1 0 C(Radical) : {0,1}, {5,1}, {6,1};
2 0 H : {0,1};
3 0 H : {0,1};
4 0 H : {0,1};
5 0 H : {1,1};
6 0 H : {1,1};
```

Figure 1-5. Adjacency list representation of ethyl radical.

3.1.2 The Bond-Electron Formalism

Reactions are "performed" in XMG by converting the reactive portion of the adjacency lists for participating reactants into a symmetric reactant matrix, as described by Grenda [51] and by the Broadbelt papers. Each row/column represents an atom; numbers in the matrix represents bonds and bond orders. Numbers on the diagonal represent radical centers. A reaction operator matrix is then added to the reactant matrix, via matrix addition; there is one reaction operator matrix for each reaction family. The result is the product matrix, which has new entries for which atoms are bonded to which. XMG then reconstructs adjacency lists based on the new bonds, and determines whether the product species are "new" by means of the canonicalization algorithm. Figure 1-6 illustrates this procedure for the addition of methyl radical to ethylene. The bond electron formalism was developed by Ugi and coworkers [67], who have made many modifications since it was adopted by the XMG developers. These changes allegedly resolve the resonant-radical and cis/trans problems previously noted.
Combined BE Matrix for C₂H₆ + CH₃⁺  

\[
\begin{array}{cccccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{C} & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
\text{C} & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 1 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

Reaction Matrix

\[
\begin{array}{cccccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{C} & -1 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{C} & 0 & -1 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\
\end{array}
\]

Product Matrix

\[
\begin{array}{cccccccc}
\text{C} & \text{C} & \text{C} & \text{C} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{C} & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 \\
\text{C} & 1 & 0 & 1 & 1 & 1 & 0 & 0 & 0 \\
\text{C} & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\text{H} & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{array}
\]

Figure 1-6. The bond-electron formalism allows the computer to “react” species with each other to produce new species. There is a separate Reaction Matrix for each reaction family.

3.2 XMG Walkthrough

3.2.1 Algorithm Overview

- DetermineXSites
- DoXReactions
- Identify Molecules
- WriteRxnExpression
- Initialization and Pool Rxns.
- Species Exploration and Reaction Construction
- Organize Reaction List
- Construct ODEs
- Integrate ODEs
- Flux Test at each tₖ:
  \( R_{\text{species}}(j) < R_{\text{min}} \) for all j?
- Increment \( X_{\text{int}} \)
- Conversion \( X_{\text{final}} \) Reached?
- Choose species j for exploration

Figure 1-7. Overview of the XMG code.

Figure 1-7 presents an overview of how XMG builds a mechanism. Except as noted, the details in this section have been published by Broadbelt, Susnow, and their coworkers [7-9;11], or have been presented by Grenda and coworkers in various conferences and papers [50-52].
At the start of mechanism generation, XMG examines the initial species and adds them to the initial pool of reactants. Any specific reactions that the user wants included from the start are also loaded via the pool reaction system developed at MIT by Dr. Preeti Aghalayam. It then initiates two lists of species: the Reacted Species list and the Unreacted Species list. The Reacted Species list holds those species which are formally part of the reaction mechanism; their reactions with all other Reacted Species have been explored. The Unreacted Species are candidates for exploration; the generator has discovered them, but their reactions have not yet been explored. A list of reactions is also maintained.

3.2.2 Species Exploration and Reaction Construction

All codes based on the NetGen program of Broadbelt et al [7-9;11] start by taking a candidate from the Unreacted Species list and exploring its reactions via a chain of function calls. This chain, called the CanReact...WriteRxnExpression sequence, applies all the relevant reaction families to the candidate species, reacting the candidate with itself and with all the species currently in the Reacted Species list. CanReact starts the sequence, determining which reaction families are relevant for the candidate.

CanReact then calls pairs of functions, of the form DetermineXSites/DoXReactions, where ‘X’ represents a reaction family. For example, if the species is a radical, ‘X’ might be “H-abstraction”, or “radical addition to an unsaturated bond”, or “beta-scission”, and so forth. These function pairs determine whether reaction is possible, and then construct and perform the matrix algebra for the reaction family as depicted in Figure 1-6. After DoXReactions, the function IdentifyMolecules builds canonical strings for the adjacency lists and sorts out which species are new and which have already been discovered.

Thermodynamic Data

IdentifyMolecules also attempts to assign thermodynamic properties from a data library to each new species. If no library data are available, the program must estimate the missing property data. In NetGen, this was accomplished with the NIST S&P program, and/or MOPAC [11]. In XMG, when library data is not available, the Group Additivity Property Predictor, GAPP [51], is used to perform a group contribution
estimate of the enthalpy, entropy and heat capacity of the species. GAPP is ExxonMobil’s proprietary, automated extension of the THERM tool of Bozzelli and coworkers [68;69]. In addition to basic thermodynamic properties, GAPP also provides a three-pseudo-frequency model to be used estimating densities of states (as per Chang [61]). Finally GAPP calculates estimates of critical temperature and pressure, and the Lennard-Jones parameters.

Rate Coefficient Data

At the end of the sequence, WriteRxnExpression builds the reaction data object and adds it to a list. If available, WriteRxnExpression selects a library value for the reaction rate constant, based on the designated reaction direction (see below). Otherwise, it selects an appropriate rate rule, as depicted in Figure 1-3.

3.2.3 Organizing the Reaction List: Degeneracy and Thermodynamic Consistency

When the reactions of a species are complete, XMG will organize them to collapse degenerate reactions. Repeated instances of the same reaction are removed: for example, XMG will initially find 6 instances of \( \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \) since there are 6 equivalent hydrogens on ethane; these are collapsed to a single reaction. Since rate rules are site-based, the rate rule coefficient must be multiplied by the pathway degeneracy when collapsing multiple instances. For example, a rate rule for abstraction of H atoms from a carbon to form a primary radical will be “per hydrogen”, while the actual reaction \( \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \), will have a rate constant equal to \( k_f^\sigma = \sigma_f k^\text{act} \), here the degeneracy \( \sigma_f = 6 \). On the other hand, rate constants from the library are stored as full-reaction rate constants and are not site-based; in these cases XMG will simply assign the library rate constant to the collapsed single reaction.

Each reaction family is designated as a “forward” or “reverse” family, roughly corresponding to whether or not it is usually exothermic. For example, the family for radical addition to a double bond is designated as forward, and radical beta scission to form a radical and a double-bonded molecule is designated as reverse. Certain families are flexible and can take either a forward or reverse direction, determined by reaction enthalpy.
If the family is a designated reverse family, XMG chooses a rate rule or library value for the *forward* direction. XMG then calculates the “true” rate constant from the rule or library parameter using the thermodynamic equilibrium constant. In this way, any pair of forward and reverse reactions in the mechanism will be thermodynamically consistent. In order to calculate the designated reverse rate constant, XMG must often calculate the forward pathway degeneracy via the function chains of **DetermineForwardRPD** (developed by this author and Dr. Grenda). Then the designated reverse rate constant may be calculated via:

\[
k_r^\infty = \frac{\sigma_i k_f^\infty}{K_C}
\]  

(1-2)

### 3.2.4 Building and Integrating the ODEs

At this point XMG adds the candidate species to the *Reacted Species* list. It then examines the reaction list, and builds the set of ordinary differential equations which represent the evolution of the *Reacted Species* in an isothermal, isobaric, homogeneous batch reactor at the temperature, pressure, and initial concentrations specified.

At the beginning of generation, the user specifies a target conversion for a single, specific component, \(X_{\text{final}}\). XMG divides the target conversion into a series of intermediate conversions \(X_{\text{int}}\). It then begins the ODE integration. At a user-specified number of “snapshot” points between \(X = 0\) and \(X = X_{\text{int}}\) (labeled as time points \(t_k\) in Figure 1-7), XMG halts integration and calculates the fluxes to the *Unreacted Species*, using the information in the reaction list and the current concentrations of all the *Reacted Species*. For each *Unreacted Species*, it stores the maximum flux value so far achieved at each snapshot point. Thus, when \(X_{\text{int}}\) is reached, each *Unreacted Species* \(j\) can be associated with a flux value \(R_{\text{species}(j)}\), which represents the maximum flux to this species from among all the snapshot points from \(X = 0\) to \(X = X_{\text{int}}\).

### 3.2.5 The Flux Criteria

XMG next examines the *Unreacted Species* maximum fluxes, \(R_{\text{species}(j)}\). From among these it chooses the largest and compares it to a flux tolerance \(R_{\text{min}}\), at the point \(X_{\text{int}}\). If the largest \(R_{\text{species}(j)}\) is less than \(R_{\text{min}}\), XMG advances \(X_{\text{int}}\) toward \(X_{\text{final}}\) and starts the integration process again. If the largest \(R_{\text{species}(j)}\) is greater than \(R_{\text{min}}\), XMG chooses this...
species as the next candidate for exploration and begins the exploration and construction process, as shown in Figure 1-7.

\( R_{\text{min}} \) is scaled to a characteristic reaction rate for the whole ODE system, by a user-specified relative tolerance \( f_{\text{min}} \):

\[
R_{\text{min}}(t) = f_{\text{min}} R_{\text{char}}(t)
\]  

(1-3)

In practice, \( f_{\text{min}} \) is usually between 0.1% and 5%, and the time \( t \) is the time at which the intermediate conversion \( X_{\text{int}} \) was reached. Equation (1-3) is the principal and key equation of rate-based termination.

\( R_{\text{char}} \), the “characteristic overall rate” for the ODE/batch reactor system, was revised from the original formula of Susnow, by Song et al [66], to be the square root of the sum of squared fluxes to all reacted species:

\[
R_{\text{char}}(t) = \sqrt{\sum_i \left( R_{\text{reacted}(i)}(t) \right)^2}
\]  

(1-4)

3.2.6 Notes on the XMG Approach

There are clear complications and difficulties with employing the flux-based termination rule, Equation (1-3), in the way described in this section. This method was extensively revised in our work; among other changes, the arbitrary divisions and snapshot points were eliminated, as described in Chapter 6.

3.3 Pressure-Dependence in XMG

3.3.1 Library-Based Pressure-Dependence

Because some capability for handling pressure-dependence was so clearly necessary, Dr. Grenda added some pressure-dependence functionality to XMG [50]. During mechanism generation, the code could explore any pressure-dependent network it found, to full extent. XMG would then examine the “net” pressure-dependent reactions of the network (see Chapter 6). If any of the net reactions could be found in the library of reaction rate constants, XMG would include these reactions in the reaction list, with the correct rate constant. Otherwise, the net reactions would be ignored, since XMG could not perform on-line calculations to estimate \( k(T,P) \). A key reason for this inability was
the size of the full networks [55;62] and the time required to calculate them, even within CHEMDIS.

3.3.2 Single-Network Exploration

Dr. Grenda also revised XMG so that it could operate in “single-network” mode. In this mode XMG would construct a single, full pressure-dependent network resulting from a specified thermal isomerization or chemical activation reaction. Each elementary step found by a family would constitute a pathway in the network. In building the network, XMG would use the high-pressure-limit rate rules, along with group additivity (GAPP) to build three-pseudofrequency models [61] for each isomer in the network. It would also calculate Arrhenius parameters for the designated reverse reaction, using Dr. Grenda’s fitting routine (the fitting procedure is discussed in more detail in Chapter 6). In this way XMG would construct CHEMDIS input files, which could then be screened and used to calculate $k(T,P)$, as described in Chapters 4 and 5.
Citations

CHAPTER 2: A PRIORI FALLOFF ANALYSIS FOR OH + NO₂
1 Introduction

1.1 An A Priori Calculation Project

This work began as an exercise in learning and developing a priori calculation techniques for \( k(T,P) \). We also wished to learn by experience how accurate an a priori \( k(T,P) \) estimate could be, without access to specific transition state information. Although no transition state frequencies or geometries are directly employed for calculation here, the case is otherwise the best possible, with detailed input data on the frequencies, rotational barriers, and geometries of the reactants and products. As it happened, this work made a significant contribution to the ongoing study of the OH + NO\(_2\) system, in suggesting (along with a few other works) that certain high-pressure measurements of the rate constant for OH + NO\(_2\) \( \rightarrow \) HONO\(_2\) were in error. This work was performed in 1998-2000, and appeared as the article: “A priori falloff analysis for OH + NO\(_2\)”, David M. Matheu and William H. Green, International Journal of Chemical Kinetics Volume 32, pages 245-262 (2000). Since that time, many other investigators have scrutinized the OH + NO\(_2\) system, though controversy remains over the correct values for the rate constant to form HONO\(_2\), and the significance of a key competing channel forming HOONO. The relation of our work to these later efforts is briefly explored in the Discussion section.

1.2 The OH + NO\(_2\) System: A Critical Atmospheric Chemistry Pathway

The reaction of OH with NO\(_2\) to form nitric acid,

\[
\text{OH} + \text{NO}_2 \xrightarrow{k_1} \text{HONO}_2
\]  

(2-1)

is an important pressure-dependent pathway in tropospheric and stratospheric chemistry, affecting ozone production, acting as a sink for OH and NO\(_2\) and governing the ratio of NO\(_x\) to NO\(_y\) [1-4]. Global atmospheric models have proved particularly sensitive to \( k_1 \) [1;2]; indeed, atmospheric modelers are concerned with errors as small as \( \pm 10\% \) in the value for \( k_1 \). The great importance of (2-1), and the need for unusually high accuracy in the rate constant estimate, have inspired an extraordinary number of theoretical and experimental studies [5-27].
In 1999, some high-pressure data for $k_I$ in helium appeared systematically too far above (and inconsistent with) data collected in other bath gases at lower pressures [8;9] (these results have since been revised downward, to closer agreement with pre-existing data [21], but discrepancies in values for $k_I$ at many pressures remain). Since the full Troe form [28] used to represent an estimate for $k_I$ requires three parameters ($k_1^0$, $k_1^w$, and $\beta_C$), accurate predictions of $k_I$ require an accurate value for the high-pressure rate constant $k_I^w$ [5]. The high-pressure limit discrepancy was therefore important and an explanation was needed. One such explanation, which we explored, is that high pressure data for $k_I$ may have been convolved, in some experiments, with a secondary channel forming peroxynitrous acid:

$$\text{OH} + \text{NO}_2 \xrightarrow{k_I} \text{HOONO}$$ (2-2)

At the beginning of our work, this possibility had also been considered by Burkholder et al. [16] and Robertshaw and Smith [17], and following our work, by many others also (e.g. [6;7;21-24;27]).

We made a priori predictions of the rate constants for (2-1) and (2-2) without any parameter adjustment to fit the data, with three goals in mind. First, we wished to understand by experience how accurate a priori rate predictions without transition states might be, under the best of conditions. This experience had important implications for our future use of a priori methods for $k(T,P)$ in automated mechanism generation. Second, we wished to investigate whether (2-2) might convolve certain high-pressure data for (2-1). Finally, we wanted to understand what steps were needed to improve any further a priori estimate for the rate constant of (2-1).

We used the inverse Laplace transform approach (ILT) [29-33] and both the modified strong collision (MSC) [34] and master equation (MEQ) treatments of collisional deactivation. The ILT approach was chosen because of its particular usefulness in reactions with no barrier to recombination, and because it requires no explicit information about the transition state. We explored the sensitivity of the rate constant predictions for (2-1) to collisional energy transfer parameters, well depth, high pressure rate constant value, treatment of OH moieties (in HOONO and HONO$_2$) as stiff vibrators, hindered rotors, or free rotors, and the inclusion or exclusion of 'adiabatic'
external rotational modes. These calculations and sensitivities pointed the way to further refinement of rate constant estimates for (2-1), suggested an answer to the question of convolution by HOONO formation, and provided a best-case estimate for unadjusted \textit{a priori} predictions of \( k(T,P) \) in the absence of specific transition state information.

2 Method of Calculation

2.1 Overview

An energy diagram (not to scale) for the system of (2-1) and (2-2) is presented in Figure 2-1. \( \varepsilon \) represents the rotational and vibrational energy of the fragments (OH and NO\(_2\)) above their zero-point energy, and \( E_R = \varepsilon + \Delta E_0^0 \) refers to the rotational and vibrational energy of the adduct. \( \Delta E_0^0 \) refers to the difference in energies between the zero points of the fragments OH and NO\(_2\) and the adduct, which may be HOONO\(_2\) or one of the HOONO conformers.

![Energy diagram](image)

**Figure 2-1.** Energy surface for OH, NO\(_2\), HOONO\(_2\), HOONO(I,II) and HOONO(III), not to scale. The barrier between HOONO and HOONO\(_2\) was considered infinite (no communication between wells).

The value of \( \Delta E_0^0 \) for HOONO\(_2\) (47.7 kcal/mol) is taken from the experimental dissociation energy cited in [13]. Sumathi and Peyerimhoff have calculated a transition
state for the isomerization of HONO$_2$ to HOONO, but the barrier height they found is well above the dissociation limit for HONO$_2$ [16]. A kinetically important transition state would need to be near or below the dissociation energy for HONO$_2$, this work assumes the HONO$_2$ and HOONO wells do not communicate. Various calculations and experiments have confirmed there is no intrinsic energy barrier for the formation of HONO$_2$ or HOONO from the reactants (e.g. [9;13]).

The two values listed for $\Delta E^0$ in the HOONO well reflect the different conformers of this species. Sumathi and Peyerimhoff [16] and McGrath and Rowland [19] verified three stable conformers of HOONO, which are related by rotations about the O-O and N-O bonds. As explained in the next section, HOONO(I) and HOONO(II) were treated as a single species, HOONO(I), with the OH arm treated as a hindered rotor having the potential energy surface calculated in [19]. HOONO(III) was considered as a separate species which did not intraconvert to HOONO(I).

$k_d(\varepsilon)$ and $k_a(\varepsilon)$ represent the microcanonical rate constants for dissociation of the reactant and association of the products. These rates were calculated using the inverse Laplace transform (ILT) technique and various approximations discussed below. The resulting expressions for $k_d(\varepsilon)$ were combined with both the modified strong collision and master equation approaches to predict the recombination rate constants $k_1(T,P)$ and $k_2(T,P)$ for (2-1) and (2-2). The predicted reaction rates are sensitive to assumptions about which modes of the adducts can rapidly exchange energy and to estimates of the density of states $\rho(\varepsilon)$ for each species. We considered the case where all rotational modes are coupled with the vibrations, and the case where only one rotational mode (corresponding to the K quantum number) is able to exchange energy with the vibrational modes.

### 2.2 Treatment of HOONO Conformers, Calculation of $\Delta E^0$ and Equilibrium Constants

There are at least three known stable conformers of HOONO [16;19]. The cis-cis HOONO(I) is planar, having a ring shape and a hydrogen bond to the terminal oxygen. A low-barrier torsion about the O-O bond converts it to the cis-perp HOONO(II), in which the hydrogen is perpendicular to the ONO plane [16]. McGrath and Rowland calculated
a potential energy surface for this rotation at the MP2/6-311+G(3df,2dp)//MP2/6-31G(d) level and fitted it to a truncated Fourier series. They found a maximum barrier of 2.6 kcal/mol (uncorrected for ZPE). Sumathi and Peyerimhoff estimated this barrier to be 1.6 kcal/mol (corrected for ZPE) at the B3LYP/6-311++G** level. The trans-perp HOONO(III) has the OH moiety trans to the terminal oxygen and is separated from HOONO(I) and HOONO(II) by a strongly hindered torsion about the N-O bond; Sumathi and Peyerimhoff found the torsional barrier to be 12.5 kcal/mol.

Sumathi and Peyerimhoff report a difference of 1.9 kcal/mol between the zero-point energies of HOONO(I) and HOONO(III). They do not report the energy difference between HOONO(I) and HOONO(II), but it cannot be greater than the calculated rotational barrier of 1.6 kcal/mol which separates (I) and (II) at the B3LYP/6-311++G** level of theory. This work approximates HOONO(I) and (II) as a single species, HOONO(I,II), with the OH moiety treated as a hindered rotor, having the potential energy surface for rotation described by McGrath and Rowland [21]. Since a large barrier (12.5 kcal/mol [18], comparable to the O-O bond strength) separates (I) and (II) from HOONO(III), isomerization between HOONO(III) and the HOONO(I) or HOONO(II) conformers was ignored and HOONO(III) was considered a separate species.

Sumathi and Peyerimhoff report a G2-level, ZPE-uncorrected energy difference of -20.3 kcal/mol between OH + NO₂ and HOONO (presumably HOONO(I), the lowest energy conformer of HOONO). This value represents the highest level calculation of HOONO energy available. Using the frequencies for HOONO(I) given by these authors, we made zero-point energy corrections to the Sumathi and Peyerimhoff G2 result. This gave ΔE₀ = -16.7 kcal/mol for OH + NO₂ → HOONO(I,II). This agrees well with the calculation of Melius, cited in Burkholder et al., of ΔE₀ = 16±2 kcal/mol (no conformer specified) [14].

A partition function was calculated for HOONO(I,II) via numerical evaluation of the direct-count density of states, in which the OH moiety was treated as a hindered rotor with the potential surface given by [19] as described in the following section. Using this partition function, the above value for ΔE₀, the statistical-mechanical formula for the equilibrium constant, and partition functions for OH and NO₂ (which included accounting of electron-spin/rotational coupling in OH; see Appendix) we found
$K_{OH + NO_2 \rightarrow HOONO(1,II)} = 1.3 \times 10^0$ [cm$^3$/mol] at 300 K. The average absolute deviation for a thermodynamic calculation using the G2 method is about 1 kcal/mol [35], which suggests $\Delta E_0^0 = -16.7 \pm 1$ kcal/mol; this error in $\Delta E_0^0$ gives a factor of 5 uncertainty in $K_{OH + NO_2 \rightarrow HOONO(1,II)}$. By comparison, a similar treatment of the equilibrium constant for $OH + NO_2 \rightarrow HONO_2$ with the OH moiety again treated as a hindered rotor, gives $K_{OH + NO_2 \rightarrow HONO_2} = 1.73 \times 10^{32}$ [cm$^3$/mol] at 300 K.

Sumathi and Peyerimhoff suggest a calculated energy difference of 1.9 kcal/mol between HOONO(I) and HOONO(III), which gives $\Delta E_0^0 = -14.8$ kcal/mol for $OH + NO_2 \rightarrow HOONO(III)$. Similar to the calculation for HOONO(I,II), the OH moiety was treated as a hindered rotor using the potential function given in [19]. A partition function for HOONO(III) was evaluated via the direct-count density of states and a resulting equilibrium constant of $K_{OH + NO_2 \rightarrow HOONO(III)} = 5 \times 10^9$ [cm$^3$/mol] was found at 300 K.

2.3 Treatment of OH Torsion in HONO$_2$ and HOONO

The OH torsion in HONO$_2$ has a fairly high rotational barrier (~7.7 kcal/mol) [17], so that at low temperatures this mode should behave similar to a stiff vibrator. To examine the effect of assumptions made for this moiety, we considered the OH torsion as a stiff (harmonic) vibrator, a free rotor, and (for some of the rate constant calculations) a hindered rotor. We conducted a BLYP/6-31G* geometry optimization/frequency calculation of HONO$_2$, using UniChem [36], which confirmed the lowest frequency of HONO$_2$ (458 cm$^{-1}$) as corresponding to OH torsion in HONO$_2$. When the OH torsion was treated as a stiff vibrator, this mode was incorporated into the molecular density of states calculations as a harmonic oscillator; when the torsion was treated as free, this mode was incorporated as a classical or quantum free rotor. To incorporate the mode as a hindered rotor, a potential surface for the OH rotation was estimated, and the energy levels for this hindered rotation were incorporated via a direct-count algorithm.

No description of the potential energy surface for OH rotation in HONO$_2$ was found in the literature. The planar geometry of HONO$_2$ suggests a symmetric double sinusoidal potential, since a rotation along the HO-N bond of 180° returns an identical
molecule. The rotational energy surface for this torsion was therefore assumed to be described (in cm\(^{-1}\)) as

\[
U(\theta) = \frac{u_0}{2} (1 - \cos 2\theta)
\]

(2-3)

where \(u_0 = 2700\) cm\(^{-1}\), the barrier found by Lee and Rice [17].

The OH hindered rotor was next assumed to have a rigid axis of rotation (the HO-N bond) attached to a rigid "frame" such that the moments of inertia for internal rotation and overall rotation were considered constant and unrelated (e.g. [37]). The potential in (2-3) was applied to a computer code by Shokhirev and Krasnoperov which evaluated the energy levels for a hindered rotor with this potential via diagonalization of the Schroedinger equation Hamiltonian for a hindered rotation [38;39]. With \(u_0 = 2700\) cm\(^{-1}\), the zero point energy and the first few levels produced by the Shokhirev-Krasnoperov code agreed well with the literature value for the harmonic frequency of this mode (458 cm\(^{-1}\)), so that (2-3) seemed a reasonable representation of the potential energy surface for this hindered rotation. The energy levels from this code were then used in a direct-count density of states algorithm, thus allowing treatment of the OH arm as a hindered rotor. The density of states was corrected by a symmetry number of 2 for this treatment.

The OH torsion in HOONO intraconverts HOONO(I) and HOONO(II), with a low overall barrier and a potential surface for hindered rotation given (in cm\(^{-1}\)) by [19]:

\[
U(\theta) = \sum_{n=1}^{4} \left( \frac{u_n}{2} \right) (1 - \cos n\theta)
\]

(2-4)

\(u_1 = 646.4\quad u_2 = -252.1\quad u_3 = 243.6\quad u_4 = 152.7\)

A BLYP/6-31G* geometry optimization/frequency optimization of HOONO(I) suggested the lowest frequency (292 cm\(^{-1}\), [16]) corresponded to OH torsion.

We treated HOONO(I) and HOONO(II) as a single species, HOONO(I,II), with a hindered rotor for OH torsion given by (2-4); the symmetry number for this rotor is 1. Torsion about the N-O bond (which would convert HOONO(I,II) to HOONO(III)) was considered as a stiff vibrator, given its high rotational barrier. A BLYP/6-31G* geometry optimization/frequency optimization of HOONO(III) suggested the second lowest frequency (292 cm\(^{-1}\), [16]) corresponded to OH torsion in this species. The OH torsion potential surface given by [19] in cm\(^{-1}\) for HOONO(III) is
\[ U(\theta) = \sum_{n=1}^{4} \left( \frac{u_n}{2} \right) (1 - \cos n\theta) \quad (2-5) \]

\[ u_1 = 398.8 \quad u_2 = 991.9 \quad u_3 = -132.0 \quad u_4 = -71.0 \]

and the symmetry number is 1.

2.4 Sources of Data

Tables 2-1 and 2-2 list data used in all the calculations. The high-pressure rate constant for forming HOONO was assumed equivalent to that for HONO₂ (as discussed below). The high-pressure rate constant for HONO₂ recombination was derived from the \textit{ab initio} CVTST calculation of Chakraborty et al. [13]. Lennard-Jones parameters for HOONO were also assumed equivalent to those for HONO₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{\text{r}} ) (HONO₂)</td>
<td>3.31E13 (at 300 K)</td>
<td>cm³/mol-sec</td>
<td>[13]</td>
</tr>
<tr>
<td>( k_{\text{r}} ) (HOONO)</td>
<td>3.31E13 (at 300 K)</td>
<td>cm³/mol-sec</td>
<td>see text</td>
</tr>
<tr>
<td>( \Delta E_{0}^{0} ) (HONO₂)</td>
<td>-47.7</td>
<td>kcal/mol</td>
<td>[13;40]</td>
</tr>
<tr>
<td>( \Delta E_{0}^{0} ) (HOONO)</td>
<td>-16.7</td>
<td>kcal/mol</td>
<td>see text</td>
</tr>
<tr>
<td>( \Delta E_{0}^{0} ) (HOONO (I))</td>
<td>-14.8</td>
<td>kcal/mol</td>
<td>see text</td>
</tr>
<tr>
<td>( \sigma_{\text{HOONO}} )</td>
<td>3.798</td>
<td>Angstroms</td>
<td>[41]</td>
</tr>
<tr>
<td>( \sigma_{\text{HNO}} )</td>
<td>2.551</td>
<td>Angstroms</td>
<td>[41]</td>
</tr>
<tr>
<td>( \sigma_{\text{HONO2}} )</td>
<td>4.24</td>
<td>Angstroms</td>
<td>[34]</td>
</tr>
<tr>
<td>( \Delta E_{\text{all}} ) (N₂)</td>
<td>-290</td>
<td>cm⁻¹</td>
<td>[42;43]</td>
</tr>
<tr>
<td>( \Delta E_{\text{all}} ) (He)</td>
<td>-150</td>
<td>cm⁻¹</td>
<td>[42;43]</td>
</tr>
<tr>
<td>( C_{\text{L}} ) (300 K)</td>
<td>1.83</td>
<td>--</td>
<td>see Appendix</td>
</tr>
<tr>
<td>( \sigma_{\text{a}} ) (NO₂)</td>
<td>2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \sigma_{\text{a}} ) (OH)</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \sigma_{\text{a}} ) (HONO₂)</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \sigma_{\text{a}} ) (HOONO)</td>
<td>1</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \gamma_{\text{a}} ) (OH)</td>
<td>2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>( \gamma_{\text{a}} ) (NO₂)</td>
<td>2</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 2-1. Sources of data for the calculations.
The values for the average energy exchanged with the bath gas, \(<\Delta E>_{\text{all}}\), were found in Dean [42], who reports them as typical values based on those of Gardiner and Troe [43]. There is much uncertainty in this parameter. Frequencies and moments of inertia used in all the calculations are listed in Table 2-2. Frequencies for HOONO(I) were taken from Sumathi and Peyerimhoff, while the moments of inertia for this conformer were calculated from our own B3LYP/6-311++G** geometry optimization, which agreed with their results. The '4th' moment of inertia listed under HOONO and HONO_2 moments refers to that for the 1-d OH rotor arm; this moment of inertia is essentially the same for the OH moiety in HONO_2 and HOONO when the rotor is assumed to have a rigid axis and to be attached to a rigid frame.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Frequencies [cm(^{-1})]</th>
<th>Moments of Inertia [amu*angstr(^{2})]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>3569</td>
<td>0.893</td>
<td>[44;45]</td>
</tr>
</tbody>
</table>
| NO\(_2\) | 1320            | 40.4            | [44;45] (freq.) 
|          | 750             | 38.3            | [13] (mom.) |
|          | 1621            | 2.1             |        |
| HONO\(_2\) | 3522           | 80.7            | [46] (freq.) |
|          | 1699            | 41.9            | [13] (mom.) |
|          | 1321            | 38.8            |        |
|          | 1304            | 0.95            |        |
|          | 879             |                 |        |
|          | 647             |                 |        |
|          | 580             |                 |        |
|          | 763             |                 |        |
|          | 458             |                 |        |
| HOONO (I) | 3535           | 87.9            | [19] (freq.) |
|          | 1670            | 64.7            |        |
|          | 1425            | 23.1            |        |
|          | 953             | 0.95            |        |
|          | 826             |                 |        |
|          | 636             |                 |        |
|          | 497             |                 |        |
|          | 358             |                 |        |
|          | 292             |                 |        |
| HOONO (III) | 3748         | 110.6           | [13]   |
|          | 1823            | 103.0           |        |
|          | 1407            | 9.26            |        |
|          | 1014            | 0.95            |        |
|          | 808             |                 |        |
|          | 459             |                 |        |
|          | 358             |                 |        |
|          | 293             |                 |        |
|          | 212             |                 |        |

Table 2-2. Frequencies and moments.

2.5 First ILT Approach (All Rotational Modes Contribute)

The question of which rotational modes should be included in the energy of the microcanonical rate constant can be confusing. We have treated the inclusion of rotational modes in two ways. In the first case (described in this section), we include in
the $E$ of $k(E)$ the energy of all the rotational modes (including the external, 2-dimensional rotational mode, or $J$ mode; see [47]) after the manner of Davies and coworkers [30].

After Forst, we approximate the adduct as a symmetric top and consider the energy in the $J$ mode available for reaction (via lowering of the barrier) to be

$$
\Delta E_r(J) = J(J + 1)(B - B^*)
$$

(2-6)

where $B$ is the rotational constant for the 2d external $J$ mode for the reactant, $B^*$ that for the transition state (see [47] and Equation 5-8, pg. 74 of the same reference for a description of how the energy in the $J$ mode may contribute to reaction even though it is not, technically, available via randomization). Thus, inclusion of all the energy in the $J$ mode approximates the limiting case where the appropriate moment of inertia of the transition state is very large and therefore $B^* = 0$ when compared to $B$ (i.e. virtually all of the energy in the $J$ mode goes to lowering the barrier to dissociation).

When the energy of the $J$ mode is thus included in the $E$ of $k(E)$, the high pressure limiting rate constant for dissociation may then be approximated:

$$
\int_{0}^{\infty} k_d(E_R) \rho^w_R(E_R) e^{-E_R/k_B T} dE_R
$$

$$
\frac{Q^w_R}{Q^w_R} = k_d^w(s)
$$

(2-7)

where $k_d$ is the dissociation rate constant for the reaction as a function of energy, $\rho^w_R$ the convolved rotational-vibrational density of states for the reactant, and $Q^w_R$ is the classical vibrational-rotational partition function for the reactant. $E_R$ is the total rotational and vibrational energy of the reactant (dissociating) molecule above its zero-point energy (see Figure 2-1). $k_d^w$ is the high pressure limit rate constant for the dissociation of the reactant R. The center of mass of the adduct is taken as the reference frame. The subscript R refers to the ‘reactant’ adduct molecule (HONO$_2$, HOONO(I,II) or HOONO(III)) and P refers to the product fragments (OH and NO$_2$); $s = 1/k_B T$, where $k_B$ is the Boltzmann constant.

Since $k_d^w$ has been calculated by CVTST in [13] and is less dependent on temperature than $k_d^w$, the equilibrium constant is used to exchange $k_d^w$ for $k_d^w$. With this
substitution, the variable change \( \varepsilon = E_R - \Delta E_0^0 \), and rewriting as a Laplace transform, (2-7) becomes

\[
L[k_d(\varepsilon)\rho_R^\varepsilon(\varepsilon + \Delta E_0^0)] = k_r^c Q_R^\varepsilon(s) \frac{Q_p(s)}{Q_R(s)}
\]  

(2-8)

where \( \varepsilon \) is the integrated variable and \( s \) is the Laplace transformed variable. \( Q_p \) and \( Q_R \) are total partition functions and involve the reduced mass translational partition function for the fragments P (OH and NO\(_2\)) as well as the standard classical rotational and vibrational partition functions for the fragments and the reactant R. \( Q_p \) and \( Q_R \) also contain electronic degeneracies, rotational symmetries, and an estimated correction factor for the spin-orbit coupling of the OH radical (see Appendix).

Separating the partition functions and deconvoluting the combined vibrational and 2-d rotational density of states yields

\[
L[k_d(\varepsilon)\rho_R^\varepsilon(\varepsilon + \Delta E_0^0)] = k_r^c C_1 L[N_p^\varepsilon(\varepsilon)]s^{-3}
\]  

(2-9)

where \( C_1 \) is a collection of constants:

\[
C_1 = V_0 C_{SO} \left( \frac{\sigma_{\text{HONO}_2}}{\sigma_{\text{NO}_2} \sigma_{OH}} \right) \left( \frac{\gamma_{\text{NO}_2} \gamma_{OH}}{\gamma_{\text{HONO}_2}} \right) \left( \frac{2I_{\text{NO}_2}^*}{h^2} \right) \left( \frac{2I_{\text{OH}}^*}{h^2} \right) \left( \frac{2I_{\text{NO}_2}^a}{h^2} \right) \left( \frac{2\pi \mu_p}{h^2} \right)^{3/2}
\]  

(2-10)

\( V_0 \) is the reference volume for the translational partition function, the \( \sigma \)s are rotational symmetries and the \( \gamma \)s are electronic degeneracies. \( N_p^\varepsilon(\varepsilon) \) is the number of vibrational states at energy \( \varepsilon \) for the fragments OH and NO\(_2\). In (2-10), the rotational modes of NO\(_2\) have been treated classically and the OH fragment's external rotational mode as classical with a correction term for coupling between electron spin and the 2-d rotational mode. NO\(_2\) is approximated as a symmetric top so that \( I_{\text{NO}_2}^* \) is the geometric mean of the two closest moments of inertia and \( I_{\text{NO}_2}^a \) is the 'odd' moment (smaller than \( I_{\text{NO}_2}^* \)). \( \mu_p \) is the reduced mass of the product fragments and \( C_{SO} \) is the estimated correction factor for the spin-orbit coupling of OH (see Appendix).

Solving the ILT in (2-9) yields
\[ k_r^\infty \int_0^\varepsilon \frac{C_1(\varepsilon - \tau)^2}{\Gamma(2)} N_r^\nu(\tau) d\tau \]

\[ k_{d}\varepsilon = \frac{\rho_{r}^\nu(\varepsilon + \Delta E_0^0)}{\rho_{r}^\nu(\varepsilon + \Delta E_0^0)} \]

(2-11)

In the derivation of (2-11), \( k_r^\infty \) has been assumed independent of temperature. Recombination reactions characteristically have weak or zero temperature dependence. The form reported by Chakraborty and coworkers reflects a weak positive temperature dependence of this constant but it explodes as \( T \to 0 \), so that it is not Laplace-transformable; furthermore the experiments of Fulle et al. suggest no measurable temperature dependence for \( k_r^\infty \) [9].

A FORTRAN code was written to evaluate (2-11) using the Whitten-Rabinovitch approximation for \( \rho_{r}^\nu \), since it is required in this equation at relatively high (> \( \Delta E_0^0 \)) energies [29;48]. The Beyer-Sweinhart/Stein-Rabinovitch direct-count algorithm [29;49-51] was used for \( N_r^\nu(\tau) \), the number of vibrational states of OH and NO\(_2\) at energy \( \tau \). The harmonic frequencies and moments of inertia used are given in Table 2-2. Equations (2-10) and (2-11) were evaluated for HONO\(_2\) assuming a stiff and free-rotor OH torsion; the hindered rotor treatment was not used in this approach. When the OH is treated as a free rotor in both the equilibrium constant and in \( \rho_r^\nu \), (2-11) is still valid and the Whitten-Rabinovitch approximation to \( \rho_r^\nu \) is modified to remove the appropriate frequency and add the 1-d rotor contribution to the partition function. We treated HONO\(_2\) as gaining a symmetry number of 2 when the OH torsion was treated as a free rotor.

Equation (2-11) was combined with both a modified strong collision approach and a master equation approach to produce predictions of \( k_{\text{rec}}(T, P) \) for HONO\(_2\). When the master equation approach was used, values for \( \rho_r^\nu \) at low energies were needed. These were computed via the Beyer-Sweinhart/Stein-Rabinovitch algorithm for the vibrational degrees of freedom, convolved with a classical treatment of the rotational degrees. The Whitten-Rabinovitch approximation [48] was used at sufficiently high energies.
2.6 Second ILT Approach (Only K Mode Contributes)

The first treatment allowed all the J modes' energy to contribute to reaction by lowering of the dissociation barrier. But as demonstrated in Forst and other sources, if the dissociating molecule is approximated as a symmetric top, only the energy of the 1-d K rotational mode is available for reaction, with the restriction that \(-J \leq K \leq J\) [47]. The angular momentum number J, and its projection M, are conserved during the reaction and the energy contained in these rotational modes cannot 'contribute' by exchanging energy with the vibrational modes. Increasing J does have the effect of lowering the barrier for reaction as the moment of inertia of the transition state is generally greater than that for the dissociating molecule. \(E_0\) then becomes dependent on J, and the microcanonical rate constant is properly written as \(k(E,J)\) where \(E\) refers to the energy in all the vibrational modes and the K rotational mode. The canonical rate constant \(k(T,P)\) is then a complicated double integral over \(E\) and \(J\) subject to \(-J \leq K \leq J\). This integral reduces to

\[
\frac{\int_0^\infty k_d(E)\rho(E)e^{-E/\hbar \omega} dE}{Q} = k_d^* \tag{2-12}
\]

in the high-pressure limit when non-ideality can be ignored and the restriction \(-J \leq K \leq J\) is dropped. In this equation, \(k_d(E)\) is the microcanonical rate constant for dissociation (\(E\) refers to energy in the vibrational and K mode) and \(\rho(E)\) is the corresponding density of states for the dissociating molecule. \(f_*\) is the 'centrifugal correction' term resulting from the independent integration with respect to J. When the moments of inertia of the transition state are very similar to the dissociating molecule, we expect \(f_* \approx 1\), and the energy in the 2-d external J mode may be assumed completely 'adiabatic' and unable to contribute to reaction via lowering of the barrier. This is equivalent to assuming \(B = B^*\) in (2-6) where \(B\) is the J-mode rotational constant of the dissociating molecule and \(B^*\) that for the transition state, which may be contrasted with the first approach in which it was assumed \(B^* \approx 0\).

Our second approach to the ILT follows these arguments by allowing only the K rotational mode to contribute to the available energy for reaction, dropping (for
tractability) the restriction \(-J \leq K \leq J\). With \(B = B^*\) (equivalently \(f_w = 1\)), (2-12) may then be approximated as

\[
\int_0^{E_R} k_d(E_R) \rho_R^{vk}(E_R) e^{-E_R s} dE_R \quad Q^*_R = k_d^*(s) \quad (2-13)
\]

\(E_R\) here represents the energy of the dissociating molecule contained in the vibrational and the \(K\) rotational mode. The \(vk\) superscripts reflect the fact that the partition function and density of states terms in (2-13) contain the vibrational and \(K\) modes only.

Paralleling the development of (2-11), approximating the adduct as a symmetric top, switching to \(k_d^*(\tau)\), making the same change of variables as in (2-8) and taking the inverse Laplace transform gives

\[
k_d^*(\epsilon_{vk}) = \frac{k_d^*(\epsilon_{vk}) \int_0^{\epsilon_{vk}} C_2(\epsilon_{vk} - \tau) N_R^*(\tau) d\tau}{\rho_R^{vk}(\epsilon_{vk} + \Delta E_0^v)} \quad (2-14)
\]

where

\[
C_2 = V_0 C_{SO} \left( \frac{\sigma_{HONO_2}}{\sigma_{OH}} \right) \left( \frac{\gamma_{NO_2} \gamma_{OH}}{\gamma_{HONO_2}} \right) \left( \frac{2I_{NO_2}^*}{h^2} \right) \left( \frac{2I_{OH}^*}{h^2} \right) \left( \frac{2I_{NO_2}^*}{h^2} \right)^{1/2} \left( \frac{2I_{HONO_2}^*}{h^2} \right) \left( \frac{2\pi \mu_p}{h^2} \right)^{3/2} \quad (2-15)
\]

and the constants are as in (2-10) and (2-11).

The \(k_d^*(\epsilon_{vk})\) values from (2-14) were used with a master equation approach to produce estimates of \(k_d(T,P)\) and \(k_{rec}(T,P)\) for (2-1) and (2-2). \(\rho_R^{vk}\) values were computed using the direct-count Beyer-Sweinhart/Stein-Rabinovich algorithm for all degrees of freedom, at lower energies. The OH torsion was treated in these calculations as a stiff vibrator, a free rotor, and a hindered rotor. Hindered rotor levels were direct-counted using the potential function described previously and the energy levels provided by the Shokhirev/Krasnoperov code. A convolved Whitten-Rabinovich approximation (in which the hindered rotor density of states was direct-counted while other degrees of freedom were evaluated via the Whitten-Rabinovich equation) was used for \(\rho_R^{vk}\) values at higher energies, when the hindered rotor treatment was employed. A FORTRAN code was written to evaluate (2-14).
2.7 Computation of $k_{rec}(T,P)$ with the Modified Strong Collision Approach

The fraction of the reactant R (HONO$_2$ or HOONO) formed at a given energy $\varepsilon$ that is stabilized by collision with the bath gas M can be approximated by

$$\phi(\varepsilon) = \frac{\beta_c k_c[M]}{\beta_c k_c[M] + k_d(\varepsilon)}$$  \hspace{1cm} (2-16)

where $k_c$ is a Lennard-Jones collision rate. $\beta_c$ represents the ‘collisional efficiency’ and is derived from the work of Troe in fitting master equation results to simpler forms [28;34]. From [34], $\beta_c$ may be written:

$$\frac{\beta_c}{1 - \beta_c^{1/\nu}} \simeq \frac{<\Delta E>_{all}}{F_E k_B T}$$  \hspace{1cm} (2-17)

where $<\Delta E>_{all}$ is the average collisional energy transfer between a bath gas molecule and the reactant R, and $F_E$ is an energy-dependence correction factor, typically between 1 and 2. We approximated $F_E$ as 1 in this work$^2$.

The recombination rate constant can then be written:

$$k_{rec}(T, P) = \frac{\int_0^\infty \rho_p^{ret}(\varepsilon) k_a(\varepsilon) \phi(\varepsilon) e^{-\Delta E/RT} d\varepsilon}{Q_p^{ret}}$$  \hspace{1cm} (2-18)

The $\rho_p^{ret}$ term in (2-18) was evaluated through a series of deconvolutions to allow evaluation of the rotational and translational portions as classical, and the vibrational density of states as a set of quantized harmonic oscillators. Both this term and the partition function $Q_p^{ret}$ contained the spin-orbit coupling correction for OH. When $k_{\gamma}^\omega$ is assumed constant with temperature, it can be shown $k_a(\varepsilon) = k_{\gamma}^\omega$. A FORTRAN code was written to evaluate (2-18) using the data listed in Table 2-1 and 2-2.

2.8 Computation of $k_{rec}(T,P)$ with the Master Equation Approach

The specific master equation for a single well is developed in many sources [24] and may be written

---

$^2$ This approximation is not really necessary since $F_E$ is easy to estimate, though the author did not realize this at the time of the work. However, it is close to 1 under the conditions studied.
\[ \frac{dn_i}{dt} = \omega \sum_j P_j n_j(t) - \omega n_i(t) - k_i n_i(t) \]  \hspace{1cm} (2-19)

where \( n_i \) refers to the population of the adduct in energy grain \( i \). In this treatment the exponential down model was used for \( P_j \). Equation (2-19) required inputs of \( k_{d}(\varepsilon) \) and \( \rho_{q}^{\infty} \) (first ILT approach) or \( \rho_{R}^{\infty} \) (second ILT approach), which were computed as described above. Equation (2-19) was solved for the dissociation rate constant \( k_{d}(T,P) \) using Shandross and Howard’s version of a master equation code which originated with Gilbert [52-55]. The minimum 100 cm\(^{-1}\) energy grains allowed by this code were insufficiently small, due to the relatively low temperature examined (300 K). We altered this code to allow 10 cm\(^{-1}\) energy grains.

Once \( k_{d}(T,P) \) was obtained, the appropriate equilibrium constant (with treatment of the OH torsion as a stiff vibrator, hindered rotor or free rotor, as appropriate) was used to convert to \( k_{rec}(T,P) \). \( \langle \Delta E_{all} \rangle \) values in Table 2-1 were converted to \( \langle \Delta E_{down} \rangle \), which is the parameter needed for the Gilbert/Shandross-Howard revised code, via (2-19), from Troe [48]:

\[ \langle \Delta E_{all} \rangle = \frac{-\langle \Delta E_{down} \rangle^2}{\langle \Delta E_{down} \rangle + F_{e}k_{q}T} \]  \hspace{1cm} (2-20)

Equation (2-20) gives \( \langle \Delta E_{down} \rangle = 433 \) cm\(^{-1}\) for \( \text{N}_2 \) and \( \langle \Delta E_{down} \rangle = 268 \) cm\(^{-1}\) for \( \text{He} \), using the \( \langle \Delta E_{all} \rangle \) values listed in Table 2-1.

2.9 \textit{A priori} calculations of \( k_{2}^{\infty} \)

To generate the predictions of \( k_{2}(T,P) \) in this work, it was assumed that the high-pressure limiting rate constants for \( \text{HOONO(I,II)} \) and \( \text{HOONO(III)} \) formation, \( k_{r,\text{HOONO(I,II)}}^{\infty} \) and \( k_{r,\text{HOONO(III)}}^{\infty} \), were equal to that for \( \text{HONO}_2 \) formation (\( k_{i}^{\infty} \) or \( k_{r,\text{HONO}}^{\infty} \)). These reactions are all barrierless radical recombinations, and the spin density in \( \text{NO}_2 \) is fairly evenly shared between the N and the O atoms, so that this assumption is not entirely unreasonable. This assumption is consistent with observations that organic radical reactions with \( \text{NO}_2 \) typically form approximately equimolar mixtures of \( \text{RNO}_2 \) and \( \text{RONO} \) species.
To test the assumption that \( k_2^\infty \) is comparable to \( k_f^\infty \), we performed \textit{ab initio} CVTST calculations for the recombination rate of \( \text{OH} + \text{NO}_2 \) to form \( \text{HOONO} \) using two different methods: UMP2 with a 6-311++G** basis, and RKS using the BLYP functional and a TZVP basis (A2 auxiliary basis). Around room temperature, the CVTST calculations were found to be sensitive to regions of the PES where the O-O bond length is greater than 2 Angstroms, and to the interaction energy between the two radicals at these moderately long distances. This leads to several difficulties. At a practical level, there are both SCF and geometry optimization convergence problems when computing the properties of weakly interacting fragments. These are reflective of the real underlying problems that there are several low-lying electronic states for two well-separated radicals, and that the PES is very floppy at long range. The electronic structure changes its character as the bond breaks; this leads for example to the famous separation of RHF and UHF potentials at long range. This effect is expected to lead to a rather large uncertainty in theoretical calculations of \( \text{D(HO-ONO)} \) discussed above. Also, conventional Gaussian basis sets we use are far from complete for these geometries. However, the CVTST "transition state geometry" is known to tighten with increasing temperature, moving in to a range where the PES is not so floppy, and the \textit{ab initio} calculations are more reliable. For this reason, we computed \( k_2^\infty \) at 3000 K as well as at lower temperatures of greater practical interest. Note that one would not expect this barrierless radical recombination rate to be strongly dependent on \( T \).

The CVTST calculations were performed treating the O-O stretch as the reaction coordinate, treating torsion about the O-O bond as a free internal rotor, and treating all other modes by the conventional rigid-rotor, harmonic-oscillator approximations. As expected, at very low \( T<150 \) K the rate is bounded by the Phase-Space Theory (i.e. very floppy TS) rate \( \sim 10^{14} \) [cm\(^3\)/mol/s]. At \( T\sim3000 \) K, the CVTST transition state moves in to \( R_{OO}\sim2 \) Angstroms, with a calculated \( k_2^\infty \sim 4 \times 10^{13} \) [cm\(^3\)/mol/s]. At moderate temperatures, the calculations were found to be highly sensitive to the difference between the energy of the long-range complexes and the completely separated fragments, a quantity which we cannot calculate precisely. However, for any reasonable value, the CVTST \( k_2^\infty \) was calculated to lie in the range of \( 10^{12} - 10^{14} \) [cm\(^3\)/mol/s]. Thus, \( k_2^\infty \) and \( k_f^\infty \sim \)
3x10¹³ [cm³/mol-s] appear to be of the same order of magnitude over the whole temperature range.

3 Results

3.1 \( k_{rc}(T,P) \) for HONO₂ in N₂ and He

In the following figures and text, the term "J-mode Included" indicates all rotational modes were allowed to contribute to reaction (first ILT approach); "K-mode Only" indicates only the K mode was allowed to contribute (second ILT approach). MSC refers to the modified strong collision approach and MEQ refers to the master equation treatment for collisional energy transfer. Pressures in all figures were calculated from bath gas concentrations using the Peng-Robinson equation and parameters from [41]. All predictions and data presented are at 300 K ± 5 unless otherwise noted.

![Figure 2-2](image_url)

**Figure 2-2.** Modified strong collision (MSC) and master equation (MEQ) \( k_{rc}(T,P) \) predictions for HONO₂ in N₂. "J-mode Included" indicates 1st ILT approach (in which all J mode energy contributes). "K-mode Only" indicates the 2nd ILT approach (in which no J mode energy contributes). All logs are common (base 10) in all figures. The J-mode Included/MSC and J-mode Included/MEQ predictions give essentially the same results, demonstrating the appropriateness of the modified strong collision approach for this system. Different treatments of the J mode energy have a large effect, and provide approximate upper and lower a priori bounds on the rate constant (see text, "Further Refinements to the \( k_{rc}(T,P) \) Prediction").
Figure 2-2 presents a J-mode Included/MSC prediction of \( k_i(T, P) \), the recombination rate constant for (2-1), in N\(_2\) with the OH arm treated as a stiff vibrator. A J-mode Included/MEQ prediction with the same OH moiety treatment, and a K-mode Only/MEQ prediction with the OH arm treated as a hindered rotor are also presented, along with data from [9], [10] and [11]. The thin dotted line represents the low-pressure limiting rate constant for the K-mode Only/MEQ prediction, estimated by the formula [29]

\[
[M] \beta_c k_s \int_0 \frac{P^k_s (\varepsilon_{sk} + \Delta E_0^k) \exp((-\varepsilon_{sk} + \Delta E_0^k)s)}{Q^k_R} d\varepsilon_{sk}
\]

(2-21)

where \( k_i^0 \) is evaluated from (2-21) by the equilibrium constant. This line confirms the K-mode Only/MEQ prediction at low pressure. The J-mode Included/MSC and K-mode Only/MEQ predictions of Figure 2-2 are within a factor of 2 above and 3 below the data, respectively. These are good accuracies for an a priori prediction of rates in which no rate data has been utilized and no parameters have been adjusted. The J-mode Included/MEQ open circles of Figure 2-2 agrees almost exactly with the J-mode Included/MSC line, confirming the appropriateness of Troe’s \( \beta_c \) formula (2-17) in single well cases.

The J-mode Included/MSC treatment in Figure 2-2 comes from the first ILT approach, and approximates a limiting case in which all of the energy in the 2-d external rotational mode, or J mode, contributes to reaction (via lowering of the barrier) and to the density of states \( \rho_R \) of the adduct in (2-11). The K-mode Only/MEQ treatment, from the second ILT approach, represents the other extreme, in which none of the energy in the J mode may participate in reaction or the density of states of the adduct. We believe these two limiting approaches to J mode participation bound the real \( k_i(T, P) \) and clearly bracket the available data at 300 K in N\(_2\). That the K-mode Only/MEQ and J-mode Included/MSC predictions approximately bound the prediction for (2-1) is supported by the relative insensitivity of these predictions to changes in parameters (such as \( \langle \Delta E_{alt} \rangle \)) or treatments of the OH moiety.
Figure 2-3 presents as a base case the $K$-mode Only/MEQ prediction of the rate constant for (2-1) with the OH moiety treated as a hindered rotor, the same as the solid line of Figure 2-2. The various thin dashed lines represent cases where the OH moiety was treated as a stiff vibrator and a free rotor, and cases where the value of $\langle \Delta E_{\text{down}} \rangle$ (from (2-20)) for $N_2$ was doubled to 866 cm$^{-1}$ and halved to 216 cm$^{-1}$. The thick dashed lines reflect different OH rotor treatments (stiff vibrator or free rotor) in the $J$-mode Included/MSC calculations.

The differences between treatment of the OH moiety as a stiff vibrator, hindered rotor, or free rotor, for both the first ILT approach ($J$-mode Included) and the second ILT approach ($K$-mode Only) are fairly small. The $K$-mode Only/MEQ treatment of the OH moiety as a free rotor results in an increase of only a factor of 1.4 in the rate constant prediction, over the ‘baseline’ $K$-mode Only/MEQ hindered rotor treatment. Treatment of the OH moiety as a stiff vibrator results in a rate constant prediction only 15% less than the hindered rotor treatment. One reason to expect this relative insensitivity to treatment of the OH moiety is that for HONO$_2$ this degree of freedom is one among ten (8 harmonic oscillators, 1 1-d or $K$ rotational mode, and the OH moiety), so that effects of the change in its treatment are lessened. Burkholder et al. in their calculation of a low-pressure limiting rate constant for (2-1) approximated the OH torsion with an adjusted stiff vibrator frequency, and found a somewhat similar insensitivity to the torsion frequency used [14]. That the treatments of the OH moiety as stiff and hindered agree so closely reflects the relatively high barrier for the OH hindered rotation, so that it behaves more like a stiff vibrator than a free rotor.
Figure 2-3. Predictions for HONO₂ in N₂ under variations in OH torsion treatment (free, stiff, hindered) and collisional energy transfer parameter. "K-mode Only" lines refer to the treatment in which only the K external rotational mode contributes to reaction (the 2nd ILT approach). "J-mode Included" predictions refer to the treatment in which both the K and J mode energies are considered to contribute (the 1st ILT approach). Data points are as in Figure 2-2. Predicted rates are only sensitive to the treatment of J-coupling in this system.

Figure 2-3 also reflects the relative insensitivity of the predictions to changes in the average downward collisional energy transfer, $\langle \Delta E_{\text{down}} \rangle$. Doubling or halving this parameter from its baseline value of 433 cm⁻¹ changes the rate constant prediction by less than a factor of 1.5. This insensitivity may be explained by the fact that at 300 K, the incoming fragments (OH and NO₂) are populated only in their lowest energy states. Their resulting adducts therefore need only lose a small amount of energy in order to be quenched below $\Delta E_0$ (see Figure 2-1). At lower temperatures, once the adduct has been quenched a little below the dissociation limit, the probability of reactivation is quite small, and therefore the calculations are relatively insensitive to the actual amount of energy transferred per collision.

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Figure 2-4. $k_r(T, P)$ predictions for HONO$_2$ under variations in $k_r^*$ and $\Delta E_0^r$. Data points are as in Figure 2. The predictions show very little sensitivity to these quantities. Prediction lines employ the $K$-mode Only/MEQ treatment (2nd ILT approach); the base case refers to $k_r^* = 3.3 \times 10^{13}$ [cm$^3$/mol-s] and $\Delta E_0^r = 47.7$ kcal/mol.

Figure 2-4 shows the effects of doubling and halving $k_r^*$ from a baseline value of $3.31 \times 10^{13}$ [cm$^3$/mol-s], and of increasing or decreasing $\Delta E_0^r$ by 1.5 kcal/mol. The effect of changing $k_r^*$ is almost negligible at lower pressures, and only becomes evident in the high pressure limit (where the calculations necessarily converge on their respective $k_r^*$ values). This effect should be expected, given the form of (2-16) and (2-18). At low pressures, $\phi(\varepsilon) = \beta r k_r[M]/k_d(\varepsilon)$. If this approximation is substituted into (2-18), with an expression such as (2-11) or (2-14) for $k_d(\varepsilon)$, the $k_r^*$ terms cancel (recall that if $k_r^*$ is independent of temperature $k_d(\varepsilon) = k_r^*$). The effect of changing $\Delta E_0^r$ is also quite small, for the same reason that the calculations are insensitive to large changes in $\langle \Delta E \rangle_{down}$. The well is quite ‘deep’ for the adducts of incoming fragments at 300 K, and small changes in its depth do not really affect the number of molecules that are quenched below the dissociation limit.
Figure 2-5. Predictions for HONO2 in He and N2 bath gas at varying temperatures, using the K-mode Only/MEQ approach in which no J mode energy contributes. The flattening of the curves at high pressure reflects the assumption of $k^-$ as insensitive to temperature.

Dransfield et al. report rate constant measurements for (2-1) at varying temperatures and at pressures of 50, 100, and 150 torr in N2 bath gas [7]. Our second ILT approach, K-mode Only/MEQ predictions (with the OH moiety treated as a hindered rotor) for $k_1(T, P)$ at 100 torr and varying temperatures are compared with their data in Figure 2-5. As is the case in Figure 2-2, this prediction is within a factor of 3 below the data, and this was consistent at 50 and 150 torr as well. Other lines in Figure 2-5 are $k_1(T, P)$ predictions for temperature dependence at 760 torr, and in the high-pressure limit ($1 \times 10^6$ Torr), where a relevant point from Fulle et al. is also displayed. The prediction in the high pressure limit is flat since $k_1^-$ was assumed constant with temperature; Fulle and coworkers found no temperature dependence for $k_1^-$ in their experimental measurements [9].
3.2 $k_{rec}(T,P)$ for HONO$_2$ and HOONO in He

Figure 2-6 shows predictions of $k_1(T,P)$ in helium bath gas. In analogy to Figure 2-2 both the first (J-mode Included) and second (K-mode Only) ILT treatments of the J mode are presented. Data from [8-11] are also presented. The two limits of J mode treatment, represented by the J-mode Included and K-mode Only predictions for HONO$_2$, again bracket the data, to within the accuracy of the $k_1$ value used. Burkholder and coworkers estimated a low-pressure limit, for a J-mode contributing case, of $k_1^0 = 1.6 \times 10^{-6}$ [cm$^6$/mol$^2$/s] in He, via the Troe formula for this limit [34]. This compares well with our value of $k_1^0 = 2.3 \times 10^{-6}$ [cm$^6$/mol$^2$/s], calculated via (2-21), for the J-mode Included case in Figure 2-6.

![Graph showing predictions for HONO2 and the summed rate constants for HOONO(I,II) and HOONO(III), written as HOONO(I,II + III), in He bath gas. As for the N2 bath gas predictions of Figure 2, differing J-mode treatments provide approximate upper and lower bounds on the rate constant for HONO2 formation. The dash-dotted line in the upper left corner indicates the sum of all recombination rate constants.]

The K-mode Only/MEQ predictions for two separate $k_2(T,P)$ calculations, the rate constants for the formation of HOONO(I,II) and HOONO(III), are also shown. The OH arm was treated in these as a hindered rotor, having the potential surfaces described by (2-4) and (2-5). The dash-dotted line beginning at log$_{10}$(P [Torr]) = 4.5 represents the
addition of the rate constant predictions for HONO₂, HOONO(I,II), and HOONO(III) formation.

4 Discussion

4.1 A Priori Estimates Without Transition State Information

The predictions for (2-1) in Figure 2-2 represent a nearly ideal scenario for estimating \(k(T,P)\) without specific transition state information. Our work employed well-estimated or measured energies, frequencies, moments of inertia, and hindered rotor potentials for all the species involved, and used a careful, full ILT approach designed specifically for the problem at hand. Importantly, it did not resort to parameter fitting and did not use measured data in its prediction of \(k(T,P)\) for (2-1). The effort yielded predictions within a factor of 3 of the data. This gives an upper bound for the expected accuracy of the similar, but more primitive, Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) approach. QRRK/MSC turns out to be the only currently-available practical method for estimating pressure-dependent rate constants on-the-fly during mechanism generation (see Chapter 3).

4.2 Further Refinements to the \(k_{ree}(T,P)\) Prediction for HONO₂ Formation

The \(K\)-mode Only/MEQ hindered rotor and \(J\)-mode Included/MSC predictions of Figure 2-2 remain the highest level, unadjusted a priori recombination rate constant predictions for the rate constant of (2-1) to date. They may be considered approximate upper and lower bounds on \(k_1(T,P)\), which represent different limiting treatments of the energy in the \(J\) or 2-d external rotational mode. All of this energy is considered to contribute to reaction in the upper-bound, first ILT approach (\(J\)-mode Included), and none of it is considered to contribute in the lower-bound, second ILT approach (\(K\)-mode Only). A thorough sensitivity analysis was not conducted, but Figures 2-3 and 2-4 imply that changes in the collisional energy transfer, \(k_c^\text{an} \) values, well depth, or treatment of the OH moiety (stiff, free or hindered) will not have an effect as strong as changes in the treatment of \(J\) mode energy. More accurate \textit{a priori} predictions of \(k_1(T,P)\) should therefore involve a more accurate treatment of the \(J\) mode energy. Explicit counting of
the $J$ states, in which the $k_d(e_{vk})$ of (2-14) becomes $k_d(e_{vk}, J)$ after Forst [47], followed by integration in both $e_{vk}$ and $J$, may be necessary.

Effects not examined in this work include vibrational mode anharmonicity, the $|K| \leq J$ restriction, and centrifugal/vibrational-rotational coupling. Of these, inclusion of anharmonicity effects in the densities of states calculations would tend to increase the predicted rate constant for recombination, through an increase in, for example, $\rho_{e^k}$. The effect might be as much as a factor of 2 increase in the rate constant prediction. The effects of applying the $K$ restriction and including centrifugal/vibrational-rotational coupling are not clear.

4.3 HOONO Channel's Effect on Experimental Attempts to Measure $k_f(T,P)$

The results in Figure 2-6 for the various HOONO channels suggest that at higher pressures (especially above 10,000 torr), the formation of HOONO might convolve efforts to measure the high-pressure limit for (2-1) via measurement of the decay of [OH]. Almost all of the experimental measurements of (2-1) were made under pseudo-first-order conditions, where $[NO_2] >> [OH]$ so the change in $[NO_2]$ over the course of the reaction is negligible. At the low temperatures and [HONO$_2$] employed, the reverse reaction HONO$_2$ $\rightarrow$ OH + NO$_2$ can be neglected. Typically the experimentalists measure the decay in [OH], and fit it to a single exponential form. This is roughly the same as setting

$$k_{expt} = (-1/\tau[NO_2]) \ln( [OH]/[OH]_0 )$$  \hspace{1cm} (2-22)

where the experimental measurement time $\tau$ is typically on the order of $1/k_f[NO_2]$.

If there are really two channels, and the second channel forming HOONO is reversible, the decays are really biexponential (though this difference from a single exponential form can be difficult to detect experimentally). We have derived the complicated analytical expressions for $k_{expt}$ as defined in Equation (2-22) in terms of $k_f$, $\tau$, $k_2$, and $K_2 = k_2/k_2$, assuming that the initial [HOONO] = 0. If $\tau = 1/k_f[NO_2]$, $k_{expt}$ will not differ by more than 10% from the true $k_f$ if $k_2/k_1 < 0.1$, or if $K_2[NO_2] < 0.22$. The latter inequality arises because no significant amount of HOONO can be formed if the
equilibrium strongly favors OH + NO₂ over HOONO. But if \( k_2/k_1 > 0.2 \) and \( K_2[NO_2] > 0.65 \), the measured \( k_{\text{expt}} \) is always significantly different from the true \( k_1 \). Although it is certainly very difficult to measure rates with an absolute error of 10\%, in this case one must be concerned about 10\% deviations: the atmospheric chemistry models are significantly sensitive to errors of this order of magnitude.

The theoretical calculations of this work are not accurate enough to allow one to be completely sure that \( k_2/k_1 > 0.1 \) above 10,000 torr, but our best a priori calculations suggest that this is true above atmospheric pressure (Figure 2-6). Density of states calculations in the low-pressure limit, via (2-21), show \( k_2/k_1 \geq 0.02 \) even in the low-pressure limit, and our CVTST calculation suggests that the ratio increases at high pressure.

Burkholder et al. made several experimental attempts to detect HOONO formation via (2-2) in the gas phase at bath gas pressures up to 850 Torr, using both direct spectroscopic detection, and measurement of the amount of HONO formed relative to OH consumed [14]. They were unable to detect significant HOONO formation with either technique, and found that HONO selectivity for the system of (2-1), (2-2) was \( 75^{\pm 25}\% \), at 300 K and pressures of 3 to 850 Torr. Their unimolecular rate constant calculations of the low-pressure limits \( k_1^0 \) and \( k_2^0 \) suggest that at low pressures in He, \( k_2/k_1 \) is in the range of 0.005-0.15. Our results in Figure 2-6 agree with this range, since we have \( k_2/k_1 \geq 0.02 \) in the low-pressure limit. At 850 Torr, Figure 2-6 suggests \( k_2/k_1 \leq 0.1 \) so that selectivity to HONO₂ would be ~90\%, well within the range established by Burkholder. The results in Figure 2-6 suggest that these researchers did not reach pressures high enough to produce HOONO in sufficient quantities for detection via the direct or indirect methods employed.

To be sure that the HOONO channel does not significantly affect measurements of \( k_1 \), experiments must be run under conditions where \( K_2[NO_2] < 0.22 \) at pressures above 10,000 Torr. At 300 K, we have calculated above that \( K_2 \sim 10^{10}\text{[cm}^3\text{/mol]} \), so the HOONO channel will not be important if the partial pressure of NO₂ < \( 10^{-6} \text{ bar} \) (e.g. ~ 1.0 ppm at 1 bar). Note that there is at least a factor of 5 uncertainty in the a priori \( K_2 \) calculation, in
part due to the uncertainties in *ab initio* calculations of $\Delta E_0^0$ (OH + NO$_2$ $\rightarrow$ HOONO) so the value of this cutoff limit is similarly uncertain.

Many experiments have been performed using very low [NO$_2$]'s below the cutoff, and these $k_1$ data are almost certainly not significantly convoluted with the HOONO kinetics. But some experiments, notably the most complete set of high pressure measurements by Fulle et al. [8;9], were performed using a much higher [NO$_2$] $\sim 2 \times 10^{-8}$ mol/cm$^3$, which gives $K_2[NO_2] \sim 200 >> 0.22$, where $K_2[NO_2] > 0.22$ implies experimental data are significantly convoluted with HOONO formation.

Hippler and coworkers recently revised the Fulle results downward by 30% [21] on the grounds that the static cell apparatus of Fulle et al. gave a systematic error. We feel values for $k_{\text{expt}}$ in the original experiments are probably significantly higher than the true $k_1$ at least partially because of HOONO formation. Our results are not accurate enough to allow us a detailed assessment of the degree of HOONO formation in the Fulle and Forster works [8;9] or in other high-pressure experiments, and we note that Hippler et al. do not give a detailed explanation of the static cell problems. In general the results of that investigation seem ambiguous concerning the possible convolution of high-pressure data for (2-1) with (2-2), and the authors do not make specific claims.

Under typical atmospheric conditions $k_2/k_1 < 0.1$, pressures are < 760 Torr, typical [NO$_2$] < 1000 ppb and $K_2[NO_2] << 0.22$. Thus our results imply that any HOONO formed via (2-2) in the atmosphere promptly falls apart, in contrast with the conditions at high-pressure, high [NO$_2$] experiments.

### 4.4 Recent Work on the OH + NO$_2$ System

Immediately following our effort, Golden and Smith published a hindered-Gorin rotor model for $k_1$ which was fitted to a subset of the data for (2-1), which they chose [22]. Their fit included a number of adjustable parameters, and so it is no surprise that the “predictive” curve for HONO$_2$ formation in their work fits the selected data better than our plot in, for example, Figure 2-3. Based on this fitting they attempted to predict the branching ratio for (2-2) and suggested that not only were certain high-pressure measurements of $k_1$ confounded by HOONO formation, but also that HOONO formation was likely important under atmospheric conditions (with $k_2/k_1$ approaching
20%). This predicted significance disagreed with our strictly a priori estimate that HOONO formation was probably less than or equal to 10% of the total OH + NO₂ rate constant under atmospheric conditions, though both works agreed that HOONO formation was a likely culprit for the differences in literature efforts to measure $k_1$. Some recent experiments disagree with Golden and Smith’s claims concerning the significance and lifetime of HOONO under atmospheric conditions [21:24].

Troe’s recent sophisticated theoretical/fitting effort addressed the treatment of the adiabatic $J$ mode energy [27], as well as many other deficiencies in both our a priori effort and the fitting work of Golden and Smith. By using a set of complicated corrective terms to the original Troe form [28], along with a SACM/CT approach to predict $k''$, Troe provided a more accurate fitting form for (2-1), for the atmospheric chemistry community, while addressing the inadequacies of the current a priori approach. Like Golden and Smith, after the fit to HONO₂ data, Troe also predicts the formation rate for HOONO. But Troe finds the HOONO branching ratio under atmospheric conditions to be 2.5% or less, and only significant at higher pressures (above 10,000 torr). That prediction agrees well with the HOONO results of our work. Neither the Troe effort nor the Golden and Smith work, however, were a priori; instead, they involved fits to existing data, making our work the only theoretical approach which did not resort to parameter fitting in order to predict the significance of HOONO formation.

In the past year, HOONO formation from OH and NO₂ in the gas phase has finally been observed both indirectly [21] and directly [25:26]. Thus the possibility of reaction (2-2) is no longer seriously in doubt (as it was when our work was published). The direct observations tentatively suggest a branching ratio of about 5% at 253 K and 20 torr of He/N₂ [25] but it is not yet clear whether the true kinetic branching ratio was measured. Recent measurements of HONO₂ formation by Donahue and coworkers [6] would imply Golden and Smith’s very high estimates for the HOONO branching ratio are correct, but this conclusion is inconsistent with the results of D’Ottone and coworkers [24], who also claim that remaining discrepancies in the low- and mid-pressure data sets for (2-1) cannot be explained entirely by HOONO formation.

Thus confusion remains concerning the exact ($\pm$ 10%) values for $k_1$, and even the high-pressure limit is still apparently unresolved. The extent to which (2-2) is significant
under atmospheric conditions remains a subject of contentious debate, which will probably only be resolved by direct observation experiments similar to Nizkorodov et al. [25,26]. In the wake of our work, along with Golden and Smith [22], and Troe [27], there does seem to be consensus that at least some experiments designed to measure the high-pressure limit of (2-1) actually measured the combined rates for (2-1) and (2-2). We presently feel that from the theoretical side, a high-level falloff calculation using a detailed potential surface in $E$ and $J$ is seriously needed before further progress can be made in predicting the significance of (2-2) in the atmosphere or at other conditions. A more solid theoretical estimate of $k_2^0$, along the lines of work by Klippenstein and Harding [56], is also necessary.

5 Conclusions

The calculations in this work represented the most accurate a priori predictions for the rate constants of reactions (2-1) and (2-2) to date (in 2001), and involved no adjustment of rate parameters. As such they demonstrate good agreement with the data. Reaction (2-1) is a simple, single-well system (if HONO$_2$ cannot isomerize to HOONO). These results therefore suggest we can expect an accuracy no greater than a factor of 3 when calculating a priori pressure-dependent rates without rate data. Such predictions are a focus of our work in systematic large kinetic model generation.

Figures 2-3 and 2-4 demonstrate the relative insensitivity of rate constant predictions to variations in the collisional energy transfer parameter $\langle \Delta E \rangle_{\text{down}}$, the high-pressure limit $k_2^0$, the well depth or dissociation limit $\Delta E_0^0$, and the treatment of the OH moiety as a stiff vibrator, hindered rotor, or free rotor. Further refinement of a priori predictions of $k_1(T,P)$ should involve more accurate treatment of the $J$ mode, possibly requiring a direct integration over the $J$ states in which the dissociation limit is dependent on $J$.

Data for the production of HONO$_2$ via (2-1) could be significantly convolved with HOONO production via (2-2) when $[NO_2] > 0.22/K_{OH+NO_2 \rightarrow HOONO}$ and $k_{r,HOONO} > 0.2k_{r,HONO_2}$. The lack of HOONO observed by Burkholder et al. may be due to the lower pressures used ($\leq 850$ Torr), such that $k_{r,HOONO} > 0.2k_{r,HONO_2}$ was not satisfied.
In light of our calculations, any data on $k_1(T, P)$ gathered with greater than 1.0 ppm NO$_2$ at high bath gas pressures (> 1000 Torr) must be regarded with caution. In particular, the extensive data measured by Fulle et al. appeared to be systematically too high due to convolution of channels (2-1) and (2-2) under their experimental conditions. Although Fulle and coworkers have recently revised their high-pressure data for (2-1), convolution of the results with (2-2) is still a real concern.

Appendix -- Spin Orbit Coupling of OH

The partition function for OH is rather different from the classical rotor expression. The OH(X$^2$Π) quantum states are labeled by |ΨJΩ⟩ where the angular momentum quantum numbers take the range:

$J = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots,$

$M = -J, -J+1, \ldots, +J$

$Ω = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ with the restriction that $|Ω| \leq J$

where $Ω$ is the quantum number for the projection of L+S on the O-H axis. The spectroscopic constants for OH are well known [52]. Using the spectroscopic energy expression, $Q_{\text{OH, quantum}}^{re}$ is very nearly linear in temperature from 200-1000 K and higher.

The classical electronic/rotational partition function is

$$Q_{\text{OH, classical}}^{re} = \gamma_{OH} \left( \frac{2 I_{OH}}{h^2} \right) k_b T; \quad \gamma_{OH} = 2$$

(2-23)

where $\gamma_{OH}$ is the electronic degeneracy. Equation (2-23) is strictly linear in temperature, and the ratio $Q_{\text{OH, quantum}}^{re} / Q_{\text{OH, classical}}^{re} = C_{SO} = 1.83$ is nearly constant with temperature.

Since $Q_{\text{OH}}^{re} = L[P_{OH}^{re}(e, \nu)]$ where L represents the Laplace transform,

$$\frac{Q_{\text{OH, quantum}}^{re}}{Q_{\text{OH, classical}}^{re}} = C_{SO} = \frac{L[P_{OH, \text{quantum}}^{re}]}{L[P_{OH, \text{classical}}^{re}]}$$

(2-24)

$P_{OH, \text{quantum}}^{re} = C_{SO} P_{OH, \text{classical}}^{re}$

if the very weak temperature dependence of $C_{SO}$ is ignored. The formula for $P_{OH, \text{quantum}}^{re}$ in (2-24) was used to include spin-orbit coupling effects in the OH density of states.
Citations

CHAPTER 3: PREDICTING $k(T,P)$ IN AUTOMATED MECHANISM GENERATION
1 Introduction

After completing the “warm-up” study of the OH + NO₂ system, we turned our attention to methods for estimating \( k(T,P) \) within the context of automated mechanism generation. As discussed in Chapter 1, we needed a fast, reasonably accurate method to predict \( k(T,P) \) for pressure-dependent networks of arbitrary size and complexity, without access to specific transition state information, or the full set of harmonic and rotational modes for each involved species. We chose the Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) code CHEMDIS, combined with the density-of-states code THERFIT, as it was the only available method that met these demands.

This chapter provides a very brief review of how the codes CHEMDIS [1] and THERFIT [2] together yield a prediction of \( k(T,P) \) which essentially requires only knowledge of the heat capacities of the isomers in a pressure-dependent network, and the high-pressure-limit modified Arrhenius forms (with meaningful activation energies) for all the network’s pathways. Certain collisional parameters are also needed, but these are discussed in later chapters.

After reviewing CHEMDIS and THERFIT, this chapter discusses the improvements and modifications we made to these codes. The modifications in Section 2 were used in all further chapters which mention CHEMDIS – the ASA screening algorithm, the H + cycloalkenes work, and the methane pyrolysis integrated example.

Next, we outline the errors and approximations associated with using CHEMDIS and THERFIT. CHEMDIS is highly approximate, and despite its practical success in this work and in many others, the use of CHEMDIS draws frequent criticism. We thus provide a justification for our use of these methods, following the discussion on error sources. Finally, based on the experience gained with these codes throughout the entire thesis, this chapter closes with recommendations for improvements to the CHEMDIS/THERFIT approach.

1.1 CHEMDIS Calculation of \( k(T,P) \)

CHEMDIS, a modified Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) code, was developed by Chang, Dean and Bozzelli to estimate
$k(T,P)$ for a multi-isomer pressure-dependent network of arbitrary complexity, without requiring specific transition state information [1]. It is based on the CHEMACT code of Dean, Bozzelli, and Ritter [3], which in turn was based on the original quantum-RRK formula of Kassel [4]. CHEMDIS brought two key improvements to QRRK/MSC techniques: a multi-frequency model for the density/number-of-states estimation, and the ability to handle a pressure-dependent network of any size and connectivity. A brief outline of the CHEMDIS code is given below; extensive details can be found in [1].

CHEMDIS first applies a graining, or “binning”, to the energies of each isomer, by partitioning the isomer’s energy distribution above the zero-point into grains of width $\Delta E$. It then calculates the microcanonical rate constant $k(E)$ from isomer $i$ to product channel or isomer $j$ by the modified QRRK formula:

$$k_{ij}(E,\Delta E) = A_{ij} T^{n_{ij}} \frac{\sum_{\Delta E} N(E-E_{ij})}{\sum_{\Delta E} N(E)}$$

(3-1)

where $k_{ij}(E,\Delta E)$ is the microcanonical $k(E)$ for the energy grain at energy $E$ above the zero-point, of width $\Delta E$. $A_{ij}$, $n_{ij}$ and $E_{ij}$ are the high-pressure-limit modified Arrhenius parameters for the channel$^1$. $\sum_{\Delta E} N(E)$ represents the number of states in width $\Delta E$ centered at energy $E$.

Note that in the set of modified Arrhenius parameters, the barrier $E_{ij}$ must have physical meaning – it must be related to the actual zero-point energy barrier for reaction. Ideally it is equal to $\Delta E_{ij}^0$, the difference in zero-point energy between the reactants and the transition state. Arrhenius parameters that have been fit carelessly, in which $E_{ij}$ has been allowed to “float” freely, are inappropriate for (3-1).

Equation (3-1) can be rewritten for convenience as:

$$k_{ij}(E,\Delta E) = A_{ij} T^{n_{ij}} \frac{\rho(E-E_{ij})}{\rho(E)}$$

(3-2)

---

$^1$ Equation (3-1) differs from the formula presented in the CHEMDIS paper, in that the temperature exponent appears here. Equation (3-1) is what actually happens in CHEMDIS.
which, when \( n_y = 0 \) and \( \Delta E \) approaches 0, becomes identical with the basic inverse Laplace transform of Forst [5]. In (3-2), \( \rho(E) \) represents the density-of-states at \( E \) calculated by taking the number of states within the width \( \Delta E \) and dividing by that width.

To evaluate Equation (3-1), CHEMDIS must calculate the number of states in the grains, \( N(E) \) and \( N(E - E_y) \). For this purpose the user supplies a set of frequencies and degeneracies for each isomer. These are meant to represent the behavior of the density-of-states and sum-of-states without being a complete listing of all the vibrational and hindered rotational modes (see below). CHEMDIS uses these frequencies and degeneracies, in a complicated \( n \)-convolved integral of gamma functions ratios, to evaluate \( N(E) \) where \( n \) is the number of frequency-degeneracy sets. For a single frequency-degeneracy pair \( (\nu, s) \) the number of states may be written:

\[
N(E/\nu) = \frac{\Gamma\left((E/\nu) + s\right)}{\Gamma\left((E/\nu) + 1\right) \Gamma(s)}
\]  

(3-3)

One instance of (3-3) exists for each frequency-degeneracy pair; these are all then convolved in a multiply-nested integral (one level for each pair) to compute the number of states \( N(E) \) or the density-of-states via \( \rho(E) = (N(E + \delta E) - N(E))/\delta E \).

CHEMDIS next combines the \( k(E) \) estimates in Equation (3-1) with a modified-strong-collision assumption, and the assumption of steady-state well populations for each energy bin. Once one has “binned” the energies into grains of \( \Delta E \), one can write down the mass balance for the concentration of each species or well \( i \) in the energy bin \( E_n \). For the case of chemical activation this balance is:

\[
\frac{d[C_i(E_n)]}{dt} = k_{wp}[R][R]f(E_n, T)\delta_{i,e} + \left\{ \sum_j (IS^T)_{i,j}[C_j(E_n)] \right\} - [C_i(E_n)]\left\{ \sum_j (IS)_{i,j} + \sum_m (PD)_{i,m} + k_i(T)[M] \right\}
\]  

(3-4)

Here \( [C_i(E_n)] \) represents the concentration of isomer \( i \) in energy bin \( E_n \). The terms of the right-hand side represent the various fluxes into and out of the energy bin. The first
right-hand term is the input channel term. It represents the flux into the bin from the
reactive collisions of the entrance adducts $R$ and $R'$, and is “active” only for that well
which is the first adduct of the entrance channel (as shown by the delta function $\delta_{i,c}$).
The high-pressure-limit rate constant $k_{\text{inp}}^\infty$ is that for the entrance channel species
combining to form the first adduct. The distribution function $f(E_n,T)$ comes from a
detailed balance involving the $k(E)$ for dissociation of the first adduct to the entrant
species.

The second term represents isomerizations from other wells to this well, via the
matrix of isomerization $k(E)$’s, $\mathbf{IS}$. The third term represents all fluxes out of isomer $i$ in
bin $E_n$. This includes isomerizations from well $i$ to other isomers $j$, exit channel pathways
to products (PD), and collisional deactivation via the modified strong collision
approximation. This last component is the classical modified-strong-collision (or “weak-
collision”) approach where:

$$k_i^i(T) = \sum_c X_c \beta_c(T) Z_c^{L-j}(T) \quad (3-5)$$

In this equation $X_c$ is the mole fraction of collider $c$ and $Z_c^{L-j}(T)$ is the Lennard-Jones
collision rate constant. $\beta_c$ is the collisional efficiency of collider $c$, and is a fraction less
than one. This parameter is at the heart of the modified strong collision assumption as
proposed by Troe and coworkers [6;7]. Its use can be interpreted as assuming that some
fraction $\beta_c$ of all collisions, between the activated species at energy $E_n$ and the bath gas
collider, instantly “thermalize” the species, deactivating it such that it undergoes no further
isomerization or decomposition in the current system. All other collisions do not affect
the species’ energy. This is clearly a gross oversimplification, but in practice it is
necessary, in order to avoid a master-equation approach. In CHEMDIS, $\beta_c$ is evaluated
from $\langle \Delta E \rangle_{\text{all}}$, the average collisional energy transferred from bath gas to species in
 collisions.

The steady-state assumption is next applied to Equation (3-4). At this point (3-4)
becomes a vector-matrix equation of the form $\mathbf{Ax} = \mathbf{b}$, and solving it yields the $k(T,P)$
rate constant estimates. An equivalent balance can be written and solved for the thermal
dissociation case.
1.2 THERFIT: The Three-Pseudofrequency Representation

CHEMDIS requires sets of frequency-degeneracy pairs for each isomer in a pressure-dependent network, in order to estimate the density-of-states or number-of-states for that isomer. In practice, three pairs of frequencies and degeneracies are used, supplied by the code THERFIT (from [2]). THERFIT examines the heat capacity data for a species, and using standard statistical-mechanical formulas, isolates that contribution to the heat capacity which comes from the vibrational and hindered or internal rotational modes of the molecule. It then assumes this contribution can be represented by a set of three frequency-degeneracy pairs, and employs a least-squares fit to find appropriate values for the frequencies and degeneracies. The degeneracies will generally not be integers.

Excellent fits to the heat capacity data can be obtained this way [2]. The high fit quality is, in some sense, no surprise, since the fitting routine involves 5 parameters (3 frequencies and 2 degeneracies, the third determined by the total number of modes in the molecule) which are typically fit to 8 heat-capacity data points. The fitted frequencies are not necessarily related to the actual modes of the molecule, hence the term “pseudofrequencies”. The three pseudofrequency-degeneracy pairs can be used as CHEMDIS inputs for the molecule.

2 Modifications to CHEMDIS and THERFIT

2.1 Boosting the Speed of CHEMDIS

The convolved approach for $k(E)$ in Equations (3-1) and (3-3) is CPU-intensive, both because of the nested integral effect and because gamma-function calculations are not fast operations. This approach is the bottleneck for CHEMDIS calculations. Even when a pre-calculated “table lookup” of gamma-functions was used, CHEMDIS still seemed too slow for on-the-fly $k(T,P)$ estimation in automated mechanism generation. We thus replaced the gamma-function method of (3-3) with a true direct-count number-of-states calculation, based on the Beyer-Swinehart method [8]. The external rotational mode, called the $k$-mode, was included using the method of Astholz and coworkers [9]. This mode, as discussed in the previous chapter, contributes to reaction and should be
included in any estimate of $k(E)$, but the nature of THERFIT is such that the three-pseudofrequency model does not include it. Thus it is added by CHEMDIS during the density-of-states calculation.

The modified version of CHEMDIS performs the direct-count sum-of-states once, at the beginning of calculation, for every isomer in the input file. The sum-of-states is then stored in a lookup array in grains of size $\delta_{\text{BS}}$, which is specified by the user but must be smaller than the calculation grain size $\Delta E$. In practice $\delta_{\text{BS}}$ is usually set to 5 or 10 cm$^{-1}$. Density-of-states or number-of-states estimates for use in Equation (3-1) are then easily and quickly derived from the sum-of-states array. The use of this fast direct-count method improved the speed of CHEMDIS calculations by a factor of 10-100, depending on the particular problem; it was this "fast" CHEMDIS which was used in all further chapters.

2.2 Modifying THERFIT for Integer Degeneracies

The above direct-count approach requires integer degeneracies for the frequency-degeneracy pairs, whereas THERFIT usually returns non-integer degeneracies. We modified THERFIT to produce integer degeneracies by first replacing its core numerical fitting routine with a true Levenberg-Marquardt non-linear fitting algorithm [10]. This algorithm allows one to "fix" certain parameters when desired, or relax them, without changing the source code.

The modified THERFIT first fits the heat-capacity data allowing non-integer degeneracies in the three-frequency model. Following this the code rounds the total number of modes (as evaluated in the original system, see [2]) to the nearest integer. Next, it checks the four possibilities for rounding of the degeneracies to the nearest integer; recall that once the total number of modes is set, one can set only two degeneracies in the three frequency-degeneracy model (the third is determined by the fact that the three degeneracies must add up to the total number of modes). The four possibilities are rounding both degeneracies upward, rounding the first up and the second down, rounding the second down and the first up, and finally, rounding both down. Each of these possibilities is examined by fixing the degeneracies at their rounded integer values and running the Levenberg-Marquardt fitting algorithm to fit the frequencies. The
modified THERFIT then selects that rounding possibility with the lowest sum of squared errors from the Levenberg-Marquardt approach.

This yields a set of three frequency/integer-degeneracy pairs which fit the heat capacity curve as well as any non-integer degeneracy and frequency model; Figure 3-1 below is typical. Indeed, it was found in the course of this work that a great many frequency/degeneracy pairs can usually fit the heat capacity data well, in part because the exercise ultimately involves fitting a five-parameter model to only eight data points. The other reason that many pseudofrequency models fit a single heat-capacity curve is that one is trying to evaluate the density-of-states, a quantized function with discrete values, by fitting to the heat capacity, which is an "integrated" collection of Boltzmann-weighted contributions to the partition function. Roughly speaking, the heat capacity "blends and smooths" density-of-states information, so that its fine structure (the quantized, discrete behavior) is very hard to extract, even if one has a large number of heat-capacity points. It is easy to go from the fine discrete structure of the density-of-states to the summed contribution heat capacity, but very difficult to go the other direction with resolution of the real discrete behavior.
Figure 3-1. Group additivity heat capacity for A2R5H (see above) in symbols, vs. integer-degeneracy 3-frequency fit. Symbols are group-additivity data points; line represents three-pseudofrequency fit with integer degeneracies. A very large number of different frequency/degeneracy pairs, integer or not, will fit a given heat-capacity curve. This curve is typical and we have almost never observed serious deviation from the heat capacity input (i.e. more than 5%) using our modified THERFIT code above.

2.3 Comparison of the Base and Fast CHEMDIS Approaches

The original and modified CHEMDIS approaches give different results for $k(T,P)$. The key reason for this is the introduction of artificial “noise” in the density/number-of-states estimates by use of the direct-count method as discussed below. Another reason may have to do with a possible bug in the original CHEMDIS code. We suspect the original code may not treat the hindered rotor contribution correctly at low energies, particularly near $E = 0$. It is hard to say for certain what the low-energy behavior should be in the original CHEMDIS, due to the complexity of the triply-convolved gamma-function system.

We quantitatively examined deviations between the “base” original version, which uses convolved gamma-functions with frequency/non-integer degeneracy pairs, and the “fast” version, which uses a direct-count sum-of-states and frequency/integer-degeneracy pairs. The “full” vinyl + O$_2$ system as studied by Chang and coworkers [1]
was chosen for study. The base and fast CHEMDIS results were compared at nine pressures (from $1.0 \times 10^{-3}$ atm to 100 atm) and fourteen temperatures (from 300 K to 3500 K) for a total of 126 $T,P$ points. The chemical activation case (vinyl + $O_2$ entrance channel) as well as the thermal dissociation of the first adduct (C*COO.), were both examined.

Over this range of $T$ and $P$, the chemical activation case revealed average differences of only 7% between the "base" and "fast" version predictions of $k(T,P)$ for each channel, with a maximum difference of 46%. Differences for the dissociation case were larger, with the average difference 30%, and the maximum difference a factor of 2. In both cases (fast and base) the worst differences were seen at the lower temperatures and pressures. Figure 3-2 shows rate constant predictions for the chemically activated system at $1.0 \times 10^{-3}$ atm and over the range of temperatures. Most predictions of the fast and base cases are not significantly different.

![Figure 3-2](image)

Figure 3-2. "Fast CHEMDIS-Integer THERFIT" and "Base CHEMDIS" predictions of $k(T,P)$ for selected channels of the chemically activated vinyl + $O_2$ system at 0.001 atm and temperatures from 300 to 3500 K. Symbols represent the modified fast CHEMDIS/integer THERFIT approach, lines represent the base CHEMDIS approach using THERFIT with non-integer degeneracies. The worst chemical-activation case disagreement between the fast and base methods, over the whole temperature-pressure space explored, is highlighted. Most base and fast predictions give essentially the same results.
2.4 Other Changes to CHEMDIS

2.4.1 Average Collisonal Energy Transfer

CHEMDIS was modified to take \( \langle \Delta E \rangle_{down} \) directly, at the user's instruction, and to calculate \( \beta_c \) from this parameter instead of \( \langle \Delta E \rangle_{all} \). This avoided the conversion from \( \langle \Delta E \rangle_{all} \) to \( \langle \Delta E \rangle_{down} \) embedded in the original method [1], but was otherwise the same approach to evaluating \( \beta_c \). This change was made on the assumption that \( \langle \Delta E \rangle_{down} \) would vary less with temperature than \( \langle \Delta E \rangle_{all} \).

2.4.2 Working with MULTIWELL

As noted in the next chapter, CHEMDIS was modified to produce tables of the densities of states with energy, for each isomer in the pressure-dependent network. It also builds tables of the microcanonical rate constants for each pathway in the network. These are formatted as inputs for the Barker MULTIWELL master-equation code [11;12]; they are exactly the same densities-of-states and microcanonical rate constants used within the CHEMDIS calculation. This ensures that the sole difference between a CHEMDIS prediction and the comparable MULTIWELL prediction is the treatment of collisional energy transfer.

3 Challenges of the CHEMDIS/THERFIT Approach

3.1 Artificial Noise in the Direct Count Method

The three-pseudofrequency fitting method of THERFIT assigns no physical significance to the frequency-degeneracy pairs, other than that they happen to reproduce the heat capacity data. They are assumed to give an appropriate representation of the density-of-states, within a smoothed, convolved gamma-function-based approach. But using a direct-count method with these frequencies inherently assigns them significance as actual harmonic modes of the molecule.

Specifically, using the direct-count method with a set of three frequency-degeneracy pairs will produce very large, artificial "spikes" in the density-of-states, at
low energies that are multiples or summed combinations of the degenerate frequencies. If, for example, a certain molecule really did have 8 modes at exactly 1200 cm\(^{-1}\), the direct-count spike would accurately reflect the huge change in densities of states when \(E\) first exceeds 1200 cm\(^{-1}\). But no real molecule is like this, and the true density-of-states will reflect a spread of separated modes. It will be much smoother than what the direct count results of the three-frequency model will reflect.

Under moderate to high temperatures and moderate or higher pressures, this effect will not be very serious, since a wide range of energies (or energy bins, in CHEMDIS) will be important for the deactivations, decompositions and isomerizations of activated species. But at low temperatures and pressures, \(k(T,P)\) calculations will depend on relatively few values of \(k(E)\), over a narrow range of energies near the barriers for reaction pathways. This is particularly true if a well has a low-energy isomerization or exit channel near its zero-point energy. In these cases \(k(T,P)\) will be strongly affected by even minor inaccuracies in the density or number-of-states estimates which feed into Equation (3-1).

3.2 The Failure to Satisfy Detailed Balancing

The modified QRRK formula for the microcanonical rate constant, expressed as (3-1) or (3-2), inherently fails to satisfy the detailed balancing requirement. To see this, consider a very simple “thermoneutral” pressure-dependent network, in which species \(C\) and \(D\) have the same zero-point energy and the same barrier to isomerization, and there are no other species in the network, as shown in Figure 3-3.

![Figure 3-3. Hypothetical, thermoneutral pressure-dependent network for demonstrating the QRRK detailed-balance failure.](image)
In this system, detailed balancing requires that

\[ k_{CD}(E) \rho_C(E) = k_{DC}(E) \rho_D(E) \tag{3-6} \]

Substituting in Equation (3-2) for the microcanonical rate constants, assuming temperature exponents are 0, and leaving out the graining \( \Delta E \), Equation (3-6) becomes:

\[ A_{eD}^w \rho_C(E - E_0) = A_{eC}^w \rho_D(E - E_0) \tag{3-7} \]

where the densities-of-states at energies \( E \) have cancelled on each side. This can be rewritten:

\[ \frac{\rho_D(E - E_0)}{\rho_c(E - E_0)} = \frac{A_{eD}^w}{A_{eC}^w} \tag{3-8} \]

which must be false, because it claims the ratio of the densities-of-states of \( D \) and \( C \) must always be fixed at every energy.

Statistical thermodynamics does require for this example that

\[ \frac{Q_D}{Q_C} = \frac{A_{eD}^w}{A_{eC}^w} = \int_0^\infty \frac{\rho_D(E) e^{-E/kT}}{\rho_C(E) e^{-E/kT}} dE \tag{3-9} \]

but this in no way implies (3-8). For example, if \( C \) and \( D \) have no relevant rotational modes and their lowest vibrational modes are \( \nu_{C,1} \) and \( \nu_{D,1} \), such that \( \nu_{C,1} < \nu_{D,1} \), then the ratio on the left-hand side of (3-8) must change in the regions around \( E - E_0 = h\nu_{C,1} \) and \( E - E_0 = h\nu_{D,1} \) even if all the rest of their modes are the same. QRRK could also violate detailed balancing in any system more complex than the simplified one illustrated here.

### 3.3 The Low-Energy \( k(E) \) Limit and Tunneling Corrections

Equation (3-1) does not have the proper low-energy Rice-Ramsperger-Kassel-Marcus (RRKM) limit for \( k(E) = \frac{1}{\hbar} \rho(E) \). This adds to prediction problems at low temperature and pressure, where \( k(E) \) values near the barrier (i.e. at low energies) become quite important. The QRRK formula also, without access to transition state or potential surface information, cannot correct for tunneling, which again can be a serious issue at low temperature.
3.4 The Modified Strong Collision Assumption

The use of the modified strong collision assumption throughout this work typically draws the most frequent criticism from the wider physical chemistry community. This assumption is actually two approximations used together: first, the populations of all activated species are assumed to be in steady-state, and second, collisions which deactivate an isomer are assumed to deactivate completely, so that the isomer undergoes no further reaction. In reality, collisions can move a species both upward and downward in energy, a single collision does not deactivate an isomer completely, and populations of the isomers are time-dependent. The time-dependent master equation is considered the most accurate way to treat a multi-well pressure-dependent network, and is reviewed in any current text on unimolecular reactions [13;14].

4 Why Choose the CHEMDIS/THERFIT Approach?

The obvious deficiencies in using the above Quantum-Rice-Ramsperger-Kassel approach, the clear difficulties inherent in the modified strong collision approximation, and the rough method for estimating densities-of-states by heat capacity fitting, are all distressing to many physical chemists. Objections to our work are generally focused on the use of these methods; Holbrook and coworkers have stated, in a popular textbook, that “the extra demands of the more realistic RRKM treatment are not much greater” and that “further refinement of the quantum RRK treatment is not justified” [13] p. 37. In practice, however, the ‘extra’ demands of RRKM are much greater – access to transition state information is expensive. Indeed, the context of mechanism generation really leaves no choice but to employ the QRRK/MSC at present, for the following reasons.

First, no automated approach to mechanism generation can seriously estimate the modes and geometries of the transition states and reacting species “on-the-fly”. The required high-level ab initio calculations can be very time-consuming (the average transition-state search taking, at a minimum, a few hours of CPU time). Computers will need to be orders-of-magnitude faster before automation of these calculations is worthwhile; still, computing power grows rapidly enough that someday these ab initio searches could be made online. More seriously, the results of such calculations are often
only meaningful in the hands of the skilled computational chemist, who provides a necessary "reality check" on any computational output. It seems to us that there are currently too many pitfalls involved in running \textit{ab initio} calculations, even for an "easy-to-use" code such as GAUSSIAN [15], to make them automatic.

Second, most master equation approaches voraciously consume CPU time. Switching from the modified strong collision approach to a master equation approach could boost the time required for a $k(T,P)$ estimate by a factor of 80,000 or more, if one chooses a popular Monte-Carlo-based trajectory approach (we have not explored more recent direct- or eigenfunction-based, publicly-available solutions to the multi-well master equation). Master-equation approaches also require expert user involvement. The user must decide when the time-dependent master equation system has reached steady-state (if at all), and whether the timescale required for it to do so is faster than the timescale of the overall problem. Some confusion still surrounds the extraction of rate constants from multi-isomer master equation solutions, so that it is difficult to pose the rigid criteria needed for automation.

Finally, for all its apparent deficiencies, the CHEMDIS/THERFIT approach \textit{works} in practice (possibly in part by error cancellation; see the next chapter). In cases where the results are compared with data or with high-level RRKM-master equation approaches, the CHEMDIS/THERFIT method does surprisingly well, typically predicting absolute or relative $k(T,P)$ values within, at least, a factor-of-10 of the data, but usually much better [1;3;16-23]. We know of no systematic study of the error bounds or accuracy of the QRRK/MSC approach; furthermore, as discussed in the next chapter, the expected accuracy of input data for automated mechanism generation rate rules is within a factor of 10.

\section{5 \textbf{Recommendations for Future Fast $k(T,P)$ Codes}}

In our view, the QRRK/MSC approach with pseudofrequency density-of-states models strikes an excellent balance of speed, accuracy and available information. Many improvements to our chosen $k(T,P)$ method are possible, however, which could resolve some of the major challenges while avoiding the need for detailed frequencies and rotational modes for all species and transition states.
5.1 Revisit the Density-of-States Estimates

As computing power rapidly improves, the need for a fast direct-count density-of-states may diminish. Thus it may be desirable to revert back to the convolved gamma-function approach in CHEMDIS, after correct treatment of the 1-d $k$-mode can be confirmed. It is even better to reconsider the derivation of density-of-states from the heat capacity.

Theoretically, one can bypass the 3-frequency fitting model entirely by using inverse Laplace transforms of the statistical-mechanical formula for the heat capacity, especially if one has a fitted form for the heat capacity curve. Numerical inverse Laplace transforms are possible, so the tractability of an analytic anti-transform may not be a serious concern. In any case, thought should be given to a smoother route from a molecule’s heat capacity data points to predictions for the number or density-of-states function. Even if the three-frequency model is used, perhaps smoothing or enforced spreading of the modes can be applied in a code like THERFIT.

Alternatively, one could rework the fitting process by first examining the chemical groups of the molecule. Certain groups or structures can often be associated with certain harmonic or rotational modes; Bozelli and coworkers have frequently exploited this fact (e.g. RADICALC [24]). The computer could construct a trial set of frequencies and hindered internal modes based on the chemical structure, and then refine it in a controlled fitting to the heat capacity data. CHEMDIS could be then modified to take full frequency and rotational barrier sets to predict the density-of-states. Ideally, this would produce a set of frequencies and hindered modes that would be closer to the real species – in any case the resultant density-of-states curve would be much smoother and more realistic. It would also be desirable to modify CHEMDIS to accept real, full frequency and internal rotational mode information where this is available.

5.2 Consider Inverse Laplace Transform for Thermodynamic Consistency

The QRRK approach violates detailed balancing, but it may be possible to avoid this while still not requiring detailed transition state information. Note that the traditional inverse Laplace transform approach would also violate detailed balancing here because the usual ILT formula is identical to (3-2) when the temperature exponent is 0. A more
complicated ILT approach could use a temperature-dependent equilibrium constant to convert the high-pressure limit $k_f^*$ for the forward direction into $k_r^*$, and then apply an anti-transform to obtain $k(E)$. Thus one could essentially transform in only one reaction direction, ensuring the opposite direction's $k(E)$ values would be thermodynamically consistent. Once again, numerical inverse transforms may be the best approach to avoid analytical tractability problems.

5.3 Develop A Fast Master Equation Algorithm

Replacing the modified strong collision assumption will be difficult, since most approaches to the master equation are computationally intensive. Furthermore, in multi-isomer cases they sometimes require the user's specific involvement in order to extract rate constants from the results, for a variety of reasons.

First, unlike the modified strong collision approach, the master equation cannot always distinguish between chemical activation processes and subsequent thermal dissociative processes. These can occur simultaneously (i.e. they can be convolved) in a master equation calculation and are not always easily separated. Any fast, automated approach to the master equation may need to resolve this issue.

A related question is that of selecting the appropriate timescale for master equation results. The master equation is of course time-dependent [13;14]. In, for example, a multi-well chemical activation case at very short times, almost all “trajectories” of the chemically activated entrance reactions are in the first adduct well; the apparent rate constant to the first isomer will thus be quite high, and the apparent rate constants to other pathways will be very small. At very long times, all trajectories must leave the system through product channels, and so apparent rate constants to all the isomers will be very small. At some range of times between very short and very long, there is often (but not always) a steady-state regime, which is used to extract the "true" rate constants. While it may be easy for a human to find the steady-state, the computer will need to do this automatically and numerically. Furthermore, one will sometimes need to be aware of the problem timescale – it may not be the same as that required for the master equation system to reach its steady-state.
Finally, we see possible confusion over what should be called a "rate constant". If isomer \( C \) in a master equation solution, at steady-state, has a distribution in energy that is significantly different than the thermal distribution, is it proper to assign a rate constant to \( C \)? In other, non-pressure-dependent reactions of a mechanism, \( C \) will be assumed thermalized, so a rate constant to non-thermal \( C \) may not be appropriate in a mechanism where \( C \) is assumed to have a thermal distribution.

Knyazev and Tsang have proposed the "pseudocomponent" method for reliably extracting meaningful rate constants from any single-well master equation result, but this has yet to be extended to multi-well systems [25]. A variant of this approach might be turned into an automated process. A compromise approach is also possible, in which the populations of activated species at different energies are still assumed to be at steady-state, but a more accurate representation of collisions is used, such as the exponential-down model. A. M. Dean, A. Y. Chang, and others have employed versions of this technique [16;26] but for reasons not clear, this compromise method sees only limited use.

5.4 Examine Low-Energy and Tunneling Corrections

The low-energy limit for \( k(E) \), \( 1/\hbar \rho(E) \), is easily estimated without transition-state information. Thus a fast \( k(T,P) \) code could automatically interpolate between an ILT or QRRK formula for \( k(E) \) and \( 1/\hbar \rho(E) \) at low energies. Adding even a crude tunneling correction, such as \( k''(T) = \kappa(T)k^{TST}(T) \), will be much harder without access to the potential surface or at least the transition state. However, it may be possible to write reaction-class-based forms for \( \kappa(T) \) [27], which could be converted into \( k(E) \) corrections. The actual importance of the tunneling correction for combustion or pyrolysis cases is probably quite small; if one is interested in generating low-temperature atmospheric chemistry mechanisms, however, it may be much more important.
Citations

CHAPTER 4: RATE-BASED SCREENING OF PRESSURE-DEPENDENT REACTION NETWORKS. THE ACTIVATED SPECIES ALGORITHM
1 Introduction

Rapidly estimating $k(T,P)$ values for any pressure-dependent network, on-the-fly, with very limited information, is only one component needed for allowing pressure-dependence in mechanism generation. Some selection of a pressure-dependent network would be needed to predict the rate of a given reaction, but how much? When fully explored, pressure-dependent networks are far too large and unwieldy for an automated approach. The vinyl radical + O$_2$ system studied by Mebel and coworkers contains at least 30 species and 62 intermediate reactions [1]; the HCCO + NO system studied by Sumathy and coworkers has at least 60 species and 120 intermediate reactions [2]. The chemically activated isopropyl radical plus isoprene system can give over 200 isomers, when only beta-scissions, intramolecular additions and hydrogen shifts are allowed. In addition to including many unimportant channels, rate predictions for these large pressure-dependent networks can be difficult.

The computer must therefore intelligently and systematically screen such networks, somehow constructing or capturing only the essential part at the conditions specified. Most researchers do this anyway, by intuition or estimation, but a computer algorithm can only be systematic. This chapter describes a reliable, automated method for truncating pressure-dependent networks, in which the error in $k(T,P)$ predictions incurred by truncation is small and bounded. It is consistent with the rate-based termination used for larger, overall mechanism generation, and avoids calculation of rates for the negligible isomers and pathways in the full pressure-dependent network. Either the user or an automated mechanism generation program can supply $R_{\text{min}}$, the rate-based termination criteria for screening.

We show that the predicted rate constants for a screened channel network (where we have not included unimportant pathways) do not differ significantly from rate constant predictions which include all possible channels. Hence a properly truncated pressure-dependent network may be used in overall mechanism generation without loss of accuracy.

The experience of the previous chapter in heavily modifying CHEMDIS allowed us to embed the method into CHEMDIS itself, so that it will screen and truncate the
network at the user's instruction. This work appeared as the article "Rate-based screening of pressure-dependent reaction networks", David M. Matheu, Thomas A. Lada, II, William H. Green, Jr., Anthony M. Dean, and Jeffrey M. Grenda, Computer Physics Communications, volume 138, pages 237-259 (2001).

1.1 Prediction of Pressure Dependent Rates

Many methods exist to predict pressure-dependent reaction rates once the connectivity of the pressure-dependent network is known; these methods incorporate varying degrees of approximation and accuracy [3-5]. Our purpose is to explore pressure-dependent networks and predict their rate constants quickly given the information available within a mechanism generation code. We have thus chosen the modified version of CHEMDIS in Chapter 3 as an efficient balance between the need for accuracy and the constraints of limited information and computation time. All information required to build a CHEMDIS input file can be obtained from data already available within many mechanism generation codes, such as rate rules, high-pressure-limit rate constants, and group-additivity thermochemistry.

CHEMDIS is an approximate code for predicting $k(T,P)$ which employs the modified strong collision assumption. This work tested the modified strong collision assumption of CHEMDIS against the more accurate master equation for selected cases, using the most recent version of the MULTIWELL code of Barker [6-8]. The results of this comparison suggest that the modified strong collision approach is accurate enough for the purposes of screening out negligible channels; the smaller, screened network could then be analyzed by the master equation, if desired, to compute $k(T,P)$.

2 Algorithm Description and Walkthrough

2.1 Overview

The algorithm is named the "Activated Species Algorithm", or ASA, since it stores chemically or thermally activated species as though they were distinct species. Like many mechanism generators, it maintains a pool of Reacted Species, whose pathways in the pressure-dependent network have been explored, and a pool of Unreacted Species which includes species that have been discovered, but not yet
explored. The connectivity of the pressure-dependent channel networks is stored in an *Activated Species Tree*.

Figure 4-1 represents an overall flowchart of the algorithm. The user supplies an input file containing the full pressure-dependent network connectivity, the high-pressure-limit Arrhenius forms for the rate constants, temperature, pressure, and a tolerance parameter \(0 < f_{\min} < 1\) which is used to compute the rate-based termination criteria \(R_{\min}\). The ASA then builds, in a step-by-step approach, a partial, 'screened' pressure dependent network, which contains only those pathways deemed important by the rate criteria. The screened pressure-dependent network is complete when the summed flux to all non-included isomers is below the rate criteria \(R_{\min}\). \(k(T,P)\) predictions are generated for all important isomers and product channels. The algorithm can also work by using a mechanism generation tool to supply the incremental connectivity changes instead of the full network connectivity [9;10].

![Flowchart of ASA Algorithm](image)

**Figure 4-1.** Overview of the ASA algorithm. Initiation steps start Activated Trees, which incorporate current knowledge of pressure-dependent reaction network connectivity; exploration and rate estimation steps add to these networks and predict the rate constants based on that knowledge.

### 2.2 Initiation

The ASA begins with a chemically or thermally activated reaction. As an example, we consider the initial, chemically-activated reaction of \(A + B \rightarrow C^*\), where \(C^*\) is an activated complex with multiple isomerization and decomposition possibilities. When the user declares this reaction as the entrance reaction to a pressure-dependent network, the ASA initiates an *Activated Species Tree* and loads it with the connectivity \(A + B \rightarrow C^*\). \(C^*\) is added as an *Unreacted Species*. The reaction \(A + B \rightarrow C^*\) is then added
to the Reaction List, with the high-pressure-limit rate constant $k^\infty$. Using $k^\infty$ as the rate constant at this stage gives the maximum possible flux, through the $A + B$ channel, to any possible species in the pressure-dependent network.

2.3 Exploration and Rate Estimation

The reactions of $C^*$ are next explored and added to the Activated Species Tree. In our example these are isomerizations to $D^*$ and $F^*$ and back-decomposition to $A + B$. The new activated species discovered, $D^*$ and $F^*$, are treated, at this stage, as product channels, and are added to the Unreacted Species pool. After exploring all reactions of $C^*$, this activated species is removed from the Unreacted Species pool and the stabilized $C$ species is added. The activated species tree at this stage is shown in Figure 4-2. The algorithm then builds the CHEMDIS input file for a pressure-dependent network with the connectivity represented in Activated Species Tree; that is, with entrant species $A$ and $B$, entrant isomer $C^*$, and “product channels” $D^*$ and $F^*$. After building the input file, the algorithm runs CHEMDIS to generate estimates of $k(T,P)$ for the reactions currently shown in the Reaction List. The reaction $A + B \rightarrow C^*$, with rate constant $k^\infty$, is then replaced with the reaction $A + B \rightarrow C$, with the rate constant $k_C(T,P)$ generated by CHEMDIS. The reactions to $D^*$ and $F^*$ are added with $k(T,P)$ estimates. The treatment of $D^*$ and $F^*$ as product channels (neglecting their back reactions) ensures computation of the maximum possible flux through these pathways, so that if they are important, they will be included by the algorithm.
EXPLORATION AND RATE ESTIMATION

- Explore reactions of C° and add to Activated Species Tree

![Diagram of reaction network]

Entrant IDs: A, B
Connectivity:

A + B ⇌ C°

D° → C°

F° → C°

C

Treat D°, F° as 'exit' or product channels.

- After $k(T, P)$ Calculation ...

Unreacted Species

D°, F°

Reaction List

$A + B \rightarrow C$  $k_c(T, P)$

$A + B \rightarrow D°$  $k_{D°}(T, P)$

$A + B \rightarrow F°$  $k_{F°}(T, P)$

Figure 4-2. Exploration and rate estimation steps.

At this point, the algorithm computes $R_{\text{leak}}$ and $R_{\text{min}}$, to define and evaluate the rate-based screening criteria. $R_{\text{leak}}$ is defined as the sum of fluxes to all non-included isomers:

$$R_{\text{leak}} = \sum_j k_j(T, P)$$  \hspace{1cm} (4-1)

In this example, $R_{\text{leak}} = (k_{D°}(T, P) + k_{F°}(T, P))$ at this stage. Note that for $R_{\text{leak}}$ to have actual units of chemical flux (e.g. molecules/cm³-s) it must be multiplied by the concentrations of the inlet species [A] and [B]. For simplicity we leave all such concentrations out of the equations in this work.

$R_{\text{min}}$ is defined as

$$R_{\text{min}} = f_{\text{min}} R_{\text{char}}$$  \hspace{1cm} (4-2)

where $R_{\text{char}}$ is the characteristic rate for the pressure-dependent system:

$$R_{\text{char}} = k_{\text{imp}}^- \hspace{1cm} (\text{chemical activation})$$  \hspace{1cm} (4-3)
\[ R_{\text{char}} = \int_{E_0} E_{\text{exc}} k^+(T)[M] \frac{\rho_c(E) \exp(-E/k_BT)}{Q_c} \text{d}E \]  

(dissociation) \hspace{1cm} (4-4)

Similar to equation (4-1), multiplying equation (4-3) by [A][B] and equation (4-4) by the concentration of the dissociating species [C] gives units of [molecules/cm^3-s]. These equations represent the total "input rate" to the pressure-dependent network. For chemical activation, this is simply the high-pressure limit rate constant (4-3). For dissociation, this input rate is the fraction of collisions between entrant isomer C and the bath gas which produce \([C'(E)]\) at energies above the lowest barrier to dissociation (4-4). A full explanation of the terms in (4-4) may be found in Chang, Bozzelli and Dean [12]; briefly, \(\rho_c(E)\) is the density of states for \(C\) at energy \(E\); \(Q_c\) is the partition function for \(C\). The example in this walkthrough is a chemical activation case \((A + B \rightarrow C')\) so that (4-3) is used to calculate \(R_{\text{char}}\).

2.4 Evaluation of \(R_{\text{min}}\) and Pathway Selection

The algorithm next examines whether the summed flux to non-included isomers is greater than \(R_{\text{min}}\), e.g. \(R_{\text{leak}} = (k_{D^*}(T,P) + k_{F^*}(T,P)) > R_{\text{min}}?\). If \(R_{\text{leak}}\) is less than \(R_{\text{min}}\), the screened network is complete and the algorithm terminates. If not, the isomer corresponding to the largest element of the sum in (4-1) (that is, the dominant pathway) is selected as the next candidate for exploration. We imagine for this illustration that \(R_{\text{leak}} > R_{\text{min}}\) and \(k_{D^*}(T,P) < k_{F^*}(T,P)\) so that the reactions of \(F^*\) are explored next. The Activated Species Tree and Reaction List are then as shown in Figure 4-3. The ASA continues in this way, exploring the reactions of activated species until the sum of all fluxes through unexplored reactions pathways is below \(R_{\text{min}}\). We have added our own routines to the modified CHEMDIS code to implement this algorithm, and present applications to single pressure-dependent networks below.
• After exploration of $F^*$ reactions ...

Figure 4-3. Activated species tree after the exploration of $F^*$

3 Examples

The ASA described above has been applied to many dissociation and chemical activation systems; in this work we show results for the vinyl + O₂ system [1;12], the phenyl + acetylene system and the 1-naphthyl + acetylene system [13]. Data for the input files were taken from the listed references; detailed potential energy surfaces can also be found in these works. All the examples we have examined (including those not in this work) illustrate the fact that rate predictions for the screened network (in which non-included isomers are treated as product channels) are virtually indistinguishable from rate constant predictions in which the entire network is used as input. This is true for all reactions whose flux is sufficiently larger than $R_{\text{min}}$ (a more precise error bound is given in Section 4). In all following sections, $R_{\text{min}}, R_{\text{leak}}$ and $R_{\text{char}}$ are considered divided by the concentrations of the entrant species (e.g. by $[A]$ and $[B]$ in (4-3)), so that they have units of the rate constant.
3.1 Vinyl + O$_2$

Vinyl radicals are important for combustion reactions and may have a strong influence on PAH formation; it is proposed that consumption of these radicals by reaction with oxygen may retard soot growth [1]. Using input data from Chang et. al. [12], we constructed an input file for a 4-isomer version of the vinyl + O$_2$ system as shown in Figure 4-4. The species and network connectivity included by the ASA for two different conditions (500 K and 3500 K at 1 atm) are also shown, for $f_{\text{min}}$ = 0.05. At 500 K, the pathway from the cyclic isomer through H$_2$C•OCHO dominates (the “•” denotes the formal radical center).

As temperature increases, the C•HCHOOH isomer pathways increase in importance, and the pathway through H$_2$C•OCHO decreases in importance, until at very high temperatures the path through H$_2$C•OCHO is unimportant and the dominant routes are C•CHO + O, C$_2$H$_2$ + HO$_2$ (1), and C$_2$H$_2$ + HO$_2$ (2) (through the C•HCHOOH isomer).

As shown in Figure 4-4, the ASA selects the important isomers at these extremes of conditions. Note that when an isomer (such as CH$_2$CHOO•) is included, all its dissociation pathways are also included, even those that are not very significant (e.g. CH$_2$O + HCO (1)); this prevents missing channels if $R_{\text{min}}$ later changes (as it will when the ASA is driven by a model generation code such as XMG).

![Figure 4-4. Vinyl + O$_2$ screened network at 1500 K and 3500 K, 1 atm, $f_{\text{min}}$ = 0.05. Italicics indicate the important parts of the network at high temperature; grey lettering and arrows at lower temperatures. Black species and pathways are included at both conditions. Calculations at 3500 K are not very realistic, but the artificially high temperature is used here to illustrate that the “important” or included fraction of a full pressure-dependent network changes with temperature.](image-url)
Figure 4-5. Rate constant predictions for vinyl + O₂ at 1500 K, 1 atm. Screened rate constant predictions are illustrated with solid bars, full predictions with hashed bars. Only two pathways are above the R_{min} criteria; however, in order to include one of these (CH₂O + HCO) the intermediate isomers C=CYCOO and H₂C-OCHO are also included.

Figure 4-5 shows the rate constant predictions for the screened and full network for the vinyl + O₂ system at 1500 K and 1 atm (f_{min} = 0.05). The screened network case excludes the C=HCHOOH isomer (treats it as a product channel). The most important feature of Figure 4-5 is that rate constant predictions for the screened network are almost identical to those for the full case, for the two reactions with rates above R_{min} (CH₂O + HCO(2) and C=CHO + O). By definition, the user is not concerned with pathways below the R_{min} cutoff, though in many cases the screened predictions for these are also accurate. This reflects the validity of the screening approach in the ASA, in which rate constant predictions are made using a partially-explored pressure-dependent network, and non-included isomers are treated as exit channels. Even though rate constants to some stabilized isomers themselves are low (e.g. C=CYCOO, H₂C-OCHO), they are important intermediates on the path to significant product channels and so are included in the truncated network.
3.2 1-Naphthyl + Acetylene

Recent work suggests the chemically activated 1-naphthyl + acetylene system is important in soot formation, fullerene production, and in polycyclic aromatic hydrocarbon (PAH) formation [13]. A diagram of the potential energy surface (not all possible reactions are shown) is presented in Figure 4-6, with labels for the different species. The ASA was applied to this system, using the data of Richter et al [13] at multiple temperatures and pressures (500-2000K, 20 torr-10 atm).

Our rate predictions for this system reflect those found by Richter et al: at low temperature and pressure, the 1-acenaphthylene (HA2R5) pathway dominates. At low pressure and midrange temperatures, the acenaphthylene (A2R5) channel becomes most important and at low pressure and high temperature, the 1-naphthylacetylene channel becomes more significant. As in the work by Richter, we find that increasing the pressure shifts this same pattern to higher temperatures. As is expected, screened-network results show these trends as well as the full-network evaluations do.

![Potential energy surface for the 1-naphthyl + acetylene system, adapted from Richter [42]. Not all possible reactions are shown. This represents the 'full' network (fmin < 0.004); screened networks contain a subset of these reactions.](image)

Figure 4-6.
Figure 4-7. Screened network rate predictions for major pathways of 1-naphthyl + acetylene at 1500 K, 10 atm, as a function of $f_{\text{min}} = R_{\text{min}}/R_{\text{char}}$. The stair-stepped dashed line represents the $R_{\text{leak}}$ criteria used to judge whether a species should be added to the network (see Equation (4-1)). Note all rate predictions above the tolerance $R_{\text{min}}$ are almost unaffected by changes in network connectivity induced by changes in $f_{\text{min}}$.

Figure 4-7 shows the changes in the rate predictions for the major channels in this system, at 1500 K and 10 atm. In this graph, $f_{\text{min}}$ is plotted on the x-axis and $\log(k(T,P))$ on the y-axis, with $k$ in units of mol/cm$^3$-s. $R_{\text{char}}$ is fixed by (4-3), so that $R_{\text{min}}$ (the thick solid line) is linear with tolerance choice $f_{\text{min}}$. The thin, stair-stepped dashed line represents the sum of fluxes to all non-included isomers, $R_{\text{leak}}$. As the user changes $f_{\text{min}}$, network connectivity changes: at certain values of $f_{\text{min}}$, $R_{\text{leak}} = R_{\text{min}}$, and lowering $f_{\text{min}}$ at this point causes a new isomer to be included. This causes a step decrease in $R_{\text{leak}}$. We note that all rate constant predictions for this system (including those not shown) are virtually unaffected by changes in $f_{\text{min}}$, once they are sufficiently above $R_{\text{min}}$. Predictions for these pathways are unaffected by changes in network connectivity. This essential feature of any screening method for pressure-dependent channel networks is visible in every case we have examined. By definition, those pathways with fluxes less than the tolerance $R_{\text{min}}$ are not of interest to the investigator, though some of these are included in
the network as a consequence of the ASA operation. A bound on the error between a rate constant predicted using an ASA-screened partial network and a full network is described in the next section.

![Graph showing network rate predictions for selected minor-pathway isomers of the 1-naphthyl + acetylene system at 1500 K, 10 atm.](image)

**Figure 4-8.** Screened network rate predictions for selected minor-pathway isomers of the 1-naphthyl + acetylene system at 1500 K, 10 atm. The stair-stepped dashed line represents the $R_{\text{leak}}$ criteria used to judge whether a species should be added to the network (4-1). When an isomer is first discovered, it is treated as an irreversible product channel. When $R_{\text{leak}} = R_{\text{min}}$ (the thick solid line), the dominant non-included isomer is treated as a true isomer, along with all the product channels associated with it. As an example, note that HA2R4 is discovered at $f_{\text{min}} = 0.03$, when A2C2H3*2 is added to the network. It is treated as a product channel, until $f_{\text{min}} < 0.008$, where it is included as an isomer.

Figure 4-8 illustrates more clearly the changes in network connectivity as the user changes the tolerance $f_{\text{min}}$ for this system at 1500 K and 10 atm. At the right end of Figure 4-8, $f_{\text{min}} = 0.6$ and only three isomers (and their attached product channels) are included in the network (A2VINS, A2C2H3*8, HA2R5). $R_{\text{leak}}$ represents the summed flux to the three non-included isomers, A2C2H3*2, A2R4H, and A2R5H, which are treated as products. Moving from right to left in Figure 4-8, $f_{\text{min}}$ decreases, and $R_{\text{min}}$ decreases linearly. $R_{\text{leak}}$ and all rate predictions remain constant (because pressure-dependent network connectivity does not change) until $f_{\text{min}} = 0.3$. At this $f_{\text{min}}$, we have $R_{\text{leak}} \geq R_{\text{min}}$ (the condition for adding a new isomer pathway). A2R5H is the dominant non-included
isomer, and so it is next included. This causes the prediction for the A2R5H rate constant to drop (most of the flux to this isomer continues to the product channel A2R5 + H) to its true value for the system. The network again remains unchanged until \( f_{\text{min}} = 0.035 \). Here, we again have \( R_{\text{leak}} \geq R_{\text{min}} \). A2C2H3*2 is the dominant non-included isomer, so it is included, and HA2R4 (connected to A2C2H3*2) is introduced and treated as a product channel. The \( R_{\text{leak}} \) line touches the \( R_{\text{min}} \) line again at \( f_{\text{min}} = 0.008 \), at which point HA2R4 is added to the network as an isomer. The final isomer is included at \( f_{\text{min}} = 0.004 \), below which the entire network is included.

### 3.2.1 MULTIWELL Master Equation Results

The above chemical activation case (1-naphthyl + acetylene, 1500 K, 10 atm) was modelled using the MULTIWELL master equation code [6] at each step of the ASA. Microcanonical rate constants, collision parameters, and densities of states were taken directly from the CHEMDIS code and used in MULTIWELL. A simple exponential-down model was chosen for collisional deactivation (other details of the MULTIWELL runs are available from the authors). The chemical activation process and the thermal dissociation processes of the separate wells are convolved in MULTIWELL so that the extraction of some of the rate constants was not straightforward. It was found, however, that at every ASA step, the decision as to which isomer to proceed with next was exactly the same as if CHEMDIS had been used. The points at which MULTIWELL predicted that the summed flux to nonincluded isomers was equal to \( R_{\text{min}} \) (i.e. the points on the \( f_{\text{min}} \) axis of the “stair steps” in Figure 4-7 and Figure 4-8) was always close (± 20%) to the CHEMDIS results. Finally, as for the CHEMDIS approach, rate constant predictions sufficiently above \( R_{\text{min}} \) were virtually unaffected by changes in network connectivity.

### 3.3 Phenylvinyl Radical Dissociation

Under many conditions, phenylvinyl radical is the dominant product of the chemically activated reaction between phenyl radical and acetylene; this system has been studied by many researchers due to its possible importance in soot formation and PAH growth [13]. A potential surface, adapted from Richter et al., is shown in Figure 4-9, with labels. Using the input data provided in Richter et al., we have applied the ASA to
the dissociation of this radical at temperatures of 1000 K, 1500 K and 2000 K and pressures of 20 torr, 1 atm and 10 atm.

\[ \text{Figure 4-9. Phenylvinyl radical dissociation potential surface [13].} \]

Selected predictions are shown plotted against \( f_{\text{min}} \) in Figure 4-10 (all plots available from the authors). Dissociation of the radical to phenyl radical and acetylene (C6H5 + C2H2) is generally the dominant path. As in the other examples, rates above \( R_{\text{min}} \) do not change significantly with changes in network connectivity. In this dissociation case, two isomers (C6H5C2H2 and C6H4C2H3) are included in the network at \( f_{\text{min}} = 0.1 \), and two are treated as a non-included isomers (HA1R4 and A1R4H). As \( f_{\text{min}} \) is lowered, HA1R4 is included (at \( f_{\text{min}} = 0.02 \)) and next A1R4H (at \( f_{\text{min}} = 0.007 \)). Predicted rates to the dominant channels (always included throughout) are almost unaffected, as are all predictions for the rates which are faster than \( R_{\text{min}} \) and are therefore of interest to the investigator.

\[ \text{3.3.1 MULTIWELL Master Equation Results} \]

As for the 1-napthyl + acetylene case, MULTIWELL was used to model the above phenylvinyl radical dissociation at 1500 K and 10 atm. Once again, it was found
that the choices of the ASA as to which isomer to proceed with next were exactly the same. Furthermore, the transition points of the algorithm (where the summed flux to nonincluded isomers is equal to $R_{\text{min}}$) were close to those for the CHEMDIS case (about 20% differences). Rate constant predictions above $R_{\text{min}}$ were once again essentially unaffected by changes in network connectivity.

**T = 1500K, P = 10 ATM, DISSOC: PHENYL + ACETYLENE**

![Graph](image)

**Figure 4-10.** ASA screened network rate predictions for the phenylvinyl radical dissociation system, as functions of the screening criteria $f_{\text{min}}$ ($T = 1500K$, $P = 10$ atm). Note all rate predictions above $R_{\text{min}}$ are almost unaffected by changes in network connectivity (e.g. changes in $f_{\text{min}}$).

## 4 Error Bounds for Pressure-Dependent Network Screening

Figure 4-7, Figure 4-8 and Figure 4-10 demonstrate through computational examples that the ASA method for screening pressure-dependent reaction networks produces rate constant predictions almost identical to those generated using full network connectivity. Significant errors appear only for those pathways near or below the $R_{\text{min}}$ cutoff, and by definition the investigator is not concerned with these pathways.

The maximum absolute error incurred by using an ASA-screened network, instead of a full network, for predicting a rate constant is $R_{\text{min}}$. To see this, consider a rate constant to an included, stabilized species or product channel $k_i^{\text{scr}}(T,P)$ which arises
from the ASA partial network (not a prediction for a non-included isomer, which has been treated as a product channel). The corresponding full network prediction is $k_{i}^{\text{true}}(T, P)$. The total flux to all non-included isomers of the screened network is $R_{\text{leak}} < R_{\text{min}}$. We always have $k_{i}^{\text{scr}}(T, P) < k_{i}^{\text{true}}(T, P)$, since adding non-included (screened) isomers returns some of the ‘leaking’ flux back into the network, potentially increasing (but never decreasing) each rate prediction $k_{i}(T, P)$. Thus any true rate constant (for the full network) $k_{i}^{\text{true}}(T, P)$ cannot be greater than $k_{i}^{\text{scr}}(T, P) + R_{\text{min}}$, and the maximum absolute error for any screened network prediction is

$$k_{i}^{\text{true}} - k_{i}^{\text{scr}} \leq R_{\text{min}}$$  \hspace{1cm} (4-5)

A rate constant prediction sufficiently above $R_{\text{min}}$ will therefore appear relatively unaffected by changes in network connectivity. We note that (4-5) is true for both chemical activation and unimolecular dissociation. In some cases, such as application within XMG, the user may be concerned with whether $k_{i}^{\text{true}}(T, P) > R_{\text{min}}$ when $k_{i}^{\text{scr}}(T, P) < R_{\text{min}}$. By the above argument we will always have $k_{i}^{\text{true}}(T, P) < 2R_{\text{min}}$ when $k_{i}^{\text{scr}}(T, P) < R_{\text{min}}$.

5 Conclusions

The Activated Species Algorithm presented here provides a way to build and screen pressure-dependent networks in a manner consistent with a rate-based termination criteria $R_{\text{min}}$. It builds only that portion of the pressure-dependent network which is important under the given conditions of temperature and pressure, thus avoiding exploring or calculating the entire network. We have shown that using partially explored pressure-dependent networks to predict rate constants gives demonstrably minor errors compared to predictions using the full network, errors which are bounded by the user's tolerance choice. Thus our results show that the ASA method of predicting pressure-dependent rates with a partial and growing knowledge of the network connectivity should work well when incorporated in automated reaction mechanism generation tools such as XMG. Use of the MULTIWELL master equation in place of the modified strong
collision assumption of CHEMDIS does not change the ASA decisions of which isomer to include next, and shifts the transition points only slightly, for the test cases examined.

When combined with the work by Grenda and coworkers [9;10], the screening approach should allow investigators to automatically construct all possible pressure-dependent reactions in a single network, efficiently determine which of those are important under given conditions, and provide reasonable estimates of $k(T,P)$ for all important pathways. But the examples so far presented have addressed well-studied cases, in which accurate calculated or experimental high-pressure limit rate constants and thermodynamic data were available as inputs to the calculations. This is a happy but very unusual circumstance for the investigator. The next chapter explores how our automated approach to generating and screening pressure-dependent reaction networks fares when it must use high-pressure limit rate rules and thermodynamic data from group contribution methods. This situation is the one that will be encountered most often during automated mechanism generation.
Citations

CHAPTER 5: CAPTURING PRESSURE-DEPENDENCE IN AUTOMATED MECHANISM GENERATION. REACTIONS THROUGH CYCLOALKYL INTERMEDIATES
1 Introduction

Chapter 3 demonstrated how modified versions of the QRRK code CHEMDIS and the density-of-states code THERFIT could allow rapid, on-the-fly estimation of \( k(T,P) \), requiring only high-pressure-limit modified Arrhenius parameters for each pressure-dependent pathway in a network, and heat capacity estimates for each isomer. This is the only information which is readily available in current automated mechanism generation tools. Next, Chapter 4 answered the challenge of determining how much of a pressure-dependent network one must explore. The exploration-and-screening approach reliably and systematically truncates a pressure-dependent network while including enough network connectivity to predict the important \( k(T,P) \) values. With that effort, it would seem that all the pieces are in place for an integrated pressure-dependent mechanism generation tool: a fast \( k(T,P) \) estimator requiring only the available input data, and a method for rationally limiting the size of pressure-dependent networks.

One serious question remained, however. The work in Chapter 4 focused on well-studied, computational examples. Other researchers had carefully constructed transition-state information and potential energy surfaces by hand for all the examples studied. But how well would our exploration-and-screening approach work “in the wild”? That is, could our approach predict needed \( k(T,P) \) values with any accuracy, when the heat capacities came mostly from group additivity estimates, the modified Arrhenius parameters came from rate rules (and not detailed \( \text{ab initio} \) calculations), and the structure of the pressure-dependent network itself came directly from the mechanism generator?

The current chapter examines this question, applying our exploration-and-screening approach to the \( \text{H + cycloalkene} \) systems studied experimentally by Stein and Rabinovitch in the 1970s. This work has been accepted for publication as “Capturing pressure-dependence in automated mechanism generation: reactions through cycloalkyl intermediates”, David M. Matheu, William H. Green, Jr., Jeffrey M. Grenda, International Journal of Chemical Kinetics (2002). Some sections of the published work, redundant with earlier chapters, have been altered or removed.
1.1 Exploration, Screening, and Estimating Pressure-Dependent Networks, “From Scratch”

This work tests a general method for building pressure-dependent reaction networks within automated mechanism generation. It combines the mechanism generation tool of Grenda and coworkers [1;2] to build the pressure-dependent networks, and the screening algorithm of Matheu and coworkers [3] to include only that part of the pressure-dependent reaction network important for the given conditions. Pressure-dependent rate estimates are made with an improved version of the CHEMDIS Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) code [4] (see Chapter 3). We apply this combined screening and exploration technique to the chemically activated H + cycloalkene systems studied by Stein and Rabinovitch [5]. Temperature, pressure, and the initial reactants (H atom and the cycloalkene) are specified; the approach discovers all the possible pathways, selects the important ones, and makes predictions for \( k(T,P) \) which we compare to experiment. The important \( \text{C}_3\text{H}_5^* + \text{C}_2\text{H}_4 \) (allyl + ethylene) and \( \text{C}_2\text{H}_5^* + \text{C}_2\text{H}_4 \) (vinyl + ethylene) systems, which share the same potential surfaces as H + cyclopentene and H + cyclobutene, are also examined. A range of temperatures and pressures are studied for these systems, to demonstrate how the approach captures dramatic changes in the importance of different channels with changing conditions. No parameters are adjusted by the user or the computer.

1.2 Expected Accuracy of Pressure-Dependent Rate Constants

Mechanism generation programs employ rate rules to predict the high-pressure limit rate constant, where library values are unavailable. These are usually sets of modified Arrhenius parameters used for a class of reactions (e.g. Curran’s rule for H additions to internal alkene double bonds, \( A^- = 8.5 \times 10^9 \text{ [mol/cm}^3\text{-s]} \), \( E_a = 2.9 \text{ [kcal/mol]} \) [6]) where a specific rate is unknown. Such estimates are seldom expected to be more accurate than a factor of ten, but this level of accuracy is suitable at the stage of mechanism generation or construction.

These “factor-of-ten” high-pressure-limit rate estimates are inputs to the QRRK/MSC approach used in our work to predict \( k(T,P) \), along with group additivity
thermodynamic parameters and the inherent inaccuracies of the QRRK/MSC. We thus cannot expect accuracy greater than an order of magnitude in our resulting relative $k(T,P)$ predictions. The results of this work suggest that the relative pressure-dependent yields given by our approach will be within a factor of 10 of the data values. This implies that our method will generate “reasonable” $k(T,P)$ estimates, in line with the expected accuracy of the high-pressure rate rules. Our approach is approximate, and not intended for cases where $k(T,P)$ values are readily available from the literature (experimental or computed). As with high-pressure-limit mechanisms, uncertainty and sensitivity analyses should be used after mechanism generation to indicate which $k(T,P)$ predictions need more thorough treatment.

2 Calculation and Prediction Method

2.1 Overview

A set of rate rules for predicting the high-pressure limit rate constants $k''(T)$ was first prepared for the systems studied in this work: three H + cycloalkene systems (H + cyclobutene, H + cyclopentene, and H + cyclohexene), and two other systems which share potential surfaces with these (vinyl + ethylene and allyl + ethylene). A thermodynamic data file was used for small species (up to C2 hydrocarbons); the remainder of thermodynamic data was calculated as needed during pressure-dependent network generation by group additivity, using the GAPP program [2]. After the thermodynamic data file and rate rule file were prepared, the computer code “XMG” (ExxonMobil Mechanism Generator) was used to generate the full pressure-dependent reaction networks for each system [1:2]. These networks ranged in size from 11 isomers and 21 product channels (H + cyclobutene) to over 90 isomers and over 200 product channels (H + cyclohexene), and represented the many possible pressure-dependent pathways available to the initial adduct, including multiple isomerization loops.

Each network was then converted into an input file suitable for the rate-based screening algorithm [3] which we have embedded in CHEMDIS [4]. The screening algorithm produced a pressure-dependent network containing only the important channels at the specified temperature, pressure, and error tolerance – in most cases the reduction in
network size was dramatic (from over 90 isomers to 3 isomers for the case of H + cyclohexene). The screened network was used for the predictions of $k(T,P)$ via the QRRK/MSC approach. In some cases, our modified version of CHEMDIS was used to generate consistent input files for the master equation code MULTIWELL [7], which then performed QRRK/master equation predictions for the screened networks. In one case, the QRRK $k(E)$ was replaced with the RRKM $k(E)$ for selected channels, to examine the effect of the QRRK assumption on the relative $k(T,P)$ results. Each of the above steps is detailed below.

2.2 Generation of the Pressure-Dependent Networks

XMG was employed to construct all the pressure-dependent systems in this study [1]. It uses planar graph, bond-electron representations of molecules in the pressure-dependent network, and the method described by Broadbelt and coworkers [8-11] for finding all possible reaction pathways. XMG discovers, from specification of only the initial reactants, all the isomers and products of a pressure-dependent network which can be produced using known types of reactions enumerated in a list. In this work, the reaction families included: a) all beta scissions and their reverse reactions, bimolecular radical additions to unsaturated bonds; b) H-shifts (intramolecular H-atom abstractions) from 1,2 to 1,6; and c) intramolecular radical addition reactions and their reverse, cyclic beta scissions, from 1,3 to 1,6. We note that the bond-electron representation considers some resonance forms of free radicals to be distinct; these were identified as equivalent and replaced by a single species before the screening and $k(T,P)$ calculations.

High-pressure limit Arrhenius parameters for each reaction, and estimates of the densities of states for each isomer, were necessary to convert the generated network into an input file for the screening algorithm and CHEMDIS predictions. These parameters were taken directly or indirectly from rate rules, which specify $A^-, n^-, E^-$ in one direction for a given class of reactions. Strictly, the rates of the reverse reactions can be written $k_{\text{reverse}}(T) = k_{\text{forward}}(T) / K_{eq}(T)$ where $K_{eq}(T)$ is the equilibrium constant. For convenience, XMG fit $k_{\text{forward}}(T) / K_{eq}(T)$ to a modified Arrhenius form to obtain $A_{\text{reverse}}^-, n_{\text{reverse}}^-, E_{-\text{reverse}}^-$. 

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$C_p(T)$ data was used to generate three-pseudofrequency models for the calculation of the density of states $\rho(E)$ of each isomer, after the method of Bozzelli et al [12]. With this information and the high-pressure limit Arrhenius parameters for each pathway, XMG constructed an input file for the CHEMDIS code and the embedded screening algorithm.

### 2.3 Prediction of Pressure Dependent Rates

#### 2.3.1 Estimating Microcanonical Reaction Rates $k(E)$

To estimate a pressure-dependent rate constant, one typically evaluates the microcanonical rate constants $k(E)$ for each channel, and then estimates the rate of collisional energy transfer from the activated species to the bath gas molecules. The CHEMDIS code [4] used in this work employs a modified QRRK formula to estimate the microcanonical rate constants $k(E)$:

$$k(E) = \frac{(A^{\text{a}}T^{n_a})\rho(E - E_a^{\text{a}})}{\rho(E)}$$  \hspace{1cm} (5-1)

where $E$ is the energy above the zero point of the molecule, $\rho$ is the density of states (estimated from the three-pseudofrequency approximation [12]) and $A^{\text{a}}, n_a^{\text{a}}, E_a^{\text{a}}$ are modified Arrhenius parameters for the high-pressure limit of the channel. $E_a^{\text{a}}$ must have physical meaning and must be close to the true barrier height. Like a linear approximation to a curved Arrhenius plot, (5-1) is very approximate; in the case where a strict Arrhenius form is used ($n_a^{\text{a}} = 0$) equation (5-1) reduces to the inverse Laplace transform result for $k(E)$. This approach is more thoroughly discussed in Chapter 3.

**RRKM Calculation of k(E) for Cyclopentyl Ring Opening**

In one case, we examined the effect of supplying a more accurate RRKM $k(E)$ for a critical pathway, the ring-opening of the cyclopentyl radical. To do this, we substituted the QRRK $k(E)$'s for ring-opening with a simple RRKM $k(E)$:

$$k(E) = \frac{L^+ W(E^*)}{h \rho(E)}$$  \hspace{1cm} (5-2)
where $L^*$ represents the pathway degeneracy, $W(E^*)$ represents the sum of states of the transition state at energy $E^*$ above the transition state, $\rho(E)$ represents the density of states of the isomer, and $h$ is Planck’s constant. Information used to evaluate $W(E^*)$ was taken from the ab initio calculations for the ring-opening of the cyclopentyl radical, described in the Appendix. Detailed balancing was used for the ring-closure $k(E)$; all other $k(E)$ values were generated by the QRRK form of (5-1). The Discussion compares the results of this calculation to the QRRK/MSC results for the H + cyclopentene system.

2.3.2 Computing $k(T,P)$ Given $k(E)$'s and Densities of States

Microcanonical rate constants $k(E)$ and density-of-states estimates $\rho(E)$ must be combined with a treatment of collisional energy transfer in order to predict $k(T,P)$. As noted in Chapter 3, the preferred method for treating collisional energy transfer is the time-dependent master equation. But the master-equation approach can be time-consuming for large systems, and is not amenable to automation. Thus the modified strong collision approach of CHEMDIS is used in this work to treat collisional deactivation. In some examples we also used the master equation approach, for comparison with modified strong collision results, as described next.

Master Equation Approach for the H + Cycloalkene Systems

MULTIWELL [7], a Monte-Carlo master equation code, was applied to the screened networks of the H + cyclobutene, H + cyclopentene, and H + cyclohexene cases, to examine the effect of the modified strong collision assumption. Microcanonical rate constants $k(E)$ and densities of states $\rho(E)$ used in the master equation were exactly the same as those used in the CHEMDIS calculation. Results were integrated to times of $1.0\times10^{-7} - 5.0\times10^{-9}$ s (H + cyclobutene), or $1.0\times10^{-5} - 5.0\times10^{-8}$ (H + cyclopentene), as needed to reach a reliable population steady state at the given pressure. For H + cyclohexene, a newer version of MULTIWELL (1.1.3) was used, which allowed specification of total collisions instead of total time; in this case total collisions were set to 1000. 10,000 Monte-Carlo trials were used for each calculated point in the H + cyclobutene and H + cyclopentene cases; 100,000 trials were used for each calculation point of H + cyclohexene. Graining of the code was set to 10 cm$^{-1}$ in the lower part of
the MULTIWELL double array, with 5000 grains ("imax1" = 5000); the upper part of the
double array used 5000 grains spaced every 30 cm\(^{-1}\) to a maximum energy to 150,000
\(\text{cm}^{-1}\).

In this work, Monte-Carlo master equation approaches for the H + cycloalkene
systems would take more than two hours for a single temperature and pressure. The
modified strong collision approximation would take far less than a second. Typically the
use of the modified strong collision assumption reduced the required computation time by
a factor of 80,000 – a Monte-Carlo master equation approach for the general, automated
calculation of pressure-dependent networks would be far too time-consuming to be
reasonable.

2.4 Screening of Pressure-Dependent Reactions

The algorithm used to identify and calculate only the important components of the
pressure-dependent network is described in [3] and Chapter 4. This algorithm has been
embedded in the modified version of CHEMDIS discussed above. The error resulting
from truncation of the pressure-dependent network (that is, use of only a partial rather
than full network to predict rates) will always be bounded absolutely by the quantity

\[
R_{\text{min}} = f_{\text{min}} R_{\text{char}}
\]

\[
k_{i}^{\text{true}} - k_{i}^{\text{screened}} \leq R_{\text{min}}
\]

(5-3)

for any product or isomer channel \(i\).

In all the examples in this work, we used \(f_{\text{min}} = 1\%\). \(R_{\text{char}},\) the characteristic rate
for the system under study, was set at \(k_{\text{imp}}(T),\) the high-pressure limit rate for the reaction
to form the first activated isomer, as described in [3]. In the H + cycloalkene cases, for
example, \(R_{\text{char}} = k_{\text{imp}} = 1.54 \times 10^{11} \text{ [cm}^{3}/\text{mol-s]}\), as given by the Curran rule for H addition
to an internal carbon atom of a double bond [6] at 300 K, multiplied by the pathway
degeneracy. Details on appropriate values for \(R_{\text{char}}\) for overall mechanisms can be found
in Song et al [13].
2.5 Thermodynamic Data, Rate Rules and Collisional Energy Transfer Parameters

2.5.1 Thermochemical Data

Most thermodynamic data was generated as required in XMG using the GAPP group additivity code [2]. Thermodynamic parameters for some smaller species (such as H, H₂, ethylene, ethyl radical) were taken from the NIST Chemistry Webbook [14] and the GRI Mech 3.0 data [15]. A table of the thermodynamic parameters for all important species in each system is given in the Supplementary Material.

2.5.2 Rate Parameters

High-pressure limit rate rules for radical additions and ring-opening/closing reactions are given in Table 5-1. Radical addition rules were taken from the work by Curran and coworkers [6], and in the case of vinyl addition, from Fahr and Stein [16]. Rate rules for cycloalkyl ring closures or openings were taken from model reactions listed by Newcomb [17] where available; otherwise these were estimated using simple (rigid-rotor harmonic oscillator) Transition State Theory (TST), and detailed ab initio calculations, as described in the Appendix. ‘Endo’ and ‘exo’ in Table 5-1 indicate different types of radical ring opening/closing, as illustrated in Figure 5-1; in ‘exo’ cycloalkyls, the radical center is beta to the carbon ring; in ‘endo’ cycloalkyls the radical site is on the ring itself.

Each rule represents a designated ‘forward’ reaction family in XMG. These were designated forward based on their likely exothermicity. Certain cycloalkyl ring openings are usually exothermic (cyclopropyl and cyclobutyl), so that the cyclic beta scissions for cyclopropyl and cyclobutyl radicals are designated forward; others (cyclopentyl and cyclohexyl) are usually endothermic and so the ring closure direction is chosen as forward. Reverse reaction high-pressure Arrhenius parameters are evaluated by fitting to the equilibrium constant as discussed earlier.
Figure 5-1. ‘Exo’ and ‘endo’ ring reactions in the H + cycloalkene systems. Typically, exo ring closures are much faster than endo ring closures (the same is true for ring openings).

<table>
<thead>
<tr>
<th>Rate Coefficient Rules</th>
<th>Modified Arrhenius Parameters</th>
<th>Ref.</th>
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</thead>
<tbody>
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<td>Additions</td>
<td></td>
<td></td>
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<tr>
<td>H addition to terminal C atom of double bond</td>
<td>1.0E+13 0.00 1.2</td>
<td>[6]</td>
</tr>
<tr>
<td>H addition to internal C atom of double bond</td>
<td>1.0E+13 0.00 2.9</td>
<td>[6]</td>
</tr>
<tr>
<td>Alkyl addition to terminal C atom of double bond</td>
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<td>[6]</td>
</tr>
<tr>
<td>Alkyl addition to internal C atom of double bond</td>
<td>8.5E+10 0.00 10.6</td>
<td>[6]</td>
</tr>
<tr>
<td>Allyl addition to terminal C atom of double bond</td>
<td>8.5E+10 0.00 11.3</td>
<td>a)</td>
</tr>
<tr>
<td>Vinyl addition to terminal C atom of double bond</td>
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<td>[16]</td>
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<tr>
<td>Ring Opening/Closure</td>
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<td></td>
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<tr>
<td>Cyclopropyl (endo) ring opening</td>
<td>7.1E+12 0.00 21.9</td>
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<td>[19]</td>
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<td>b)</td>
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<td>[17]</td>
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<td>Intra 1,5 addition (endo)</td>
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<td>Intra 1,5 addition (exo)</td>
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<td>Intra 1,6 addition (endo)</td>
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Table 5-1. High-pressure limit rate rules used in the pressure-dependence calculations. Intra-1,5 and intra-1,6 additions are the reverse of cyclopentyl and cyclohexyl ring opening reactions. a) R. Sumathi, from CBS-Q evaluation, private communication. b) Present work, from CBS-Q calculation, see Appendix. c) Present work, from B3LYP calculation (see Appendix). Rate rules are per-site; multiply by pathway degeneracy for rate constant prediction. Units of $A$ are cm$^3$ mol$^{-1}$ s$^{-1}$ K$^n$; units of $E_a$ are kcal/mol.

Rules used for H-shift reactions are presented in Table 5-2; these are derived from the results of high level (B3LYP-ccpVDZ) quantum calculations from Sumathi [20]. We are aware of the work by Viskolcz et al [21,22] to develop such rules, but that work ignored hindered rotations, which can be important for determining Arrhenius A-factors;
the "rotor loss" effects are included in the rules of Table 5-2. Parameters for H-shift
types not listed (e.g. 1,3 secondary to allylic radical) were estimated by Evans-Polanyi
rules derived from the results of the above ab-initio calculations, combined with an
estimate of the ring strain energy for the particular H-shift transition state to predict the
activation energy:

$$E_a = E_{rs} + a + b\Delta H_{rxn}$$  \hspace{1cm} (5-4)

where $E_{rs}$ is the ring-strain energy estimate and $a$ and $b$ are Evans-Polanyi parameters.
$A^\circ$ and $n^\circ$ were taken from Table 5-2 for the appropriate H-shift. The Evans-Polanyi
parameters are given at the bottom of Table 5-2. Details on the development and use of
the H-shift rules are given in the Appendix.
<table>
<thead>
<tr>
<th>Rate Estimates for Intramolecular H-Abstractions</th>
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<td><strong>Modified Arrhenius Parameters</strong></td>
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<table>
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<tr>
<th>1,2 H-shifts</th>
<th>A</th>
<th>n</th>
<th>Ea</th>
<th>Basis Reactant for Ea</th>
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<tr>
<td>p-&gt;p</td>
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<td>40.0</td>
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<td>40.0</td>
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<th>Ea</th>
<th>Basis Reactant for Ea</th>
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<td>CC(C)CC.</td>
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<td>t-&gt;t</td>
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<td>36.6</td>
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<th>1,4 H-shifts</th>
<th>A</th>
<th>n</th>
<th>Ea</th>
<th>Basis Reactant for Ea</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-&gt;p</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>23.1</td>
<td>CCC.C.</td>
</tr>
<tr>
<td>p-&gt;s</td>
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<td>-0.12</td>
<td>20.6</td>
<td>CCC.CC.</td>
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<tr>
<td>p-&gt;t</td>
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<td>18.3</td>
<td>CC(C)CCC.</td>
</tr>
<tr>
<td>p-&gt;a</td>
<td>3.67E+12</td>
<td>-0.6</td>
<td>15.3</td>
<td>C*CCCCC.</td>
</tr>
<tr>
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<td>-0.12</td>
<td>23.5</td>
<td>CCC.C.C</td>
</tr>
<tr>
<td>s-&gt;t</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>20.6</td>
<td>CC(C)CCC.C</td>
</tr>
<tr>
<td>t-&gt;t</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>19.4</td>
<td>CC(C)CCC.(C)C</td>
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### Rate Estimates for Intramolecular H-Abstractions (continued)

<table>
<thead>
<tr>
<th>1,5 H-shifts</th>
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<th>E</th>
<th>Basis Reactant for Ea</th>
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</thead>
<tbody>
<tr>
<td>p-&gt;p</td>
<td>3.67E+12</td>
<td>-0.6</td>
<td>15.3</td>
<td>CCCCC</td>
</tr>
</tbody>
</table>

**1,6 H-shifts**

| (all)        | 2.80E+10 | 0   | see Appendix |

<table>
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<tr>
<th>Evans-Polyani Parameters (see Appendix)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>Ers-3</td>
</tr>
<tr>
<td>Ers-4</td>
</tr>
<tr>
<td>Ers-5</td>
</tr>
<tr>
<td>Ers-6</td>
</tr>
</tbody>
</table>

**Table 5-2.** High-pressure limit H-shift rate rules used in the pressure-dependence calculations. See Appendix. The letters ‘p’, ‘s’, ‘t’, ‘v’, ‘a’ indicate primary, secondary, tertiary, vinylic and allylic radicals, so that “p->t” under the 1,3 H-shift family indicates a 1,3 H-shift from a primary alkyl radical to form a tertiary alkyl radical. "Basis Reactant" indicates the source reactant for TST estimate of Ea. String notation of Dean is used to denote basis reactant: the string represents the carbon backbone, a "*" indicates a double bond, a '.' indicates a radical center and '(' indicate a branch. Units of A are cm³ mol⁻¹ s⁻¹ K⁻⁰; units of Eₐ are kcal/mol.

The average downward collisional energy transfer parameter, \( \langle \Delta E \rangle_{down} = 224 \, \text{cm}^{-1} \), was taken from data provided by Oref and Tardy for azulene-H₂ collisions (H₂ is the bath gas of interest in this work) at activation energies closest to those for H + cyclobutene and H + cyclopentene [23]; these authors give \( \langle \Delta E_{at} \rangle = -100 \, \text{cm}^{-1} \) for H₂ and azulene at 15000 cm⁻¹ of activation (this corresponds to \( \langle \Delta E \rangle_{down} = 224 \, \text{cm}^{-1} \)). Many different values are possible for this parameter; for example, D. C. Tardy has suggested values of 350-400 cm⁻¹ for this system [24]. An accurate guess for \( \langle \Delta E \rangle_{down} \) is hard to make, but in general the results of this work are not especially sensitive to the choice of \( \langle \Delta E \rangle_{down} \). Lennard-Jones parameters were the same as those suggested by Stein and Rabinovitch [5]. The parameters for hydrogen gas are from Reid et al [25]. These pressure-dependence parameters are summarized in Table 5-3.
Collisional Energy Transfer

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$: Delta-E-down</td>
<td>224 cm$^{-1}$</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Lennard-Jones Parameters</th>
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<th>well depth (K)</th>
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</thead>
<tbody>
<tr>
<td>H$_2$</td>
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<tr>
<td>Isomers of cyclobutyl radical</td>
<td>4.70</td>
<td>244</td>
</tr>
<tr>
<td>Isomers of cyclopentyl</td>
<td>5.20</td>
<td>320</td>
</tr>
<tr>
<td>Isomers of cyclohexyl</td>
<td>5.87</td>
<td>325</td>
</tr>
</tbody>
</table>

Table 5-3. Collisional energy transfer parameters for the H + cycloalkene systems.

3 Application to H + Cycloalkenes, Vinyl + Ethylene and Allyl + Ethylene

3.1 H + Cycloalkenes

The pressure-dependent reactions of cycloalkyl radicals have been experimentally studied by many researchers, including (but not limited to) Carter and Tardy [26;27], Scherzer and coworkers [28], Gierczak and coworkers [29] and Stein and Rabinovitch [5]. We chose the work of Stein and Rabinovitch [5] for study because it was most easily compared quantitatively to the single-network systems generated in this work. In addition, these researchers used a well-defined system for trapping radical species, and the competing reactions could be easily considered.

Stein and Rabinovitch examined the effects of chemically activated H atom addition to cycloalkenes in H$_2$ bath gas, using Hg photosensitization of H$_2$ as a source of H atoms [5]. Pyrex or quartz vessels were filled with H$_2$, the cycloalkene substrate, and in many runs, a “getter” precursor, ethylene. H attack on ethylene produced ethyl radicals, which would then “get”, via radical recombination and disproportionation, the radical products of H attack on the cycloalkene substrate. Other runs used self-getting, where the radical products were expected to recombine and disproportionate with each other faster than other processes in the system. Molar ratios H$_2$:C$_2$H$_4$:cycloalkene of the starting materials appear to have been about 50:8:1 for the ethyl-getted runs (though this ratio was reported for only one set of runs); reaction times were typically 10 minutes – 2 hours, at 300 K and various pressures. Substrate conversion was reported to range
between 0.2-1.5%. At the end of each run, stable products were condensed and measured in a gas chromatograph.

From prior estimates of disproportionation and recombination ratios for the self-and ethyl-getting reactions, Stein and Rabinovitch estimated values for S/D with pressure, where S/D is the ratio of the first collisionally stabilized product to all decomposition products. In the H + cycloalkene cases examined in this work, only one other isomer (besides the first adduct) was found to be significant, so that the experimental S/D should reflect the ratio of the rate constants \( k(T, P)_{1st\ isom} / k(T, P)_{other\ isom} \). We have converted these S/D ratios to yields (S/(S+D) or D/(S+D)) in the Results section to compare with our predictions, noting that since these experiments are steady-state, an absolute comparison of rates is not possible.

We applied our approach to the H + cyclobutene, cyclopentene and cyclohexene systems at the conditions of the Stein and Rabinovitch experiments. Full pressure-dependent networks, describing all possible reaction pathways, were constructed for each of these systems. They were then truncated and used to predict \( k(T,P) \) for each pathway of the truncated network. The screened network was also used for the MULTIWELL master equation predictions.

### 3.2 Vinyl + Ethylene and Allyl + Ethylene

Addition of vinyl to ethylene takes place over the same potential surface as for H + cyclobutene. Vinyl radical is an important intermediate in many pyrolysis and combustion systems, and its addition pathways have been suggested as a significant route to higher hydrocarbons in some systems. Despite this radical’s importance, there is very little experimental work available on its addition reactions to alkenes. Fahr and Stein studied this system experimentally in the low-pressure limit [16]; Benson and Haugen made an estimate for the rate of production of butadiene and H atom based thermodynamic reversibility, in an attempt to model the shock-tube experiments of Skinner and Sokoloski [30;31]. We applied our approach to screen the vinyl + ethylene system (using the full network already generated for H + cyclobutene) and predict \( k(T,P) \) for temperatures of 300 K-1500 K and pressures of 10 millitorr, 1 atm and 100 atm. The lowest pressure results were compared qualitatively with those of Fahr and Stein [16].
The allyl + ethylene pressure-dependent network could be important in some pyrolysis or combustion processes, as both species are common in these systems. It shares the same potential surface as H + cyclopentene, but with a different entrance channel. We applied our approach to this system at 1 atm and temperatures of 300-1500K. The results for the minor H + cyclopentene production channel were compared with the recommendation of Tsang for this rate constant (based on 1,7 octadiene shock tube studies) [32].

4 Results

4.1 H + Cyclobutene

4.1.1 Exploration and Screening

The network of all possible chemically activated reactions for H + cyclobutene includes 12 isomers and over 20 separate product channels; the estimated potential surface is shown in Figure 5-2, with selected pathways labeled (the CHEMDIS input file which represents this surface is available in the Supplementary Material). This surface illustrates all the possible H-shifts, beta scissions, and intra-radical additions the isomers of cyclobutyl may undergo.

The first few channels in Figure 5-2 lead to the expected ring-opened isomer 3-buten-1-yl, the well-known ring closure to cyclopropylcarbiny1, and the product channels H + butadiene and vinyl + ethylene. Other interesting possibilities following 3-buten-1-yl formation include formation of an allylic radical via 1,2 H-shift (3-buten-2-yl), and (via a number of isomerizations) formation of the resonance-stabilized isobutenyl radical. Though some of these channels may seem unlikely to be important from a glance at Figure 5-2, our approach rules out no pathway a priori.
The ASA algorithm discussed above was applied to the system in Figure 5-2 with a screening tolerance of $f_{\text{min}} = 1\%$. This gave the truncated, simplified network shown in Figure 5-3, for all pressures of the Stein and Rabinovitch study. CHEMDIS $k(T,P)$ predictions were made for each isomer and product channel in Figure 5-3.

4.1.2 Comparison with Experimental Results

In agreement with Stein and Rabinovitch, our approach predicts cyclobutyl radical and 3-buten-yl radical to be the only significant isomers of the reaction network at 300 K, with no important product channels. While our algorithm includes cyclopropylcarbinyl radical, this radical ring-opens almost immediately back to 3-buten-1-yl, so that only a very small amount is collisionally stabilized and would not be measured in the Stein and Rabinovitch experiments.
Figure 5.3. H + cyclobutene network after screening at 300K and pressures of Stein and Rabinovitch experiment. Only two channels are significant at these conditions (cyclobutyl radical and butenyl radical); the cyclopropylcarbinyl isomer is formed and ring-opened very quickly, so that the overall rate to this isomer is small.

Figure 5.4 compares predicted yields from our $k(T,P)$ calculations against data from the Stein and Rabinovitch experiments. Master equation predictions (using the same $k(E)$ and $\rho(E)$ as the modified strong collision approach) of the MULTIWELL code are also included. Both the modified strong collision and master equation predictions agree reasonably well with the experimental data; modified strong collision predictions are within a factor of 3 and master equation results within a factor of 1.5 of the experimentally estimated relative rate constants. In these predictions and all others of this work, no parameters have been adjusted – data for the CHEMDIS and MULTIWELL predictions are entirely from the rate rules of Table 5-1, Table 5-2, and thermodynamic values as described above.
Figure 5-4. Yields from rate constant predictions $k(T,P)$ for the H + cyclobutene system at 300 K in H$_2$ bath gas. Dotted lines represent modified strong collision results; solid lines are master equation results, symbols are data from Stein and Rabinovitch. The upper set of data and lines are for cyclobutyl radical; the lower set are for the butenyl radical.

Figure 5-5. Rate constant predictions for the H + cyclobutene system at 115 torr and 300 – 1500 K in H$_2$ bath gas. Note the narrow regime near 600 K where as many as four channels may be important, in sharp contrast to the lower temperatures where cyclobutyl radical is the primary product.
4.1.3 *H + Cyclobutene at Higher Temperatures*

Figure 5-5 shows the results of application of the ASA to the H + cyclobutene system at 115 torr and temperatures from 300 to 1500 K. We predict large changes would be observed as temperature is increased. Four separate channels are predicted to be roughly equally important near 600 K (3-buten-1-yl, cyclobutyl, 3-buten-2-yl, and butadiene + H); at higher temperatures 1,3-butadiene and hydrogen atom are the dominant products by as much as three orders of magnitude. The approach adapts to the changing temperature by gradually including more isomers in the network as they are needed for accurate $k(T,P)$ estimates. At 300 K, the screened network contains three isomers; at 1300 K, it contains seven.

We note that at the higher temperatures (near 1500 K) and lower pressures of this work, the modified strong collision assumption may be inaccurate. In particular the individual well populations may not achieve any degree of steady-state behavior, as discussed generally by Tsang and coworkers [33;34]. We have made no attempt to examine the validity of the steady-state assumption at these temperatures.

4.2 *Vinyl + Ethylene*

Addition of vinyl to ethylene takes place over the same potential surface as in Figure 5-3, for H + cyclobutene. The screening approach above was applied to predict rate constants for the vinyl + ethylene system at 300-1500 K and three Argon pressures (10 mtorr, 1 atm and 100 atm). This gave networks containing from two to seven isomers depending on the pressure and temperature conditions. Yield predictions from the screened networks are given in Figure 5-6.

Figure 5-6a shows results for 10 millitorr, approximately the pressure used in the Fahr and Stein work and very likely in the low-pressure limit at 1000-1330 K. The predictions agree with the experimental result that H + butadiene is the overwhelmingly dominant product in the 1000-1330 K range at low pressure.

The predicted relative rate constants also reflect the dramatic changes in the importance of different channels with temperature and pressure. In the low-pressure limit, the reaction goes entirely to butadiene, even at low temperatures. At 1 atm,
formation of butenyl radical dominates at lower temperatures, until ~800 K where the allylic C.C*CC isomer and the butadiene channel are roughly equally important. As temperature increases, the butadiene channel becomes more important. A similar pattern appears at 100 atm, but this time with the crossover point shifted to a much higher temperature (1500 K). This pattern of branching ratio crossover points shifting to higher temperatures as pressure is increased has been observed in other multichannel studies [35].
Figure 5-6. Yield (relative rate constant) predictions (excluding back reaction) for the vinyl + ethylene system at 300-1500 K and Ar bath gas pressures of a) 10 millitorr; b) 1 atm; and c) 100 atm. The lowest pressure (a) is similar to that in the Fahr and Stein experiments. The pattern of the yield crossover points moving from low to high temperature as pressure increases is typical for multi-isomer, multi-channel systems.
4.3  H + Cyclopentene

4.3.1  Exploration and Screening

Application of the XMG code to H + cyclopentene resulted in a network with 32 isomers and 70 product channels; the full network is illustrated in Figure 5-7 and Figure 5-8. The ASA/CHEMDIS screening approach, again using a 1% tolerance, reduced this system to a three-isomer version as shown in Figure 5-9 for the conditions of the experiments.

4.3.2  Comparison with Experimental Results

As in the previous case, Stein and Rabinovitch reported detection of no significant isomers or products other than the initially formed cyclopentyl radical and the first ring-opened product, 4-penten-1-yl radical. The ASA selects these two isomers as important, along with cyclobutylcarbinyl radical; again, however, the cyclobutylcarbinyl radical (like cyclopropylcarbinyl in the previous case) is formed and ring-opened quickly, so that very little stabilized isomer is formed. The predicted truncated network thus agrees with the results of Stein and Rabinovitch.
Figure 5-7. Full H + cyclopentene system, broken into two halves, a) and b). There are 32 possible isomers and 70 separate product channels. "I" label denotes an isomer; "P" denotes a product channel. Chemical drawings for each isomer and product channel label are given in the next figure. In b), arrow with 'I16' denotes connection to that portion of the surface illustrated in a). To make the graph readable, most connections between wells have been partially deleted; "stubs" remain which indicate pathways to other wells.
Figure 5-9. Screened network for the H + cyclopentene system. The original system of over 30 isomers was reduced to the one shown above by the ASA algorithm for pressures of 0.1 to 100 torr. This network is all that is necessary to predict rate constants for the system at almost any pressure, up to 500 K.

Relative rate constant predictions using CHEMDIS are presented in Figure 5-10, along with the Stein and Rabinovitch yields. As found in the experiment, the cyclopentyl radical formation is the dominant process, with the ring-opened pentenyl radical the largest of the minor channels. The CHEMDIS predictions agree less well with the data in this case, with predictions for the ring-opened product within a factor of 6 at 100 torr. The master equation predictions in Figure 5-10 differ from the CHEMDIS results by only a factor of 2.5, but in this case this puts the prediction for the pentenyl channel slightly more than a factor of 10 above the data. Possible reasons for the discrepancy are explored in the Discussion.
Figure 5-10. Yield (relative rate constant) predictions for the H + cyclopentene system at 300 K. As noted previously, dotted lines represent the modified strong collision approach, solid lines represent the master equation results; symbols are data from Stein and Rabinovich.

4.4 Allyl + Ethylene

The full network of all possible channels for allyl + ethylene is the same as that for H + cyclopentene; in this case the ASA was applied with allyl + ethylene as the entrance channel, at 760 torr Ar and temperatures from 300 to 1500 K. Results for the dominant channels are shown in Figure 5-11. Most of the penteny radical initially formed at the higher temperatures (> 1000 K) falls back apart to reactants. Rate constant predictions for the other product and isomer channels show formation of penteny radical is the dominant over most of the temperature range. The allylic penteny radical and the cyclopentene + H channel become more significant at higher temperatures. The predictions for cyclopentene + H agree with the recommendation of Tsang [32].
Figure 5-11. Allyl + ethylene predicted products in Ar bath gas at 1 atmosphere. Note dominance of the pentenyl radical channel for most of the temperature range; this system has a potential surface similar to H + cyclobutene and identical to H + cyclopentene but quite different behavior. Symbols represent Tsang’s recommendation for the cyclopentene channel based on shock tube experiments and are not actual data points. The “bump” in some predictions near 1000 K is an artifact of the screening process whose effect is bounded; see [3].

4.5 H + Cyclohexene

4.5.1 Exploration and Screening

Application of our approach to the H + cyclohexene system generated a network with over 90 isomers and more than 200 product channels. Using a 1% tolerance, the ASA/CHEMDIS screening reduced this system to the three-isomer version shown in Figure 5-12, for pressures up to about 20 torr. Above this pressure, only a single-isomer network is needed at the 1% screening tolerance, but in order to predict the minor-channel yields we have preserved the three-isomer network for the range of conditions used in the Stein and Rabinovitch experiment.

In this case the well depth for the first ring-opened product (5-hexen-1-yl) is quite shallow. Barriers from the 5-hexen-1-yl to the cyclohexyl and the cyclopentylmethyl are 5.9 and 6.8 kcal/mol, respectively. One might expect to find that the allylic 2-hexen-1-yl (not shown), resulting from a 1,4 H-shift of the 5-hexen-1-yl, is an important isomer in
this system. Instead, since the barrier for this pathway is about 15 kcal/mol, it does not compete at the experimental conditions with the much faster ring-closure channels.

![Figure 5-12. Screened network for the H + cyclohexene system. The original system of over 90 isomers was reduced to the one shown above by the screening algorithm for the conditions of the Stein and Rabinovitch experiments. Note that under pressures greater than about 20 torr, the 3-isomer network reduces (with the \( f_{\text{min}} = 1\% \) criteria) to a single isomer network (only cyclohexyl radical). The barrier to allylic radical formation from 5-hexen-1-yl is low (~15 kcal/mol) but still much higher than the barrier to cyclohexyl or cyclopentylmethyl radical; under the experimental conditions (300 K, 0.1-80 torr) our algorithm rules out this isomer as unimportant.]

### 4.5.2 Comparison with Experimental Results

The truncated network is in agreement with the experimental detection of cyclohexyl and cyclopentylmethyl radicals as the dominant species by Stein and Rabinovitch. Cyclopentylmethyl forms from the exo-ring closure of the 5-hexen-1-yl as Figure 5-12 illustrates. Unlike the H + cyclobutene and H + cyclopentene cases, the exo-ring closure product is more stable than the ring-opened species, and is kinetically significant at the experimental conditions, as our results reflect.

Stein and Rabinovitch did not detect the first ring-opened product, 5-hexen-1-yl, in their experiments; they observed cyclohexyl radical as the dominant channel and cyclopentylmethyl as a secondary channel. Our initial prediction, however, gave a measurable rate constant for 5-hexen-1-yl formation from the chemically activated H + cycloalkene addition. It turns out that 5-hexen-1-yl, due to its shallow well depth as
illustrated in Figure 5-12, very likely reacted completely via thermal unimolecular reaction, after it was formed by the original chemical activation process.

*Correction for Thermal Isomerization in the H + Cyclohexene Experiments*

We used CHEMDIS to predict \( k(T,P) \) for thermal unimolecular reaction of 5-hexen-1-yl. The results suggest this species isomerizes to cyclohexyl and cyclopentylmethyl at the rate of \( 10^3 - 10^5 \) sec under the pressures and temperature used by Stein and Rabinovitch (this is due to the very shallow well for this species, as shown in Figure 5-12). This rate is many orders of magnitude faster than the frequency at which radicals would have been captured at these pressures (~0.01-8/sec; see Appendix for discussion of the getting frequency). Thus the collisionally stabilized 5-hexen-1-yl would have isomerized to cyclohexyl or cyclopentylmethyl radical long before it could be trapped by radical recombination, so that Stein and Rabinovitch would not have been able to detect the 5-hexen-1-yl species.

Results of the CHEMDIS calculations for this system were thus adjusted to reflect the presence of 5-hexen-1-yl thermal reaction occurring in the Stein and Rabinovitch experiments, a correction of as much as 25% for the cyclopentylmethyl channel. We converted the CHEMDIS predicted chemical activation rate constants for this system to apparent rate constants, those that would have been measured in the Stein and Rabinovitch experiments, by accounting for thermal dissociation of 5-hexen-1-yl. It is assumed, as suggested by our CHEMDIS calculations for unimolecular reaction of this species, that the 5-hexen-1-yl radical dissociates entirely to cyclohexyl and cyclopentylmethyl radicals at the experimental conditions. The branching ratios for this unimolecular reaction were evaluated using CHEMDIS (Table 5-4).
Table 5-4. Predicted CHEMDIS branching ratios for thermal reaction of 5-hexen-1-yl radical at 300 K and 0.1 to 80 torr.

The predicted rate of 5-hexen-1-yl formation (from H + cyclohexene) was then multiplied by the thermal branching ratio for cyclohexyl; this value was added to the original, chemical activation rate constant prediction for cyclohexyl radical formation, to give the apparent rate constant to cyclohexyl radical in the experiment. Similarly, the rate constant for cyclopentylmethyl formation via chemical activation was augmented by the rate constant for 5-hexen-1-yl formation, multiplied by the thermal dissociation branching ratio for cyclopentylmethyl. An example, at 20 torr, is illustrated in Figure 5-13. It is yields from these adjusted CHEMDIS predictions which are compared with the Stein and Rabinovitch results. These are not true $k(T,P)$ rate constants but have been adjusted to reflect the fact that radical getting was too slow in the experiments to capture 5-hexen-1-yl formation.
\[ H + \text{cyclohexyl} \rightarrow \text{cyclohexyl} \cdot \]

**Chemical Activation**

\[ k_{\text{chem.act.}}^{\text{cyclohexyl}} (300\text{K, 20 torr}) = 3.8 \times 10^8 \text{ [cm}^3\text{/mol-s]} \]

\[ H + \text{5-6exyl} \rightarrow \text{5-6exyl} \cdot \rightarrow \text{cyclopentylmethyl} \cdot \]

**Chemical Activation**

\[ k_{\text{chem.act.}}^{\text{5-6exyl}} (300\text{K, 20 torr}) = 1.2 \times 10^9 \]

**Thermal Isomerization**

\[ \text{78%} \]

\[ \text{22%} \]

\[ k_{\text{apparent}}^{\text{cyclopentylmethyl}} (300\text{K, 20 torr}) = 3.8 \times 10^8 + (0.22) \cdot 1.2 \times 10^9 = 6.4 \times 10^8 \]

**Figure 5-13.** Formation of cyclohexyl and cyclopentylmethyl radical via separate pathways under the conditions of the \( H + \text{cyclohexene} \) experiment. The ring-opened species 5-hexen-1-yl is formed by chemical activation, but dissociates thermally and rapidly to cyclohexyl and cyclopentylmethyl radicals faster than the experimental time scale of Stein and Rabinovitch.

The apparent relative rate constants for cyclohexyl and cyclopentylmethyl radical formation are presented in Figure 5-14, and they agree well with the Stein and Rabinovitch measurements above 1 torr. The difference at the lower pressure (~0.1 torr) for the cyclopentylmethyl channel is large but still within a factor of 10.
Figure 5.14. Predictions for the H + cyclohexene system. Dotted lines represent the modified strong collision approach; solid lines represent master equation results; symbols are data from Stein and Rabinovitch. Note that the 5-hexen-1-yl radical thermally isomerizes to cyclopentylmethyl radical much faster than the radical capture frequency, so that it was not observed in the Stein and Rabinovitch experiments. The predicted values (dotted and solid lines) represent apparent rate constants, which account for 5-hexen-1-yl unimolecular reaction (see text).

5 Discussion

In all cases where experimental data was available, our approach of combined exploration (with XMG) and screening (with the ASA code of [3]) identifies all experimentally important channels of the pressure-dependent network, “from scratch”. The computer is allowed to generate and screen rate pathways without intervention, using only rate rules, group additivity thermodynamics and the QRRK/Modified Strong Collision (CHEMDIS) approach. This produces pressure-dependent yield predictions, from calculated \( k(T,P) \), for all important channels within a factor of 10 of the data. Such accuracy is acceptable for an automated generation code, and in fact many of the high-pressure-limit \( k^*(T) \) estimates used as inputs to the \( k(T,P) \) calculation could be uncertain by an order of magnitude. In practice, key reactions would be refined, in order to build a higher-accuracy model for specific reaction conditions. The current approach insures that
important pressure-dependent pathways will not be ignored, avoiding errors such as those discovered by Dean [36].

5.1 H + Cyclobutene and H + Cyclopentene

5.1.1 H + Cyclobutene

As noted previously, CHEMDIS yield predictions for this system were within a factor of 3 of the experimental data, so that agreement is acceptable for mechanism generation. Nonetheless, two plausible causes, other than uncertainty in the inputs, were examined for the difference between prediction and data. First, the possibility that thermal dissociation of the cyclobutyl radical in the experiments might occur faster than capture by radical recombination (getting) was studied. Second, the possibility of a pathological problem for the modified strong collision approach was explored.

Hand calculations and SENKIN [37] simulations of the experimental conditions were used to examine whether the “getting frequency” – the rate of species capture by a getter molecule (i.e. ethyl radical) – was too slow to prevent thermal dissociation of cyclobutyl radical. If the getting frequency is slow enough, some cyclobutyl radicals could have thermally isomerized before they were captured; this may be considered a separate process from the chemical activation case for which CHEMDIS and other codes make \( k(T,P) \) predictions. The Stein and Rabinovitch S/D ratio would then not reflect \( k(T,P) \) ratios for chemical activation. Our calculations suggest, however, a getting frequency of around 8/second, compared to a thermal isomerization frequency 3 times lower, for the lowest pressure H + cyclobutene cases. This implies thermal dissociation was too slow to affect the S/D ratio. Details of the estimates for the getting frequency are given in the Appendix.

A look at the H + cyclobutene estimated potential surface (Figure 5-3) shows that the difference between the entrance channel barrier height and that of the ring-opening of the cyclobutyl radical is about 8 kcal/mol. Dean has already noted that “intermediate” barrier height differences in this range give rise to the least accurate estimates where the modified strong collision approach is used [38]. The slightly improved agreement of the master equation approach for this case supports this explanation, that the modified strong collision approximation is breaking down for H + cyclobutene at 300 K.
5.1.2 $H + Cyclopentene$

Again, the agreement between the screened CHEMDIS predictions and the data for this system (within a factor of 10) are acceptable for mechanism generation techniques. We examined two issues that could explain, in part, the difference between the screened CHEMDIS predictions and the data: thermal isomerization of the pentenyl radical, and sensitivity to the difference between the energy of the entrance channel barrier and the cyclopentyl-pentenyl isomerization barrier.

Hand calculations for the much lower pressures of the $H + cyclopentene$ experiments revealed that ethyl-getting, self-getting, and thermal dissociation of the pentenyl radical all take place on the same timescale (~0.05/s) at the lower pressures (see Appendix). We used SENKIN to simulate the system and found that this fact could be responsible for a factor of 2 difference in the S/D ratios measured by Stein and Rabinovitch at low pressure. Above 100 torr, however, our calculations suggest thermal dissociation would be too slow to compete with the getting reactions.

A second possible explanation lies with the sensitivity of the calculations to the barrier height for $H$ addition to cyclopentene and the ring opening of cyclopentyl radical to pentenyl. The ring opening barrier height is derived from a rule based on a CBS-Q calculation, and is uncertain by at least $\pm 1$ kcal/mol. But a 1 kcal/mol increase in the ring-opening barrier leads to a factor of 3 difference in the rate constant for pentenyl, bringing that rate prediction much closer to the pentenyl data of Stein and Rabinovitch in Figure 5-10. Lowering the barrier for $H$ addition in the first step produces almost the same effect. At higher temperatures this sensitivity would be considerably reduced.

5.2 $H + Cyclohexene$

5.2.1 Agreement with Experimental Data

CHEMDIS predictions for the pressure-dependent yield of cyclohexyl and cyclopentylmethyl radical agree reasonably well with the data above 1 torr, after thermal dissociation of the 5-hexen-1-yl is accounted for. The low-pressure discrepancy drifts toward a factor of 8. As in the $H + cyclopentene$ case, a possible explanation for this difference is that the CHEMDIS prediction is quite sensitive to a barrier height difference, in this case the difference in isomerization barriers for 5-hexen-1-yl. These
barriers differ by only 1.5 kcal/mol, and the formation of cyclopentylmethyl radical is sensitive to this barrier height difference especially at low pressure. A change of 1.0 kcal/mol in the barrier height difference (e.g. -0.75 kcal/mol for the ring closure of 5-hexen-1-yl to cyclopentylmethyl; + 0.25 for the ring closure of 5-hexen-1-yl to cyclohexyl) is enough to bring the low-pressure yield prediction from a factor of 8 below the data into agreement within 10% (other combinations of small changes in the barrier heights have similar strong effects). The low temperature and pressure of the experiments accentuates such sensitivity. Other likely reasons include the failure of error cancellation, as described in the following sections.

Note that in an overall mechanism generation context, our algorithm would first identify formation of stabilized 5-hexen-1-yl via chemical activation and estimate the rate constant. It would then discover that 5-hexen-1-yl thermal isomerization is rapid, and estimate rate constants for this process, so that chemical activation and thermal activation would be included separately in an overall mechanism for the H + cyclohexene experiment. We have simulated the effect of this by our simplified inclusion of thermal reaction.

5.2.2 Absolute Rate Constant for H Addition to Cyclohexene

Whereas Stein and Rabinovitch measured relative rates for the products of H + cyclohexene, at least four groups [39-42] have directly measured the absolute rate of total H addition to cyclohexene. At temperatures near 300 K and pressures above 1 torr, those researchers who looked for other products found only cyclohexyl radical [40;41], which agrees qualitatively with the results of this work and of Stein and Rabinovitch. These measurements have all been at or near 300 K, and since back-dissociation of the cyclohexyl radical does not appear significant at this temperature, the measured rate of these experiments is probably close to the high-pressure limit for H addition to cyclohexene. Their results for $k_{\text{inp}}^\omega (300K)$ range from $4-6 \times 10^{11}$ [cm$^3$/mol-s], which compares with the $k_{\text{inp}}^\omega (300K) = 1.54 \times 10^{11}$ [cm$^3$/mol-s] derived from the Curran rate rule for H addition to an internal double bond, used in this work for the H + cyclohexene input (see Table 5-1). The experimental H + cyclohexene $k_{\text{inp}}^\omega (300K)$ from Melville and Robb [39] (who measured the absolute rate under very similar conditions and with the
same H activation method) can be used to convert Stein and Rabinovitch relative rate data to absolute rate constants. When this is done, we find our absolute rate constant predictions for the cyclohexyl and cyclopentylmethyl pathways are within an order of magnitude of the converted experimental data, except at pressures below 0.5 torr. Below this pressure, predictions for the cyclopentylmethyl channel are slightly more than a factor of 10 below the data.

5.3 Vinyl + Ethylene and Allyl + Ethylene

The results of these cases, possibly important for some pyrolysis and combustion systems, agree very well with the little available data. They provide estimates of the behavior of these systems under conditions so far unstudied. They also suggest the ASA shows promise in adapting to widely varying conditions. Figure 5-5, Figure 5-6 and Figure 5-11 show that while dramatic change with temperature is possible – with different channels turning on and off with temperature changes – it may not always occur. The H + cyclobutene system has multiple “crossovers” where the dominant channel changes, and the vinyl + ethylene system has a prominent yield crossover. But for allyl + ethylene, the same channel is dominant over a wide range. Both of these systems have similar complex potential surfaces; use of the ASA will capture the behavior of both, without resorting to “rules of thumb” or guesses based on the shape of the potential surface.

5.4 Sensitivity to Choice of \( \langle \Delta E \rangle_{\text{down}} \)

As noted above, it is difficult to select an appropriate value for the average downward collisional energy transfer, \( \langle \Delta E \rangle_{\text{down}} \), in these cases. The effect of choosing \( \langle \Delta E \rangle_{\text{down}} = 350 \text{ cm}^{-1} \) (as suggested by values in Tardy and Rabinovitch [24]) was found for all H + cycloalkene cases to be small, and not more than a factor of 1.5 for the secondary channel in Figure 5-4, Figure 5-10 and Figure 5-14.

5.5 Other Sources of Error in the Screened CHEMDIS Predictions

The QRRK/MSC approximation of CHEMDIS relies on a number of issues which may, in addition to the points above, partially explain differences between the \( k(T,P) \)
predictions and the H + cycloalkene experimental data. First, equation (5-1) does not obey detailed balancing; $k_{1-2}(E)\rho_1(E)$ for one direction will not equal the reverse direction $k_{2-1}(E)\rho_2(E)$, as required by statistical mechanics. Second, equation (5-1) is inherently less correct than the RRKM $k(E)$. In particular, it has the wrong low-energy limit. As $(E-E_0)$ approaches 0, the RRKM $k(E)$ approaches $1/h\rho(E)$ multiplied by some correction for adiabatic rotations [43]; this is clearly not what happens in (5-1). Low temperatures exacerbate this error since in these cases the low-energy $k(E)$ values are especially important. Third, the three-pseudofrequency model for $\rho(E)$ is not unique; a number of 3-frequency and degeneracy sets may give equivalent fits of $C_p$. Fourth, tunneling corrections (possibly important at these temperatures) are neglected in all calculations. Finally, the direct-count method to evaluate the approximate 3-frequency $\rho(E)$ in CHEMDIS may introduce numerical noise in the $k(E)$ values.

We suspect these errors may sometimes combine with the modified strong collision approach to produce an error cancellation effect. This is suggested by Figure 5-15, where we have replaced the QRRK $k(E)$ approximations for the ring opening and closure of cyclopentyl radical with RRKM $k(E)$ values, for the master equation approach. The CHEMDIS calculation lines (dashed) are the same as in Figure 5-10. Correcting some of the $k(E)$ values and the modified strong collision approximation simultaneously does lead to improved predictions for $k(T,P)$ in the H + cyclopentene system. Our goal, however, is not to show that continuous improvement (RRKM $k(E)$'s for every pathway, multidimensional tunneling corrections, and so forth) will lead to better predictions for $k(T,P)$. Instead, we demonstrate that the approach we have outlined for including pressure-dependent pathways in mechanism generation will be reasonably accurate (within a factor of 10) and allow reliable automatic generation of a complex kinetic mechanism.
Figure 5-15. Predictions for the H + cyclopentene system at 300 K, where the k(E) values used in the master equation approach have been changed from QRRK to RRKM for the ring-opening and closing of cyclopentyl. Dashed lines represent the CHEMDIS QRRK/MSC predictions as before; solid lines represent RRKM master equation results. Compare with QRRK master equation results of Figure 5-10; this suggests error cancellation operating in the CHEMDIS predictions for this case.

Almost all of the above errors will probably be at their worst under the low-temperature, low-pressure conditions studied in this work for the H + cycloalkene systems. Numerical noise in the k(E) values will be ameliorated by the generally broader population distributions at higher temperatures; higher temperature and pressure will also lead to more thermal averaging, lessening the problem of a non-unique 3-pseudofrequency fit of the density of states to C_p data. Thus, we expect improved behavior of this approach at the higher temperatures and pressures of most industrially interesting systems (except for atmospheric chemistry mechanisms), though the accuracy of all the cases studied here is sufficient for mechanism generation.

5.6 Conclusions

A general approach for including pressure-dependent pathways on-the-fly in automated mechanism generation has been demonstrated. Examples are presented for the H + cycloalkene systems studied by Stein and Rabinovich, and the related vinyl +
ethylene and allyl + ethylene systems; new rate estimation rules for intramolecular radical additions and H abstractions have also been presented. This approach will reliably approximate $k(T,P)$ where library values are not available, and high-level *ab initio* calculations and RRKM analysis are not practical. The combined screening and exploration approach also shows an ability to capture widely varying types of behavior.

The accuracy of our automated pressure-dependence approach has been shown to be sufficient for mechanism generation and is expected to improve with increasing temperature and pressure. The computed $k(T,P)$ values appear to be as accurate as the $k^\ast(T)$ on which they are based – the pressure-dependent yield predictions are within a factor of 10 of the experimental data. The many approximations made in the automated treatment have been tested in various ways. This work thus sets the stage for incorporation of pressure-dependence in automated mechanism generation.

6 Appendix: Rate Rule Development and Getting Frequency Estimation

Rate rules for the cycloalkyl ring-opening or intraradical closure reactions, and for the intraradical H-shift reactions, were taken from literature results or estimated from high-level *ab initio* and transition state theory (TST) calculations as described below. The TST calculations were all performed using the computer code of Sumathi [44]. *Ab initio* calculations for H-shift rate rules in this work were performed by or with the assistance of R. Sumathi and will be described in detail in an upcoming work [20]. The optimized structures, energies, and frequencies from the *ab initio* calculations used in developing the cycloalkyl radical ring-opening or closure rules are reported in the Supplementary Material.

6.1 Cycloalkyl Radical Ring-Opening Rules

The exo-cycloalkyl ring-opening rules in Table 5-1 were derived from literature *ab-initio* estimates or liquid-phase experimental rate constants for the simplest example of that type of reaction. The rule for cyclopropyl (exo) ring openings was taken from the well-known literature rate for the cyclopropylcarbinyl radical ring opening [19]. This
rule was used for any exo-cyclopropyl ring opening even though some substituent effects on the rate constant are well-studied [17].

In the above work by Smith et al., high-level ab initio calculations combined with transition state theory agreed very well with the liquid-phase experimental data. Since, in addition, solution effects are generally not reported as important in these reactions, we felt justified in similarly formulating high-pressure limit gas-phase rate rules from well-established liquid phase rate constant data for the cyclobutyl and cyclopentyl (exo) ring openings. Thus the rate rule for cyclobutyl (exo) ring openings was taken from the Newcomb review value for the cyclobutylnorcaranyl ring opening [17]. The rule for ring closures to cyclopentyl (exo) rings was taken from data on the reaction of 5-hexen-1-yl closing to cyclopentyl norcaranyl, in the same work. The ring-closure to cyclopentyl (exo) radicals is typically exothermic, so the ring closure direction was designated forward and used as the rate rule in this case.

We were unable to find directly measured or calculated values for the cycloalkyl (endo) ring opening/closing reactions (except cyclopropyl-endo), so we used high-level ab initio calculations and conventional transition state theory (TST) to estimate rate rules for these reactions. The rate constant for the ring opening of the cyclobutyl radical was evaluated by first calculating the CBS-Q geometries, energies, and frequencies of the cyclobutyl radical and the ring-opening transition state using GAUSSIAN98 [45]. Conventional transition state theory [46] with the common rigid-rotor harmonic oscillator approximation, neglecting tunneling, was used to calculate values of $k^*$ for this reaction at temperatures from 300 to 1500 K. A modified Arrhenius form, in which $E_a^*$ was fixed at the zero-point CBS-Q energy difference between the cyclobutyl radical and the transition state, was then fit to the TST rate constant. This Arrhenius form was then used as a rate rule for all cyclobutyl (endo) ring-opening reactions.

Similar CBS-Q calculations were performed for the cyclopentyl radical ring-opening reaction. The conformer used was the “twisted-chair”, similar to the one identified in Liu and Allinger [47]. Frequencies for the radical and transition state were calculated at the B3LYP/6-31G* level. Significant spin contamination ($< S^2 > = 1.0$) was found for the CBS-Q calculation of the ring-opening transition state, so B3LYP-ccpVTZ optimizations (starting with the CBS-Q geometries as initial guesses) were performed to
check the CBS-Q results. We found only a small difference between the CBS-Q and B3LYP-ccpVTZ calculations, for the zero point energy barrier $\Delta E^0$ of the ring opening (0.6 kcal/mol), and concluded that in this case the CBS-Q empirical correction for spin contamination was sufficient. From the CBS-Q results for the cyclopentyl radical ring opening, a TST calculation was performed for the ring opening to obtain estimates of the high-pressure rate constant from 300 to 1500 K. Thermodynamic parameters from GAPP were then used to evaluate the reverse rate constant for exothermic ring closure. Finally, $A^\omega, n^\omega, E^\omega_a$ were fit to the ring closure rate predictions, so that the rate rule would be posed in the exothermic direction. $E^\omega_a$ was again fixed to the zero-point energy difference between the transition state and the linear species 4-penten-1-yl evaluated by the CBS-Q method. This rule was used for all cyclopentyl (endo) ring closures.

The rate rule for the cyclohexyl (endo) ring closure was similarly estimated from a B3LYP-ccpVTZ calculation of the energies and optimized geometries of the cyclohexyl radical and ring-opening transition state (awareness of spin-contamination for the cyclopentyl radical transition state led us to start with density functional theory in this case). The chair conformer (believed lowest in energy, [47]) was used for the cyclohexyl radical. Frequencies were evaluated for the transition state and cyclohexyl radical at the B3LYP/6-31G* level, using the geometry and energy optimized at that level. Arrhenius parameters for the cyclohexyl (endo) ring closure rule were then developed as for the cyclopentyl case.

6.2 Intramolecular Hydrogen Transfer (H-shift) Rules

6.2.1 1,2 Through 1,4 H-shifts

The 1,2; 1,3; and 1,4 H-shift rules in Table 5-2 were developed by first considering the primary alkyl-primary alkyl neutral reaction for the family, e.g. ethyl radical to ethyl radical for the 1,2 H-shifts, 1-propyl radical to 1-propyl radical for the 1,3 H-shifts, and 1-butyl to 1-butyl radical for the 1,4 H-shifts. A "full" TST calculation was performed for this reaction, including explicit hindered rotor effects, using information from \textit{ab initio} B3LYP-ccpVDZ calculations for the reactant and transition state [20]. $A^\omega, n^\omega$ and $E^\omega_a$ were derived from fitting to the TST $k^\omega(T)$ from 300 K to 1500 K.
Subsequent rate rules in the family used the same $A^\omega$ and $n^\omega$ parameters, as the neutral primary-primary H-shift was assumed to capture the dominant effect of rotor loss and the addition of low-frequency ring vibrational modes between the stable radical and the transition state. The $E^\omega_{n}$ for these rate rules were estimated using the B3LYP-ccpVDZ zero-point energy difference of a model reaction; for example, the secondary-tertiary radical 1,2 H-shift rule ($s \rightarrow t$) was generated by examining the reaction of 3-methyl-2-butyl radical to form the tertiary radical 3-methyl-3-butyl.

6.2.2 Other 1,2 Through 1,4 H-shifts: Evans-Polanyi/Ringstrain Rules

Clearly, not all types of possible 1,2 through 1,4 H-shifts which XMG evaluated are included in Table 5-2 and the above discussion. For those types not covered, an Evans-Polanyi rule was formulated based on ring strain and intrinsic activation energy for the 1,2 through 1,5 H-shifts. To do this, $\Delta H_{\text{rxn}}^{298}$ was calculated via GAPP for each reaction explicitly given in Table 5-2. The 5 parameters $a, b, E_{1,2}^{rs}, E_{1,3}^{rs}, E_{1,4}^{rs}$ were least-squares adjusted to bring the Evans-Polanyi activation energy $E_{a}^{\text{pred}} = a + b\Delta H_{\text{rxn}}^{298} + E_{t}^{rs}$ into agreement with the B3LYP-ccpVDZ evaluated energy in Table 5-2. This produced the values at the bottom of Table 5-2, which were used to estimate $E_{a}^{\omega}$ where the specific type was unavailable. Predicted vs. calculated $E_{a}^{\omega}$ are shown in the Supplementary Material. Average absolute differences are $\pm 0.75$ kcal/mol but maximum differences are above 2 kcal/mol, so that this method is not always reliable for predicting H-shift barrier heights. Work continues on improving and adding to the list of explicit H-shift rules, and adapting the XMG tool to make use of this differentiation. H-shifts involving the vinyl radical were found problematic for this fitting approach; $E_{a}^{\omega}$ for these reactions was set to that for the primary-primary H-shift of the family.

In cases where an allylic radical was formed outside the transition state ring, thus involving an additional rotor loss, $A^\omega$ and $n^\omega$ were sometimes chosen from the next larger rule; that is, a 1,3 H-shift to form an allylic radical not in the transition state ring would use the 1,4 H-shift $A^\omega$ and $n^\omega$. For example, the reaction
is a 1,3 H-shift, but the bond adjacent to the reactant double bond must give up an internal rotation to form the allylic radical, so the 1,4 H-shift \( A^\pi \) and \( n^\pi \) were used for this reaction. Similarly, if a double bond was involved in the transition state, the next smaller rule's \( A^\pi \) and \( n^\pi \) would be used, since one less rotor is lost in this case.

6.2.3 The 1,4 "Cross-Ring" H-Shift

The 1,4 H-shift ring-strain \( E_{rs,5} \) given in Table 5-2 is not appropriate when the H-shift occurs across an existing ring, as shown for cyclopentylmethyl:

\[
\text{\includegraphics[width=0.5\textwidth]{cyclopentylmethyl.png}}
\]

(5-5)

In this case, we expect the torsion induced in the existing cyclopentyl ring will add significant additional ring strain to the transition state. We constructed a crude estimate of the ring-strain energy for "cross-ring" 1,4 H-shifts by first noting that the well-studied norbornene molecule has a ring structure similar to that of the transition state for (5-5). The experimental heat of formation of norbornene is approximately 21 kcal/mol [48]; comparing this value with the group additivity result (with no ring strain correction) suggests a ring-strain energy of about 20 kcal/mol for a norbornene-like structure. Subtracting Benson's ring strain energy for cyclopentane [49] suggests a ring-strain energy of 14.7 kcal/mol to form the norbornene-like transition state ring from the cyclopentylmethyl radical. This value can be compared with the 8.35 kcal/mol ring strain energy of the normal 1,4 H-shift in Table 5-3. This crude value (14.7 kcal/mol) was used for the ring-strain energy of the 1,4 H-shift in cases like that illustrated above, where the 1,4 H-shift occurs across the existing ring. We did not correct other types of cross-ring H-shifts; even using the normal H-shift rules, these had barriers too high to be important under the conditions investigated.
6.2.4 1,5 and 1,6 H-shifts

$A^\sigma, n^\sigma, E_\sigma^\sigma$ were evaluated for the primary 1,5 H-shift of 1-pentyl radical. The Evans-Polanyi + ring strain energy estimation discussed above was used for all other 1,5 H-shifts (except those involving vinyl radical).

The 1,6 H-shift rule is very approximate; the A-factor was estimated by taking the 1,5 H-shift pre-exponential factor at 300 K and adjusting downward by 2.5 entropy units (2.5 cal/mol K), as per Benson's technique for estimating rotor-loss A-factors [49]. $E_\sigma^\sigma$ was estimated using the Evans-Polanyi/ringstrain method described above, with ringstrain for the 7-member 1,6 H-shift transition state estimated at 5 kcal/mol. This in turn was estimated from the Benson ring correction enthalpy for cycloheptane, less 1.5 kcal/mol, since all the ringstrain energies in Table 5-2 are typically lower than Benson alkane ring corrections by about 1.5 kcal/mol.

6.3 Estimation of Getting Frequency in H + Cycloalkene Experiments

In the Stein and Rabinovitch experiments, ethyl radicals, formed from the addition of H to ethylene, captured products of the chemical activation by radical recombination, giving stable species that could be measured in a gas chromatograph. If the trapping rate, however, was slower than the rate at which thermal cycloalkyl radical isomerized or broke apart, then the S/D ratio measured in the experiment would not reflect the true branching ratio of the chemically activated reaction. Because the trapping rate was not very fast under Stein and Rabinovitch conditions, some of the collisionally stabilized radical could have thermally reacted before capture, leading to an experimental yield that would be different than the actual chemical activation rate constant. This possibility is examined for the H + cyclobutene case below.

Assume back-dissociation of cyclobutyl is negligible in the experiments (supported by the results of our H + cyclobutene calculations), and that all other consumption processes for the cyclobutene substrate are also insignificant. The rate of consumption of cyclobutene can then be set equal to approximately the conversion of substrate divided by the experimental time:

$$k_{H+CB}^n[H\cdot][CB] = \frac{X[CB]}{t}$$  (5-6)
where \([CB]\) is the substrate concentration, \(X\) is the total conversion, and \(t\) is the time of the experiment. Since conversion is small (< 1%) \([CB]\) may be assumed constant at the ideal gas value evaluated from the 50:8:1 molar ratio given by Stein and Rabinovitch as typical [5]. For this example, we consider the lowest pressure of the \(H +\) cyclobutene experiments, \(~ 100\) torr. \(X\) is taken as 1% and \(t\) as 1 hour; these appear to be typical values from the Stein and Rabinovitch work though specific values are not given (the final result is relatively insensitive to \(X\) and \(t\) in their experimental range). Equation (5-6) with these values gives 
\[ [H^\bullet]_{ss} = 2 \times 10^{-17} \text{ [mol/cm}^3\text{-s]} \]

The steady-state ethyl radical concentration can now be estimated by balancing the principal production and loss processes. We assume production is entirely from \(H\) atom addition to ethylene, and that the dominant loss processes for ethyl radical are recombination and disproportionation (appropriate since there is much more ethylene than cyclobutene). This gives
\[
[C_2H_5]_{ss} = \sqrt{\frac{k_{H^+ + C_2H_4}[H^\bullet]_{ss}[C_2H_4]}{(k_{rec} + k_{dis})}} \tag{5-7}
\]
where \(k_{H^+ + C_2H_4}\) is calculated from the Baulch et al recommended value at 300 K and 115 torr [50], and \(k_{rec} + k_{dis}\) are taken from the recommended values of Tsang and Hampson [51]. Finally, given a value for the steady-state ethyl radical concentration, and assuming that the recombination rate constant for ethyl radical with cyclobutyl radical is approximately the same as the rate constant for ethyl radical recombination with itself, the "getting frequency" may be estimated as
\[
getting = k_{rec}[C_2H_5^\bullet]_{ss} \tag{5-8}
\]
which turns out to be 8/sec at 300 K and 115 torr. The thermal dissociation rate of cyclobutyl radical under these conditions, estimated with CHEMDIS (using the same potential energy surface and screened network), is three times lower; thus in this case the getting is fast enough that thermal dissociation is probably not important. Since S/D ratios for the self-getting results were quite similar to those for ethyl-getting, we have assumed self-getting is also not affected by possible cyclobutyl thermal dissociation. The above assumptions have been tested and found valid by simulation of the entire experimental setup using SENKIN.

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At the lower pressures of the H + cyclopentene case, however, an evaluation similar to that above implies that getting and thermal isomerization would have been competitive processes. For H + cyclohexene, the thermal isomerization of the 5-hexen-1-yl radical would have been much faster than getting at all pressures in the experiment (10^3/sec vs. 0.01-8/sec). This is why only two isomers (cyclohexyl and cyclopentylmethyl) were observed, despite the fact that a significant amount of 5-hexen-1-yl would have reached a room-temperature Boltzmann energy distribution during the experiment.
Citations


SUPPLEMENT TO CHAPTER 5
1 Thermodynamic Parameters

Table 5S-1 presents selected thermodynamic parameters for species in the screened pressure-dependent networks produced by the ASA. It includes thermochemical data for each species which was an isomer or product channel of the screened network, as well as for many species which were non-included isomers, at the edge of the screened network. GAPP provided estimates for any species not included in Table 5S-1, but part of the full pressure-dependent networks discussed.

2 Rate Rule Development and Ab Initio Calculations

2.1 H-shift Evans –Polanyi Table

Table 5S-2 provides a more detailed look at the development of the Evans-Polanyi rule for alkyl radical-based intra-radical H-shifts. It lists absolute differences between Sumathi’s results for the barrier $\Delta E_0$ [1] and the Evans-Polanyi “prediction”. Average deviation is about 0.75 kcal/mol but maximum deviations approach 2.5 kcal/mol. We note Sumathi has shown that an Evans-Polanyi relationship will fail to capture important effects, and has improved greatly on the results in Table 5S-2; the reader is directed to Sumathi’s extensive work [1-3] for more information.

2.2 Cycloalkyl Radical Ab Initio Calculations

Ab initio calculations of the cycloalkyl radicals cyclobutyl, cyclopentyl, and cyclohexyl, and their transition states for ring-opening beta-scissions, provided data for the ring-opening or ring-closure rate rules presented in the work. Simple transition state theory (rigid rotor, harmonic oscillator, no adiabatic correction; as described in [4]) produced estimates of the high-pressure limit rate constants for each ring-opening reactions. The ring-opening direction was chosen since it involved no internal rotors, making the RRHO treatment more reasonable.

With $k^*$ from TST for each ring opening, we fit modified Arrhenius parameters directly to the TST results from 300 to 1500 K, fixing $E_a$ at the zero-point energy difference $\Delta E_0^*$ for cyclobutyl ring-opening to butenyl. For cyclopentyl and cyclohexyl,
we reversed the direction using the data in Table 5S-1 and fit modified Arrhenius parameters for the reverse direction, this time fixing $E_a$ to $\Delta E^0$ for the reverse direction, using the linear species' zero-point energy.

Tables 5S-3 through 5S-8 show geometric parameters resulting from the \textit{ab initio} optimizations of this work, performed via Gaussian [5]. The rest of the tables present frequencies, rotational constants and energies.
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**Table SS-1. Thermodynamic data for selected species in the H + cycloalkene networks.** Any species not listed but appearing in the network was evaluated using the GAPP group additivity code. Reference key: GAPP = GAPP group additivity code [6]; NIST = NIST Chemistry Webbook [7]; GRI 3.0 = GRI Mech 3.0 [8]. As in Chang et al [9] abbreviated string notation is used; in this notation hydrogens are left out, a '+' indicates a double bond; '#' indicates a triple bond; '·' indicates a radical site; 'CY[...]' indicates a cycle, and '(...)' indicates a branch. For example, 'CY[CCC][CC]' represents the cyclobutyl radical, and C*CCC represents 4-penten-1-yl.
**Average Deviation of E-P Prediction of Barrier**

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**Average Deviation for Set** 0.75

*Table 5S-2.* Predicted (via Evans-Polyani) vs. calculated activation barriers for the H-shift reactions; see Appendix for description. Units are kcal/mol. Ers-n indicates ring strain correction for n-member (1,n H-shift) transition state.
### Table 5S-3

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Table 5S-4. Z-matrix for cyclobutyl radical ring-opening transition state at the CBS-Q level.
### Table 5S-5. Z-matrix for cyclopentyl radical, optimized at the B3LYP/cc-pVTZ level.

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### Table 55-6

Z-matrix for transition state of cyclopentyl radical ring-opening reaction, optimized at the B3LYP/cc-pVTZ level.
Table SS-7. Z-matrix for cyclohexyl radical, chair conformer, optimized at B3LYP/ccpVTZ.

| c  | ccc2 | ccc3 | ccc4 | ccc5 | ccc6 | dih4 | dih5 | dih6 | dih7 | dih8 | dih9 | dih10 | dih11 | dih12 | dih13 | dih14 | dih15 | dih16 | dih17 | dih18 |
|----|------|------|------|------|------|------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|
|    |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| c  | 1    | cc2  | 1    | ccc3 | ccc4 | 2    | ccc5 | 3    | ccc6 | 4    | ccc7 | 5    | ccc8  | 6    | ccc9  | 7    | ccc10 | 8    | ccc11 | 9    |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| c  | 2    | cc3  | 1    | ccc3 | ccc4 | 2    | ccc5 | 3    | ccc6 | 4    | ccc7 | 3    | ccc8  | 2    | ccc9  | 3    | ccc10 | 4    | ccc11 | 4    |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 4    | hc7  | 3    | hcc7 | 2    | dih7 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 5    | hc8  | 4    | hcc8 | 3    | dih8 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 6    | hc9  | 4    | hcc9 | 3    | dih9 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 6    | hc10 | 5    | hcc10 | 4   | dih10 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 6    | hc11 | 5    | hcc11 | 4   | dih11 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 1    | hc12 | 2    | hcc12 | 3   | dih12 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 1    | hc13 | 2    | hcc13 | 3   | dih13 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 2    | hc14 | 3    | hcc14 | 4   | dih14 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 2    | hc15 | 3    | hcc15 | 4   | dih15 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 3    | hc16 | 2    | hcc16 | 1   | dih16 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
|    |      |      |      |      |      |      |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |
| h  | 3    | hc17 | 2    | hcc17 | 1   | dih17 |      |      |      |      |      |      |       |       |       |       |       |       |       |       |       |       |
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Table 5S-8. Z-matrix for transition state of cyclohexyl ring-opening, optimized at the B3LYP/6-31G(d,p) level.
### Ab Initio CBS-Q Results for Cyclobutyl Radical

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Table 5S-9. Results of CBS-Q optimization and energy calculation for cyclobutyl radical, from Gaussian98. Frequencies are also at CBS-Q level.

### Ab Initio CBS-Q Results for Cyclobutyl Ring-Opening TS

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Table 5S-10. CBS-Q results for the cyclobutyl radical beta-scission to butenyl transition state. Frequencies are also at the CBS-Q level.
### Ab Initio Results for Cyclopentyl Radical

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**Table 5S-11.** *Ab Initio* results for cyclopentyl radical. Energy and geometry are at the B3LYP/cc-pVTZ level; frequencies are at the B3LYP/6-31G* level. Frequencies scaled by 0.96.

### Ab Initio Results for Cyclopentyl Ring-Opening TS

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**Table 5S-12.** *Ab Initio* results for cyclopentyl ring-opening transition state. Energy and geometry are at the B3LYP/cc-pVTZ level; frequencies are at the B3LYP/6-31G* level. Frequencies scaled by 0.96.
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Table 5S-13. *Ab Initio* results for the cyclohexyl radical, chair conformation. Energy and geometry are at the B3LYP/cc-pVTZ level; frequencies are at the B3LYP/6-31G* level. Frequencies scaled by 0.96.
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<tr>
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<td>3008.0</td>
<td>3026.3</td>
</tr>
<tr>
<td></td>
<td>3033.2</td>
<td>3092.5</td>
<td>3104.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
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<th>3.7</th>
<th>2.3</th>
</tr>
</thead>
<tbody>
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<td></td>
</tr>
<tr>
<td>(&lt;S^2&gt;)</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 55-14.** *Ab Initio* results for the cyclohexyl radical ring opening. Energy and geometry are at the B3LYP/cc-pVTZ level; frequencies are at the B3LYP/6-31G* level. Frequencies scaled by 0.96.
Citations

CHAPTER 6: MECHANISM GENERATION ALGORITHM
WITH INTEGRATED PRESSURE DEPENDENCE
1 Introduction

The H + cycloalkene cases of the previous chapter were built using an extension to the original XMG/NetGen software [1-6], which could build a single, full pressure-dependent network from scratch. This network could then be screened with the ASA [7;8]. Thus Chapter 5 demonstrated that a mechanism generator could explore, screen, and calculate pressure-dependent networks on-the-fly, with reasonable accuracy. It remained to integrate the single-network approach of Chapter 5 into a true, fully pressure-dependent mechanism generation algorithm.

Despite appearances, the single-network approach of Chapter 5 needed considerable changes before inclusion in mechanism generation. Certain questions arose only within the context of an integrated (as opposed to single-network) approach, such as: How should pressure-dependent network leakage fluxes be treated in comparison to unreacted species fluxes? At what point in the main mechanism generation loop should leakage fluxes be tested and networks explored? Obvious changes were also made – for example, though the approach of Chapter 5 explores the full network and then screens it, our approach here will only explore as needed.

This chapter thus describes our integrated algorithm for including pressure-dependence in mechanism generation, based on the results of Chapters 3-5. By carefully knitting this algorithm into the existing XMG/NetGen software, we have built the first known mechanism generator to include pressure-dependence in a general and systematic fashion. This new mechanism generator is called “XMG-PDep”.

1.1 Background and Preparatory Work

Our integrated approach to pressure-dependence in mechanism generation was first sketched out early in the work, in 1998. Before implementing it, however, we needed to prove that truncating pressure-dependent networks would not lead to large errors in \( k(T,P) \) (Chapter 4) and that reasonable estimates of \( k(T,P) \) could be made using high-pressure limit rate rules, group-additivity thermodynamics, and a QRRK/MSC code (Chapter 5). The author then designed, in detail, an integrated algorithm which would include pressure-dependent reactions naturally during mechanism generation.
Before translating this algorithm into computer code, a full month was spent researching good coding practice as outlined by McConnell [9]. We then built a modular framework, with restricted data objects and a controlled approach to routine design, to ensure our code would be robust and easy to work with. The modular design was also constructed so that adaptation to the Unified-Modelling-Language (UML)-based mechanism generator, under development by Jing Song and others, would be facile.

1.2 Chapter Overview

First, to give context to the following major sections, the integrated pressure-dependence algorithm is summarized in Section 1.4. Section 2 describes fundamental and minor changes to the original XMG software which were required for the integrated algorithm to work. Section 3 explores two key assumptions of this integrated approach, followed by an in-depth description of the algorithm and its modular framework. The Source Code Supplement section (not included in the public thesis) is a full listing of the original source code described in Section 3. Finally, Section 4 is devoted to known difficulties with the approach and possible resolutions. Throughout this chapter, boldface is used to designate specific modules and italics are used to denote objects, lists, or data (when not used to describe variables in equations).

1.3 A Note About the Source Code Supplement

The source code of this work is almost entirely original. Occasionally, however, certain sections of existing XMG code were cut-and-pasted, then modified slightly, to perform similar tasks in the pressure-dependence module. The source code also, unavoidably, references certain XMG data objects, function names, and header files. For these reasons, the Source Code Supplement is bound by the ExxonMobil Confidentiality Agreement. It can only be released to those who have signed this agreement in conference with ExxonMobil representatives. The Source Code Supplement is intended to guide the user interested in modifying the code, and such users will have generally signed an agreement in any case. To obtain this supplement, contact:
1.4 The Integrated Algorithm, In Brief

XMG builds a chemical mechanism by constructing all the possible reactions of a particular molecule with those species it has already included in the mechanism. These species, whose reactions have already been explored, are called the Reacted Species. In exploring and constructing reactions, XMG discovers new species, which become candidates for exploration and inclusion in the mechanism. These candidate species are called Unreacted Species. When XMG exhausts all the reactive possibilities for a given particular candidate, that species becomes part of the mechanism, and is moved from the list of Unreacted Species to the list of Reacted Species.

During the exploration of the reactions of a species, our integrated algorithm recognizes any reaction of the form $A + B \rightarrow C$, $B \rightarrow C$, or $B \rightarrow C + D$ as potentially pressure-dependent. It initiates a pressure-dependent network (a data object with placeholders for all necessary information to build a CHEMDIS input file) for each such "entrant" reaction. At the end of the species exploration step, all the new partial pressure-dependent networks are converted into CHEMDIS input files. Pathways to isomers not yet included in each network are treated as product channels, as described in Matheu et al. [7]. The integrated algorithm then uses CHEMDIS to estimate $k(T,P)$ values for each pressure-dependent reaction of each network.

Next, the DASSL integrator [10] solves the set of ordinary differential equations describing the Reacted Species (species whose reactions have been explored), out to time steps as specified by DASSL's Gear algorithm. At each DASSL time step, our integrated algorithm evaluates the set of fluxes $R_{\text{leak}(i)}$ for each partial pressure-dependent network $i$, where $R_{\text{leak}(i)}$ represents the total flux to all non-included isomers of the network. The integrated algorithm also examines the set of fluxes $R_{\text{species}(j)}$ which are fluxes to the
species of the Unreacted Species list (species not yet included in the mechanism). As soon as the largest flux among these is greater than the flux criteria $R_{\text{min}}$, integration halts.

If the largest flux belongs to a species from the Unreacted Species list, the algorithm proceeds as before, exploring the reactions of that candidate species as described in the above paragraphs. If it belongs to a pressure-dependent network, the integrated algorithm explores that network by iterating all the possible isomerizations and decompositions of its most important, non-included isomer. The algorithm then constructs new net pressure-dependent reactions, and it updates the list of reactions with new estimates of $k(T,P)$ based on the new network structure. The DASSL integration steps are then repeated.

The algorithm continues in this way until all fluxes $R_{\text{leak}}(i,j)$ to the non-included isomers of pressure-dependent networks, and all fluxes $R_{\text{species}}(i,j)$ to Unreacted Species, are less than the criteria $R_{\text{min}}$ over the entire integration to the user-specified conversion.

2 Major Changes to the XMG Software

This section documents the major changes made to the XMG software to prepare the ground for the integrated pressure-dependence approach. Some of these changes are rather important, such as the revision of the main exploration loop; others were simple in application but represent an important change in thinking and design. The detailed descriptions below are intended for readers who are either working heavily with the integrated pressure-dependence approach in XMG, or who are porting this approach to another mechanism generator. Other readers may wish to skip to Section 3, which describes the integrated algorithm in detail.

2.1 Revision of the Main Exploration Loop

The main exploration loop, by which XMG discovers new species and reactions, integrates the system of ordinary differential equations (ODEs) representing the explored species, and selects new candidates for exploration, is described in Chapter 1. This loop was rewritten to operate without arbitrary, user-specified time-steps, and to allow repeated integration steps in which only pressure-dependent networks were explored and calculated. The main loop now works as follows.
Once the ODEs of the Reacted Species are prepared, XMG integrates them to the first DASSL time-step. The DASSL time-steps are chosen by a sophisticated Gear-algorithm approach [10] which reflects the stiffness of the system and the rate at which important variables are changing. At the first DASSL time-step, XMG calculates the flux to each Unreacted Species, \( R_{\text{species}(j)} \). Similarly, it evaluates the fluxes \( R_{\text{leak}(i)} \) through the truncated pathways of each pressure-dependent network \( i \). \( R_{\text{min}} = f_{\text{min}}R_{\text{char}} \) is also calculated. XMG chooses the largest value from the set of \( R_{\text{species}(j)} \) and \( R_{\text{leak}(i)} \).

If this largest flux is less than \( R_{\text{min}} \), integration proceeds to the next DASSL time-step, where the above process is repeated. At some point the largest flux exceeds \( R_{\text{min}} \) and integration halts. The integrated approach proceeds to explore either a species or a network, as described in Section 3. XMG then rebuilds the ODEs and begins integration all over again.

The new ConvStat module tracks the status of conversion, and is updated at each DASSL time step. When the user-specified convergence is reached, this module alerts the main loop, which stops the mechanism-building process, and the code then organizes and prints the final output files.

### 2.2 Rate Rule Thermodynamic Consistency

As described in Chapter 1, rate rules are usually posed in XMG in only one direction, the designated “forward” direction. It is assumed this direction is exothermic. When XMG finds the reverse version of this reaction, and this reaction is part of a pressure-dependent network, then it must estimate Arrhenius parameters for this “designated reverse” reaction based on the forward rule.

XMG estimates these reverse Arrhenius parameters in two steps. First, it approximates the reverse activation energy by:

\[
E_{a,r} = E_{a,f} + \Delta H_{rn}(T_{\text{ref}})
\]  \hspace{1cm} (6-1)

where \( E_{a,f} \) is the forward activation energy and \( \Delta H_{rn}(T_{\text{ref}}) \) is the reaction enthalpy at a reference temperature (typically 298 K). Second, Arrhenius parameters \( A_r^\infty \) and \( n_r^\infty \) are fit by a least-squares form to evaluations of \( k_r^\infty = k_f^\infty / K_C \) where \( K_C \) is the equilibrium constant. “Fixing” \( E_{a,r} \) via (6-1) is necessary in order to ensure consistent inputs to a
pressure-dependent $k(T,P)$ calculation. XMG originally assumed that all reactions of certain subfamilies (particularly radical addition or intra-radical addition) would be exothermic, and that their companion reverse reactions (beta-scissions or cyclic beta-scissions) would always be endothermic.

In fact, most reaction families can be exothermic or endothermic, though one case usually predominates. Equation (6-1) can lead to negative estimates of $E_{a,r}$ if the reaction has been incorrectly assumed exothermic and $|\Delta H_{rm}(T_{ref})|$ is large enough. The routines of XMG which assign rate rules were thus re-written to address this issue, in particular for radical additions/beta scissions and intra-radical additions/cyclic beta-scissions.

When a reaction is discovered, XMG now makes a provisional rate rule assignment using the designated forward direction. If the designated forward direction is then found to be endothermic, XMG corrects the rule. For example, upon discovering the beta-scission:

\[ \text{\includegraphics[width=0.5\textwidth]{reaction_diagram}} \]

the code recognizes this reaction as a designated reverse reaction. It thus considers the forward version of this reaction to be radical addition to an internal double bond to form a non-terminal radical. The code looks up $A_j^\sigma$, $n_j^\sigma$ and $E_{a,f}$ for the forward version. Upon discovering the above reaction is an exothermic beta-scission (and not the typical endothermic case), $E_{a,r}$ is set equal to $E_{a,f}$ and the fitting procedure to obtain $A_j^\sigma$ and $n_j^\sigma$ continues as before. Note this is the same as adding the absolute value of the heat of reaction $|\Delta H_{rm}(T_{ref})|$ to $E_{a,f}$ and proceeding with (6-1). Similar changes were made for other sub-families.

### 2.3 Rate Rule Differentiation

Code was added to XMG to allow it to distinguish various subfamilies in some of the larger reactions families, such as intraradical H-abstractions (H-shifts) and intraradical ring closures. Dr. Preeti Aghalayam, at MIT, wrote the initial code to allow
limited H-shift differentiation; this was expanded, debugged, and modularized by the author.

2.3.1 H-shift Differentiation

Each H-shift family is now subdivided into fifteen sub-families which designate the nature of the initial and final radical as indicated in Table 6-1. All of these are assumed exothermic in the direction written, though XMG applies the correction of Section 2.2 where necessary.

<table>
<thead>
<tr>
<th>vinyllic → vinyllic</th>
</tr>
</thead>
<tbody>
<tr>
<td>vinyllic → primary</td>
</tr>
<tr>
<td>vinyllic → secondary</td>
</tr>
<tr>
<td>vinyllic → tertiary</td>
</tr>
<tr>
<td>vinyllic → allylic</td>
</tr>
<tr>
<td>primary → primary</td>
</tr>
<tr>
<td>primary → secondary</td>
</tr>
<tr>
<td>primary → tertiary</td>
</tr>
<tr>
<td>primary → allylic</td>
</tr>
<tr>
<td>secondary → secondary</td>
</tr>
<tr>
<td>secondary → tertiary</td>
</tr>
<tr>
<td>secondary → allylic</td>
</tr>
<tr>
<td>tertiary → tertiary</td>
</tr>
<tr>
<td>tertiary → allylic</td>
</tr>
<tr>
<td>allylic → allylic</td>
</tr>
</tbody>
</table>

Table 6-1. Subfamilies of H-shift reactions. Radical type on left is the starting radical; type on right is ending radical. Each H-shift family (1.2 through 1.5) was subdivided into these sub-families.

2.3.2 Radical Ring Closure Differentiation

Several examples in the course of work showed that the old method of designating a single rate rule for an intraradical addition reaction was inadequate. We divided these first into “exo” and “endo” type ring closures (where an endo ring-closure product has the radical site on the formed ring, and the exo ring-closure leaves the radical site beta to a ring site). Exo and endo intra-radical additions divide further, into
“strained-TS” and unstrained ring closures. In strained transition state ring-closures, the transition state for intraradical addition resembles a strained ring (with two consecutive double bonds, or a triple bond, in the transition-state ring), as shown below:

Additional subdivisions occur when the radical must break allylic stabilization in order to undergo ring closure, as is the case for 2,4-pentadien-1-yl closing to a cyclopentenyl radical. All of these changes are accompanied by coding changes in the corresponding reverse reaction families, to ensure consistency; that is, any subdivisions of a designated forward reaction must be recognized by the code in the reverse direction, so that the proper rate rule can be applied or reversed as needed.

2.4 Prohibited Reactions and Species

Because XMG had no simple way of allowing or disallowing certain species to appear, the source code for each reaction family was edited to prevent them from occurring. We forbid strained ring structures, having two consecutive double bonds or a triple bond (for up to six ring members), from appearing in any reaction family. While such reactions are possible, they are deemed unlikely for the present work, and in any case the thermodynamic property estimator GAPP always failed for such species. In addition, their highly strained nature means that the normal rate rules for their creation and destruction reactions would probably be incorrect.

Similarly, certain reactions deemed to pass through a highly-strained transition state were also prohibited. For example, H-shifts across a consecutive double-bond or a triple bond are prohibited, and H-shifts across rings (but not 1,2 H-shifts along a ring) are also forbidden. Finally, certain reactions were restricted because the group-additivity predictor (GAPP, [5;6]) would generally be unreliable for their products; for this reason intra-radical additions of radicals that were already cyclic were prohibited. While such reactions are certainly possible, they are assumed to be unimportant under the conditions of all the example cases (including methane pyrolysis). Using normal rate rules (such as the H-shift rule types listed in Table 6-1) for these cases would almost certainly give
seriously flawed results, and developing the correct rate rules for such cases was outside the scope of this thesis.

2.5 Setting Rates

The original code evaluated rate constants at multiple times and at various points in the code for a single reaction, leading to organizational chaos whenever substantial code changes were made. This was re-organized so that one module, SetRates, controls the setting or calculation of rate constants. In cases where the reaction is not pressure-dependent, SetRates evaluates \( k(T) \) according to the Arrhenius parameters, and according to whether the reaction has been designated “forward” or “reverse”. In cases where the rate constant is pressure-dependent, and from a library (i.e. having a Troe or third-body form to describe the rate constant), SetRates evaluates \( k(T,P) \) according to the formalism. Evaluation of the bath gas concentration \( [M] \) in either formalism is the same as that used in CHEMKIN [11], but must be calculated inside the integration routine RunDassl, since this is the only place in the code where species concentrations are available. When the reaction is pressure-dependent and is derived from a partial pressure-dependent network, its rate constant is already set, as described later in this chapter.

2.6 Flux Snapshots

In gas-phase mechanisms it is desirable to know which reactions are net producers of radicals, which reactions are net consumers, and their relative importance. The FluxSnap module evaluates these questions and reports “snapshots” of the most important radical producing and consuming reactions at a user-selected set of time points. Note that CHEMKIN and similar packages do not supply this information; their sensitivity and rate-of-production analyses answer separate questions.

2.7 File Output

Major changes were made to the format and content of the copious output files produced by XMG. Some of these are described below and are related to the pressure-dependence modules; others helped make sense of the code’s progress and aided in debugging. Like the setting of the rate constant, printing routines were scattered
throughout the code, and a major effort was made to consolidate and organize printing functions in a rational manner, in the `xmgPrint` module.

2.8 CHEMKIN File Output

The CHEMKIN package [11] can perform sensitivity and rate-of-production analyses on chemical reaction mechanisms. To allow the analysis of XMG-generated mechanisms in CHEMKIN, the `PrintChemkinList` function and associated functions were written with the assistance of Dr. Preeti Aghalayam. These routines build a CHEMKIN-compatible chemical reaction file ("chem.inp") which reflects all the reactions among the reacted species, and a "therm.dat" file of NASA polynomials for each species in the mechanism. At the user's discretion, the "chem.inp" is a set of CHEMKIN-reversible reactions or a set of irreversible (one-direction) reactions. The chem.inp file typically requires some manual editing to repair misnamed "duplicate" reactions (reactions which have the same reactants and products, but proceed via different transition states or pressure-dependent networks). This is because the nature of reaction list storage in the XMG code makes it very difficult to identify duplicate reactions with complete accuracy.

2.8.1 Difficulties with Resonant Radicals

The CHEMKIN-compatible mechanism will normally differ from the actual mechanism used in XMG in one important aspect. Inside XMG, resonance-stabilized radicals (such as propargyl), which have two or more different formal structures, can only be treated as distinct entities. XMG's bond-electron formalism does not allow resonant structures. For example, propargyl radical is actually stored in XMG as the two "separate" species illustrated below:

```
\begin{align*}
\text{\includegraphics[width=0.2\textwidth]{propargyl_radical}}
\end{align*}
```

However, XMG assigns these the same "abbreviated string" indicator, C#CC., which is used as a key in looking up library thermodynamic and rate data. This abbreviated string is also the species identifier used in the CHEMKIN-compatible files, so that one abbreviated string serves to represent what to XMG are two separate species. XMG uses
a fake "reaction" (the triple or double-bond resonance reactions) to allow these species to interconvert very rapidly, as though they were one species.

In the last chapter, we could fix XMG's problems with resonant structures by hand. But note here that the use of a single abbreviated string for both instances above will cause CHEMkin to consider "propargyl" as one species, where XMG considers it as two. This is a source of discrepancy between predicted concentration profiles in XMG, and those resulting from a CHEMkin solution with the "same" mechanism under the same conditions.

2.9 Other Changes

A multitude of other changes and debugging edits were required to allow XMG to run smoothly by itself and with the pressure-dependent modules. Most of these are embedded within the over 50,000 lines of proprietary code and are not meaningful out of their specific context. While the more substantial changes have been listed in this chapter, approximately 200 additional changes were made which are only documented inside the XMG source code.

3 The Integrated Pressure-Dependence Algorithm: XMG-PDep

This section describes the integrated pressure-dependence algorithm, in which our ASA is woven into the existing mechanism generation algorithm XMG, to create "XMG-PDep". The description is, we hope, detailed enough to allow another researcher to understand the algorithm, and reproduce it, within the context of another mechanism generator. The reader interested in broader concepts may be content with the outline given above (Section 1.3), and the discussion of key assumptions below (Section 3.1).

3.1 Key Assumptions of the Approach

In addition to the assumptions involved in a QRRK/Modified-Strong-Collision calculation based on rate rules and group-additivity thermodynamics, two further key assumptions are inherent in our integrated pressure-dependence approach. First, leakage fluxes through pressure-dependent networks are treated "on-par" with fluxes to species in the Unreacted Species listing. Second, rate constants are assumed a function of temperature and pressure, when in reality they should be a function of temperature, and
the set of collider or bath gas concentrations \([M]_i\), where \(i\) runs over all significant bath gases. Further discussion of these issues, and possible resolutions, are presented in Section 4.

3.1.1 The On-Par Assumption

As noted in the algorithm overview (Section 1.3), each partial pressure-dependent network \(i\) has a value \(R_{\text{leak}(i)}\) associated with it, which describes the maximum possible flux to non-included parts of the network. This is illustrated in Figure 6-1 below.

![Diagram of PDep NW #72](image)

**Figure 6-1.** \(R_{\text{leak}}\) in a hypothetical partial-pressure dependent network “#72”. The dotted enclosure marks the partial pressure-dependent network; species \(D^*\) and \(E^*\) are non-included isomers, treated as product channels in the \(k(T,F)\) calculation. The \(R_{\text{leak}}\) flux represents the summed flux to all non-included pathways; it is the maximum possible flux to any path of the network not yet explored.

When considering candidates for exploration, our approach treats each \(R_{\text{leak}}\) flux as having the same “weight” as each Unreacted Species flux. Thus if integration stops because the \(R_{\text{min}}\) criteria has been violated, the code will explore the reactions of an unreacted species \(j\) only if it has the largest instantaneous flux among the set of all fluxes \(R_{\text{leak}(i)}\) and \(R_{\text{species}(j)}\). Alternatively, it will explore the reactions of one isomer of the pressure-dependent network \(i\) if that network has the largest flux \(R_{\text{leak}(i)}\) from among the same set. There is, however, no clear reason that these separate sets of fluxes should be given equal consideration; it might be as reasonable to consider pressure-dependent network fluxes only half as important, or twice as important, as species fluxes.

A further consequence of this assumption is that there is no contributing flux to any Unreacted Species on the edge of a partial pressure-dependent network. In other words, suppose species \(D\) in Figure 6-1 is also an Unreacted Species, which XMG might later pick for exploration and subsequent inclusion in the mechanism. The flux
$k_D^A[B]$ does not contribute to the fluxes which produce $D$ in our approach; that is, it is not included in $R_{\text{species}(D)}$. This flux is instead contained within $R_{\text{leak}(72)}$ in the example above. Normally, this should be a safe assumption. But cases are possible in which $D$ exists at the edge of many pressure-dependent networks, whose $R_{\text{leak}}$ fluxes are all too small to cause further exploration by the main algorithm. It can happen that, if all of these networks were to be explored, so that $D$ was included in all of them, then $D$ might suddenly have a large enough flux $R_{\text{species}(D)}$ to be chosen as a candidate species by the generator. Thus, unreacted species may “hide” at the edges of pressure-dependent networks. Exploration of these networks could cause these species to have $R_{\text{species}(j)}>R_{\text{min}}$.

3.1.2 The “Constant” $k(T,P)$ Assumption

The current version of the code considers as a bath gas any species whose \textit{initial} concentration, at the start of integration, is greater than 10\% (mole). It then builds input files for CHEMDIS according to the initial distribution of bath gases, and it uses the initial concentrations of each throughout the code. Bath gas concentrations never change from their initial concentrations. This assumption effectively restricts our approach to dilute or neat cases, where the concentrations of the main colliders do not change much over the timescale of interest.

Relaxing this assumption is difficult because $k(T,P)$ must become $k(T(t),[M],(t))$ where bath gas concentrations and temperature change with time, $t$. The rate constants must then be written in terms of differential equations (since they now change with time) and integrated along with concentrations, even though the temperature and pressure of the system may be constant. While DASSL can technically solve such a problem, rewriting the entire equation-building structure of XMG to allow this was beyond the scope of the present work. Furthermore, our pressure-dependence calculation scheme only evaluates $k(T,P)$ at specific values of $T$ and $P$; a scanning-and-fitting algorithm is needed to develop a functional form that represents $k(T(t),[M],(t))$ over a defined region of $(T,[M],)$ space.
3.2 The Integrated Algorithm in Detail

3.2.1 Definitions

In the following sections, the word "entrant" is used to denote a reaction (in the chemically-activated case) or an isomer (in a thermally-activated case) which initiates a pressure-dependent network. The word "pathway" refers to an individual, elementary step within a pressure-dependent network, and the phrase "net pressure-dependent reaction" refers to the net reaction resulting from the network with the specified entrant. A "well" or "isomer" refers to one of the adducts of the network. The pressure-dependent network data object stores all these data types. Figure 6-2 illustrates these concepts.

As before, boldface denotes sub-modules or functions within the pressure-dependence or XMG codes. Italicics usually denote memory or data objects, or reactions specifically.

![Diagram](image)

**Figure 6-2.** Entrant reaction, pathway reactions, and net reactions for a pressure-dependent network. Isomers or wells in this system are \( C \) and \( F \). \( k(T,P) \) will be computed for the net reactions and for non-included isomer \( D \), which is treated as a product channel. The net reactions are part of the reaction list in XMG, from which the overall mechanism is constructed. The pathway reactions, however, are local to the network object.
The data object \textit{PDepNetwork} is used to store all the necessary information to understand a partial pressure-dependent network, at any given point, within the pressure-dependence module. The list of these objects is called the \textit{PDepNetworkList}. Data objects are covered in detail in Section 3.3. The "module" is the overall pressure-dependence module, which runs the integrated algorithm. It is made up of various sub-modules, which are discussed in Section 3.5.

3.2.2 Algorithm Flowchart

Figure 6-3 shows the main steps of the integrated pressure-dependence algorithm within XMG. The following sections describe each algorithm step in detail.

**Figure 6-3.** Detailed overview of the integrated pressure-dependence algorithm. Shaded blocks indicate pre-existing sections of code in XMG; solid blocks are new parts added in separate modules for the pressure-dependence algorithm.
3.2.3 Module Initialization

The \textit{PDepNetworkList} is initialized at the beginning of a mechanism generation run, along with the list of bath gases and other main module variables.

3.2.4 Species Exploration and Reaction Construction

\textit{Normal Species Exploration and Reaction Construction}

XMG explores and builds the reactions of a single candidate species at a time; it receives this candidate from the flux test described later. Using the \textbf{CanReact-...-WriteRxnExpression} sequence, it builds all the possible reactions of the candidate species with itself, and with all other species in the \textit{Reacted Species} list.

Upon construction of each reaction in \textbf{WriteRxnExpression}, the pressure-dependence module examines it to check whether it could initialize a pressure-dependent network. Currently any reaction of the form \( A + B \rightarrow C \), \( B \rightarrow C \), or \( B \rightarrow C + D \) is considered to initiate a pressure-dependent network. Of these three types, \( A + B \rightarrow C \) is a chemically-activated initiation of a pressure-dependent network, while \( B \rightarrow C \) and \( B \rightarrow C + D \) are thermally-activated entrant reactions. The pressure-dependence module then creates initial pressure-dependent networks, with these reactions as entrants.

\textit{First Pass Species Exploration and Reaction Construction}

The species exploration and reaction construction steps are slightly different on the first pass through than they are on every other pass. \textit{All} the initial species of the input file are first explored for all the possible reactions among them, using the \textbf{CanReact-DetermineXSites-DoXReactions-IdentifyMolecules-WriteRxnExpression} sequence of XMG. “Pool reactions” also are treated specially in this step. All the initial species are then added to the \textit{Reacted Species} lists. Pressure-dependent networks are created during the first pass in the same manner as during normal species exploration.

3.2.5 Creation of Initial Pressure-Dependent Networks

When the pressure-dependence module identifies a chemically-activated reaction (of the form \( A + B \rightarrow C \)), it initiates a \textit{PDepNetwork} with this reaction as the entrant. If a network already exists with this entrant reaction, however, the module updates the pathway degeneracy of the entrant reaction within that network.
Similarly, when the module finds a thermally-activated entrant reaction, it searches the \textit{PDepNetworkList} for a thermally-activated network whose first isomer is the reactant species ("B", for types $B \rightarrow C$ and $B \rightarrow C + D$). If no such network is found, the module initiates a \textit{PDepNetwork}. If a network is found, but the particular reaction pathway does not exist in the network, the module creates a new pathway within that network. If the network exists, and a pathway in it also exists which exactly matches the discovered pathway, the module increments the pathway degeneracy within the network. Each time a new \textit{PDepNetwork} is built, it is given a unique integer (the \textit{PDepID}); the module keeps count of the total number of networks in the list (\textit{mUniquePDepCount}).

For example, upon exploring the reactions of CH$_4$, the generator will find the first instance of the reaction CH$_4$ $\rightarrow$ CH$_3$ + H. The pressure-dependence module will identify this as a reaction which initiates a pressure-dependent network, and will start a \textit{PDepNetwork} object with this reaction as the entrant. Control is returned to XMG, which promptly finds the next instance of CH$_4$ $\rightarrow$ CH$_3$ + H. The module finds the network that starts with CH$_4$ as the first isomer. It then discovers that this network already has the pathway CH$_4$ $\rightarrow$ CH$_3$ + H, so it increments the degeneracy for this pathway. Since the pathway degeneracy is 4, the module will do this two more times.

A consequence of this approach is that the "same" pressure-dependence system may appear in multiple networks, with different entrant channels. Figure 6-4 illustrates an example "full" pressure-dependence system. The module might first initiate a partial pressure-dependent network starting from the chemically-activated entrant $A + B$. It could then later discover the thermally activated entrant channel $D \rightarrow G + H$, and it would initiate a separate \textit{PDepNetwork} for this starting point. For this example there are four possible \textit{PDepNetworks}; the module may or may not initiate all of them. Each \textit{PDepNetwork} it does initiate will be explored independently according to its particular $R_{\text{leak}}$ value.
The module’s processing functions determine whether these initial pathways are to product channels, non-included isomers, or included isomers. When first initiated, a chemically activated system such as \( A + B \rightarrow C \) is considered to have one non-included isomer pathway, \( A + B \rightarrow C \), which happens to be identical to the entrant channel. Thermally-activated networks will have a set of reactions to non-included isomers and product channels when first initiated. The pressure-dependence module also constructs the appropriate net reactions when new pathways are discovered.

### 3.2.6 Building and Calculating Networks

After species exploration and reaction construction, the module goes through the list of pressure-dependent networks and prepares them for computation. It then builds CHEMDIS input files and runs CHEMDIS for each network that requires a new calculation of \( k(T,P) \). In general, the module only does this when the network structure has changed (due to exploration of an isomer), or when the network is currently new and has not yet been calculated. Note that special cases, like an unexplored chemically-activated system, do not need to be calculated, as for these cases we already know \( R_{\text{net}} = k^- [A][B] \) where \( A \) and \( B \) are the entrant species and \( k^- \) is the high-pressure limit rate constant to the first adduct. The sections below describe how each network needing calculation is prepared and processed.
Bath Gas and Collision Properties

First, the module loads bath gas collider properties from a data file, followed by a search for Lennard-Jones collision parameters appropriate for the first isomer. If these parameters are not available from a data file, the module calculates them via GAPP. Although usually successful, a GAPP failure causes the module to select default Lennard-Jones parameters based on the size of the isomer. In either case, the Lennard-Jones parameters of the first isomer are assumed appropriate for all other isomers in the network. This is a common assumption in pressure-dependent reaction analysis, and probably not an important one, since $k(T,P)$ results are rarely very sensitive to Lennard-Jones parameters. Finally, the module loads a specific collisional energy transfer parameter $\langle \Delta E \rangle_{\text{down}}$ for this bath gas-isomer pair, if the user has supplied it. Normally such specific information is unavailable, and the module reads a general $\langle \Delta E \rangle_{\text{down}}$ from the bath gas input file.

High-Pressure Library Data Search

The module searches a library of high-pressure limit Arrhenius parameters for $A^\infty$, $n^\infty$ and $E_a$ data. Usually, of course, this data is not available, and the high-pressure limit rate rules discussed earlier provide these parameters.

Calculation of Pathway Degeneracy

As noted earlier, rate rules are posed in a single direction, usually the exothermic direction. If a pathway is a designated reverse reaction, and no high-pressure limit data is available for either direction, the module must estimate $A_r^\infty$, $n_r^\infty$ and $E_{a,r}$ from the rate rule for the designated forward case, using Equation (6-1) and the equilibrium constant evaluated from thermodynamic data. In order to do this, the module must know the pathway degeneracy for the designated forward direction. For example, the pathway:

\[ \cdot \quad \rightarrow \quad \ \ + \quad \text{H} \]

would be a designated reverse reaction. The rate rule for the designated forward direction would be that for H addition to an internal double bond to make a non-primary radical. While the actual direction's pathway degeneracy, 2, is known, we need the
degeneracy of the designated forward direction (H addition to the double bond) to evaluate $k_r^-$:

$$k_r^- = \frac{\sigma_f k_{r, site}^-}{K_c} \quad (6-2)$$

where $\sigma_f$ is the pathway degeneracy in the forward direction and $k_{r, site}^-$ is the site-based rate rule for the designated forward reaction.

The pressure-dependence module calculates the forward degeneracy in these cases by taking the products of the reaction and running them through the appropriate **DetermineXSites/DoXReactions** chain (via the author's function **DetermineForwardRPD**). This forces explicit iteration of every possible designated forward version of the reaction, allowing calculation of $\sigma_f$.

**Calculation of Reverse Arrhenius Parameters**

Once the reverse pathway degeneracies are ready, the module estimates Arrhenius parameters for them. This is done by fixing $E_{a,r}$ via (6-1) and calculating $k_r^-$ at various temperatures via (6-2). A short FORTRAN code developed by Dr. Jeffrey Grenda then performs a least-squares fit to estimate $A_r^-$ and $n_r^-$.  

**Isomer Frequencies and Degeneracies**

Our modified, fast version of CHEMDIS requires a set of integer degeneracies for each frequency of the 3-pseudofrequency model, because it uses a direct-count method to estimate the densities of states. While this modification to CHEMDIS saves much computational time, it does not work well with the non-integer degeneracies supplied by GAPP. Our module thus examines each well, or isomer, to determine whether pseudofrequencies and degeneracies need to be estimated.

If they do, the module builds an input file for an author-modified version of Bozzelli’s THERFIT code. THERFIT is an implementation of the Chang, Dean and Bozzelli method for representing the density of states of a molecule by fitting a set of pseudofrequencies and degeneracies to heat capacity data [12]. The module then runs THERFIT, which produces a 3-frequency fit to the heat capacity data, with integer
degeneracies. The module loads the 3 pseudofrequencies and corresponding
degeneracies to the well’s data object; a record of each such frequency calculation is also
archived.

*Building the CHEMDIS Input*

At this point, the *PDepNetwork* data object contains all the information necessary
to build a CHEMDIS input. Our module constructs an input file for the network, treating
pathways to non-included isomers as product channels. Temperature and pressure are
taken from the main user input file. It archives the input file (for later examination) and
then runs CHEMDIS, to produce estimates of \( k(T,P) \) for each net reaction of the network.

*Reading the CHEMDIS Output*

Following calculation of \( k(T,P) \) for each net reaction of the network, the pressure-
dependence module opens the output file and interprets the results. We have modified
CHEMDIS to produce a special, very simple output file which is more easily read by a
machine. The module loads \( k(T,P) \) for each net reaction of the network, and for each
reaction to a non-included isomer. Elementary checks are performed to ensure the
pressure-dependence calculation has not gone awry. The module then archives the
CHEMDIS output file, and the working files for running CHEMDIS are deleted.

3.2.7 *Updating the Reaction List*

Once \( k(T,P) \) estimates are stored in the *PDepNetwork*, the module looks for
library values which might supercede the CHEMDIS calculation of \( k(T,P) \) for a specific
net reaction. It examines the rate constant library and looks for explicitly pressure-
dependent reactions; that is, reactions written in a Troe or Lindemann form. If it finds a
match to a net reaction, it replaces the CHEMDIS estimate of the rate constant with the
library value, though the CHEMDIS estimate is stored separately for comparison. A later
module examines all net reactions for which a library rate constant was available, and
alerts the user when the CHEMDIS and library rate constants differ by more than a factor
of 10.

Once the library replacements are finished, the module goes through the
network’s list of net reactions again. For each one, it scans the global list of reactions in
XMG which make up the current mechanism. When it finds a reaction in the global list
matching the net reaction, it overwrites the global reaction’s \( k(T,P) \) with the newly calculated (or library-derived) value. If the net reaction is new, and has not yet been added to the global list, then the module adds it and assigns it the correct \( PDepID \), to indicate which \( PDepNetwork \) it has come from. The module also examines all net reactions to non-included isomers for a given network. It sums up their rate constants and stores the value in the \( PDepNetwork \) as \( k_{\text{leak(i)}} \). Note that individual pathway reactions (as shown in Figure 6-2) are never added to the global reaction list. Only net reactions are added.

3.2.8 The Integration Step

XMG next examines the global reaction list, and from it, constructs the set of ordinary differential equations (ODEs) which describe how all the Reacted Species evolve under the specified conditions. It then integrates the ODEs using DASSL, advancing just one DASSL time step. It computes \( R_{\text{species(j)}} \), the flux to each Unreacted Species \( j \), using the concentrations from the DASSL solution and the global reaction list. It next evaluates \( R_{\text{leak(i)}} \), the flux to all non-included isomers, for each network \( i \). To do so, the module multiplies the value \( k_{\text{leak(i)}} \) described above, for each network, by the appropriate species concentrations, to produce the flux \( R_{\text{leak(i)}} \).

3.2.9 The Flux Test

The module then examines the combined set of fluxes \( R_{\text{species(j)}} \) and \( R_{\text{leak(i)}} \). If all of these are less than \( R_{\text{min}} = f_{\text{min}} R_{\text{char}} \), integration continues to the next DASSL time step, as depicted in Figure 6-3. If one or more of these fluxes is greater than \( R_{\text{min}} \), integration halts. If the largest of these fluxes is a species flux \( R_{\text{species(j)}} \), control returns to XMG, which takes that unreacted species and explores it, effectively going through the steps of Section 3.2.4 with a new species. If it is a leakage flux \( R_{\text{leak(i)}} \), then the module passes the associated \( PDepNetwork \) to a sub-module, where the network is explored by one non-included isomer. The characteristic, overall mechanism rate \( R_{\text{char}} \) is calculated by Song’s formula [13]:

\[
R_{\text{char}}(t) = \sqrt{\sum_i \left( R_{\text{reacted(i)}}(t) \right)^2}
\]  

(6-3)
3.2.10 PDepNetwork Exploration

Our module first picks a non-included isomer for exploration according to whether or not it has the largest rate constant among all the non-included isomers of the network. It then passes the species and network to a sub-module which acts similar to the CanReact function discussed in Chapter 1. CanReact itself cannot be used to do this, since only particular isomerizations and decompositions of the isomer are possible within the network; it is assumed that activated species will not react with species in the bulk gas phase.

The sub-module initiates the appropriate DetermineXSites-DoXReactions-IdentifyMolecules-WriteRxnExpression sequences to discover all the possible pressure-dependent pathway reactions of the selected isomer. The main pressure-dependence module intercepts reactions constructed in WriteRxnExpression and adds them as pathways to the PDepNetwork, or updates the pathway degeneracies, as appropriate. After all possible pathways have been explored, the sub-module adds the isomer to the network, changes the correct non-included pathways to isomer pathways, and builds the appropriate net reactions to the new isomer and its associated product channels.

After exploration of one non-included isomer of the PDepNetwork, our module builds the network input file. The rate constants $k(T,P)$ are calculated just as described in Section 3.2.6. After calculation, the appropriate net reactions in the global list are updated with new $k(T,P)$ values (Section 3.2.7) and the code proceeds to once again build and integrate the ODEs of the mechanism. Figure 6-3 shows this loop.

3.2.11 Continuation and Termination of the Integrated Algorithm

The integrated algorithm proceeds in this way, exploring the reactions of species (and initiating pressure-dependent networks along the way) or exploring the reactions of pressure-dependent networks as appropriate. The integrated algorithm continues around one or the other of the two main loops in Figure 6-3 until the conversion test is satisfied (in the ConvStat module). Once this test is passed, a final DASSL run provides data for the FluxSnap module, the production of CHEMKIN-compatible files, and other outputs.
3.3 Data Objects in Detail

3.3.1 The PDepNetwork Object

The most important data object of the pressure-dependence modules is the PDepNetwork object. It is this object which is passed, processed, calculated and checked by the pressure-dependence sub-modules, and at any given time it stores all of the information necessary to build a CHEMDIS input file that describes the network. A complete description of this object is not given here; the source code for it is reasonably well-documented in the Source Code Supplement, as the file “PDepNetworkMod.h”. It may be helpful to “follow along in the source” as this object is described. The main pressure-dependence module maintains a list of these objects, one for every pressure-dependent network in the system.

PDepNetwork

The PDepNetwork contains four main substructures: the PDepInfo object, the PDepWellList, the NetPDepList and the Rleak object, as illustrated in Figure 6-5. The PDepInfo structure contains general information about the network. PDepWellList is a linked list of PDepWell objects, one for each included isomer in the network. A linked list of net pressure-dependent reactions for the network is held as NetPDepList. Rleak holds the values of the summed rate constants to non-included isomers and the net leakage flux, as well as other values needed for calculation.

![Diagram](image)

Figure 6-5. The PDepNetwork object.
PDepInfo

PDepInfo holds general information required to build a CHEMDIS input file, as well as information required for bookkeeping. PDepID is the unique network ID number, assigned when the network is created. The IsChemAct flag indicates whether the entrant is a chemically activated pathway or a thermally activated species. EntrantID1 and EntrantID2 store the molecule IDs of the entrant molecule(s); FirstWellID stores the molecule ID of the first adduct or isomer. EntrantRxn is a pointer to a Reaction structure (as defined in the XMG source) which describes the entrant reaction for this network (in the case where that reaction is chemically activated). Among much other data, Reaction stores the Arrhenius parameters and the enthalpy and entropy of reaction, as well as molecule IDs for all the species involved in the pathway. IsUpdated describes whether the network has been changed and requires a new k(T,P) calculation. The IsomColl and BathGasList objects hold collision parameters for the bath gases.

PDepWellList and PDepWell

PDepWellList is a linked list of PDepWell objects, one for each isomer in the network. Figure 6-6 depicts the PDepWell. Each PDepWell contains a WellID, the molecule ID of the isomer, and a linked list of PDepPath objects.

![Diagram](image_url)

**Figure 6-6.** The PDepWell and PDepPath objects.
PDepPath

Each PDepPath describes an elementary pathway in the pressure-dependent network. There is one PDepPath for each elementary pathway starting from the PDepWell, except the entrant pathway in chemical activation cases (this is stored in PDepInfo). The PDepPath stores a pointer to a Reaction structure which describes the pathway, as well as the PathType, which indicates whether the pathway is to an isomer, a product channel, the entrance channel, or a non-included isomer. Additional flags describe the state of the PDepPath as regards pathway degeneracy and Arrhenius fitting if it is a designated reverse reaction.

NetPDepList

Net reactions of the network are stored in NetPDepList, a linked list of Reaction objects. These contain thermodynamic information for each reaction, as well as the current estimate or library value for k(T,P).

Rleak

The Rleak object contains, in addition to the variables Rleak and RleakFlux, the current concentrations of the entrant species or entrant isomer. These are needed to calculate Rleak(i) from the summed rate constants to all non-included species of the network (kleak(i)).

3.3.2 Other Objects

Almost all other data objects in the pressure-dependence module are objects local to particular submodules. A key module-wide object is PDepModuleStat, which tracks the overall state of the module. The entire pressure-dependence module is always in one of two states: “exploring network” or “not exploring network”. The module switches to “exploring network” when it is discovering the pathways of a single PDepNetwork; that is, it is exploring a network. It is “not exploring network” at all other times; in particular, it is in the “not exploring network” state when the main XMG software is constructing the reactions of a species via the main CanReact-DetermineXSites-DoXReactions-IdentifyMolecules-WriteRxnExpression sequence discussed in Chapter 1.
3.4 Module Layout Overview

The layout of the pressure-dependence module is illustrated below in Figure 6-7. The dotted enclosure signifies the pressure-dependence main module; the sub-modules are shown along with the major functional connections between them (not all connections are shown). Solid double arrows indicate control is passed to and from the module. Dotted single-arrows indicate, conceptually, that the module on the starting end more or less maintains control, and probes the other module for information. This figure represents only the conceptual layout of the sub-modules; the access each sub-module has to different structure types and objects is a separate issue, discussed briefly later in the chapter.

Because the XMG code is extremely complicated (over 50,000 lines of largely uncommented code), and has been modified by multiple authors, a "barrier" sub-module, PDepNetwork, sits between it and the rest of the pressure-dependence sub-modules, as suggested by McConnell for these situations [9]. All calls to the pressure-dependence module from the XMG main routines are through PDepNetwork, which then calls the other sub-modules to perform the appropriate tasks. When these tasks are complete, PDepNetwork returns control to the main XMG process. This helps limit the confusion and complexity resulting from interaction with the larger XMG software. It also simplifies maintenance, as the module dependencies are clearer.

PDepCanReact is an exception, and is allowed to directly call the DetermineXSites-DoXReactions-IdentifyMolecules-WriteRxnExpression sequence embedded in the XMG code. However, these calls are "encapsulated" - control is maintained in the PDepCanReact sub-module (hence the single-direction arrow).

Almost all the sub-modules directly use Broadbelt's linked-list module (called List), as well as many functions related to the ChemGraph structure (properties of the molecule or radical, including the adjacency list, are stored in the ChemGraph). These calls occur without passing through PDepNetwork (and thus break the good-coding-practice rules) but it was felt these basic modules, essentially unchanged since the original NetGen of 1994 [1], were unlikely to be altered, and were reliable enough to be called directly. Many of the sub-modules also call a set of proprietary string handling and parsing routines written by Dr. Jeffrey Grenda.
Most of the sub-modules call print functions in **PDepPrint**. **PDepCheck** interacts directly with many of the sub-modules to trap subtle errors in the networks at different stages. **PDepCheck** resolves the errors if it can and issues error messages when it cannot. The great majority of the errors found stem from bugs in the XMG or GAPP codes which are only noticed deep within the pressure-dependence sub-modules. Not all connections are shown in Figure 6-7, and most sub-modules call a few functions (usually testing utilities) in other sub-modules.

![Diagram](image)

**Figure 6-7.** Conceptual layout of the pressure-dependence module. The large enclosure marks the boundary of the pressure-dependence module. Inside are separate sub-modules for performing separate tasks. Each sub-module corresponds to a *.c* file. Solid double arrows indicate strongly interacting sub-modules in which conceptual control changes hands; dotted arrows indicate cases where one sub-module calls functions within another to perform specific tasks.

### 3.5 Individual Sub-Module Descriptions

Very brief discussions of some of the important sub-modules are given here. These essentially mirror the description of the algorithm given previously but are now organized by sub-module name. The source code comments of each sub-module contain further documentation.
3.5.1 PDepNetwork

This sub-module is the general gateway to the other pressure-dependence modules. The XMG main routines call functions in this sub-module, which then transfer the work to other, specific sub-modules. Thus each function in PDepNetwork is called by the XMG main thread directly; the XMG source is not allowed to call any other pressure-dependent sub-module directly (this is arranged through header file construction).

3.5.2 PDepInit

PDepInit allocates memory for new PDepNetwork objects and initializes their variables where needed. It also contains routines to allocate and initialize memory for all the sub-objects of the PDepNetwork (PDepInfo, PDepWell, PDepPath ...). It includes a few testing utilities (e.g. the boolean test “WellIsFirstWell”) used by other sub-modules.

3.5.3 PDepProcess

PDepProcess is a collection of three smaller sub-modules. The first (ProcessEntrantPathway) is active when the pressure-dependence module is in the “not exploring network” state. It takes reactions passed to it via PDepNetwork during the main XMG sequence, when XMG is building the reactions of a species, and checks to determine whether the reaction could be pressure-dependent. If it is, and a new network is needed, PDepProcess directs PDepInit to construct a new PDepNetwork, and this reaction is made the entrant reaction (or entrant species if thermally activated). If the reaction is pressure-dependent but the appropriate PDepNetwork exists, the entrant pathway degeneracy is incremented.

The second sub-module (ProcessIntmRxn) is active when the overall module is in the “exploring network” state. This sub-module examines reactions generated by WriteRxnExpression and passed through PDepNetwork during the exploration of a particular pressure-dependent network. It then constructs the PDepPath objects and net reactions, as needed, and adds them to the PDepNetwork. PDepProcess also determines whether a pathway is to an isomer, product channel, entrant species, or non-included isomer.

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The third sub-module is a set of utilities and functions which serve the other two sub-modules. It includes specific tests on various features of the PDepNetwork; these tests are used often by other components of the pressure-dependence module as well.

3.5.4 PDepCalc

PDepCalc is the calculational workhorse of the pressure-dependence module set. It performs all the tasks required to transform the PDepNetwork into a CHEMDIS input file, including replacement of rate-rule high-pressure limit parameters with library parameters where available, fitting of reverse Arrhenius parameters where needed, and calculation of integer degeneracy and frequency sets for each PDepWell via PDepIntFreq. It oversees the CHEMDIS run and archives input and output files for later examination.

3.5.5 PDepResults

A separate sub-module, PDepResults, is required to read in and correctly interpret the text-file output of the CHEMDIS run. Results for $k(T,P)$, and the summed rate constant to non-included species, are loaded to the PDepNetwork.

3.5.6 PDepUpdate

After results have been loaded to the network, PDepUpdate replaces $k(T,P)$ values for net reactions with library Troe or Lindemann forms, if these are available. It then searches the XMG global reaction list, and updates the appropriate reactions in that list with new $k(T,P)$ values. If necessary it adds net reactions from the PDepNetwork to the global list.

3.5.7 PDepExplore

This routine governs the incremental exploration of a PDepNetwork. It includes a small sub-module that determines which non-included isomer of the network is dominant. Once the non-included isomer is chosen, PDepExplore transfers control to PDepCanReact, to determine all the possible pathways for this isomer. After this, PDepExplore modifies PDepPath objects to ensure that the formerly non-included
isomer is now treated as a true isomer, and that the newly discovered paths have the correct types.

3.5.8  **PDepCanReact**

This sub-module receives a *PDepNetwork* and a *ChemGraph* from *PDepExplore*, where the *ChemGraph* corresponds to the non-included isomer chosen for exploration. It then calls the *DetermineXSites-DoXReactions-IdentifyMolecules-WriteRxnExpression* sequences to find the pathways of the isomer. During this time the module state is “exploring network”, so *PDepProcess* is capturing the reaction pathway information and adding it to the *PDepNetwork*.

3.5.9  **Module Structure and Function Access**

The header file “PDepNetworkMod.h” declares the structure of all the objects used in the pressure-dependence modules. All the sub-modules have access to these structures or object types, as well as the *ChemGraph* type, *Reaction* type, and other types declared in the XMG header file “ChemGraph.h”. In addition, each sub-module technically has access to all the functions of any other sub-module. While not the best coding practice, this allowed one general header file (PDepNetworkMod.h) to be used for the entire pressure-dependence module. The larger XMG code cannot access any functions or structures of the pressure-dependence module except those detailed in the public header “PDepNetworkPub.h”. In general, function prototypes for the public functions of *PDepNetwork* are included in this header, since *PDepNetwork* is the gateway sub-module.

3.5.10  **Module Variable Access**

The main XMG code is not allowed access to *any* variables of the pressure-dependence module. Conceptually, access from XMG to the pressure-dependence module occurs only through the gateway *PDepNetwork*. This is a key practice which should be preserved in any implementation of the module. Similarly, the sub-module *xmgaccess* controls the communication between the pressure-dependence module and XMG’s global variables for most cases. Because of XMG’s non-modular structure, however, it was impossible to prevent access to many XMG global variables by the
pressure-dependence module. Instead, coding discipline and specific prototypes ("extern" statements) were used to make the access obvious and controlled, where xmgaccess was not employed. In particular, searching XMG's linked global lists through xmgaccess proved too cumbersome, so that these lists are sometimes accessed directly (the access is read-only in these cases).

3.6 Issues for Implementation in Other Mechanism Generators

While much effort has been spent to design a reasonably modular and easily maintained pressure-dependence code, this work has been done wholly in the context of XMG. Certain non-modular features of the code presented here, which worked well in the XMG context, would become stumbling blocks during implementation in a more modular, structured generator.

First, as mentioned above, many of the sub-modules employ utilities located in other sub-modules, and each of the sub-modules can access another sub-module's functions. Before porting the module to another generator, the utility functions used by multiple modules should be properly collected into specific utility modules, and access to them should be more controlled. In most cases, moving utility functions to different files should not be difficult, but better access control should make the modules more portable and maintainable. In particular, there are a number of separate routines (IsEntrantPDep, IsRxnPDep, IsPDepOn) which determine whether a reaction could be pressure-dependent or not. These are in different sub-modules, and changes to them must be synchronized with each other and with compiler definitions in the Makefiles. This makes them a confusing aspect of the code, and their functions should be collated into a separate, single sub-module.

Second, the pressure-dependence module often directly accesses global lists of reactions and species in XMG. This is because it was quite difficult (given the nature of the XMG source) to avoid direct access. Other mechanism generators will certainly have different lists (probably not simple linked lists) and different controls on accessing them. In fact, a good mechanism generation code would not allow the pressure-dependence module to ever see these lists directly but would force access through a separate interface. Before attempting to port the module, a sub-module should be designed which would

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handle access requests, searches, and changes to the generator's globally maintained species and reaction lists.

4 Known Challenges and Possible Remedies

4.1 The On-Par Assumption

The on-par assumption discussed in Section 3.1.1 could allow unreacted species to "hide" at the edges of partially explored pressure-dependent networks, as non-included species. If these species potentially feed into autocatalytic pathways, serious problems might emerge with the above approach. Three proposed remedies are explored here.

4.1.1 Non-included Flux Calculation

At a given point during the run, the module could examine the flux to each non-included species of each network, and calculate the summed flux $R_{\text{incl}(n)}$ to each non-included species $n$ across all partially-explored pressure-dependent networks. For example, suppose species $B$ is a non-included isomer of pressure-dependent networks 1, 2, and 3. We could calculate $R_{\text{incl}(B,1)}$, $R_{\text{incl}(B,2)}$ and $R_{\text{incl}(B,3)}$ as the fluxes to $B$ from networks 1, 2 and 3 respectively. Then $R_{\text{incl}(B)} = R_{\text{incl}(B,1)} + R_{\text{incl}(B,2)} + R_{\text{incl}(B,3)}$. The code could then check whether $R_{\text{incl}(B)} > R_{\text{min}}$, and if so, force exploration of some or all of networks 1, 2, and 3 on non-included isomer $B$. This would prevent $B$ from hiding at the edges of networks, at the expense of additional network exploration.

4.1.2 Weighted Leakage Flux

There is no special reason that the set of $R_{\text{leak}(i)}$ should be compared evenly to $R_{\text{spec}(j)}$. Instead, we could imagine boosting $R_{\text{leak}(i)}$ by a weighting factor, so that values of $w_{\text{leak}}R_{\text{leak}(i)}$ are compared to $R_{\text{min}}$, where $w_{\text{leak}} > 1$. The weighting factor could be chosen by the user, or scaled to a parameter of each network. For example, it might be helpful to set $w_{\text{leak}}$ equal to the number of non-included isomers in the network. This technique is very simple to implement, but could be more expensive in terms of network
exploration than the non-included flux calculation. It is also not yet clear what value $w_{\text{leak}}$ should have.

4.1.3 Non-included Species Contribution Approach

Suppose species $j$ is an Unreacted Species with unreacted species flux $R_{\text{species}(j)}$. If $j$ is also a non-included isomer in a pressure-dependent network, the flux to $j$ as a non-included species is not part of $R_{\text{species}(j)}$. $R_{\text{species}(j)}$ is made up only of fluxes to $j$ from net pressure-dependent reactions and pressure-independent reactions. In theory a very different approach is possible, which would not depend on $R_{\text{leak}(i)}$. We could allow each non-included pathway to $j$ from any pressure-dependent network to contribute directly to $R_{\text{species}(j)}$. Then, $R_{\text{species}(j)}$ would be the summed flux contributions from each pressure-independent reaction, each net pressure-dependent reaction, and each non-included pathway which produces $j$.

When $R_{\text{species}(j)} > R_{\text{min}}$ and species $j$ is thus chosen for exploration, we could force exploration of all, or a significant fraction of, the pressure-dependent networks which have $j$ as a non-included isomer. After this step exploration of species $j$ could continue in the normal manner. Exploration of all networks with $j$ as a non-included isomer could greatly increase the number of networks explored, so it would probably be wiser to explore just the top one or two networks which contribute to $j$ in this scheme. At first glance this remedy appears to eliminate the possibility that species might hide on the edges of the network.

This approach was proposed by the author very early in the work, and was ultimately rejected for two reasons. First, it seemed quite difficult to implement, and did not lend itself to modular construction. Second, when networks are explored in this way, the bound for the network truncation error in $k(T,P)$ predictions is no longer clear. In theory, the $R_{\text{leak}(i)}$ screening approach of Chapter 4, and this remedy approach, could be overlaid in order to bound the truncation error. Despite the obvious coding difficulties, this “non-included-isomer-contributes” approach remains a valid alternative, which was not pursued beyond the design stage in our work.
4.2 Single-Point \( k(T,P) \) Values

As currently implemented, the \textit{PDepNetwork} object represents a network designed for one temperature, and one pressure. In practice this will not be sufficient, as most users will need \( k(T,P) \) predictions (and hence, appropriately sized networks) over a certain range of \( (T,P) \). To complicate matters further, \( k(T,P) \) is really \( k(T(t),[M_i](t)) \) where \( [M_i](t) \) is the concentration of bath gas \( i \) at time \( t \). This second point could matter – it is well-known that certain colliders (such as water) can be many times more powerful than others (such as nitrogen) in removing energy from a chemically activated species. Thus the rapid appearance of water in, for example, a stoichiometric combustion process could change certain \( k(T,[M_i](t)) \) in an important way. Finally, in most real systems, temperature will change with time and extent of reaction.

It will at least be necessary to change sub-modules such as \textit{PDepCalc} and \textit{PDepResults} so that they scan a temperature and pressure range. A module could be then used to build a fitting form, or at least an interpolation grid, to represent \( k(T,P) \) over this range for each net reaction in the network. The summed rate constant to all non-included isomers, \( k_{\text{leak}}(T,P) \), should also be represented by a fitting form, so that the leakage flux \( R_{\text{leak}} \) can be estimated at any \( T \) and \( P \) in the space scanned. Fitting forms should also provide reasonable estimates of the derivatives for each channel and the leakage flux:

\[
\frac{\partial k(T,P)}{\partial T}, \frac{\partial k(T,P)}{\partial P}, \frac{\partial R_{\text{leak}}}{\partial T}, \frac{\partial R_{\text{leak}}}{\partial P}
\]

It is these derivatives which are required in the method of Song et al [13]. Without them, construction of a mechanism over a range of temperatures and pressures is very difficult. Note that the above derivatives become more complex (but not intractable) when the rate constant is treated more rigorously as \( k(T,[M_i](t)) \). As long as only a few bath gases are important at any given point during mechanism development, there are not too many more derivatives to consider.

Possible fitting forms for multi-well \( k(T,P) \) include the 12-parameter form of Kazakov, Wang and Frenklach [14], but even a 12-parameter form may be too many parameters. A 12-parameter fitting form would require many more than 12 sampling
points on a T,P grid; a judicious finite-element interpolation may prove more successful. However, the Kazakov approach should be examined closely for simplification opportunities.

5 Conclusions

This chapter demonstrates how we have integrated the pressure-dependent network truncation algorithm of the previous chapters into a combined algorithm for exploring pressure-dependent networks and species. We thus describe the first known mechanism generator to incorporate pressure-dependent reactions in a general and rational manner. It provides for calculation of \( k(T,P) \) where needed, on-the-fly, and builds individual pressure-dependent networks only as much as is necessary. Given the temperature, pressure, initial species concentrations, and desired conversion, this approach will construct the appropriate mechanism “from scratch”, in an unbiased and systematic manner, using the same flux criteria \( R_{min} \) to both add species and explore pressure-dependent networks. We have labeled this integrated mechanism generation software “XMG-PDep”, for “ExxonMobil Mechanism Generator with Integrated Pressure-Dependence”. A successful application of XMG-PDep to methane pyrolysis, which yields a new mechanism to explain that system’s autocatalytic behavior, is discussed in the next chapter.
Citation List

CHAPTER 7: APPLICATION TO METHANE PYROLYSIS
1 Introduction

Methane pyrolysis has been extensively studied for many decades, both for its potential to convert methane to more valuable hydrocarbons, and its importance within larger combustion and pyrolysis mechanisms (references [1-13] provide a sample of recent work in this area). Pyrolysis of methane often produces large quantities of coke, carbon, and hydrogen, since these are the thermodynamically-favored products at almost all practical temperatures [7]. This seriously limits its straightforward industrial application [10], so that research focuses on novel reactor designs and catalysts which could kinetically trap desirable products before coke and soot dominate (for example, [14]). Proper understanding of the homogeneous, gas-phase mechanism of methane pyrolysis is thus crucial for successful reactor and catalyst design [2]. In addition, correct modeling of combustion in fuel-rich regimes sometimes requires a methane pyrolysis sub-mechanism [6].

These demands have driven various attempts at a mechanistic understanding, over a wide range of temperatures and pressures. At lower temperatures and moderate pressures (below 1100 K and 0.5-1.0 atm), Chen and coworkers performed numerous experiments on methane pyrolysis [15-17], and discovered a sharp autocatalysis which neither surface reactions nor the then-current gas-phase understanding could account for. Indeed, they found autocatalysis a general but inexplicable feature of lower-temperature (< 1100 K) methane pyrolysis. The fact that the autocatalytic effect appeared at extremely small methane conversions (less than 1%) only added to the mystery. Despite the early models of Roscoe and Thompson [18], this autocatalytic behavior defied explanation until the work of Dean [19].

Dean proposed a number of previously unconsidered pathways which could account for autocatalysis under the conditions of Back and coworkers (1038 K, 0.58 atm, neat batch pyrolysis). In particular, he stressed the importance of cyclopentadiene, formed via the pressure-dependent pathways of Equation (7-1):
Cyclopentadiene, once formed, may function as a chain-brancher by dissociating into the resonantly stabilized cyclopentadienyl radical, and a hydrogen atom:

\[
\text{Cyclopentadiene} \leftrightarrow \text{Cyclopentadienyl radical} + \text{H}
\]  
(7-2)

Both the cyclopentadienyl radical and the hydrogen atom abstract hydrogens from CH\textsubscript{4} under the experimental conditions:

\[
\text{Cyclopentadienyl radical} + \text{CH}_4 \rightarrow \text{Cyclopentadiene} + \text{CH}_3
\]  
(7-3)

The cyclopentadiene product can dissociate to cause chain branching once again. In this way Dean provided the first plausible explanation for the autocatalytic upturn measured by Back et al., and the work found broader use in illustrating the crucial role of cyclopentadiene in various other pyrolysis and combustion processes.

However, recent experimental and theoretical data on the enthalpy and entropy of formation for cyclopentadienyl [20-25] suggest that reactions (7-1)-(7-3) alone are not sufficient to explain autocatalytic behavior [26;27]. Dean used a cyclopentadienyl enthalpy of formation close to that of McMillen and Golden (\(\Delta H_f^{298} = 58\ \text{kcal/mol}\) [28], whereas more recent values from various research groups are about 4 kcal/mol higher (clustered around 62 kcal/mol). With the more widely accepted thermochemical parameters for cyclopentadienyl, reaction (7-2) no longer proceeds rapidly enough to drive autocatalysis to the extent observed. Figure 7-1 below shows how the Dean mechanism changes when more recent data for cyclopentadienyl radical is used. That mechanism is now clearly unable to explain most of the autocatalysis in methane pyrolysis, and a new mechanism is needed.

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Figure 7-1. Attempts to explain autocatalysis in methane pyrolysis at 1038 K and 0.58 atm for very low conversions of methane. The most recent mechanism for these conditions [19] no longer explains the autocatalysis. Open symbols represents various data sets of Back and coworkers. The dotted line represents the prediction of the original mechanism of Dean in 1990. The solid line illustrates the Dean mechanism once again, but this time with updated values for the thermodynamic data of cyclopentadienyl and other species, as well as an improved QRRK method for calculating pressure-dependent rate constants.

In this chapter we apply our computerized mechanism generation tool with integrated pressure-dependence, "XMG-PDep", to the problem of methane pyrolysis under the conditions of Chen, Back and Back [15-17]. We use the integrated pressure-dependence algorithm of the previous chapter to build the mechanism "from scratch", systematically, using the scaled flux termination criteria $R_{\text{min}}$. This criteria ensures that the mechanism contains the important pathways, but is not combinatorially and unmanageably large. Bias in mechanism development is thus constrained to the design of the reaction families; that is, the specification of broad classes of possible reaction types which the generator will examine. The approach suggests a number of "new" pathways that could be crucial to autocatalysis. Some of these pathways have never been considered in previous methane pyrolysis work, and are rarely, if ever, given consideration in larger combustion or pyrolysis mechanisms. This chapter also represents
the first application of automated pressure-dependent mechanism generation to a real-world process.

The integrated approach to pressure-dependent mechanism generation, "XMG-PDep", was described in the previous chapter. Section 2 describes the specifics of our application to methane pyrolysis, and the thermodynamic and reaction rate data used in building the mechanism. Section 3 describes the mechanism briefly and shows the agreement with the experimental data of Back et al. Section 4 discusses the sources of autocatalysis in the mechanism, as well as other results of the flux and sensitivity analyses. Finally, Section 5 discusses the conclusions and recommendations of this portion of the thesis.

2 Method

We modeled the Chen, Back and Back experiments by assuming a homogeneous, isobaric, isothermal batch pyrolysis starting with pure methane at the conditions they specified [15,17]. Our integrated mechanism generation approach implicitly assumes this model when building and integrating the ordinary differential equations (ODEs) required to calculate fluxes. Given the small conversions and slow process evolution, as well as experimental work showing surface reactions were not significant [17], the isothermal, isobaric batch model for the experiments seemed appropriate.

We applied XMG-PDep to generate a lower-temperature methane pyrolysis mechanism appropriate for the conditions of Back et al. The XMG-PDep mechanism generator is described fully in Chapter 6; a brief review is given below. Next are descriptions of the input data, reaction families, thermochemical data, rate constant data, and rate rules that the generator used to build the mechanism.

2.1 A Brief Review of XMG-PDep

XMG-PDep uses a set of reaction families to explore the possible reactions of chemical species, as described in Chapter 1. The families are broad classes of reactions, from which XMG-PDep creates specific instances based on the species under consideration. At the start of generation, XMG-PDep adds the user-specified starting species to the mechanism and generates a set of initial reactions using the families. In doing so it generates new species, as well as partial pressure-dependent networks, which
become candidates for exploration. XMG-PDep constructs and integrates a set of ordinary differential equations (ODEs) representing the evolution of the system described by the current mechanism in an isothermal, isobaric batch reactor. It can then evaluate the mechanistic importance of each partial pressure-dependent network, and each non-included species, based on its flux.

XMG-PDep next selects the most important species or pressure-dependent network and explores its reactions using the families. It adds the new reactions or species to the mechanism as appropriate, and redoes the ODE integration. XMG-PDep repeats the process of exploration and integration until the flux criteria in Chapter 6 is satisfied for all species left out of the mechanism, and for all pressure-dependent networks which have been left partially explored. In this way mechanism growth is rationally terminated.

The rate constants and thermochemical parameters required for the mechanism are taken, when available, from small electronic libraries of such data. Usually, however, the correct rate constant or thermochemical data for a given discovered reaction is not available from literature. In these cases rate rules are used for the pressure-independent rate constants, and group additivity predictions are used for thermochemical parameters. Pressure-dependent rate constants are evaluated from partial pressure-dependent networks with a modified version of the Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision code "CHEMDIS", as described in Chapters 3 and 6. High-pressure limit Arrhenius parameters and heat capacity data are the primary inputs to this code for evaluating $k(T,P)$.

2.2 Initial Input Data

Generation began with an input file specifying temperature $T = 1038 \, K$, pressure $P = 0.58 \, atm$, and $x_{0,CH4} = 1.0$ where $x_{0,CH4}$ is the starting mole fraction of methane. The generator explored the possible pressure-dependent and pressure-independent reactions that methane and the subsequent intermediates would undergo, according to the $R_{min} = f_{min} R_{char}$ flux criteria as discussed in Chapters 1 and 6. We used a tolerance $f_{min} = 0.01$ and specified a final conversion of methane $X_{F,CH4} = 0.0055$, or 0.55% methane conversion, in order to build a model covering the timescale of the experiments.
2.3 Reaction Families

Mechanism generation in XMG-PDep still uses the basic bond-electron formalism and graph-theory approach of NetGen [29]. Thus the generator only discovers elementary reactions which have been coded in the source as reaction families. Each family has an associated reaction matrix by which graph-theory algebra is applied to produce new species and specific reactions [30-32]. The allowed reaction families, with example instances, are given in Table 7-1. Elementary-step families in Table 7-1 of the form \( A + B \rightarrow C \), \( C \rightarrow A + B \) and \( C \rightarrow D \) are also used to generate the pressure-dependent pathways in each pressure-dependent network, as discussed in Chapter 5.
<table>
<thead>
<tr>
<th>FAMILY</th>
<th>DESCRIPTION</th>
<th>EXAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation</td>
<td>C-C and C-H bond dissociation of a molecule</td>
<td><img src="image" alt="C-C and C-H bond dissociation" /> + CH₃</td>
</tr>
<tr>
<td>Recombination</td>
<td>Reverse of Dissociation</td>
<td>H + <img src="image" alt="H and C-H bond" /></td>
</tr>
<tr>
<td>Radical Addition</td>
<td>Radical addition to double or triple bond of a molecule</td>
<td><img src="image" alt="Radical addition" /></td>
</tr>
<tr>
<td>Beta-scission</td>
<td>Reverse of Radical Addition</td>
<td><img src="image" alt="Beta-scission" /> + H</td>
</tr>
<tr>
<td>H-abstraction</td>
<td>Abstraction of H atom from a molecule by a radical</td>
<td><img src="image" alt="H-abstraction" /> + <img src="image" alt="H addition" /></td>
</tr>
<tr>
<td>Disproportionation</td>
<td>Radical disprop. to form two molecules</td>
<td><img src="image" alt="Disproportionation" /> + CH₄</td>
</tr>
<tr>
<td>Molecular Addition</td>
<td>Reverse of disprop.</td>
<td><img src="image" alt="Molecular Addition" /> + <img src="image" alt="Molecular Addition" /></td>
</tr>
<tr>
<td>H-shift (1,2 through 1,6)</td>
<td>Intra-radical H-abstraction</td>
<td><img src="image" alt="H-shift" /></td>
</tr>
<tr>
<td>Intra-radical Addition (1,5 and 1,6)</td>
<td>Intra-radical addition to a double or triple bond (1,5 and 1,6 only)</td>
<td><img src="image" alt="Intra-radical Addition" /></td>
</tr>
<tr>
<td>Cyclic Beta-scission</td>
<td>Cyclic beta scission which opens a ring radical (reverse of Intra-radical addition)</td>
<td><img src="image" alt="Cyclic Beta-scission" /></td>
</tr>
</tbody>
</table>

Table 7-1. Elementary-step reaction families for methane pyrolysis mechanism generation at lower temperatures and low conversion of methane. These represent all the “possible” elementary reaction types which the generation tool will explore. Upon choosing a species or pressure-dependent isomer for exploration, the generator will explore all possible instances of each family in which that species might take part.

### 2.3.1 Prohibited or Restricted Families

XMG-PDep, built on the framework of the original NetGen software, cannot handle reactions of diradical species. Thus all the families above (and further reaction
families specific to diradicals) ignore the possibility of diradical formation, or reaction through diradical intermediates. We have assumed that diradical reactions would be largely unimportant at the low temperature, oxygen-free conditions studied in this work.

Other reaction families were restricted as discussed in Chapter 6, for a number of reasons. First, these reactions are likely to be unimportant under low-temperature conditions. Second, accurate rate rules for them were unavailable. Finally, in some cases our group-additivity property predictor (GAPP, by Grenda et al [33]) would fail for most versions of the product. For example, H-shift reactions were not allowed across rings (though 1,2 H-shifts along a ring were allowed) because the normal rate rules of this chapter would be highly incorrect for these cases, and because these cases would be expected to have high barriers due to the required ring torsion. The intra-radical additions of cyclic radicals which also had an unsaturated bond were prohibited, because GAPP could not generally handle multi-ringed radical species. Topomerizations and concerted elimination reactions were not considered for similar reasons.

Finally, 1,3 and 1,4 intra-radical additions, while certainly possible, were prohibited because of their higher barriers, and because GAPP failure on the product species was too frequent to be manageable. Note that GAPP is an ExxonMobil proprietary software which could not be altered by the author, so that each GAPP failure would have to be remedied by hand for the particular species involved using the manual group-additivity/hydrogen-bond-increment software THERM [34-36]. In the case of 1,3 and 1,4 intra-radical additions, such failures occurred so frequently that individual species repairs became impossible, and these sub-families were turned off.

We prohibited the above cases for a combination of practical and scientific reasons, but the decisions above represent a bias introduced into our mechanism construction approach. Table 7-1 is also biased, since, by definition, it does not include unknown but possibly important reaction families. The advantage here is that the bias is clearly defined and easily stated, and that mechanism construction proceeds in a very systematic manner given these rules. Accuracy of the generated mechanism rests in part on the assumptions that, under the conditions examined, 1,3 and 1,4 additions are unimportant, diradical reactions are not important, and H-shifts across rings are not important.
2.3.2 Pool Reactions

Although XMG-PDep could not build or discover reactions through diradical intermediates, it was felt that the well-known allene-propyne isomerization system should be included in the mechanism, because the system barriers for isomerization are lower than those for dissociation to propargyl + H atom (see, for example, [37;38]). In this system allene may isomerize to cyclopropene, which in turn will rapidly isomerize back to allene or to propyne, all at rates much faster than dissociation to propargyl and hydrogen atom. We thus added three reactions directly to the reaction mechanism at the start of generation, via the Pool Reactions system of Dr. Preeti Aghalayam (MIT), as illustrated below:

\[
\begin{align*}
\text{\ldots} & \quad \Rightarrow & \quad \text{\ldots} \\
\text{\ldots} & \quad \Rightarrow & \quad \text{\ldots} + \text{H} \\
\text{\ldots} & \quad \Rightarrow & \quad \text{\ldots} + \text{H}
\end{align*}
\]

These are not elementary but net reactions, which result from pressure-dependent networks, constructed from results of a CHEMDIS analysis of the rate constants for the allene-propyne-cyclopropene system at 1038 K and 0.58 atm in CH₄ (see Appendix). CHEMDIS input files were built by hand using the potential surface of Davis and coworkers [37], and the results of Harding and Klippenstein for recombination of H with propargyl [39].

2.4 Thermodynamic Library

Usually, XMG-PDep uses Grenda’s Group Additivity Property Predictor (GAPP) [33] to provide automated group contribution predictions for the thermochemistry of the species it discovers. But since good literature thermodynamic data is preferable to group additivity, XMG-PDep consults an electronic library of literature results before resorting to GAPP.

For the current methane pyrolysis study, Table 7-2 presents the 38 species whose thermodynamic parameters were adapted in part, or wholly, from the literature. Often
only a few values, such as the enthalpy of formation, could be found for a species. In these cases we used THERM to combine available literature values with group-additivity predictions in order to build a NASA polynomial representation of the thermodynamic data. The Appendix holds the same data of Table 7-2, represented as NASA polynomials. All other species were estimated via GAPP, or (in cases of on-line GAPP failure) using THERM.

Table 7-2 and other tables in this work use Dean's string abbreviations: hydrogens are omitted, a ' # ' represents a triple-bond; a ' * ' represents a double bond, a ' . ' represents a radical center, the CY[...] symbols enclose a ring, and the (...) symbols describe a branch. Thus “CY[C(C.)C*CC*C]” represents a 1,3-cyclopentadienyl-5-carbiny radical. Further abbreviations are: CY13PD = cyclopentadiene, CY13PD5. = 1,3-cyclopentadien-5-yl, CY13PD2. = 1,3-cyclopentadien-2-yl, CY13PD1. = 1,3-cyclopentadien-1-yl, CYPENE3. = cyclopenten-3-yl, CYPENE4. = cyclopenten-4-yl, CHD13 = 1,3-cyclohexadiene, CHD14 = 1,4 cyclohexadiene, CYC6H7 = 2,4-cyclohexadien-1-yl, and CYC6H5. = phenyl radical.

<table>
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<tr>
<th>Species</th>
<th>$\Delta H_f^{298}$</th>
<th>$S_0^{298}$</th>
<th>$C_p^{300}$</th>
<th>$C_p^{400}$</th>
<th>$C_p^{500}$</th>
<th>$C_p^{600}$</th>
<th>$C_p^{800}$</th>
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<td>7.3</td>
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### Library Thermochemical Parameters

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Table 7-2. Library thermochemical parameters. These values were placed in a library at the beginning of the generation run, so that XMG-PDep would use them for the species parameters when that species was discovered. All other species' thermochemical parameters were estimated via GAPP. Units are kcal/mol for $\Delta H_f(298)$ and cal/mol-K for $S$ and $C_P$. In some cases, such as C#CC.C*C, a highly-accurate value for a precursor species was chosen from the literature, followed by the use of group-additivity/hydrogen-bond-increment arithmetic in THERM to produce values for the desired species.

### 2.5 Rate Constant Library

Although XMG-PDep must usually resort to rate rules to predict rate constants for the reactions it discovers, reliable literature data is preferable, where available. This is especially so for important or sensitive reactions of the mechanism. Table 7-3 gives the 49 reactions of our example for which a literature value was used, along with a reference (all of the thousands of other rate constants used to construct the full model were computed on-the-fly in the present work). In many cases only the high-pressure limit
data were available, as the experimental pressure-dependent rate constants were not available or not appropriate for our conditions.

For many of the reactions in Table 7-3, high-pressure limit Arrhenius parameters were calculated via simple Transition-State Theory (TST) from transition-state information supplied in the reference given. In other cases, we fit modified Arrhenius parameters to data or calculations presented for a reaction in the high-pressure limit in the opposite direction (as for the dissociation of cyclopentadiene from [21]). Finally, we performed one set of *ab initio* calculations to estimate the barrier and transition state properties for the ring-opening beta-scission of 1,3-cyclopentadien-2-yl (CY13PD2). The Appendix presents details of that calculation. For all reactions of the mechanism which are not in Table 7-3, rate constants were calculated using the high-pressure limit rate rules and CHEMDIS, or the pressure-independent rate rules for non-pressure-dependent reactions.
<table>
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<th>Reaction</th>
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<th>$n^\circ$</th>
<th>$E_a$</th>
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<td>$n$</td>
<td>$E_a$</td>
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<td>-----------</td>
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<td>2.25E+04</td>
<td>3.00</td>
<td>8.75</td>
<td>[54]</td>
</tr>
<tr>
<td>H + C2H6 =&gt; H2 + C2H5</td>
<td>5.53E+02</td>
<td>3.5</td>
<td>5.17</td>
<td>[54]</td>
</tr>
<tr>
<td>H + C2H4 =&gt; H2 + C2H3</td>
<td>5.42E+14</td>
<td>--</td>
<td>14.9</td>
<td>[48]</td>
</tr>
<tr>
<td>CH3 + C2H6 =&gt; CH4 + C2H5</td>
<td>5.50E-01</td>
<td>4.0</td>
<td>8.29</td>
<td>[54]</td>
</tr>
<tr>
<td>C&quot;CC + CH3 =&gt; C&quot;CC. + CH4</td>
<td>2.21E+00</td>
<td>3.5</td>
<td>5.7</td>
<td>[48]</td>
</tr>
<tr>
<td>C#CC + CH3 =&gt; CH4 + C#CC.</td>
<td>2.21E+00</td>
<td>3.5</td>
<td>5.7</td>
<td>[48]</td>
</tr>
<tr>
<td>C2H4 + CH3 =&gt; C2H3 + CH4</td>
<td>6.62E+00</td>
<td>3.7</td>
<td>9.5</td>
<td>[48]</td>
</tr>
<tr>
<td>C2H5 + C2H4 =&gt; C2H6 + C2H3</td>
<td>6.32E+02</td>
<td>3.13</td>
<td>18</td>
<td>[48]</td>
</tr>
<tr>
<td>C2H + CH4 =&gt; C2H2 + CH3</td>
<td>1.81E+12</td>
<td>--</td>
<td>0.5</td>
<td>[48]</td>
</tr>
<tr>
<td>CY13PD1. =&gt; CY13PD5.</td>
<td>8.98E+10</td>
<td>1.3</td>
<td>33.6</td>
<td>[51]</td>
</tr>
<tr>
<td>C&quot;CCC&quot;C. =&gt; CYPENE4.</td>
<td>7.00E+11</td>
<td>--</td>
<td>14</td>
<td>[53]</td>
</tr>
<tr>
<td>C&quot;CC&quot;C. =&gt; CY13PD1.</td>
<td>8.23E+11</td>
<td>0.07</td>
<td>17.4</td>
<td>[51]</td>
</tr>
<tr>
<td>C#CC&quot;C. =&gt; CY13PD1.</td>
<td>8.23E+11</td>
<td>0.07</td>
<td>13.7</td>
<td>[51]</td>
</tr>
<tr>
<td>CH3 + CY13PD =&gt; CH4 + CY13PD5.</td>
<td>2.50E+11</td>
<td>--</td>
<td>5.5</td>
<td>[19]</td>
</tr>
<tr>
<td>C&quot;CC.C&quot;C =&gt; CYPENE3.</td>
<td>7.00E+11</td>
<td>--</td>
<td>31.1</td>
<td>[55], A from above for CYPENE4.</td>
</tr>
</tbody>
</table>

Table 7-3. Library of rate constants used in mechanism generation, in CHEMKIN format [56]. Units are in (kcal/mol, cm³, s) for a modified Arrhenius form $A T^{n} e^{E_a/kT}$. Troe parameterizations are indicated by the LOW and TROE keywords. LOW indicates low-pressure limit modified Arrhenius parameters $A$, $n$, and $E$ in order. TROE indicates the Troe fitting parameters $\alpha$, $T^{**}$, $T^*$, and $T^{**}$. We added an efficiency of 0.5 for CH4 bath gas for C2H6 dissociation, based on the efficiency of 1.0 assumed by Baulch for C2H6 bath in this case.
2.6 High-Pressure Limit Rate Rules

Tables 7-4 and 7-5 present high-pressure limit rate rules used in the CHEMDIS calculations; Table 7-6 presents the pressure-independent rate rules. These rate rules were developed from a variety of sources. When from the literature, these tables give the source; in other cases these rules were estimated based on our experience with calculations and specific literature values for instances of the reaction. Though these rate rules are modified Arrhenius parameter sets, the activation energies given have real significance – they are estimates of the true barrier for reaction and thus are appropriate as inputs to the pressure-dependence code CHEMDIS as described in Chapter 3.

Table 7-4 shows high-pressure-limit rate rules, as modified Arrhenius parameters, for recombinations, radical additions, specific H-shifts, and intra-radical ring closures. Recall that all rate rules are posed in only one direction, the “designated forward” direction; the mechanism generator fits modified Arrhenius parameters for the reverse instance of the reaction.
# High-Pressure-Limit Rate Rules

<table>
<thead>
<tr>
<th>Rate Rule</th>
<th>$A^\infty$</th>
<th>$n^\infty$</th>
<th>$E_a$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Recombination</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H recombination w/any radical</td>
<td>1.00E+14</td>
<td>--</td>
<td>--</td>
<td>[57]</td>
</tr>
<tr>
<td>CH3 recombination w/any radical</td>
<td>1.00E+13</td>
<td>--</td>
<td>--</td>
<td>[57]</td>
</tr>
<tr>
<td>Generic radical recombinations</td>
<td>8.00E+12</td>
<td>--</td>
<td>--</td>
<td>[57]</td>
</tr>
<tr>
<td><strong>Radical Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H addition to terminal carbon of a double bond</td>
<td>1.00E+13</td>
<td>--</td>
<td>1.2</td>
<td>[57]</td>
</tr>
<tr>
<td>H addition to internal carbon of a double bond</td>
<td>1.00E+13</td>
<td>--</td>
<td>2.9</td>
<td>[57]</td>
</tr>
<tr>
<td>H addition to terminal carbon of a triple bond</td>
<td>1.70E+11</td>
<td>0.97</td>
<td>2.8</td>
<td>from [37]</td>
</tr>
<tr>
<td>H addition to internal carbon of a triple bond</td>
<td>2.03E+11</td>
<td>0.77</td>
<td>6.75</td>
<td>from [37]</td>
</tr>
<tr>
<td>CH3 addition to terminal carbon of a double bond</td>
<td>8.50E+10</td>
<td>--</td>
<td>7.8</td>
<td>[57]</td>
</tr>
<tr>
<td>CH3 addition to internal carbon of a double bond</td>
<td>8.50E+10</td>
<td>--</td>
<td>10.6</td>
<td>[57]</td>
</tr>
<tr>
<td>CH3 addition to terminal carbon of a triple bond</td>
<td>1.50E+07</td>
<td>1.87</td>
<td>8.2</td>
<td>from [37]</td>
</tr>
<tr>
<td>CH3 addition to internal carbon of a triple bond</td>
<td>8.50E+10</td>
<td>0</td>
<td>10.6</td>
<td>[57]</td>
</tr>
<tr>
<td>Generic radical addition to terminal carbon</td>
<td>8.50E+10</td>
<td>--</td>
<td>7.8</td>
<td>from [57]</td>
</tr>
<tr>
<td>Generic radical addition to internal carbon</td>
<td>8.50E+10</td>
<td>--</td>
<td>10.6</td>
<td>from [57]</td>
</tr>
<tr>
<td><strong>1,2 H-Shift</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v-&gt;a</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>38.7</td>
<td>[58]</td>
</tr>
<tr>
<td>p-&gt;p</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>40.0</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;s</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>37.3</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;t</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>34.6</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;a</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>29.6</td>
<td>[59]</td>
</tr>
<tr>
<td>s-&gt;s</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>39.1</td>
<td>[59]</td>
</tr>
<tr>
<td>s-&gt;t</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>37.7</td>
<td>[59]</td>
</tr>
<tr>
<td>s-&gt;a</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>31.5</td>
<td>[59]</td>
</tr>
<tr>
<td>t-&gt;t</td>
<td>3.56E+10</td>
<td>0.88</td>
<td>40.0</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>1,3 H-Shift</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v-&gt;a</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>38.7</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;p</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>38.8</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;s</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>36.6</td>
<td>[59]</td>
</tr>
<tr>
<td>p-&gt;t</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>34.3</td>
<td>[59]</td>
</tr>
<tr>
<td>s-&gt;s</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>38.2</td>
<td>[59]</td>
</tr>
<tr>
<td>s-&gt;t</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>36.1</td>
<td>[59]</td>
</tr>
</tbody>
</table>
### High-Pressure-Limit Rate Rules

<table>
<thead>
<tr>
<th>Rate Rule</th>
<th>$A$</th>
<th>$n$</th>
<th>$E_a$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>t$\Rightarrow$t</td>
<td>3.80E+10</td>
<td>0.67</td>
<td>36.6</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>1,4 H-Shift</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$\Rightarrow$p</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>23.1</td>
<td>[59]</td>
</tr>
<tr>
<td>p$\Rightarrow$s</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>20.6</td>
<td>[59]</td>
</tr>
<tr>
<td>p$\Rightarrow$t</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>18.3</td>
<td>[59]</td>
</tr>
<tr>
<td>p$\Rightarrow$a</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>15.3</td>
<td>[59]</td>
</tr>
<tr>
<td>s$\Rightarrow$s</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>23.5</td>
<td>[59]</td>
</tr>
<tr>
<td>s$\Rightarrow$t</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>20.6</td>
<td>[59]</td>
</tr>
<tr>
<td>t$\Rightarrow$t</td>
<td>7.85E+11</td>
<td>-0.12</td>
<td>19.4</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>1,5 H-Shift</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$\Rightarrow$p</td>
<td>3.67E+12</td>
<td>-0.6</td>
<td>15.3</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>1,6 H-Shift</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p$\Rightarrow$p</td>
<td>2.80E+10</td>
<td>--</td>
<td>20.3</td>
<td>[59]</td>
</tr>
<tr>
<td><strong>1,5 Intra-Radical Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endo ring-closure</td>
<td>1.22E+08</td>
<td>1.05</td>
<td>15.82</td>
<td>[59]</td>
</tr>
<tr>
<td>Exo ring-closure</td>
<td>2.51E+10</td>
<td>--</td>
<td>6.85</td>
<td>[59]</td>
</tr>
<tr>
<td>Strained endo ring-closure</td>
<td>1.22E+08</td>
<td>1.05</td>
<td>17.42</td>
<td>see text</td>
</tr>
<tr>
<td>Strained exo ring-closure</td>
<td>2.51E+10</td>
<td>--</td>
<td>8.05</td>
<td>see text</td>
</tr>
<tr>
<td><strong>1,6 Intra-Radical Addition</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Endo ring-closure</td>
<td>1.00E+08</td>
<td>0.855</td>
<td>5.9</td>
<td>[59]</td>
</tr>
<tr>
<td>Strained endo ring-closure</td>
<td>1.00E+08</td>
<td>0.855</td>
<td>7.5</td>
<td>see text</td>
</tr>
</tbody>
</table>

Allylic radical ring-closure correction | 15 | see text |

**Table 7-4.** High-pressure-limit rate rules, used as inputs to pressure-dependent CHEMDIS calculations. Abbreviations in H-shifts: $v =$ vinylic, $p =$ primary, $s =$ secondary, $t =$ tertiary, $a =$ allylic. “Exo” and “endo” do not refer to the heat of reaction in this context; they are different types of intra-radical addition (see text). Units are kcal/mol, cm$^3$, s with a modified Arrhenius form $Ae^{\frac{E_a}{RT}}$. 
<table>
<thead>
<tr>
<th>Rotor Loss $A^-$ and $n^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotor Loss</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ringstrain Corrections $E_{rs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring Size</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>6</td>
</tr>
<tr>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Evans-Polanyi</th>
<th>$a$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>13.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 7-5. General H-shift parameters. Rotor loss $A$ and $n$ are chosen according to how many rotors are lost in going from the reactant to the transition state. Ring strain $E_{rs}$ for use in (7-4) chosen according to how many members are in the transition-state ring for the intra-radical H-abstraction. Units are as for Table 3. These rate rules (specifically for H-shifts) are from Matheu and coworkers [59].

2.6.1 H-shifts

The “specific” H-shifts in Table 7-4 are used for the specified unimolecular transformation from the radical of the first type to the radical of the second. For example, the “1-2 H-Shift, $p\rightarrow s$” is a rate rule for an H-shift reaction starting with a primary radical and going to a secondary radical. Table 7-5 represents parameters used to evaluate general H-shifts, where a specific type was not available. In these cases, $A^-$ and $n^-$ were selected from Table 7-5’s “Rotor-loss $A^-$” and $n^-$’ values, as described in Matheu et al. [59]. The generator then evaluates the barrier height $E_a$ via:

$$E_a^* = E_{rs} + a + b\Delta H_{rs}^{396}$$

(7-4)

where $E_{rs}$ is the appropriate ring-strain correction and $a$ and $b$ are Evans-Polanyi parameters, all chosen from Table Y. For endothermic H-shifts, the exothermic direction
would be chosen for estimation first, followed by reverse Arrhenius parameter fitting as described earlier.

2.6.2 *Intra-radical Ring Closures*

Rate rules for intra-radical ring closures are first divided into "exo" and "endo" forms. In exo- ring closures, the radical site adds to the unsaturated bond in such a way that the product radical site is not on the formed ring. In endo-closures, the radical site ends up on the formed ring, as discussed in Chapter 4. These are further divided into strained and unstrained ring-closures. Based on the work of Moskaleva and Lin [51], a correction of 1.6 kcal/mol was added to the barrier for cases where the transition state for the ring-closure would be "strained"; that is, it would have two consecutive partial double bonds, or a partial triple bond, in the transition state.

Finally, in light of the work of Martinez and Cooksy [55] and our own calculation for the ring-opening transition state of CY13PD2, we added 15 kcal/mol to any ring-closure which starts from an allylic-stabilized reactant. Current work suggests that such reactants must give up their allylic stabilization in order to undergo ring closure; the 15 kcal/mol penalty used above is roughly the difference between the barrier for 1,3-pentadien-5-yl ring closure as predicted by Martinez and Cooksy, and the barrier from the normal 1,5 endo ring closure rule.
2.7 Pressure-Independent Rate Rules

Table 7-6 shows the rate rules used for non-pressure-dependent reactions in this work. These are from various sources as shown.

<table>
<thead>
<tr>
<th>Rate Rule</th>
<th>$A$</th>
<th>$n$</th>
<th>$E_a$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H Abstraction by H (generic)</td>
<td>4.55E+06</td>
<td>2.0</td>
<td>5.0</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by H to form primary radical</td>
<td>9.33E+06</td>
<td>2.0</td>
<td>7.7</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by H to form secondary radical</td>
<td>4.55E+06</td>
<td>2.0</td>
<td>5.0</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by H to form tertiary radical</td>
<td>1.26E+14</td>
<td>--</td>
<td>7.3</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by CH3 (generic)</td>
<td>2.00E+11</td>
<td>--</td>
<td>9.5</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by CH3 to form primary radical</td>
<td>2.17E+11</td>
<td>--</td>
<td>11.6</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by CH3 to form secondary radical</td>
<td>2.00E+11</td>
<td>--</td>
<td>9.5</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abstraction by CH3 to form tertiary radical</td>
<td>1.00E+11</td>
<td>--</td>
<td>7.9</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abs. by C2H5 (generic)</td>
<td>2.50E+10</td>
<td>--</td>
<td>10.4</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abs. by C2H5 to form primary radical</td>
<td>1.67E+10</td>
<td>--</td>
<td>13.4</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abs. by C2H5 to form secondary radical</td>
<td>2.50E+10</td>
<td>--</td>
<td>10.4</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abs. by C2H5 to form tertiary radical</td>
<td>1.00E+11</td>
<td>--</td>
<td>7.9</td>
<td>[57]</td>
</tr>
<tr>
<td>H Abs. by C2H3 (generic)</td>
<td>1.02E+03</td>
<td>3.1</td>
<td>8.8</td>
<td>from abs. from C3H8 to i-C3H7 in [49]</td>
</tr>
<tr>
<td>H Abs. by C2H3 to form primary radical</td>
<td>6.02E+02</td>
<td>3.3</td>
<td>10.5</td>
<td>from abs. from C3H8 to n-C3H7 in [49]</td>
</tr>
<tr>
<td>H Abs. by C2H3 to form secondary radical</td>
<td>1.02E+03</td>
<td>3.1</td>
<td>8.8</td>
<td>from abs. from C3H8 to i-C3H7 in [49]</td>
</tr>
<tr>
<td>H Abs. by C2H3 to form tertiary radical</td>
<td>9.03E-01</td>
<td>3.5</td>
<td>2.61</td>
<td>from abs. from i-C4H10 to t-buty1 in [60]</td>
</tr>
<tr>
<td>H Abstraction by Generic Radical</td>
<td>2.50E+10</td>
<td>--</td>
<td>10.4</td>
<td>from above for “H Abs. by C2H5”</td>
</tr>
<tr>
<td>Generic H Abstraction to form primary radical</td>
<td>1.67E+10</td>
<td>--</td>
<td>13.4</td>
<td>from above for C2H5</td>
</tr>
<tr>
<td>Generic H Abstraction to form secondary radical</td>
<td>2.50E+10</td>
<td>--</td>
<td>10.4</td>
<td>from above for C2H5</td>
</tr>
<tr>
<td>Generic H Abstraction to form tertiary radical</td>
<td>1.00E+11</td>
<td>--</td>
<td>7.9</td>
<td>from above for C2H5</td>
</tr>
<tr>
<td>Disproportionation (all)</td>
<td>1.00E+12</td>
<td>--</td>
<td>--</td>
<td>[61]</td>
</tr>
</tbody>
</table>

Table 7-6. Rate rules for non-pressure-dependent reactions. The secondary radical rule is chosen in each case as the general rule, also. Units are as for other tables (kcal/mol, cm$^3$/mol, s).
2.8 Other Data

Table II of Dean, Bozzelli and Ritter [62] provided Lennard-Jones parameters and \( \langle \Delta E \rangle_{all} \) for methane as a bath gas; from their value of \( \langle \Delta E \rangle_{all} \) we estimated \( \langle \Delta E \rangle_{down} = 1285 \text{ cm}^{-1} \) at 1038 K. Lennard-Jones collision parameters for most other species were provided by GAPP, or by default values based on the number of heavy atoms and whether or not the species was cyclic. In general the CHEMDIS calculations were not very sensitive to the Lennard-Jones values used.

2.9 Thermodynamic Consistency

The non-pressure-dependent reactions of the generated mechanism, and all those reactions whose rates were taken from a library, are completely thermodynamically consistent; in addition, all these reactions will appear in both directions as a property of the generation algorithm. As noted in Chapter 3, however, the CHEMDIS tool for predicting \( k(T,P) \) is not an inherently thermodynamically consistent tool. The CHEMDIS predictions of \( k(T,P) \) for a reaction such as \( A + B \rightarrow C \) and its reverse, \( C \rightarrow A + B \), will not always fit the equation \( k_f/k_r = K_e \) where \( K_e \) is the equilibrium constant. Furthermore, our algorithm will naturally select some pressure-dependent reactions in one direction only. For example, XMG-PDep may build a network for the dissociation of allyl radical to a variety of products and isomers. But it may not build a network for certain entrance channels, such as \( H + \text{allene} \rightarrow \text{allyl} \), since it is simply not called for by the flux criteria of Chapter 6. Thus the mechanism will technically require the allyl dissociation in only "one" direction, the addition of \( H \) to allene to form allyl directly being an insignificant back-reaction.

In the construction of a final mechanism, therefore, XMG-PDep will write CHEMDIS-derived reactions in only one direction. In this work we found the pressure-dependent networks for allyl radical dissociation, and for methyl addition to ethylene, to be the most important pressure-dependent reactions in our system. These systems were made internally thermodynamically consistent, by hand-editing of the final CHEMKIN [56] mechanism file. In the end these changes had little effect on the final mechanism

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predictions, and no important changes to the results occur when using the unadjusted final CHEMKIN mechanism built by the generator.

3 Results: The Methane Pyrolysis Mechanism

XMG-PDep examined over 12,000 candidate species and 12,000 possible pressure-dependent networks as it automatically constructed a methane pyrolysis mechanism for the Chen, Back and Back experiments. The code performed over 200 on-the-fly $k(T,P)$ estimations via CHEMDIS. The final generated mechanism has approximately 100 species and about 1000 reversible reactions; it may be the first known accurate mechanism developed systematically via a flux-limit criteria. That is, at any given time $t$ from 0 to $\sim 2500$ seconds (the point at which the target conversion is reached) the flux to any species not included in the mechanism, or through the non-included pathways of any pressure-dependent network, is less than $R_{\min}(t) = f_{\min}R_{\text{char}}(t)$. No attempt has been made to reduce or condense the mechanism.

The Appendix presents this mechanism in CHEMKIN format, including the changes made to ensure thermodynamic consistency for important pressure-dependent reactions. Recall that all rate constants in this mechanism which do not appear in Table 7-3 have been estimated via the rate rules or via CHEMDIS calculations based on the rate rules. Similarly all thermodynamic parameters are estimated via GAPP or THERM unless they appear in Table 7-2. A record of each active pressure-dependent network, with sufficient information to build the CHEMDIS input file and produce QRRK/MSC estimates of $k(T,P)$, is included in the attached electronic media.

Figure 7-2 highlights the generated mechanism’s ability to capture autocatalysis. Our prediction for the ethane mole fraction agrees well with the data of Chen, Back and Back from various experiments; no rate or thermodynamic parameters were adjusted to fit the data. The generated mechanism prediction does miss the ethane plateau concentration by about 20%, but falls within the error of repeated runs once within the autocatalytic regime ($t > 2000$ sec).
In addition to ethane, the principal stable products of methane pyrolysis under these conditions and at low conversion are hydrogen, ethylene, acetylene, propene, allene, and propyne; of these Back and coworkers measured all but propyne. Figures 7-3 through 7-7 show how the mechanism agrees with measured concentrations of these species. Note that predictions for acetylene and propene concentrations in particular are much improved over the earlier Dean mechanism.
Figure 7-3. XMG-PDep predicted hydrogen mole fraction vs. experimental data.

Figure 7-4. XMG-PDep predicted ethylene mole fraction vs. experimental data.
Figure 7-5. Acetylene mole fraction prediction vs. experimental data. Compare this graph to Figure 4 of Dean [19] and note improvement in prediction of this important species.

Figure 7-6. Propene mole fraction prediction vs. experimental data.
The last plot, Figure 7-7, shows some discrepancy between the measured and predicted concentrations of allene at later times; this is addressed in the Discussion. In all other cases, agreement of the unadjusted, unfitted mechanism with the data is quite good. Thus our pressure-dependent mechanism generation algorithm succeeds in capturing the vital elements of methane pyrolysis under these conditions, with no fitting or adjustment of any mechanism parameters to the experimental data.

4 Discussion

4.1 The Source of Autocatalysis

Sensitivity analyses and rate-of-production/consumption calculations are not sufficient when trying to understand how the generated XMG-PDep mechanism explains autocatalysis. Thus we used radical flux analysis, which examines only those reactions generating a net increase or decrease in the total number of radicals. Reactions generating a net increase in radicals can be chain branching, and thus can explain the
abrupt increase in ethane, and almost every other measured product, at around 2000-2500 seconds as shown in Figures 7-3 through 7-7. Combining radical flux, sensitivity, and rate-of-production/consumption provides a comprehensive picture of pathways in methane pyrolysis under these conditions.

4.1.1 Radical Production Analysis

The top three radical-producing reactions, along with selected other reactions, are shown in Figure 7-8, with their net production rates as a function of time. Cyclopentadiene is still important as a chain brancher, but molecular addition reactions (i.e. reverse disproportionations) are also quite important for radical production. In particular the molecular addition of allene and methane to form allyl radical and methyl radical is crucial.
Figure 7-8. Main radical production routes for autocatalysis in methane pyrolysis. Each curve represents a net rate, in which the reverse recombination or disproportionation flux has been taken into account. Note the early importance of the allene + methane pathway. There are three or four other pathways with curves very similar to those for fulvene + methane; these have been left out for clarity.

"New" Route to Cyclopentadienyl

As noted previously, the allyl + acetylene channel, Equation (7-1), does not produce sufficient cyclopentadiene to account for autocatalysis. Instead, the mechanism generator found a "new" chemically-activated pathway which produces cyclopentadienyl radical directly (in the Appendix see Pressure-Dependent Network 158):

\[
\text{propargyl + acetylene} \rightarrow \text{cyclopentadienyl radical}
\]

The net pressure-dependent reaction of propargyl + acetylene \( \rightarrow \) cyclopentadienyl accounts for almost all the cyclopentadienyl radical production in our system. The
cyclopentadienyl then abstracts H atoms from CH₄, to form a cyclopentadiene which dissociates relatively quickly, in a chain-branching reaction. To our knowledge no previous methane pyrolysis mechanism has ever included the propargyl + acetylene pathway. Note that without integrated pressure-dependence, our mechanism generator could not have discovered this important pressure-dependent reaction.

At first the ring-closure step in Equation (7-5) might seem too strained to be reasonable. But Moskaleva and Lin recently performed a detailed computational study of the potential surface for the cyclopentadienyl dissociation system, which included the propargyl + acetylene channel [51]. They found the barrier for the ring closure to be only slightly more than that for an unstrained ring closure such as that forming cyclopentyl [59]. In addition, Knyazev and Slagle [63] have found strong experimental evidence for a C₃H₅ product of propargyl addition to acetylene. Its thermal stability, and experimental agreement with the prediction of Moskaleva and Lin, suggest this species is cyclopentadienyl formed via the chemically activated pathway of (7-5). Thus cyclopentadienyl formation via propargyl + acetylene is quite reasonable and should be expected under our methane pyrolysis conditions.

*Importance of Molecular Addition Reactions*

Figure 7-8 shows that the molecular addition (or reverse disproportionation) of allene and methane to form allyl and methyl radicals is key to explaining autocatalysis in methane pyrolysis; the cyclopentadiene chain-branching reaction, though dominant, accounts for only 25% of radical production at 2450 seconds (the endpoint of model integration, where X_{CH₄} = 0.0055). Other researchers have considered reactions of this type to be only marginally important for lower-temperature methane pyrolysis. But, especially as a group, molecular additions appear quite important and account for over half of the radical production in the autocatalytic regime, as Figure 7-9 suggests.
Figure 7-9. Total radical production from all molecular addition reactions, compared to radical production from all other reactions except methane dissociation, which produces radicals at a constant $1.3 \times 10^{12}$ mol/cm$^3$-sec.

To predict the molecular addition rate constants, XMG-PDep uses thermodynamic reversibility and the single disproportionation rule in Table 7-6 as given by Dahm [61]. In general, disproportionation reactions are not well-studied experimentally or theoretically, but the Dahm rate rule could be considered somewhat high. Tsang’s review [48] suggests a rate constant of $3.3 \times 10^{11}$ [cm$^3$/mol-s] compared to the Dahm rate rule of $1.0 \times 10^{12}$ for the reverse of the key molecular addition:

\[ \text{C} + \text{CH}_4 \rightarrow \cdot + \text{CH}_3 \]  

(7-6)

Using Tsang’s recommendation for this reaction has little effect on the predicted ethane concentration, however, lowering it by less than 15% in the autocatalytic regime. Effects on the other measured species of Figures 7-3 through 7-7 are similarly small.
In addition, Dahm’s "fast" rate rule is within the range of disproportionation rate constants suggested by the Allara and Shaw tables [64]; these authors give estimates anywhere from $1.6 \times 10^{11}$ to $2.0 \times 10^{12}$ [cm$^3$/mol-s] per hydrogen for the disproportionation of small alkyl radicals with each other. Disproportionations in which hydrogen atom is the abstractor can be higher by an order of magnitude, so it is not clear that Dahm's rule is necessarily too fast, if one is applying a general rule for all disproportionations.

Radical production via molecular addition is not merely a consequence of the Dahm rate rule. Cutting the Dahm rule by a factor of 3 for the top five molecular addition reactions has the effect shown in Figure 7-10 on predicted ethane concentration. The autocatalytic effect is still present though it is clearly weaker with the reduced rate rule. Thus while Dahm's rule may be primitive, the generated mechanism shows that, as a class, molecular additions are critical to explaining the radical production which leads to methane autocatalysis at lower temperatures. The importance of molecular addition also implies further work is needed in understanding disproportionation rate constants.

![Figure 7-10. Predicted ethane concentration when the disproportionation rate rule is lowered by a factor of three for the top five molecular addition reactions. The autocatalytic effect is still pronounced and is still within the data scatter at around 2400 sec, reinforcing the suggestion that molecular additions are key to explaining autocatalytic effects in methane pyrolysis. Plots for other species in this case (1/3 disproportionation rate) show little change, or mild improvement, in terms of agreement with data.](image-url)
4.1.2 Sensitivity and Rate-of-Production/Consumption Analysis

Normalized sensitivities from SENKIN [56] for ethane are presented in Figure 7-11. Since conversion of methane is quite low, methane dissociation dominates the sensitivities. Unimolecular ethane decomposition to methyl radicals has the strongest negative influence. The disproportionation of methyl and allyl radical appears again in this analysis; ethane concentration is actually sensitive to the reverse step, whose rate constant would also increase if one increased the disproportionation rate constant (since this is a reversible reaction). The pressure-dependent addition of methyl radical to ethylene, to form propene and hydrogen atom, appears to be a key step, as is the pressure-dependent beta scission of propyl radical. In fact, of the four reactions with significant positive sensitivities, three "produce" allyl radical or propene (the disproportionation reaction net flux is toward allyl and CH₃). This suggests allyl or propene formation is rate-limiting for production of ethane.
Figure 7-11. Normalized sensitivity coefficients for ethane formation in the autocatalysis regime. The "noise" in the curves is a consequence of solving the sensitivity equations with a loose tolerance and is not physically significant.

A relative rate-of-consumption analysis confirms the idea that propene and allyl formation are rate-limiting, as suggested by Figure 7-12. Propene or allyl formation are entrance points to "loop" pathways with significant chain branching and methane consumption. First, over half the propene at 2450 seconds forms allyl radical. Most (65%) of the allyl will form propyne or allene by direct beta-scission, or by a pressure-dependent H-shift followed by beta-scission. Propyne and allene are rapidly equilibrated via the isomerizations through cylopropene, as studied by Davis [37], so that propyne in excess of equilibrium quickly becomes allene. Next, some of the allene undergoes direct molecular addition with methane to re-form allyl radical. This process is chain-branching, so that the reaction "loop" from allyl to allene, followed by the chain-branching conversion of methane to methyl, is a powerful acceleration mechanism.
Figure 7.12. Important net fluxes during autocatalysis at 2450 seconds. Not all pathways are shown. Dotted connections are to species which can effectively re-enter the allene loop via beta-scission (to propyne or allene). Some of the propargyl formed by this loop will combine with acetylene, initiating a more powerful cyclopentadiene autocatalysis loop. While most cyclopentadiene is actually "consumed" by methyl radical abstraction of hydrogen, the net effect of this reversible reaction is to produce cyclopentadiene from cyclopentadienyl. Note that this is not a steady-state picture, but represents predicted fluxes in the autocatalytic regime.

Much of the remaining allene will undergo other molecular additions in which it is the hydrogen donor (rather than the abstractor), to give propargyl radical – in all, 65% of the allene participates in chain-branching molecular addition of some kind. The great majority of the propargyl abstracts hydrogen from CH₄ to re-form propyne which is equilibrated with allene, closing the outer loop.

Finally, some of the propargyl adds to acetylene to form cyclopentadienyl radical via Equation (7-5). The cyclopentadienyl loop in Figure 7-12 represents a second chain-branching system, since cyclopentadienyl recombination with H atom is not significant under these conditions. Most cyclopentadienyl will abstract a hydrogen from methane, forming cyclopentadiene which either dissociates or undergoes molecular addition to re-
form cyclopentadienyl. Figure 7-8 would suggest the cyclopentadienyl and allene-allyl loops are, roughly, equally important in explaining methane autocatalysis, though the relative significance of the cyclopentadienyl system grows with increasing methane conversion.

**Sensitivity to Allyl Beta-Scission Barrier**

Figure 7-12 implies that allyl dissociation to allene + hydrogen atom could be quite important. In XMG-PDep the barrier for allyl radical beta-scission is calculated from the reverse of the library parameters for H addition to allene to form allyl radical in Table 7-3. We find that increasing the barrier by 2 kcal/mol in the relevant pressure-dependent networks has only a weak affect on the predicted allene concentration or the predicted ethane concentration (as Figure 7-11 would imply, in that beta-scission of allyl radical does not appear as a sensitive reaction). A possible explanation lies in Figure 7-12 itself: decreased allene formation by direct allyl beta scission simply means more allyl radical converts to propyne, which then finds its way to allene. This explanation is only tentative, however, since the barriers for the pressure-dependent H-shift and beta scission which turn allyl radical into propyne and hydrogen atom are also uncertain.

4.1.3 Adding Allene or Propene to Methane Pyrolysis

The comprehensive picture in Figure 7-12 might lead one to conclude that adding a very small amount of propene or allene to methane at the start of pyrolysis, under the conditions of Chen, Back and Back, could have a strong effect on the results. Figure 7-13 shows that this is partly true. Adding propene or allene at a very small concentration (1.0×10⁻³ mole fraction) would appear to boost the concentration of ethane in the autocatalytic regime by about 40-50%. Adding the same amount of ethane, however, has a similar (though diminished) effect, probably because the ethane will convert to methyl radical and/or ethylene, which together readily form propene. In fact, almost any stable alkane, alkene or alkyne could form the ubiquitous allyl or propargyl radicals in just a few steps under these conditions, providing an alternate entry point to these radicals in Figure 7-12. Indeed we find that adding any one of many stable species of the mechanism (acetylene, 1-butyne, 2-butyne, 1,2 butadiene, 1-methyl-1,3-cyclopentadiene), in a very small concentration, has an effect similar to that for propene.
or allene in Figure 7-13. Notable exceptions include hydrogen gas and benzene, which have no effect at the low mole fraction of $1.0 \times 10^{-5}$ and the low conversions of this work.

Though small, the difference between the effects of incremental amounts of ethane, benzene and allene at least suggest simple experiments to examine whether an incremental amount of allene would have a more pronounced effect on methane pyrolysis than the same amount of ethane, or hydrogen, or benzene. Such an experiment would be a helpful test of our mechanism's accuracy.

![Graph](image)

**Figure 7-13.** Predicted response of ethane product in methane pyrolysis to adding very small amounts of allene, propene, or ethane at the beginning of the Chen et al. experiments. Note that adding almost any small alkane or alkene will have a promotional effect.

### 4.2 Allene Concentration

As noted earlier, Figure 7-7 shows some discrepancy between the predicted and measured allene concentrations. There is only one data set for allene concentration under the conditions of Chen and coworkers [17]; despite many experiments and reviews on
methane pyrolysis by these researchers [15-17;65-67] the allene measurement was never repeated. It stands alone as the only data set not reported from previous work, in the review chapter of Back and Back [15]. This seems odd, since in Figure 4 of [17] allene is the only measured species which appears to plateau after the autocatalytic regime has set in. Such behavior should mark it as a species of interest. For various reasons our mechanism generator was halted at the methane conversion specified above and could not predict whether allene would plateau after 2500 seconds, as the Chen, Back and Back figure implied.

4.2.1 Adding the Propargyl + Propargyl System

Assuming the measured allene profile represented the real behavior, we attempted to correct our model prediction by adding a version of the propargyl + propargyl pressure-dependent reaction network as studied by Miller and Melius [68]. It is believed that via a chemically activated, pressure-dependent network, propargyl radicals may combine to form benzene and fulvene, as well as the direct recombination isomers. Unfortunately, XMG-PDep cannot handle reactions through diradical intermediates, and did not have the reaction families which would represent some of the isomerizations which occur in the propargyl + propargyl network. Thus the mechanism generator could not have found this system "on its own".

We thus used A. M. Dean’s hand-constructed CHEMDIS input file, representing the head-to-head, head-to-tail and tail-to-tail chemical activation channels for this system (based on the surface of Miller and Melius). The resultant net reactions were added reversibly to the generated CHEMKIN mechanism. This lead to a marked improvement in the allene prediction as compared with the experimental result, as Figure 7-7 shows.

The addition of the propargyl + propargyl system weakly affects other species concentration predictions in Figures 7-2 through 7-6, in the regimes where experimental data is available. Predicted ethane concentration increases by about 30% at 2450 seconds, putting it just above the highest data point in Figure 7-2; other species profiles increase by amounts of 10-40% in the autocatalytic regime. The predicted concentration of hydrogen in Figure 7-3 increases by a factor of 2 at 2500 seconds, but no data is available in this range. In general the results of Figures 7-2 through 7-6 are not seriously
perturbed, and are largely unchanged in the regions where data are present. The broad
effect of autocatalysis is still clearly expressed. We note that the combination of adding
the propargyl + propargyl system and reducing the rate constants of the top 5
disproportionation reactions by a factor of 3 offers no change, or slight improvement, for
each species, compared to the case with just the propargyl + propargyl system added.

It may seem odd that allene, so important in Figure 7-12, could be halved in
centration with only small effect on other species. The likely explanation is that
many species can perform the role of allene in Figure 7-12. In particular, fulvene (a key
product of the propargyl + propargyl recombination) undergoes molecular addition to
form resonantly stabilized radicals; the importance of fulvene is already implied by
Figure 7-11. Probably, fulvene makes up the chain-branching deficiency left by depleted
allene in this hand-adjusted mechanism, so that other species concentrations remain
unaffected. In any case, the generated mechanism is likely more accurate with the
propargyl system added in.

4.3 Accuracy of the QRRK/MSC Approach

As discussed extensively in earlier chapters, XMG-PDep uses CHEMDIS, a
QRRK/MSC approach, to estimate $k(T,P)$ rapidly. The accuracy of this approximate
method has never been systematically studied. However, certain systems in this work
provided the opportunity to test CHEMDIS's accuracy against experiment. In particular,
we examined the results of CHEMDIS against measured data for the allene-propyne-
cyclopropene system cited by Davis [37], the propargyl + acetylene results of [51], and
all the reactions for which we had a Troe form available in the literature (see Table 7-3).
While this approach is not systematic, we can say that in all these cases the CHEMDIS
results were within a factor of 10 of the higher-level calculations or the experimental
results, and were usually within a factor of 5.

4.4 Directions for Model Improvement

4.4.1 Disproportionation and Molecular Addition

Figures 7-10 through 7-12 suggest the need for more accurate disproportionation
rate constants, as the molecular addition rates are derived from these. Unfortunately
these reactions are not widely studied. Kinetic experiments and computational work in lower-temperature methane pyrolysis should focus on the disproportionation of allyl and methyl radical; the rates for disproportionation and molecular addition in our mechanism can then be improved.

4.4.2 Missing Families and the Propargyl System

Propargyl and allyl radicals are probably the most important radicals at the onset of autocatalysis. Unfortunately, XMG-PDep in its current form is unable to handle the diradical intermediates that can be formed when propargyl radicals recombine; these diradicals may then form fulvene and benzene as suggested by Miller and Melius. It is not reasonable to proceed further with automated methane pyrolysis mechanism development until diradical-intermediate isomerization families can be added systematically, since it seems clear from the previous section that such reactions become important. If one uses our mechanism as a starting point for lower-temperature methane pyrolysis, these reactions need to be added by hand, as well as topomerization reactions (e.g. Bettinger et al [69]) and the diradical isomerizations of cyclopentadiene and similar species [70]. Indeed, the diradical intermediate isomerization of propyne and allene (through cyclopropene) seems possible for any triple-bonded or allenic species, and should be considered for species like 1,2 butadiene. Finally, ene reactions, concerted eliminations, 1,3 and 1,4 intra-radical additions, and retro-Diels-Alder reactions are among the families not considered in this work; extension of this mechanism may need to include such families.

4.4.3 Treatment of Resonant Species

As noted in Chapter 5, XMG-PDep (and the original XMG) treat resonant radical species as though they were separate species with different formal structures. This of course is not correct, and it also leads to differences between the XMG-PDep-integrated ordinary differential equations and the final CHEMKIN mechanism. The differences stem from the fact that rate constants from the library are written assuming single species representations for resonant species. The differences in predicted concentrations between XMG-PDep and the final CHEMKIN mechanism are not severe but they are noticeable,
and in any case this treatment needs to be repaired in XMG-PDep before continuing with the later stages of pyrolysis.

4.4.4 Range Analysis and $k(T,P)$

The mechanism generated in this work is technically appropriate only for 1038 K and 0.58 atm of neat methane, at very low methane conversion; it is only under these conditions that satisfaction of the flux criteria $R_{\text{min}}$ is assured. To be truly useful, this mechanism needs to be combined with a range analysis [71], and each $k(T,P)$ estimate fitted to a functional form over a given $T,P$ grid. While our current XMG-PDep cannot do this, all the information required to do so is available in the mechanism's pressure-dependent network files of the attached media.

4.4.5 Improved $k(T,P)$ Estimates

Clearly the QRRK/MSC method of CHEMDIS is approximate, and certain pressure-dependent reactions should have their $k(T,P)$ estimates replaced with detailed Troe forms. These should be based on careful RRKM-$k(E,J)$ and master-equation analysis, or experimental data for the rarer cases where conditions appropriate to this work have been examined. Further resolution of QRRK/MSC accuracy and error bounds awaits a systematic study, or an upgrade to a true inverse-Laplace-transform method (which incorporates a temperature-exponential in the Arrhenius form properly) to ensure strict thermodynamic consistency for $k(T,P)$ estimates.

4.4.6 Improving the Allene Concentration Prediction

Despite addition of the propargyl + propargyl system, Figure 7-7 still shows a significant discrepancy in the predicted allene concentration. The discrepancy is of special concern due to the importance of allene in Figure 7-12. Pursuing the above recommended changes (adding missing families, finding more accurate disproportionation rates or rules) may improve this prediction. If they do not, the allene prediction will need serious attention before the mechanism is improved further.
5 Conclusions

5.1 Automated Mechanism Generation

This chapter provides a successful demonstration of the first known mechanism generation tool with incorporated pressure-dependence. The XMG-PDep tool systematically built a mechanism for low-temperature methane pyrolysis, from scratch, which adequately explains that system’s autocatalytic behavior. In applying it, this work is the first to resolve the mystery of low-temperature methane autocatalysis while employing accurate thermodynamic parameters for the important species. Automated generation of the methane pyrolysis mechanism would have been impossible without an integrated pressure-dependence tool; this is a problem only a pressure-dependent mechanism generator (as opposed to other generators) could have approached. This demonstration application also highlights needed improvements in mechanism generation, which are reviewed in the next chapter.

5.2 A New Model for Lower-Temperature Methane Pyrolysis

This chapter presents a new mechanism for methane pyrolysis which can explain the lower-temperature (below 1100 K) autocatalytic behavior. Predicted concentration profiles from this mechanism agree well with almost all measured data at 1038 K and 0.58 atm. The new model suggests that autocatalysis stems in large part from a set of rarely-considered molecular addition reactions. The cyclopentadiene chain-branching system cited by Dean [19] is also quite important, especially at later times, but its source is now the direct formation of cyclopentadienyl from propargyl and acetylene, not the formation of cyclopentadiene from allyl and acetylene. While the current model is appropriate only for low conversion of methane around 1038 K and 0.58 atm, any model operating near this regime probably needs to account for the chain-branching loops of molecular additions in Figure 7-12.

Model analysis suggests that the molecular addition of allene and methane is a key step, but that other species could easily play the role allene does in this study. Experiments in which very small amounts of allene or certain other species are added to methane at the start of pyrolysis might help confirm the mechanism presented here, in
that our work predicts allene or other reactive unsaturated species will have a stronger effect than the same amount of ethane, hydrogen, or benzene.

In any case, it seems that the best avenue for quantitatively improving this mechanism, at the conditions of the Chen, Back and Back experiments, is to add a full and accurate representation of the propargyl + propargyl system. This should be followed by a closer study of disproportionation/molecular addition reactions generally. Next, any model extension to higher conversions must include general reactions through diradical intermediates, and the isomerizations of triple bonds and allenic bond systems via cyclopropenes. These should be added systematically if possible. Finally, application of this mechanism to a range of conditions awaits a reasonable fitting algorithm for $k(T,P)$ in multi-well systems, though our results provide a good starting point for automated or by-hand refinement.
6 Appendix

This section of the Appendix describes the calculations for the cyclopropene-allene-propyne system that were used in the pool reactions at the start of mechanism generation. It also describes the development of the rate rule barrier correction for resonant-stabilized ring closure. Finally, this section presents the pressure-dependent network for the propargyl + propargyl system, added to the mechanism to produce the dotted-line curve in Figure 7-7. The final mechanism, in CHEMKIN format, is included in the Supplement, along with the listing for the propargyl + acetylene pressure-dependent network (number 158).

6.1 Allene-Propyne-Cyclopropene Isomerization

XMG-PDep did not have reaction families which would produce the well-known direct isomerizations between allene and propyne through cyclopropene. These reactions were added to the mechanism at the start of generation via the pool reaction system. To do this, we constructed modified Arrhenius forms from the calculational results of Davis and coworkers for this system [37], using Sumathi’s TST code [72]. This allowed us to build the CHEMDIS input file representing the allene-propyne-cyclopropene system, shown below:

```
Allene-Cyclopropene-Propyne
TEMP 1 1000.0
PRES 1 1.0
XMG DISSOC INPONLY
CV[C*C]
MASS 40.00
PARAMETERS (Lennard Jones: Angstr. K)
  4.440  265.28
DRDOWN
INT 0.10
BSGS 5.00
XMG COLLIDER
!N2 1.00  28.01  3.798  71.4  290.0  ! 290 cm-1 from Davis for N2 ...
WELL 1 C*C*C
```
Figure 7-14. CHEMDIS input file representing the allene-propyne-cyclopropene system of Davis and coworkers.

Using this file, CHEMDIS calculated the thermal dissociation rate constants for allene, propyne, and cyclopropene. These are shown below:
Thermal Dissociation Rate Constants at 1038 K, 0.58 atm CH₄

<table>
<thead>
<tr>
<th>CY[C*CC] to:</th>
<th>k (1/sec)</th>
<th>fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>C^*C^*C</td>
<td>8.90E+04</td>
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<tr>
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<td>1.50E+00</td>
<td>0.00</td>
</tr>
<tr>
<td>C#CC</td>
<td>7.10E+05</td>
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</tr>
<tr>
<td>C2H + CH₃</td>
<td>4.50E-09</td>
<td>0.00</td>
</tr>
<tr>
<td>C.#CC + H</td>
<td>7.40E-12</td>
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</tr>
<tr>
<td>C#CC. + H</td>
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<td>0.00</td>
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C^*C^*C to:

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<td>C^*C^*C. + H</td>
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<tr>
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<tr>
<td>C#CC</td>
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<td>C2H + CH₃</td>
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<tr>
<td>C.#CC + H</td>
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<tr>
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<td>2.89E-06</td>
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C#CC to:

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<tr>
<td>C^*C^*C. + H</td>
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<td>CY[C*CC]</td>
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<tr>
<td>C2H + CH₃</td>
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<td>C.#CC + H</td>
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<tr>
<td>C#CC. + H</td>
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</tr>
</tbody>
</table>

Table 7-7. CHEMDIS results for the allene-cyclopropene-allene systems. These results were compiled into net reactions which assumed cyclopropene was a very short-lived intermediate.

Note that cyclopropene rapidly re-dissociates back to allene or propyne. We assume this process happens fast enough that reactions of cyclopropene with other species are not important (this assumption is necessary because 1,3 intra-radical additions and beta-scissions were prohibited). With this assumption we were able to write out three net reversible reactions to describe the allene-propyne isomerization and dissociations to propargyl and H atom:

| C^*C^*C ↔ C#CC. + H | 1.34E-03 | 0.0 | 0.0 | ! from Davis calcs |
| C^*C^*C ↔ C#CC      | 5.60E+00 | 0.0 | 0.0 | ! from Davis calcs |
| C#CC ↔ C#CC. + H    | 7.53E-04 | 0.0 | 0.0 | ! from Davis calcs |
6.2 Intra-radical Addition (Ring-Closure) of Resonance-Stabilized Species

Early results of this work suggested that the normal ring-opening/closure rate rules for ring-closure of resonance-stabilized radicals were far too fast. These radicals must give up their allylic stabilization to close, so that the normal 1.5 intra-radical addition rule barrier, in Table 7-4, was not appropriate. The recent work of Martinez and Cooksy supported this assessment [55]. On the presumption that any discovered route to a cyclopentadienyl radical should be studied carefully, we performed an \textit{ab initio} optimization of the geometries of 1,3-cyclopentadien-2-yl and the transition state of the ring-opening:

\begin{align*}
\text{\includegraphics[width=0.2\textwidth]{cyclopentadienyl.png}} & \rightleftharpoons \text{\includegraphics[width=0.2\textwidth]{cyclopentadienyl-yl.png}}
\end{align*}

The resonance-stabilized pent-2-ene-4-yn-1-yl radical on the right is delocalized over three carbon positions, and forms readily from various reactions in the mechanism. Thus, if rapid enough, ring closure of this radical to a cyclopentadienyl could be important.

Calculations of the optimized geometries and frequencies for the 1,3-cyclopentadien-2-yl and the transition state to the ring opened product were performed at the B3LYP/6-311G** level using GAUSSIAN 98 [73]. Optimized geometries are presented below, along with tables of the frequencies and the rotational constants. Sumathi’s TST code provided calculations of the high-pressure-limit rate constant. These were fitted to Arrhenius forms over the temperature range 300-1500 K, to give Arrhenius parameters $A^\prime = 1.98 \times 10^{11}$, $n^\prime = 0.91$ and $E_a = 32.3$ kcal/mol (for $A1^\prime$ in units of 1/sec). When thermodynamically reversed for the ring-closure direction, the ring-closure barrier is about 27.5 kcal/mol, which is close to Martinez and Cooksy’s value for the ring-closure barrier of 1,4-pentadien-3-yl to cyclopenten-3-yl of 31 kcal/mol.

Compare the 31 kcal/mol barrier for the 1,4-pentadien-3-yl closure, or the 27.5 kcal/mol barrier for the pent-2-ene-4-yn-1-yl ring closure, with the normal 1,5 intra-radical addition barrier of 15.8 kcal/mol (Table 7-4). The two resonance-breaking ring closures have barriers 15 and 11 kcal/mol greater than the normal ring-closure barrier. We thus posed a 15 kcal/mol rate-rule correction to the barrier height, for intra-radical
ring closures in which resonance stabilization is broken to close the ring. This is reflected in Table 7-4’s “allylic radical ring-closure correction”.

```
zmat angstroms
  c
  c  1 cc2  1 ccc3
  c  2 cc3
  c  3 cc4  2 ccc4
  c  4 cc5  3 ccc5  1 dih4
  h  1 hc6  2 hcc6  3 dih6
  h  2 hc7  3 hcc7  4 dih7
  h  4 hc8  3 hcc8  2 dih8
  h  5 hc9  4 hcc9  3 dih9
  h  5 hc10  4 hcc10  3 dih10
```

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**Table 7-8.** Z-matrix in angstroms and degrees for 1,3-cyclopentadien-2-yl optimized at the B3LYP/6-311G** level.
zmat angstroms

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Table 7-9. Z-matrix in angstroms and degrees for the ring-opening beta-scission transition state of 1,3-cyclopenta[a]fien-2-yl radical to pent-2-ene-4-yn-1-yl, optimized at the B3LYP/6-311G** level.
Ab Initio B3LYP/6-311G** Results for 1,3-cyclopentadien-2-yl

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| <S²>                           | 0.76       |

Table 7-10. Frequencies, rotational constants and zero-point energy for 1,3-cyclopentadien-2-yl. Frequencies scaled by 0.9613; in zero-point energy correction they are scaled by 0.98.

Ab Initio B3LYP/6-311G** Results for Ring-Opening TS

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<td>498.3</td>
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<td>674.0</td>
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<td>786.2</td>
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| <S²>                           | 0.79       |

Table 7-11. Frequencies, rotational constants and zero-point energy for 1,3-cyclopentadienyl ring-opening transition state. Frequencies and zero-point correction scaled as above.

6.3 The Propargyl + Propargyl System

This CHEMDIS input file was obtained personally from A. M. Dean and H.-H. Carstensen, and is based on the oft-cited BAC-MP4 potential energy surface of Miller and Melius [68]. We used this file to construct net pressure-dependent reactions representing more accurately the recombination of propargyl radicals to form fulvene and benzene. In doing so we removed all CHEMDIS predictions for the propargyl + propargyl system (XMG-PDep does allow the first adducts to form). Adding this system
(which XMG-PDep cannot discover on its own) lowers the predicted allene concentration in Figure 7.7 by about half.

propargyl + propargyl 9/3/98 Melius calc. for input and
TEMP
  1 1038.0
# 9 300. 500. 750. 1000. 1300. 1650. 2000. 2400. 3000.
pres
  1 0.58
# 9 1.e-3 0.01 0.1 1.0 3.0 10.0 30. 60.0 100.
dissoc
chemact
INPUT (A, n, E kcal)
  7.2e+13 0. 0. 0.  (Morier et al 1994)
MASS
  78.
PARAMETERS (Angstrom, K)
    5.82 517.
OLDRHO
DEDOWN
INT
  0.1
BSGS
  5.00
Collider
!CH4
  1.00 16.000 3.750 141.40 1285.0
WELL 1
C#CCCC#C
freq
  3 501.5 10.613 549.4 4.672 1976.8 13.215
REACTANT
  C#CC. + C#CC.
  4.22e+23 -1.89 0. 60.86 (Keq)
ISOMER
  C*C*CC*C*C
  5.2E+10 0.482 0. 27.7
WELL 2
C*C*CC*C*C
freq
  3 318.4 9.509 800.3 5.700 2147.7 14.290
ISOMER
  C#CCCC#C
  2.2e+10 0.658 0. 34.5 (Keq)
ISOMER
  ME2CYBE
  2.5E+10 0.538 0. 21.7
ISOMER
  FULVENE(:)
  2.1E+10 0.54 0. 31.4
WELL 3
ME2CYBE
freq
  3 250.0 1.990 965.5 18.713 2487.3 9.296

274
ISOMER
  C*C*CC*C*C
  9.7e+11 0.608 0. 39.2 (Keq)
WELL 4
FULVENE(6)
freq
3 250.0 1.990 965.5 18.713 2487.3 9.296
ISOMER
  C*C*CC*C*C
  3.7E+11 0.609 0. 14.5 (KEQ)
ISOMER
FULVENE
1.2E+11 0.502 0. 12.0
WELL 5
FULVENE
freq
3 250.0 1.990 965.5 18.713 2487.3 9.296
ISOMER
FULVENE(6)
9.1E+11 0.501 0. 74.0 (KEQ)
ISOMER
CY2(C5C3)
9.7E+11 0.323 0. 38.8
WELL 6
CY2(C5C3)
freq
3 250.0 1.990 965.5 18.713 2487.3 9.296
ISOMER
FULVENE
9.8E+11 0.321 0. 1.3 (KEQ)
ISOMER
BENZENE
2.2E+12 0.254 0. 35.7
WELL 7
BENZENE
freq
3 250.0 1.990 965.5 18.713 2487.3 9.296
ISOMER
CY2(C5C3)
4.53E+13 0.253 0. 108.4 (Keq)
PRODUCT
CYC6H5 + H
9.66E+17 -0.6104 0. 116.2 (from Keq with kf=4e13)
END

275
Citations

editor, National Institutes of Standards and Technology: Gaithersburg, MD, 20899, 2001.
SUPPLEMENT TO CHAPTER 7

1 CHEMKin Mechanism

The generated mechanism, in CHEMKin format (the “chem.inp” file), is presented in the following pages. Most species names are in the Bozzelli/Dean string format used in the rest of this work. For species in which the generated string was too long, or is otherwise not clear, an “SPC” string appears for the species name. These are translated into diagrams at the end of this section. Note that some resonant species appear more than once in the species listing; this is a consequence of XMG-PDep’s treatment of resonant-stabilized species as separate iterations of their formal structures. It does not adversely affect the running of the file. Following the mechanism is the thermodynamic data file in NASA format, and last, a selection from the pressure-dependent network summary file, which shows Network 158, mentioned in the text.
COC + CYC(C)(CC(OC)OC) >= CYC(C)(CC(OC)OC) 2.00e+12  0.00e+00  0.00  1.1  n536  -unknown- from CHIMDES NM 1532
CYC(C)(CC(OC)OC) >= C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n541
dispropRecept L0
C2H2 + CYC(C)(CC(OC)OC) >= CYC(C)(CC(OC)OC) 2.00e+12  0.00e+00  0.00  1.1  n542
dispropRecept L0
COC + CYC(C)(CC(OC)OC) 3.00e+12  0.00e+00  0.00  1.1  n543
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n544
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n545
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n546
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n547
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n548
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n549
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n550
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n551
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n552
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n553
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n554
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n555
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n556
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n557
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n558
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n559
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n560
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n561
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n562
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n563
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n564
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n565
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n566
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n567
dispropRecept L0
COC + CYC(C)(CC(OC)OC) => C2H4 + HCYC24PD 3.00e+12  0.00e+00  0.00  1.1  n568
1.1 Species Translations

C*C*C*C*V:

SPC1915:

SPC1923:

SPC1987:

SPC1996:

SPC1839:
1.2 Thermodynamic Data File

A file in NASA format containing the NASA polynomial representations of species thermodynamic parameters for the CHEMKIN mechanism (see a CHEMKIN manual).
2 Pressure-Dependent Network Summary

A summary listing of all active pressure-dependent networks, with enough information to reproduce the CHEMDIS input file of each, would consume over 300 pages. This information is included on a ZIP disk associated with the thesis. Below, a summary of Network 158, which describes the propargyl + acetylene system, is presented.

PRESSURE-DEPENDENT NETWORK: NUMBER 158

CHEMICAL ACTIVATION: Entrant Reaction:

C2H2 + C#CC. => C#CCC*C. ( 45 + 5 => 150 )
addition ( 6 )

Pathway HP Parameters

A: 1.24E+10 n: 0.84 E: 14.33

Rate Source:

HP parameters read from reaction-library-strict.data

PDEP WELL C#CCC*C. ID: 150

---

REACTANT C#CCC*C. => C2H2 + C#CC. ( 150 => 45 + 5 )

beta scission ( 5 ) REVERSE

Pathway HP Parameters

A: 1.32E+13 n: 0.45 E: 25.10
Ar: 1.24E+10 nr: 0.84 Er: 14.33

Fitted Arr. Parameters incurred average error of 16.95 %

Rate Source:

HP parameters read from reaction-library-strict.data

PRODUCT C#CCC*C. => C#CCC#C + H ( 150 => 785 + 6 )
H beta scission \( (38) \) REVERSE

Pathway HP Parameters

\[
\begin{align*}
A: & \quad 3.75E+11 \quad n: \quad 0.58 \quad E: \quad 33.25 \\
Ar: & \quad 4.06E+11 \quad nr: \quad 0.77 \quad Er: \quad 6.75 \\
\end{align*}
\]

degeneracy: 1 \quad RPDfor: 2 \quad RPDrev: 1 \\
bondadtype: 6 \quad hshifftype: 26

Fitted Arr. Parameters incurred average error of 7.11 \%

Rate Source:

-

HP rate estimated from rate rules

Comments:

(hadd-ter3-pri) reverse of H addition to triple bond (terminal) 
rate estimate, primary vinylic 
- final \( A = 2.03e+11 \quad n = 7.70e-01 \quad E = 6.750000 \)

NONINCLUDED \( C\#CCC\#C. \Rightarrow C\#C.C\#C (150 => 838) \)

1-2 H shift \( (10) \) FORWARD

Pathway HP Parameters

\[
\begin{align*}
A: & \quad 3.56E+10 \quad n: \quad 0.88 \quad E: \quad 40.00 \\
\end{align*}
\]

degeneracy: 1 \quad RPDfor: 1 \quad RPDrev: 1 \\
hshifftype: 15

Rate Source:

-

HP rate estimated from rate rules

Comments:

Found rule for (onetwoh-pp) in place of (onetwoh-vv) onetwoh reaction with A,n,E type rate rule

NONINCLUDED \( C\#CCC\#C. \Rightarrow C\#CC.C\#C (150 => 839) \)

1-3 H shift \( (11) \) FORWARD

Pathway HP Parameters

\[
\begin{align*}
A: & \quad 7.60E+10 \quad n: \quad 0.67 \quad E: \quad 38.70 \\
\end{align*}
\]

degeneracy: 2 \quad RPDfor: 2 \quad RPDrev: 1 \\
rotorloss: 1 \quad hshifftype: 25
Rate Source: 
---------
HP rate estimated from rate rules

Comments: 
--------
onethreeh-va
onethreeh reaction with A,n,E type rate rule

-----------------------------------------------
ISOMER  C#CCC*C.C.  =>  CY13PD1.  ( 150 => 840 )
-----------------------------------------------
1-5 intramol add  ( 17 )  FORWARD

Pathway HP Parameters
----------------------------
A:  8.23E+11  n:  0.07  E:  13.70
----------------------------

Rate Source: 
---------
HP parameters read from reaction-library-strict.data

===============================================
PDEP WELL CY13PD1.  ID: 840
===============================================

-----------------------------------------------
ISOMER  CY13PD1.  =>  C#CCC*C.C.  ( 840 => 150 )
-----------------------------------------------
beta scission  ( 5 )  REVERSE

Pathway HP Parameters
----------------------------
A:  1.84E+13  n:  0.43  E:  49.71
Ar:  8.23E+11  nr:  0.07  Er:  13.70
----------------------------
Fitted Arr. Parameters incurred average error of 5.75 %

Rate Source: 
---------
HP parameters read from reaction-library-strict.data

-----------------------------------------------
NONINCLUDED  CY13PD1.  =>  C.*CC*C*C  ( 840 => 157 )
-----------------------------------------------
beta scission  ( 5 )  REVERSE

Pathway HP Parameters
----------------------------
A:  5.35E+07  n:  1.79  E:  48.64
----------------------------
Ar: 1.22E+08 nr: 1.05 Er: 17.42

---------------------------------
degeneracy: 1 RPDfor: 1 RPDrev: 1
bondadtype: -35 hshifttype: 25

Fitted Arr. Parameters incurred average error of 6.32 %
---------------------------------

Rate Source:
-----------
HP rate estimated from rate rules

Comments:
--------

(in15add-en-st) reverse intraradical endo 1-5 addition reaction rate estimate
  - final A = 1.22e+08 n = 1.05e+00 E = 17.420000

---------------------------------
NONINCLUDED CY13PD1. => CY13PD2. ( 840 => 5119 )
---------------------------------

1-2 H shift ( 10 ) FORWARD

Pathway HP Parameters
--------------------
A: 3.56E+10 n: 0.88 E: 40.00

---------------------------------
degeneracy: 1 RPDfor: 1 RPDrev: 1
hshifttype: 15

Rate Source:
-----------
HP rate estimated from rate rules

Comments:
--------

Found rule for (onetwoh-pp) in place of (onetwoh-vv)
onetwoh reaction with A,n,E type rate rule

---------------------------------
ISOMER CY13PD1. => CY13PD5. ( 840 => 5120 )
---------------------------------

1-2 H shift ( 10 ) FORWARD

Pathway HP Parameters
--------------------
A: 8.98E+10 n: 1.30 E: 33.60

Rate Source:
-----------
HP parameters read from reaction-library-strict.data
PDEP WELL CY13PD5. ID: 5120

ISOMER CY13PD5. => CY13PD1. ( 5120 => 840 )

1-2 H shift ( 10 ) REVERSE

Pathway HP Parameters

A: 2.81E+13 n: 0.77 E: 59.25
Ar: 8.98E+10 nr: 1.30 Er: 33.60

Fitted Arr. Parameters incurred average error of 14.73 %

Rate Source:

HP parameters read from reaction-library-strict.data

NET P-DEP REACTIONS for THIS NETWORK (k in [cm3-mol-s])

C2H2 + C#CC. => C#CCC#C + H  4.20E+06
C2H2 + C#CC. => C#CCC+C.  1.00E+08
C2H2 + C#CC. => CY13PD1.  6.70E+07
C2H2 + C#CC. => CY13PD5.  1.10E+09

RLEAK: 1.38E+08  RLEAKFLUX: 1.16E-13
CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS
1 Conclusions of the Thesis

Advances in the understanding of a great many gas phase processes, including combustion, pyrolysis, hydrocarbon cracking, next-generation engines, and atmospheric pollutant fates, now depend in part on the accuracy and availability of very large chemical kinetic models. Building such large, complex chemical mechanisms by hand can be unsystematic, prone to bias, and can conceal hidden inaccuracies; hence the periodic interest in computerized, automated mechanism generators over the last three decades. These generator tools lacked wide employment, however – partly because, until now, they could not handle the crucial pressure-dependent behavior of most interesting gas-phase kinetic systems.

This thesis represents the first known automated mechanism generation tool to incorporate pressure-dependence in a systematic, flexible, and reliable way. The approach assembled and described in this work includes pressure-dependent reactions using the same, flux-based termination criteria which rationally limits mechanism growth, the $R_{\text{min}}(t)$ criteria [1-4]. By constructing only those parts of a pressure-dependent network which are appropriate for the specified conditions of temperature and pressure, our approach allows any mechanism generation tool to include pressure-dependent reactions.

The following paragraphs review the specific results of each chapter of the work. Next, we summarize recommendations for improvements to our automated pressure-dependence approach. Finally, this chapter suggests broader directions for the field of mechanism generation, based on the experience gained here.

1.1 Chapter 2: A Priori Falloff Analysis for OH + NO₂

Chapter 2 described a series of a priori predictions for the rate constants of the important reactions OH + NO₂ → HONO₂ and OH + NO₂ → HOONO. These were based on a full inverse Laplace transform approach, followed by a master equation treatment of energy transfer. The unadjusted “from scratch” predictions for HONO₂ formation bounded the experimental results within a factor of three. This implied a
“best-case” bound for expected accuracy when doing a priori pressure-dependence calculations from scratch, without direct access to transition-state information.

The results suggested that further improvement in any a priori evaluation of \( k(T,P) \) for this system depended on improved treatment of the J-mode; the later work of Troe included such a treatment as a key feature (among other improvements) [5]. The calculations of Chapter 2 also suggested that HONO formation convolved the results of certain experiments designed to measure the high-pressure limit for \( \text{OH} + \text{NO}_2 \rightarrow \text{HONO}_2 \) (though its significance under atmospheric conditions was less clear). At the time HONO had not been observed in the gas phase. Recently, experimental measurements have confirmed HONO formation from OH and NO\(_2\), in rough agreement with the approximations of our work [6;7].

1.2 Chapter 3: Predicting \( k(T,P) \) in Automated Mechanism Generation

Chapter 3 explained how the modified Quantum-Rice-Ramsperger-Kassel/Modified Strong Collision (QRRK/MSC) approach, CHEMDIS [8], and the density-of-states fitting code, THERFIT [9], could be combined to make rapid estimates of \( k(T,P) \) while requiring only high-pressure-limit Arrhenius parameters and heat capacities. It outlined our successful efforts to boost the speed of CHEMDIS by a factor of 10-100, making it more suitable for an on-line approach.

The QRRK/MSC is clearly approximate, involving unphysical assumptions, so the sources of error in this approach were thoroughly, if qualitatively, explored. The choice of the QRRK/MSC method for on-line pressure-dependence is justified by its speed, and by the fact that the information it requires to evaluate \( k(T,P) \) happens to be all that is practically available in a mechanism generation tool. Online ab initio calculations of transition state properties and the modes of every needed stable species, required for any higher-level approach, are simply not feasible. The QRRK/MSC presents the best available balance of speed, accuracy, and required inputs. Nonetheless we made a number of recommendations for improving predicted \( k(T,P) \) accuracy while preserving feasibility for on-line mechanism generation.
1.3 Chapter 4: Rate-Based Screening of Pressure-Dependent Networks: The Activated Species Algorithm (ASA)

Pressure-dependent reactions are not isolated systems but are each part of larger networks of successive isomerizations, dissociations, and collisional activations and stabilizations. Some knowledge of the appropriate network is required to predict $k(T,P)$ with any reliability. But it is not obvious which parts of a network need to be included for $k(T,P)$ estimates, under what conditions. Furthermore, since networks may grow to arbitrary size if their full exploration is forced, screening of such networks cannot be avoided. Chapter 4 resolved the question of how to truncate a pressure-dependent network in a systematic way, with an algorithm called the “Activated Species Algorithm”.

The key feature of the approach was its treatment of isomer channels not yet included in the network as though they were product channels, for the purposes of calculating $k(T,P)$. The summed rate through all channels not yet included in the pressure-dependent network could then be evaluated. Dubbed “$R_{\text{leak}}$”, this summed rate could be used with the rate-based termination criteria $R_{\text{min}}$. Our screening algorithm would build the pressure-dependent network, one isomer at a time, until $R_{\text{leak}}$ was less than the desired flux criteria $R_{\text{min}}$. This screening approach ensured that the flux to all non-included pathways is bounded; this in turn bounded the “truncation error” in any $k(T,P)$ prediction of the truncated network. We thus developed the first known method for systematically screening a pressure-dependent network to include only those portions necessary for predicting $k(T,P)$ under arbitrary conditions. This algorithm was implemented within the modified CHEMDIS of Chapter 3.

1.4 Chapter 5: Capturing Pressure-Dependence in Automated Mechanism Generation: Reactions Through Cycloalkyl Intermediates

Chapter 4 dealt with well-studied examples for which a great deal of computational or experimental data was available. But how would the approach work in a real automated mechanism generator, when high-pressure-limit data and density-of-states information would come from simple rate rules and group additivity estimates of
the thermodynamic parameters? Chapter 4 examined these questions in a detailed application to the H + cycloalkene systems of Stein and Rabinovitch [10].

The XMG automated generator of Grenda was used to build full pressure-dependent networks, using rate rules and group additivity. These were then subjected to our automated screening approach. In each case the approach captured all of the important channels found in the experiments, and predicted yields agreed with the data within a factor of 10, usually better. While we did not conduct a systematic study of expected accuracy, we found factor-of-10 accuracy in predicted \( k(T,P) \). This accuracy was reasonable for the low-temperature, low-pressure conditions at which the QRRK/MSC approach would be expected to be at its worst. The screening approach was highly robust; errors in the \( k(T,P) \) prediction stemmed entirely from the QRRK/MSC approach used, and the inaccuracies in the rate rule and thermodynamic inputs.

1.5 Chapter 6: Mechanism Generation Algorithm with Integrated Pressure-Dependence: XMG-PDep

Chapter 6 presented, in detail, an integrated approach to pressure-dependence in automated mechanism generation. This approach knitted together the work of Chapters 3-5, and the original XMG, into a fully-pressure-dependent mechanism generation code called "XMG-PDep". As XMG-PDep explores the reactions of a candidate species, it recognizes reactions of the type \( A + B \rightarrow C \), \( B \rightarrow C \), and \( B \rightarrow C + D \) as potential "entrance channels" to pressure-dependent networks. Upon discovering a new reaction of any of these three types, it initiates a new pressure-dependent network data object (or modifies an existing one if appropriate), which later holds all information needed to calculate \( k(T,P) \).

After completing the reactions of a candidate species, the generator builds the set of ordinary differential equations that represents the behavior of all explored species. It integrates these, stopping at every solver time-step to calculate the flux criteria \( R_{\text{min}}(t) = f_{\text{min}}R_{\text{char}}(t) \). It also evaluates the flux to each candidate species, \( R_{\text{species}(j)}(t) \), and the flux through all non-included pathways of each pressure-dependent network, \( R_{\text{leak}(i)}(t) \). From the set of \( R_{\text{species}(j)}(t) \) and \( R_{\text{leak}(i)}(t) \) it chooses the largest value. If this value is less than \( R_{\text{min}}(t) \), integration continues to the next solver time-step and the
comparison is repeated. If the largest value is greater than $R_{\text{min}}(t)$, and it is a species flux $R_{\text{species}(j)}(t)$, the generator explores the reactions of that species. But if the largest value is a pressure-dependent network leakage flux, $R_{\text{leak}(i)}(t)$, the generator explores a portion of network $i$. This adds some of the non-included pathways to the network, and allows new ones to be discovered.

The generator then calls CHEMDIS to estimate $k(T,P)$ for the reactions of the explored network. Integration with the solver starts anew, with updated $k(T,P)$ values for the reactions associated with the newly-extended network. The generator will continue in this fashion, exploring species and pressure-dependent networks, until the user-desired conversion of reactant is reached. At this point, the user is assured that for all time $t$ from $t = 0$ to the time at which conversion is reached, $R_{\text{species}(j)}(t)$ and $R_{\text{leak}(i)}(t)$ are less than $R_{\text{min}}(t)$. That is, no flux to a species not yet included in the mechanism, or through the non-included pathways of a pressure-dependent network, exceed the rate-based $R_{\text{min}}$ criteria.

1.6 Chapter 7: Mechanism Generation with Pressure-Dependence: Application to Methane Pyrolysis

The new mechanism generator with integrated pressure-dependence, XMG-PDep, was applied to the methane pyrolysis system studied by Chen and coworkers [11;12], Roscoe and Thompson [13], and Dean [14]. Chen and coworkers found experimentally that at temperatures near 1038 K and pressures near 0.58 atm, the neat batch pyrolysis of methane showed a strong autocatalytic behavior at very low methane conversion (less than 1%). This behavior defied mechanistic explanation until Dean proposed a chain-branching pathway through cyclopentadienyl radical. But this explanation fell short when more accurate thermodynamic parameters were used for cyclopentadienyl [15;16]. Since methane pyrolysis also enjoys periodic industrial interest and is important as a subset of wider combustion and pyrolysis systems, we used XMG-PDep to systematically construct a mechanism for the conditions of Chen and coworkers.

XMG-PDep successfully built a new model which captured the autocatalytic behavior of methane pyrolysis, without any fitting or adjustment of data or input.
parameters. Construction required only a small library of rate constants and thermodynamic parameters, with a larger library of high-pressure-limit rate rules. Most imput data came from the rate rules and from group-additivity estimates. The cyclopentadienyl system was still important in the generated mechanism, but accounted only for about 25% of the autocatalytic behavior. In addition, it no longer came from the allyl + acetylene pathway proposed by Dean. Instead, cyclopentadienyl forms directly from the pressure-dependent addition of propargyl radical to acetylene. To our knowledge no methane pyrolysis mechanism has ever included this pathway before; our mechanism generator could not have discovered it without an integrated pressure-dependent capability.

Roughly half the autocatalysis appears to come from molecular addition reactions, which are rarely given serious treatment in gas-phase mechanisms. Indeed, as a group these reactions (or their reverse, radical disproportionation) are not well-studied. But the molecular addition of allene and methane to form allyl and methyl radicals plays a fundamental chain-branching role in methane autocatalysis, according to the generated mechanism. Allene, while a key species, is not unique in its role. Our pressure-dependent mechanism generator has revealed new pathways for a specific system, which might not have otherwise been discovered. Further improvements to our methane pyrolysis mechanism await improved values for disproportionation or molecular addition rates, and the addition of key diradical reaction families to the generator.

2 Recommendations and Further Research

2.1 Recommendations for Automated Pressure-Dependence

The approach of this thesis for including pressure-dependence in mechanism generation has proved successful in application to methane pyrolysis, and to reactions through cycloalkyl intermediates. There remain many opportunities for improving the approach. Some of the more important challenges, and the best opportunities for improvement, are offered below.
2.1.1 Recommendation 1: Improve $k(T,P)$ Prediction in Mechanism Generation

Systematically Assess Errors in the QRRK/MSC

A key weakness of XMG-PDep is its reliance on the QRRK/MSC method for predicting $k(T,P)$, even though no other currently available method is practical. We know of no systematic study of the sources of error in this method and what the expected accuracy might be, although some work (including our own) exists for specific systems. It would be very useful to quantify the accuracy of QRRK/MSC; this would guide its application in our method and in other cases. Such work would also prepare the way for advanced uncertainty analysis tools such as that of Tatang [17;18].

Implement an ILT/Fast-MEQ Method

The QRRK/MSC approach could, theoretically, be upgraded to a thermodynamically consistent inverse Laplace transform method for $k(E)$, followed by a fast master equation treatment of collisional activation and deactivation. A carefully-implemented inverse Laplace transform would require no more information than the QRRK approximation now used, but would be thermodynamically consistent (it could be made to follow detailed balancing). Since our work’s reliance on the QRRK/MSC method routinely draws criticism from the wider physical chemistry community (in the absence of any systematic study of its accuracy), a full, thermodynamically-consistent ILT approach for $k(E)$ should be implemented in future automated pressure-dependence approaches. Both numerical and analytical methods are available.

For various reasons a fast master equation approach may require a compromise method which retains the steady-state assumption for activated isomers but allows a full distribution of collisions. We know of no publicly-available code to accomplish this, which would be applicable to general, multi-isomer systems of arbitrary complexity. Though the physical chemistry field is currently focused on ever-more-sophisticated, complex numerical master-equation solvers, work is needed in understanding and implementing accurate, approximate master equation approaches which retain the speed and simplicity of the modified strong collision assumptions.
Revisit the Density of States Approximations

Whether or not an ILT/MEQ approach is used, other issues contribute to inaccuracy in automated \( k(T,P) \) calculations. The three-pseudofrequency model for the density of states may need to be re-examined. A next-generation code should incorporate real frequency and rotational data (in order to calculate a "real" density of states) when such information is available. Also, since chemical functional groups often have very characteristic frequencies, geometries, and hindered rotation barriers, it may be possible to replace the three-pseudofrequency fitting approach almost entirely, with "assumed frequency sets" for new molecules (whose actual frequencies and other modes are unknown). These could be reconciled and adjusted to match heat-capacity data, yet might be much better representations of the "true" density-of-states, for the purposes of calculating \( k(E) \).

2.1.2 Recommendation 2: Check the Assumptions of the Integrated Approach

The "On-Par" assumption and the "Constant \( k(T,P) \)" assumption were both discussed in Chapter 6 as key assumptions of our integrated pressure-dependent exploration algorithm. The on-par assumption states that each partially-explored pressure-dependent network is "as important" as each unreacted, candidate species for exploration, even though a candidate species and a partial pressure-dependent network are completely different entities. A consequence of this assumption is that important unreacted species can "hide" at the edges of partial pressure-dependent networks. Of the three solutions proposed for the hiding-species problem, a variant of the "non-included flux calculation" would seem the easiest and most practical to implement; future adaptations of the integrated pressure-dependence approach should at least consider the non-included flux calculation method.

The pressure-dependent rate constant for any system is really a concentration-dependent value, \( k(T(t),[M_i](t)) \) where \([M_i](t)\) is the concentration of bath gas \( i \) at time \( t \). We have assumed throughout this work, however that \( k(T(t),[M_i](t)) = k(T,P) \),

\[ k(T(t),[M_i](t)) = k(T,P) \]

---

\[ ^3 \text{Dr. Albert Chang, formerly of Exxon Research and Engineering, now with the Jet Propulsion Laboratory, worked on a generalized inverse Laplace transform approach in 1996. This work was unfortunately never published and remains proprietary.} \]
where one bath gas is the dominant collider. In principle, this assumption is easily relaxed, as the CHEMDIS QRRK/MSC approach already treats multiple colliders in different fractions, as do most other pressure-dependence codes. It does mean, however, that since \([M](t)\) will change with time during a given process, a parameterization may be required during the integration step of DASSL. Alternatively, any fitting routine for \(k(T,P)\) will really need to span multiple bath gases and not just one “pressure”, unless these bath gas concentrations and collisional efficiencies can be mapped to an “effective pressure”.

2.1.3 Recommendation 3: Connect the Approach to Range Analysis

XMG-PDep is designed to work with a single a single, user-specified temperature and pressure, and a single set of initial concentrations. In reality, the user will always want a mechanism designed for a range of temperatures, pressures, and concentrations. Song’s approach will accomplish this in the high-pressure-limit [4]; it remains to integrate the pressure-dependent approach here with Song’s range analysis.

Connecting range analysis and pressure-dependence requires a fitting routine for \(k(T,P)\), so that first-order derivatives with respect to temperature and pressure can be estimated. We know of no suitable fitting routines in the literature; most of those proposed employ far too many fitting parameters to be useful in an automated approach. Indeed, simple linear interpolation over an \(n\)-by-\(n\) temperature-pressure grid would be much better than the approaches of Venkatesh (requiring ~50 parameters) [19;20] or even Kazakov and coworkers (requiring about 12) [21]. Curves of \(k(T,P)\) follow well-behaved forms, so it is not clear why simpler fitting routines have not yet been proposed. Finite element methods may provide a way to estimate \(k(T,P)\) values and possibly, derivatives, from a pressure-dependent network using only a limited number of \((T,P)\) points.

2.2 Future Directions for Automated Mechanism Generation

The inclusion of pressure-dependence is only one feature among many that have long been needed to make automated mechanism generation truly useful to the chemist or engineer. Range analysis, automated mechanism reduction, improved rate rules and thermodynamic data (and improved bookkeeping of these), a more reliable and robust
code, user-friendly interfaces, and a flexible system for adding and testing reaction families are all much-needed improvements. A selection of ideas for future work in mechanism generation is presented below.

2.2.1 Reaction Family And Structure Issues

Reaction Templates

XMG-PDep and its predecessors, XMG and NetGen, all use “hard-coded” reaction families, in which each reaction family is embedded in the program source. In addition to having a hard-coded matrix for bond-electron algebra, each family has a particular logic and order of functions and list searches. This makes it quite difficult to add new families. The software user must become a good ‘C’ programmer in order to “teach” the code about, say, diradical reactions.

The reaction family system must be changed so that new families can easily be constructed and specified. A true template-matching system (as opposed to the bond-electron formalism) may be the best choice; such an approach can be combined with a graphical user interface to design templates that represent reactions. The entire, cumbersome \texttt{DetermineXSites-DoXReactions} system can then be greatly simplified to a template-matching and construction system, working with the user-defined set of templates. A template system simultaneously eliminates many deficiencies of the bond-electron formalism, including its inability to handle delocalized electrons.

Missing Species Types

A key problem in Chapter 7 was XMG-PDep’s inability to understand or allow diradical intermediate species. The NetGen/XMG/XMG-PDep codes also struggle with proper identification of electronically excited species such as singlet methenyl, which can be important in many combustion and atmospheric chemistry systems. These species types need to be incorporated rationally into any future mechanism generation effort.

Missing Reaction Families

Retro-Diels-Alder, \textit{ene}-reactions, insertions, and concerted eliminations are among the many reaction families not included in the XMG family of codes (in part because some of these may proceed through diradical intermediates or are primarily diradical-type reactions). The importance of such families is well-known, and further use
of the generators without such families may not be very useful. They need to be studied and added, preferrably with a template-based family system.

Resonant Species and Aromatic Species

A key problem, repeatedly mentioned, with the XMG-based codes is their incorrect treatment of resonance-stabilized and aromatic species. Since the most important radicals of many systems are resonance-stabilized, a more accurate method for treating these must be found. All formal structures of a resonance-stabilized or aromatic species can be represented by a single graph; with some modification, the data structure can also store information required to reconstruct each formal structure.

The application of rate rules to these species, which have multiple possibilities for formal structures, will also have to change. For example, consider the addition of propargyl radical to ethylene, in which two reaction path possibilities arise from the two formal structures of propargyl:

\[
\begin{align*}
\text{\textbullet} \quad & + \quad \text{\textbullet} \\
\text{\textbullet} \quad & + \quad \text{\textbullet}
\end{align*}
\]

The current mechanism generator would choose a high-pressure limit rate rule for radical addition to the terminal carbon of the double bond, for both of these reactions. But if a rate rule is used here, it should be divided among the formal structure possibilities for propargyl. Thus the appropriate rate rule for addition should be partitioned, to, say, 60% as the first type of addition and 40% as the second type. Exactly how rate rules should be partitioned in these cases is not clear, however. More research is needed to devise a partitioning system or rule-of-thumb for resonant-species and aromatic-species reactions.

Cis/Trans and Stereochemistry

Most mechanism generators cannot resolve stereochemistry or cis/trans features, because the graph-theoretical structure cannot represent them. Ugi and coworkers have presented a number of methods for extending graph-theory structures to include cis/trans and even detailed stereochemistry, but it is not clear whether these are suitable for large-scale, gas-phase mechanism generation [22]. It may be worthwhile to examine ways of
including cis/trans features, though once included, the rate rules will need to be altered just as for resonant and aromatic species above. In most instances there will probably not be enough information to justify any specific partitioning between, say, the cis and trans product possibilities of a reaction; this is even more true for other stereochemistry differences.

2.2.2 Data Source Improvement

The accuracy of mechanism generation hinges on reliable thermochemical and kinetic data for important reactions, and on reliable methods for estimation when these data are not available. Therefore continued improvement of the reaction data library, the thermodynamic library, the rate rule library, and the group-additivity methods is imperative. The general application of group additivity to transition-state theory (GA-TST) [23;24] should allow users to build more accurate rate rules for many gas-phase reactions; these should be incorporated in any future use of XMG-PDep or another mechanism generator. Alternatively, the GA-TST method could be added directly to a mechanism generation tool.

2.2.3 Useful Reactor Models

XMG-PDep builds and solves the ordinary differential equations for evaluating $R_{char}$ and $R_{min}$ assuming a homogeneous, isobaric, isothermal batch reactor. Most systems of interest are not well-modeled by these assumptions; indeed, methane pyrolysis was chosen as the previous chapter's example in part because the experiments seemed to fit these assumptions. The other classical chemical engineering reactor models (laminar plug flow, continuous-stirred-tank, packed catalyst bed) probably need to be considered as alternate templates for building the ODEs. The isobaric and isothermal constraints also should certainly be relaxed, though this will make the ODEs more difficult to solve.

Certainly one can generate models using the isothermal, isobaric batch reactor assumptions, and then apply them to a wide variety of real-world systems. It is not clear how to do this systematically, however. What batch reactor initial conditions will build the right model for a continuous-stirred-tank reactor? It is also unclear where and when new batch-reactor-based mechanisms would be necessary. These problems persist even if one proposes that the batch-reactor-based generator be used to build mechanisms for
individual sets of “cells” or elements of a computational fluid dynamics (CFD) code. A systematic approach to these issues would be most useful; the reactor model question is in some ways related to the range analysis problem.

2.2.4 The Autocatalytic Pathway Problem

Perhaps the most interesting unsolved problem in automated mechanism construction is the detection of autocatalytic pathways. Recall that the flux criteria $R_{\text{min}}$ is set by $R_{\text{min}}(t) = f_{\text{min}} R_{\text{char}}(t)$, and while $R_{\text{char}}(t)$ may be set using Song’s formula [4], the tolerance $f_{\text{min}}$ is set by the user. In the previous chapter’s methane pyrolysis example, $f_{\text{min}} = 0.01$ was fortunately sufficient to capture the important autocatalytic pathways, but there is no a priori guideline for what $f_{\text{min}}$ should be.

More seriously, autocatalytic pathways could escape capture by the mechanism generator even when a low tolerance is used. Continued lowering of $f_{\text{min}}$ will rapidly lead to larger and larger mechanisms [1], so this is not a practical solution. One possible remedy would include using different $f_{\text{min}}$ values for radicals and stable molecules, or assigning weights to the fluxes in $R_{\text{char}}(t)$ based on family type. If a certain type of family is known to be a key step in an autocatalytic route, the generator could add a high weight to all fluxes from such families. Reactions could also be added based on the degree to which they increase the total net radical production, a key feature of autocatalytic systems.

It might also be possible to estimate the theoretical autocatalytic potential for any species on the “edge” of the mechanism at a particular point, using a radical-chain-length estimate. The generator could examine a set of non-included, candidate species, and attempt to answer the question “how many new radicals would each new molecule of this candidate species produce?” An algorithm might estimate the answer by examining only the radical production reactions the candidate could participate in, or even what its products might participate in, without forcing full exploration of all the possible reactions. Using the current state of the mechanism for input data, the algorithm could generate a rough estimate of the “radical producing power” of a new species and use this in conjunction with $R_{\text{min}}$ to decide whether or not to formally add it.

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3 Final Comments

In this work we have presented the first known mechanism generator which can truly include pressure-dependent reactions and systems. We have used this tool to discover previously unrecognized or neglected pathways, which, in turn, explain the persistent, decades-old mystery of low-temperature methane autocatalysis. Much work remains to turn automated mechanism generation into a truly useful, broad tool – the kind of tool with the power to remove the fictional elements of gas-phase mechanisms and replace them with processes closer to the truth. But both the field of gas-phase chemistry, and computing power, have now advanced to the point that all of this needed work seems feasible.

Indeed, automated mechanism generation may finally be acquiring the startling potential it was thought to posses in its early days – one conference attendee (at the 17th International Symposium on Gas Kinetics in Essen, Germany) recently labeled this work “automated grant proposal generation”. If our simple and rudimentary tool could uncover an explanation for methane pyrolysis which eluded 20 years of research, what else can be discovered with new advances and better tools?
Citations
