Uncertainty Analysis in Automatic Reaction Mechanism Generation: Neopentyl + O_2

by

Sarah V. Petway

B.S. Chemical Engineering
Georgia Institute of Technology, 2003

SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT THE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY

SEPTEMBER 2006

Signature of Author:______________________________
Department of Chemical Engineering
August 11, 2006

Certified by:______________________________
William H. Green, Jr.
Associate Professor of Chemical Engineering
Thesis Supervisor

Accepted by:______________________________
William M. Deen
Professor of Chemical Engineering
Chairman, Committee for Graduate Students

Uncertainty Analysis in Automatic Reaction Mechanism Generation: Neopentyl + O_2

by

Sarah V. Petway

Submitted to the Department of Chemical Engineering
on August 11, 2006 in Partial Fulfillment of the
Requirements for the Degree of Master of Science in
Chemical Engineering

ABSTRACT

The process of building accurate chemical mechanisms for hydrocarbon oxidation systems is difficult since these mechanisms can have hundreds of species and thousands of reactions. Computer programs have recently been developed to construct these models automatically, but until this work, these programs did not include tools for the propagation of uncertainty. Rate constants and thermodynamic properties are not known precisely, and this can lead to large errors in model predictions.

This work presents tools for sensitivity analysis and uncertainty propagation within an automatic reaction mechanism generator. A function for calculating first-order sensitivity coefficients with respect to rate and thermodynamic parameters and initial conditions is implemented in the MIT Reaction Mechanism Generator (RMG). An algorithm for generating error bounds on model output using first-order sensitivity coefficients and uncertainties in model parameters is also implemented.

These tools are applied to an automatically generated model for the oxidation of the neopentyl radical, and results are compared to experimental observations. Comparison of the model with experimental data allowed identification of two rate constants. At 673 K and 60 Torr, $k_{C5H11+O2 \rightarrow OH+C5H10O} = 1.9 \times 10^{-14} \pm 6 \times 10^{-15}$ cm^3/molecule-s, and $k_{OH+C5H11I \rightarrow C5H10I+H2O} = 3.1 \times 10^{-12} \pm 1.5 \times 10^{-12}$ cm^3/molecule-s.The computer-generated model is consistent with two prior literature studies.

Thesis Supervisor: William H. Green, Jr.
Title: Associate Professor of Chemical Engineering

Table of Contents

1. Introduction

Accurate chemical mechanisms are important for understanding hydrocarbon combustion systems. Manually constructed mechanisms are often incomplete, and the process of building them is very slow. Computer programs for the automatic construction of reaction mechanisms have recently been used to generate large models efficiently, but these programs usually do not include tools for the propagation of uncertainty. Uncertainties in rate constants and thermodynamic parameters used to generate these models can lead to large errors in the model predictions.

Sensitivity analysis computes the change in model output when an uncertain input parameter is varied. The sensitivity coefficients can be used to estimate uncertainty in the model output resulting from uncertain input parameters. In chemical kinetic models, the uncertain inputs include thermochemistry estimates and parameters used to estimate rate constants at the temperature and pressure of interest. When the thermochemistry or rate constant of interest has not been measured, one is forced to use estimates, so one would like to compute sensitivities of the model output to all the parameters used to estimate a rate constant or thermodynamic parameter. Unfortunately, most sensitivity analysis codes compute sensitivities for all rate constants in the model without consideration of thermochemistry or how the rate constants were estimated.

In this work, tools for sensitivity analysis and uncertainty propagation are implemented in an automatic reaction mechanism generator. These tools are used to generate and analyze a model for the oxidation of the neopentyl radical, and model predictions are compared to experimental results. Error bounds on the rate constant for the direct chemically activated reaction $C_5H_{11} + O_2 \rightarrow OH + $ 3,3-dimethyloxetane are determined from a comparison of the model with experimental results. This rate constant is compared to RRKM master equation results and QRRK/MSC calculations. Error bounds on the rate constant for $C_5H_{11}I + OH \rightarrow C_5H_{10}I + H_2O$ are also presented.

2. Background

2.1 Sensitivity Analysis

Sensitivity analysis investigates the relationship between changes in input parameters and model output. This relationship can be expressed as a Taylor series expansion,

$$C_i(t,\underline{\alpha}+\Delta\underline{\alpha}) = C_i(t,\underline{\alpha}) + \sum_j \frac{\partial C_i}{\partial \alpha_j}\Delta\alpha_j + \frac{1}{2}\sum_l \sum_j \frac{\partial^2 C_i}{\partial \alpha_l \partial \alpha_j}\Delta\alpha_l \Delta\alpha_j + \ldots \quad , \qquad (2.1)$$

where $\partial C_i/\partial \alpha_j$ are the first-order local concentration sensitivity coefficients and $\partial^2 C_i/\partial \alpha_l \partial \alpha_j$ are second-order local concentration sensitivity coefficients. Methods for the calculation of first-order sensitivity coefficients have been reviewed by Rabitz et al. [1] and Turányi [2].

The simplest method for calculating local sensitivities is the brute-force method in which individual parameters are perturbed and sensitivities are calculated by finite difference approximations. This method is easy to implement but is inaccurate and computationally inefficient. Another class of methods involves the solution of the following set of differential equations:

$$\frac{d}{dt}\frac{\partial \underline{C}}{\partial \alpha_j} = \sum_l \frac{\partial \underline{f}}{\partial C_l}\frac{\partial C_l}{\partial \alpha_j} + \frac{\partial \underline{f}(t)}{\partial \alpha_j}, \qquad (2.2)$$

where $d\underline{C}/dt = \underline{f}(\underline{C},\underline{k})$. This set of equations can be solved simultaneously with the kinetic equations. Since both sets of equations have the same Jacobian, it is more efficient to use a decoupled direct method which solves the kinetic equations first, followed by the solution of equation 2.2 at each time step [3, 4]. The simultaneous corrector [5] and staggered corrector [6] methods reduce the computational cost of the decoupled direct method by minimizing the number of Jacobian factorizations needed to solve the sensitivity equations. The Green's function method solves equation 2.2 by first calculating the solution of the homogeneous part and then determining the particular solutions that correspond to each parameter [7]. Variations on this method include the scaled Green function method [8] and the analytically integrated Magnus version [9]. The adjoint sensitivity analysis procedure is efficient for computing sensitivities in systems where the number of parameters is larger than the number of model responses, but it requires the solution of an adjoint model, which can be difficult to construct [10].

Local sensitivity coefficients can be used to obtain estimates of uncertainties in a model's output. If the uncertain model parameters have a normal distribution and covariance is neglected, the variance in the model output can be estimated from the first-order sensitivity coefficients and the variances of the input parameters [11]:

$$\sigma^2(C_i) \approx \sum_j \left(\frac{\partial C_i}{\partial \alpha_j} \right)^2 \sigma^2(\alpha_j). \tag{2.3}$$

The individual terms in Equation 2.3 can be used to estimate the contributions of uncertainties from individual parameters to the total uncertainty in an output concentration. The output concentrations can also be extrapolated to a new set of parametric conditions by parametric scaling:

$$C_i(\underline{\alpha} + \Delta\underline{\alpha}) \approx C_i(\underline{\alpha}) + \sum_j \frac{\partial C_i}{\partial \alpha_j} \Delta\alpha_j \,. \tag{2.4}$$

The truncated Taylor series in Equation 2.4 can result in physically unrealistic predictions such as negative concentrations. Since species concentrations behave exponentially, it is more useful to write a first-order Taylor series in the transformed variable $z = ln|C_i - C_l|$, where C_l can be zero or a known mass conservation limit [1, 2]. Setting C_l equal to zero and solving for C_i gives the following equation:

$$C_i(\underline{\alpha} + \Delta\underline{\alpha}) \approx C_i(\underline{\alpha}) \exp\left[\sum_j \frac{\partial C_i}{\partial \alpha_j} \frac{\Delta\alpha_j}{C_i(\underline{\alpha})} \right]. \tag{2.5}$$

Using first-order sensitivity coefficients to predict uncertainties in model predictions is computationally efficient, but the Taylor series approximation is only valid near nominal values of the input parameters. Since rate constants and thermodynamic parameters can have large uncertainties, these methods provide rough approximations.

Including second-order terms in the Taylor series expansion extends the range over which parameter variation is valid and allows interactions of parameters to be examined. Brute-force, decoupled direct, and Green's function methods have been used to calculate second-order sensitivity coefficients [12, 13]. Second-order sensitivity analysis improves the accuracy of the predictions when sensitivity coefficients are used to estimate concentration changes, but calculating the higher order sensitivity coefficients requires considerable computer time. The computational cost of calculating second-order sensitivities scales with the square of the number of parameters, while first-order sensitivity analysis scales only linearly with the number of parameters. Özyurt and Barton developed the directional second-order adjoint method, which has only a weak dependence on the number of parameters [14].

2.2 Uncertainty Propagation

Global methods for uncertainty propagation precisely calculate the uncertainty of model output from uncertainties in the model parameters. Unlike local sensitivity analysis, these methods can handle large uncertainties in the input parameters, and many can determine uncertainties in the output resulting from each parameter [11]. The Fourier Amplitude Sensitivity Test (FAST) method was the first widely used global method [15]. In this method, the rate parameters are perturbed simultaneously by sine functions with incommensurate frequencies, and the Fourier coefficients are evaluated and used to obtain variances of the output concentrations. The FAST method is computationally expensive, requiring $1.2\times m^{2.5}$ model simulations, where m is the number of parameters. Similar methods based on other orthonormal perturbation functions have been developed, but all require a large number of model simulations and therefore much computer time.

Monte Carlo methods use a random number generator to select values of parameters according to their probability density functions [11]. The model is then solved for each parameter combination, and the results are analyzed statistically. Monte Carlo methods are simple to implement, but the computational cost scales exponentially with the number of parameters. In the Latin hypercube method, parameter combinations are chosen according to a Latin hypercube to ensure that the sample values cover the entire range of uncertainty [16, 17]. This reduces the computer time by approximately an order of magnitude. Quasi-Monte Carlo methods have been developed and applied by Saltelli et al. [18, 19], but the number of simulations required is still about two orders of magnitude greater than the number of parameters.

Response surface methods were developed to reduce the amount of computer time required by the Monte Carlo approach. These methods replace complicated output functions with analytic approximations called "response surfaces" [20]. Tatang developed the Deterministic Equivalent Modeling Method (DEMM), which transforms a stochastic model into its deterministic equivalent [21]. In this approach, the probability density distributions of uncertain model parameters are represented as polynomial chaos expansions. Distributions of model output are calculated using orthogonal collocation. DEMM was applied to a model for supercritical water oxidation and required approximately two orders of magnitude fewer simulations than the Monte Carlo method [22].

High-dimensional model representations (HDMR) have been developed for the efficient analysis of high dimensional input-output systems [23, 24]. HDMR expresses the model output as an expansion of component functions of the input parameters. These component functions can be represented by orthonormal polynomials to reduce the required sampling effort. This technique can be used to determine the variance of model output and to decompose this variance into contributions from individual input parameters and from interactions among multiple parameters. The number of model simulations needed to describe the system scales as n^l, where n is the number of parameters and l is the cooperativity order. HDMR expansions to second order ($l = 2$) are sufficient for most systems.

Methods for global uncertainty analysis require knowledge of the probability distribution functions of input parameters. Sufficient data are not always available to construct sophisticated probability distributions for kinetic and thermodynamic parameters. To ensure that rate constants can have only positive values, a log-normal distribution is sometimes assumed for forward rate constants. Heats of formation can be assigned normal probability distributions so that the reverse rate constants are also log-normally distributed [22]. When sufficient experimental data are available, Bayesian analysis can be used to characterize the probability distributions of uncertain parameters. The Bayesian approach is used to determine a posterior density function from a prior density function and a likelihood function [25].

2.3 Automatic Reaction Mechanism Generation

Several computer programs have been developed for the automatic generation of reaction mechanisms. Côme et al. [26], Vogin [27], Chevalier et al. [28, 29], Ranzi et al. [30], Blurock [31], and Broadbelt et al. [32-34] have used automatic reaction modeling software to generate mechanisms for the oxidation of hydrocarbons. These programs all have limitations, and none are widely available.

Jing Song developed Reaction Mechanism Generator (RMG), an automatic reaction model generation program that combines a rate-based iterative model generation algorithm [35] with the integrated pressure-dependence algorithm developed by Matheu et al [36]. The algorithm is described in detail in reference 37 and is briefly summarized here. At the beginning of the model generation process, only reactants specified in the input file are included in the model. RMG generates all possible reactions of these species using rate rules stored in a database. The set of ordinary differential equations describing the system is integrated using DASPK 3.0 [38], and formation rates of all reaction products not already included in the model are calculated. Each reaction of the form A + B → C, B → C, and B → C + D is considered to initiate a partial pressure-dependent network. These networks are explored by adding one activated isomer at a time. RMG constructs net pressure-dependent reactions from these networks and estimates their rate constants k(T,P). For each partial pressure-dependent network, a leakage flux is calculated, which represents the flux to all unexplored parts of the network. At each time step, all leakage fluxes and fluxes to possible product species are compared to the minimum formation rate, R_{min}, expressed as

$$R_{\min}(t) = \varepsilon \cdot R_{char}(t),$$

where ε is a user-specified tolerance and the characteristic rate R_{char} is the L-2 norm of the reacted species flux vector, $R_{char}(t) = \sqrt{\sum_i R_i^2(t)}$. $R_i(t)$ is the rate of change in the concentration of each species already included in the mechanism. RMG identifies the maximum flux from the formation rates of species not included in the model and fluxes to pressure-dependent networks. If the maximum flux belongs to a chemical species, RMG adds that species to the mechanism with all reactions producing it and generates all possible reactions of that species with other species in the model. If the maximum flux is to a partial pressure-dependent network, one more activated isomer is added to the network with all its reaction pathways, and rate constants k(T,P) are calculated for all reactions in the network. If all fluxes are less than R_{min}, RMG proceeds to the next time step. Otherwise, the system of ODEs is changed, and the integration starts again at t = 0. The mechanism is complete when all fluxes are less than R_{min} at all time points.

To estimate pressure-dependent rate constants, a microcanonical rate constant k(E) is evaluated for each channel, and the rate of collisional energy transfer from the activated species to the bath gas molecules is estimated. Methods for estimating k(E) include Rice-Ramsperger-Kassel-Marcus (RRKM) [39-41], inverse Laplace transform (ILT) [42,43] and Quantum-Rice-Ramsperger-Kassel (QRRK) approximations [44,45]. RRKM requires knowledge of the transition state frequencies and geometries. Since this information is not available in an automatic reaction model generation program, RMG uses CHEMDIS [46], which employs the QRRK approximation to predict k(E) and a modified strong collision approximation to estimate energy transfer properties. CHEMDIS first partitions the isomer's energy distribution above the zero-point into bins of width ΔE and calculates the microcanonical rate constant from isomer i to product channel or isomer j from:

$$k_{ij}(E,\Delta E)=\frac{\left(A_{ij}^{\infty}T^{n_{ij}^{\infty}}\right)\rho\left(E-E_{a,ij}^{\infty}\right)}{\rho(E)} \tag{2.6}$$

where E is the energy above the zero point of the molecule, ρ is the density of states estimated from the heat capacities, and A^{∞}, n^{∞}, and E_a^{∞} are high-pressure-limit Arrhenius parameters. To estimate the density of states, RMG uses THERFIT [47] to derive a reduced set of vibrational frequencies and degeneracies from heat capacity data.

The preferred method for treating collisional energy transfer is the master equation approach. This approach assumes a probability distribution for energy transfer between the activated species and the bath gas molecules and models the system using a set of coupled differential equations. This approach is too time-consuming to use in an automatic reaction mechanism generation code. CHEMDIS uses the modified strong collision approximation (MSC) of Troe [48,49] to estimate the energy transfer properties. This method assumes that populations of all activated species are at steady state and that the rate of collisional stabilization is equal to $\beta_C k_S[M]$, where [M] is the concentration of the bath gas, and k_S is the Lennard-Jones collision rate. β_C is a fraction less than 1 and can be estimated by:

$$\beta_C = \frac{1}{\Delta}\left(\frac{\langle \Delta E \rangle_{down}}{\langle \Delta E \rangle_{down} + F_E k_B T}\right)^2 \tag{2.7}$$

where $\langle \Delta E \rangle_{down}$ is the average downward collisional energy transferred from the activated species to the bath gas, F_E is an integral involving the density of states of the isomer, and Δ is a function of the density of states of the isomer and temperature. This suggests that some fraction of collisions with the bath gas molecule will stabilize. After combining the k(E) estimates with the MSC approximation, CHEMDIS constructs the mass balance for each species i in the energy bin E_n. For the chemical activation case, the mass balance is:

$$\begin{aligned} \frac{d[C_i(E_n)]}{dt} &= k_{inp}^{\infty}[R][R']f(E_n,T)\delta_{i,e} + \left\{\sum_j \left(IS^T\right)_{i,j}[C_j(E_n)]\right\} \\ &- [C_i(E_n)]\left\{\sum_j (IS)_{i,j} + \sum_m (PD)_{i,m} + k_i^s(T)[M]\right\} \end{aligned} \tag{2.8}$$

where $[C_i(E_n)]$ is the concentration of isomer i in energy bin E_n. The first term on the right-hand side represents the flux into the bin from collisions of R and R', the entrance adducts. This term is only active for the first adduct of the entrance channel. k_{inp}^{∞} is the high-pressure-limit rate constant for the entry reaction, and $f(E_n,T)$ is a distribution function that comes from a detailed balance involving k(E) for the dissociation of the first adduct back to the entrant species. The second right-hand term represents isomerizations from other wells to well i. The last term represents fluxes out of isomer i in bin E_n, which includes fluxes to other isomers and product channels and collisional stabilization. The steady-state assumption is applied to Equation 2.8, and a vector-matrix equation is solved to get estimates for k(T,P).

RMG stores thermodynamic parameters and high-pressure-limit rate parameters in a hierarchical database based on functional groups. Thermodynamic parameters for specific molecules are included in a primary thermodynamic library, and thermodynamic properties for all other molecules are estimated using group additivity. RMG's kinetics database is divided into 34 reaction families. Small molecule oxidation reactions that cannot be described by reaction families are included in a primary reaction library.

2.4 Neopentyl + O_2

Reactions of alkyl radicals with oxygen are thought to be important for understanding preignition chemistry and for predicting negative temperature coefficient (NTC) behavior. Alkyl radicals react with molecular oxygen to form an alkyl peroxy radical, RO_2, that can form a hydroperoxy alkyl radical, QOOH, via intra-molecular hydrogen abstraction. The QOOH radical can decompose to OH and a cyclic ether or undergo a second O_2 addition that leads to chain branching. The reaction of the neopentyl radical with O_2 is particularly interesting because the formation of a conjugate alkene + HO_2 is impossible, allowing the isomerization of RO_2 to QOOH to be highlighted. Since all hydrogen atoms of the neopentane molecule are equivalent, this reaction is simpler than other hydrocarbon oxidation reactions.

The oxidation of neopentane has been investigated by several groups. Slow-flow reactor experiments were performed by Walker and coworkers, who analyzed the reaction products and proposed a mechanism to explain their results [69-71]. Hughes et al. measured OH production following pulsed photolysis of neopentyl iodide in the presence of oxygen and derived a rate constant for the isomerization of the neopentyl peroxy radical [72-73]. Curran et al. developed a detailed mechanism for the oxidation of neopentane and compared it to available experimental results [74]. The mechanism was later modified based on data from high-pressure flow reactor experiments [75]. DeSain et al. measured OH and HO_2 production in Cl-initiated neopentane oxidation and proposed a simple model based on analogous time-dependent master equation calculations for the reaction of *n*-propyl with O_2 [76]. They concluded that direct pathways for chemical activation reactions, such as direct production of OH from R + O_2, are necessary to correctly model oxidation systems. Sun and Bozzelli used ab initio and density functional methods to calculate thermochemical and kinetic properties for important species in the oxidation of the neopentyl radical [77].

The previous studies have attempted to determine rate constants for such reactions as

$R+O_2 \rightarrow OH+3,3\text{-dimethyloxetane},$ (2.9)

$R+O_2 \rightarrow QOOH,$ (2.10)

and

$R+O_2 \rightarrow RO_2.$ (2.11)

However, due to the complexity of the chemistry, it was difficult for these researchers to firmly determine any of these rate constants. Here we analyze the prior experimental data as well as some new measurements combined with the best available quantum chemistry to firmly determine two rate constants of interest.

3. Sensitivity Analysis in RMG

An option to automatically perform first-order sensitivity analysis was implemented in RMG using DASPK 3.0, which can calculate first-order sensitivity coefficients using staggered direct, simultaneous corrector, and staggered corrector methods. When the sensitivity analysis option is turned on, RMG calculates sensitivities of user-selected species to rate constants, heats of formation of all species, and initial concentrations of all reactants.

An algorithm for computing sensitivities to high-pressure-limit pre-exponential factors and activation energies of the pressure-dependent path reactions and to enthalpies and entropies of formation for isomers in the pressure-dependent network was added to RMG. Because RMG does not have an analytical expression for the pressure-dependent rate constants as a function of the high-pressure-limit rate parameters in the network, sensitivities to these parameters are estimated from the sensitivity of the model output to the pressure-dependent rate constants and the sensitivities of those pressure-dependent rate constants to the high-pressure-limit rate parameters. The equations used to calculate the sensitivity of species i to the pre-exponential factor and activation energy of the pressure-dependent path reaction j are shown in Equations 3.1 and 3.2:

$$\frac{\partial \ln C_i}{\partial \ln A_j^{\infty}} = \sum_{\substack{p\text{-}dep \\ net\ rxns\ l}} \frac{\partial \ln C_i}{\partial \ln k_l} \frac{\partial \ln k_l}{\partial \ln A_j^{\infty}} \tag{3.1}$$

$$\frac{\partial \ln C_i}{\partial E_{a,j}^{\infty}} = \sum_{\substack{p\text{-}dep \\ net\ rxns\ l}} \frac{\partial \ln C_i}{\partial \ln k_l} \frac{\partial \ln k_l}{\partial E_{a,j}^{\infty}}. \tag{3.2}$$

Sensitivities to pre-exponential factors are normalized sensitivities, and sensitivities to activation energies are semi-normalized. Sensitivities to the net pressure-dependent rate constants $\left(\frac{\partial \ln C_i}{\partial \ln k_l}\right)$ are calculated by DASPK 3.0 using a staggered direct method holding constant all other rate constants and thermochemistry. It is not possible to calculate the sensitivities of the pressure-dependent rate constants to the high-pressure-limit parameters $\left(\frac{\partial \ln k_l}{\partial \ln A_j^{\infty}} \text{ and } \frac{\partial \ln k_l}{\partial E_{a,j}^{\infty}}\right)$ analytically, so these derivatives are estimated using finite differences. It would be possible to calculate the sensitivity coefficients

$\left(\frac{\partial \ln C_i}{\partial \ln A_j^{\infty}} \text{ and } \frac{\partial \ln C_i}{\partial E_{a,j}^{\infty}}\right)$ directly using finite differences, but that would involve re-running the pressure-dependent code and solving the kinetic equations for each parameter. The method employed here requires the pressure-dependent calculation for each parameter but not the solution of the kinetic equations.

Sensitivities of the output concentrations to enthalpies and entropies of formation for isomers in a pressure-dependent network are more complicated because the non-pressure-dependent reverse rate constants also depend on these parameters. The method described here is for a system with externally controlled temperature and pressure. The equations for computing the sensitivity of species i to the enthalpy and entropy of isomer A at the temperature of interest are shown in Equations 3.3 and 3.4:

$$\begin{aligned}\left.\frac{\partial \ln C_i}{\partial \Delta H_f(A)}\right|_{\substack{\text{all } kf,\\ \text{all } S,\\ H(\text{all } B\neq A)}} &= \sum_{\substack{\text{non-p-dep}\\ \text{reverse rxns } m}} \left(\frac{\partial \ln C_i}{\partial \ln k_{m,r}}\right)_{\substack{\text{all } kf,\\ \text{all } kr(j\neq m)}} \left(\frac{\partial \ln k_{m,r}}{\partial \Delta H_f(A)}\right)_{\substack{\text{all } kf,\\ \text{all } S,\\ H(\text{all } B\neq A)}} \\ &+ \sum_{\substack{\text{p-dep}\\ \text{net rxns } l}} \left(\frac{\partial \ln C_i}{\partial \ln k_l}\right)_{\substack{\text{all } k(j\neq l),\\ \text{all } H,S}} \left(\frac{\partial \ln k_l}{\partial \Delta H_f(A)}\right)_{\substack{\text{all } kf,\\ \text{all } S,\\ H(\text{all } B\neq A)}}\end{aligned} \tag{3.3}$$

$$\begin{aligned}\left.\frac{\partial \ln C_i}{\partial S(A)}\right|_{\substack{\text{all } kf,\\ \text{all } H,\\ S(\text{all } B\neq A)}} &= \sum_{\substack{\text{non-p-dep}\\ \text{reverse rxns } m}} \left(\frac{\partial \ln C_i}{\partial \ln k_{m,r}}\right)_{\substack{\text{all } kf,\\ \text{all } kr(j\neq m)}} \left(\frac{\partial \ln k_{m,r}}{\partial S(A)}\right)_{\substack{\text{all } kf,\\ \text{all } H,\\ S(\text{all } B\neq A)}} \\ &+ \sum_{\substack{\text{p-dep}\\ \text{net rxns } l}} \left(\frac{\partial \ln C_i}{\partial \ln k_l}\right)_{\substack{\text{all } k(j\neq l),\\ \text{all } H,S}} \left(\frac{\partial \ln k_l}{\partial S(A)}\right)_{\substack{\text{all } kf,\\ \text{all } H,\\ S(\text{all } B\neq A)}}.\end{aligned} \tag{3.4}$$

The second terms on the right-hand sides of Equations 3.3 and 3.4 are calculated using the same method as the sensitivities to high-pressure-limit activation energies. Sensitivities of species i to the pressure-dependent rate constants are calculated using DASPK holding constant all other forward rate constants and all thermochemistry, and sensitivities of the pressure-dependent rate constants to enthalpy and entropy are estimated using finite differences holding constant all forward rate constants and thermochemistry for all other species. The first terms on the right-hand sides of Equations 3.3 and 3.4 are the contributions from reverse rate constants. The sensitivities to reverse rate constants $\left(\frac{\partial \ln C_i}{\partial \ln k_{m,r}}\right)$ are calculated using DASPK holding constant all forward rate constants and reverse rate constants for all reactions except reaction m. To calculate the $\frac{\partial \ln k_{m,r}}{\partial \Delta H_f(A)}$ and $\frac{\partial \ln k_{m,r}}{\partial S(A)}$ terms, the reverse rate constant is written as $k_r = k_f/K_{eq}$, and K_{eq} is expressed as:

$$K_{eq} = e^{-\Delta G/RT}(RT)^{-\Delta n} = e^{-\Delta H_{rxn}/RT} e^{\Delta S_{rxn}/R}(RT)^{-\Delta n}, \tag{3.5}$$

so the reverse rate constant can be written as:

$$\ln k_r = \ln k_f - \ln K_{eq} = \ln k_f + \frac{\Delta H_{rxn}}{RT} - \frac{\Delta S_{rxn}}{R} + \Delta n \ln\left(\frac{RT}{1\,atm}\right). \tag{3.6}$$

The $\frac{\partial \ln k_{m,r}}{\partial \Delta H_f(A)}$ and $\frac{\partial \ln k_{m,r}}{\partial S(A)}$ terms are:

$$\frac{\partial \ln k_{m,r}}{\partial \Delta H_f(A)} = \begin{cases} 1/RT, & A\ is\ prod\ in\ rxn\ m \\ -1/RT, & A\ is\ react\ in\ rxn\ m \\ 0, & no\ A\ in\ rxn\ m \end{cases} \tag{3.7}$$

$$\frac{\partial \ln k_{m,r}}{\partial S(A)} = \begin{cases} -1/R, & A\ is\ prod\ in\ rxn\ m \\ 1/R, & A\ is\ react\ in\ rxn\ m \\ 0, & no\ A\ in\ rxn\ m \end{cases}. \tag{3.8}$$

Sensitivities to heat capacity data have not been considered in this work. The heat capacities affect the densities of states used to estimate the microcanonical rate constants as well as $H_f(T)$ and $S(T)$.

4. Error Propagation in RMG

An algorithm to generate approximate error bars on model predictions was implemented in RMG. Before uncertainties in the output concentrations could be calculated, it was necessary to estimate uncertainties in rate constants and thermodynamic parameters in the RMG database. The RMG kinetics database, constructed by J. Song, S. Raman, and C. D. Wijaya, contains rate rules from literature sources [50-63] and unpublished quantum calculations. C. D. Wijaya assigned a rank to each rate rule to describe the quality of the kinetic parameters [64]. Uncertainties in rate rules in the RMG database were taken from literature sources when available. Uncertainties not available in the literature were estimated from other rate rules in the database with the same rank. J. Yu built the thermal group library that contains thermodynamic data from Benson [65], Stein and Fahr [66], and Sumathi and Green [67, 68]. Since these literature sources do not include uncertainty contributions from individual functional groups, those uncertainties had to be estimated. When sufficient experimental data were available, uncertainties in thermodynamic parameters were determined using linear regression. Uncertainties in thermodynamic data for functional groups for which no experimental data were available were estimated from uncertainties in similar functional groups.

A function for calculating upper and lower bounds on model predictions using first-order sensitivity coefficients was implemented in RMG. To avoid negative lower bound concentrations, the algorithm uses Equation 2.5 to calculate these error bounds. Error bounds on the rate constants are determined from uncertainties in RMG's kinetics database. To calculate upper bounds on model predictions, the $\Delta\alpha_j$ terms in Equation 2.5 are taken as the difference in the rate constant's upper bound and nominal value for reactions with a positive sensitivity coefficient and the difference in the lower bound and nominal value for reactions with a negative sensitivity. Lower bounds on model output are calculated using the difference in the upper bound and nominal rate constant for negative sensitivities and the difference in the lower bound and nominal rate constant for positive sensitivities. The contribution of each reaction to the total uncertainty in a species' output concentration is estimated by multiplying the sensitivity coefficient by the uncertainty in the rate constant. RMG's output file includes the five reactions that contribute most to the uncertainty in each species. This approximate method was chosen because global methods for uncertainty propagation are too computationally expensive to be practical for the large models generated by RMG, and most require detailed information about the probability distributions of the uncertain parameters, which is not available in the RMG database.

5. RMG model for neopentyl + O_2

In this work, a mechanism for the oxidation of the neopentyl radical is generated automatically using RMG, and model predictions are compared to experimental results for OH production following pulsed photolysis of neopentyl iodide in the presence of O_2. Constraints on the rate constants for

$$C_5H_{11} + O_2 \rightarrow OH + \text{3,3-dimethyloxetane} \tag{5.1}$$

and

$$C_5H_{11}I + OH \rightarrow C_5H_{10}I + H_2O \tag{5.2}$$

are determined based on comparison of the model with experimental results.

Experiments were performed by Huzeifa Ismail, Edgar G. Estupiñán, Leonard E. Jusinski, and Craig A. Taatjes at Sandia National Laboratories. They measured time-dependent production of OH following pulsed photolysis of neopentyl iodide in the presence of O_2. Experiments were performed at three temperatures (673, 700 and 725 K), two pressures (30 and 60 Torr), and two initial neopentyl iodide concentrations ([RI] $= 9\times10^{14}$ and 3×10^{15} molecules/cm^3). Oxygen concentrations varied from 6×10^{16} to 6×10^{17} molecules/cm^3 with the balance composed of helium.

A model was generated at these initial conditions using RMG. High-pressure-limit rate constants and thermodynamic parameters from Sun and Bozzelli [9] were added to the RMG database. Using a tolerance of $\varepsilon = 0.001$, RMG generated a model with 57 species and 881 reactions. Predicted and experimental OH concentration profiles are shown in Figure 5.1. RMG predictions show good qualitative agreement with experimental measurements, but the peak OH concentrations are overpredicted, and the modeled OH decay is more rapid than that observed experimentally.

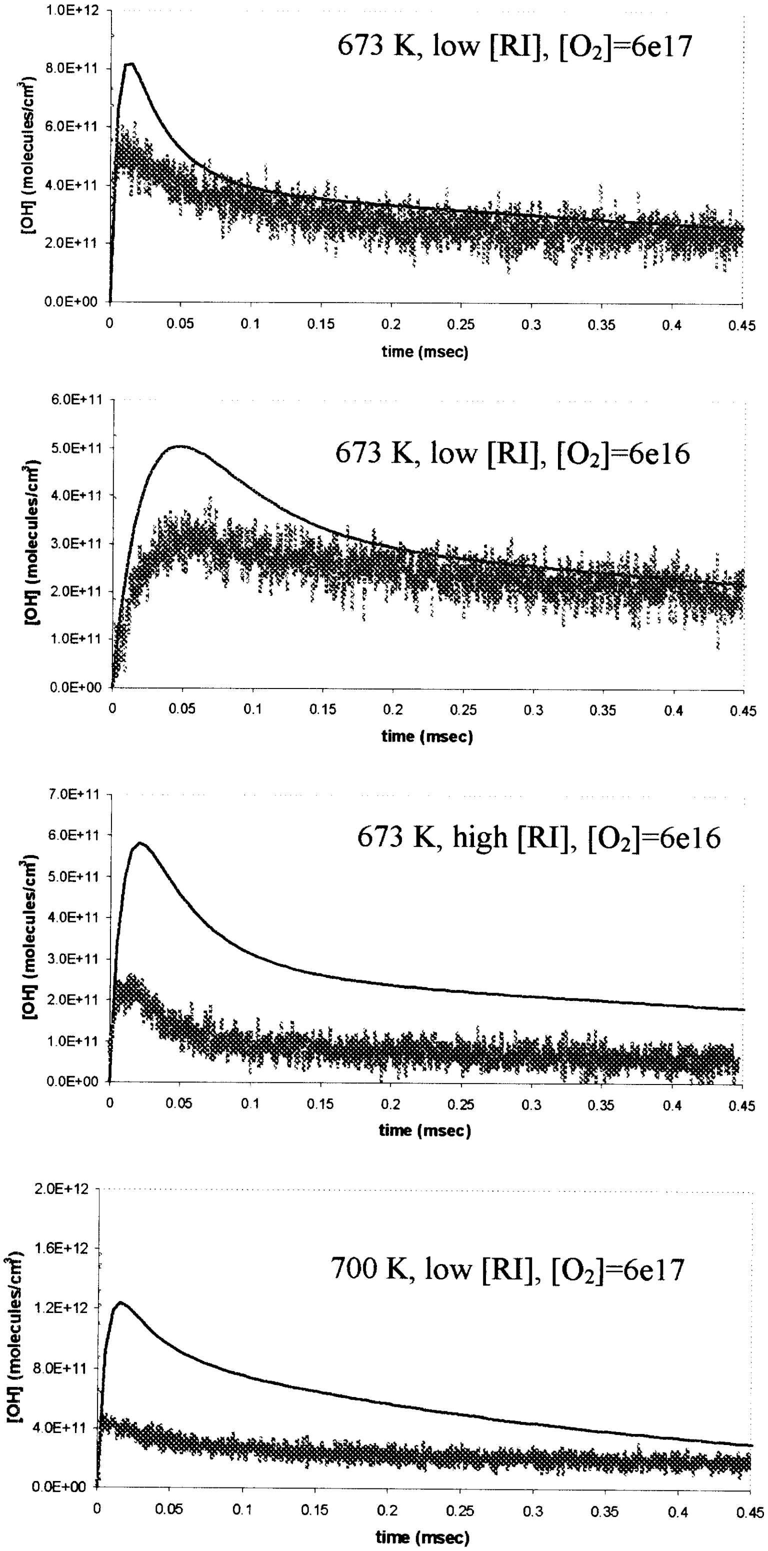

Figure 5.1 Experimental and predicted OH concentration profiles using unadjusted model parameters.

Normalized first-order sensitivity coefficients were automatically calculated by RMG. These sensitivity coefficients are shown in Figure 5.2. In the initial time following photolysis, the OH concentration is sensitive only to the direct reaction of the neopentyl radical with oxygen producing OH and 3,3-dimethyloxetane. At later times, OH is most sensitive to Reaction 5.2. As the neopentyl radical is consumed, production of OH from

$$RO_2 \rightarrow OH + \text{3,3-dimethyloxetane} \tag{5.3}$$

and

$$QOOH \rightarrow OH + \text{3,3-dimethyloxetane} \tag{5.4}$$

also becomes important. The sensitivity of OH to

$$R + O_2 \rightarrow RO_2 \tag{5.5}$$

is negative at early times because this reaction competes with the direct reaction producing OH and 3,3-dimethyloxetane. This sensitivity becomes positive at later times because production of OH from the RO_2 and QOOH radicals becomes more important than the direct reaction. The conventional sensitivity analysis employed at this stage does not consider that increasing the high-pressure-limit rate constant for Reaction 5.5 also increases the chemically-activated rate constant for Reaction 5.1.

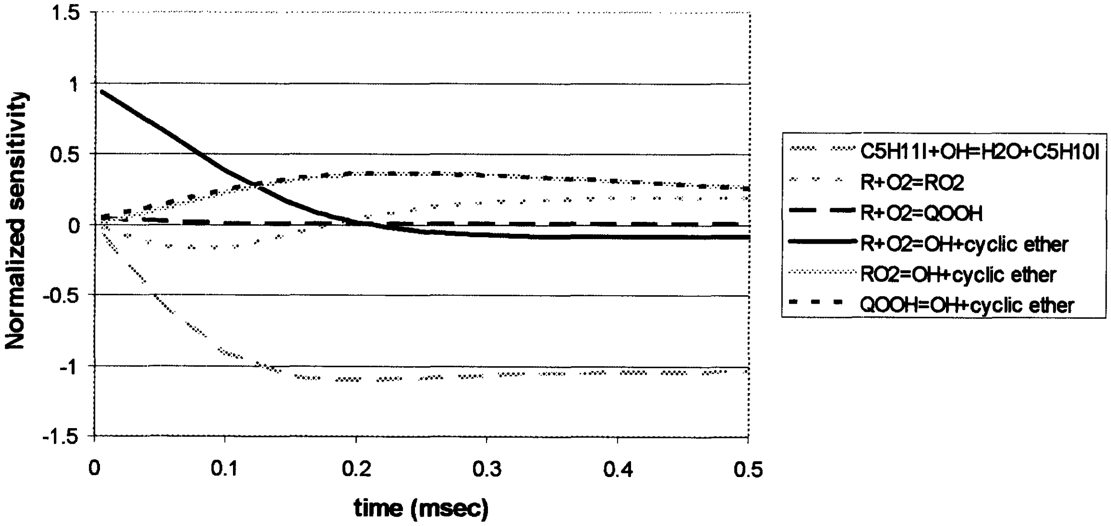

Figure 5.2 Normalized sensitivities of OH for unadjusted model

The decay of OH is most sensitive to the reaction of OH with neopentyl iodide (Reaction 5.2). RMG's prediction for this rate constant is $2.37\times10^{7}T^{1.8}e^{-0.278\,(\mathrm{kcal/mol})/RT}$

cm^3/mol-s based on a transition state theory calculation by Cohen [78] for the reaction of OH with neopentane. Cohen's pre-exponential factor of 3.16×10^7 cm^3/mol-s is multiplied by 9/12 to correct for the number of reaction sites. A recent literature review by Atkinson [79] suggests a rate rule of $1.12\times10^7T^{2.00}e^{-0.41\ (kcal/mol)/RT}$ cm^3/mol-s for OH + neopentane, which is slightly higher than Cohen's rate constant. Both rate rules agree reasonably well with those given in the literature reviews by Baulch et al. [80] and Walker et al. [81] ($4.79\times10^6T^{2.08}e^{-0.14\ (kcal/mol)/RT}$ and $1.41\times10^{10}T^{1.00}e^{-1.29\ (kcal/mol)/RT}$ cm^3/mol-s, respectively). To improve the predicted OH fall and steady-state concentration, RMG's rate rule was reduced by a factor of 1.5. This rate gives better agreement with Tully et al. [82], who measured the rate constant for OH + neopentane using flash photolysis. They report a rate rule of $6.58\times10^3T^{3.02}e^{-0.70\ (kcal/mol)/RT}$ cm^3/mol-s, which is lower than the value calculated by Cohen by approximately a factor of 2.

Reducing the rate constant for Reaction 5.1 is necessary to correctly predict the peak OH concentration. The sensitivity of this reaction to high-pressure-limit rate constants and thermodynamic parameters for isomers in the pressure-dependent network was examined since the direct rate constant depends on these parameters. Sensitivities to pre-exponential factors were calculated by multiplying the pre-exponential factor of the high-pressure-limit forward reactions by 2 while holding thermochemical quantities fixed and calculating the change in the pressure-dependent rate constant. Since reverse rate constants are calculated from the forward rate constants and thermodynamic properties, doubling the forward rate constant causes the reverse rate constant to double as well. Sensitivities to activation energies and heats of formation were calculated by increasing the energy by 1 kcal/mol, and sensitivities to entropy were calculated by increasing S by 1 cal/mol-K.

Increasing the pre-exponential factor for Reaction 5.5 by a factor of two causes an 80% increase in the rate constant for Reaction 5.1. Doubling the pre-exponential factors for the isomerization of RO_2 to QOOH and for the decomposition of QOOH to OH + 3,3-dimethyloxetane causes the direct rate constant to increase by approximately 40 and 30%, respectively. Increasing the activation energies for these reactions by 1 kcal/mol causes the direct rate to decrease by 20 and 25%. Reaction 5.1 is more sensitive to the activation energy for the QOOH decomposition than to the activation energy for the isomerization reaction because the energy of the transition state for Reaction 5.4 is much closer to the energy of the entrance channel. The sensitivity of Reaction 5.1 to the heat of formation of the RO_2 radical and to the entropies of RO_2 and QOOH is low. Its sensitivity to the heat of formation for QOOH is similar to its sensitivity to the activation energy for Reaction 5.4. This suggests that the direct reaction is sensitive to the energy of the transition state for Reaction 5.4 relative to the energy of the entrance channel.

The sensitivity of [OH] to the high-pressure-limit rate constants and thermodynamic parameters in the pressure-dependent network was also examined since these parameters also affect other reactions producing OH. These sensitivities are shown in Figure 5.3.

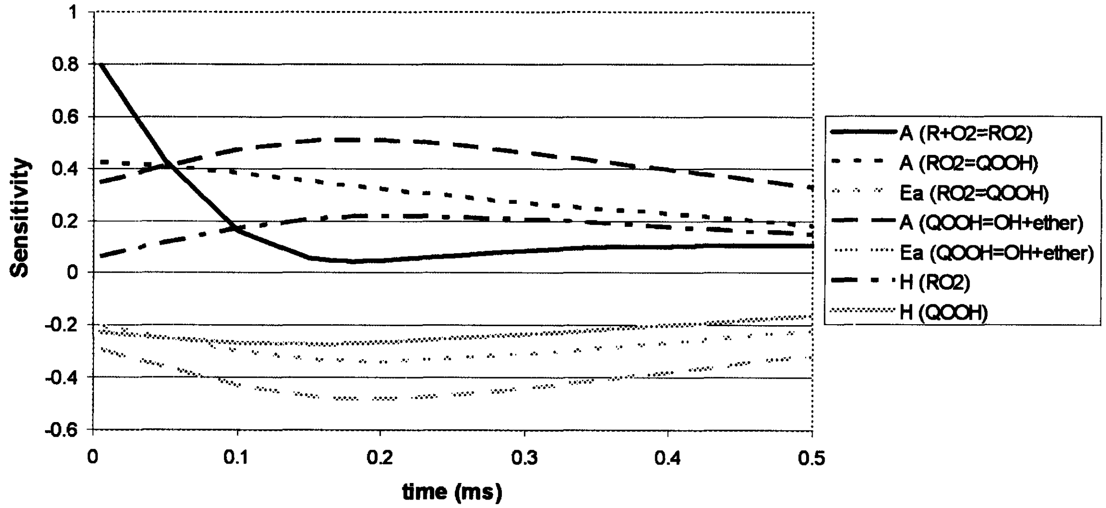

Figure 5.3 Sensitivity of OH concentration to thermodynamic and high-pressure-limit rate parameters in the pressure-dependent network for unadjusted model. Sensitivities to pre-exponential factors are normalized sensitivities ($\Delta\ln[OH]/\Delta\ln A$). Sensitivities to activation energies and heats of formation are semi-normalized ($\Delta\ln[OH]/\Delta Ea$ or $\Delta\ln[OH]/\Delta(\Delta H_f)$) and have units of mol/kcal.

Sensitivities were calculated by changing the pre-exponential factor by a factor of 2 or changing the activation energy or heat of formation by 1 kcal/mol and observing the change in the predicted OH concentration. Initially, OH is most sensitive to the pre-exponential factor for Reaction 5.5. This sensitivity decreases quickly and is lower than the sensitivities to other parameters after about 0.1 ms. The pre-exponential factors and activation energies for the RO_2 isomerization and QOOH decomposition reactions are also important at early times.

Rate and thermodynamic parameters in the pressure-dependent network were varied within their estimated uncertainties to find the combination of parameters that best matches experimental data. The best overall agreement between model and experiment was obtained by increasing the activation energy of the QOOH decomposition by 0.8 kcal/mol and increasing the activation energy of the RO_2 isomerization by 1.2 kcal/mol because the model is sensitive to these parameters in the region where the unadjusted model disagrees with experimental data. A comparison of several observed OH profiles with the adjusted model is shown in Figure 5.4. Model predictions show excellent agreement with experimental results at 673 K. The absolute OH concentration is over-predicted at higher temperatures, but the qualitative agreement is very good. Predicted concentration profiles for other major species are shown in Figure 5.5. Most of the neopentyl radical reacts with oxygen to produce RO_2, but smaller fractions go directly to QOOH and to OH + 3,3-dimethyloxetane. Most of the QOOH radical is produced directly from noepentyl + O_2. After the neopentyl radical is consumed, some QOOH is produced from the isomerization of the neopentylperoxy radical. The most significant reaction consuming the QOOH radical is the reverse isomerization. A smaller fraction of QOOH is consumed in Reaction 5.4. This model gives near perfect agreement with experimental results of Hughes et al [73]. A comparison of their data with the adjusted model is shown in Figure 5.6.

To estimate the uncertainty in the predicted OH concentrations, high-pressure-limit rate constants were changed to their upper or lower bounds based on the sign of the sensitivity of [OH] to that parameter, and the kinetic equations were solved. Uncertainties in the rate parameters from Sun and Bozzelli were estimated as a factor of 2 for pre-exponential factors and 2 kcal/mol for activation energies. The resulting error bounds on a predicted OH concentration profile are shown in Figure 5.7. The contribution of each rate constant to the total uncertainty in [OH] was estimated as the product of the sensitivity coefficient and uncertainty in the rate constant. Before 0.01 ms, virtually all of the uncertainty is from the direct reaction producing OH and 3,3-dimethyloxetane. At later times, over half of the uncertainty is from the reaction of neopentyl iodide with OH.

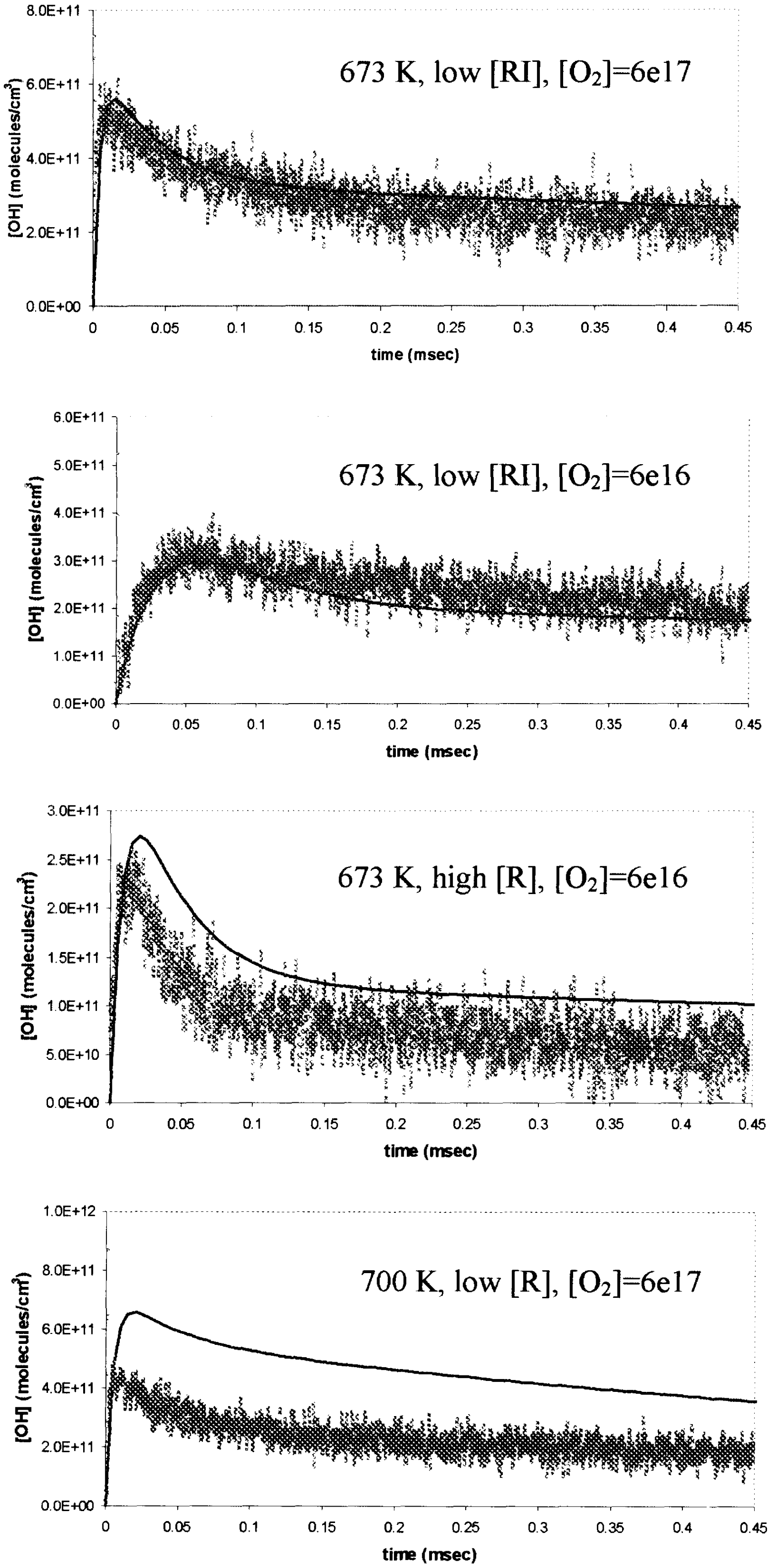

Figure 5.4 Predicted and experimental OH concentration profiles using the best model (adjusted activation energies and lower $k_{5.2}$)

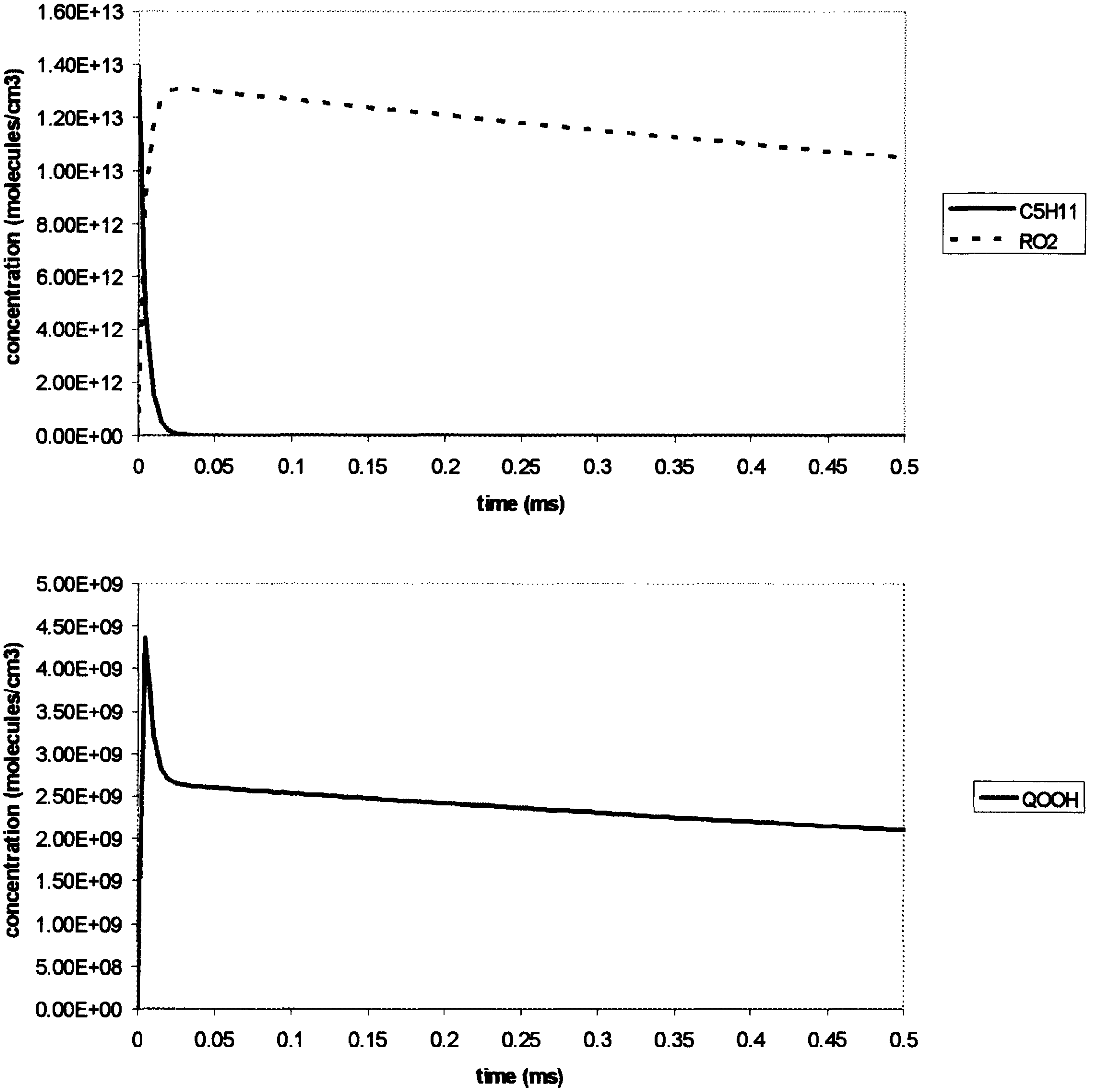

Figure 5.5 Predicted concentration profiles for C_5H_{11}, $C_5H_{11}O_2$ and QOOH. Initial conditions are 673 K, 60 Torr, $[O_2]_o = 6e17\ cm^{-3}$, $[RI]_o = 9e14\ cm^{-3}$, $[R]_o = [I]_o = 1.4e13\ cm^{-3}$.

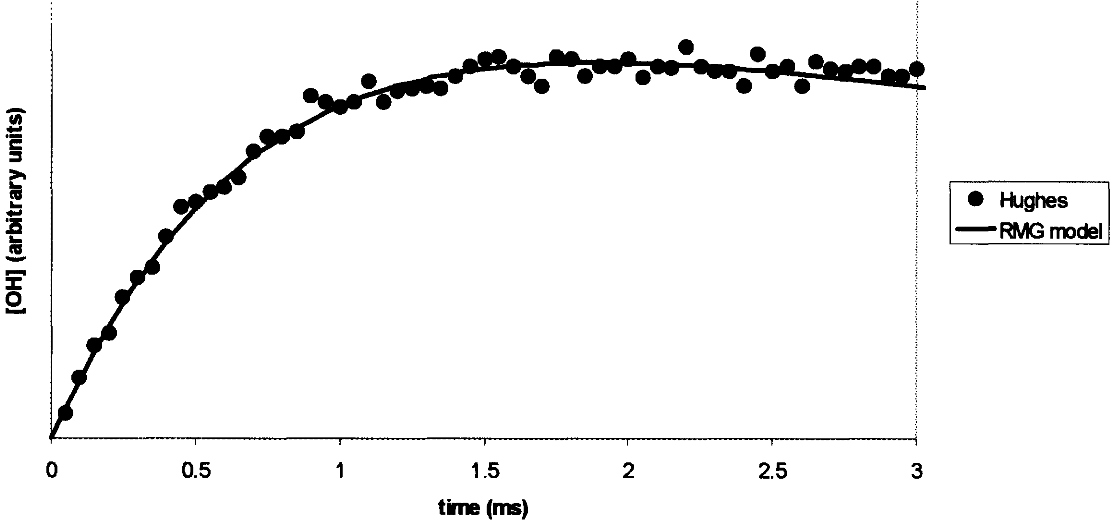

Figure 5.6 Comparison of RMG model with experimental results of Hughes et al.[73] Profiles are scaled to the same peak height since absolute concentrations were not measured.

Upper and lower bounds on the rate constant for Reaction 5.1 were determined using experimental data since OH production at early times is sensitive only to this reaction. These error bounds were found so that all experimental data points plus uncertainty contributions from all other rate constants were within the error bounds on the predicted OH concentration at times less than 0.01 ms. Figure 5.8 shows error bounds on the OH predictions using these experimentally determined bounds on the direct rate constant. This method gives conservative estimates for the limits on this rate constant because of scatter in the data. More realistic error bounds were determined from the standard deviation calculated from a least-squares fit of the data at early times. Upper and lower bounds on the rate constant for Reaction 5.1 represent two standard deviations above and below the best value determined from a least-squares fit. Table 5.1 shows the values for the direct rate constant calculated from a least-squares fit of the data at early times, and Table 5.2 shows the conservative uncertainty estimates compared with those determined from the least-squares fit.

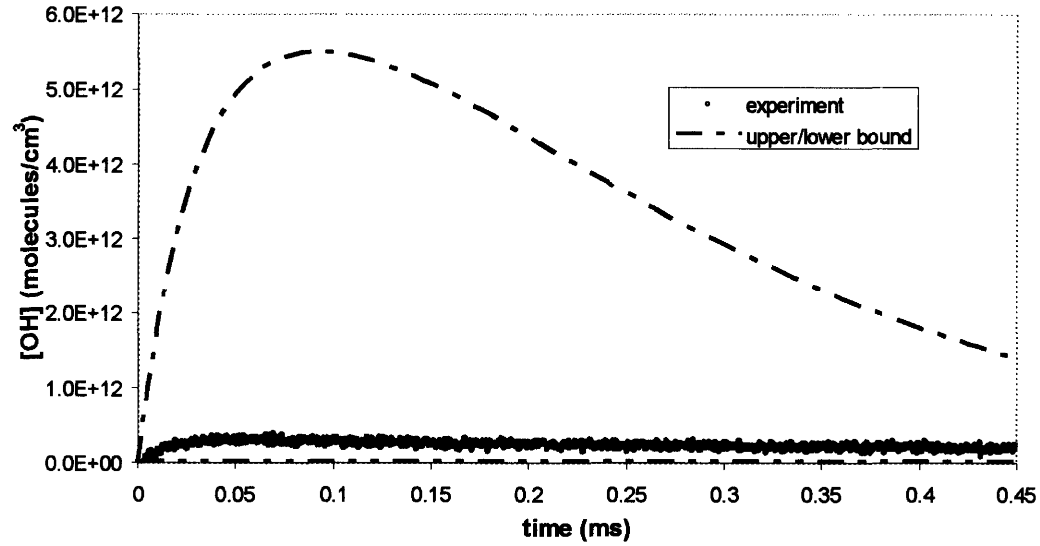

Figure 5.7 Uncertainty in predicted [OH] based on the large uncertainties in rate constants prior to this work. Uncertainties in high-pressure limit rate parameters from Sun and Bozzelli are estimated as a factor of 2 for A-factors and 2 kcal/mol for activation energies. Initial conditions are 673 K, 60 Torr, $[O_2]_o$ = 6e16 cm^{-3}, $[RI]_o$ = 9e14 cm^{-3}, $[R]_o$ = $[I]_o$ = 1.4e13 cm^{-3}.

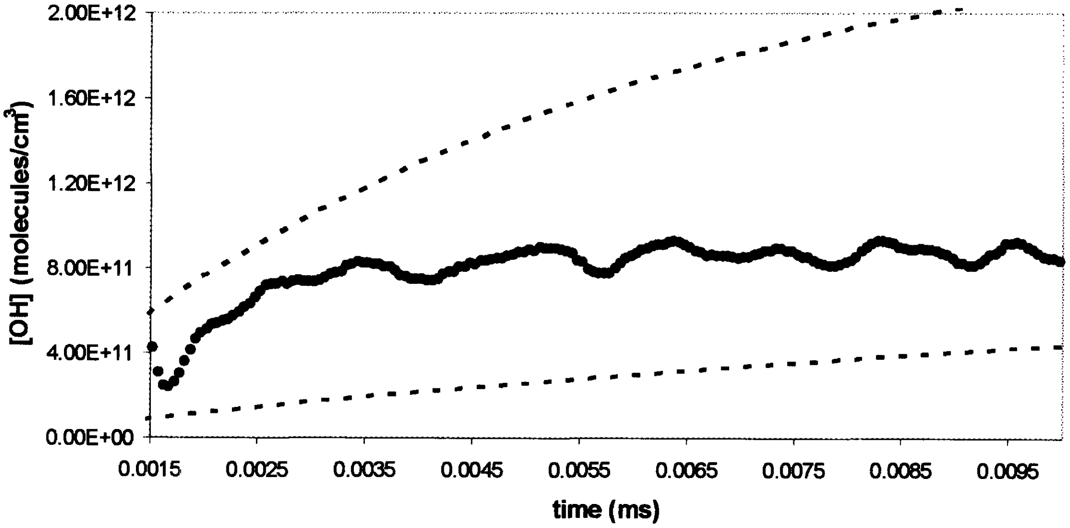

Figure 5.8 Error bounds on predicted [OH] at early times using experimentally determined error bounds on $k_{5.1}$. Upper and lower bounds on $k_{5.1}$ were calculated so that all experimental data points are within error bounds on predicted [OH]. The dotted lines are upper and lower bounds on OH predictions using the new experimentally determined error bounds on $k_{5.1}$, and circles are experimental data points.

Table 5.1 $k_{5.1}$ from least squares fit (cm^3/mol-s)

	60 Torr	30 Torr
673 K	1.15×10^{10}	1.29×10^{10}
700 K	1.37×10^{10}	1.73×10^{10}
725 K	1.91×10^{10}	2.17×10^{10}

Table 5.2 Upper and lower bounds on $k_{5.1}$ (cm^3/mol-s)

Temperature (K)	Pressure (Torr)	Upper bound (conservative)	Lower bound (conservative)	Upper bound (least squares)	Lower bound (least squares)
673K	60	2.48×10^{10}	3.83×10^{9}	1.50×10^{10}	7.95×10^{9}
700K	60	2.74×10^{10}	5.07×10^{9}	1.87×10^{10}	8.73×10^{9}
725K	60	3.33×10^{10}	7.31×10^{9}	3.30×10^{10}	9.80×10^{9}
673K	30	2.30×10^{10}	3.83×10^{9}	1.88×10^{10}	7.00×10^{9}
700K	30	3.38×10^{10}	6.04×10^{9}	2.73×10^{10}	7.43×10^{9}
725K	30	3.75×10^{10}	6.09×10^{9}	2.78×10^{10}	1.04×10^{10}

Error bounds on the rate constant for Reaction 5.2 were estimated since this reaction contributes most to the uncertainty in [OH] at late times. Upper and lower bounds on the rate constant were determined so that all data points and errors from all other rate constants were within the error bounds on the model predictions at times greater than 0.3 ms. These error bounds are still rather large because the model is also sensitive to other reactions in this region. The experimentally determined error bounds on the rate constant for Reaction 5.2 are shown in Table 5.3.

Table 5.3 Upper and lower bounds on $k_{5.2}$ (cm^3/mol-s)

Temperature (K)	Upper bound	Lower bound	Nominal $k_{5.2}$
673	2.76×10^{12}	9.21×10^{11}	2.37×10^{12}
700	4.27×10^{12}	1.42×10^{12}	2.57×10^{12}
725	5.98×10^{12}	1.99×10^{12}	2.75×10^{12}

Figure 5.9 shows the predicted uncertainty in an OH concentration profile using experimentally determined error bounds on Reactions 5.1 and 5.2 compared with the original error bounds calculated from RMG's estimated uncertainties in these rate constants. Using the new experimentally determined error bounds significantly reduces the uncertainty in the predicted OH concentration profile.

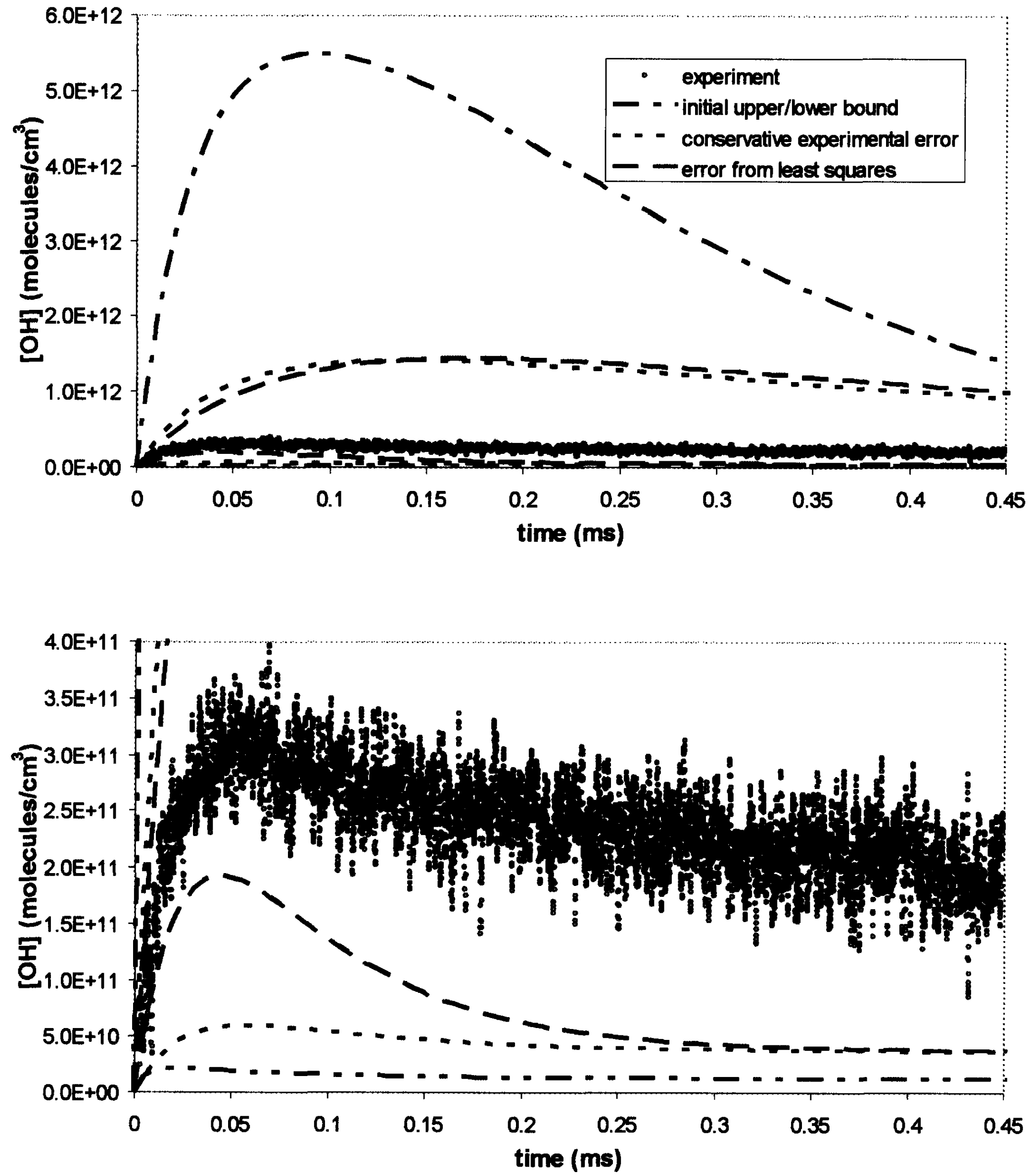

Figure 5.9 Error bounds on predicted [OH]. The largest error bounds are those calculated using only information available prior to these experiments. The two tighter error bounds use the new experimentally determined error bounds on $k_{5.1}$ and $k_{5.2}$. Initial conditions are 673 K, 60 Torr, $[O_2]_o = 6e16\ cm^{-3}$, $[RI]_o = 9e14\ cm^{-3}$, $[R]_o = [I]_o = 1.4e13\ cm^{-3}$.

OH production in chlorine-initiated neopentane oxidation was modeled using initial conditions described in the experimental investigation by DeSain et al [76]. Rate constants from DeSain et al. for important reactions involving chlorine were added to the RMG database. This model uses the adjusted activation energies determined from the neopentyl iodide experiments. Figure 5.10 shows a comparison of predicted and experimental OH profiles at several temperatures. The model agrees with experimental observations reasonably well. Error bounds on the predicted OH concentration are shown in Figure 5.11. These error bounds were calculated using the conservative experimentally determined error bounds on the rate constant for Reaction 5.1 and estimated uncertainties in the RMG database for all other rate constants.

Normalized sensitivities of OH for the most sensitive reactions in this system are shown as a function of time in Figure 5.12. Like in the neopentyl iodide system, [OH] in Cl-initiated neopentane oxidation is very sensitive to Reaction 5.1, but the sensitivity to this reaction remains high at later times. The concentration of OH in this system is also sensitive to

$$C_5H_{12} + Cl \rightarrow C_5H_{11} + HCl. \tag{5.6}$$

The sensitivity of [OH] to Reaction 5.5 is similar to its sensitivity in the neopentyl iodide system. The OH decay is most sensitive to

$$C_5H_{11}Cl + OH \rightarrow C_5H_{10}Cl + H_2O, \tag{5.7}$$

but OH is also consumed by

$$C_5H_{12} + OH \rightarrow C_5H_{11} + H_2O \tag{5.8}$$

and

$$C_5H_{11}O_2 + OH \rightarrow C_5H_{11}O + HO_2. \tag{5.9}$$

At later times, the OH concentration becomes sensitive to

$$C_5H_{11} + Cl_2 \rightarrow C_5H_{11}Cl + Cl, \tag{5.10}$$

which competes with Reaction 5.1. The concentration of OH is more sensitive to Reaction 5.7 than to Reaction 5.8 because as neopentane is consumed in Reaction 5.6, the concentration of neopentyl chloride produced in reaction 5.10 becomes higher than the concentration of neopentane.

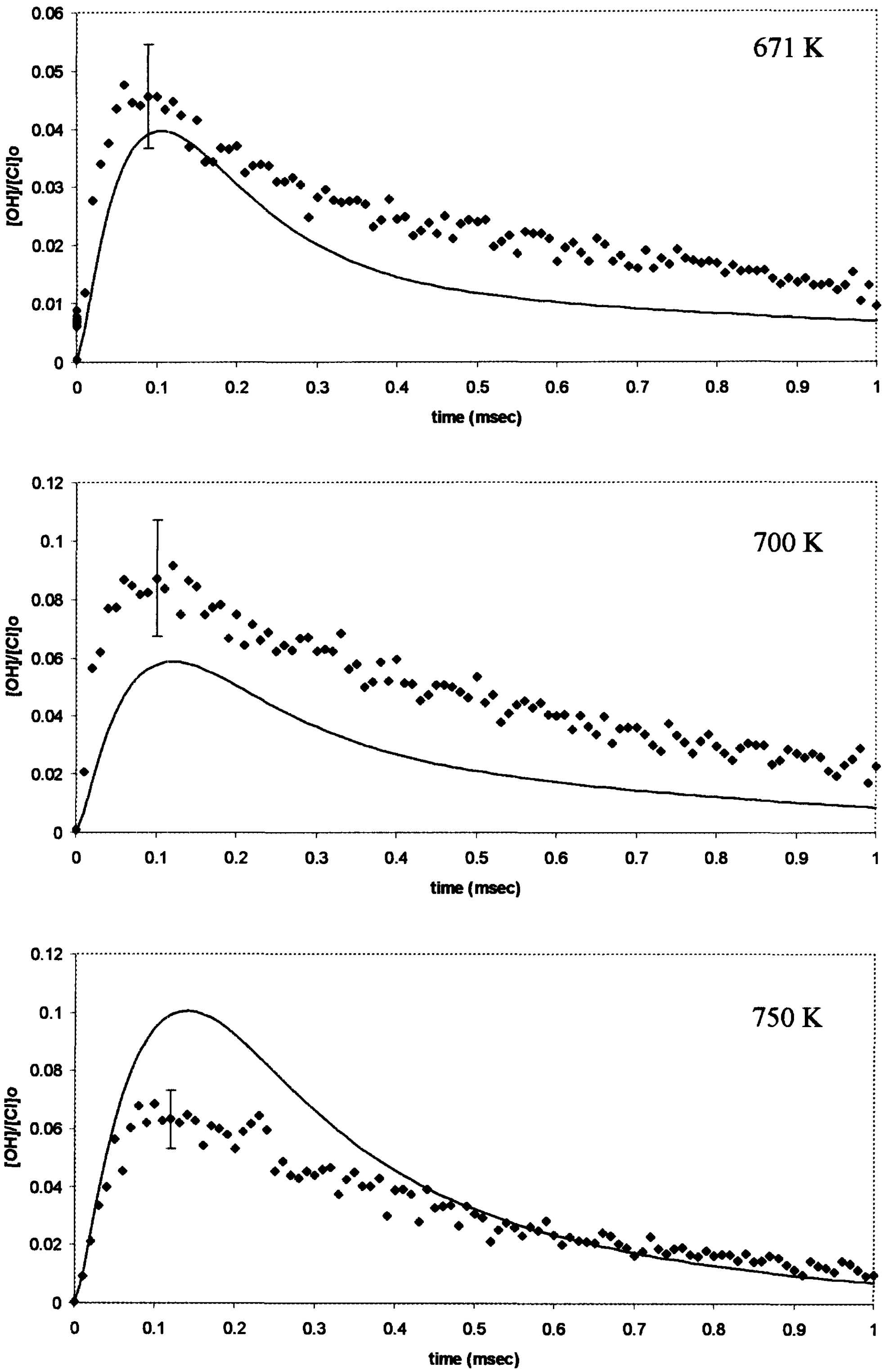

Figure 5.10 Predicted and experimental OH concentration profiles for Cl-initiated neopentane oxidation using adjusted parameter values from the RI experiments. Solid lines are model predictions, and symbols are experimental data. Representative experimental uncertainties in the observed peak OH concentration are shown.

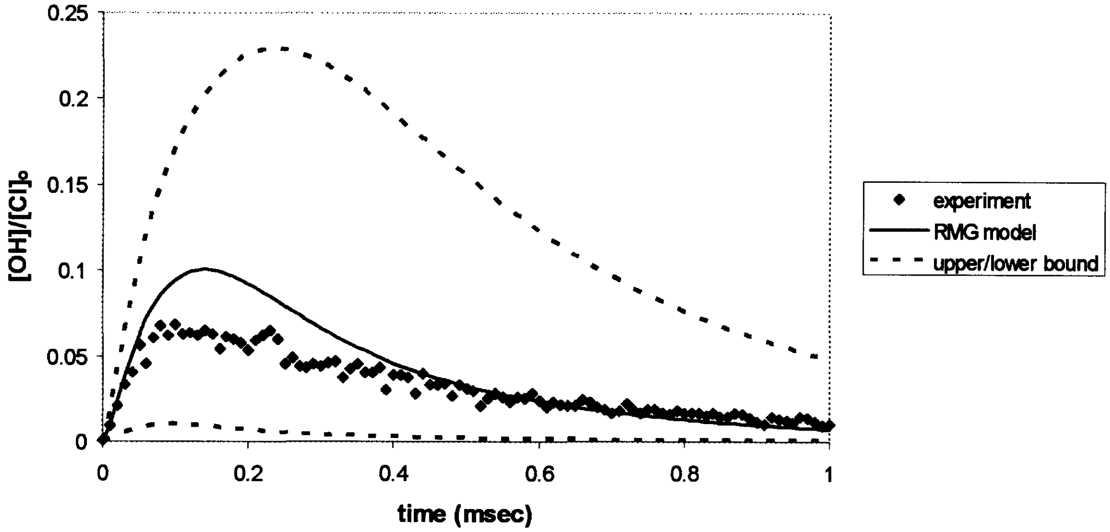

Figure 5.11 Upper and lower bounds on OH predictions for Cl-initiated neopentane oxidation at 750 K using experimentally determined uncertainty in $k_{5.1}$ (conservative error bounds).

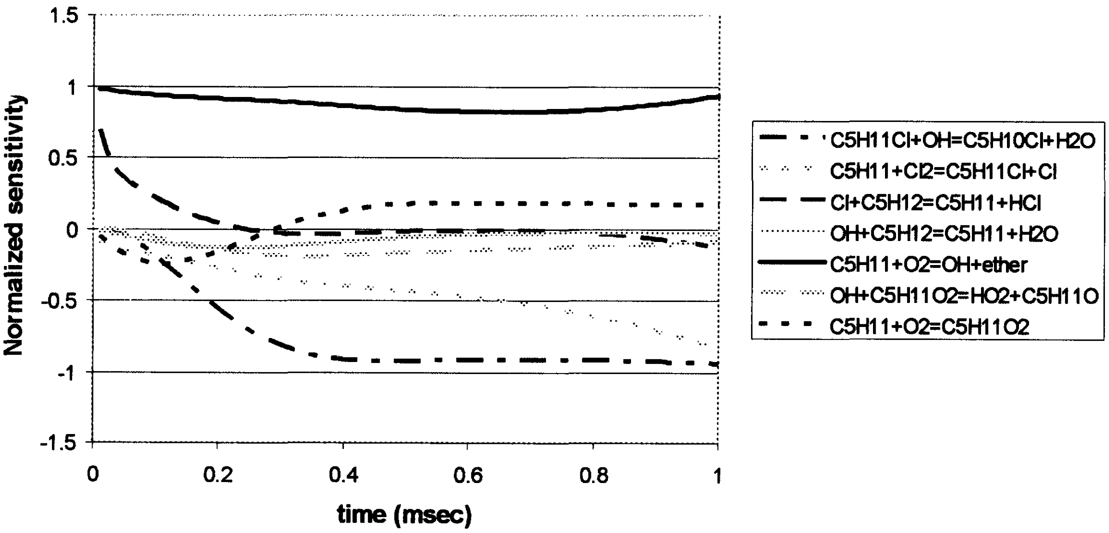

Figure 5.12 Normalized sensitivities of OH in Cl-initiated neopentane oxidation at 750 K using adjusted parameters from RI experiments.

Using a QRRK/MSC approach to estimate the pressure-dependent rate constants may explain differences in experimental and modeled results. To estimate the error from using this approach, master equation calculations were performed using VariFlex [83]. Structures and frequencies from reference 9 were used for reactants, wells, and transition states. Internal rotors were treated classically, and an Eckart tunneling correction was used. The values for $k_{5.1}(T,P)$ obtained from the master equation analysis are compared to those calculated using CHEMDIS and those determined experimentally in Figure 5.13. These results are also compared to results from Sun and Bozzelli, who used a QRRK approach to estimate the microcanonical rate constants and master equation analysis for pressure falloff.

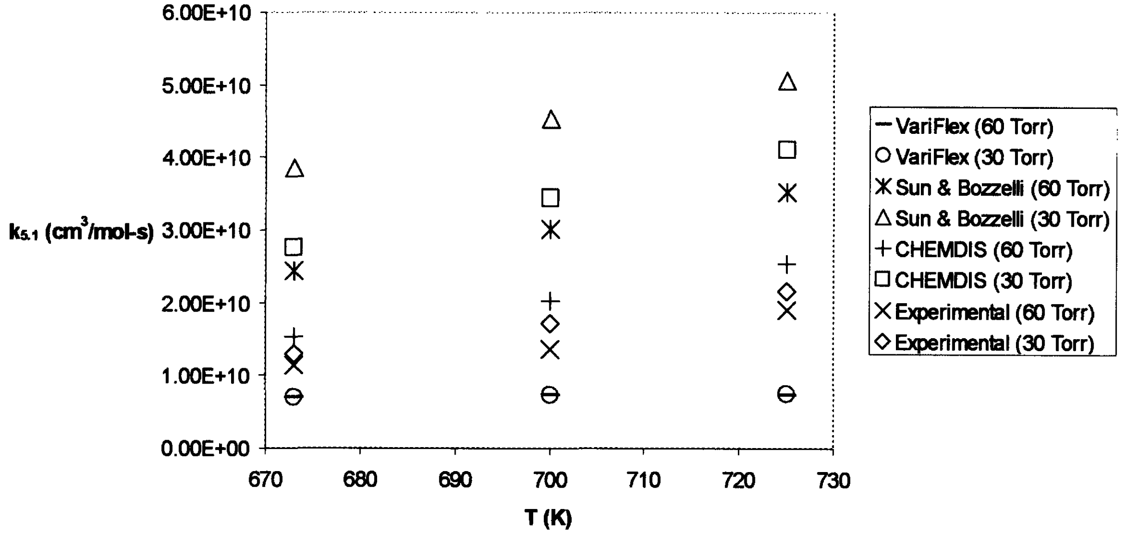

Figure 5.13 Comparison of $k_{5.1}$(T,P) calculated using QRRK/MSC approach (CHEMDIS) with master equation results (VariFlex and Sun & Bozzelli) and experimentally determined $k_{5.1}$. CHEMDIS calculations use high-pressure-limit rate parameters and thermodynamic properties from Sun and Bozzelli.

Rate constants calculated using VariFlex are lower than those determined experimentally by a factor of 1.5 to 3, while Sun and Bozzelli's calculations are higher than the experimental values by approximately the same amount. Values of $k_{5.1}$ calculated using CHEMDIS show good agreement with experimental results at 60 Torr but disagree by approximately a factor of 2 at 30 Torr. CHEMDIS estimates and results from Sun and Bozzelli overestimate the pressure-dependence of $k_{5.1}$. While CHEMDIS results suggest higher barriers for the RO_2 isomerization and QOOH decomposition, VariFlex calculations suggest these barriers are actually lower than those calculated by Sun and Bozzelli. The energies of these transition states were varied within their estimated uncertainty ranges, and VariFlex simulations were run to determine the barrier heights that gave the best agreement with experimental results. Decreasing the barriers for the RO_2 isomerization and QOOH decomposition by 1 and 2 kcal/mol, respectively, gave the best agreement with the experimentally determined values for $k_{5.1}$. A potential energy diagram adapted from Sun and Bozzelli is shown in Figure 5.14 with the suggested activation energies and transition state energies. The Variflex calculation is the most accurate but is expected to slightly underestimate k(E) because it treats the internal rotors classically. Therefore it is expected that E_o for $RO_2 \rightarrow QOOH$ is greater than or equal to 22.8 kcal/mole and that the transition state for QOOH→OH+3,3-dimethyloxetane is lower than the energy of the entrance channel $R+O_2$ by no more than 6.5 kcal/mole.

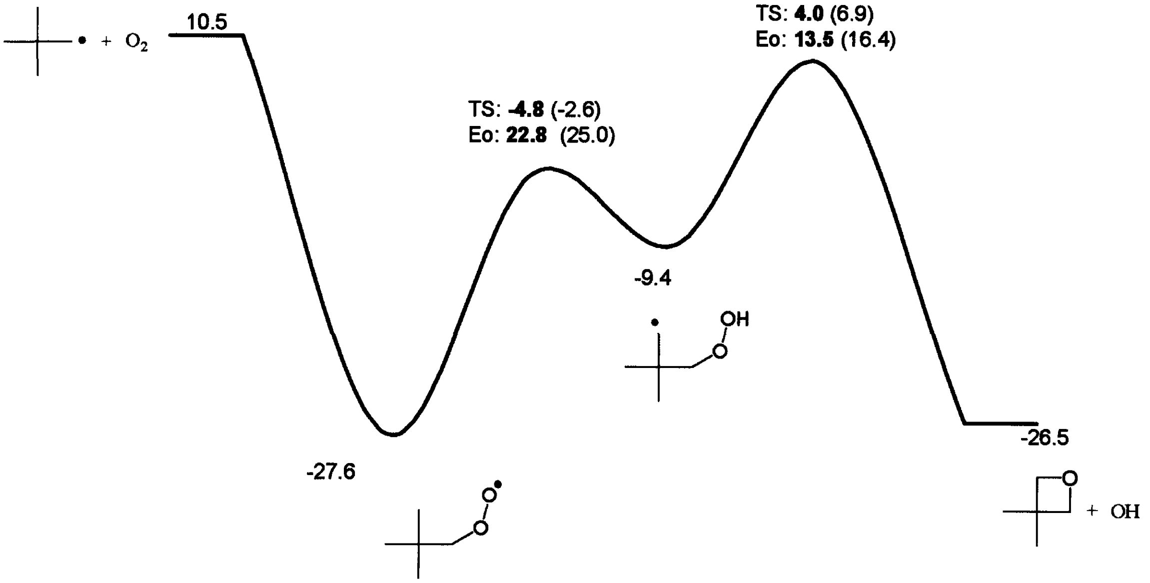

Figure 5.14 Zero point energy corrected potential energy diagram. Numbers in bold are energies determined from Variflex calculations, and numbers in parentheses are those determined from CHEMDIS calculations. Units are kcal/mol.

6. Conclusions

An algorithm to automatically calculate first-order sensitivity coefficients with respect to rate constants, enthalpies of formation, and initial concentrations was implemented in the MIT Reaction Mechanism Generator. A method for calculating sensitivities to high-pressure-limit rate parameters and thermodynamic properties of isomers in pressure-dependent networks was also developed and implemented. The option to automatically generate error bars on model predictions using first-order sensitivity coefficients and uncertainties in rate and thermodynamic parameters was incorporated in an automatic reaction model generation program for the first time.

RMG successfully generated a mechanism for the oxidation of the neopentyl radical. The comparison of this model with experimental results confirms the importance of the direct chemically activated reaction $R + O_2 \rightarrow OH + \text{ether}$ for the production of OH. Predicted OH concentration profiles agree reasonably well with results from several experimental investigations. The results suggest barriers of 22.8-25.0 and 13.5-16.4 kcal/mol for the isomerization of the neopentyl peroxy radical and decomposition of the hydroperoxy neopentyl radical, respectively. The production of OH is most sensitive to the direct reaction of the neopentyl radical with O_2 producing OH and 3,3-dimethyloxetane and the reaction of neopentyl iodide with OH. Upper and lower limits on these rate constants were calculated by comparing the RMG model to experimental data.

7. Recommendations for Future Work

The error propagation method presented here is only an approximation based on first-order sensitivity analysis. A method that can handle large uncertainties in input parameters is needed to generate accurate error bounds on RMG model predictions. Monte Carlo or response surface methods would give detailed information about the probability distribution of the model output, but these methods are computationally expensive. To save computer time, the current method could be used as a screening tool to identify model parameters that contribute significantly to the uncertainty, and a more accurate method could be applied only to those parameters. RMG currently only explores the effects of parametric uncertainties. Errors from other sources such as using a QRRK/MSC approach for estimating pressure-dependent rate constants and model truncation errors should also be considered.

RMG's termination rule is only guaranteed to be satisfied at the nominal parameter point used to generate the model. Since rate and thermodynamic parameters are not known precisely, it would be useful to generate models that are valid over the entire range of uncertainty for all input parameters. Song et al. [84] developed a method to identify the valid ranges of automatically generated models and to generate models valid over user-specified parameter ranges. This method is based on first-order sensitivity analysis and only guarantees that a model is valid at the vertices of the hyper-rectangle that describes the parameter range. Oluwole et al. [85] developed a more rigorous method to identify the valid range of a reduced model. Either of these methods could be implemented in RMG to automatically generate models that are valid over the entire range of uncertain parameters.

8. References

[1] Rabitz, H., Kramer, M. and Dacol, D., "Sensitivity Analysis in Chemical Kinetics", *Ann. Rev. Phys. Chem.* **34**, pp. 419-461, 1983;

[2] Turányi, T., "Sensitivity Analysis of Complex Kinetic Systems: Tools and Applications", *Journal of Mathematical Chemistry* **5**, pp. 203-248, 1990;

[3] Dunker, A. M., "The Decoupled Direct Method for Calculating Sensitivity Coefficients in Chemical Kinetics", *J. Chem. Phys.* **81**, pp. 2385-2393, 1984;

[4] Dunker, A. M., "Efficient Calculation of Sensitivity Coefficients for Complex Atmospheric Models", *Atm. Environ.* **15**, pp. 1155-1161, 1981;

[5] Maly, T. and Petzold, L., "Numerical Methods and Software for Sensitivity Analysis of Differential-Algebraic Systems", *Applied Numerical Mathematics* **20**, pp. 57-79, 1996;

[6] Feehery, W. F., Tolsma, J. E. and Barton, P. I., "Efficient Sensitivity Analysis of Large-Scale Differential-Algebraic Systems", *Applied Numerical Mathematics* **25**, pp. 41-54, 1997;

[7] Hwang, J. T., Dougherty, E. P., Rabitz, S. and Rabitz, H., "The Green's Function Method of Sensitivity Analysis in Chemical Kinetics", *J. Chem. Phys.* **69**, pp. 5180-5191, 1978;

[8] Hwang, J. T., "The Scaled Green's Function Method of Sensitivity Analysis and its Application to Chemical Reaction Systems", *Proc. Natl. Sci. Council B. Republic of China, Part B: Basic Science* **6**, pp. 37-44, 1982;

[9] Kramer, M. A., Calo, J. M. and Rabitz, H., *Appl. Math. Modelling* **5**, p. 432, 1981;

[10] Cacuci, D. G., "Sensitivity Theory for Nonlinear Systems I. Nonlinear Functional Analysis Approach", *J. Math. Phys.* **22**, p. 2794, 1981;

[11] Tomlin, A. S., Turányi, T. and Pilling, M. J., "Mathematical Tools for the Construction, Investigation, and Reduction of combustion Mechanisms", *Low Temperature Combustion and Autoignition. Comprehensive Chemical Kinetics.* M. J. Pilling and G. Hancock. Amsterdam, Elsevier **35**, pp. 293-437, 1997;

[12] Vuilleumier, L., Harley, R. A. and Brown, N. J., "First- and Second- Order Sensitivity Analysis of a Photochemically Reactive System (a Green's Function Approach)", *Environ. Sci. Technol.* **31**, pp. 1206-1217, 1997;

[13] Hakami, A., Odman, M. T. and Russell, A. G., "High-Order, Direct Sensitivity Analysis of Multidimensional Air Quality Models", *Environ. Sci. Technol.* **37**,

pp. 2442-2452, 2003;

[14] Özyurt, D. B. and Barton, P. I., "Large-Scale Dynamic Optimization Using the Directional Second-Order Adjoint Method", *Ind. Eng. Chem. Res.* **44**, pp. 1804-1811, 2005;

[15] Cukier, R. I., Levine, H. B. and Shuler, K. E., "Nonlinear Sensitivity Analysis of Multi-parameter Model Systems", *J. Comp. Phys.* **26**, pp. 1-42, 1978;

[16] Derwent, R. G., "Treating Uncertainty in Models of the Atmospheric Chemistry of Nitrogen-Compounds", *Atm. Environ.* **21**, pp. 1445-1454, 1987;

[17] Derwent, R. G. and Hov, O., "Application of Sensitivity and Uncertainty Analysis Techniques to a Photochemical Ozone Model", *J. Geophys. Res. (Atm.)* **93**, pp. 5185-5199, 1988;

[18] Saltelli, A., Andres, T. H. and Homma, T., "Sensitivity Analysis of Model Output: An Investigation of New Techniques", *Comput. Stat. Data Anal.* **15**, pp. 211-238, 1993;

[19] Saltelli, A. and Hjorth, J., "Uncertainty and Sensitivity Analyses of OH-Initiated Dimethylsulphide (DMS) Oxidation Kinetics", *J. Atmos. Chem.* **21**, pp. 187-221, 1995;

[20] Cox, D. C. and Baybutt, P., "Methods for Uncertainty Analysis: A Comparative Survey", *Risk Analysis* **1**, p. 251, 1981;

[21] Tatang, M. A., *Direct Incorporation of Uncertainty in Chemical and Environmental Engineering Systems (Stochastic Models)*, 1995;

[22] Phenix, B. D., Dinaro, J. L., Tatang, M. A., Tester, J. W., Howard, J. B. and McRae, G. J., "Incorporation of Parametric Uncertainty into Complex Kinetic Mechanisms: Application to Hydrogen Oxidation in Supercritical Water", *Combustion and Flame* **112**, pp. 132-146, 1998;

[23] Li, G., Rosenthal, C. and Rabitz, H., "High Dimensional Model Representations", *J. Phys. Chem.* **105**, pp. 7765-7777, 2001;

[24] Li, G., Wang, S., Rabitz, H., Wang, S. and Jaffé, P., "Global Uncertainty Assessments by High Dimensional Model Representations (HDMR)", *Chem. Eng. Sci.* **57**, pp. 4445-4460, 2002;

[25] Stewart, W. E., Caracotsios, M. and Sørensen, J. P., "Parameter estimation from multiresponse data", *AIChE Journal* **38**, pp. 641-650, 1992;

[26] Côme, G. M., Azay, P., Alran, D. and Niclause, M., AIChE 72nd Annual Meeting,

San Francisco, 1979;

[27] Vogin, L., PhD thesis, University of Nancy, 1983;

[28] Chevalier, C., Warnatz, J. and Melenk, H., "Automatic Generation of Reaction Mechanisms for the Description of the Oxidation of Higher Hydrocarbons", *Ber. Bunsenges. Phys. Chem.* **94**, pp. 1362-1367, 1990;

[29] Chevalier, C., Pitz, W. J., Warnatz, J., Westbrook, C. K. and Melenk, H., "Hydrocarbon Ignition: Automatic Generation of Reaction Mechanisms and Application to Modeling of Engine Knock", 24th Symp. (Int.) Comb., pp. 93-101, 1992;

[30] Ranzi, E., Faravelli, T., Gaffuri, P. and Sogaro, A., "Low Temperature Combustion: Automatic Generation of Primary Oxidation Reactions and Lumping Procedures", *Combustion and Flame* **102**, pp. 179-192, 1995;

[31] Blurock, E. S., "Reaction: System for Modelling Chemical Reactions", *J. Chem. Info. Comp. Sci.* **35**, pp. 607-616, 1995;

[32] Broadbelt, L. J., Stark, S. M. and Klein, M. T., "Computer Generated Pyrolysis Modelling: On-the-Fly Generation of Reactions, Rates and Predictions", *Ind. Eng. Chem. Res.*, pp. 790-799, 1994;

[33] Broadbelt, L. J., Stark, S. M. and Klein, M. T., "Computer Generated Reaction Modelling: On-the-Fly Calculation of Species' Properties Using Computational Quantum Chemistry", *Chem. Eng. Sci.* **49**, pp. 4991-5010, 1994;

[34] Broadbelt, L. J., Stark, S. M. and Klein, M. T., "Computer Generated Reaction Modelling: Decomposition and Encoding Algorithms for Determining Species Uniqueness", *Comp. Chem. Eng.* **20**, pp. 113-129, 1996;

[35] Susnow, R. G., Dean, A. M. and Green, W. H., Jr., "Rate-Based Construction of Kinetic Models for Complex Systems", *J. Phys. Chem. A.* **101**, pp. 3731-3740, 1997;

[36] Matheu, D. M., Dean, A. M., Grenda, J. M. and Green, W. H, Jr., "Mechanism Generation with Integrated Pressure Dependence: A New Model for Methane Pyrolysis", *J. Phys. Chem. A.* **107**, pp. 8552-8565, 2003;

[37] Song, Jing, "Building Robust Chemical Reaction Mechanisms: Next Generation of Automatic Model Construction Software", 2004;

[38] Li, S. and Petzold, L. R., "Design of New DASPK for Sensitivity Analysis", UCSB Technical Report, 1999;

[39] Marcus, R. A., “Dissociation and Isomerization of Vibrationally Excited Species. III.”, *J. Chem. Phys.* **43**, pp. 2658-2661, 1965;

[40] Marcus, R. A., “Unimolecular Dissociations and Free-radical Recombination Reactions”, *J. Chem. Phys.* **20**, pp. 359-364, 1952;

[41] Wieder, G. M., Marcus, R. A., “Dissociation and Isomerization of Vibrationally Excited Species. II.”, *J. Chem. Phys.* **37**, pp. 1835-1852, 1962;

[42] Forst, W., “Unimolecular Rate Theory Test in Thermal Reactions”, *J. Phys. Chem.* **76**, pp. 342-348, 1972;

[43] Forst, W. Theory of Unimolecular Reactions; Academic Press: New York, 1973;

[44] Kassel, L. S., “Studies in Homogeneous Gas Reactions. II. Introduction of Quantum Theory”, *J. Phys. Chem.* **32**, pp. 1065-1079, 1928;

[45] Dean, A. M., “Predictions of Pressure and Temperature Effects Upon Radical Addition and Recombination Reactions”, *J. Phys. Chem.* **89**, pp. 4600-4608, 1985;

[46] Chang, A. Y., Bozzelli, J. W., Dean, A.M., “Kinetic Analysis of Complex Chemical Activation and Unimolecular Dissociation Reactions using QRRK Theory and the Modified Strong Collision Approximation”, *Z. Phys. Chem.* **214**, pp. 1533-1568, 2000;

[47] Bozzelli, J. W.; Chang, A. Y.; Dean, A. M., “Molecular Density of States from Estimated Vapor Phase Heat Capacities”, *Int. J. Chem. Kinet.* **29**, pp. 161-170, 1997;

[48] Troe, J., “Predictive Possibilities of Unimolecular Rate Theory”, *J. Phys. Chem.* **83**, pp. 114-126, 1979;

[49] Troe, J., “Theory of Thermal Unimolecular Reactions at Low Pressures. II. Strong Collision Rate Constants. Applications.”, *J. Chem. Phys.* **66**, pp. 4758-4775, 1977;

[50] Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Rossi, M. J. and Troe, J., “Evaluated Kinetic, Photochemical and Heterogeneous Data for Atmospheric Chemistry: Supplement V, IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry”, *J. Phys. Chem. Ref. Data* **26**, pp. 521-1013, 1997;

[51] Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., Rossi, M. J. and Troe, J., “IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry”, *J. Phys. Chem. Ref. Data* **26**, pp. 1329-1499, 1997;

[52] Baulch, D. L., Cobos, C. J., Cox, R. A., Frank, P., Hayman, G., Just, T., Kerr, J. A.,

Murrells, T., Pilling, M. J., Troe, J., Walker, R. W. and Warnatz, J., "Evaluated Kinetic Data for Combustion Modeling. Supplement I", *J. Phys. Chem. Ref. Data* **23**, pp. 847-1033, 1994;

[53] Baulch, D. L., Cobos, C. J., Cox, R. A., Esser, C., Frank, P., Just, T., Kerr, J. A., Pilling, M. J., Troe, J., Walker, R. W. and Warnatz, J., "Evaluated Kinetic Data for Combustion Modeling", *J. Phys. Chem. Ref. Data* **21**, pp. 411-734, 1992;

[54] Tsang, W., "Chemical Kinetic Database for Combustion Chemistry. Part V. Propene", *J. Phys. Chem. Ref. Data* **20**, pp. 221-273, 1991;

[55] Tsang, W., "Chemical Kinetic Database for Combustion Chemistry. Part 4. Isobutane", *J. Phys. Chem. Ref. Data* **19**, pp. 1-68, 1990;

[56] Tsang, W., "Chemical Kinetic Database for Combustion Chemistry. Part 3. Propane", *J. Phys. Chem. Ref. Data* **17**, pp. 887-951, 1988;

[57] Tsang, W., "Chemical Kinetic Database for Combustion Chemistry. Part 2. Methanol", *J. Phys. Chem. Ref. Data* **16**, pp. 471-508, 1987;

[58] Tsang, W. and Hampson, R. F., "Chemical Kinetic Database for Combustion Chemistry. Part 1. Methane and Related Compounds", *J. Phys. Chem. Ref. Data* **15**, pp. 1087-1279, 1986;

[59] Sumathi, R., Carstensen, H. H. and Green, W. H., Jr., "Reaction Rate Prediction via Group Additivity Part 1: H abstraction from Alkanes by H and CH_3", *J. Phys. Chem. A* **105**, pp. 6910-6925, 2001;

[60] Sumathi, R., Carstensen, H. H. and Green, W. H., Jr., "Reaction Rate Prediction via Group Additivity Part 2: H-abstraction from alkenes, alkynes, alcohols, aldehydes and acids by H atoms", *J. Phys. Chem. A* **105**, pp. 8969-8984, 2001;

[61] Sumathi, R., Carstensen, H. H. and Green, W. H., Jr., "Reaction Rate Prediction via Group Additivity Part 3: Effect of Substituents with CH_2 as the Mediator", *J. Phys. Chem. A* **106**, pp. 5474-5489, 2002;

[62] Sumathi, R. and Green, W. H., Jr., "A priori rate constants for kinetic modeling", *Theor. Chem. Acc.* **108**, pp. 187-213, 2002;

[63] Wijaya, C. D., Sumathi, R. and Green, W. H., Jr., "Thermodynamic Properties and Kinetic Parameters for Cyclic Ether Formation from Hydroperoxyalkyl Radicals", *J. Phys. Chem. A* **107**, pp. 4908-4920, 2003;

[64] Wijaya, C. D., "Developing Fundamentally Based Models for Autoignition", 2003;

[65] Benson, S. W., *Thermochemical Kinetics*, John Wiley & Sons, New York, 2nd

edition, 1976;

[66] Stein, S. E. and Fahr, A., "High-temperature stabilities of hydrocarbons", *Journal of Physical Chemistry* **89**, pp. 3714-3725, 1985;

[67] Sumathi, R. and Green, W. H., Jr., "Thermodynamic properties of ketenes: Group additivity values from quantum chemical calculations", *Journal of Physical Chemistry A* **106**, pp. 7937-7949, 2002;

[68] Sumathi, R. and Green, W. H., Jr., "Missing thermochemical groups for large unsaturated hydrocarbons: Contrasting predictions of G2 and CBS-Q", *Journal of Physical Chemistry A* **106**, pp. 11141-11149, 2002;

[69] Baldwin, R. R., Hisham, M. W. M., Walker, R. W., "Arrhenius Parameters of Elementary Reactions Involved in the Oxidation of Neopentane", *J. Chem. Soc., Faraday Trans.* **78**, pp. 1615-1627, 1982;

[70] Baker, R. R., Baldwin, R. R., Everett, C. J., Walker, R. W., "Addition of Neopentane to Slowly Reacting Mixtures of Hydrogen and Oxygen at 480 deg. I. Formation of Primary Products from Neopentane", *Combust. Flame* **25**, pp. 285 -300, 1975;

[71] Baker, R. R., Baldwin, R. R., Walker, R. W., "Addition of Neopentane to Slowly Reacting Mixtures of Molecular Hydrogen + Molecular Oxygen at 480 deg. Part II. The Addition of the Primary Products from Neopentane, and the Rate Constants for Atomic Hydrogen and Hydroxy Attack on Neopentane", *Combust. Flame* **27**, pp. 147-161, 1976;

[72] Hughes, K. J., Lightfoot, P. D., Pilling, M. J., "Direct Measurements of the Peroxy-Hydroperoxy Radical Isomerization, a Key Step in Hydrocarbon Combustion", *Chem. Phys. Lett.* **191**, pp. 581-586, 1992;

[73] Hughes, K. J., Halford-Maw, P. A., Lightfoot, P. D., Turanyi, T., Pilling, M. J., "Direct Measurements of the Neopentylperoxy-Hydroperoxy Radical Isomerization Over the Temperature Range 660-750 K", *Symp. Int. Combust. Proc.* **24**, pp. 645-652, 1992;

[74] Curran, H. J., Pitz, W. J., Westbrook, C. K., Hisham, M. W. M., Walker, R. W., "An Intermediate Temperature Modeling Study of the Combustion of Neopentane", *Symp. Int. Combust. Proc.* **26**, pp. 641-649, 1996;

[75] Wang, S. M., David, L., Cernansky, N. P., Curran, H. J., Pitz, W. J., Westbrook, C. K., "A Flow Reactor Study of Neopentane Oxidation at 8 Atmospheres: Experiments and Modeling", *Combust. Flame* **118**, pp. 415-430, 1999;

[76] DeSain, J. D., Klippenstein, S. J., Taatjes, C. A., "Time-resolved Measurements of

OH and HO_2 Product Formation in Pulsed-Photolytic Chlorine Atom Initiated Oxidation of Neopentane", *Phys. Chem. Chem. Phys.* **5**, pp. 1584-1592, 2003;

[77] Sun, H., Bozzelli, J. W., "Thermochemical and Kinetic Analysis on the Reactions of Neopentyl and Hydroperoxy-Neopentyl Radicals with Oxygen: Part I. OH and Initial Stable HC Product Formation", *J. Phys. Chem. A* **108**, pp. 1694-1711, 2004;

[78] Cohen, N., "Are Reaction Rate Coefficients Additive? Revised Transition State Theory Calculations for OH + Alkane Reactions", *Int. J. Chem. Kinet.* **23**, pp. 397-417, 1991;

[79] Atkinson, R., "Kinetics of the Gas-Phase Reactions of OH Radicals with Alkanes and Cycloalkanes", *Atmos. Chem. Phys.* **3**, pp. 2233-2307, 2003;

[80] Baulch, D. L., Bowers, D. G., Malcolm, D. G., Tuckersman, R. T., "Evaluated Kinetic Data for High-Temperature Reactions. Volume 5. Part 1. Homogeneous Gas-Phase Reactions of the Hydroxyl Radical with Alkanes", *J. Phys. Chem. Ref. Data* **15**, pp. 465-592, 1986;

[81] Walker, R. W., "Temperature Coefficients for Reactions of OH Radicals with Alkanes between 300 and 1000 K", *Int. J. Chem. Kinet.* **17**, pp. 573-582, 1985;

[82] Tully, F. P., Koszykowski, M. L., Binkley, J. S., "Hydrogen-atom Abstraction from Alkanes by Hydroxyl Radical. I. Neopentane and Neooctane", *Symp. Int. Combust. Proc.***20**, pp. 715-721, 1985;

[83] Klippenstein, S. J., Wagner, A. F., Dunbar, R. C., Wardlaw, D. M., Robertson, S. H., Miller, J. A. VariFlex, 1.13m ed., 2002;

[84] Song, J., Stephanopoulos, G. and Green, W. H., Jr., "Valid Parameter Range Analyses for Chemical Reaction Kinetic Models", *Chem. Eng. Sci.* **57**, pp. 4475-4491, 2002;

[85] Oluwole, O. O., Bhattacharjee, B., Tolsma, J. E., Barton, P. I. and Green, W. H., Jr., "Rigorous Valid Ranges for Optimally-Reduced Kinetic Models", submitted to *Combustion and Flame*, 2005;

Appendix: RMG Mechanism for Neopentyl + O_2

```
ELEMENTS H C O N I He Ne Ar END
SPECIES
       N2
       He
       Ar
       Ne
       CH
       IO2.
       C3CC.
       CH2HCO
       C2H6
       C4H2
       C3.CCOOH
       CO2
       OH
       C3CCI
       H2
       O2
       HO2
       C(COOH)CYCCOC
       C2C(COOH)COO.
       C2H3
       C2.C(COOH)2
       C4H10
       C3H2
       C3CCOO.
       CH2I
       C2H5
       C4H9_2
       H2O
       HCCO
       I2
       C2H2
       C4H8
       CH2OH
       HCO
       CH3
       CO
       C4H9_1
       CH2CO
       H2CCCH
       HI
       H2CCCCH
       C3H6
       HIO
       CH2(S)
       CH4
       C3H5
       H
       O
       C5H11IO2
       C2CYCCOC
       C2H4
       I
       H2O2
       CH2
       CH3O
       IO.
       CH3O2
       C3.CCI
       C3H4
       CH2O
       C2H
END
```

```
THERMO ALL
   300.000  1000.000  5000.000
CH                       C   1H   1I   00   00   300.000  5000.000 1447.000      1
 2.85628327E+00 9.08655604E-04-1.63589434E-07 1.11834596E-11-1.22961181E-16    2
 7.07087581E+04 5.73133966E+00 3.25449498E+00 1.17415028E-03-1.87905007E-06    3
 1.46245582E-09-3.62236991E-13 7.04558867E+04 3.17642721E+00                   4

IO2.                     C   0H   0I   1O   20   300.000  5000.000 1393.000      1
 5.93899775E+00 1.28657224E-03-6.03332359E-07 1.01241536E-10-6.03684425E-15    2
 9.75677600E+03-2.23694135E+00 4.18622764E+00 6.05249821E-03-5.78832850E-06    3
 2.72468320E-09-5.14940435E-13 1.03104400E+04 6.95870206E+00                   4

C3CC.                    C   5H  11I   00   00   300.000  5000.000 1393.000      1
 1.59939147E+01 2.19818827E-02-6.94245532E-06 1.02878312E-09-5.79956309E-14    2
-2.44822515E+03-6.05426253E+01-5.16303228E-01 6.32143640E-02-4.70859551E-05    3
 1.90747021E-08-3.19434136E-12 3.01848384E+03 2.71824592E+01                   4

CH2HCO                   C   2H   3I   0O   10   300.000  5000.000 1396.000      1
 7.18970376E+00 7.05973844E-03-2.26238682E-06 3.36561511E-10-1.89994018E-14    2
-1.02693775E+01-1.34274592E+01 1.14626984E+00 2.21761856E-02-1.68825660E-05    3
 6.81502222E-09-1.12277551E-12 1.97437272E+03 1.86517362E+01                   4

C2H6                     C   2H   6I   00   00   300.000  5000.000 1382.000      1
 6.08086952E+00 1.25171107E-02-4.01175468E-06 5.97185370E-10-3.37178215E-14    2
-1.36304028E+04-1.25992236E+01-1.14904307E-01 2.44514785E-02-1.16796722E-05    3
 2.24550750E-09-3.45872965E-14-1.12204982E+04 2.15840046E+01                   4

C4H2                     C   4H   2I   00   00   300.000  5000.000 1409.000      1
 9.25454825E+00 5.44118548E-03-1.59076052E-06 2.18701167E-10-1.16233717E-14    2
 4.94910726E+04-2.50275080E+01 3.31796477E+00 2.54954331E-02-2.69864418E-05    3
 1.43154524E-08-2.88741170E-12 5.09325359E+04 4.65836002E+00                   4

C3.CCOOH                 C   5H  11I   0O   20   300.000  5000.000 1387.000      1
 2.16121087E+01 2.15822397E-02-7.09043891E-06 1.08580487E-09-6.26552582E-14    2
-1.47530308E+04-8.14901214E+01 1.61160741E+00 6.90156428E-02-5.04038384E-05    3
 1.92383503E-08-3.00807655E-12-7.88516131E+03 2.56637166E+01                   4

CO2                      C   1H   0I   0O   20   300.000  5000.000 1394.000      1
 5.06417736E+00 2.20377103E-03-7.68793535E-07 1.18999736E-10-6.87336235E-15    2
-4.92612118E+04-4.46228085E+00 2.47501265E+00 8.44770393E-03-6.49552774E-06    3
 2.49180713E-09-3.81352538E-13-4.83934180E+04 9.35423355E+00                   4

OH                       C   0H   1I   0O   10   300.000  5000.000 1453.000      1
 2.75911618E+00 1.17572134E-03-2.95628092E-07 3.51411616E-11-1.62980032E-15    2
 3.74586897E+03 6.33029598E+00 3.87703800E+00-1.48031854E-03 2.00443618E-06    3
-8.17307837E-10 1.10626212E-13 3.37785760E+03 3.68110581E-01                   4

C3CCI                    C   5H  11I   1O   00   300.000  5000.000 1394.000      1
 1.89461037E+01 2.26307760E-02-7.41656530E-06 1.11769134E-09-6.36015293E-14    2
-1.67955833E+04-7.62037676E+01-1.52071856E+00 7.45137293E-02-5.86593494E-05    3
 2.44354281E-08-4.15398572E-12-1.01117895E+04 3.22447997E+01                   4

H2                       C   0H   2I   00   00   300.000  5000.000 1448.000      1
 2.77742098E+00 9.88956630E-04-1.86537311E-07 1.41596340E-11-2.71191041E-16    2
-7.22323249E+02-9.35271024E-02 3.32038250E+00 8.51211645E-04-1.47824911E-06    3
 1.26678962E-09-3.27418244E-13-1.01709425E+03-3.39966900E+00                   4

O2                       C   0H   0I   0O   20   300.000  5000.000 1480.000      1
 3.61249258E+00 9.20628182E-04-3.46614008E-07 5.65645739E-11-3.37952713E-15    2
-1.24324080E+03 3.56282985E+00 3.21873711E+00 8.08363677E-04 9.86282017E-07    3
-1.09861586E-09 2.85329865E-13-1.00227303E+03 6.04551737E+00                   4

HO2                      C   0H   1I   0O   20   300.000  5000.000 1506.000      1
 3.66884473E+00 3.15305647E-03-1.06239645E-06 1.61467637E-10-9.20904098E-15    2
-1.17198484E+03 5.44556796E+00 3.75687734E+00 7.22079138E-04 3.64224682E-06    3
-2.96503545E-09 6.87098035E-13-9.62444201E+02 5.79156045E+00                   4
```

```
C(COOH)CYCCOC           C   5H  10I   0O   30   300.000  5000.000 1385.000      1
 2.23897262E+01 2.24296165E-02-7.61684296E-06 1.18821010E-09-6.93487108E-14    2
-3.72687038E+04-8.95069933E+01-1.76833290E+00 7.79637578E-02-5.58783351E-05    3
 2.00763510E-08-2.88517591E-12-2.88389632E+04 4.04759651E+01                   4

C2C(COOH)COO.           C   5H  11I   0O   40   300.000  5000.000 1387.000      1
 2.71499901E+01 2.14828964E-02-7.25665131E-06 1.13620351E-09-6.65769431E-14    2
-3.36936954E+04-1.07972268E+02 1.21433537E+00 8.36926393E-02-6.45968477E-05    3
 2.53150967E-08-3.99953476E-12-2.48930287E+04 3.06728984E+01                   4

C2H3                    C   2H   3I   00   00   300.000  5000.000 1401.000      1
 5.16208800E+00 6.18002840E-03-1.90928299E-06 2.76195724E-10-1.52825474E-14    2
 3.37518389E+04-3.72967306E+00 1.00287985E+00 1.67468389E-02-1.22996990E-05    3
 4.95242642E-09-8.22453602E-13 3.51002033E+04 1.82876649E+01                   4

C2.C(COOH)2             C   5H  11I   0O   40   300.000  5000.000 1385.000      1
 2.76428220E+01 2.07706308E-02-7.05120399E-06 1.10933373E-09-6.52155375E-14    2
-2.50454022E+04-1.06861614E+02 2.83549487E+00 7.95595167E-02-6.05100683E-05    3
 2.33429621E-08-3.63579565E-12-1.65436246E+04 2.60264351E+01                   4

C4H10                   C   4H  10I   00   00   300.000  5000.000 1382.000      1
 1.27419107E+01 2.09851709E-02-6.85440917E-06 1.03705299E-09-5.92437651E-14    2
-2.19626008E+04-4.56104425E+01-5.32848242E-01 4.85878253E-02-2.75818655E-05    3
 7.58174664E-09-7.60825957E-13-1.70006354E+04 2.69117512E+01                   4

C3H2                    C   3H   2I   00   00   300.000  5000.000 1420.000      1
 4.09085842E+00 8.47717150E-03-2.32286271E-06 2.93349199E-10-1.43693561E-14    2
 5.95445316E+04 6.09649666E+00 2.44014784E+00 1.91259564E-02-2.03357537E-05    3
 1.19979737E-08-2.63694354E-12 5.94754040E+04 1.26118803E+01                   4

C3CCOO.                 C   5H  11I   0O   20   300.000  5000.000 1390.000      1
 2.10907473E+01 2.23533051E-02-7.30093979E-06 1.11195347E-09-6.39238263E-14    2
-2.39286992E+04-8.43534749E+01-9.79613467E-01 7.61206206E-02-5.78537686E-05    3
 2.29145091E-08-3.69275371E-12-1.65189763E+04 3.33398492E+01                   4

CH2I                    C   1H   2I   1O   00   300.000  5000.000 1398.000      1
 6.83325877E+00 1.21191330E-03-5.00592483E-07 8.30879845E-11-4.98466734E-15    2
 2.52569927E+04-6.63013258E+00 3.50451085E+00 1.04839442E-02-1.05169328E-05    3
 5.00450276E-09-9.22382867E-13 2.62525330E+04 1.06988601E+01                   4

C2H5                    C   2H   5I   00   00   300.000  5000.000 1402.000      1
 4.20963761E+00 1.22478245E-02-3.72122404E-06 5.27308472E-10-2.86624904E-14    2
 1.21391080E+04 1.64792626E+00 4.59769373E-01 2.16654284E-02-1.31486645E-05    3
 4.95468957E-09-8.37206426E-13 1.34002895E+04 2.15940190E+01                   4

C4H9_2                  C   4H   9I   00   00   300.000  5000.000 1370.000      1
 1.04344305E+01 2.10937072E-02-6.97841359E-06 1.06198838E-09-6.08431289E-14    2
 2.32241901E+03-2.85707801E+01 1.80266755E+00 3.34434391E-02-9.13212018E-06    3
-2.29293754E-09 1.18298310E-12 6.15836866E+03 2.06548537E+01                   4

H2O                     C   0H   2I   0O   10   300.000  5000.000 1422.000      1
 2.67329335E+00 3.01140286E-03-8.28913345E-07 1.08858853E-10-5.57093023E-15    2
-2.98899736E+04 6.89577739E+00 4.00642224E+00-6.07323247E-04 2.82015586E-06    3
-1.51355826E-09 2.63230821E-13-3.02786490E+04-4.57677622E-02                   4

HCCO                    C   2H   1I   0O   10   300.000  5000.000 1409.000      1
 6.17855423E+00 2.95226567E-03-8.65868790E-07 1.19993428E-10-6.42703952E-15    2
 2.18578126E+04-6.89810224E+00 3.20211411E+00 1.25506156E-02-1.26118823E-05    3
 6.48430337E-09-1.28291559E-12 2.26229063E+04 8.14203104E+00                   4

I2                      C   0H   0I   2O   00   300.000  5000.000 1409.000      1
 3.37036441E+00 2.00110970E-03-9.14235352E-07 1.40001568E-10-7.70138607E-15    2
 6.58436087E+03 1.19526729E+01 4.45638877E+00 2.10346231E-04-5.61149138E-07    3
 7.52381310E-10-2.55537824E-13 6.17437730E+03 5.92421081E+00                   4

C2H2                    C   2H   2I   00   00   300.000  5000.000 1417.000      1
 5.05015444E+00 3.88605317E-03-1.06584508E-06 1.38158132E-10-6.98820352E-15    2
```

```
 2.53134713E+04-6.02066667E+00 2.17789252E+00 1.42644181E-02-1.47196485E-05    3
 7.87444004E-09-1.60181339E-12 2.59380849E+04 8.09323398E+00                   4

C4H8                    C   4H   8I   00   00   300.000  5000.000 1381.000      1
 1.15040944E+01 1.74701582E-02-5.72717965E-06 8.68009442E-10-4.96314650E-14    2
-7.75153206E+03-3.87446809E+01 9.32420183E-01 3.90066318E-02-2.13811291E-05    3
 5.53761007E-09-4.93505318E-13-3.74596333E+03 1.91839479E+01                   4

CH2OE                   C   1H   3I   0O   10   300.000  5000.000 1401.000      1
 5.83153875E+00 4.85565570E-03-1.47022064E-06 2.12656353E-10-1.18128397E-14    2
-4.21572054E+03-6.32004637E+00 1.70971478E+00 1.56028929E-02-1.23134914E-05    3
 5.20865358E-09-8.91802016E-13-2.91107826E+03 1.53951269E+01                   4

HCO                     C   1H   1I   0O   10   300.000  5000.000 1448.000      1
 7.56895558E+00-1.71493615E-03 3.22113619E-08 6.11036931E-11-6.17453648E-15    2
 2.00614609E+03-1.77218337E+01 3.92290171E+00-1.44056602E-03 1.00232377E-05    3
-9.23915324E-09 2.39055329E-12 4.05701149E+03 4.72036257E+00                   4

CH3                     C   1H   3I   00   00   300.000  5000.000 1403.000      1
 4.19498816E+00 3.52776858E-03-9.96658191E-07 1.37342735E-10-7.36938819E-15    2
 1.59675943E+04-1.89303225E+00 2.93067309E+00 6.78450303E-03-4.29254423E-06    3
 1.67984695E-09-2.85369427E-13 1.63782821E+04 4.79260809E+00                   4

CO                      C   1H   0I   0O   10   300.000  5000.000 1443.000      1
 6.71188887E+00-3.12521060E-03 5.29696703E-07-1.77404143E-11-1.53635040E-15    2
-1.60171559E+04-1.52966237E+01 4.02200850E+00-4.17322773E-03 1.05914044E-05    3
-8.78625014E-09 2.21210742E-12-1.43873574E+04 1.69040100E+00                   4

C4H9_1                  C   4H   9I   00   00   300.000  5000.000 1382.000      1
 1.22820701E+01 1.89411639E-02-6.19148632E-06 9.37626228E-10-5.36013547E-14    2
 3.11259620E+03-3.96003773E+01 2.48139616E-01 4.39949593E-02-2.50683069E-05    3
 6.94417779E-09-7.09234775E-13 7.60997187E+03 2.61358409E+01                   4

CH2CO                   C   2H   2I   0O   10   300.000  5000.000 1399.000      1
 6.36034318E+00 5.28125369E-03-1.65660876E-06 2.42345171E-10-1.35151569E-14    2
-8.28617439E+03-1.04937355E+01 2.27832513E+00 1.60657234E-02-1.27801586E-05    3
 5.51146737E-09-9.69480524E-13-6.99797184E+03 1.09787720E+01                   4

H2CCCH                  C   3H   3I   00   00   300.000  5000.000 1398.000      1
 7.34586691E+00 6.94446587E-03-2.19924185E-06 3.23904186E-10-1.81478125E-14    2
 3.79462589E+04-1.51832368E+01 1.92963770E+00 2.10310442E-02-1.65049871E-05    3
 7.00901216E-09-1.21796828E-12 3.96793287E+04 1.33892431E+01                   4

HI                      C   0H   1I   1O   00   300.000  5000.000 1000.000      1
 3.76055252E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.06449836E+03 3.42542331E+00 3.76055252E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.06449836E+03 3.42542331E+00                   4

H2CCCCH                 C   4H   3I   00   00   300.000  5000.000 1405.000      1
 8.46784475E+00 9.21402563E-03-2.82347010E-06 4.01164885E-10-2.18309347E-14    2
 5.59601912E+04-1.75081236E+01 2.46672477E+00 2.76461209E-02-2.47696599E-05    3
 1.21430813E-08-2.36731034E-12 5.76177308E+04 1.31803486E+01                   4

C3H6                    C   3H   6I   00   00   300.000  5000.000 1381.000      1
 8.22469956E+00 1.31601408E-02-4.29422326E-06 6.48201989E-10-3.69592178E-14    2
-1.91538353E+03-2.10720355E+01 4.07066322E-01 2.87937403E-02-1.51684788E-05    3
 3.55915084E-09-2.29478618E-13 1.06614078E+03 2.18527848E+01                   4

HIO                     C   0H   1I   1O   10   300.000  5000.000 1406.000      1
 2.06871685E+00 2.56575775E-04-1.22548629E-08 1.32456411E-12-1.57905126E-16    2
-1.72793692E+04-7.12765290E+00 1.62422073E+00-1.81024346E-04 2.35717542E-06    3
-2.03256911E-09 5.19018815E-13-1.70005666E+04-4.25530690E+00                   4

CH2(S)                  C   1H   2I   00   00   300.000  5000.000 1415.000      1
 3.86777055E+00 1.75725158E-03-4.69946474E-07 6.22600837E-11-3.24658763E-15    2
 5.00499708E+04 6.39263427E-01 3.28338152E+00 3.43443242E-03-2.33792020E-06    3
 1.00451096E-09-1.82412342E-13 5.02208354E+04 3.66549852E+00                   4
```

```
CH4                     C   1H   4I   00   00   300.000  5000.000 1531.000     1
 2.94204993E+00 8.03803547E-03-2.57226419E-06 3.81289105E-10-2.14372133E-14    2
-1.06214186E+04 2.56203214E+00 2.42393375E+00 5.01676431E-03 4.97602334E-06    3
-5.02510459E-09 1.22574452E-12-9.98884136E+03 6.89493290E+00                   4

C3H5                    C   3H   5I   00   00   300.000  5000.000 1396.000     1
 8.54466507E+00 1.07922076E-02-3.44788751E-06 5.11675037E-10-2.88352293E-14    2
 1.63999401E+04-2.28718907E+01-5.77389399E-01 3.36328080E-02-2.55517694E-05    3
 1.03067543E-08-1.69689181E-12 1.93917611E+04 2.55380812E+01                   4

H                       C   0H   1I   00   00   300.000  5000.000 1000.000     1
 2.50003774E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.54750466E+04-4.44508791E-01 2.50003774E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.54750466E+04-4.44508791E-01                   4

O                       C   0H   0I   0O   10   300.000  5000.000 1000.000     1
 2.55352371E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 2.92084706E+04 4.82196261E+00 2.55352371E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 2.92084706E+04 4.82196261E+00                   4

C5H11IO2                C   5H  11I   1O   20   300.000  5000.000 1375.000     1
 2.60992657E+01 1.85647832E-02-6.75135115E-06 1.10728823E-09-6.67697761E-14    2
-5.09581348E+04-1.24090160E+02-1.14236127E+00 7.74930650E-02-5.31469284E-05    3
 1.66726608E-08-1.89426205E-12-4.11161580E+04 2.37405753E+01                   4

C2CYCCOC                C   5H  10I   0O   10   300.000  5000.000 1387.000     1
 1.62420701E+01 2.33664766E-02-7.70154742E-06 1.17178151E-09-6.71963472E-14    2
-2.62969727E+04-6.38398497E+01-2.62239089E+00 6.59948385E-02-4.39874718E-05    3
 1.50313149E-08-2.07645081E-12-1.96223962E+04 3.79519645E+01                   4

C2H4                    C   2H   4I   00   00   300.000  5000.000 1392.000     1
 5.34387695E+00 8.50901642E-03-2.70002295E-06 3.98547466E-10-2.23706648E-14    2
 3.60784350E+03-8.01479399E+00 7.90908675E-02 2.02619466E-02-1.24679753E-05    3
 3.97959042E-09-5.09018538E-13 5.47932514E+03 2.04349242E+01                   4

I                       C   0H   0I   1O   00   300.000  5000.000 3000.000     1
 2.50320089E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 1.20971533E+04 7.37843514E+00 2.50320089E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 1.20971533E+04 7.37843514E+00                   4

H2O2                    C   0H   2I   0O   20   300.000  5000.000 1402.000     1
 5.23636014E+00 3.37908972E-03-1.01382346E-06 1.44589042E-10-7.93309048E-15    2
-1.83515839E+04-3.30283178E+00 2.95408656E+00 9.64515990E-03-7.73469085E-06    3
 3.44202866E-09-6.23732936E-13-1.76542733E+04 8.61978529E+00                   4

CH2                     C   1H   2I   00   00   300.000  5000.000 1415.000     1
 3.86777055E+00 1.75725158E-03-4.69946474E-07 6.22600837E-11-3.24658763E-15    2
 4.51883704E+04 6.39263427E-01 3.28338152E+00 3.43443242E-03-2.33792020E-06    3
 1.00451096E-09-1.82412342E-13 4.53592350E+04 3.66549852E+00                   4

CH3O                    C   1H   3I   0O   10   300.000  5000.000 2007.000     1
 4.13584420E+00 7.21405768E-03-2.44022166E-06 3.79123315E-10-2.20955342E-14    2
 1.73464417E+02 2.63315442E+00 1.56157949E+00 1.19046962E-02-4.87427111E-06    3
 5.22420568E-10 8.92190648E-14 1.14591943E+03 1.68593301E+01                   4

IO.                     C   0H   0I   1O   10   300.000  5000.000 1000.000     1
 4.28319096E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
 1.26635806E+04 4.49897392E+00 4.28319096E+00 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00 1.26635806E+04 4.49897392E+00                   4

CH3O2                   C   1H   3I   0O   20   300.000  5000.000 1373.000     1
 5.75573849E+00 8.36992198E-03-2.71684245E-06 4.06313891E-10-2.29769711E-14    2
-4.05704250E+02-3.55078926E+00 3.73538432E+00 1.03496454E-02-1.50591532E-06    3
-1.45281262E-09 4.92357219E-13 6.06295990E+02 8.33237830E+00                   4

C3.CCI                  C   5H  10I   1O   00   300.000  5000.000 1396.000     1
```

```
 1.89252392E+01 2.00865506E-02-6.53865848E-06 9.80729127E-10-5.56305355E-14    2
 9.45241373E+03-7.11259168E+01-7.08968106E-01 7.20087140E-02-6.01768927E-05    3
 2.64435732E-08-4.68748891E-12 1.56454262E+04 3.21416134E+01                   4

C3H4                    C   3H   4I   00   00   300.000  5000.000 1392.000     1
 7.84419500E+00 8.98963753E-03-2.90804113E-06 4.35358501E-10-2.46779477E-14    2
 1.98839586E+04-1.97402936E+01 8.83827810E-01 2.55633929E-02-1.80465055E-05    3
 6.74912321E-09-1.03857141E-12 2.22597001E+04 1.75133850E+01                   4

CH2O                    C   1H   2I   0O   10   300.000  5000.000 1453.000     1
 7.55612865E+00 7.76678203E-04-8.18374117E-07 1.93079157E-10-1.38297861E-14    2
-1.66142829E+04-1.94924249E+01 3.31222002E+00 4.83384071E-04 1.19962439E-05    3
-1.13969006E-08 2.94069754E-12-1.41537646E+04 6.86695544E+00                   4

C2H                     C   2H   1I   00   00   300.000  5000.000 1424.000     1
 3.06052718E+00 3.81104217E-03-1.00003510E-06 1.19555213E-10-5.51897009E-15    2
 6.66866985E+04 8.05616857E+00 4.28108889E+00 3.61162218E-03-4.30989472E-06    3
 3.32272375E-09-8.50462563E-13 6.60333304E+04 6.18665648E-01                   4

Ne                120186Ne  1               G  0300.00   5000.00  1000.00      1
 0.02500000E+02 0.00000000E+00 0.00000000E+00 0.00000000E+00 0.00000000E+00    2
-0.07453750E+04 0.04366001E+02 0.02500000E+02 0.00000000E+00 0.00000000E+00    3
 0.00000000E+00 0.00000000E+00-0.07453750E+04 0.04366001E+02                   4

N2                121286N   2               G  0300.00   5000.00  1000.00      1
 0.02926640e+02 0.01487977e-01-0.05684761e-05 0.01009704e-08-0.06753351e-13    2
-0.09227977e+04 0.05980528e+02 0.03298677e+02 0.01408240e-01-0.03963222e-04    3
 0.05641515e-07-0.02444855e-10-0.01020900e+05 0.03950372e+02                   4

Ar                120186Ar  1               G  0300.00   5000.00  1000.00      1
 0.02500000e+02 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
-0.07453750e+04 0.04366001e+02 0.02500000e+02 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00-0.07453750e+04 0.04366001e+02                   4

He                120186He  1               G   300.000  5000.000 1000.00      1
 2.50000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00 0.00000000e+00    2
-7.45375000e+02 9.15348900e-01 2.50000000e+00 0.00000000e+00 0.00000000e+00    3
 0.00000000e+00 0.00000000e+00-7.45375000e+02 9.15348800e-01                   4

END
REACTIONS     KCAL/MOLE
 HIO+C2H3=IO.+C2H4 14.400   3.100  6.940
 CH2O+OH=HCO+H2O 3.430E9    1.180  -0.447
 HIO+CH3=IO.+CH4 1.487E3    2.386  9.690
 C4H10+C3.CCI=C3CCI+C4H9_1 3.954E3 2.710  12.920
 C4H10+C3.CCI=C3CCI+C4H9_2 6.160E3 2.660  10.100
 C2H4+O=>C2H3+OH 1.512E7    1.910  3.740
 O2+CH3O=CH2O+HO2 2.170E10  0.000  1.749
 O2+CH2OH=HO2+CH2O 1.140E13 0.000  0.000
 HI+C2H5=C2H6+I 9.228E9     0.860  28.332
 HIO+C3.CCI=C3CCI+IO. 1.487E3      2.386  9.690
 H2O2-CH3=CH4+HO2 1.390E14  -1.100 2.630
 HI+C2H=I+C2H2 9.228E9      0.860  28.332
 O2+C2H=CO2+CH 9.050E12     0.000  0.000
 CH2+CH2OH=CH3+CH2O 1.210E12 0.000  0.000
 CH2+CH3O=CH3+CH2O 1.506E13 0.000  0.000
 C3.CCI+C3H5=C3CCI+C3H4 9.640E11     0.000  -0.130
 C2H3+HO2=C2H4+O2 3.000E11  0.000  0.000
 HO2+C3H5=H2O2+C3H4 6.030E12 0.000  0.000
 CH3+CH3O=CH4+CH2O 9.570E12 -0.173 -1.806E-3
 CH3+CH2OH=CH4+CH2O 8.490E13 0.000  0.000
 C4H9_1+HO2=O2+C4H10 3.000E11      0.000  0.000
 C4H9_2+HO2=O2+C4H10 3.000E11      0.000  0.000
 H+I=HI 1.499E13     -0.150 0.292
 CH2+HO2=CH3+O2 1.046E13    0.000  0.000
 C2H6+OH=C2H5+H2O 7.230E6   2.000  0.865
 C2H4+C2H=C2H3+C2H2 8.852E9 0.696  9.952
```

```
C2H3+C3H5=C2H4+C3H4 2.410E12      0.000  0.000
CH4+CH=C2H4+H 3.010E13     0.000  -0.397
H2O2+OH=H2O+HO2 7.830E12   0.000  1.331
HCO+HCO=CH2O+CO 3.010E13   0.000  0.000
HI+C3H5=C3H6+I 9.228E9     0.860  28.332
CH2+C3H5=CH3+C3H4 4.234E12 -0.050 -0.057
CH4+OH=CH3+H2O 1.570E7     1.830  2.781
CH2CO+H=CH3+CO 1.810E13    0.000  3.376
C4H10+HO2=C4H9_2+H2O2 1.120E13    0.000  17.678
C4H10+HO2=C4H9_1+H2O2 1.680E13    0.000  20.425
H2+O=OH+H 5.120E4   2.670  6.276
C3H5+CH2OH=C3H6+CH2O 1.810E13     0.000  0.000
C3H5+CH3O=C3H6+CH2O 9.570E12      -0.173 -1.806E-3
C4H9_1=C4H9_2 3.876E10     0.890  35.800
IO.+O=IO2. 1.000E13 0.000  0.000
C2H2+O=CH2+CO 2.170E6      2.100  1.570
H+C3H5=C3H4+H2 1.810E13    0.000  0.000
IO.+C3H5=HIO+C3H4 6.030E12 0.000  0.000
O2+CH=CO+OH 1.660E13 0.000  0.000
IO.+HO2=HIO+O2 2.920E9     0.000  -3.275
HI+C3.CCI=C3CCI+I 9.228E9  0.860  28.332
CH2O+CH2=>HCO+CH3 6.040E9  0.000  0.000
O2+CH2=CO2+H+H 5.430E12    0.000  1.491
CH4+C2H3=CH3+C2H4 6.360E14 0.000  13.700
C4H10+CH2=>CH3+C4H9_1 9.999E5     2.326  3.700
C4H10+CH2=>CH3+C4H9_2 3.020 3.460  7.470
CH+O=CO+H 3.970E13  0.000  0.000
C2H2+C2H=C4H2+H 9.030E13   0.000  0.000
C3CCI+CH3=C3.CCI+CH4 2.502E6      1.900  11.050
HIO+H=IO.+H2 1.063E10      1.105  8.910
CH+CH3=C2H3+H 3.000E13     0.000  0.000
C2H5+C3H5=C3H4+C2H6 9.640E11      0.000  -0.130
C3H5+C2H5=C3H6+C2H4 1.146E13      -0.350 -0.130
C2H4+OH=C2H3+H2O 2.050E13  0.000  5.939
C2H4+H=C2H3+H2 5.420E14    0.000  14.897
H2O2+H=OH+H2O 2.410E13     0.000  3.963
I+HO2=O2+HI 3.000E11 0.000  0.000
CH3+C3H5=CH4+C3H4 3.010E12 -0.320 -0.130
CH2O+C3.CCI=C3CCI+HCO 5.500E3     2.810  5.860
CH2O+HO2=HCO+H2O2 4.110E4  2.500  10.196
H2+CH2(S)=CH3+H 7.230E13   0.000  0.000
H2+CH2=>CH3+H 1.846E10     0.860  28.332
OH+O=HO2 1.000E13   0.000  0.000
OH+OH=O+H2O 1.510E9 1.140  0.100
OH+HCO=H2O+CO 1.020E14     0.000  0.000
CH2O+O=HCO+OH 4.160E11     0.570  2.762
CH2+C2H3=C2H2+CH3 1.810E13 0.000  0.000
C2H+C3H5=C2H2+C3H4 5.413E12-0.089 -0.037
HIO+C2H5=IO.+C2H6 1.487E3  2.386  9.690
C2H+CH2OH=C2H2+CH2O 3.610E13      0.000  0.000
C2H+CH3O=C2H2+CH2O 9.570E12-0.173 -1.806E-3
HCO+CH2OH=CH2O+CH2O 1.810E14      0.000  0.000
HCO+CH3O=CH2O+CH2O 9.570E12-0.173 -1.806E-3
CH2+OH=CH2O+H 1.810E13     0.000  0.000
C2H6+C2H=C2H5+C2H2 3.612E12 0.000  0.000
O+C3H5=C3H4+OH 4.234E12    -0.050 -0.057
HI+CH2=>CH3+I 9.228E9      0.860  28.332
C2H6+C4H9_1=>C4H10+C2H5 3.954E3   2.710  12.920
C4H10+C2H5=>C2H6+C4H9_1 3.954E3   2.710  12.920
C4H10+C2H5=C2H6+C4H9_2 6.160E3    2.660  10.100
HO2+HO2=H2O2+O2 1.870E12   0.000  1.541
H2O2+H=HO2+H2 1.690E12     0.000  3.753
H2O2+IO.=HIO+HO2 34.600    3.400  -1.140
O2+HCO=HO2+CO 5.120E13     0.000  1.694
I+I=I2 1.499E13     -0.150 0.292
CH+CH2=C2H2+H 4.000E13     0.000  0.000
HO2+CH2OH=H2O2+CH2O 1.210E13      0.000  0.000
```

```
HO2+CH3O=H2O2+CH2O 9.570E12 -0.173 -1.806E-3
O+CH2OH=CH2O+OH 9.040E13   0.000  0.000
O+CH3O=CH2O+OH 1.506E13    0.000  0.000
CH2CO+O=CH2O+CO 4.580E11   0.000  1.350
C3CCI+H=C3.CCI+H2 5.652E8  1.750  7.510
H+CH2OH=CH2O+H2 2.000E13   0.000  0.000
H+CH3O=CH2O+H2 1.810E13    0.000  0.000
C4H10+CH3=CH4+C4H9_1 1.668E6      1.900  11.050
C4H10+CH3=CH4+C4H9_2 5.800E6      1.770  8.530
C4H10+IO.=HIO+C4H9_2 3.139E12     0.000  11.343
HIO+C4H9_1=C4H10+IO. 1.487E3      2.386  9.690
CH2O+H=HCO+H2 1.260E8      1.620  2.164
C2H6+O=C2H5+OH 1.000E9     1.500  5.800
O2+H+H2O=HO2+H2O 6.890E15  0.000  -2.086
IO.+H=HIO 1.499E13  -0.150 0.292
C2H6+C3.CCI=C3CCI+C2H5 3.954E3    2.710  12.920
C3H5+HO2=C3H6+O2 3.000E11  0.000  0.000
O2+CH3=CH2O+OH 3.310E11    0.000  8.939
I+CH2OH=CH2O+HI 9.505E12   -0.027 -0.468
I+CH3O=CH2O+HI 9.570E12    -0.173 -1.806E-3
C2H6+H=C2H5+H2 1.450E9     1.500  7.408
CH3+C2H5=CH4+C2H4 4.710E10 0.680  0.000
O2+CH2=CH2O+O 4.200E12     0.000  1.491
O2+CH2=CO+H2O 1.480E12     0.000  1.491
C2H5+HO2=C2H6+O2 3.000E11  0.000  0.000
H+HO2=OH+OH 1.690E14 0.000  0.874
CH4+CH2=CH3+CH3 4.300E12   0.000  10.033
CH4+CH2(S)=CH3+CH3 7.000E13 0.000  0.000
O2+CH2(S)=CO+OH+H 3.130E13 0.000  0.000
O2+CH2=CO+CH+H 8.150E12    0.000  1.491
C2H4+CH=C3H4+H 1.320E14    0.000  -0.344
HIO+CH2=>IO.+CH3 14.400    3.100  6.940
H+HO2=H2O+O 3.010E13 0.000  1.720
C2H5+O=CH2O+CH3 6.620E13   0.000  0.000
O+HCO=CO+OH 3.010E13 0.000  0.000
O+HCO=CO2+H 3.010E13 0.000  0.000
CO+OH=CO2+H 1.660E7 1.300  -0.764
CH2O+C3H5=HCO+C3H6 5.500E3 2.810  5.860
C3CCI+OH=C3.CCI+H2O 2.37E7 1.800  0.278
CH2+O=CO+H2 4.800E13 0.000  0.000
OH+CH2OH=H2O+CH2O 2.410E13 0.000  0.000
OH+CH3O=H2O+CH2O 9.570E12  -0.173 -1.806E-3
CH+C2H3=CH2+C2H2 5.000E13  0.000  0.000
CH2+CH3=C2H4+H 4.220E13    0.000  0.000
C3H6+C4H9_1=C4H10+C3H5 1.680E12   0.000  12.400
C3H6+C4H9_2=C4H10+C3H5 8.610E11   0.000  12.300
HCO+C2H5=CH2O+C2H4 9.570E12 -0.173 -1.806E-3
CH2+HCO=CH3+CO 1.810E13    0.000  0.000
CH3+HO2=CH4+O2 3.000E11    0.000  0.000
O2+CH2O=HCO+HO2 6.020E13   0.000  40.638
C3CCI+O=>C3.CCI+OH 7.695E4 3.050  3.123
HI+IO.=HIO+I 1.400E4 2.690  11.300
H2O2+O=OH+HO2 6.620E11     0.000  3.973
C3H6+CH2=>C3H5+CH3 5.000E5 2.326  3.700
OH+C3H5=H2O+C3H4 6.030E12  0.000  0.000
HO2+C2H5=H2O2+C2H4 1.206E13 0.000  0.000
CH+OH=HCO+H 3.000E13 0.000  0.000
C2H6+CH=C2H4+CH3 1.080E14  0.000  -0.263
C4H10+C4H9_1=C4H10+C4H9_2 6.160E3 2.660  10.100
H2O+H=H2+OH 4.520E8 1.600  18.414
C2H6+CH2(S)=CH3+C2H5 2.400E14     0.000  0.000
C2H6+CH2=>C2H5+CH3 9.999E5 2.326  3.700
C3.CCI+HO2=C3CCI+O2 3.000E11      0.000  0.000
CH2CO+O=HCO+HCO 2.520E11   0.000  1.350
HI+CH3=I+CH4 8.100E5 1.870  13.000
HI+HCO=I+CH2O 9.228E9      0.860  28.332
IO.+CH2OH=HIO+CH2O 1.708E13 0.000  0.000
```

```
IO.+CH3O=HIO+CH2O 9.570E12  -0.173  -1.806E-3
OH+I=HIO 1.499E13    -0.150  0.292
O2+CO=CO2+O 1.260E13 0.000   47.038
H2O2+C3H5=HO2+C3H6 2.973E3  2.386   9.690
H2O2+C2H3=C2H4+HO2 28.800   3.100   6.940
HI+OH=H2O+I 1.200E6  2.000   10.100
C4H10+C2H3=C2H4+C4H9_1 8.700E3      2.900   8.830
C4H10+C2H3=C2H4+C4H9_2 2.040E3      3.100   8.820
C2H3+O=CO+CH3 3.000E13      0.000   0.000
HI+O=>OH+I 1.700E8   1.500   6.600
OH+C2H5=H2O+C2H4 1.206E13   0.000   0.000
CO2+CH=HCO+CO 3.430E12      0.000   0.686
HI+H=I+H2 2.400E8    1.500   9.400
CH2+O=CO+H+H 7.200E13       0.000   0.000
CH3+O=CH2O+H 8.430E13       0.000   0.000
HIO+O=>IO.+OH 1.000E13      0.000   4.690
I+C2H5=C2H4+HI 9.570E12     -0.173  -1.806E-3
C3H6+C2H3=C3H5+C2H4 2.319E13        0.000   7.500
CH2O+CH=CH2+HCO 9.640E13    0.000   -0.516
H+CH2OH=CH3+OH 1.020E13     0.000   0.000
C3H6+H=C3H5+H2 1.299E6      2.380   2.800
CH2+CH2=C2H2+H2 1.200E13    0.000   0.796
C2H2+CH2=>C2H+CH3 1.846E10  0.860   28.332
CH3+HCO=CH4+CO 1.200E14     0.000   0.000
H+CH2=CH+H2 6.020E12 0.000   -1.787
CH2O+C2H3=HCO+C2H4 5.420E3  2.810   5.860
CH4+O=CH3+OH 7.230E8 1.560   8.481
OH+HO2=H2O+O2 2.890E13      0.000   -0.497
C3H6+C2H5=C2H6+C3H5 1.680E12        0.000   12.400
C3.CCI+CH3O=C3CCI+CH2O 9.570E12     -0.173  -1.806E-3
C3.CCI+CH2OH=C3CCI+CH2O 2.410E12    0.000   0.000
HI+HO2=I+H2O2 1.400E4       2.690   11.300
C3H6+IO.=C3H5+HIO 6.824E7   1.700   3.644
CH2O+C2H=HCO+C2H2 1.443E8   1.320   5.129
O+HO2=O2+OH 3.190E13 0.000   0.000
IO.+C2H5=HIO+C2H4 1.206E13  0.000   0.000
O2+C2H3=HCO+CH2O 5.420E12   0.000   0.000
CH2+CH2=C2H2+H+H 1.080E14   0.000   0.796
C4H10+C2H=C2H2+C4H9_1 3.612E12      0.000   0.000
C4H10+C2H=C2H2+C4H9_2 2.420E12      0.000   0.000
H2O2+C3.CCI=C3CCI+HO2 1.824E15      -0.700  7.200
O2+CH2=CO2+H2 5.430E12      0.000   1.491
C3CCI+CH2=>C3.CCI+CH3 1.500E6       2.326   3.700
C3H6+CH3=C3H5+CH4 241.200   2.920   7.160
CH3+CH3=C2H5+H 3.010E13     0.000   13.507
CH4+C2H=CH3+C2H2 1.812E12   0.000   0.500
CH2CO+O=CH2+CO2 1.330E12    0.000   1.350
C2H6+C2H3=C2H5+C2H4 8.700E3 2.900   8.830
CH3O=CH2OH 8.893E9   0.769   38.000
HIO+C2H=IO.+C2H2 1.210E12   0.000   0.000
C3H6+C2H=C3H5+C2H2 1.806E12 0.000   0.000
C2H4+CH2=>C2H3+CH3 1.908E9 1.305   5.685
C3CCI+C2H3=C3.CCI+C2H4 1.305E4      2.900   8.830
CH2CO+OH=CH3+CO2 2.520E12   0.000   0.000
C3H6+O=>C3H5+OH 2.565E4     3.050   3.123
H+HO2=H2+O2 4.280E13 0.000   1.409
O2+H=OH+O 9.756E13   0.000   14.838
C2H3+C2H5=C2H4+C2H4 7.590E13        -0.700  0.000
HI+C2H3=I+C2H4 9.228E9      0.860   28.332
CH2O+IO.=HIO+HCO 6.483E7    1.250   6.595
CH2CO+O=HCO+H+CO 2.520E11   0.000   1.350
H+CH2(S)=CH2+H 2.000E14     0.000   0.000
C2H+C2H5=C2H2+C2H4 1.806E12 0.000   0.000
C3H5+C3H5=C3H4+C3H6 8.430E10        0.000   -0.260
H2O2+CH2=>HO2+CH3 28.800    3.100   6.940
O2+I=IO2. 6.859E12   0.089   3.250
C2H2+O=>C2H+OH 3.400E8      1.500   6.600
```

```
 CH3+HO2=CH3O+OH 1.800E13    0.000  0.000
 CO+HO2=CO2+OH 1.510E14      0.000  23.655
 O+C2H5=C2H4+OH 1.506E13     0.000  0.000
 C4H10+H=H2+C4H9_1 3.768E8   1.750  7.510
 C4H10+H=H2+C4H9_2 5.200E8   1.690  4.780
 H2+C2H=C2H2+H 1.080E13      0.000  2.170
 H2O2+C2H=HO2+C2H2 2.420E12 0.000  0.000
 CO+H=HCO 1.180E11   0.000  2.720
 C3.CCI+C2H5=C3CCI+C2H4 1.149E13    -0.350 0.000
 C2H6+CH3=C2H5+CH4 1.510E-7 6.000  6.044
 O2+C3H5=HO2+C3H4 1.210E12  0.000  13.550
 C2H3+CH3O=C2H4+CH2O 9.570E12       -0.173 -1.806E-3
 C2H3+CH2OH=C2H4+CH2O 3.010E13      0.000  0.000
 C2H+O=CH+CO 1.000E13 0.000  0.000
 CH2CO+OH=CH2OH+CO 4.680E12 0.000  0.000
 H+C2H5=C2H4+H2 1.806E12    0.000  0.000
 C2H2+CH=C2H+CH2 2.110E14   0.000  -0.122
 C2H4+O=CH2CO+H2 6.800E5    1.880  0.179
 C3CCI+C2H=C3.CCI+C2H2 5.418E12     0.000  0.000
 C2CYCCOC=CH2O+C4H8 3.800E15 0.000  60.622
 C2H+OH=CH2+CO 1.810E13     0.000  0.000
 C4H9_2+C3H5=C3H4+C4H10 4.580E12    -0.350 -0.130
 C4H9_1+C3H5=C3H4+C4H10 9.640E11    0.000  -0.130
 C2H4+O=CH3+HCO 8.130E6     1.880  0.179
 I+O=IO. 1.000E13    0.000  0.000
 C2H+HO2=C2H2+O2 3.000E11   0.000  0.000
 C4H9_2+C2H5=C2H4+C4H10 1.056E14    -0.700 0.000
 C4H9_1+C2H5=C2H4+C4H10 1.149E13    -0.350 0.000
 I+C3H5=C3H4+HI 5.413E12    -0.089 -0.037
 CH3+OH=CH2(S)+H2O 7.230E13 0.000  2.781
 H2O+CH2=>OH+CH3 1.447E8    1.433  9.820
 C2H2+OH=C2H+H2O 6.000E13   0.000  12.910
 C2H5+C2H5=C2H6+C2H4 1.149E13       -0.350 0.000
 CH2O+C2H5=C2H6+HCO 5.500E3 2.810  5.860
 HI+C4H9_2=C4H10+I 9.228E9  0.860  28.332
 HI+C4H9_1=C4H10+I 9.228E9  0.860  28.332
 O2+C2H5=HO2+C2H4 6.300E10  0.000  0.000
 HIO+OH=IO.-H2O 17.300      3.400  -1.140
 C4H10+O=>OH+C4H9_1 5.130E4 3.050  3.123
 C4H10+O=>OH+C4H9_2 1.908E5 2.710  2.106
 C2H5+CH3O=C2H6+CH2O 9.570E12       -0.173 -1.806E-3
 C2H5+CH2OH=C2H6+CH2O 2.410E12      0.000  0.000
 C2H6+HO2=H2O2+C2H5 1.320E13 0.000  20.456
 C2H4+CH2(S)=C3H6 9.640E13  0.000  0.000
 C4H9_2+CH3O=C4H10+CH2O 9.570E12    -0.173 -1.806E-3
 C4H9_2+CH2OH=CH2O+C4H10 2.350E12   0.000  0.000
 CH2+C2H5=CH3+C2H4 1.506E13 0.000  0.000
 C4H9_1+CH3O=CH2O+C4H10 9.570E12    -0.173 -1.806E-3
 C4H9_1+CH2OH=C4H10+CH2O 2.410E12   0.000  0.000
 C4H10+OH=H2O+C4H9_1 1.105E8 1.800  0.278
 C4H10-OH=H2O+C4H9_2 3.600E6 2.000  -1.133
 C3H6+C3.CCI=C3CCI+C3H5 1.680E12    0.000  12.400
 CH2O+CH3=CH4+HCO 4.090E12  0.000  8.827
 CH2O+C4H9_2=C4H10+HCO 1.080E11     0.000  6.960
 CH2O+C4H9_1=C4H10+HCO 5.500E3      2.810  5.860
 C2H2+CH2=C3H4 1.200E13     0.000  6.615
 O2+CH=CO2+H 1.660E13 0.000  0.000
 H+HCO=CO+H2 9.030E13 0.000  0.000
 HCO+C3H5=CH2O+C3H4 5.413E12 -0.089 -0.037
 C3H6+OH=C3H5+H2O 6.824E7   1.700  3.644
 CO2+CH2=CH2O+CO 2.350E10   0.000  0.000
 CH4+H=CH3+H2 1.224E8 1.870  10.590
 H+O+m=OH+m   1.180E19      -1.000 0.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 H+H+m=H2+m   1.870E18      -1.000 0.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
```

```
CO2/1.5/ H2/0.0/ O2/0.4/
 CH2C+m=HCO+H+m       1.400E36       -5.540 96.651
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 C2H2+H(+m)=C2H3(+m)  8.430E12       0.000  2.582
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
LOW/3.430E18  0.000  1.469/
TROE/1.0      1.0    1.0    1231.0/

 H+CH3(+m)=CH4(+m)    1.688E14       0.000  0.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
LOW/1.408E24  -1.800 0.000/
TROE/0.37     3315.0 61.0/

 C2H4+m=C2H2+H2+m     9.970E16       0.000  71.505
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 CH2O+m=H2+CO+m       3.260E36       -5.540 96.651
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 C2H4+H(+m)=C2H5(+m)  3.970E91.280  1.290
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
LOW/1.350E19  0.000  0.755/
TROE/0.76     40.0   1025.0/

 CH2(S)+m=CH2+m       1.510E13       0.000  0.000
C2H2/3.2/ H2O/6.5/ C2H6/1.44/ N2/0.4/ CH4/0.48/ CO/0.75/
C2H4/1.6/ Ar/0.24/ CO2/1.5/ O2/0.4/
 O2+H+m=HO2+m 2.100E18       -0.800 0.000
H2O/0.0/ C2H6/3.0/ N2/0.67/ CH4/3.0/ CO/0.75/ Ar/0.29/
CO2/1.5/ O2/0.4/
 CH2CO+m=CH2+CO+m     6.570E15       0.000  57.580
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 H+OH+m=H2O+m 5.530E22       -2.000 0.000
H2O/2.55/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.15/
CO2/1.5/ O2/0.4/
 O+O+m=O2+m   5.400E13       0.000  -1.787
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 CH3O+m=CH2O+H+m      1.550E14       0.000  13.488
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 CH2OH+m=CH2O+H+m     1.260E16       0.000  30.005
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 OH+OH(+m)=H2O2(+m)   7.230E13       -0.370 0.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
LOW/5.530E19  -0.760 0.000/
TROE/1.0      1.0    1.0    1040.0/

 CH3+CH3(+m)=C2H6(+m) 3.610E13       0.000  0.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
LOW/3.630E41  -7.000 2.762/
TROE/0.62     73.0   1180.0/

 CH3+m=CH2+H+m2.910E16       0.000  90.573
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 CO+O+m=CO2+m 1.540E15       0.000  3.000
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
```

```
 C2H4+m=C2H3+H+m      7.400E17       0.000  96.534
H2O/6.5/ C2H6/3.0/ N2/0.4/ CH4/3.0/ CO/0.75/ Ar/0.35/
CO2/1.5/ O2/0.4/
 C2H6(+m)=>C2H5+H(+m)1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /  -30.21086    1.35380   -0.24012   -0.01985 /
CHEB /   29.72985    0.46763    0.15072   -0.01199 /
CHEB /   -1.30331    0.18788    0.08155    0.01106 /
CHEB /   -0.64755    0.04845    0.03346    0.01438 /
CHEB /   -0.32010    0.00130    0.01104    0.01266 /
CHEB /   -0.15549   -0.00831    0.00424    0.01197 /
CHEB /   -0.07461   -0.00800    0.00298    0.01182 /


 O2+C3CC.(+m)=>C3CCOO.(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   10.85361    0.54313   -0.08517   -0.01288 /
CHEB /   -1.75749    0.89361   -0.11814   -0.02899 /
CHEB /   -0.71167    0.46459   -0.01558   -0.02832 /
CHEB /   -0.22189    0.07980    0.04981   -0.01433 /
CHEB /    0.00602   -0.09574    0.04866    0.00524 /
CHEB /    0.04975   -0.08956    0.01610    0.01595 /
CHEB /    0.01221   -0.02106   -0.00430    0.01362 /


 O2+C3CC.(+m)=>C3.CCOOH(+m)  1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /    8.40216   -0.67693   -0.23178   -0.00757 /
CHEB /    0.50713    1.87918   -0.19213   -0.07211 /
CHEB /   -0.53820    0.70265    0.07947   -0.06124 /
CHEB /   -0.45477    0.01666    0.11290   -0.00132 /
CHEB /   -0.16171   -0.15371    0.04509    0.02631 /
CHEB /    0.00725   -0.09477   -0.00014    0.02115 /
CHEB /    0.04429   -0.01283   -0.00453    0.01119 /


 O2+C3CC.(+m)=>C2CYCCOC+OH(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /    7.40202   -2.55326   -0.24355   -0.00321 /
CHEB /    3.18520    1.93696   -0.15461   -0.07508 /
CHEB /   -0.28250    0.58845    0.12550   -0.05236 /
CHEB /   -0.44566   -0.08241    0.11175    0.01255 /
CHEB /   -0.13782   -0.17268    0.01604    0.02758 /
CHEB /    0.01849   -0.06674   -0.02802    0.01128 /
CHEB /    0.04138    0.01876   -0.02225   -0.00156 /


 C3CCOO.(+m)=>O2+C3CC.(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   -1.69801    0.51270   -0.10027   -0.01623 /
CHEB /    9.85647    0.83769   -0.14706   -0.03584 /
CHEB /   -1.25563    0.42205   -0.04116   -0.03556 /
CHEB /   -0.56502    0.05528    0.02846   -0.02216 /
CHEB /   -0.20977   -0.10251    0.03131   -0.00326 /
CHEB /   -0.06397   -0.08286    0.00187    0.00694 /
CHEB /   -0.02764   -0.00711   -0.01627    0.00462 /


 C3CCOO.(+m)=>C3.CCOOH(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   -0.71931    0.24455    3.78392    1.87203 /
```

```
CHEB /    2.61471    0.19041    7.57601    3.68014 /
CHEB /   -4.78307   -0.40312    7.46341    3.53181 /
CHEB /   -4.14846   -0.85554    7.07750    3.32834 /
CHEB /   -3.53298   -1.01885    6.42722    3.04904 /
CHEB /   -2.96703   -0.97085    5.59745    2.67662 /
CHEB /   -2.41930   -0.81762    4.64386    2.22348 /


 C3CCOO.(+m)=>C2CYCCOC+OH(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   -1.84081   -0.87652   -0.23156   -0.01101 /
CHEB /   11.44259    1.67079   -0.24882   -0.06895 /
CHEB /   -0.82107    0.72969    0.00052   -0.07199 /
CHEB /   -0.45975    0.12121    0.06609   -0.02490 /
CHEB /   -0.11454   -0.08993    0.03153    0.00619 /
CHEB /    0.01716   -0.09064   -0.00248    0.00819 /
CHEB /    0.02387   -0.03121   -0.01327    0.00169 /


 C5H11IO2(+m)=>C3CC.+IO2.(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /  -24.90227    1.81731   -0.09916   -0.03259 /
CHEB /   31.67438    0.25766    0.13568    0.04075 /
CHEB /   -2.21862   -0.06811   -0.02855   -0.00181 /
CHEB /   -0.93456   -0.01802   -0.01451   -0.00866 /
CHEB /   -0.34394    0.00820    0.00401    0.00056 /
CHEB /   -0.09942    0.00464    0.00342    0.00196 /
CHEB /   -0.01169   -0.00068   -0.00012    0.00028 /


 C5H11IO2(+m)=>C3CCOO.+I(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   -9.75534    0.63164   -0.02696    0.00080 /
CHEB /   21.07458    1.01547   -0.02300   -0.00130 /
CHEB /   -2.18800    0.48455    0.02582   -0.00324 /
CHEB /   -1.10506    0.05434    0.03347    0.00058 /
CHEB /   -0.34664   -0.10412    0.00727    0.00347 /
CHEB /    0.01444   -0.08054   -0.01146    0.00125 /
CHEB /    0.10779   -0.02255   -0.00921   -0.00159 /


 CH3O2+I(+m)=>CH3+IO2.(+m)  1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /    0.41221 -4.22491E-8 -3.10979E-8 -1.60378E-8 /
CHEB /   -9.79867 -7.91359E-8 -1.67630E-8 -4.55600E-8 /
CHEB /    0.40267 -1.04740E-8 -8.88877E-9 -3.53477E-9 /
CHEB /   -0.02724 1.70772E-9 1.29849E-9 6.32724E-10 /
CHEB /   -0.17765 -1.29644E-9 -2.07407E-10 -7.71529E-10 /
CHEB /    0.09420 2.53950E-10 -1.92510E-10 2.38346E-10 /
CHEB /    0.05738 6.22793E-10 2.09377E-10 3.29578E-10 /


 CH3O2+I(+m)=>CH3O+IO.(+m)  1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   12.25058   -0.00021   -0.00014 -8.12258E-5 /
CHEB /   -0.49455   -0.00030   -0.00021   -0.00012 /
CHEB /   -0.11128   -0.00010 -7.13903E-5 -4.02505E-5 /
CHEB /    0.02458 -1.92492E-6 -1.33011E-6 -7.36383E-7 /
CHEB /   -0.00308 4.93682E-6 3.44542E-6 1.94580E-6 /
CHEB /   -0.00061 -1.20915E-6 -8.44073E-7 -4.76927E-7 /
CHEB /    0.00038 -8.49832E-8 -5.92463E-8 -3.33866E-8 /
```

```
 C3H6(+m)=>C2H3+CH3(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -23.66750    0.39840   -0.06268   -0.01849 /
CHEB /   31.96562    0.67851   -0.09085   -0.04259 /
CHEB /   -0.97915    0.42618   -0.03178   -0.04518 /
CHEB /   -0.60221    0.19202    0.00328   -0.03763 /
CHEB /   -0.33167    0.05211    0.00692   -0.02643 /
CHEB /   -0.16057   -0.00184   -0.00256   -0.01878 /
CHEB /   -0.06600   -0.01000   -0.00950   -0.01529 /


 C3H6(+m)=>C3H5+H(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -25.47612    0.17082   -0.01356   -0.01309 /
CHEB /   26.39567    0.31607   -0.02340   -0.02562 /
CHEB /   -0.86649    0.24895   -0.01433   -0.02388 /
CHEB /   -0.50513    0.16377   -0.00477   -0.02094 /
CHEB /   -0.30438    0.08577    0.00104   -0.01714 /
CHEB /   -0.17206    0.03097    0.00185   -0.01314 /
CHEB /   -0.08687    0.00230   -0.00056   -0.00962 /


 C3.CCOOH(+m)=>C2CYCCOC+OH(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    5.03491    0.64274   -0.12837   -0.00311 /
CHEB /    4.52290    0.90022   -0.10416   -0.04400 /
CHEB /   -0.41490    0.33517    0.04618   -0.04409 /
CHEB /   -0.17624    0.03767    0.05376   -0.00681 /
CHEB /   -0.05678   -0.03261    0.01317    0.01038 /
CHEB /   -0.00724   -0.03005   -0.00284    0.00356 /
CHEB /    0.01179   -0.01795   -0.00125   -0.00330 /


 C3.CCOOH(+m)=>C3CCOO.(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    6.44693    0.93703   -0.17213   -0.00810 /
CHEB /    0.82093    1.50656   -0.21117   -0.04515 /
CHEB /   -0.67550    0.82980   -0.02627   -0.05537 /
CHEB /   -0.31311    0.30196    0.04893   -0.02644 /
CHEB /   -0.07522    0.03357    0.04018    0.00257 /
CHEB /    0.02910   -0.05437    0.01534    0.01138 /
CHEB /    0.04827   -0.05741    0.00323    0.00743 /


 C3.CCOOH(+m)=>O2+C3CC.(+m)  1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    1.09912   -0.70132   -0.24897   -0.00721 /
CHEB /    6.11802    1.80239   -0.20761   -0.07712 /
CHEB /   -0.94182    0.63659    0.06602   -0.06339 /
CHEB /   -0.64491   -0.01581    0.09743   -0.00280 /
CHEB /   -0.27281   -0.16020    0.03330    0.02202 /
CHEB /   -0.04505   -0.08489   -0.00908    0.01479 /
CHEB /    0.03228    0.00591   -0.01367    0.00382 /


 H2O2(+m)=>HO2+H(+m)  1.0E0  0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -31.07363    1.99952   -0.00033   -0.00019 /
CHEB /   25.63916    0.00054    0.00038    0.00021 /
CHEB /   -0.95520 -5.13481E-5 -3.57545E-5 -2.01142E-5 /
```

```
CHEB /   -0.41146 -1.68662E-5 -1.17755E-5 -6.65488E-6 /
CHEB /   -0.18952 -4.33052E-6 -3.01900E-6 -1.70667E-6 /
CHEB /   -0.08791 -7.40041E-7 -5.19785E-7 -2.93999E-7 /
CHEB /   -0.03779 3.80215E-7 2.69068E-7 1.51655E-7 /


 C3CCOO.+I(+m)=>C5H11IO2(+m) 1.0E0  0.0  0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   11.05328    0.63214   -0.02681    0.00084 /
CHEB /   -2.71746    1.01640   -0.02272   -0.00123 /
CHEB /   -1.78068    0.48530    0.02605   -0.00319 /
CHEB /   -0.75170    0.05483    0.03363    0.00062 /
CHEB /   -0.07333   -0.10392    0.00736    0.00350 /
CHEB /    0.20430   -0.08060   -0.01144    0.00127 /
CHEB /    0.22447   -0.02280   -0.00924   -0.00159 /


 C3CCOO.+I(+m)=>C3CC.+IO2.(+m)      1.0E0  0.0  0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   -1.67837   -0.25750   -0.12839   -0.03291 /
CHEB /   12.15104    0.36576    0.17653    0.03997 /
CHEB /   -0.80244   -0.08412   -0.02973    0.00313 /
CHEB /   -0.95079   -0.06384   -0.03837   -0.01488 /
CHEB /   -0.04403    0.03748    0.01566    0.00049 /
CHEB /    0.02680    0.02042    0.01384    0.00683 /
CHEB /   -0.21979   -0.02254   -0.00967   -0.00057 /


 C2.C(COOH)2(+m)=>C(COOH)CYCCOC+OH(+m)     1.0E0  0.0  0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    9.89449    1.99981   -0.00013 -7.32079E-5 /
CHEB /   -0.17253   -0.00032   -0.00023   -0.00013 /
CHEB /   -0.00169   -0.00028   -0.00020   -0.00011 /
CHEB /    0.00340   -0.00022   -0.00015 -8.73055E-5 /
CHEB /    0.01026   -0.00017   -0.00012 -6.59051E-5 /
CHEB /    0.01516   -0.00012 -8.49017E-5 -4.78454E-5 /
CHEB /    0.00971 -8.43496E-5 -5.87914E-5 -3.31230E-5 /


 C2.C(COOH)2(+m)=>C2C(COOH)COO.(+m) 1.0E0  0.0  0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    5.69904    0.93219   -0.13429   -0.00560 /
CHEB /   -1.49104   -1.55290    0.17471    0.02451 /
CHEB /   -0.97049    0.90172   -0.01139   -0.03401 /
CHEB /    0.57082   -0.35897   -0.06877    0.01794 /
CHEB /   -0.28804    0.08654    0.05900    0.00244 /
CHEB /    0.14000    0.00281   -0.02732   -0.00828 /
CHEB /   -0.06749   -0.02330    0.01028    0.00445 /


 C2.C(COOH)2(+m)=>C3.CCOOH+O2(+m)   1.0E0  0.0  0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    2.23050   -0.75024   -0.18826   -0.00336 /
CHEB /   -5.70947   -1.85552    0.17219    0.04196 /
CHEB /   -0.84431    0.75271    0.07852   -0.04299 /
CHEB /    0.70081   -0.08397   -0.12077    0.00256 /
CHEB /   -0.31888   -0.07653    0.04962    0.01940 /
CHEB /    0.09916    0.04187   -0.00195   -0.01190 /
CHEB /   -0.02515   -0.00591   -0.00596    0.00123 /


 C3CCOO.+CH3(+m)=>C3CC.+CH3O2(+m)   1.0E0  0.0  0.0
```

```
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    5.18448   -0.44941   -0.17548   -0.02011 /
CHEB /   -5.92237   -0.55681   -0.19513   -0.00549 /
CHEB /    0.56215   -0.04071    0.01834    0.02567 /
CHEB /    0.00354    0.08095    0.03752    0.00516 /
CHEB /   -0.02880   -0.01014   -0.01423   -0.00992 /
CHEB /    0.01414   -0.01736   -0.00700    0.00053 /
CHEB /   -0.01120    0.01066    0.00777    0.00372 /


 CH3+O2(+m)=>CH3O2(+m)       1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   10.67997    1.56312   -0.18419   -0.02870 /
CHEB /   -1.55257    0.40960    0.15497    0.01082 /
CHEB /   -0.71340    0.05811    0.03733    0.01437 /
CHEB /   -0.26288   -0.01768   -0.00241    0.00372 /
CHEB /   -0.05645   -0.01690   -0.00736   -0.00090 /
CHEB /    0.01962   -0.00716   -0.00413   -0.00131 /
CHEB /    0.03506   -0.00145   -0.00129   -0.00071 /


 CH3+O2(+m)=>CH3O+O(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    0.16789   -0.00607   -0.00421   -0.00235 /
CHEB /    9.66771    0.00680    0.00472    0.00263 /
CHEB /    0.28092   -0.00024   -0.00016 -7.91294E-5 /
CHEB /    0.02882   -0.00039   -0.00027   -0.00015 /
CHEB /   -0.23483   -0.00023   -0.00016 -8.95250E-5 /
CHEB /   -0.28926   -0.00011 -7.55469E-5 -4.27758E-5 /
CHEB /   -0.14728 -1.70496E-5 -1.19335E-5 -6.77901E-6 /


 CH3O(+m)=>O+CH3(+m)  1.0E0  0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -23.39327    1.73791   -0.12983   -0.03414 /
CHEB /   27.65208    0.39784    0.20563    0.05520 /
CHEB /   -0.80890    0.02882    0.04063    0.03301 /
CHEB /   -0.38856   -0.02223   -0.00936    0.00206 /
CHEB /   -0.18707   -0.03699   -0.02519   -0.00994 /
CHEB /   -0.09734   -0.05017   -0.03625   -0.01708 /
CHEB /   -0.04956   -0.05740   -0.04345   -0.02317 /


 C4H10(+m)=>C4H9_1+H(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -29.75032    0.43883   -0.09906   -0.01074 /
CHEB /   29.39028    0.72615   -0.14534   -0.03009 /
CHEB /   -1.76930    0.40837   -0.05189   -0.03418 /
CHEB /   -0.98592    0.12143    0.01085   -0.02350 /
CHEB /   -0.49358   -0.03171    0.02377   -0.00659 /
CHEB /   -0.20210   -0.06816    0.01091    0.00427 /
CHEB /   -0.04759   -0.05129   -0.00239    0.00695 /


 C4H10(+m)=>C2H5+C2H5(+m)    1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -17.65202    0.31667   -0.06149   -0.00963 /
CHEB /   26.65288    0.56320   -0.10451   -0.01969 /
CHEB /   -1.23823    0.38850   -0.06126   -0.01920 /
CHEB /   -0.77728    0.18985   -0.01862   -0.01506 /
CHEB /   -0.43605    0.03883    0.00518   -0.00764 /
```

```
CHEB /   -0.19919   -0.03726    0.00896   -0.00040 /
CHEB /   -0.05946   -0.05284    0.00280    0.00352 /


 C4H10(+m)=>C4H9_2+H(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /  -29.05447    0.41143   -0.08849   -0.01023 /
CHEB /   28.46353    0.69453   -0.13542   -0.02580 /
CHEB /   -1.79165    0.41015   -0.05493   -0.02891 /
CHEB /   -0.98535    0.13894    0.00407   -0.02071 /
CHEB /   -0.49963   -0.01873    0.02039   -0.00662 /
CHEB /   -0.20653   -0.06556    0.01094    0.00335 /
CHEB /   -0.05220   -0.05431   -0.00139    0.00609 /


 C4H9_2(+m)=>C3H6+CH3(+m)    1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   -0.15181    0.55581   -0.08222   -0.01312 /
CHEB /    9.43589    0.87671   -0.10189   -0.03425 /
CHEB /   -0.97726    0.40865   -0.00792   -0.03206 /
CHEB /   -0.42549    0.04261    0.02626   -0.01279 /
CHEB /   -0.09621   -0.10158    0.00964    0.00396 /
CHEB /    0.03710   -0.09300   -0.01045    0.00753 /
CHEB /    0.05438   -0.03816   -0.01278    0.00397 /


 C3CC.+I(+m)=>C3CCI(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /   12.06741    0.50663   -0.04142   -0.00416 /
CHEB /   -0.95871    0.86830   -0.05769   -0.01024 /
CHEB /   -0.65026    0.52425   -0.00611   -0.01219 /
CHEB /   -0.25184    0.17382    0.02803   -0.00908 /
CHEB /    0.02226   -0.03914    0.02632   -0.00265 /
CHEB /    0.13089   -0.09525    0.00526    0.00120 /
CHEB /    0.11915   -0.06161   -0.01024    0.00018 /


 C3CC.+I(+m)=>C3.CCI+H(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /  -13.96369   -0.48206   -0.19931   -0.02707 /
CHEB /   15.69824    0.54048    0.19111   -0.00194 /
CHEB /   -1.72120   -0.01579    0.02254    0.02380 /
CHEB /   -0.95999   -0.11033   -0.04464   -0.00124 /
CHEB /   -0.12400   -0.01287   -0.02043   -0.01325 /
CHEB /   -0.28074    0.01407    0.00616   -0.00043 /
CHEB /    0.03536    0.00609    0.00739    0.00508 /


 C3CC.(+m)=>C4H8+CH3(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /    0.26515    0.51585   -0.09400   -0.01335 /
CHEB /    9.18189    0.81664   -0.13360   -0.03124 /
CHEB /   -1.00406    0.36577   -0.03935   -0.02896 /
CHEB /   -0.39705    0.00264    0.00684   -0.01180 /
CHEB /   -0.07780   -0.13495    0.00286    0.00454 /
CHEB /    0.04336   -0.10996   -0.00798    0.00885 /
CHEB /    0.03778   -0.03842   -0.00354    0.00604 /


 C4H2(+m)=>C2H+C2H(+m)       1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
```

```
CHEB /  -50.03820    0.11515   -0.05355    0.01038 /
CHEB /   53.16303    0.16767   -0.07149    0.00707 /
CHEB /   -0.83569    0.08099   -0.02861   -0.00347 /
CHEB /   -0.44565    0.01723    0.00029   -0.00810 /
CHEB /   -0.22845   -0.00457    0.00761   -0.00670 /
CHEB /   -0.10627   -0.00427    0.00534   -0.00422 /
CHEB /   -0.04427   -0.00047    0.00239   -0.00252 /


 C3CCI(+m)=>C3CC.+I(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   -5.02518    0.50663   -0.04142   -0.00416 /
CHEB /   15.07548    0.86830   -0.05769   -0.01024 /
CHEB /   -1.13674    0.52425   -0.00611   -0.01219 /
CHEB /   -0.58379    0.17382    0.02803   -0.00908 /
CHEB /   -0.20839   -0.03914    0.02632   -0.00265 /
CHEB /   -0.01861   -0.09525    0.00526    0.00120 /
CHEB /    0.03356   -0.06161   -0.01024    0.00018 /


 C3CCI(+m)=>C3.CCI+H(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -31.65494    1.59346   -0.17376   -0.02533 /
CHEB /   29.25089    0.50939    0.21230    0.02471 /
CHEB /   -1.96150    0.03474    0.03904    0.01940 /
CHEB /   -0.88575   -0.06999   -0.03853   -0.01993 /
CHEB /   -0.36207   -0.04439   -0.04090   -0.03496 /
CHEB /   -0.13615   -0.01185   -0.02093   -0.02604 /
CHEB /   -0.05577    0.00281   -0.00423   -0.00966 /


 C3.CCOOH+O2(+m)=>C2C(COOH)COO.(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   11.00255    0.43385   -0.10964   -0.00696 /
CHEB /   -1.49793    0.71170   -0.16679   -0.01992 /
CHEB /   -0.54604    0.36914   -0.06008   -0.02663 /
CHEB /   -0.16032    0.07320    0.01608   -0.02114 /
CHEB /   -0.00386   -0.05235    0.03184   -0.00801 /
CHEB /    0.01711   -0.04436    0.01586    0.00060 /
CHEB /   -0.00816   -0.00068    0.00350    0.00090 /


 C4H9_1(+m)=>C2H4+C2H5(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    1.10048    0.87737   -0.09991    0.00298 /
CHEB /    8.47339    0.99083    0.02748   -0.03564 /
CHEB /   -1.19763    0.28833    0.06936   -0.01485 /
CHEB /   -0.37199   -0.01882    0.02022   -0.00839 /
CHEB /    0.00251   -0.06712   -0.01333   -0.01661 /
CHEB /    0.10267   -0.03198   -0.01729   -0.02211 /
CHEB /    0.07934 -2.66641E-5   -0.01113   -0.02139 /


 C3H5(+m)=>C3H4+H(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -15.64652    0.27458   -0.06538   -0.00441 /
CHEB /   17.00873    0.48971   -0.10975   -0.01143 /
CHEB /   -1.09835    0.34398   -0.06098   -0.01587 /
CHEB /   -0.61867    0.18233   -0.01336   -0.01650 /
CHEB /   -0.32895    0.06215    0.01353   -0.01199 /
CHEB /   -0.14987    0.00056    0.01900   -0.00575 /
CHEB /   -0.05220   -0.01731    0.01350   -0.00150 /
```

```
 C3.CCI(+m)=>C4H8+CH2I(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    3.92123    0.93808   -0.07904   -0.00239 /
CHEB /    5.95327    1.08632    0.02649   -0.03189 /
CHEB /   -1.03241    0.20636    0.07149   -0.01187 /
CHEB /   -0.15450   -0.10187    0.01037   -0.00669 /
CHEB /    0.08329   -0.07328   -0.01997   -0.01601 /
CHEB /    0.04868   -0.00444   -0.01507   -0.01901 /
CHEB /   -0.01463    0.01389   -0.00853   -0.01621 /


 C2C(COOH)CCO.(+m)=>C3.CCOOH+O2(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    0.57168    0.36441   -0.12759    0.01103 /
CHEB /    8.31325    0.58439   -0.19952    0.01288 /
CHEB /   -1.13029    0.27288   -0.08456   -0.00254 /
CHEB /   -0.52302    0.01784    0.00202   -0.00916 /
CHEB /   -0.22320   -0.06840    0.02705   -0.00873 /
CHEB /   -0.09489   -0.03154    0.01694   -0.01069 /
CHEB /   -0.04551    0.02688    0.00659   -0.01686 /


 C2C(COOH)COO.(+m)=>C2.C(COOH)2(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -12.24889    4.71216   13.86752   -5.79656 /
CHEB /   -7.66945    4.81210   26.21568  -10.32931 /
CHEB /  -12.61697    3.13842   21.93995   -6.81079 /
CHEB /   -8.65545    0.82972   15.70632   -1.80011 /
CHEB /   -4.16725   -1.57026    8.68068    3.61153 /
CHEB /   -0.05266   -3.54777    2.15639    8.24104 /
CHEB /    2.91195   -4.71508   -2.73136   11.07524 /


 C2C(COOH)COO.(+m)=>C(COOH)CYCCOC+OH(+m)   1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /    1.98237    0.29549   -0.10351    0.00800 /
CHEB /    6.18840    0.50807   -0.17502    0.01097 /
CHEB /   -0.46839    0.31003   -0.09993 4.64095E-5 /
CHEB /   -0.26251    0.10743   -0.02591   -0.00889 /
CHEB /   -0.11015   -0.01288    0.01534   -0.01211 /
CHEB /   -0.03172   -0.03737    0.02271   -0.01203 /
CHEB /   -0.00830   -0.00946    0.01474   -0.01241 /


 C2H2(+m)=>C2H+H(+m)  1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -42.27897    0.00645   -0.00446    0.00248 /
CHEB /   41.70493   -0.00243    0.00168   -0.00093 /
CHEB /   -0.63764    0.00042   -0.00030    0.00017 /
CHEB /   -0.29389   -0.00086    0.00059   -0.00032 /
CHEB /   -0.14414   -0.00034    0.00024   -0.00013 /
CHEB /   -0.06754 4.32522E-5 -2.70779E-5 1.19648E-5 /
CHEB /   -0.03092 7.37030E-5 -4.95826E-5 2.60021E-5 /


 CH3O2(+m)=>CH3O+O(+m)       1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -13.32330    1.99455   -0.00379   -0.00212 /
CHEB /   18.26667    0.00634    0.00440    0.00245 /
```

```
CHEB /   -0.67561   -0.00055   -0.00038   -0.00020 /
CHEB /   -0.31367   -0.00040   -0.00028   -0.00016 /
CHEB /   -0.12991   -0.00011 -7.71277E-5 -4.40091E-5 /
CHEB /   -0.04234 -4.07718E-6 -2.96159E-6 -1.79744E-6 /
CHEB /   -0.00504 1.98954E-5 1.38755E-5 7.82143E-6 /


 CH3O2(+m)=>CH3+O2(+m)       1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /    0.37131    1.56312   -0.18419   -0.02870 /
CHEB /    8.18966    0.40960    0.15497    0.01082 /
CHEB /   -0.84577    0.05811    0.03733    0.01437 /
CHEB /   -0.33422   -0.01769   -0.00241    0.00372 /
CHEB /   -0.10223   -0.01690   -0.00736   -0.00090 /
CHEB /   -0.01138   -0.00716   -0.00413   -0.00131 /
CHEB /    0.01433   -0.00145   -0.00129   -0.00071 /


 C3H4+HCO=H2CCCH+CH2O 2.080E4       2.820  28.600
 C3H4+H=H2CCCH+H2 1.012E8   1.980  11.780
 C3CCI+C3H2=>C3.CCI+H2CCCH 2.610E4  2.900  8.830
 IO.+CH2HCO=HIO+CH2CO 5.413E12      -0.089 -0.037
      DUP
 IO.+CH2HCO=HIO+CH2CO 4.234E12      -0.050 -0.057
      DUP
 C3H4+HCCO=H2CCCH+CH2CO 5.880E13    0.000  13.100
 H2O2+C3H2=>HO2+H2CCCH 57.600       3.100  6.940
 H2CCCH+C3H5=C3H4+C3H4 2.410E12     0.000  0.000
 C2H+CH2HCO=C2H2+CH2CO 4.234E12     -0.050 -0.057
      DUP
 C2H+CH2HCO=C2H2+CH2CO 5.413E12     -0.089 -0.037
      DUP
 CH2HCO(+m)=>C2H3+O(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /       PCHEB / 0.01 100.0 /
CHEB / 7       4 /
CHEB /  -36.82857    1.78054   -0.11274   -0.02864 /
CHEB /   38.91195    0.34656    0.19237    0.07067 /
CHEB /   -0.95043    0.00285    0.02660    0.03674 /
CHEB /   -0.46037   -0.02956   -0.01181    0.00575 /
CHEB /   -0.21876   -0.03461   -0.02291   -0.00975 /
CHEB /   -0.09680   -0.03909   -0.03299   -0.02498 /
CHEB /   -0.03945   -0.03835   -0.03913   -0.03809 /


 C3H2+CH2HCO=>H2CCCH+CH2CO 8.468E12-0.050 -0.057
      DUP
 C3H2+CH2HCO=>H2CCCH+CH2CO 1.083E13-0.089 -0.037
      DUP
 C3CCI+HCCO=C3.CCI+CH2CO 1.305E4    2.900  8.830
 C2H2+CH2(S)=H2CCCH+H 1.750E14      0.000  0.000
 C4H2+O=C3H2+CO 7.890E12     0.000  1.347
 O2+CH2HCO=HO2+CH2CO 1.594E11       0.000  2.710
      DUP
 O2+CH2HCO=HO2+CH2CO 1.210E12       0.000  13.550
      DUP
 C4H2+OH=C3H2+HCO 6.680E12  0.000  -0.409
 C2H+OH=HCCO+H 2.000E13      0.000  0.000
 OH+HCCO=CH2O+CO 1.000E13    0.000  0.000
 HCCO+HO2=CH2CO+O2 3.000E11 0.000  0.000
 C3H5+CH2HCO=C3H6+CH2CO 5.413E12    -0.089 -0.037
      DUP
 C3H5+CH2HCO=C3H6+CH2CO 4.234E12    -0.050 -0.057
      DUP
 C3H4+C3H5=C3H6+H2CCCH 2.144E14     0.000  30.700
 H2CCCH+CH2HCO=C3H4+CH2CO 5.413E12 -0.089 -0.037
      DUP
```

```
 H2CCCH+CH2HCO=C3H4+CH2CO 4.234E12  -0.050 -0.057
       DUP
 O2+HCCO=CO+CO+OH 1.630E12  0.000  0.855
 CH3+CH2HCO=CH4+CH2CO 5.413E12      -0.089 -0.037
       DUP
 CH3+CH2HCO=CH4+CH2CO 4.234E12      -0.050 -0.057
       DUP
 HI+C3H2=>H2CCCH+I 1.846E10 0.860  28.332
 HCCO(+m)=>C2H+O(+m) 1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -48.52509    1.83318   -0.11805   -0.05700 /
CHEB /   48.51437    0.29549    0.13865    0.02886 /
CHEB /   -0.71277   -0.00080    0.02757    0.02573 /
CHEB /   -0.36124   -0.03290    0.02498    0.03436 /
CHEB /   -0.18671   -0.04225    0.00908    0.03069 /
CHEB /   -0.08614   -0.04171   -0.02542    0.00322 /
CHEB /   -0.03193   -0.03234   -0.04873   -0.02892 /


 C3H4+CH3=H2CCCH+CH4 1.296E4 2.580  14.040
 HIO+C3H2=>IO.+H2CCCH 28.800 3.100  6.940
 C4H10+C3H2=>H2CCCH+C4H9_1 1.740E4 2.900  8.830
 C4H10+C3H2=>H2CCCH+C4H9_2 4.080E3 3.100  8.820
 C3H4+C3H2=>H2CCCH+H2CCCH 1.176E14 0.000  13.100
 HCCO+C2H5=CH2CO+C2H4 7.590E13      -0.700 0.000
 C2H3+CH2HCO=C2H4+CH2CO 4.234E12    -0.050 -0.057
       DUP
 C2H3+CH2HCO=C2H4+CH2CO 5.413E12    -0.089 -0.037
       DUP
 HI+H2CCCH=C3H4+I 9.228E9   0.860  28.332
 C2H4+C3H2=>C2H3+H2CCCH 1.176E14    0.000  13.100
 C3H4(+m)=>H2CCCH+H(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -24.47035 9.32174E-6 -6.48654E-6 3.63578E-6 /
CHEB /   26.31068 1.45209E-5 -1.01509E-5 5.75819E-6 /
CHEB /   -0.89120 7.37874E-6 -5.14783E-6 2.90505E-6 /
CHEB /   -0.48195 1.56152E-6 -1.08920E-6 6.14365E-7 /
CHEB /   -0.26887 -8.67735E-7 6.05638E-7 -3.42158E-7 /
CHEB /   -0.13406 -6.65198E-7 4.64230E-7 -2.62199E-7 /
CHEB /   -0.06036 1.54391E-7 -1.07673E-7 6.07081E-8 /


 HCCO+CH2OH=CH2CO+CH2O 3.010E13     0.000  0.000
 HCCO+CH3O=CH2CO+CH2O 9.570E12      -0.173 -1.806E-3
 C3H2+C3H5=>H2CCCH+C3H4 4.820E12    0.000  0.000
 H2O+C3H2=>OH+H2CCCH 968.000 2.900  14.860
 C3H2+HO2=>H2CCCH+O2 6.000E11       0.000  0.000
 C3H4+O=>H2CCCH+OH 1.512E7  1.910  3.740
 CH2CO+OH=HCCO+H2O 1.026E13 0.000  5.940
 H2O2+H2CCCH=HO2+C3H4 28.800 3.100  6.940
 CH2CO(+m)=>HCCO+H(+m)      1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /  -31.66319 9.84519E-5 -6.86600E-5 3.87131E-5 /
CHEB /   32.33515 6.18662E-5 -4.31789E-5 2.43969E-5 /
CHEB /   -0.73345 1.30015E-5 -9.07351E-6 5.12382E-6 /
CHEB /   -0.36359 -1.86385E-5 1.29969E-5 -7.32814E-6 /
CHEB /   -0.18743 -1.44934E-5 1.01082E-5 -5.70133E-6 /
CHEB /   -0.09165 -2.10736E-6 1.47165E-6 -8.32153E-7 /
CHEB /   -0.03957 5.50111E-6 -3.83467E-6 2.16063E-6 /


 HCCO+C3H5=CH2CO+C3H4 2.410E12      0.000  0.000
 O2+H2CCCH=CH2CO+HCO 3.010E10       0.000  2.867
 H2CCCH+CH2OH=C3H4+CH2O 3.010E13    0.000  0.000
```

```
 H2CCCH+CH3O=C3H4+CH2O 9.570E12    -0.173 -1.806E-3
 H2CCCCH(+m)=>C4H2+H(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   -8.47208    0.16409   -0.01744   -0.00632 /
CHEB /   11.30020    0.30476   -0.03015   -0.01232 /
CHEB /   -0.76095    0.24265   -0.01831   -0.01120 /
CHEB /   -0.40535    0.16215   -0.00488   -0.00903 /
CHEB /   -0.22831    0.08606    0.00472   -0.00594 /
CHEB /   -0.12025    0.03019    0.00803   -0.00257 /
CHEB /   -0.05435   -0.00084    0.00613    0.00020 /


 CH2O+HCCO=CH2CO+HCO 5.420E3 2.810  5.860
 C3H2+CH2OH=>H2CCCH+CH2O 6.020E13  0.000  0.000
 C3H2+CH3O=>H2CCCH+CH2O 1.914E13   -0.173 -1.806E-3
 HCCO+HCCO=C2H2+CO+CO 1.000E13     0.000  0.000
 C2H2+O=HCCO+H 5.060E6      2.100  1.570
 C3H4+C2H=H2CCCH+C2H2 8.852E9      0.696  9.952
 CH2+CH2HCO=CH3+CH2CO 4.234E12     -0.050 -0.057
       DUP
 CH2+CH2HCO=CH3+CH2CO 4.234E12     -0.050 -0.057
       DUP
 C3H4+C2H3=H2CCCH+C2H4 5.880E13    0.000  13.100
 H2+C3H2=>H2CCCH+H 1.796E13 0.000  10.300
 O2+C3H2=HCO+HCCO 1.000E13  0.000  0.000
 HI+HCCO=I+CH2CO 9.228E9    0.860  28.332
 CH+HCCO=C2H2+CO 5.000E13   0.000  0.000
 O+HCCO=H+CO+CO 9.640E13    0.000  0.000
 H2+HCCO=CH2CO+H 8.980E12   0.000  10.300
 C3H6+HCCO=C3H5+CH2CO 2.319E13     0.000  7.500
 C3H6+C3H2=>C3H5+H2CCCH 4.638E13   0.000  7.500
 C2H5+CH2HCO=C2H6+CH2CO 5.413E12   -0.089 -0.037
       DUP
 C2H5+CH2HCO=C2H6+CH2CO 4.234E12   -0.050 -0.057
       DUP
 H2CCCH+HO2=C3H4+O2 3.000E11 0.000  0.000
 C4H10+HCCO=CH2CO+C4H9_2 2.040E3   3.100  8.820
 C4H10+HCCO=CH2CO+C4H9_1 8.700E3   2.900  8.830
 CH2HCO(+m)=>CH2CO+H(+m)     1.0E0 0.0 0.0
TCHEB / 300.0 3000.0 /      PCHEB / 0.01 100.0 /
CHEB / 7      4 /
CHEB /   -7.75405    0.50590   -0.07174    0.00526 /
CHEB /   10.00214    0.81479   -0.07531   -0.00657 /
CHEB /   -1.12137    0.44955    0.01647   -0.01605 /
CHEB /   -0.53242    0.15907    0.04962   -0.00633 /
CHEB /   -0.23415    0.01302    0.03477    0.00503 /
CHEB /   -0.08825   -0.03038    0.01050    0.00727 /
CHEB /   -0.02367   -0.02836   -0.00336    0.00342 /


 CH2+HCCO=C2H+CH2O 1.000E13 0.000  2.000
 C2H6+C3H2=>C2H5+H2CCCH 1.740E4    2.900  8.830
 C3H4+C3.CCI=C3CCI+H2CCCH 3.128E13 0.000  19.700
 HIO+HCCO=IO.+CH2CO 14.400  3.100  6.940
 C3H4+C4H9_2=C4H10+H2CCCH 1.300E13 0.000  20.200
 C3H4+C4H9_1=C4H10+H2CCCH 3.128E13 0.000  19.700
 CO+CH=HCCO 2.770E11 0.000  -1.708
 HCCO+CH2HCO=CH2CO+CH2CO 5.413E12  -0.089 -0.037
       DUP
 HCCO+CH2HCO=CH2CO+CH2CO 4.234E12  -0.050 -0.057
       DUP
 C2H2+C2H2=H2CCCCH+H 2.000E9 0.000  57.812
 O2+C2H=HCCO+O 9.050E12     0.000  0.000
 H2CCCH+C2H5=C3H4+C2H4 7.590E13    -0.700 0.000
 C2H2+C3H2=>C2H+H2CCCH 3.721E9     1.510  21.428
 CH2CO+C3H2=>HCCO+H2CCCH 5.880E13  0.000  13.100
```

```
CH2O+C3H2=>HCO+H2CCCH 1.084E4      2.810  5.860
C3H4+OH=H2CCCH+H2O 2.052E13 0.000  5.940
CH2CO+CH2=>HCCO+CH3 9.541E8 1.305  5.685
C3H2+C2H5=>H2CCCH+C2H4 1.518E14    -0.700 0.000
C3H4+CH2=>H2CCCH+CH3 1.908E9       1.305  5.685
C2H4+O=H+CH2HCO 4.740E6     1.880  0.179
H+CH2HCO=CH2CO+H2 4.234E12 -0.050 -0.057
      DUP
H+CH2HCO=CH2CO+H2 5.413E12 -0.089 -0.037
      DUP
C2H4+HCCO=C2H3+CH2CO 5.880E13      0.000  13.100
OH+HCCO=HCO+HCO 1.000E13    0.000  0.000
OH+CH2HCO=H2O+CH2CO 5.413E12       -0.089 -0.037
      DUP
OH+CH2HCO=H2O+CH2CO 4.234E12       -0.050 -0.057
      DUP
H2CCCH+O=C2H2+CO+H 1.390E14 0.000  0.000
CH2CO+C2H=HCCO+C2H2 4.426E9 0.696  9.952
CH2+HCCO=C2H3+CO 3.000E13  0.000  0.000
HCO+CH2HCO=CH2O+CH2CO 4.234E12     -0.050 -0.057
      DUP
HCO+CH2HCO=CH2O+CH2CO 5.413E12     -0.089 -0.037
      DUP
C3H4+C2H5=H2CCCH+C2H6 3.128E13     0.000  19.700
CH4+C3H2=>CH3+H2CCCH 1.272E15      0.000  13.700
H+HCCO=CH2+CO 1.510E14      0.000  0.000
C3H4+IO.=H2CCCH+HIO 2.052E13       0.000  5.940
CH4+HCCO=CH3+CH2CO 6.360E14 0.000  13.700
C3.CCI+CH2HCO=C3CCI+CH2CO 5.413E12 -0.089 -0.037
      DUP
C3.CCI+CH2HCO=C3CCI+CH2CO 4.234E12 -0.050 -0.057
      DUP
H2O2+HCCO=CH2CO+HO2 28.800 3.100  6.940
C4H9_1+CH2HCO=C4H10+CH2CO 4.234E12 -0.050 -0.057
      DUP
C4H9_1+CH2HCO=C4H10+CH2CO 5.413E12 -0.089 -0.037
      DUP
C4H9_2+CH2HCO=CH2CO+C4H10 4.234E12 -0.050 -0.057
      DUP
C4H9_2+CH2HCO=CH2CO+C4H10 5.413E12 -0.089 -0.037
      DUP
I+CH2HCO=CH2CO+HI 4.234E12 -0.050 -0.057
      DUP
I+CH2HCO=CH2CO+HI 5.413E12 -0.089 -0.037
      DUP
CH2CO+O=>HCCO+OH 7.560E6    1.910  3.740
HO2+CH2HCO=H2O2+CH2CO 5.413E12     -0.089 -0.037
      DUP
HO2+CH2HCO=H2O2+CH2CO 4.234E12     -0.050 -0.057
      DUP
C2H6+HCCO=C2H5+CH2CO 8.700E3       2.900  8.830
C3H2+H=>H2CCCH 2.420E14     0.000  0.000
O+CH2HCO=CH2CO+OH 4.234E12 -0.050 -0.057
      DUP
O+CH2HCO=CH2CO+OH 4.234E12 -0.050 -0.057
      DUP
END
```