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CHEMICAL KINETIC MODELING OF OXIDATION OF HYDROCARBON EMISSIONS IN SPARK IGNITION ENGINES

by

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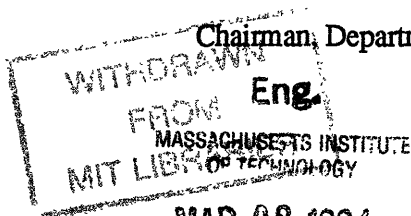
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ABSTRACT

Hydrocarbon emissions from spark ignition engines are significantly affected by the type of fuel used. Furthermore, the type and amount of each chemical species leaving the exhaust are a very strong function of the fuel type. In order to model the process through which unburned hydrocarbons are oxidized in the exhaust process, one needs to take into account the transport of cold layers to the bulk gases and chemistry of oxidation of these mixtures. The objective of this work is to study the effect of fuels on the resulting hydrocarbon emissions by using existing detailed chemical kinetic mechanisms of oxidation of hydrocarbons. Because of computational time constraints, only fully-mixed time-dependent problems were considered. A parametric study of the effects of pressure, equivalence ratio, temperature and fraction of unburned gas on characteristic chemical time scales for fuel oxidation and total hydrocarbon oxidation were made to provide useful information about hydrocarbon oxidation under relevant kinetically-controlled conditions. In addition, detailed kinetic models have been used to investigate the interactions between two components in a binary fuel, which is the first step for exploring the influence between different types of components in real fuels. Moreover, one-step expressions have been fitted from the numerical results of detailed chemical mechanisms so they can be used in more sophisticated transport models for better predictions. Correlations between reaction time and total hydrocarbon emissions from engines operating on single substance fuels show the practical use of the simple zero dimensional approach.

A second part of the work was devoted to combine a simple physical thermal model and detailed chemical kinetic models to simulate the oxidation of unburned hydrocarbons through the exhaust port. The results show that measured extents of oxidation of the unburned fuel through the exhaust cannot be reproduced by the simulations using the well mixed (average) temperatures in the exhaust, but that the experimental results can be bracketed by the average and core temperatures. Investigations of the temperature limits for kinetic control in the exhaust port, the effect of super-equilibrium radicals, and the behavior of intermediate combustion products were made for further understanding the mechanisms of hydrocarbon oxidation. The analysis shows that most of the oxidation occurs at the very early exhaust times, when temperatures in the exhaust are in excess of approximately 1200 K. For the fuels considered, it is suggested that oxidation is controlled by mixing rates at the initial stages of exhaust, where temperatures are high and the cold unburned mixture emerges from the wall layers in to the exhaust jet.

Thesis Advisor : Simone Hochgreb,
Assistance Professor of Mechanical Engineering

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CHAPTER 1

INTRODUCTION

1.1 Background

Hydrocarbon (HC) emissions from spark ignition (SI) engines have faced increasingly stringent regulations since the United States Clean Air Act of 1970 and, with the adoption of the United States Clean Air Act of 1990, further tightening of hydrocarbon emissions is under way. Therefore, tailpipe emissions are a critical consideration for engine system designers, who must optimize for emissions, fuel economy, performance, cost, and durability. In addition, new fuels, such as alcohol fuels, are also being tested as alternatives to mitigate the effects of hydrocarbon products emitted into the atmosphere. With this in mind, automotive companies in collaboration with research institutions, and universities have recently engaged in extensive experimental and analytical studies in order to clarify the mechanisms of production and reduction of hydrocarbon emissions from spark ignition engines for control of hydrocarbon emissions.

1.2 Relevant experiments and analytical approach

Perhaps because of the relative complexity of processes involved the development of fundamental physical and chemical models of hydrocarbon formation and oxidation in the cylinder and exhaust system are still in their infancy. A few physically based, semi-empirical models have been developed for the formation of hydrocarbons via crevices, quench and oil layers, and partial burn, followed by in-cylinder or port oxidation [1-3]. Other investigators used more sophisticated fluid mechanical models [4,5] to correlate observed trends with engine operating conditions. These models have also utilized empirically fitted parameters for the

calculation of oxidation of rates of hydrocarbons, and did not attempt to quantify the products of partial oxidation.

The extensive tests performed under the Air Quality Improvement Research Program have generated a large and useful database on the effect of different fuel variables on total and speciated emissions from spark ignition engines [6]. Other researchers have experimentally studied the effect of single-species fuels on emissions at steady state operation [7-10]. In particular, recent hydrocarbon emissions experiments were performed on simple, pure fuels by Kaiser et al. [7-9] : lean and rich mixtures were studied at steady engine operating conditions, and the effect of changing engine speed and spark timing was investigated for the lean mixtures. This work is particularly useful for comparison with the present numerical results because the different fuels were studied in the same engine under the same operating conditions, and because chemical kinetic mechanisms have already been formulated for these small hydrocarbons.

1.3 Motivation and objectives

Although the current federal regulation specifies maximum values for the total non-methane organic gas (NMOG), the speciated hydrocarbon emissions are of increasing importance because the state of California will regulate hydrocarbon emissions based on their reactivity in forming ozone in the atmosphere in the near future [12]. In addition, even though experiments indicated that fuel effects on hydrocarbon emissions are relevant [7-9], there has been no attempt to incorporate them into modeling. Therefore, the purpose of the current work is the application of fully detailed chemical kinetic mechanisms to investigate evolution of oxidation processes of unburned fuel, combustion intermediates, and total hydrocarbons in the ranges expected to be encountered in the cylinder and exhaust port using zero-dimensional models without transport. The objectives are to:

- determine how fuel chemistry affects the oxidation rates and partial combustion products

- determine how the parameters (temperature, equivalence ratio, unburned mixture fraction, and pressure) influence the characteristic times of hydrocarbon oxidation.
- correlate the zero-dimensional simulation results with experimental data
- fit one-step expressions for fuel destruction and hydrocarbon oxidation to produce approximate estimations of reaction rates over the relevant conditions
- investigate the interactions between the different types of fuels and how the intermediate combustion products affect the behavior of their parent fuels
- incorporate the physical engine simulation models with full chemical mechanisms to study the exhaust port oxidation process
- quantitatively and qualitatively analyze the experimental and simulated results of the oxidation of hydrocarbons in the exhaust.

CHAPTER 2

APPROACH and MODEL

2.1 Background

During the normal combustion process in spark ignition engines, a fraction of the fuel inducted into the cylinder is prevented from burning through storage in cold wall layers, generally called hydrocarbon sources [11] (crevices, deposits, oil layers, and flame quenching, shown in Fig. 2.1) . These unburned hydrocarbons emerge out of the different sources into the burned gas during the expansion and exhaust process and some of the unburned hydrocarbons exit the cylinder into the exhaust port and manifold. Oxidation occurs in the cylinder and exhaust system as hydrocarbons mix with the bulk burned gas. The oxidation of the unburned hydrocarbons is governed both by the rate of mixing into the burned gas as well as by the chemical kinetic rate of oxidation. However, transport processes cannot currently be combined with the detailed chemistry mechanisms because the computational expense of such of a treatment would be prohibitive. Therefore, efforts to incorporate some of these processes into two dimensional fluid mechanical models (KIVA) have only used one-step reduced chemical reaction mechanisms [4,5]. No attempts have been made at modeling the hydrocarbon oxidation during the expansion and exhaust processes in spark ignition engines using a detailed chemical kinetics model. In addition, critical experimental information about the nature of turbulence near the liner walls, as well as on the thickness of thermal boundary layer around the regions where unburned hydrocarbons emerge is scarce. Hence it is very difficult to predict the unburned hydrocarbon oxidation processes with accurate transport models coupled with full chemistry. Nevertheless, because of the possible regulation on speciated hydrocarbon emissions based on their reactivity in forming ozone in the atmosphere in the near future [12], and experimental indication that fuel

effects on hydrocarbon emissions are relevant, the focus of the current work is to apply existing chemical kinetic mechanisms of oxidation of hydrocarbons to the engine hydrocarbon emissions problem using zero-dimensional, time-dependent modeling. Real fuels are clearly too complex to be realistically modeled at present. Only single component fuels such as simple paraffins, olefins, oxygenated fuels, and aromatics whose detailed chemical mechanisms of oxidation are currently available are studied. For zero-dimensional modeling, more attention was given to port oxidation instead of in-cylinder oxidation, since zero-dimensional model is more suitable for modeling the former. More details on modeling and approaching the hydrocarbon emissions problem are described as following.

2.2 Chemical kinetic mechanisms

Because reduced chemical mechanisms determined from experimental data or detailed chemical kinetics calculations have been typically validated only for specific conditions (particularly flame propagation) or for very narrow parameter ranges, they are not suitable for the present purposes. In addition, simplified mechanisms usually do not provide information on the intermediate species formed during the reactions. "Comprehensive" detailed chemical kinetic mechanisms which have been validated over a wide range of conditions (pressure, temperature, and equivalence ratio) make possible the prediction of chemical behavior under a wide range of conditions. In general, interpolation within the range of conditions covered by a comprehensive mechanism is more reliable than extrapolation from a model validated at a single set of conditions. Therefore, detailed chemical kinetic mechanisms were used to simulate hydrocarbon oxidation.

All the detailed, elementary step mechanisms for the current study were drawn from the literature. Present detailed chemical schemes for oxidation simulation have included four straight-chain paraffins (methane, ethane, propane, n-butane), one branched-chain paraffin

(isooctane), one aromatic fuel (toluene), and two oxygenated fuels (methanol and MTBE). In the interest of consistency, chemical kinetic mechanisms for the oxidation of methane, ethane, propane, and n-butane validated over wide temperature, pressure, and equivalence ratio with jet-stirred reactor and shock tube data were chosen from the same group (the work of Dagaut, Cathonnet and coworkers [13-16]). The mechanisms for methane and ethane include the same reactions and rate parameters since the methyl radical recombination chemistry is included in the methane mechanism [13]. The propane mechanism was a subset of that of butane, since chemical reaction models are often constructed in a hierarchical manner. Furthermore, models for simple olefins (ethylene, propene, and 1-butene) were already included in kinetic models for their parent paraffins (ethane, propane, and n-butane) since olefins are byproducts of paraffin oxidation. Detailed reaction mechanisms for large molecules : isooctane, toluene, and MTBE were included because of the interest in their behavior within real fuels, even though they have been only validated with limited experimental data. The mechanism for MTBE is a combination of reaction mechanisms of MTBE, isobutene, [21] and n-butane [16]. Table 2.1 lists the sources for the chemical kinetic mechanisms used and the parameter ranges over which they have been validated.

All the chemical kinetic mechanisms for the oxidation study were verified against published experimental data using the CHEMKIN interpreter and integration computer codes [26]. In particular, more experimental data ([18],[19],[22],[25]) than those available in the original literature have been compared with the mechanisms which had been only validated at narrow range of conditions in order to check the possibility of extension of these models (see Appendix). However, since validation is still limited by the lack of experimental data available , the results of the simulations have to be considered with caution. As an example, in the MTBE mechanism, some modifications were made to pre-exponential factors of reactions $C_4H_9OCH_3 + X = C_4H_9OCH_2 + HX$ (increased by a factor of 10 , where X refer to H, O, OH, and HO₂ radicals) and $C_4H_9OCH_3 = IC_4H_8 + CH_3OH$ (increased by a factor of 2) to match flow reactor data [25] and shock tube data [24].

Table 2.1. Chemical kinetic mechanisms used in simulations

Fuel	Reference	Apparatus*	T (K)	P (atm)	ϕ
methane	[13]	JSR	900 - 2000	1 - 13	0.1 - 2.0
ethane	[14]	JSR	800 - 2000	1 - 10	0.1 - 2.0
propane	[15]	JSR	900 - 2000	1- 10	0.15 - 4.0
n-butane	[16]	JSR	900 - 2000	1- 10	0.15 - 4.0
i-octane	[17]/[18]	PFR	1080/1135-1235	1.0	0.99/0.5-2.2
	[19]	ST	1250-1450	1.7-4.8	0.99
toluene	[20,21]	PFR	1188,1190	1.0	0.69,1.33
	[22]	ST	1334-1611	2.0-6.0	0.33-1.0
methanol	[23]	PFR	1025-1090	1.0	0.6-1.6
MTBE	[24]	ST	1100-1600	3.45	1.0
	[25]	PFR	1024,1115	1.0	0.95

* Experimental data used in mechanism validation. JSR: jet stirred reactor, PFR: plug flow reactor, ST: shock tube

2.3 Physical models

An accurate simulation for the hydrocarbon oxidation process would include chemical reactions and species transport effects. However, this is computationally infeasible at this point in time. This section describes the physical models used in the current computations which do not include transport phenomena. The plug flow reactor model was used for calculating the characteristic time scales and port oxidation simulations. Results using the perfectly stirred reactor (PSR) model were also studied and compared to those of the plug flow reactor model. Both are described below. Finally, the engine-exhaust simulation models which generated histories of the mass flow rate exiting the cylinder and the cylinder and exhaust port gas temperature and pressure to drive the detailed chemical port oxidation simulations are described.

Plug flow reactor model

An important class of idealized combustion systems are collectively called plug flow reactors. These systems are characterized by high linear flow rates with negligible recirculation flow. Each element of gas reacts as it moves, with the characteristic time scale for heat and mass transfer by diffusion in the cross stream direction being much faster than that for convective motion so that each cross section has uniform properties. Therefore, for a reacting system without turbulent or molecular transport, the species and temperature evolution equation is :

$$\frac{Dy_i}{Dt} = \frac{w_i}{\rho} \text{ and } \frac{DT}{Dt} = -\frac{\sum w_i h_i^\circ}{\rho C_p}$$

where y_i is the mass species concentration , w_i the mass reaction rate and ρ the local mass density. The operator

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \frac{dx}{dt} \frac{\partial}{\partial x}$$

For steady one dimensional flow,

$$\frac{\partial}{\partial t} = 0 \text{ and } \frac{\partial x}{\partial t} = \frac{dx}{dt} \text{ so that } \frac{Dy_i}{Dt} = v \frac{\partial}{\partial x} = \frac{dy_i}{dt}$$

For purposes of comparison to experimental data in steady flow, distance is converted to time by means of velocity measurements. Based on the assumption of this model, gas flow which contains the burned and unburned mixture is discretized into several sections, and there are no temperature, pressure, and concentration gradients existing in each element of mixture.

Stirred reactor model

Another important idealized combustion system which can be considered to be spatially uniform is the perfectly stirred reactor (PSR). The PSR utilizes rapid mixing to achieve spatial homogeneity. Reactants are injected at a uniform rate into a combustor through a number of inlets. Within the perfectly stirred reactor, reactions take place, and energy is released in the uniform region, and the product gases (with the same properties as the uniform region) are

removed through the exhaust opening. The characteristic time scale is the average residence time in the reactor. Thus, a well-stirred reactor can be modeled as a flow system in which a mixture flows into a control volume where it is perfectly mixed with recirculation flow of combustion products, which flow out at the same conditions as those prevailing inside the chamber, so that the governing equation for a steady perfectly stirred reactor is :

$$\frac{y_i - y_{io}}{\tau} = \frac{w_i(\mathbf{y}, T)}{\rho}$$

where, $y_i(0) = y_{io}$ and $y_i(\tau) = y_i$.

A comparison of calculation results of plug and stirred reactor models

From a physical point of view, the plug flow model is an isolated, moving control volume (if we interchange the space coordinates with time, we can treat it as a static control volume) which contains the homogeneous reacting mixture; and the perfectly stirred reactor model is a control volume where steady-state incoming and outgoing flows cross over and uniform mixing of new inflows and remaining mixture occurs continuously at an infinite rate. From a numerical point of view, modeling plug flow reactor requires solving systems of time-dependent initial value problems; modeling well-stirred reactors requires solving systems of boundary value problems. The kinetic equations for plug or stirred reaction models were integrated using the CHEMKIN library which will be described in the following section. Plug or stirred reactor calculation results for the extent of reaction as a function of residence time differ only very little for the same inlet conditions and isothermal reaction, with exception of methane, for which time scales are one order of magnitude shorter for the perfectly stirred reactor model. Therefore, in the following chapters, the plug flow reactor model will be used for characteristic time scale computations and exhaust port oxidation simulations, and the results of well-stirred reactor models will be compared with those of plug flow models where they are obviously different.

Engine simulation models

For the simulations of hydrocarbon oxidation in the exhaust port, which will be discussed in Chapter 4, data about the temperature and initial concentration history through the exhaust port must be obtained in order to drive the detailed chemical kinetic models. However, there are not enough data available on the accurate time-resolved temperature profile for exhaust gases through the exhaust port so far. Therefore, engine and exhaust port thermal simulation models must be used to predict in-cylinder and port temperature histories and the mass flow rates exiting the cylinder in order to drive the simulation of hydrocarbon oxidation in the port.

A two-zone, zero-dimensional thermodynamic model for the state of the gas in a four-stroke spark ignition engine [27] was used to predict the pressure and temperature of the gas and the mass flow rate through the valves as a function of crank angle. The total mass exiting the cylinder was discretized into ten elements and the temperature histories in the exhaust port were calculated for each mass element based on heat transfer relationships derived by Caton et al. [28] based on experimental measurements of exhaust temperatures. A plug flow model was used for each exhaust gas element, and the initial conditions for the exhaust temperature were calculated from the thermodynamic model of the engine cylinder mentioned above; the boundary conditions for the in-cylinder and port calculations were obtained from the bulk thermal model of the entire engine [29], which predicts the engine component temperature, including the coolant and oil circuits and the exhaust system.

2.4 Numerical methodology

The solution to the systems of ordinary differential equations of the detailed chemical kinetic schemes were made using the CHEMKIN-II chemical kinetics package [26]. This set of application codes was compiled and executed on a Hewlett Packard 9000/720 workstation.

CHEMKIN is a fortran software package for the solution of gas-phase chemical kinetic problems. The chemical kinetic reactions and a thermodynamic database which contains appropriate thermochemical information (specific heat at constant pressure, standard-state enthalpy, and entropy) of species involved in the reactions are read by its interpreter, and a binary linking file which holds all the pertinent information on elements, species, and reactions in the mechanism is produced for use by CHEMKIN subroutines and other application codes. The thermodynamic data for most of the species involved in the simulation were obtained from Kee et al. [30], and Burcat et al. [31]. The computer program THERM [32], which uses the group additivity method, was used to calculate the thermochemical coefficients of the species not available in the CHEMKIN database. Nevertheless, since the data computed from THERM have uncertainties associated with the inputs, reverse reaction rate constants have been included in the current chemical reaction mechanisms if available in the literature, rather than from forward rate constants and equilibrium constants calculated using the thermodynamic database.

For the simulations of plug flow reactors and shock tubes, CHEMKIN-based application code named SENKIN (Lutz et al., 1991) was used which predicts homogeneous gas-phase mixture chemical kinetics by integrating the time dependent conservation equations of species and energy. The characteristic time scales in the plug flow model which will be discussed in detailed in Chapter 3 are calculated at constant pressure and temperature; simulations of shock tube models are computed based on the assumptions of constant density (volume) and adiabatic condition. This code has been also modified in order to include the option of varying temperature and pressure histories. This temperature and pressure programming is used to determine the levels of super-equilibrium radicals in the exhaust gas using the predicted in-cylinder temperatures and pressures. In addition, the exhaust port hydrocarbon oxidation simulations were carried out by temperature programming at constant pressure in SENKIN. In addition to SENKIN, the PSR program [33] was used to compute the simulations of perfectly stirred reactors; and the initial composition of gas mixture at equilibrium is obtained by running the STANJAN computer code [34].

2.5 Approach

In order to determine chemical reaction time scales of unburned hydrocarbons in burned gas mixtures, homogeneous mixtures of the bulk burned gas and various concentrations of unburned mixture assumed to consist of unreacted air and fuel (unburned mixture fraction) were considered as the initial composition for the present zero-dimensional computations. The composition of the burned gas consists of products of combustion of the gaseous fuel under equilibrium conditions, or non-equilibrium as described below. Since active radicals (OH, H, O), which are responsible for the attack on the unburned hydrocarbons, do not recombine at a rate sufficiently high to match the equilibrium composition during the expansion process in the cylinder, the effect of non-equilibrium radical concentrations was initially investigated. The predicted in-cylinder pressures and temperatures (Fig. 2.2), from the engine simulations were used for kinetic temperature and pressure programming in order to simulate how the non-equilibrium radicals deviate from the equilibrium states. Initial conditions for these simulations are the assumptions that the burned gases are mixture in chemical equilibrium at peak pressure. Figure 2.2 also depicts the deviation of hydroxyl (OH) concentration from the equilibrium state as a function of crank angles (CAD). The radical concentrations depart from equilibrium by one order of magnitude at exhaust valve opening (EVO). The effect of super-equilibrium radicals on the evolution of hydrocarbon oxidation is illustrated in Fig. 2.3(a) and (b). Figure 2.3(a) shows a typical plot of concentrations of fuel and partial oxidation products, starting with a mixture of burned gas in equilibrium and unburned fuel-air mixture at 1200 K. Figure 2.3(b) shows the effect of using initial conditions at 1200 K with super-equilibrium radicals from the engine simulation : there is immediate reaction with excess radicals, followed by a behavior similar to that of Fig. 2.3(a) for a mixture of equilibrium burned products. Note that the time scale for the overall reaction is not significantly affected by the different radical concentrations, and that the profiles of stable intermediates are almost identical as a function of extent of reaction of fuel. Accordingly, for simplicity purposes of comparison among fuels, the chemical characteristic time

scales involved in the oxidation of fuels and total hydrocarbons are investigated as a function of temperature, pressure, equivalence ratio, and fraction of unburned mixture in an equilibrium burned gas mixture using a zero-dimensional, detailed chemistry calculation. The exhaust port oxidation process was assumed to be that of a perfect mixture of unburned gas and burned gas which contains the super-equilibrium radicals traveling through the exhaust port subject to programmed temperature history. Details about the initial conditions for defining the characteristic time scales and calculating the extent of port oxidation will be described in the following chapter.

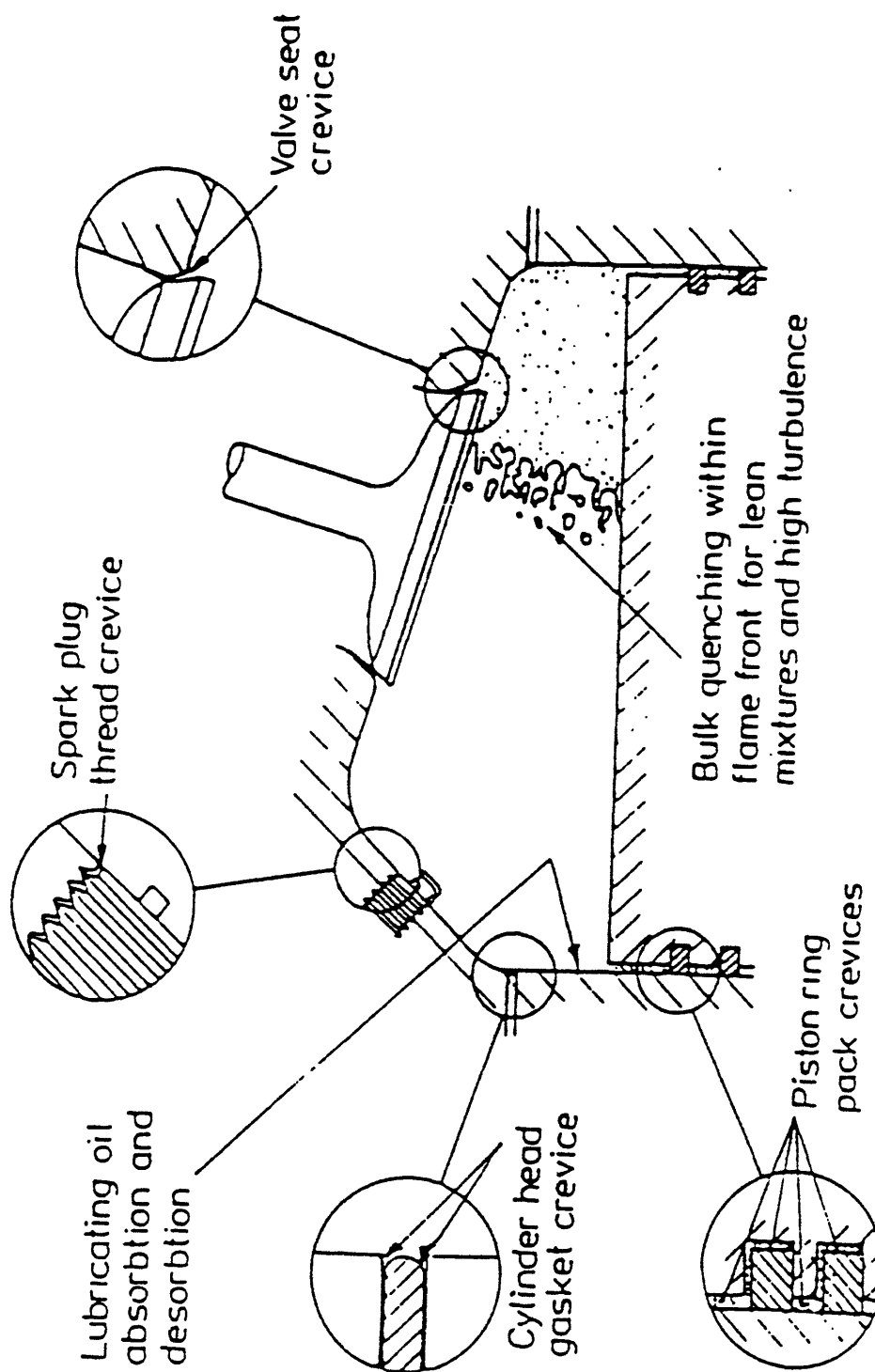


Figure 2.1: A schematic view of the hydrocarbon emissions mechanisms.

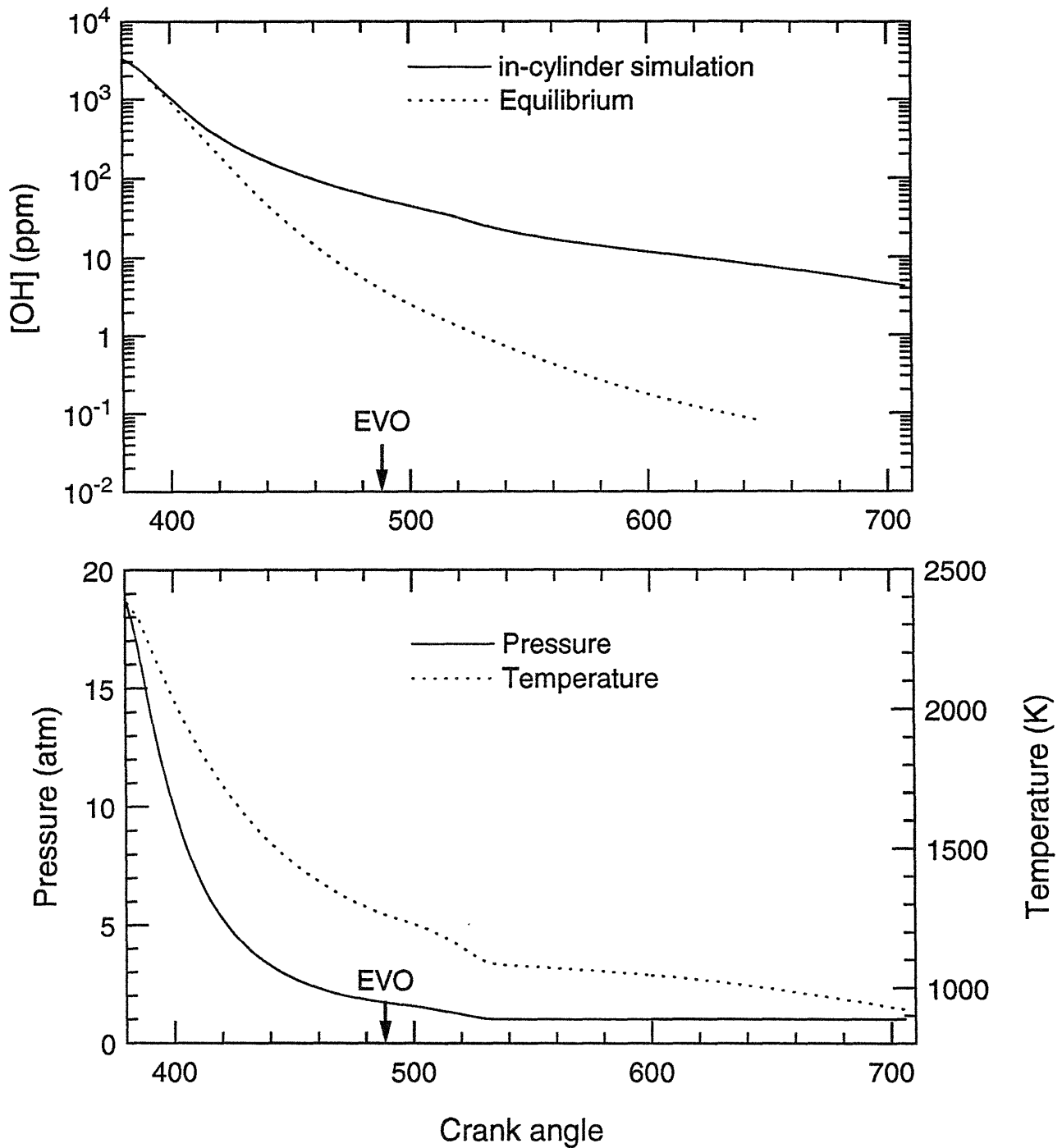


Figure 2.2: Simulated in-cylinder temperature and pressure for the baseline case of Kaiser et al. (top) [5] ($\Phi=0.9$, 1500 rpm, 3.75 kpa IMEP, MBT spark timing. Fuel : propane), and simulated deviation of in-cylinder hydroxyl (OH) mole fractions from the equilibrium state as a function of crank angle (bottom).

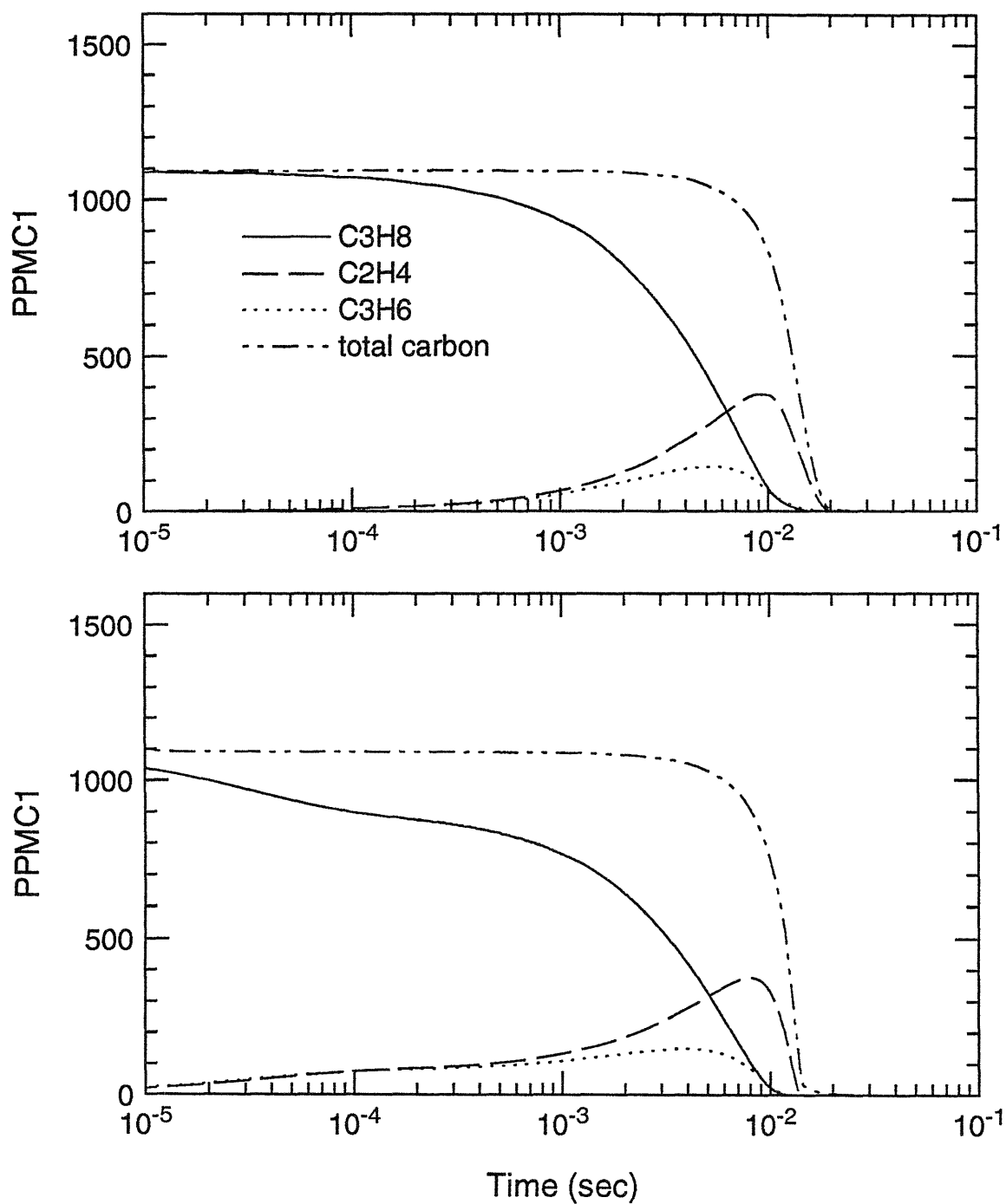


Figure 2.3: Mole fractions of propane and its primary products of partial oxidation for $T=1200$ K, unburned mixture fraction : 1%, $\Phi=0.9$.(top) burned gas composition in equilibrium at 1200 K; (bottom) burned gas composition from the in-cylinder simulation at 1200 K.

CHAPTER 3

PARAMETRIC STUDY OF HYDROCARBON OXIDATION

3.1 Introduction

Because of limitations on computer time, and by insufficient available experimental information for detailed physical models of the oxidation process of hydrocarbon emissions in spark ignition engines, the problem of hydrocarbon emission modeling was initially approached by application of detailed chemical kinetic to perform zero-dimensional computations for a uniform mixture of burned gas at different initial temperatures, pressures, and compositions expected to be encountered in the process of hydrocarbon oxidation through the cylinder and exhaust. Using these chemical models (mostly comprehensive mechanisms validated over a range of conditions) a group of systematic numerical predictions have been made. These results provide systematic information about the possible chemical behavior of unburned hydrocarbons over a wide range of conditions. Not only did the simulation results supply a clearer picture about the role of hydrocarbon oxidation in spark ignition engines in a quantitative sense, but they were also used to fit reduced one-step mechanisms to produce approximate estimations of reaction rates over the relevant conditions that can be used in more sophisticated models including fluid mechanics and heat transfer effects.

Parameter matrix

Since hydrocarbon oxidation occurring in the cylinder and exhaust port is an unsteady and non-uniform phenomenon, the current study used four parameters (pressure, temperature, equivalence ratio, and fraction of unburned gas in the mixture), which vary with time and space

during the exhaust process, so that the parameter matrix would bracket the situations in the engines. The ranges of parameters are listed in Table 3.1 and will be discussed as follows.

Table 3.1 Ranges of parameters used in simulations

Parameter	Range
Temperature (K)	800, 1000, 1200, 1400
Fuel/Air equivalence ratio Φ	0.9, 1.0, 1.15
Unburned mixture fraction (%)	0.1, 1.0, 10
Pressure (atm)	1.0, 10

(a) Temperature

As will be shown in Section 3.3, the simulation results show that when the temperature is above 1400 K, most hydrocarbons are burned within 0.1 millisecond, roughly 1 crank angle for an average 1500 rpm engine speed; when the temperature is below 800 K, the mixture composition is practically frozen. Therefore, the range 800-1400 K is focus of our present interest, even though the temperature range spans a wider range than this during the expansion and exhaust processes.

(b) Fuel/air equivalence ratio (Φ)

The definition of equivalence ratio is that the ratio of the actual fuel/air concentration ratio to the stoichiometric ratio.

$$\Phi = \frac{\left(\frac{[Fuel]}{[Air]}\right)_{actual}}{\left(\frac{[Fuel]}{[Air]}\right)_{stoich}} \quad (3.1)$$

Equivalence ratios 0.9, 1.0 and 1.15 have been used for the parametric study to check the evolution of species involved in the oxidation processes under lean, stoichiometric and rich conditions, respectively. Typical operating conditions are stoichiometric, with small excursions to the lean and rich sides. These specific values were originally selected for comparison with existing experimental results [5].

(c) Unburned mixture fraction

The unburned mixture fraction is the ratio of the volume of unburned gas mixture to the volume of total mixture which includes the burned and unburned gas. Based on the ideal gas law, this gas volume ratio equals the molar ratio. From the assumption of perfect and adiabatic mixing, the fraction of unburned cold gas is limited if the final mixture temperature is to be higher than a minimum temperature of 800 K. Therefore, 10%, 1%, and 0.1% of unburned gas in the whole mixture were selected. Typical fuel molar fractions in the exhaust are of the order of 2000 ppmC1, which roughly equals 1 to 3% unburned mixture fraction.

(d) Pressure

Pressure values between 1 and 10 atm were chosen for the current parametric study because these values correspond to the range of pressures among which unburned hydrocarbons start outgassing from sources and emerge at temperature low enough for the chemical time scales to be controlling (Fig. 2.2).

Computation details

There are $72 \left(2 \left(1, 10 \text{ ATM} \right) * 4 \left(800 \text{ K}, 1000 \text{ K}, 1200 \text{ K}, \text{ and } 1400 \text{ K} \right) * 3 \left(\text{equivalence ratio } 0.9, 1.0, 1.15 \right) * 3 \left(10\%, 1\%, \text{ and } 0.1\% \text{ unburned gas fraction} \right) \right)$ simulations for each fuel. For each simulation, the initial composition of mixture is a combination of the composition of equilibrium burned gas, which is calculated using STANJAN [34] and that of unburned gas which includes fuel and the corresponding amount of air. The ratio of fuel to air is

according to the assigned equivalence ratio and composition of the air is assumed to be only oxygen and nitrogen ($O_2 : N_2 = 1 : 3.773$). For the current study, it is assumed that the unburned mixture is coming from the crevice or wall quenching, and that the mixture consists of a fixed ratio of air and unburned fuel. Hydrocarbons emitted from the oil layers and deposits typically consist of fuel only and have not been studied in detail, since the very rich case is beyond the validated range of present models. Computation starts at the specific initial composition of the mixture, constant pressure and temperature.

3.2 Speciation results

One of the advantages of detailed chemical kinetic mechanisms is the ability to follow the evolution of all chemical species. The total hydrocarbon concentration (in ppmC1) obtained by adding up the mole fraction of all species times the number of carbon in each molecule (C1) except for carbon monoxide (CO) and carbon dioxide (CO₂), is then an index of the extent of the oxidation of the original fuel.

Figures 3.1 to 3.4 show the evolution of major species for propane, n-butane, iso-octane, toluene under fuel lean ($\Phi = 0.9$) and rich ($\Phi = 1.15$) conditions. Since the previous simulation results [35] indicated that the distributions of products is not significantly changed by temperature or initial concentration, but strongly affected by the equivalence ratio, the simulations for 1% unburned gas at 1200 K can provide enough information about the hydrocarbon oxidation process.

The simulated results showed that the type and proportion of major products is primarily a function of the structure of the compound and equivalence ratio. For example, ethylene and propene are the major products of propane and n-butane oxidation, both straight-paraffinic fuels. Iso-octane, which is a branched-paraffinic fuel, produces a large amount of iso-butene; and a large amount of methane is produced at rich conditions rather than lean conditions. In

addition, results showed that the time scales for fuel decomposition and total carbon conversion are of the same order of magnitude for smaller molecular fuels such as methane, ethane, ethylene, propane, n-butane and methanol. However, carbon conversion times are much longer than the fuel decomposition times for larger molecular fuels such as iso-octane and MTBE. These observed trends can be explained by the fact that large molecules break easily into many small, longer-lived segments so that it takes much more time to oxidize all the species into carbon monoxide and carbon dioxide.

3.3 Time scale results

Time scales for oxidation of fuels under plug-flow conditions provide useful quantitative benchmarks for further understanding of the oxidation rate of hydrocarbons. The time scales for the oxidation of a fuel or total carbon is defined here as the time at which 50% of the fuel was reacted and 50% of carbon was converted into CO or CO₂, respectively. Computations showed that 50% reaction times are of the same order of magnitude as 10% or 90% reaction time for most simulation cases. Therefore, the half lives of hydrocarbons represent time scales at which the complete conversion of hydrocarbons occurs.

Parametric effects

The effect of five parameters (temperature, fuel/air equivalence ratio, fraction of unburned gas, fuel type and pressure) was investigated. Although in general it is easy to predict the qualitative trends of oxidation rates according to the trends of temperature and pressure, quantitative measures of sensitivity require detailed analysis. In addition, changes in one parameter can cause change in more than one rate-determining factor so that it is hard to decide the trend of oxidation speed directly by qualitative predictions. For instance, reducing the fraction of unburned gas in the mixture makes the concentration of fuel smaller so as to retard the

reaction rate; on the other hand, the effect of the extra oxygen in the burned gas may speed up reactions at fuel lean conditions when the unburned gas concentration becomes smaller. Therefore, only systematic numerical simulation results provide a clear picture about how these parameters quantitatively affect the reaction time scales.

(a) Temperature effect

The 50% reaction time scales of the whole fuel matrix as functions of the reciprocal of temperature are shown in figure 3.5 (a) to 3.15 (a), for fuel decomposition; and in figure 3.5 (b) to 3.15 (b), for carbon conversion, respectively. These plots obviously show that temperature is the most important parameter on the oxidation time scales. Within the temperature range of interest, 800 K to 1400 K, the time scales span six orders of magnitude. In particular, reaction times change by two orders of magnitude with a 200 K change in temperature.

Data points whose times exceed 10^4 seconds (3 hours) are not shown in the graphs. This occurs because of the low temperature for some unreactive species or lack of oxygen in the carbon conversion process. Considering the practical residence time scales in spark ignition engines, reactions can be treated as frozen if the time scale is beyond 1 second. This point will be discussed later.

(b) Fuel/air equivalence ratio effect

Compared to temperature, equivalence ratio has little effect upon time scales for oxidation. Except for methane and toluene, calculation results at fuel/air equivalence ratio 0.9 (lean), 1.0 (stoichiometric), and 1.15 (rich) conditions showed that the variations of the half-lives of fuels are within one order of magnitude. Moreover, for most cases the changes in reaction times were within a factor of three. Computations indicated that reaction times for methane are more sensitive to equivalence ratio, changing by an order of magnitude difference in 50% reaction times was made by the relatively narrow variations of equivalence ratio. This may probably be explained by the fact that the stable molecular structure of methane makes the

decomposition of methane more difficult than other fuels so that the conversion times are more dependent on the concentration of fuel and oxygen.

One thing should be noticed is that because the lack of oxygen at fuel rich conditions ($\Phi = 1.15$) the 90% of conversion of total carbon into carbon monoxide (CO) and carbon dioxide (CO₂) is hard to achieve, even the 50% conversion may be achieved and probably the time scales be the same order of magnitude as those at lean and stoichiometric conditions.

(c) Unburned mixture fraction effect

Similarly to the effect of equivalence ratio, the concentration of unburned gas does not affect the conversion times very much. For most simulation results, the variations are limited within the same order of magnitude. For the most stoichiometric and rich conditions, the reaction times are longer when the unburned mixture fractions become smaller. Conversely, there are opposite trends observed at most fuel lean conditions. Although not all simulated results are consistent with the tendency described above, the exceptions are still within a factor of two, which may be accounted within the range of uncertainties (model accuracy, or the precise representative meaning of 50% reaction time (only one points) for the whole oxidation process etc.). The explanations for these observations are apparently that the dilution of burned gas slows down the reaction rates since the concentrations of fuel and oxygen become small, but the extra oxygen, whose concentration is large relative to that of the unburned fuel, in the burned gas speeds up the reactions at the fuel lean conditions. The most apparent trends are observed for the simulated results of methane.

(D) Pressure effect

At the same temperature, higher pressure means that the density and the collision rates are higher. Therefore, in general time scales are shorter if the pressure increases. Simulation results showed that the time scales are moderately affected by varying the pressure from 1 atm to 10 atm. The ratios of two time scales (1 atm : 10 atm) vary from nearly one to roughly an order

of magnitude and the values strongly depend on temperature and fuel type (shown in Fig 3.16). The effect of pressure on the time scales and the dependency of the fuel type is smaller at high temperature than at low temperature. Since chemical kinetic models for iso-octane and toluene were not validated at high pressure in their original publications and the shock tube experimental data were usually carried out at higher temperatures, the simulated results should be used with caution.

(e) Fuel type effect

The extent of reaction as a function of time for the entire fuel matrix is plotted in Figs. 3.17 (a) and (b), for the parent fuels, and in Figs. 3.18 (a) and (b), for the total hydrocarbon under the conditions of 1200 K, 1 atm, stoichiometric fuel/air ratio, and 1% unburned fuel-air mixture. The rank of oxidation rates changes little with temperature (Figs. 3.5 - 3.15), since the different groups of fuels have similar activation energies. Methane shows the slowest oxidation rate of the hydrocarbons tested, followed by toluene, both fuels of well-known stable chemical structure. The fastest rates of fuel decomposition were found for ethane, isooctane, MTBE and methanol; the fastest oxidation speeds for total carbon were found for ethane, ethylene, and methanol. Since the rate of decomposition of intermediate products is in general different from that of the fuel itself as discussed above, fuel destruction times are shorter than overall carbon conversion times. The difference is very apparent for the large molecules such as iso-octane and MTBE, since they rapidly decompose into longer-lived intermediate hydrocarbons. Therefore, in the current test matrix, isooctane and MTBE have fast fuel decomposition times but their carbon conversion times are not the fastest. The fastest carbon conversion rates were found for smaller molecules such as ethane, ethylene, and methanol which produce less intermediate products.

A comparison with residence time scales in spark ignition engines

The range of temperatures where oxidation rates are likely to control hydrocarbon destruction in spark ignition engines can be obtained by an order-of-magnitude comparison

between the chemical kinetic time scales and the residence times of internal combustion engines. A group of fuels was selected to make this comparison : methane, n-butane, isooctane (two paraffins which are significant components of real fuel), toluene (important component of real fuels), MTBE, methanol (oxygenated fuels) and 1-butene (olefinic fuel). Because of the differences observed between results from plug flow model and stirred reactor model for methane, both results were plotted for comparison. Furthermore, since temperature is the primary parameter controlling time scales, comparisons were made for constant pressure (1 atm), fuel/air ratio ($\Phi = 1.0$), and fraction of unburned gas (1% of unburned fuel-air mixture) and various temperatures (800 K, 1000 K, 1200 K, and 1400 K). Figures 3.19 and 3.20 show the calculated half lives for fuel and total carbon oxidation for selected fuels as a function of reciprocal temperature. Typical residence times for the exhaust gas are also indicated in the same figure. Ten milliseconds is the order of magnitude of the in-cylinder residence time process, 1 to 100 milliseconds is the range of the residence time for the exhaust gas through the exhaust port, if both of the conditions of gas passing through and staying in the port after EVC (exhaust valve closed) are considered. Therefore, the time scale comparison shows that above approximately 1400 K all hydrocarbons are completely oxidized in less than the residence time of 10 milliseconds, conversely, there is no substantial oxidation below 1000 K at the longest residence times of 100 milliseconds.

3.4 Global expressions

In order to explore more realistic fluid mechanical models, simplified one-step expressions are desirable to minimize computational time, at the expense of chemical detail and accuracy. There exist already many reduced mechanisms in the literature for the simpler hydrocarbons. However, most have been developed for flame propagation, which is in general very different from the problem considered here. In the former, temperatures are high (≥ 2000 K),

molecular diffusion dominates and many reactions are partially equilibrated, none of which are necessarily true in the low temperature, turbulence mixing situation considered in hydrocarbon emissions problems. One-step expressions representing the approximate trends of the oxidation of hydrocarbons were obtained from the detailed models for further exploration of the emission problems. The procedure for fitting one-step expressions from the data sets calculated from the detailed chemical kinetic mechanisms and comparisons with simulations of full kinetic models will be discussed below.

Approach

According to the definition of characteristic reaction rate, the current global expressions are defined as a pseudo first order rate:

$$-\frac{1}{[f]} \frac{d[f]}{dt} \text{ or } -\frac{1}{[HC]} \frac{d[HC]}{dt} = \frac{1}{\tau} = A(\rho_{fo})^\alpha (\rho_o)^\beta e^{\left(-\frac{E}{RT}\right)} \quad (3.2)$$

ρ_{fo} : Initial fuel concentration (mole/cm³)

ρ_o : Initial oxygen concentration (mole/cm³)

R : Universal gas constant (1.986 kcal/kmol · K)

T : Temperature (K)

The characteristic reaction rate of the fuel or overall hydrocarbon is defined as the time derivative of the natural logarithm of fuel concentration. It obviously corresponds to the reciprocal characteristic reaction time τ , at which 1/e of original fuel or total carbon still remains unreacted. variables are the initial fuel and oxygen concentration, temperature. The pre-exponential term A, and the dependence on fuel (α), oxygen concentration (β), and the activation energy E are unknowns obtained by fitting the numerical simulation results.

In general, there are 36 data points used for fitting the global mechanisms, : 4 (temperatures : 800 K, 1000 K, 1200 K, and 1400 K) * 3 (equivalence ratios Φ : 0.9, 1.0, and

1.15) * 3 (unburned mixture fraction : 10%, 1%, and 0.1%) * 1 (pressure : 1 atm), corresponding to the characteristic time for (1-1/e) reaction at each condition. Some data points were excluded from the set as they exceed the assigned maximum time limit (10^4 seconds), so that there are less than 36 points used for fitting the one-step expressions in some cases. The global mechanisms are fitted by standard square error minimization.

Results

The fitted parameters α , β , and E for the one-step expressions for the whole test matrix are listed in Table 3.2 and Table 3.3, for fuel decomposition and for carbon conversion, respectively. For the predictions of characteristic reaction times for fuel destruction, Methane results are poorly predicted at rich conditions; and toluene has those poor results for rich conditions at 800 K. The poorest results have one to two orders of magnitude differences in the predicted characteristic times. Fitted expression for ethane and ethylene are the poorest predictions of total hydrocarbon conversion times for the conditions that the equivalence ratio equals 1.15 and unburned mixture fractions are 1% and 0.1%. Except for these few poor results, most of these expressions can make reasonable approximations, which almost all the estimating times are within the same order of magnitude as full mechanism data. A comparison for propane is shown in Fig 3.21. Under low temperature rich conditions the carbon conversion into CO or CO₂ is very difficult to be completed and the first order decay behavior of hydrocarbons specified from the one-step models cannot reproduce this behavior. Accordingly, a set of coefficients for the hydrocarbon oxidation was calculated by only including lean and stoichiometric cases. Table 3.4 lists the expressions which only apply to lean and stoichiometric conditions. An improvement of the accuracy of prediction of characteristic time scales of hydrocarbon conversion for all fuels was observed by entirely excluding the rich cases from the data sets. Better predictions for fuel destruction times from methane and toluene one-step expressions can also be achieved by excluding the exceptional cases. (For methane, all rich cases are excluded; for toluene, only the conditions of 800 K and $\Phi = 1.15$ are excluded from the

whole data set to get a satisfactory result). The specialized global expressions are also shown in Table 3.2.

The predicted trends of fuel decomposition and hydrocarbon oxidation from one-step expressions are compared to those from detailed chemical kinetic mechanisms (shown in Fig. 3.22). Most simulation results from full chemical kinetic mechanisms indicated the trends of fuel destruction are approximately a first order decay, whereas this is not a good approximation for total hydrocarbon conversion, since the latter involves more complicated oxidation mechanisms.

3.5 Correlation of full chemistry simulations with experimental data

Because the present zero-dimensional models are very simplified compared to the processes occurring inside the cylinder, simulated results are not expected to compare directly to experimental data. Therefore correlations of the simulated results with existing experimental data were made to assess the usefulness of zero-dimensional models of oxidation of unburned hydrocarbon in explaining observed differences between fuels. The experimental data on speciated hydrocarbon emissions from Kaiser et al. [5,6] were obtained from tests in a single cylinder engine under operation with different single substance gaseous and liquid fuels. The calculated time scales, which can be considered as a representation of the reactivity of species, were used to correlate with the experimental data. Figure 3.23 shows the correlation between the calculated ratio of the time scale of fuel consumption over that of total hydrocarbon conversion and the percentage contribution of unburned fuel to the total engine-out hydrocarbon emissions. As expected, fuels which are oxidized much faster than the total hydrocarbons show smaller resulting fractions of unburned fuel in total hydrocarbon emission and vice-versa. In Fig. 3.24, calculated half lives of total hydrocarbon are plotted against measured exhaust hydrocarbons normalized by the total charge in the engine. There is certainly a positive correlation, meaning that fuels that are oxidized faster yield lower overall emissions. For the two liquid fuels tested

(toluene and isooctane) the correlation is not very strong. A possible explanation for this fact is that the main source of unburned hydrocarbon emissions in the case of gaseous fuels is crevice storage, whereas oil layers and act as additional sources of hydrocarbons in the case of liquid fuels, shifting the measurements towards higher levels of hydrocarbon emissions. Peak burned gas temperatures are similar for all these fuels (about 2800 K except for toluene, about 60 K higher), so that the observed values should reflect hydrocarbon storage effects (e.g. oil layer effect for liquid fuels) and chemical oxidation rates.

3.6 Binary fuel study

The interaction between the different types of fuels is an interesting topic since the real fuel consists of many different types of fuel components. In addition, for simulations of exhaust port oxidation Chapter 4, for single component fuels, it is necessary to consider the role of initial concentrations of intermediate byproducts on the overall reaction. However, there is no validated comprehensive mechanism and experimental data available for many binary mixtures of interest. The current approach is then to study the interaction between the olefin and its parent paraffin since the experiment-verified mechanisms can be applied to both of them. In addition, a combination of kinetic mechanisms of butane and toluene has been built to study how they affect each other.

This binary-fuel mechanism consists of the original butane [16] and toluene [20,21] oxidation mechanisms. However, there are many different reaction rate expressions for the repeated reactions between the two mechanisms since they came from different authors. For the present study, all the repeated reactions were selected from butane mechanisms for its higher reliability. The single fuel simulation results from the modified mechanism has been compared with those from the original ones and the comparisons showed very good consistency.

Figure 3.25 shows the interaction between propane (paraffin) and ethylene (olefin). The propane-ethylene oxidation is plotted as an example since interactions of olefinic intermediate product and its parent paraffin were observed to be similar. In Fig. 3.25, two cases are depicted for comparison : pure propane oxidation and initial propane-ethylene mixture (the initial concentrations for propane and ethylene are 800 ppmC1 and 200 ppmC1, which are similar to the compositions at cylinder exit observed in quenching experimental data [35]). The same amount of pure ethylene (200 ppmC1) oxidation is also plotted for comparison. The comparison showed that the addition of the olefinic fuel has almost no effect on the oxidation process of the parent fuel (propane) and its partial oxidation product (ethylene), but the decomposition speed of pure ethylene is faster than that of the binary mixture. The reason is that olefins are much more stable than paraffins. Thus, if both of them co-exist, paraffin has a higher chance to be consumed than olefin. Therefore, the simulation indicates that the small amount of stable olefin does not affect the destruction of paraffin but the relative large amount of paraffin affects the reaction rate of olefin. Accordingly, since the experimental data showed that intermediate byproducts make up only a small fraction of total emissions (< 20%, on a carbon base [35]), simulated results indicated the effects of intermediates on the evolution of fuel destruction in the exhaust should be trivial (shown in Fig 3.26). However, methane is once again an exception because very few amounts of byproducts were measured in the experiments (< 5%) and its major combustion byproducts are ethane, ethylene and formaldehyde (formaldehyde is difficult to measure so that there are no data shown in some experiments such as Kaiser et al.[5,6,7] and Drobot et al.[35], but it should be a major byproduct for methane combustion [36]). Fig. 3.27 indicates that these small amounts of intermediates do affect the reaction times of methane by a factor of two. Therefore the intermediate products effect for methane will be taken into account for the study of the oxidation of hydrocarbons in the exhaust Chapter 4.

Similar trends are observed in the butane-toluene case. The only difference between this case and paraffin-olefin case is that butane and toluene cannot produce each other. Figs 3.28(a) and (b) show the simulated trends of evolution of toluene and butane at different ratios between

two fuels. Results show that butane is little affected by toluene addition except when relatively large amounts of toluene (butane : toluene = 1 : 9 in the 1% unburned mixture) are added at fuel rich conditions. Five times longer reaction times of original pure butane are observed with the addition of toluene. Comparatively, toluene is affected more significantly by butane. More than an order-of-magnitude change in reaction times were observed in simulations. However, since the mechanism for toluene is only validated over a very narrow range around the stoichiometric condition, the simulated results should be used with caution.

3.7 Summary

This Chapter illustrated the fundamental applications of detailed chemical kinetic mechanisms on the study of hydrocarbon emissions. The first approach was a systematic study of the effects of parameters which are variable in real engines to gain perspective on the controlling factors. All simulations were performed at specific constant temperature and pressure conditions and information on all species involved the oxidation mechanisms has been generated. The behavior of partial oxidation products and the total hydrocarbon has been simulated under a range of conditions. In addition, the time scales for fuel disappearance and overall hydrocarbon oxidation have also been extensively discussed and, not surprisingly, temperature has the most significant effect on the reaction times. Variations in the other parameters (pressure, unburned mixture fraction, and equivalence ratio) lead to changes roughly within an order of magnitude of time scale. A quantitative comparison between the computed time scales and practical engine residence times indicates that chemical kinetics controls oxidation rates within roughly the temperature range of 1000 K to 1400 K for fuel and total hydrocarbon oxidation. One-step expressions for characteristic oxidation times were fitted from the systematically calculated data sets and reasonable agreement was attained by these in predicting of the behavior of fuel destruction and hydrocarbon conversion. Correlations between calculated reaction time scales

from zero-dimensional modeling and exhaust emission data show that the zero-dimensional model can provide a qualitative estimate about the expected emissions, but quantitative explanations for the experimental data will still need further effort to incorporate more realistic physical models. Finally, the binary mixture study indicated that the intermediate byproducts should not affect the fuel destruction in the exhaust since their amounts measured in the relevant experimental conditions are relatively small.

3.2 Coefficients of one-step expressions for fuel destruction

$$-\frac{1}{[f]} \frac{d[f]}{dt} = \frac{1}{\tau} = A(\rho_{fo})^{\alpha}(\rho_o)^{\beta} e^{(-\frac{E}{RT})}$$

	A	α	β	E (kcal/kmol)
methane	3.0416E-20	1.9572E-01	-1.3807E+00	6.1788E+04
methane ¹	1.0219E-16	3.7933E-01	-1.2299E+00	5.6661E+04
ethane	5.0188E-15	-1.3295E-01	-2.3661E-01	4.8541E+04
ethylene	8.4560E-15	-3.6429E-01	-7.0518E-02	4.6569E+04
propane	2.2594E-14	-9.3065E-02	-1.0268E-01	5.3700E+04
propene	4.9990E-13	2.1987E-01	-5.1803E-01	4.7736E+04
n-butane	5.1991E-15	-2.7509E-01	4.1759E-02	5.3419E+04
1-butene	3.0998E-14	7.7893E-02	3.6515E-02	6.1041E+04
iso-octane	1.4388E-15	-4.1223E-03	-2.0917E-01	5.5896E+04
toluene	1.0753E-10	2.4584E-01	-6.5609E-01	3.5000E+04
toluene ²	2.9061E-12	3.0942E-01	-8.2626E-01	3.9887E+04
methanol	8.3011E-13	-1.3537E-01	-2.1926E-01	4.0036E+04
MTBE	9.6235E-15	1.9800E-01	-4.4270E-01	4.9548E+04

¹Rich conditions are excluded

²Conditions of 800 K and $\Phi=1.15$ (rich) are excluded

3.3 Coefficients of one-step expressions for overall hydrocarbon conversion

$$-\frac{1}{[HC]} \frac{d[HC]}{dt} = \frac{1}{\tau} = A(\rho_{fo})^{\alpha}(\rho_o)^{\beta} e^{\left(-\frac{E}{RT}\right)}$$

	A	α	β	E (kcal/kmol)
methane	4.2528E-19	3.0158E-01	-1.5353E+00	5.5082E+04
ethane	4.2015E-19	-8.4695E-02	-1.3034E+00	3.8801E+04
ethylene	5.2816E-20	-2.5546E-01	-1.1379E+00	4.2772E+04
propane	5.9388E-17	4.9660E-02	-1.0209E+00	4.5376E+04
propene	6.4903E-16	1.7920E-01	-1.1493E+00	4.1269E+04
n-butane	6.4545E-16	-5.4080E-02	-7.7426E-01	4.3796E+04
1-butene	7.0997E-14	2.1392E-01	-8.2810E-01	4.3355E+04
iso-octane	1.5733E-16	1.6446E-01	-1.0807E+00	4.7615E+04
toluene	2.2987E-15	4.1741E-01	-1.5145E+00	4.0239E+04
methanol	4.9016E-13	-1.5004E-01	-2.4028E-01	4.0187E+04
MTBE	3.8168E-14	1.5728E-01	-4.8934E-01	5.4906E+04

3.4 Coefficients of one-step expressions for overall hydrocarbon conversion (limited within lean and stoichiometric conditions)

$$-\frac{1}{[HC]} \frac{d[HC]}{dt} = \frac{1}{\tau} = A(\rho_{fo})^{\alpha}(\rho_o)^{\beta} e^{\left(-\frac{E}{RT}\right)}$$

	A	α	β	E (kcal/kmol)
methane	1.2481E-16	3.6581E-01	-1.2142E+00	5.6357E+04
ethane	5.5003E-17	-2.7517E-01	-4.6594E-01	4.8057E+04
ethylene	2.8895E-17	-3.6107E-01	-4.3409E-01	4.7762E+04
propane	8.0530E-16	1.1393E-01	-9.0282E-01	4.6499E+04
propene	6.7238E-15	2.2814E-01	-1.0350E+00	4.2110E+04
n-butane	4.6248E-16	6.0595E-02	-9.3613E-01	4.4099E+04
1-butene	3.2870E-13	2.6028E-01	-7.6506E-01	4.4161E+04
iso-octane	1.2975E-14	1.2411E-01	-7.0269E-01	4.8782E+04
toluene	7.9252E-14	2.8595E-01	-1.0588E+00	4.1661E+04
methanol	2.9454E-13	-1.2842E-01	-3.1206E-01	3.9802E+04
MTBE	1.4921E-14	1.8346E-01	-6.2150E-01	5.3750E+04

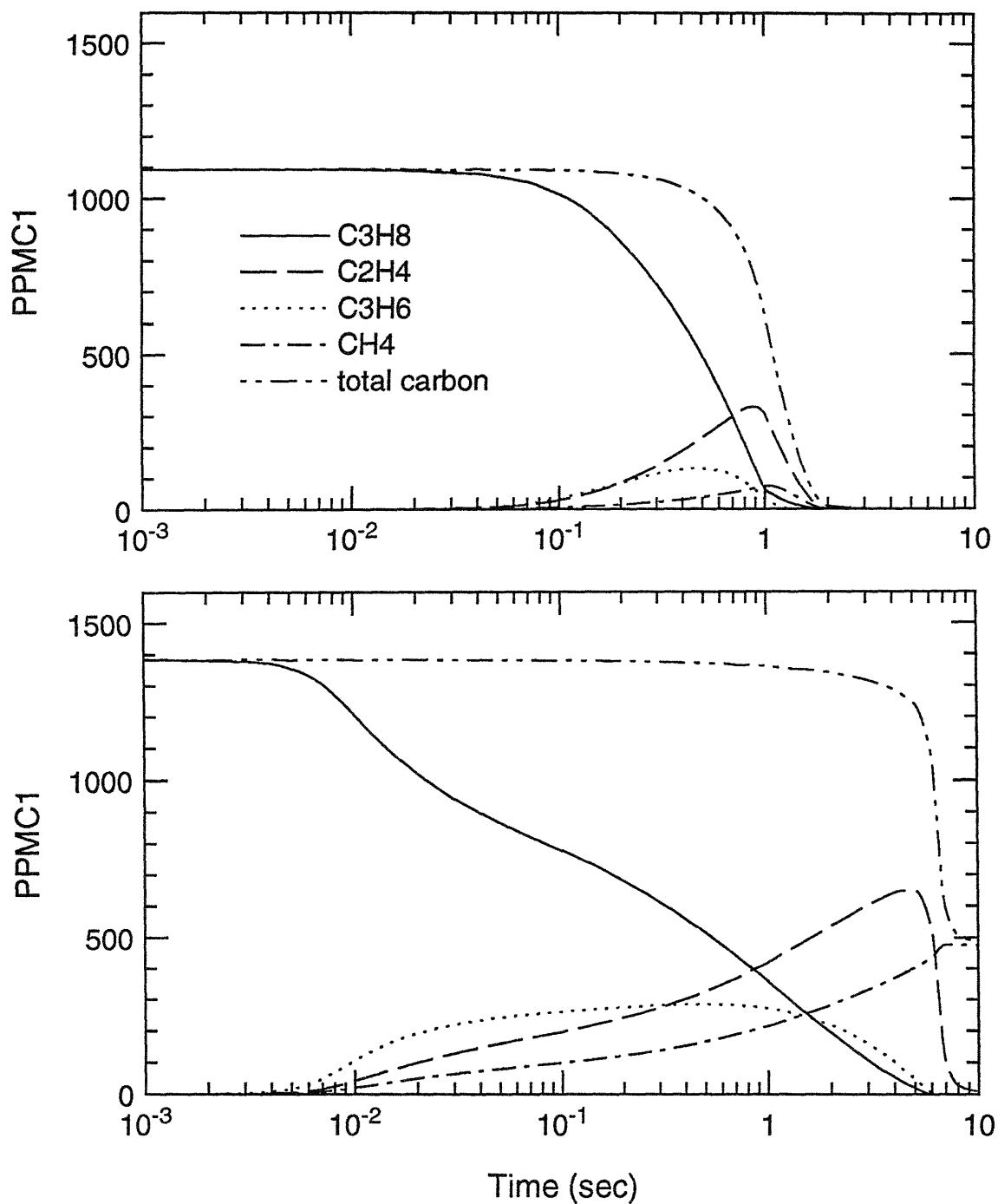


Figure 3.1: Mole fractions of propane and its primary products of partial oxidation for $T=1000$ K, X_u (fraction of unburned gas)=0.01, (top) lean mixture ($\Phi=0.9$); (bottom) rich mixture ($\Phi=1.15$).

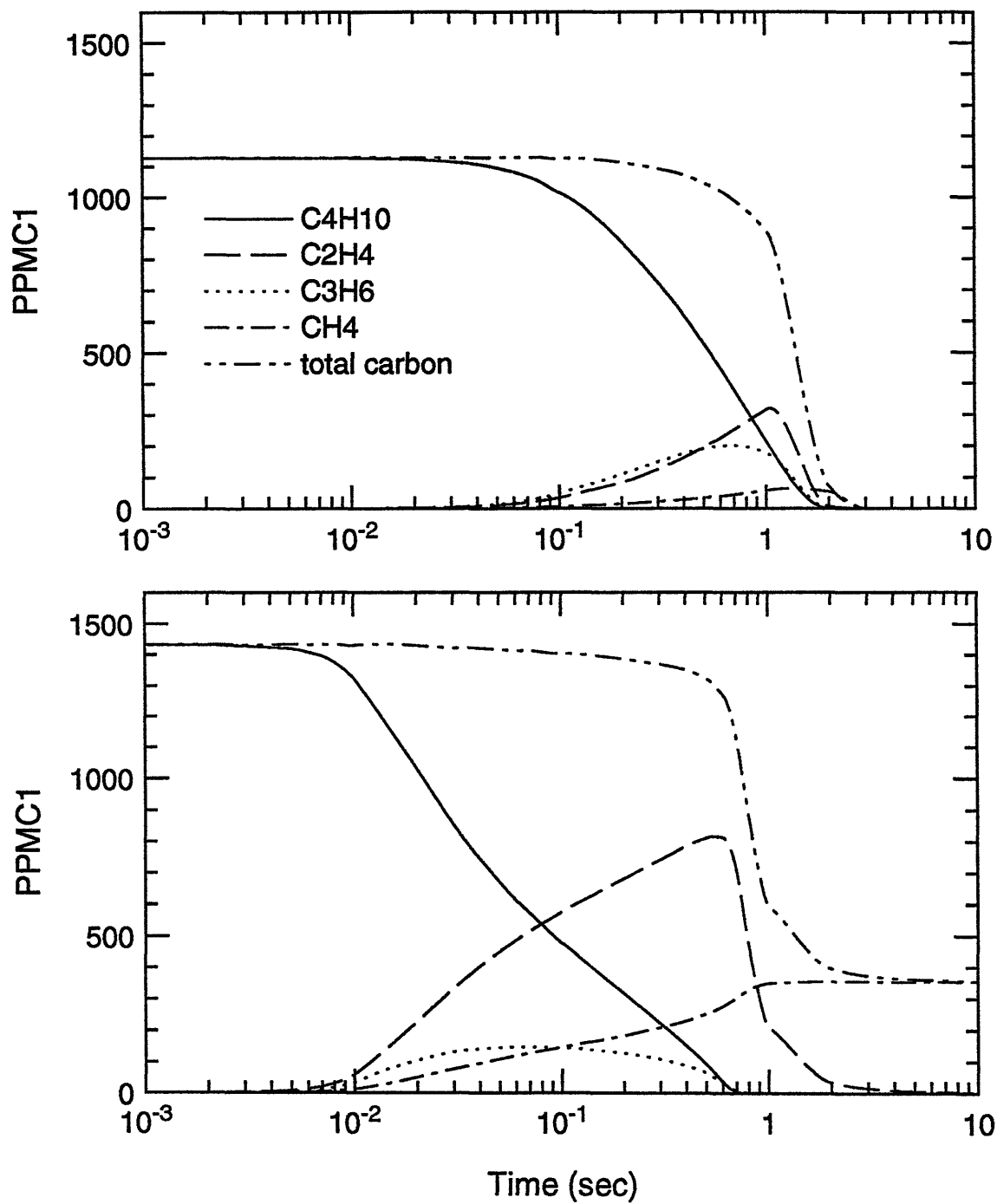


Figure 3.2: Mole fractions of n-butane and its primary products of partial oxidation for $T=1000$ K, X_u (fraction of unburned gas)=0.01, (top) lean mixture ($\Phi=0.9$); (bottom) rich mixture ($\Phi=1.15$).

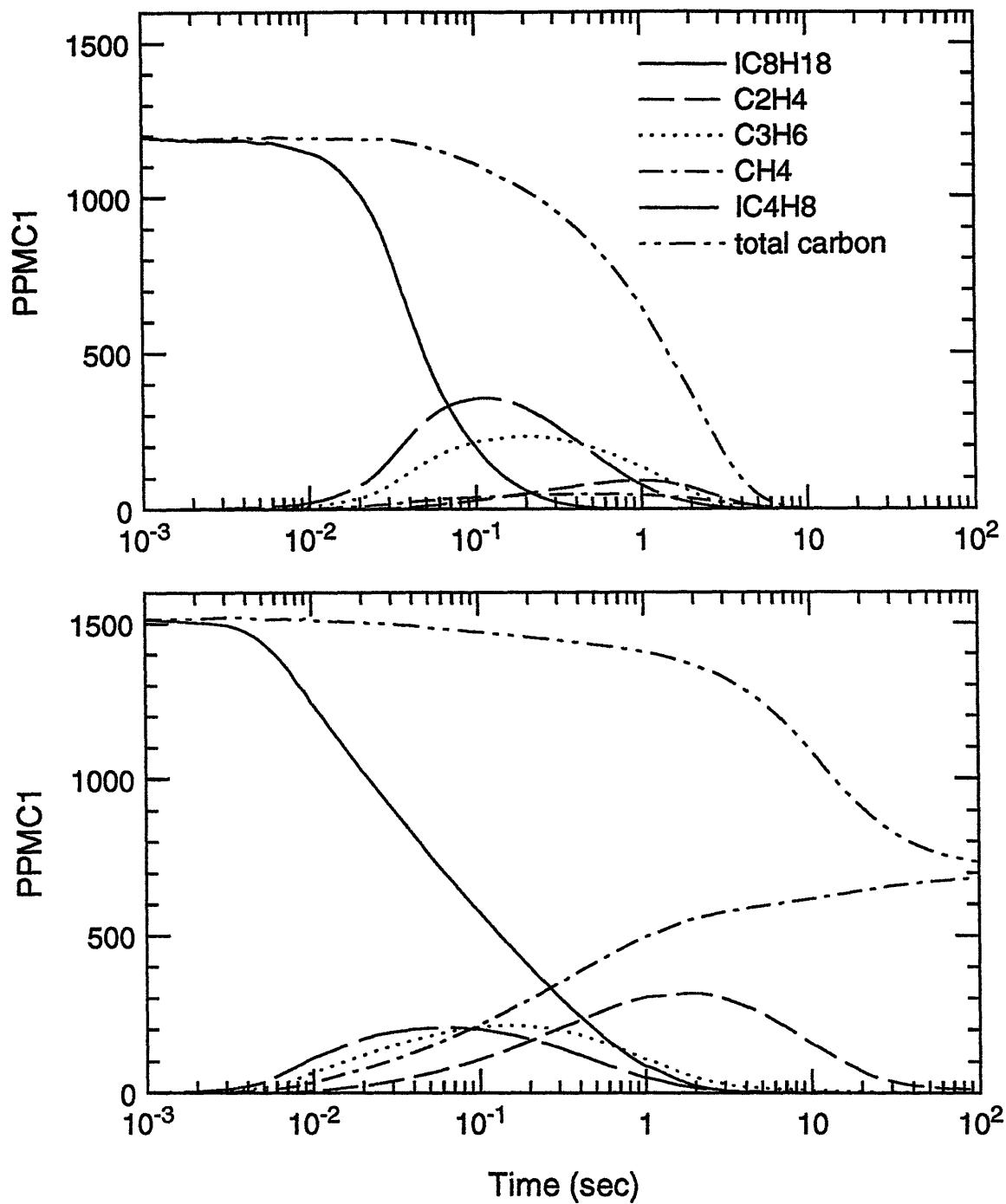


Figure 3.3: Mole fractions of iso-octane and its primary products of partial oxidation for $T=1000$ K, X_u (fraction of unburned gas)=0.01, (top) lean mixture ($\Phi=0.9$); (bottom) rich mixture ($\Phi=1.15$).

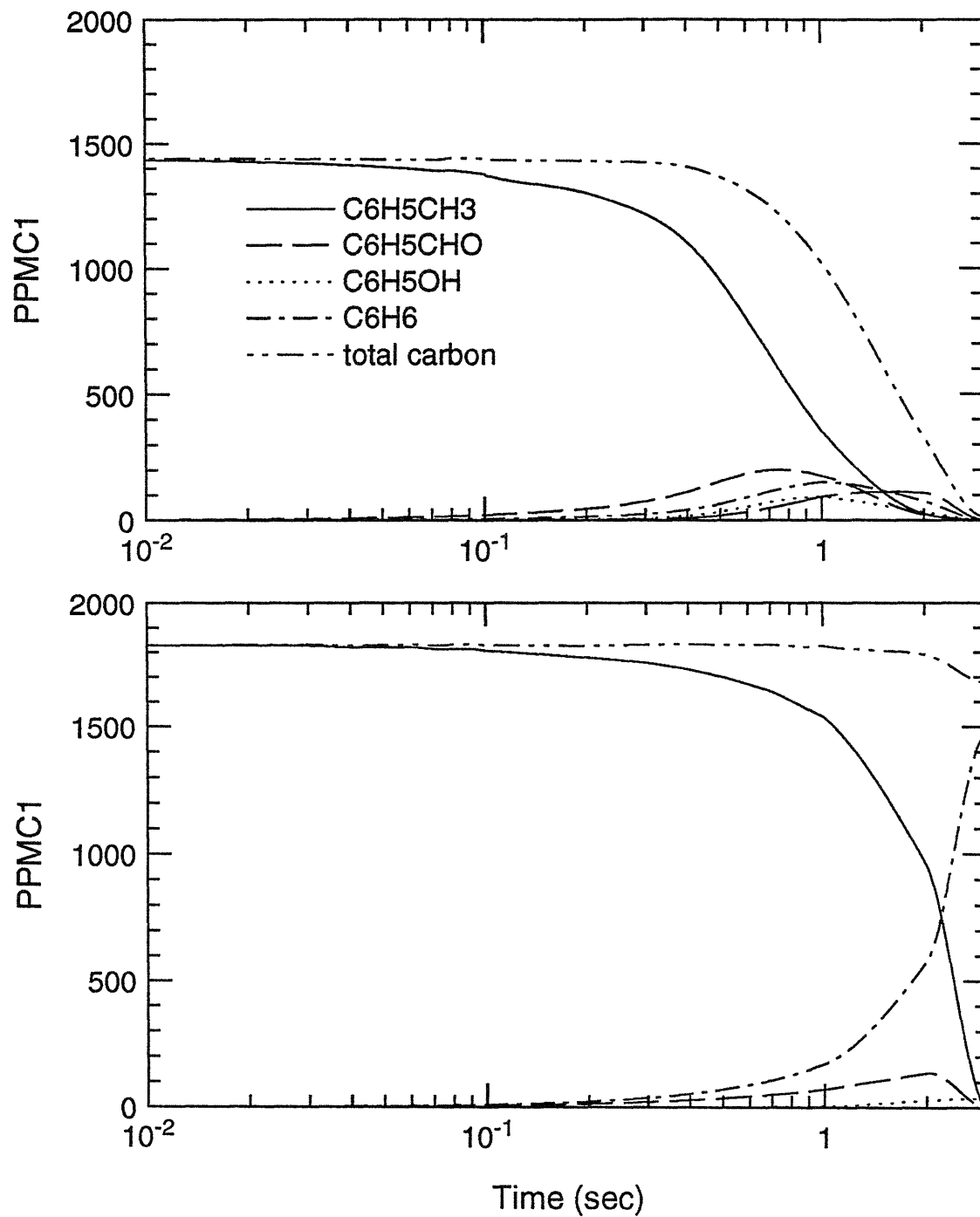


Figure 3.4: Mole fractions of toluene and its primary products of partial oxidation for $T=1000$ K, X_u (fraction of unburned gas)=0.01, (top) lean mixture ($\Phi=0.9$); (bottom) rich mixture ($\Phi=1.15$).

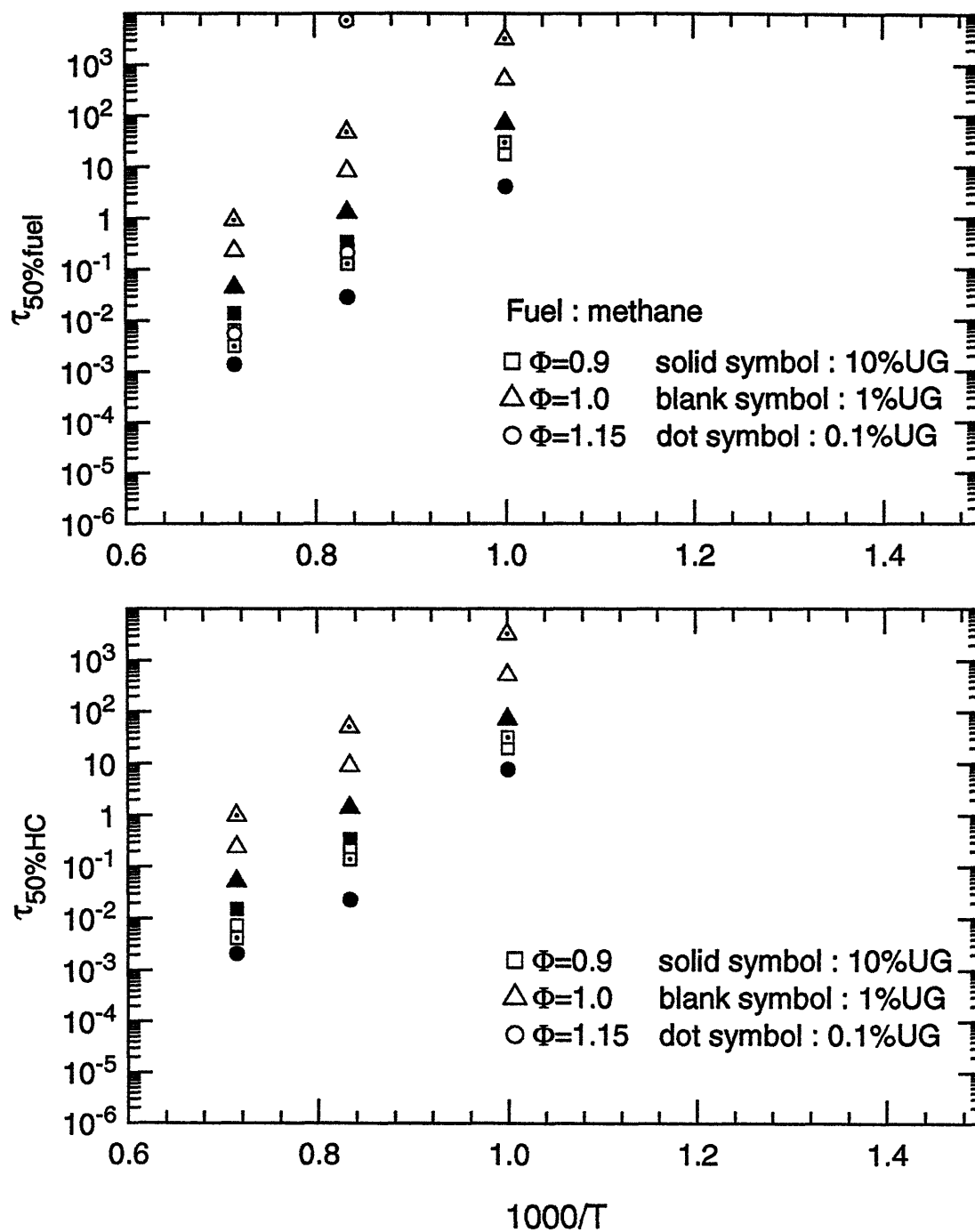


Figure 3.5: Characteristic 50% reaction time scales for methane as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

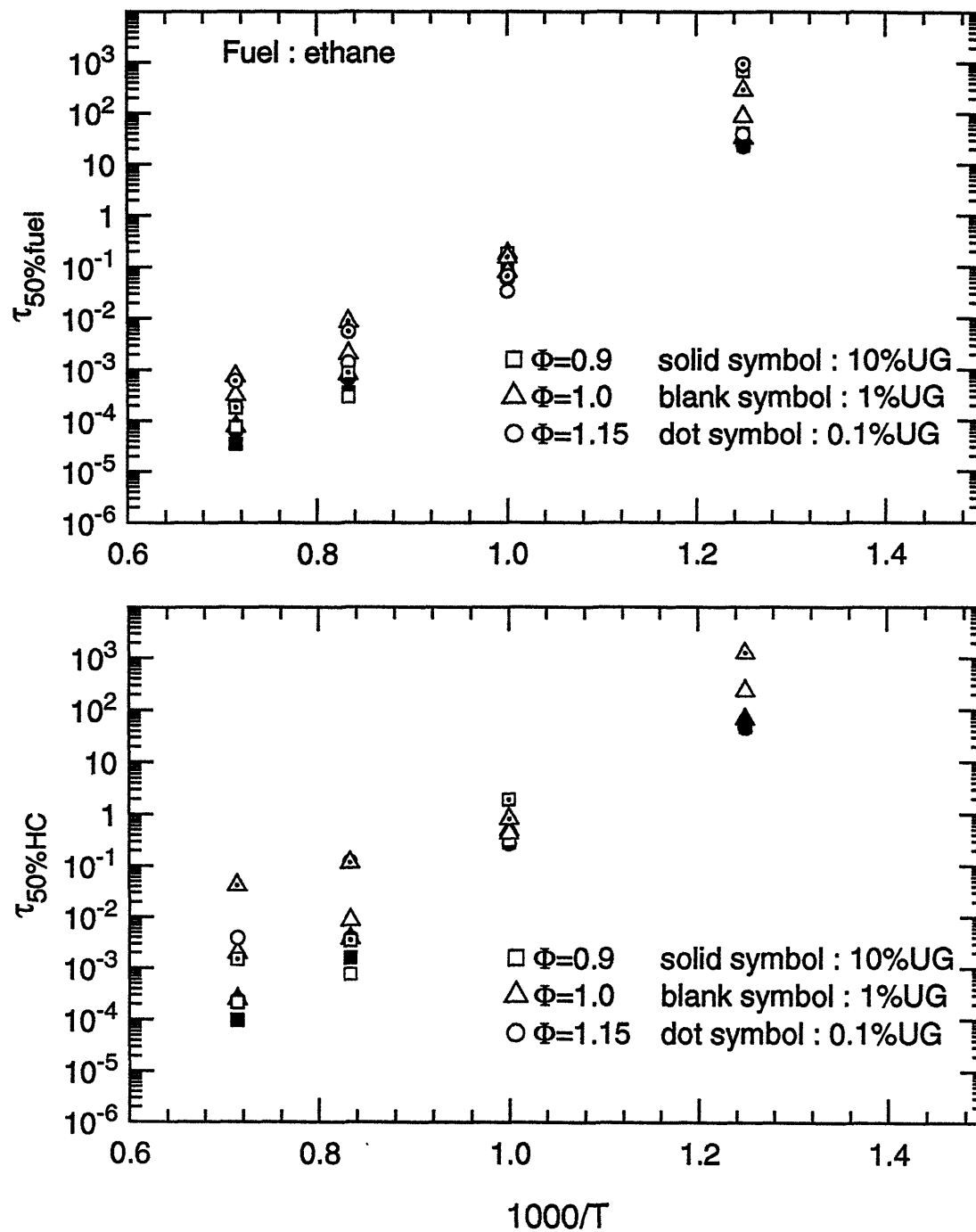


Figure 3.6: Characteristic 50% reaction time scales for ethane as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

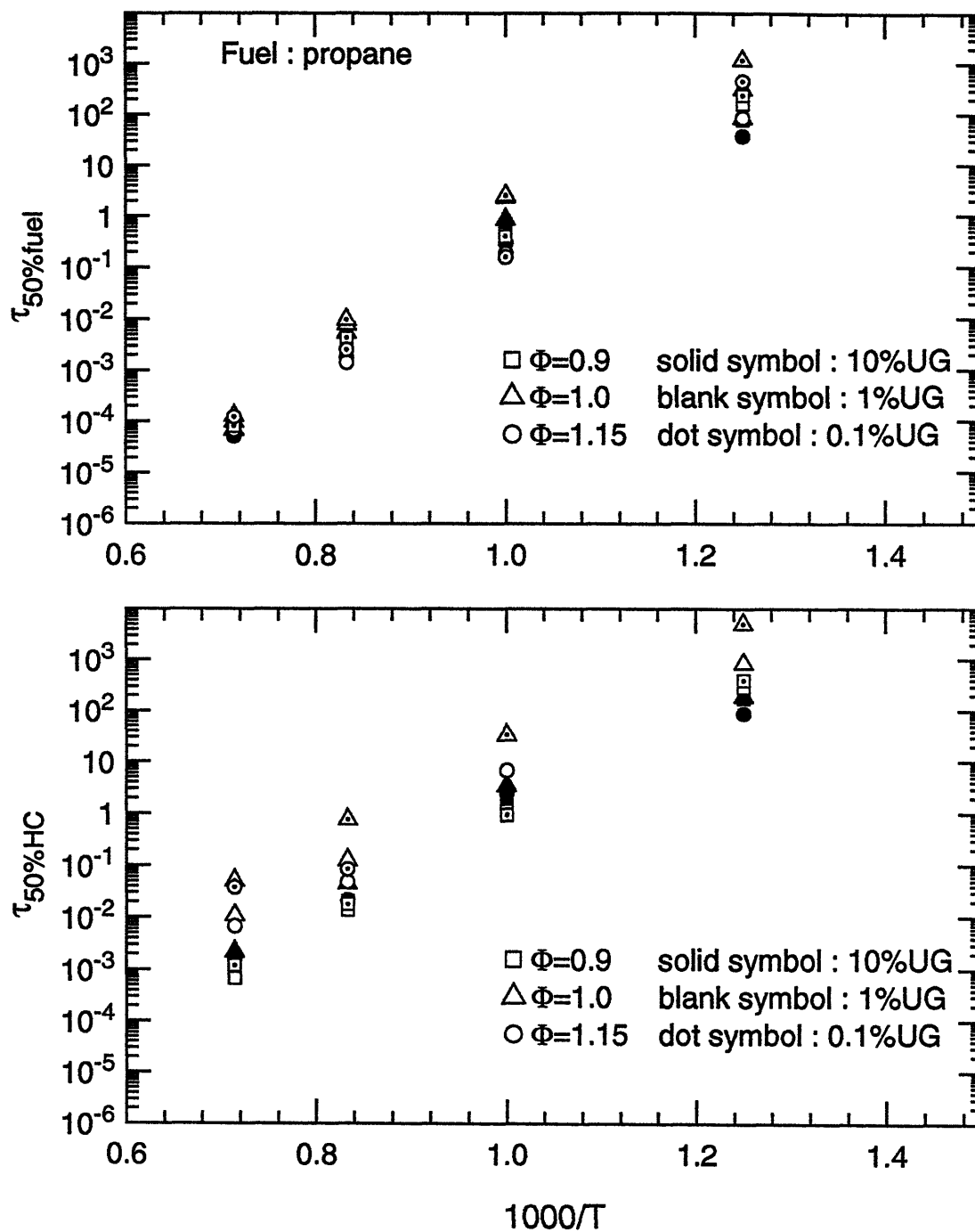


Figure 3.7: Characteristic 50% reaction time scales for propane as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

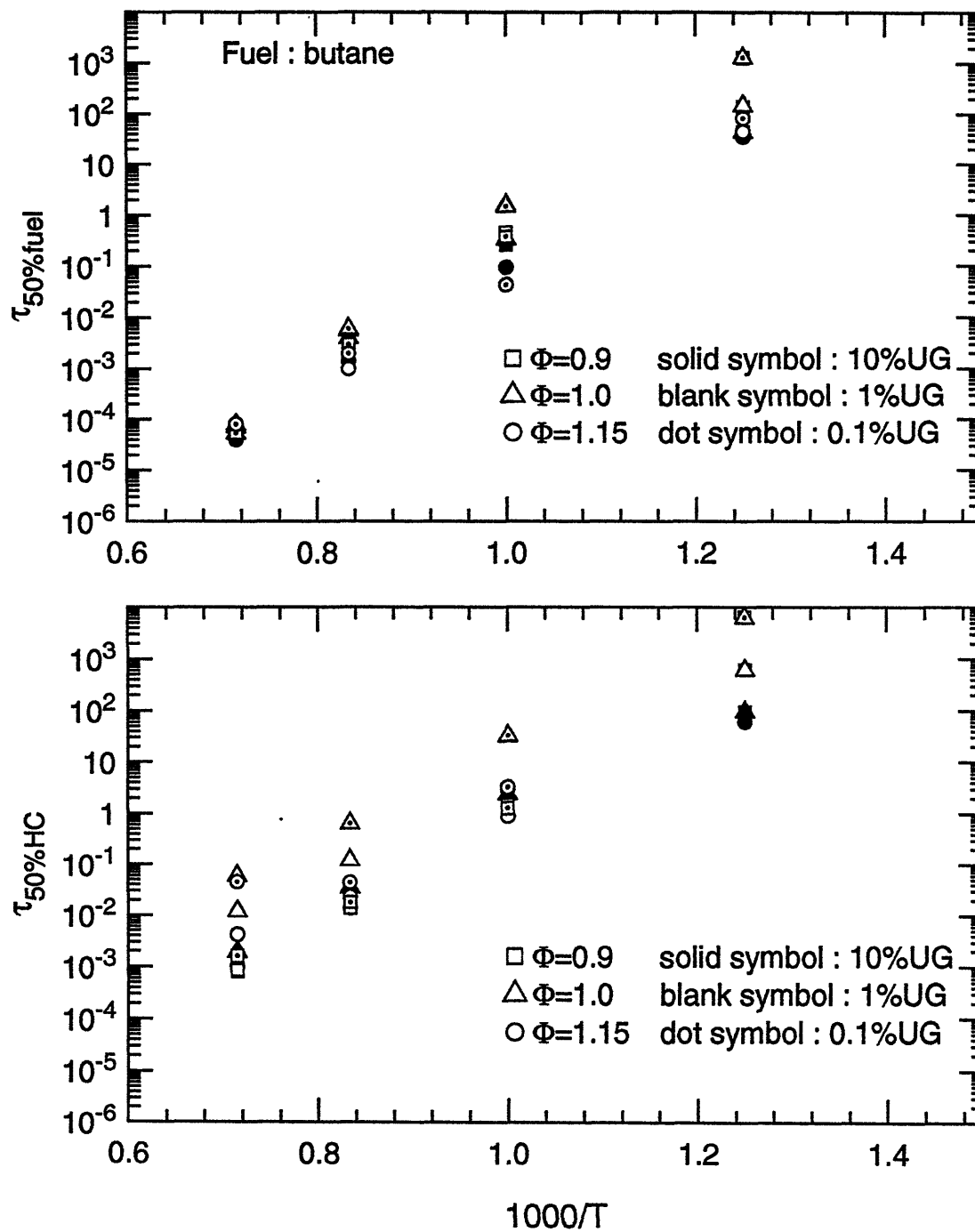


Figure 3.8: Characteristic 50% reaction time scales for n-butane as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

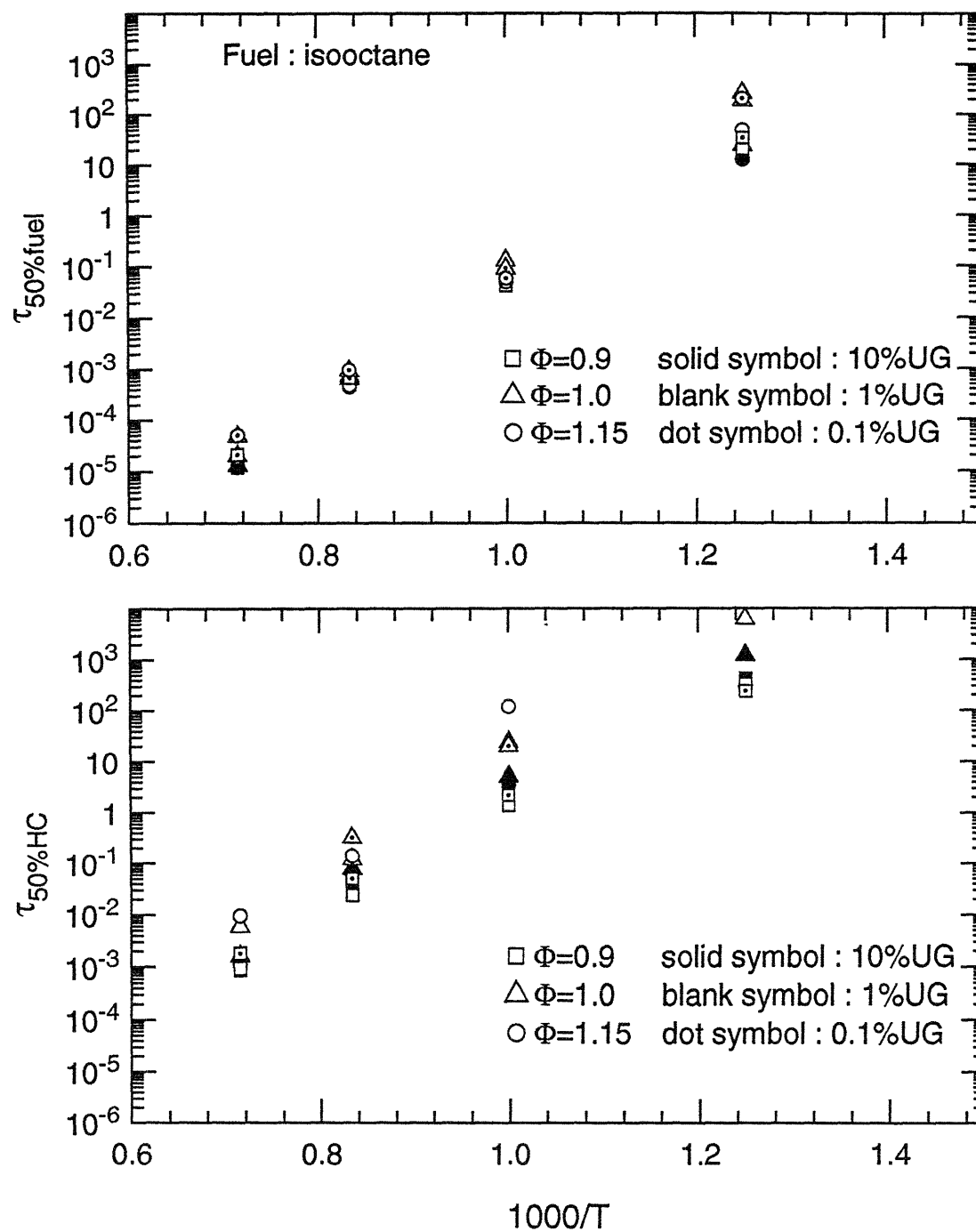


Figure 3.9: Characteristic 50% reaction time scales for iso-octane as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

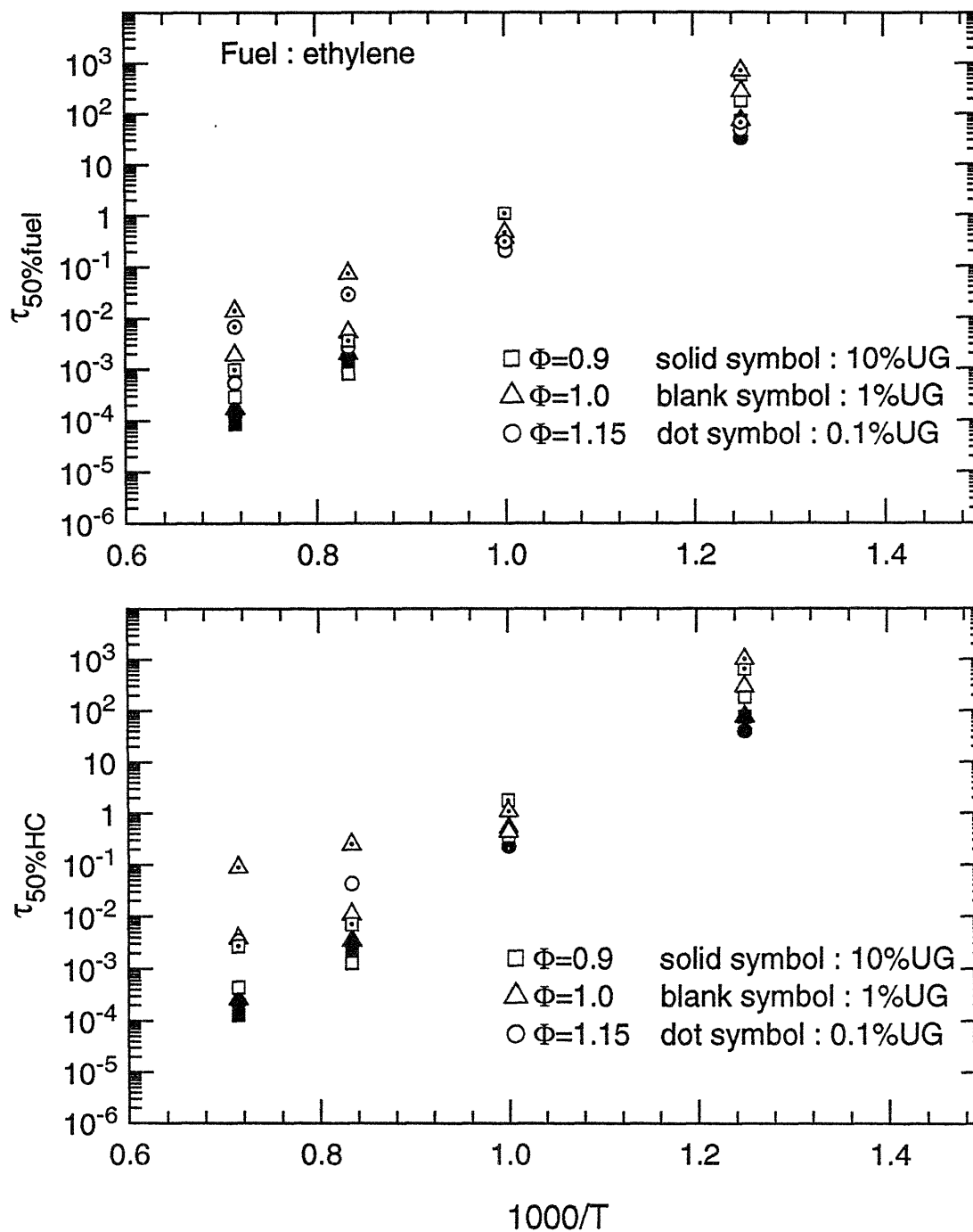


Figure 3.10: Characteristic 50% reaction time scales for ethylene as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

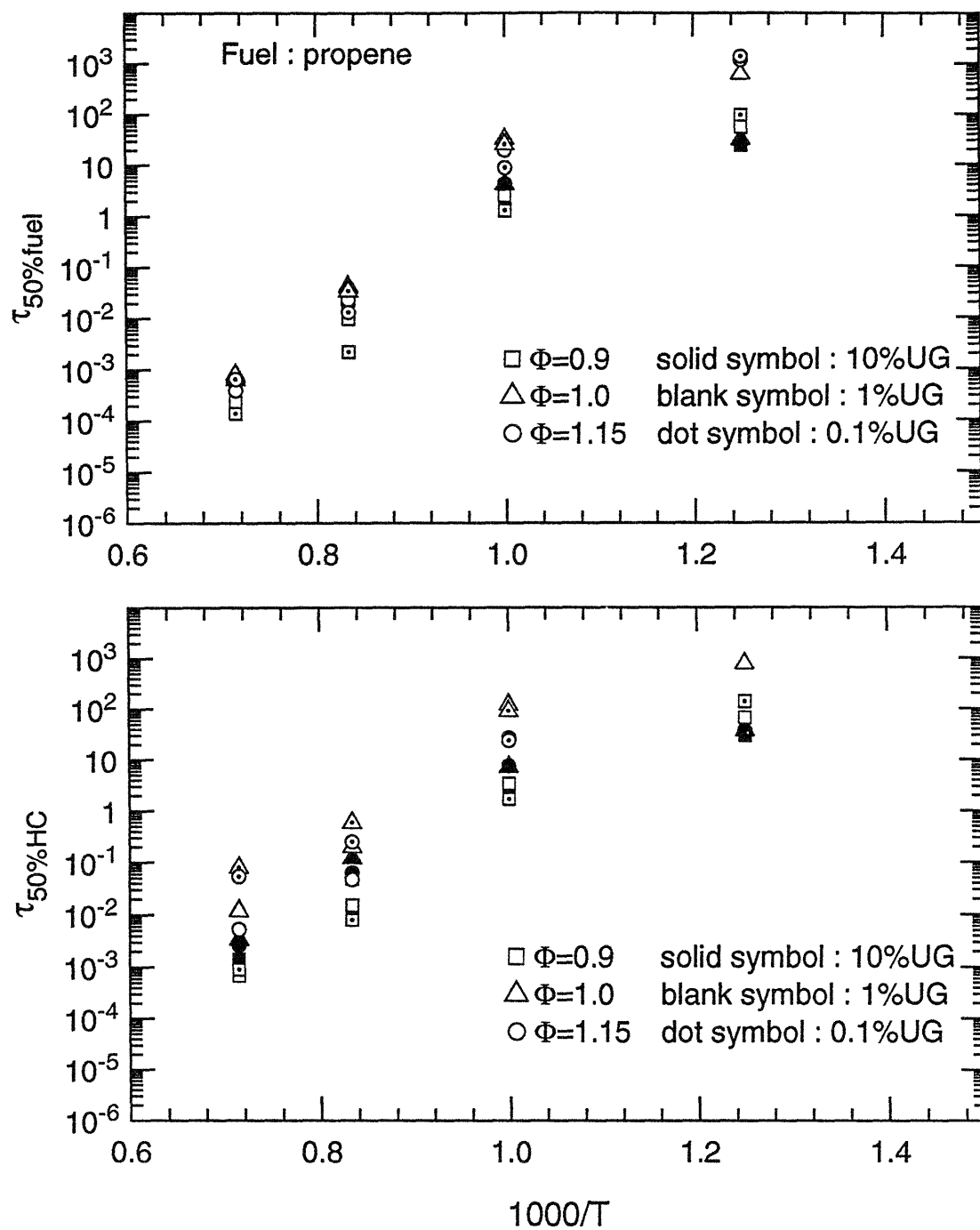


Figure 3.11: Characteristic 50% reaction time scales for propene as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

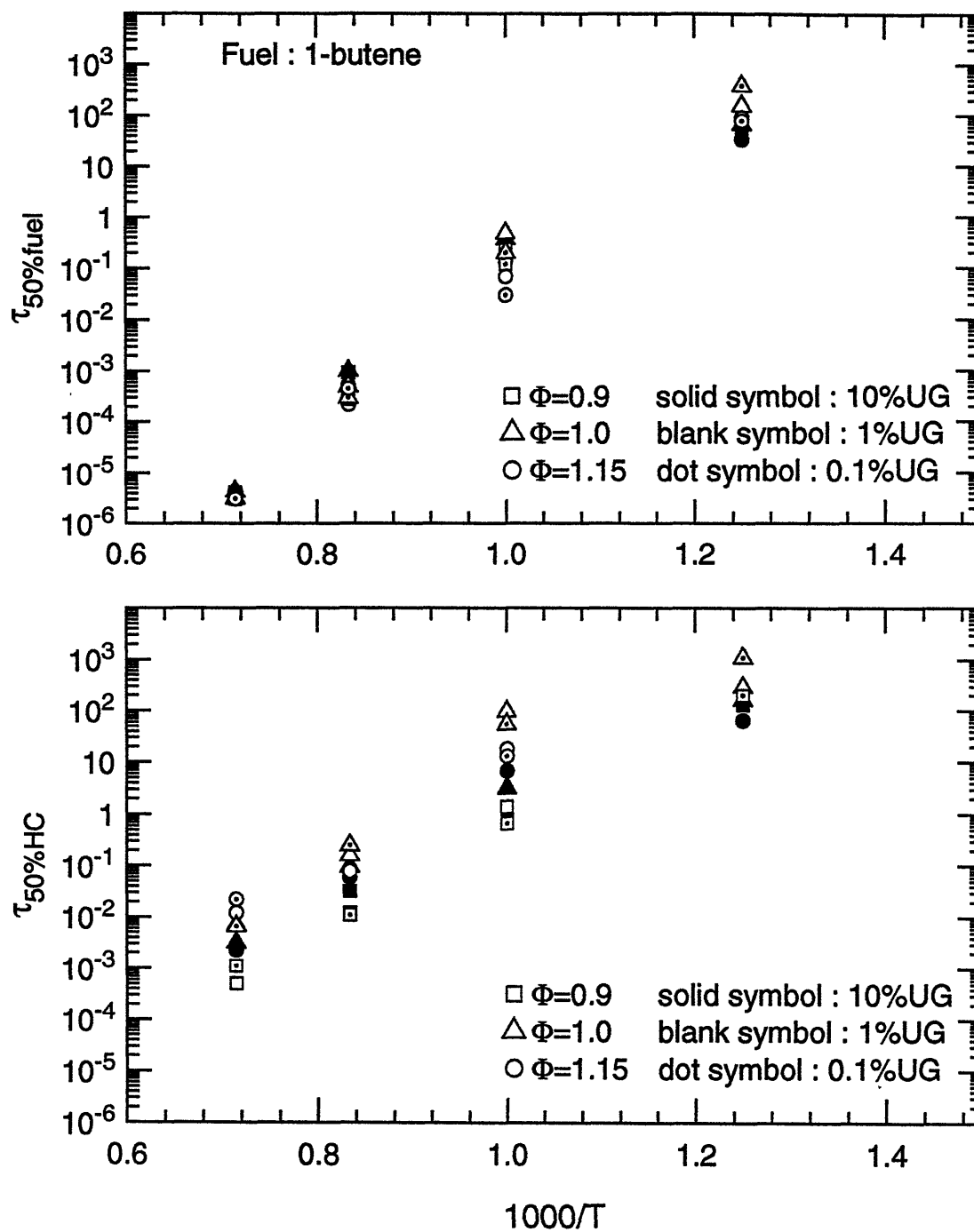


Figure 3.12: Characteristic 50% reaction time scales for 1-butene as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

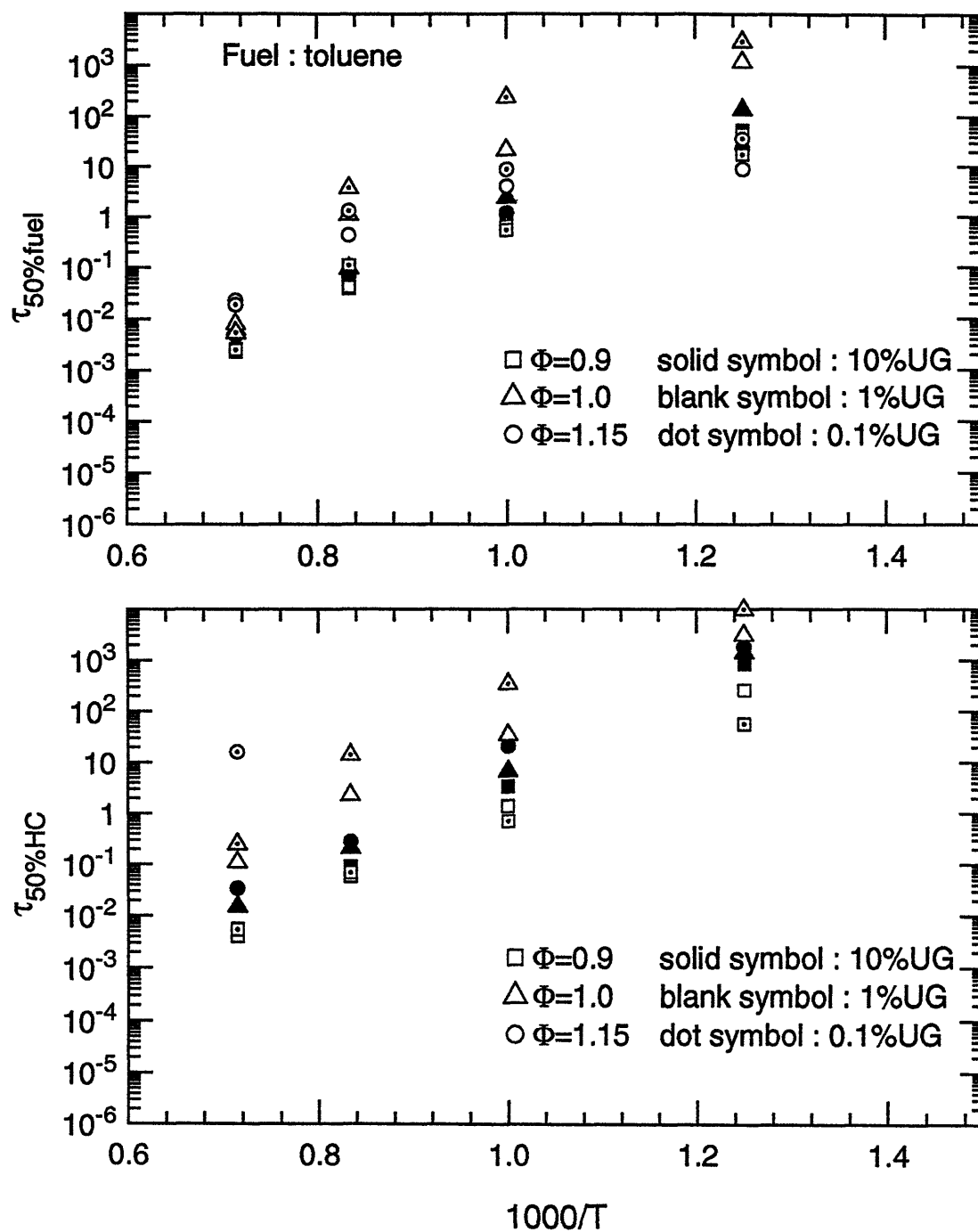


Figure 3.13: Characteristic 50% reaction time scales for toluene as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

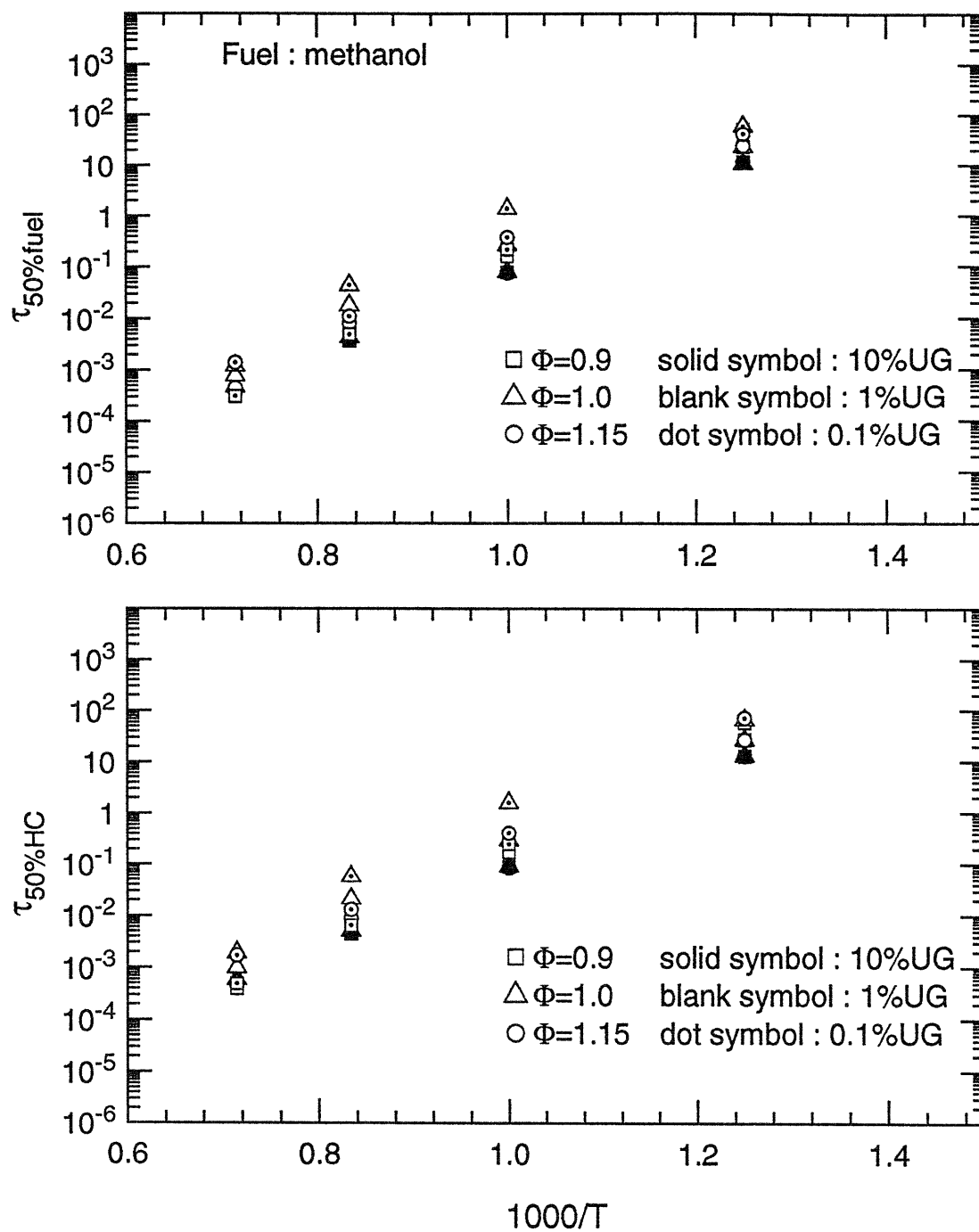


Figure 3.14: Characteristic 50% reaction time scales for methanol as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

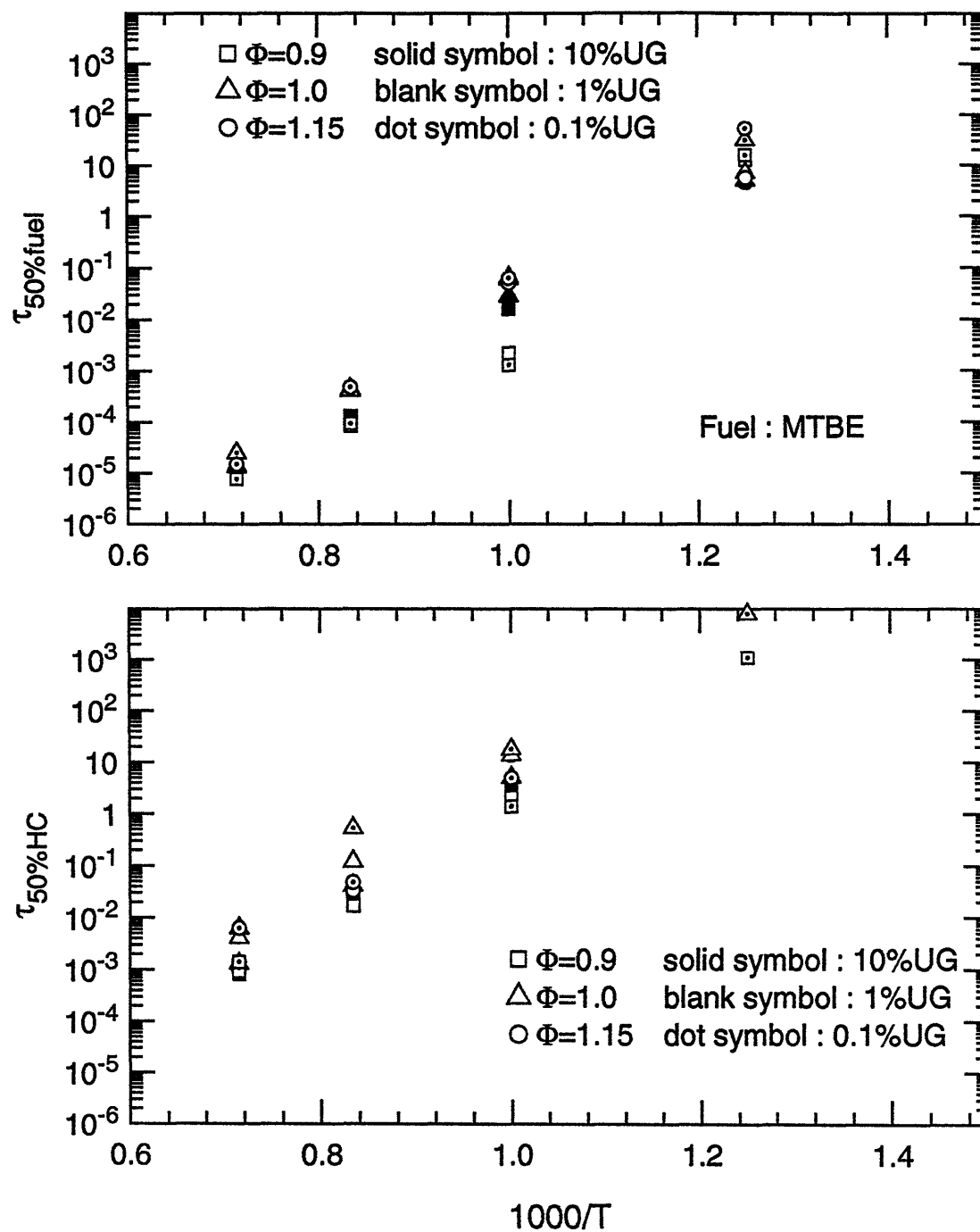


Figure 3.15: Characteristic 50% reaction time scales for MTBE as a function of reciprocal temperature for (top) fuel destruction; (bottom) overall hydrocarbon conversion.

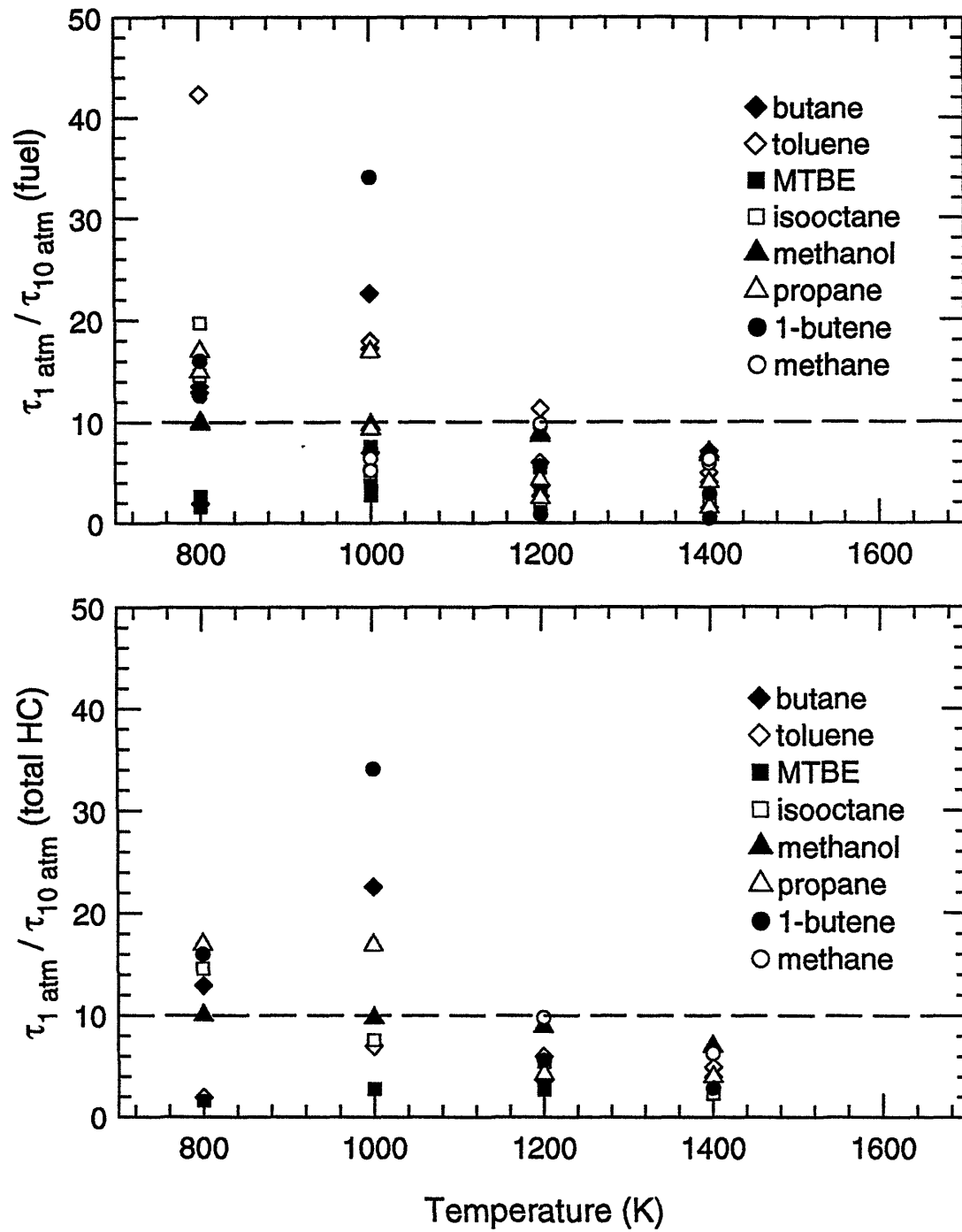


Figure 3.16: The ratio of the 50% reaction times at 1 atm to 10 atm as a function temperature for several selected fuels. ($\Phi=1.0$, 10% unburned mixture)

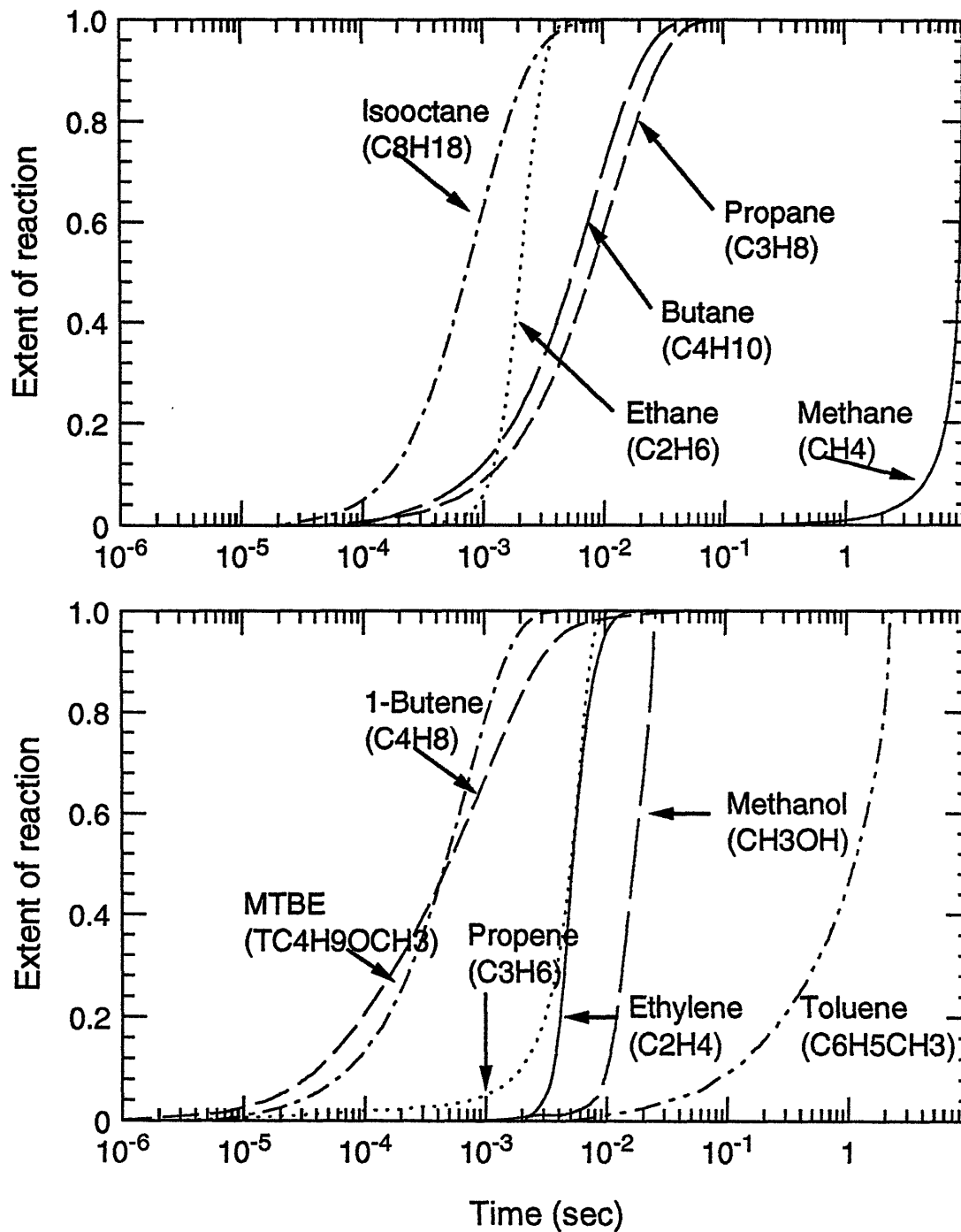


Figure 3.17: A comparison of the extents of fuel destruction for (top) paraffins; (bottom) olefins, oxygenated fuels, and toluene in and burned gas environment: $P=1$ atm, $\Phi=1.0$, $T=1200$ K, and initial concentration : 1% unburned gas mixture.

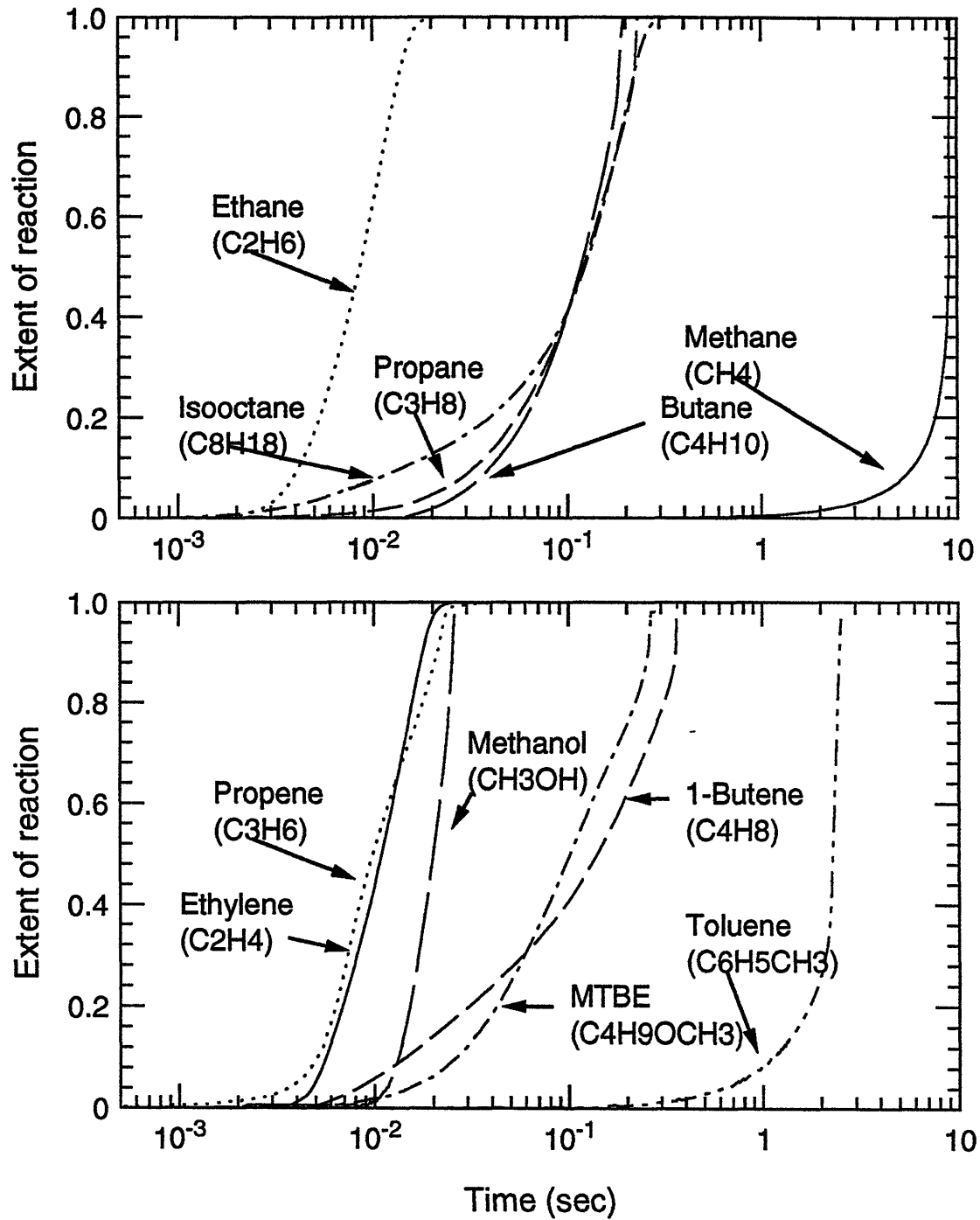


Figure 3.18: A comparison of the extents of overall hydrocarbon conversion for (top) paraffins; (bottom) olefins, oxygenated fuels, and toluene in an burned gas environment: $P=1$ atm, $\Phi=1.0$, $T=1200$ K, and initial concentration : 1% unburned gas mixture.

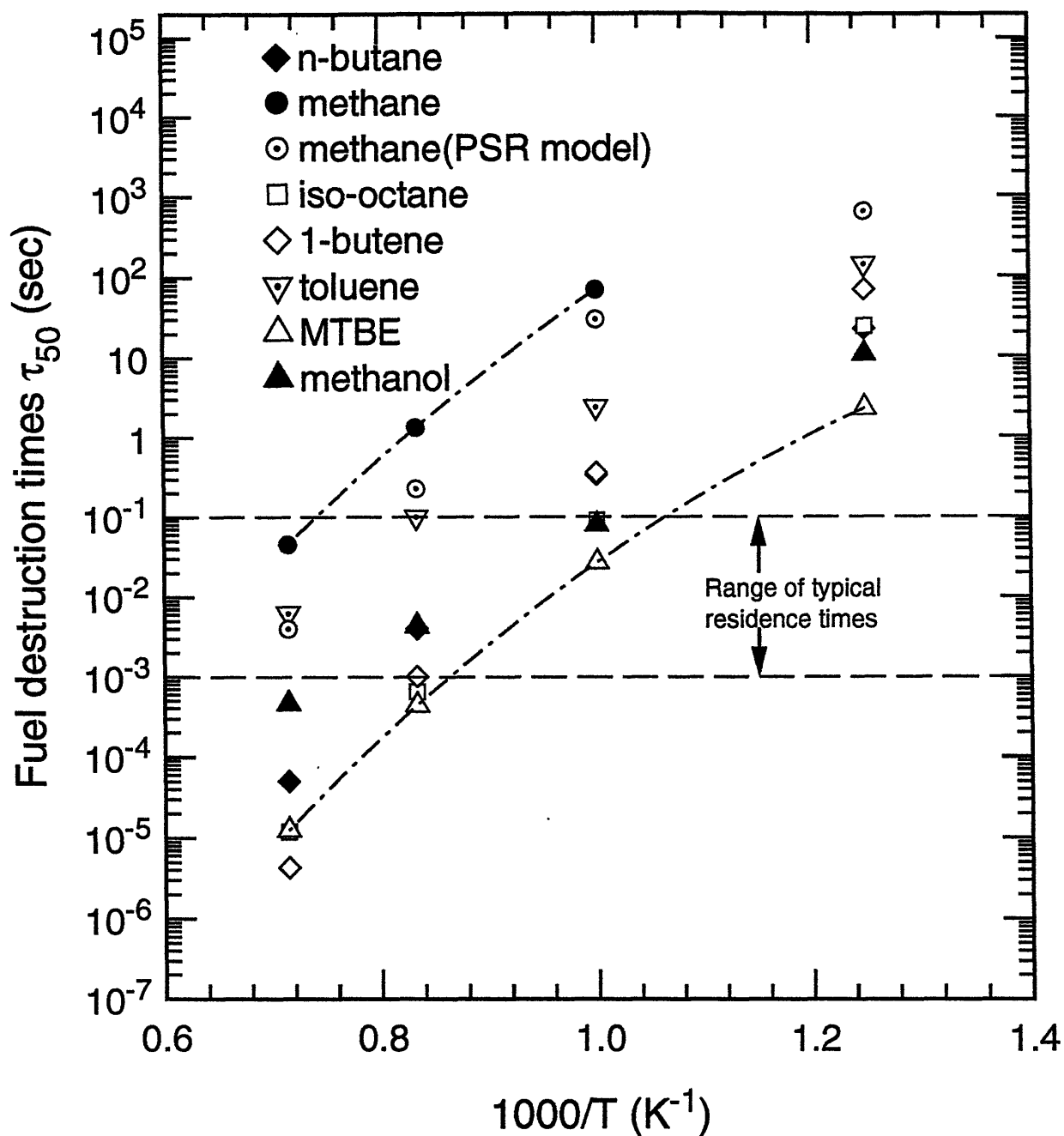


Figure 3.19: A comparison of practical residence times in SI engines (lines) and calculated half lives of fuels (symbols) during oxidation in a burned gas environment as a function of reciprocal temperature: $P=1$ atm, $\Phi=1.0$, and initial concentration : 1% unburned gas mixture.

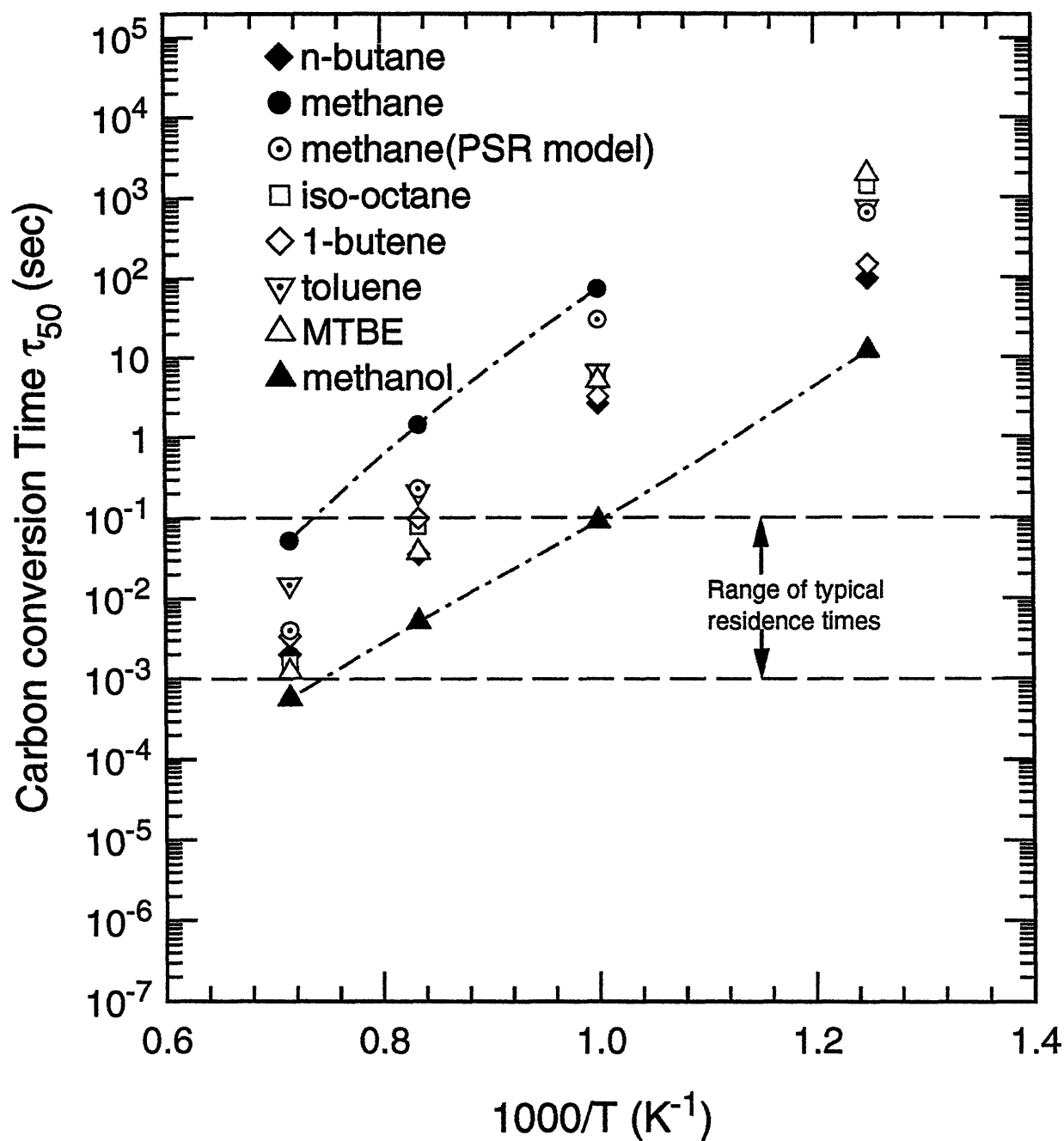


Figure 3.20: A comparison of practical residence times in SI engines (lines) and calculated half lives of total hydrocarbon (symbols) during oxidation in a burned gas environment as a function of reciprocal temperature: $P=1$ atm, $\Phi=1.0$, and initial concentration : 1% unburned gas mixture.

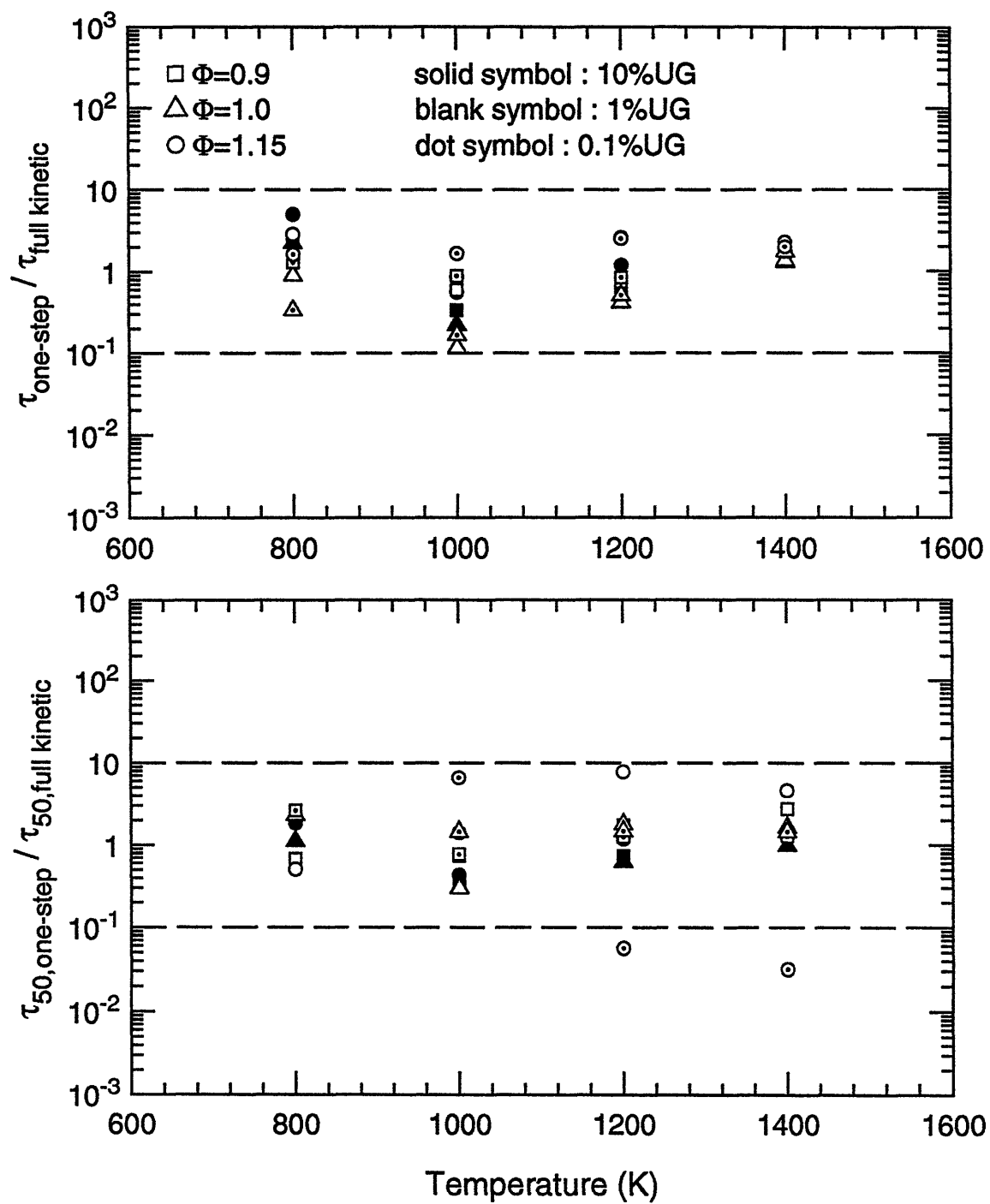


Figure 3.21: The ratios of characteristic reaction times for (top) fuel destruction (bottom) hydrocarbon conversion computed from one-step expressions to full kinetic mechanisms as a function of temperature. (Fuel : propane)

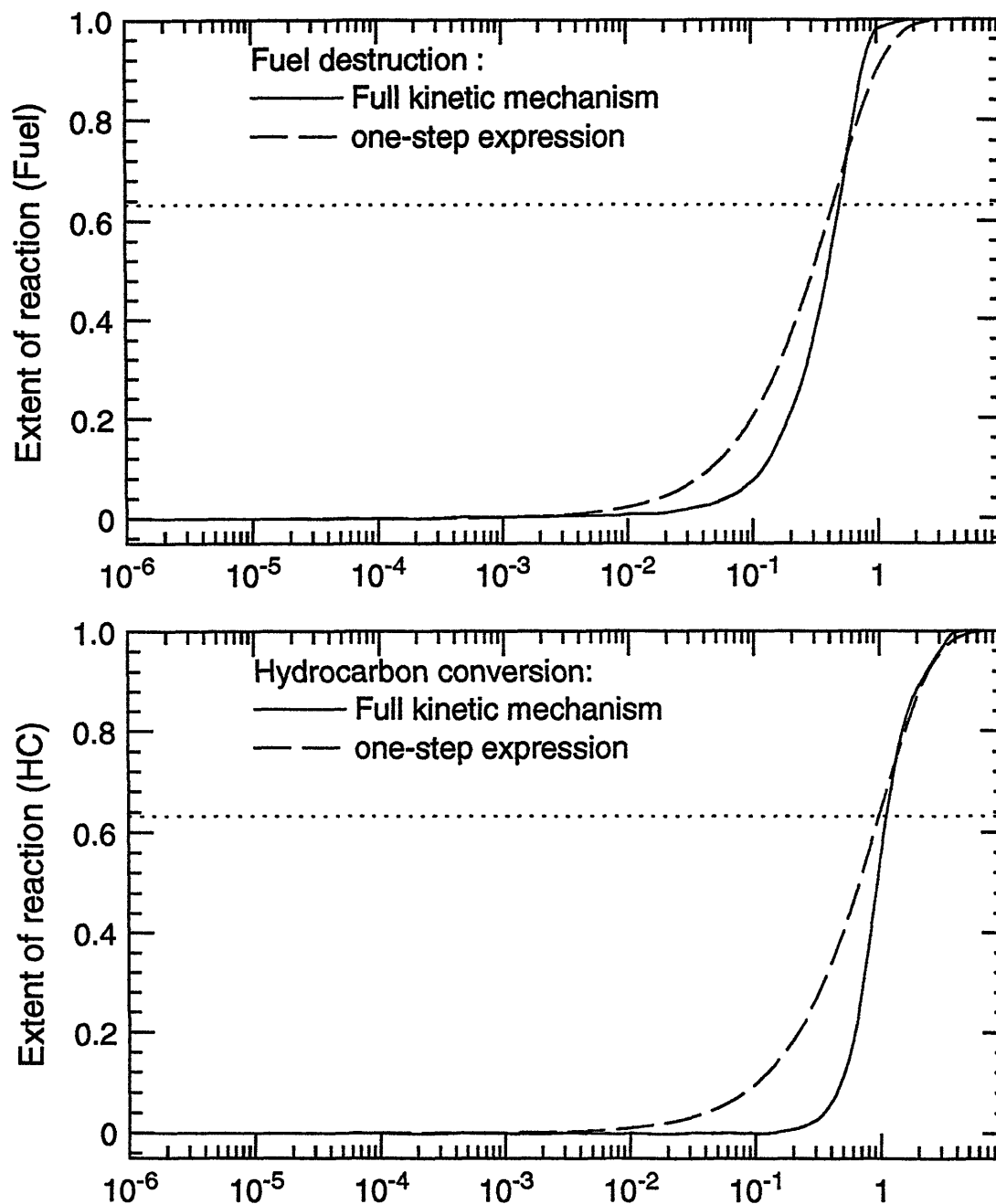


Figure 3.22: A comparison of the predictions of the behaviors of fuel destruction and overall hydrocarbon conversion from a one-step mechanism (dashed lines) and a detailed chemical kinetic mechanism (solid lines). Fuel : propane. A good match in the predictions of characteristic reaction times from two models is achieved in this case.

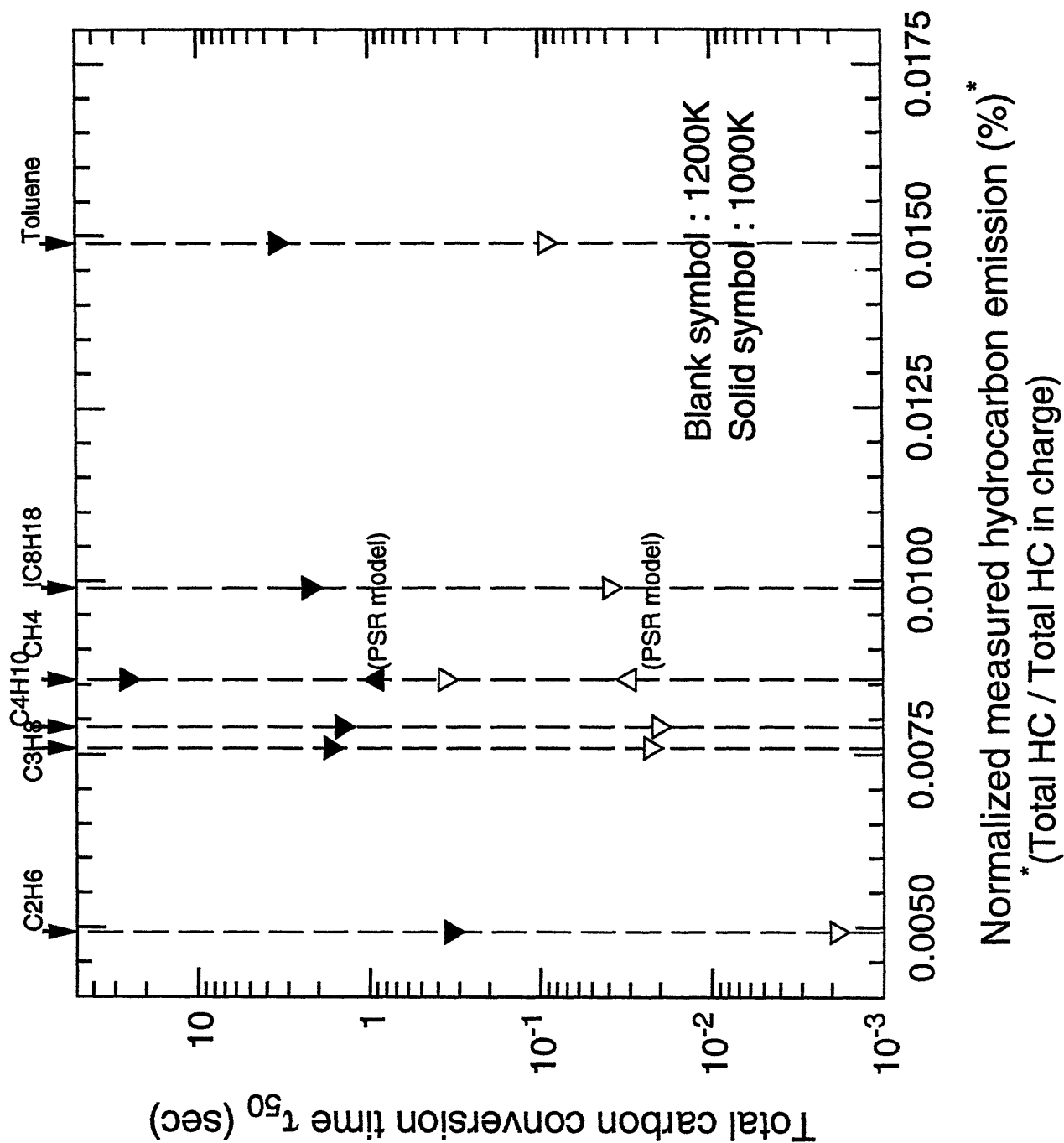


Figure 3.23 Calculated ratio of half lives for fuel oxidation and total hydrocarbon oxidation ($\Phi=0.9$, $P=1$ atm, $X_u=10\%$), plotted as a function of measured fraction of unburned fuel in the total hydrocarbons

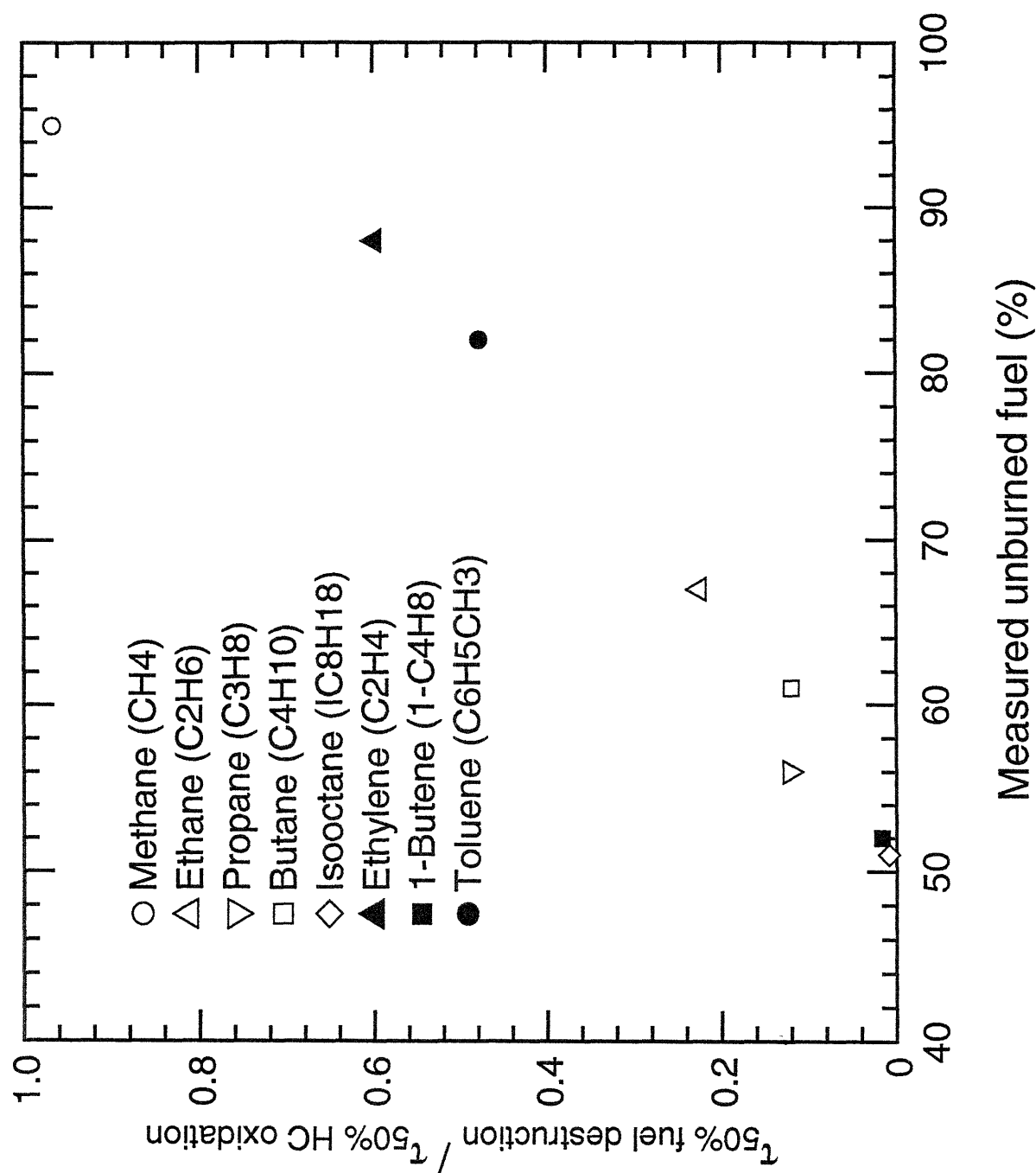


Figure 3.24: Calculated half lives for fuel oxidation plotted as a function of measured normalized hydrocarbon emissions ($\Phi=0.9$, $P=1$ atm, $X_u=10\%$). Two calculated values are shown for methane, for a plug flow and a stirred reactor simulation.

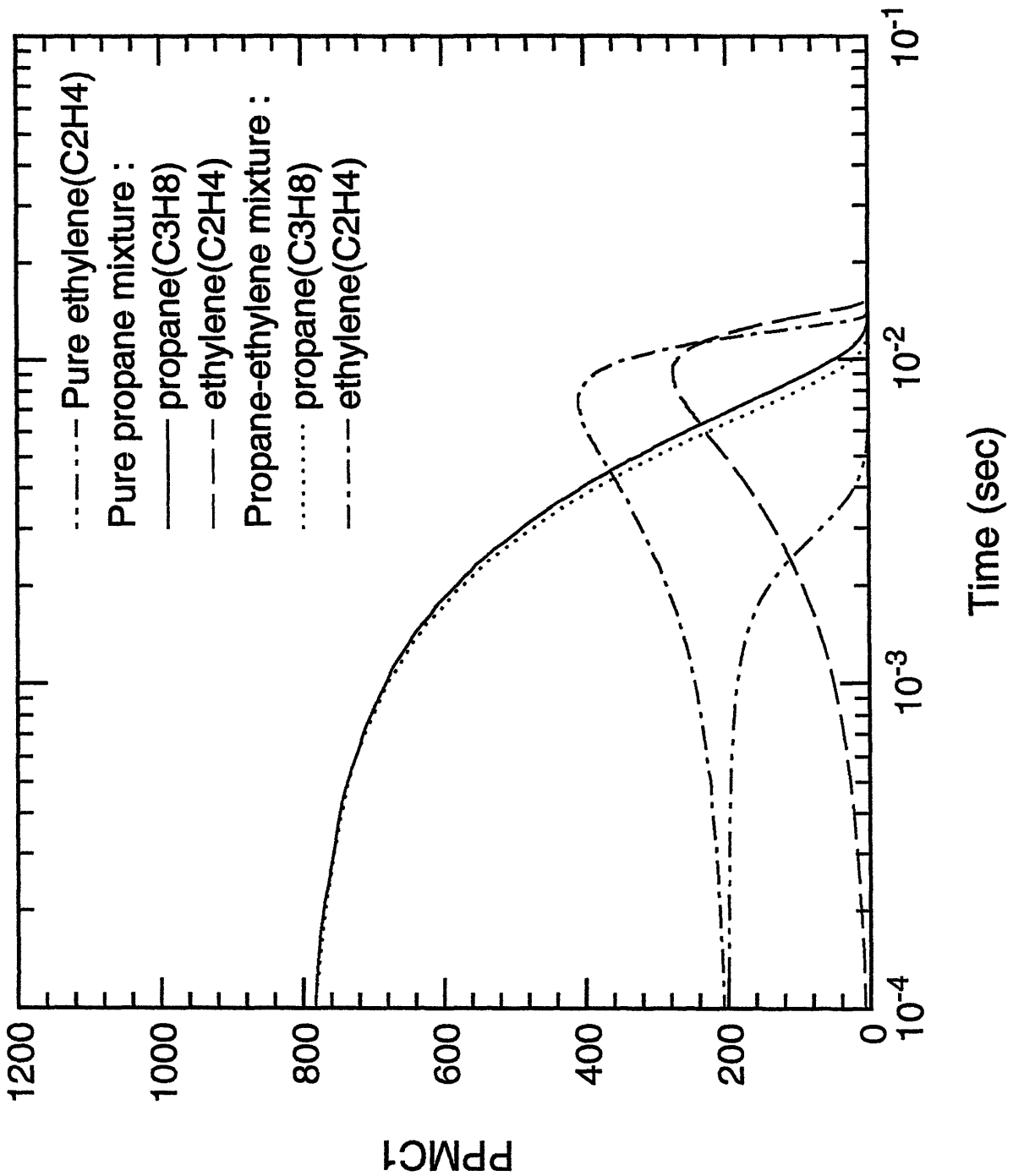


Figure 3.25: Calculated profiles of mole fractions of propane and ethylene in a burned gas environment as a function of time: $P=1$ atm, $T=1200$ K, total initial concentration : 1000 ppmC1. The ratio of initial concentration (propane : ethylene = 4 : 1). The calculated profiles of pure fuel destruction with the corresponding initial concentrations are also plotted for comparison.

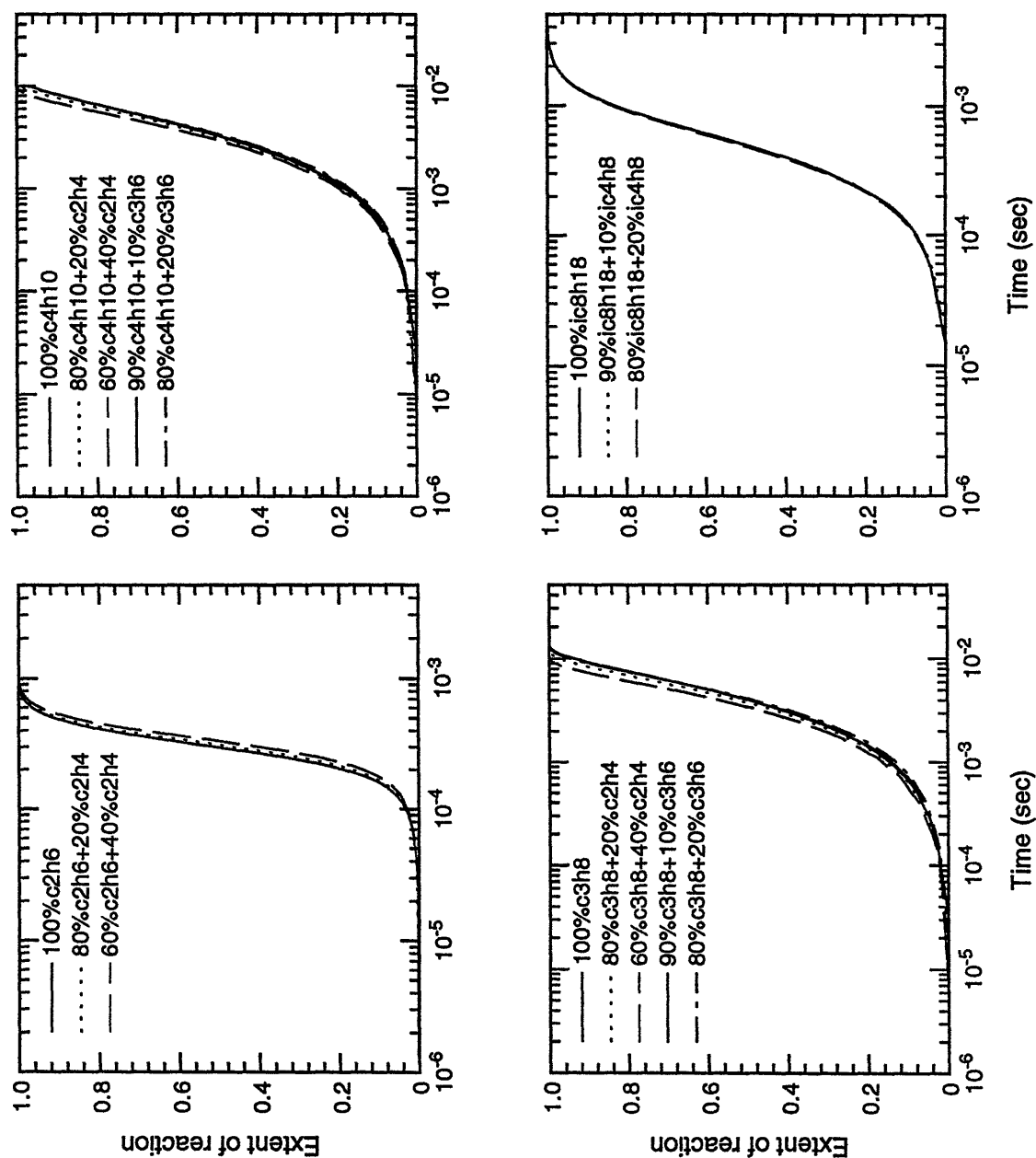


Figure 3.26: The effects of intermediate byproducts on the calculated extent of fuel reaction for ethane, propane, butane, and isooctane. ($T=1200$ K, unburned mixture fraction : 1%, $\Phi=0.9$)

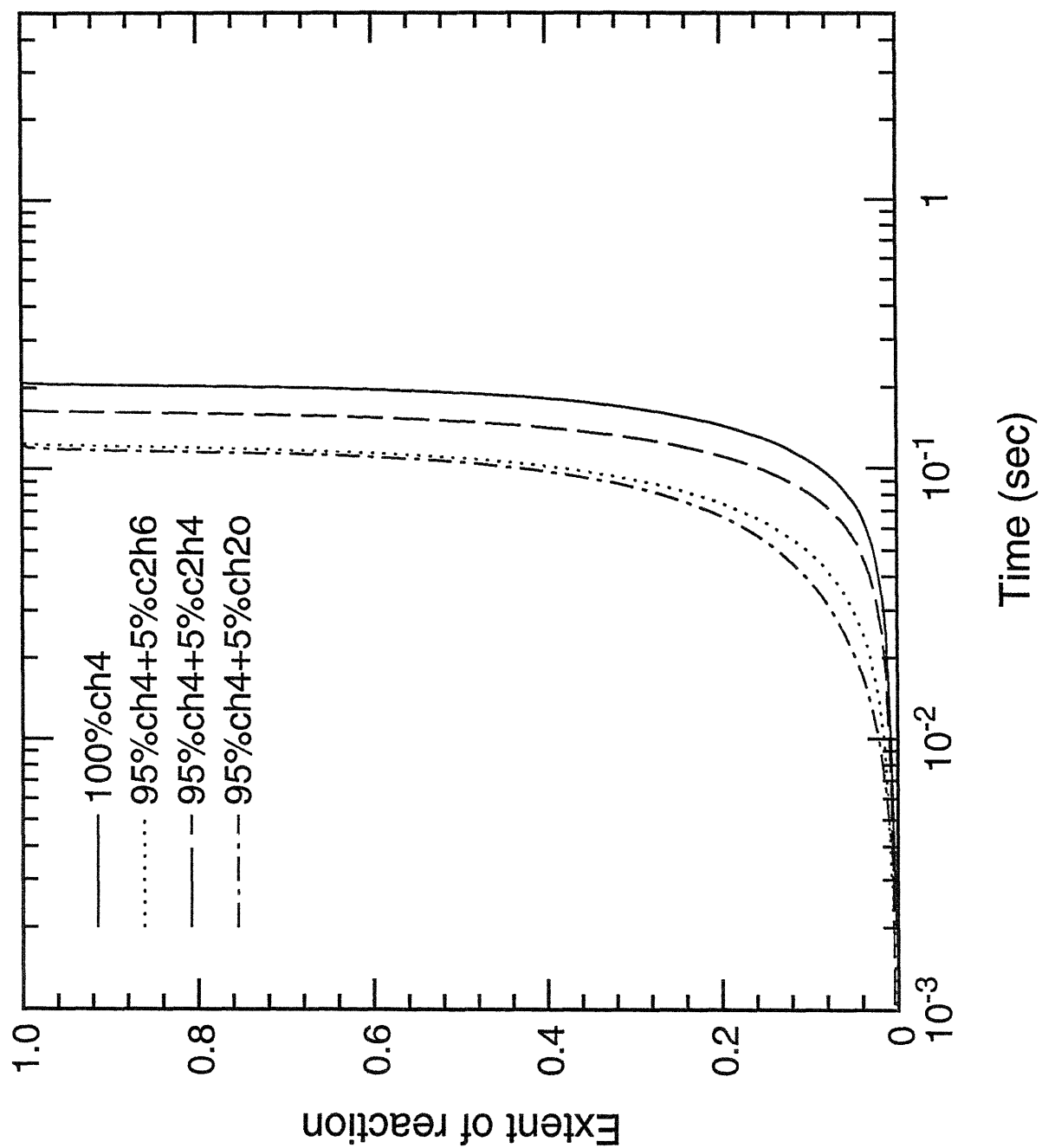


Figure 3.27: Calculated extent of fuel destruction for unburned mixture with different intermediates addition (ethane, ethylene, or formaldehyde) for methane. ($T=1200$ K, unburned mixture fraction : 1%, $\Phi=0.9$)

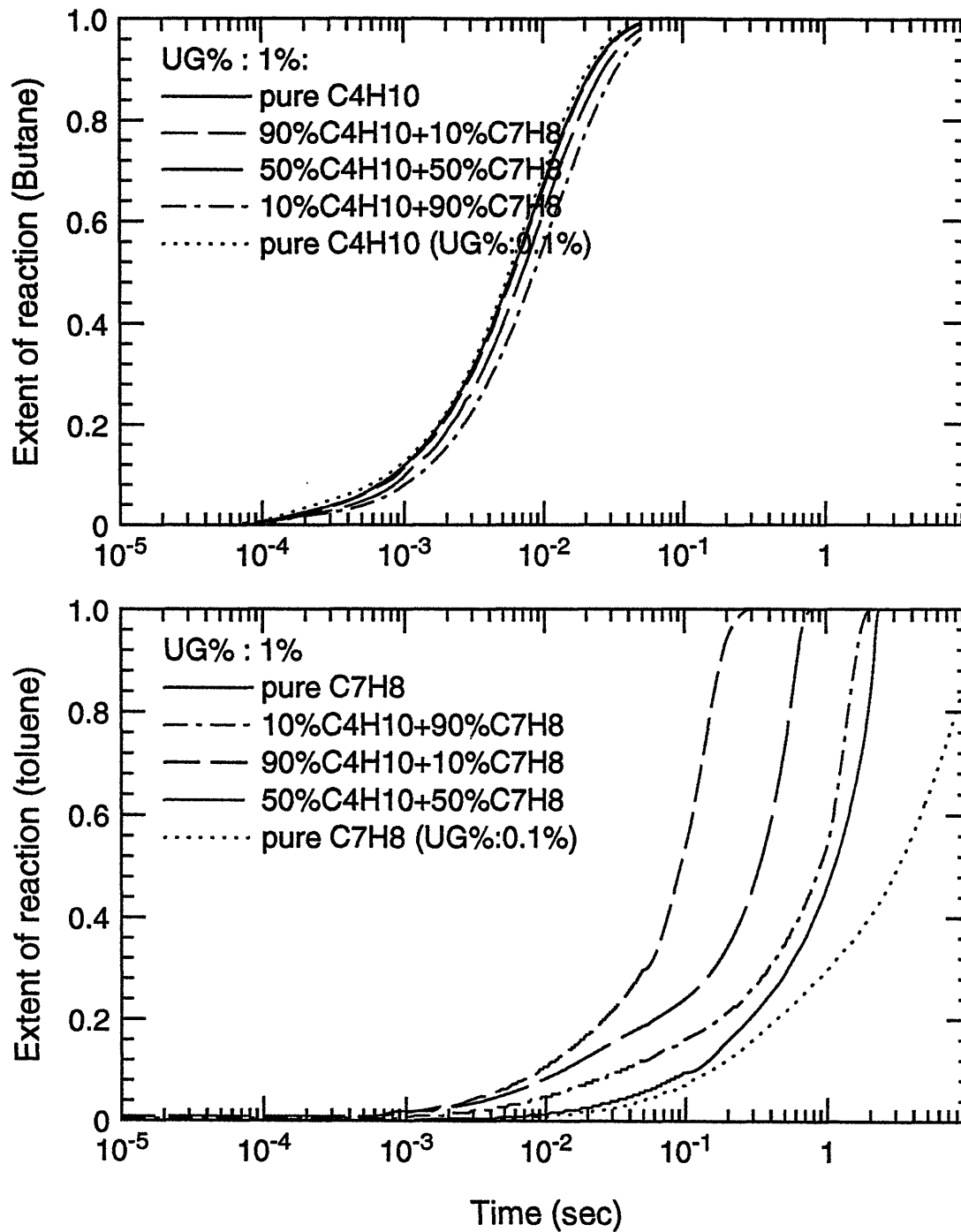


Figure 3.28: Comparisons of calculated extents of fuel destruction for (top) butane and (bottom) toluene for the different proportions of initial concentrations between two fuels in the 1% unburned mixtures. The corresponding extent of reaction of pure fuel in the 0.1% unburned gas are also plotted for comparison.

CHAPTER 4

EXHAUST PORT OXIDATION STUDY

4.1 Introduction

In the last Chapter, we focused on the behavior of chemical species during the oxidation process at constant conditions. Reaction time scales were chosen to be an index of characteristic of species for the parametric study. In this chapter, the focus is on a physically realistic model of the oxidation of unburned hydrocarbons in the region between the cylinder exhaust port and the tailpipe. The motivation for this study was based on several factors :

- the existence of speciated experimental data for comparison [35];
- the conjecture that much of the production of reactive intermediate hydrocarbons occurred under the low temperature conditions in the exhaust;
- the expectation of a fast mixing, homogeneous, kinetically controlled situation in the exhaust port

A thermal model for the exhaust temperatures is combined with the detailed chemical kinetic mechanisms to study the extent of reaction of fuels through the exhaust port.

As shown in Fig. 4.1, the exhaust port is defined as a region between the exhaust valve seat and the plane connected with the manifold (or exhaust runner). When the exhaust valves open during the expansion process the hot core gas and the cold unburned mixture which escaped combustion through different mechanisms are pushed out of the engine cylinder into the exhaust port through the blowdown event and exhaust process. Because the temperature of the mixture is still high when the gas passes through the exhaust port, about a third of the hydrocarbons leaving the cylinder are observed to be oxidized in the exhaust port [35]. The details about the

assumptions made in the simulation and the comparison between simulation and experimental data are discussed below.

4.2 Model assumptions

The temperature and concentration fields in the exhaust port are non-uniform and unsteady [37],[38]. At some distance downstream, the mixture of burned gases and cold unburned air-fuel mixture becomes increasingly uniform. The exhaust port hydrocarbon oxidation problem basically is an unsteady, multi-dimensional problem. Many of the initial and boundary conditions, as well as the turbulent mixing rates are not well known. Instead of attempting to solve the multi-dimensional unsteady problem, simplifying assumptions were made in order to provide bounds for the extent of oxidation.

The following assumptions were made in order to simulate the oxidation of unburned hydrocarbons in the exhaust port :

- **infinitely fast mixing** : the mixture of burned gases and unburned hydrocarbon and air is assumed to be uniform.
- **plug flow** : the calculation is performed by following the evolution of each mass segment exiting the cylinder exhaust port as a plug flow element that does not interact with other elements leaving at different times.
- **super-equilibrium radicals** : allowance was made for the existence of super-equilibrium concentrations of radicals in the burned gas mixture (Chapter 2).
- **heat transfer and temperature profiles** : temperature profiles were calculated from engine simulations (see below) and heat transfer correlations.

Because there were no accurate time-resolved measurements of hydrocarbons emissions at the cylinder and exhaust port for this set of experiments, a constant unburned fuel molar fraction was assumed and varied as a parameter. Typical average measurement values for hydrocarbon at

cylinder exit are around 1000 to 2000 ppmC1, varying through the cycle from 300 to 5000 ppmC1. The values 300 ppmC1 and 4500 ppmC1 were chosen to bracket the concentration range and check the effects of unburned mixture concentration on the extent of oxidation of unburned hydrocarbons. In this chapter, the unit ppmC1, which is usually used in measurement of emissions, will be adopted for easy comparison between experimental data and simulation results instead of the use the unburned gas mixture. The conversion of two units given by :

$$X_{\text{HC}} (\text{ppmC1}) = 10^6 X_u \frac{\Phi}{\Phi + a(1 + 3.773)} b$$

X_u : unburned gas mixture (4.1)

Φ : fuel / air equivalence ratio

a : stoichiometric number of moles of air per mole of fuel

b : number of carbons per molecule

For most fuels, one percent of unburned mixture fraction correspond to about 1000 to 1500 ppmC1. Experimental data [35] show that the initial concentrations of intermediate products are not zero at the inlet of the exhaust port. However, it has been shown in Chapter 3 that fuel oxidation rates are not significantly affected by initial concentrations of their intermediate products at the concentrations measured. The unburned gas was assumed to consist only of fuel and air when the extent of reaction of fuel was the first concern. The behavior of intermediate reaction products will also be studied in a later section. Therefore, under the present assumptions, the unburned fuel/air mixture and the super-equilibrium burned gas mix perfectly at the inlet of the exhaust port and react at constant pressure and programmed temperature as it flows as a plug along the exhaust port.

4.3 Results

In order to simplify the calculations, the total mass in the cylinder was discretized into ten equal mass elements and the residence times and temperature histories were calculated for each segment from engine simulations. The port oxidation simulations were performed for each discretized element according to its corresponding temperature history and residence time. Fig. 4.2 shows simulation results for the extent of reaction of each element that leaves the cylinder for propane at two different engine speeds. The residence time in the exhaust port decreases as the engine speed increases, and the temperature increases because the heat transfer is reduced when the residence time is shorter for heat loss (shown in Fig. 4.2(a)) Therefore, a comparison of simulated results at two different speeds provides a chance to compare the effects of temperature and residence time on the extent of reaction in the port. Results indicate that unburned hydrocarbons leaving the cylinder early will have a much better chance at oxidation in the exhaust than those leaving at later crank angles and the effect of increasing speed is primarily an exhaust temperature increase due to reduced heat transfer, which more than compensates for the reduced residence time in the exhaust port.

Results from an exhaust port quenching experiment carried out by Drobot et al. [35] were compared with the simulation results. A schematic of the experimental set up is shown in Fig. 4.1. A cold quench gas is injected into the exhaust system at either the cylinder exit (plane 1 in Fig. 4.1) or the port exit (plane 2 in Fig. 4.1) during the whole exhaust procedure in order to stop the oxidation. The level of oxidation in the exhaust port is then quantified by the difference in hydrocarbon concentration under quenching at plane 1 and quenching at plane 2 conditions. Because measurements are only integrated over time, no time-resolved data are available, and simulation results for every element leaving the cylinder at different crank angles must be summed up for comparison. In Fig. 4.3, the calculated total extent of reaction in the port of the conditions in Fig. 4.2 is compared to the experimental results. Clearly, the calculations largely underpredict the observed extent of reaction in the port. The possible causes of the discrepancy

could be : (a) an underprediction of the average temperatures due to inadequate heat transfer correlations in the engine or exhaust and (b) incomplete mixing leading to a partially or totally mixing-controlled situation instead of fully-mixed, kinetically controlled process. The latter possibility was not taken into account in this study, even though mixing rates may play an important role on the extent of oxidation in the exhaust port. Mixing rate control will be included the next phase of this project. Option (a) is certainly a possible explanation, since heat transfer correlations for cylinder and exhaust port are not very accurate. In order to investigate the role of temperature uncertainties, two temperature profiles have been chosen to bracket the maximum and minimum temperatures for reaction by two extremes (shown in Fig. 4.4) :

(a) the original temperature profile predicted from the engine simulation codes, which assumes full mixing of the boundary layer and core gas, i.e. it is the average cylinder and exhaust temperatures (low temperature limit);

(b) the predicted temperature profile calculated by assuming a different heat transfer correlation in the cylinder. Because of the reduction of heat loss in the cylinder, the temperature of the gas exiting through the exhaust port is closer to that of the core gas. In order to check the maximum limits of the extent of reaction in the port, no heat transfer in the exhaust port is assumed, i.e. it is the adiabatic core temperature without mixing with the boundary layer (high temperature limit).

The final calculated extent of reaction for the total mass of fuel that leaves the cylinder (Fig. 4.5) shows that the experimental data considered, which cover 30 to 50 percent reduction in hydrocarbon concentration in the exhaust port section, are bracketed by two limits. The upper limits indicates that except for methane, hydrocarbons would be completely oxidized at core temperatures. The lower temperature limit results show that the oxidation level should depend strongly on fuel type and somewhat less on the initial concentration of unburned fuel. The fuel concentration effect on the oxidation level is in part a result of super-equilibrium radicals in the

burned gas. For smaller fuel concentrations, this effect is very apparent, but for larger fuel concentrations (beyond 1000 ppmC1) the oxidation level is not significantly affected by non-equilibrium radicals. This will be discussed in more detail in section 4.4. The assumption of plug flow rather than stirred reactor does not affect the resulting extent of reactions for all fuels except methane. Fig. 4.6 shows the difference between the calculated extent of reaction from plug flow and stirred reactor models. The simulated result from stirred reactor can be treated as the extremely highest limit for methane reaction in the port. However, although further oxidation would be achieved at the same level of temperature in a stirred configuration because of product recirculation in this case, the accompanying temperature drop due to stirring with colder gas would more than compensate for that effect.

4.4 Discussion

The quenching experiments showed that, for all fuels tested, roughly forty percent of the cylinder-out unburned fuel is oxidized in the exhaust port [35]. The relative lack of sensitivity of the extent of reaction in the exhaust port to fuel type implies that the process is mainly controlled by the rate of mixing of the cold hydrocarbon layers with the burned gas, since mixing processes are controlled primarily by the fluid mechanical processes in the engine and they should have little dependence on the type of fuel used. However, the slight increase in intermediate oxidation products indicates that the process must be at least partially controlled by chemical kinetic rates. In addition, other experiments showed that temperature and species concentrations are certainly not uniform at the exit of the cylinder [37,38]. The observations imply that the picture may be such that of hot gases squeezing through the open exhaust port while some of the cold boundary layer next to the cylinder wall, containing unburned hydrocarbons, emerges into the exhaust port, and mixes with the bulk hot gases as it travels through the port. Full mixing becoming complete at some distance downstream. The full mixing calculation with average temperatures, which we

have done in this chapter, can be envisioned as one of the limits of oxidation if mixing did occur fast enough. In addition, the adiabatic core temperature simulations not only provide the upper limits for the fuel destruction in the exhaust but also the information about that the oxidation take place in distributed pockets under molecular diffusion-controlled conditions in the regions where temperatures are still high enough. Accordingly, it is not surprising that simulations of two temperature limits did not make good predictions for the oxidation in the exhaust port. However, the work done in this chapter provide a clear picture of how the hydrocarbons react if they were completely mixed. In this section, quantitative and qualitative analysis are performed to study the switch-over temperatures at which mixing rates should become controlling, initial concentration and super-equilibrium effects, and the concentration of intermediate combustion products observed in the experiments in order to further approach the hydrocarbon port oxidation problem.

Switch-over temperature between mixing controlled and kinetically controlled process

Typical residence times in the exhaust port during EVO are between 1 and 10 milliseconds for moderate engine speeds. Mixing times, although not well defined, should be in the same range as residence times if mixing is complete at some distance downstream in the exhaust. Therefore, a residence time of one millisecond (approximately 9 crank angles at 1500 rpm) was chosen for investigating the temperature region beyond which chemical reactions are shorter than mixing times, here called switch-over temperature. One can define it conveniently as the temperature at which most of the fuel is oxidized at a fixed residence time, assumed to be equal to the mixing time. The actual level of oxidation chosen in the definition is not important, since at a fixed residence time extents of reaction from 20% to 80% are realized within 50 K (Fig. 4.7). Fig. 4.7 shows the sensitivity of the extent of reaction as a function of temperature for different residence times. The switchover temperature decreases by approximately 100 K if the mixing time increases from 1 to 10 milliseconds. Because the current results were obtained from constant temperature calculations rather than the quickly dropping temperature in the port, the

switch-over temperatures would be underpredicted by the results of residence times of 10 milliseconds. Thus, the calculated results from the residence times of one millisecond would be a better choice to compensate the temperature for drop effects. Figures 4.8 (a) and (b) show the extent of reaction as a function of temperature for fuel decomposition and hydrocarbon oxidation at a fixed residence time of one millisecond for different fuels, respectively. From the comparison of switch-over temperatures and predicted temperature profiles through the exhaust port, one can identify temperature regions where the reaction rate of each fuel is so high that the disappearance of fuel is primarily controlled by mixing or, conversely, so low that it would be kinetically controlled. Figure 4.9 shows the extent of reaction for two different fuels for different temperatures and a fixed residence time in the exhaust port. The switch-over temperature between mixing-controlled and kinetically-controlled process at typical port residence times is about 1300 K for most fuels at a residence time of 1 millisecond, except for methane, whose calculated result from plug flow model is closer to 1500 K and, for the stirred reactor results, closer to 1400 K. For the baseline case considered, the maximum core temperatures are about 1500 K, and maximum average temperatures (lower temperature limit) are of the order of 1300 K. Therefore, from the comparisons, there is a period during which the oxidation process is mixing-controlled or partially mixing-controlled when temperatures in the exhaust are in excess of 1200 K, followed by a region where the process is controlled by the slower chemical kinetics.

Super-equilibrium radicals and initial concentration effect

Since the reaction rates of reactive radicals (H, O, and OH) are very fast, the level of concentrations of radicals kept very low during the fuel oxidation process. During the initial phase of reaction, super-equilibrium radicals, which exist in the core burned gas due to insufficient time for recombination during the fast blowdown process, mix with unburned fuel and oxygen and react very fast until the concentrations of radicals return to the normal level. Figure 4.10, 4.11, and 4.12 show the effects of super-equilibrium radicals on the fuel and total hydrocarbon disappearance for different initial butane concentrations (10%, 1%, and 0.1%

unburned gas) at different temperatures (1400 K, 1200 K, and 800 K), respectively. Results indicate that, for very small initial concentrations (0.1% unburned fuel which roughly equal 100 ppmC1), the behavior of hydrocarbon oxidation is significantly accelerated by one to two orders of magnitude because the extra radicals can quickly attack this small amount of hydrocarbons. As the initial fuel concentration increases, only part of the unburned fuel reacts within a very short time period (approximately 10^{-4} seconds) and the remainder reacts similarly to that of the equilibrium burned gas case. The larger the initial concentration is, the relative smaller fraction of unburned hydrocarbon is quickly depleted by super-equilibrium radicals. Radical effects on hydrocarbon reactions are more pronounced at lower temperatures, since the active radical concentration difference between the equilibrium and super-equilibrium burned gas is larger at lower temperature (Fig. 2.2 shows the deviation of OH radical from equilibrium states during the exhaust process, the lower temperature corresponding to a later crank angle shows larger deviation from equilibrium states).

In addition, because the concentrations at the inlet of the exhaust port are not uniform, simulations with a step variation in initial concentrations were performed to investigate the sensitivity of final calculated extent of fuel destruction to the variations in the initial concentrations. Profiles of the initial concentrations are plotted in Fig. 4.13(a). One is a high-step concentration (4500 ppmC1) at the beginning and followed by low concentration step (300 ppmC1) (profiles A and B), the other has the opposite profile, which has low step at the beginning and finally followed by a high step (profiles D and E). Approximate 10% (profiles A and D) and 20 % (profiles B and E) exiting mass were assumed contain 4500 ppmC1 unburned fuel to bracket the constant 1000 ppmC1 results (profile C) for comparison in each profile. Fig. 4.13(b) indicates that the oxidation level is significantly determined by the extent of reaction of the high-step concentration because of the weighting factor of high concentration in the integration. Thus, the constant concentration assumption would underpredict the oxidation level if the gas with high level of hydrocarbon concentration exits the cylinder at the early stage so that the temperature is still high enough for relatively large extent of reaction, and vice versa. The real

concentration profile may be more likely a two-peak profile, which has one peak at the beginning (unburned hydrocarbon emitting from the crevice near the cylinder head at the blowdown process) and the other at the end of exhaust process (unburned hydrocarbon scraped by the piston upward movement). The rough estimation (profile F, the first 4500 ppmC1 high step at the beginning and the other at the end) indicated that the effect of the first peak would be compensated by the second one. However, the precise estimate still need accurate time-resolved concentration and temperature data in the future.

Intermediate product study

The intermediate products of combustion observed in the experiment offer another opportunity to explore the model capabilities. Intermediate products are produced through decomposition of the unburned fuel and finally are converted into final products (H_2O and CO_2). Non-fuel hydrocarbons were measured at the engine cylinder exit and the exhaust port exit showing that the concentration levels are roughly unchanged. Since there are no accurate time-resolved speciated experimental data available, it is difficult to determine what fractions of the intermediates in the mixture leave the engine at different crank angles or whether or not the parent fuel and the intermediates are fully mixed together. In the current work, the investigation for the interactions between the unburned fuel and its partially oxidized products in a homogeneous mixture were made. The study in the Chapter 3.6 (binary fuel study) indicated that the intermediate species do not affect the behavior of fuel reaction significantly if the amounts of partially oxidized products are relatively small compared to the parent fuel. Actually, the computations show that almost no changes in fuel decomposition behavior are caused even the fractions of intermediate products increase to the portions which are two times of experimental results. Even for the extreme case, methane with 5% ethane (2% ethane occurred is the experimental data), whose reaction times can be shorten a factor of two by adding a small portion of ethane, no apparent alteration was found in the port simulations (shown in Fig. 4.14).

Therefore, to start with pure fuel does not change the predictions significantly. It supports the assumption made in the earlier sections.

A parametric study on the mechanism of the production and destruction of intermediate products in the exhaust port was made. Since there are too many unknowns to carry out the detailed port simulations, only a qualitative discussion is presented on the experimental fact that the concentrations of intermediates keep approximately constant when quenching is at the inlet and outlet of exhaust port. Figure 4.15 illustrates how a uniform mixture of propane and ethylene (propane : ethylene = 4 : 1, on a ppmC1 base, which is similar to experimental values) reacts at different temperatures (shown in Figs 4.15 (A), (B), and (C)) which are assumed to be encountered at different regions in the port. Simulations indicate that at high temperature (Fig. 4.15 (A)), which exceeds the mixing-controlled temperature limit, all species are totally oxidized very quickly. Thus, both fuel and intermediates are consumed at this stage if they are mixed in the hot core gas. Conversely, all reactions become frozen at the temperature which is below the switch-over temperature (Fig 4.15 (C)). Only at the middle temperature, it is observed that, during the residence time in the port, part of fuel is destructed and the concentrations of the intermediate products increase because the production rate is higher than the destruction rate. Accordingly, simulations show that the phenomenon of intermediates in the port can be reasonably explained because the concentration balance can be achieved by the production and depletion of products at different stages.

4.5 Summary

In this chapter, zero-dimensional, detailed chemical kinetic models have been applied to the investigation of the oxidation of hydrocarbons in the engine exhaust port. Since some assumptions were made to simplify the complex phenomena to meet the current computational capability, many sets of simulations were designed to broaden the windows of the prediction.

Computation results demonstrate that temperature is the key factor for the hydrocarbon oxidation in the exhaust port. Furthermore, a comparison with the high speed case reveals that temperature is more important than residence time for the level of the fuel disappearance and hydrocarbon oxidation because the quick decrease in temperature cause the reactions to stop, so that most oxidation happens at early stages but not through the whole residence period. Some parametric simulations were made for further understanding of the oxidation process in the exhaust. From the comparison of the temperature histories in the port and the switch-over temperature region for a typical residence time scale, the exhaust process can be considered as an initially mixing controlled process, followed by a process which is controlled by the slow kinetics. The duration of each controlled process depends on crank angles at which the gas mixtures exit out of the cylinder. Moreover, it has been found that small fraction of unburned fuel, approximately hundreds of ppmC1, can be consumed very quickly by the extra radicals present at super-equilibrium concentration. In addition, intermediate oxidation products are noticed to have little influence on the fuel decomposition, so that each chemical species in the exhaust inlet can be considered independently. Simulations for the mixture of parent fuel and intermediates at different temperature limits suggest that intermediate products may be destructed and generated at different temperature stages during the exhaust process so that the amount of intermediate passing both the inlet and outlet of the exhaust port remains almost unchanged.

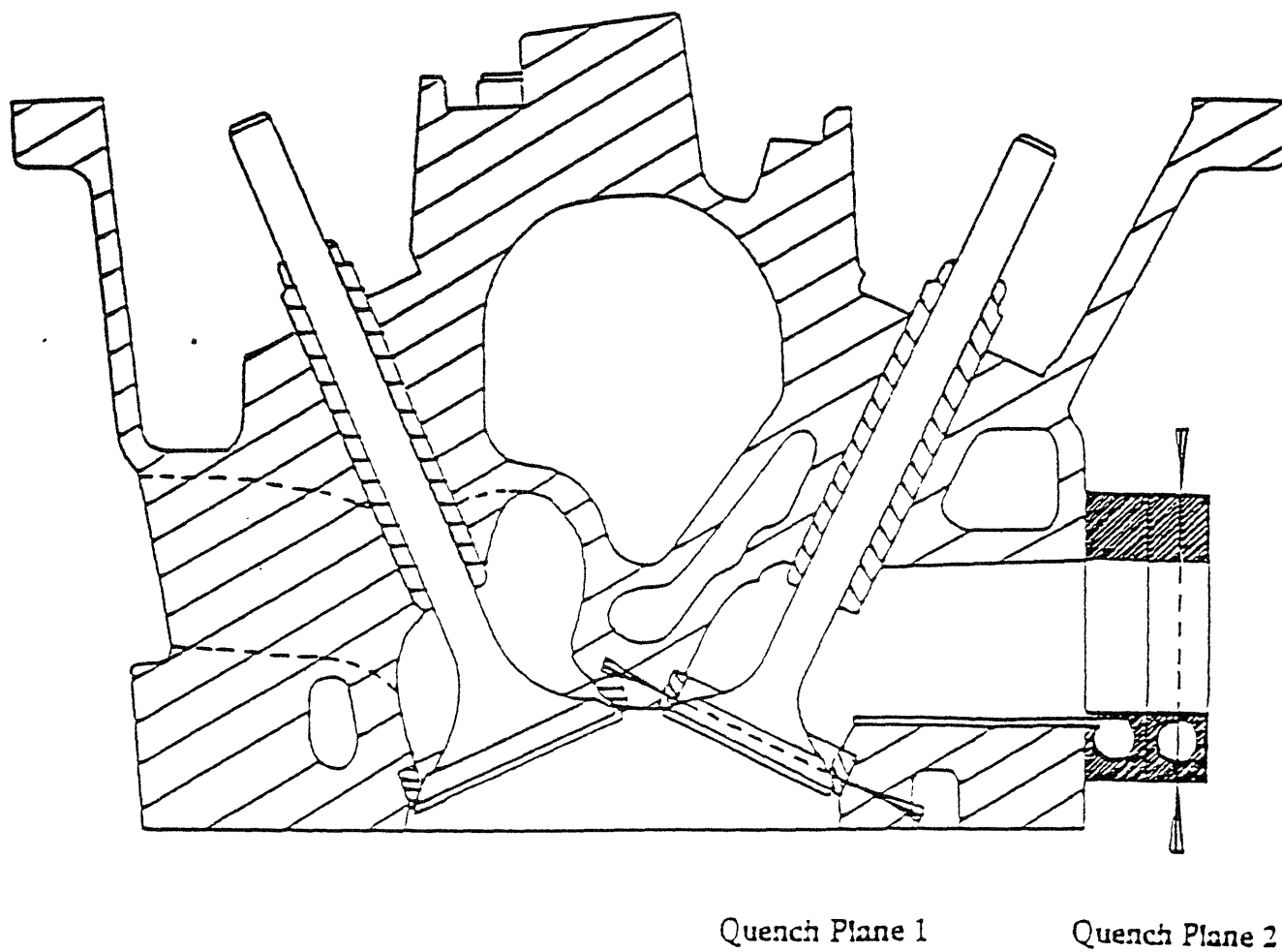


Figure 4.1: A schematic view of the cross section of an engine exhaust port.

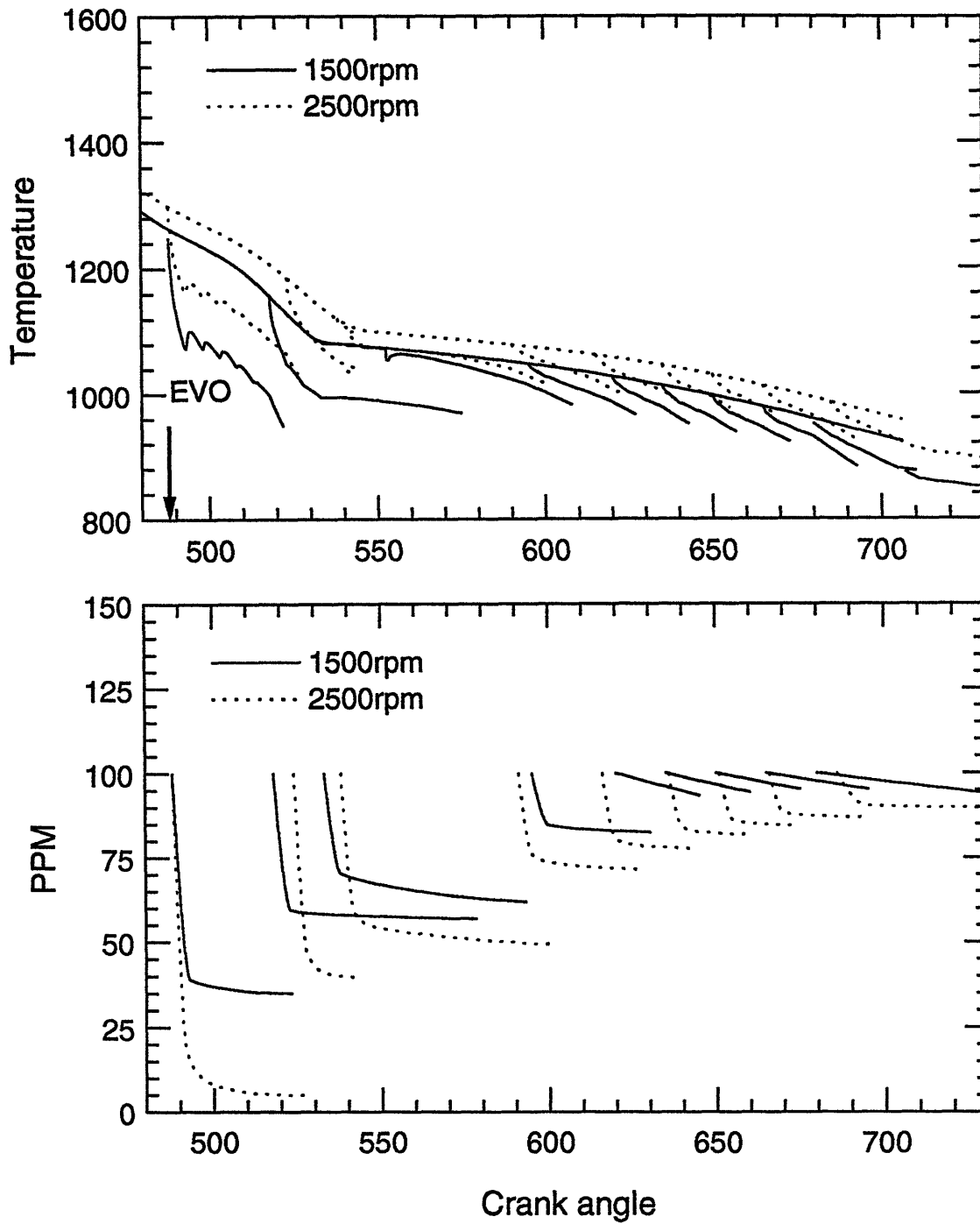


Figure 4.2: Calculated average temperatures for each mass element leaving the cylinder at two different speeds (top) and corresponding fuel concentration profiles for each element as a function of crank angle (bottom). Fuel : propane, initial concentration (bottom) : 300 ppmC1. Operating conditions : $\Phi=0.9$, 3.75 kpa IMEP.

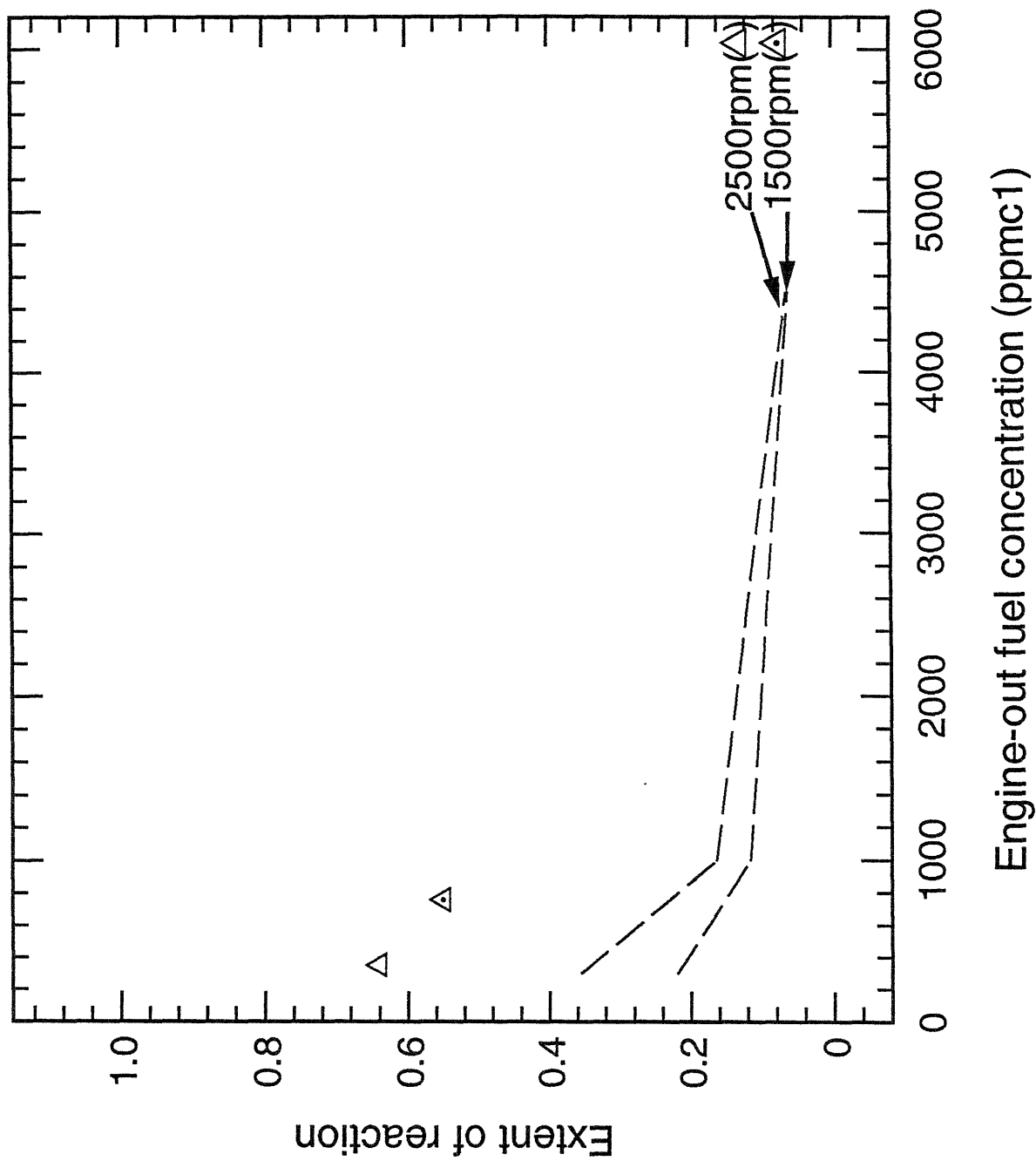


Figure 4.3: Calculated extent of reaction in the exhaust port (lines) and measured values (symbols, blank symbol :2500 rpm, dot symbol : 1500 rpm) for two different operating conditions. Operating conditions : $\Phi=0.9$, 3.75 kpa IMEP.

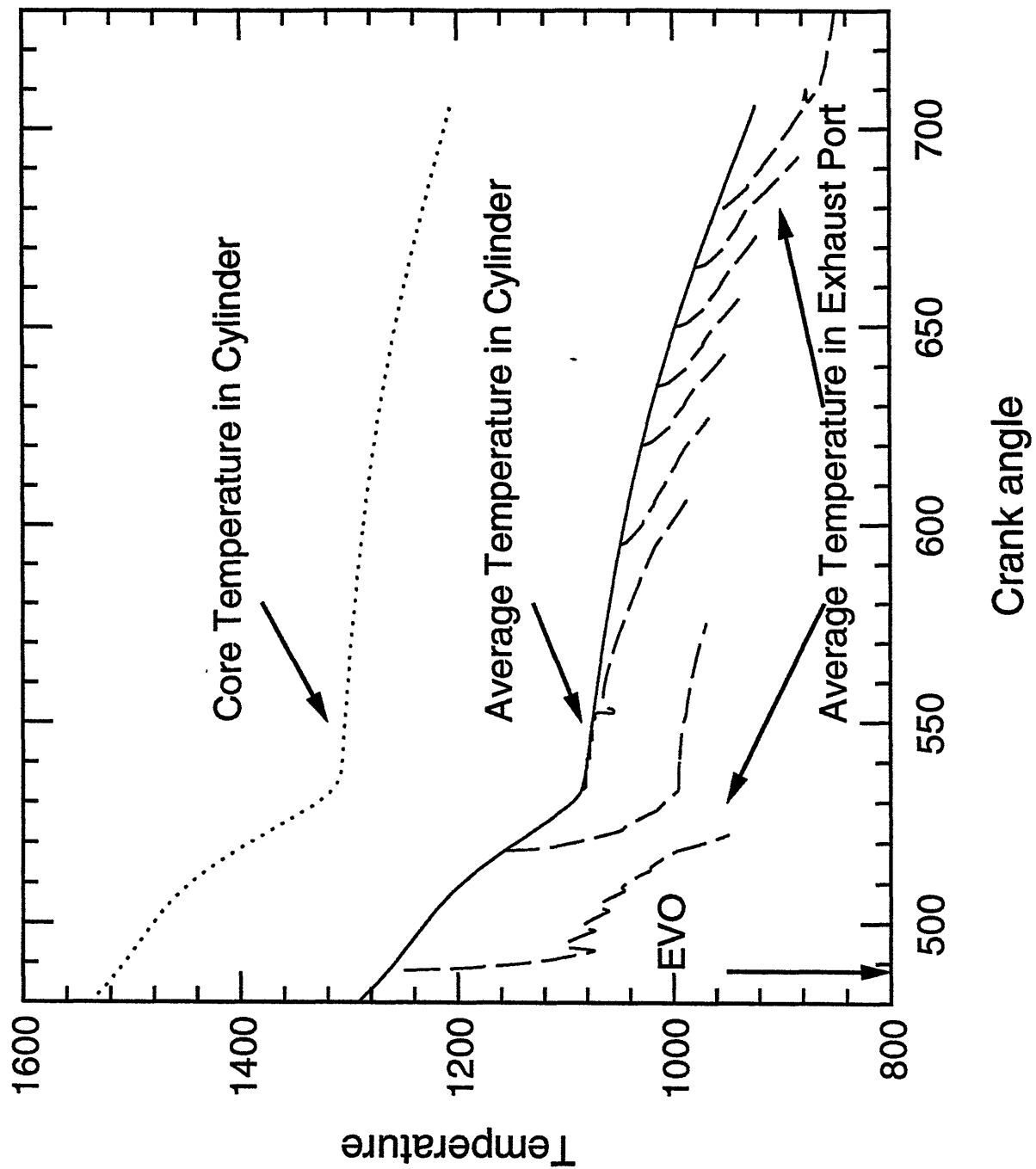


Figure 4.4: Calculated core and average temperatures in cylinder and exhaust port as a function of crank angle. The drop in temperature for each element leaving the cylinder is due to heat loss to the walls. Operating conditions: $\Phi=0.9$, 1500 rpm, 3.75 kpa IMEP and MBT spark timing.

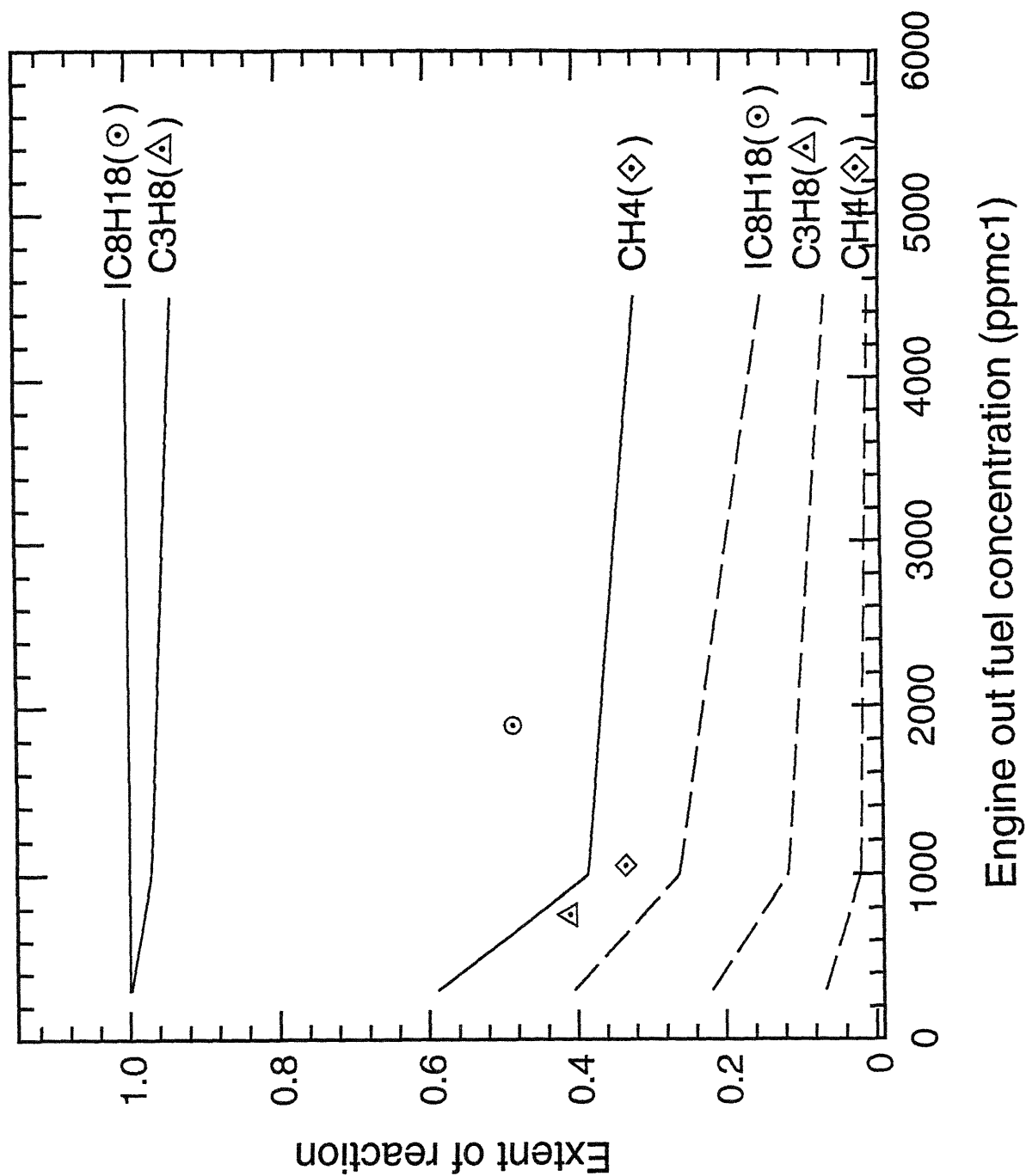


Figure 4.5: Calculated extent of reaction in the exhaust port (lines) and measured values (symbols). Solid lines are simulations performed with core temperatures, dashed lines are simulations with average temperatures. Symbols represent the experimental measurement values. Operating conditions: $\Phi=0.9$, 1500 rpm, 3.75 kpa IMEP and MBT spark timing.

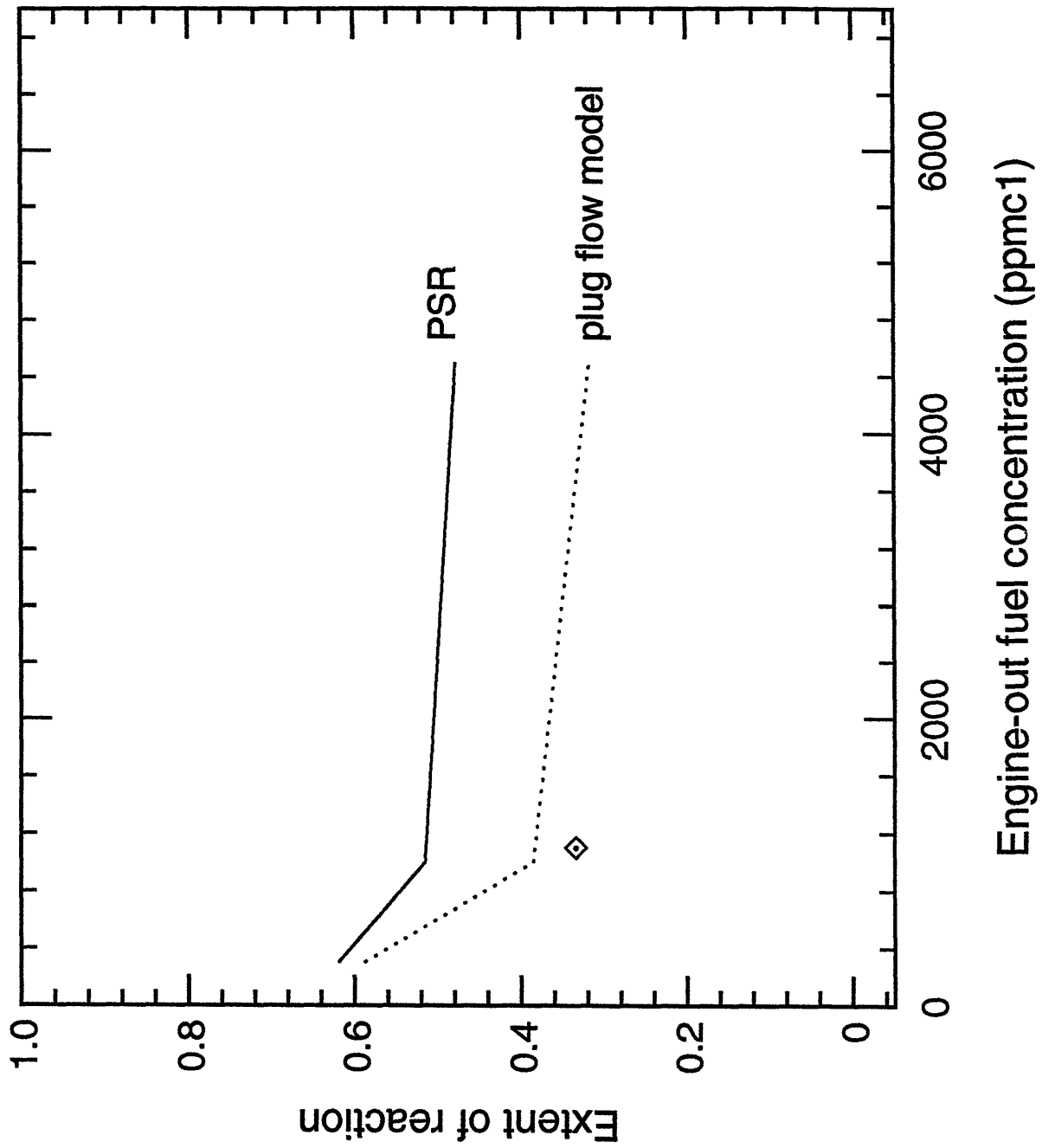


Figure 4.6: A comparison of calculated extent of reaction in the exhaust port using plug flow model (solid line) and stirred reactor model (dot line). Both simulations are performed with the assumption of no heat loss to the walls. The symbol represents the experimental measurement value. Operating condition : $\Phi=0.9$, 1500 rpm, 3.75 kpa IMEP, MBT spark timing.

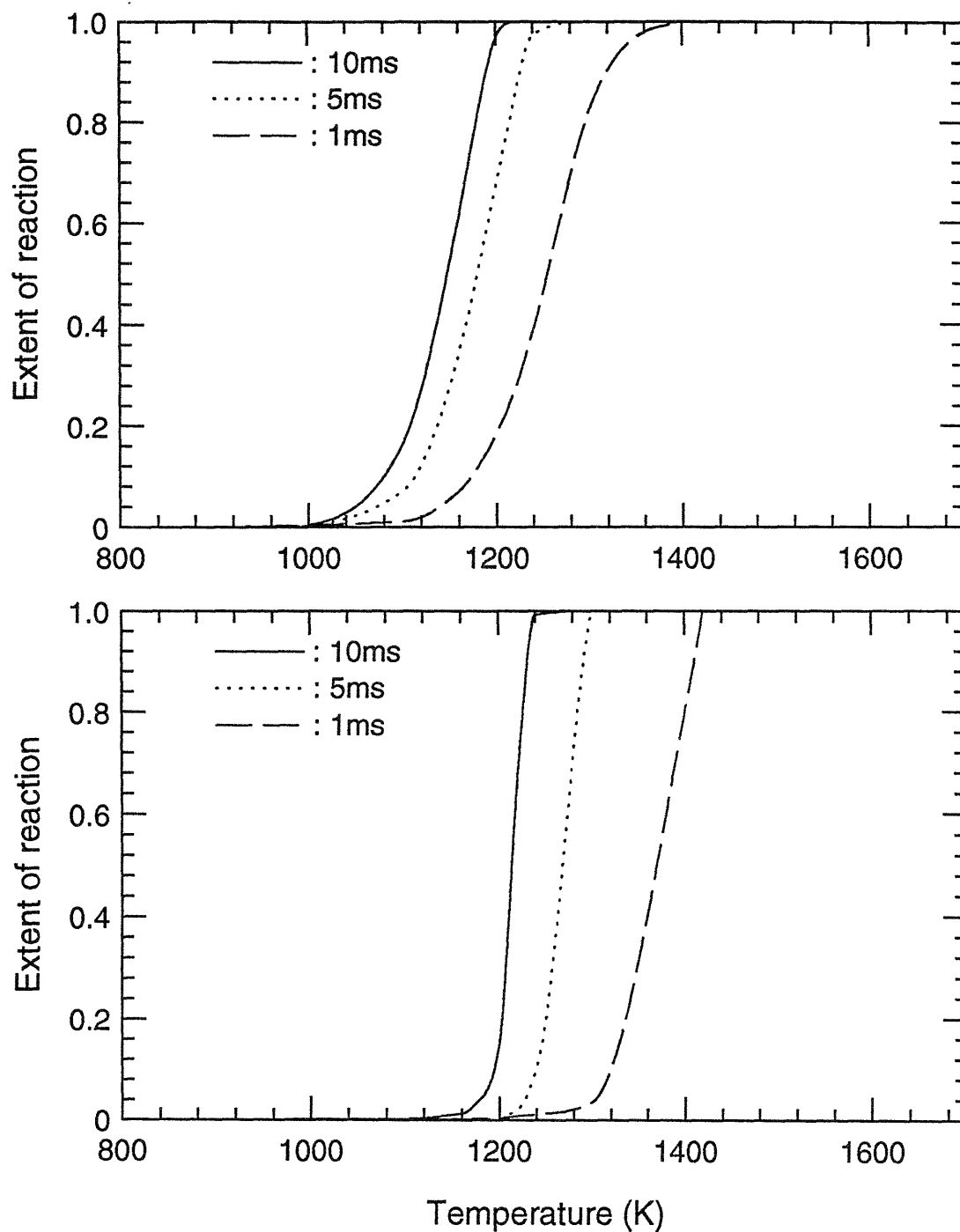


Figure 4.7: Calculated extent of fuel destruction (top) and hydrocarbon conversion (bottom) for n-butane as a function of temperature at the different residence times. (solid line : 10ms, dot line : 5 ms, and dashed line : 1ms). ($P=1$ atm, $\Phi=0.9$, $X_u=1\%$)

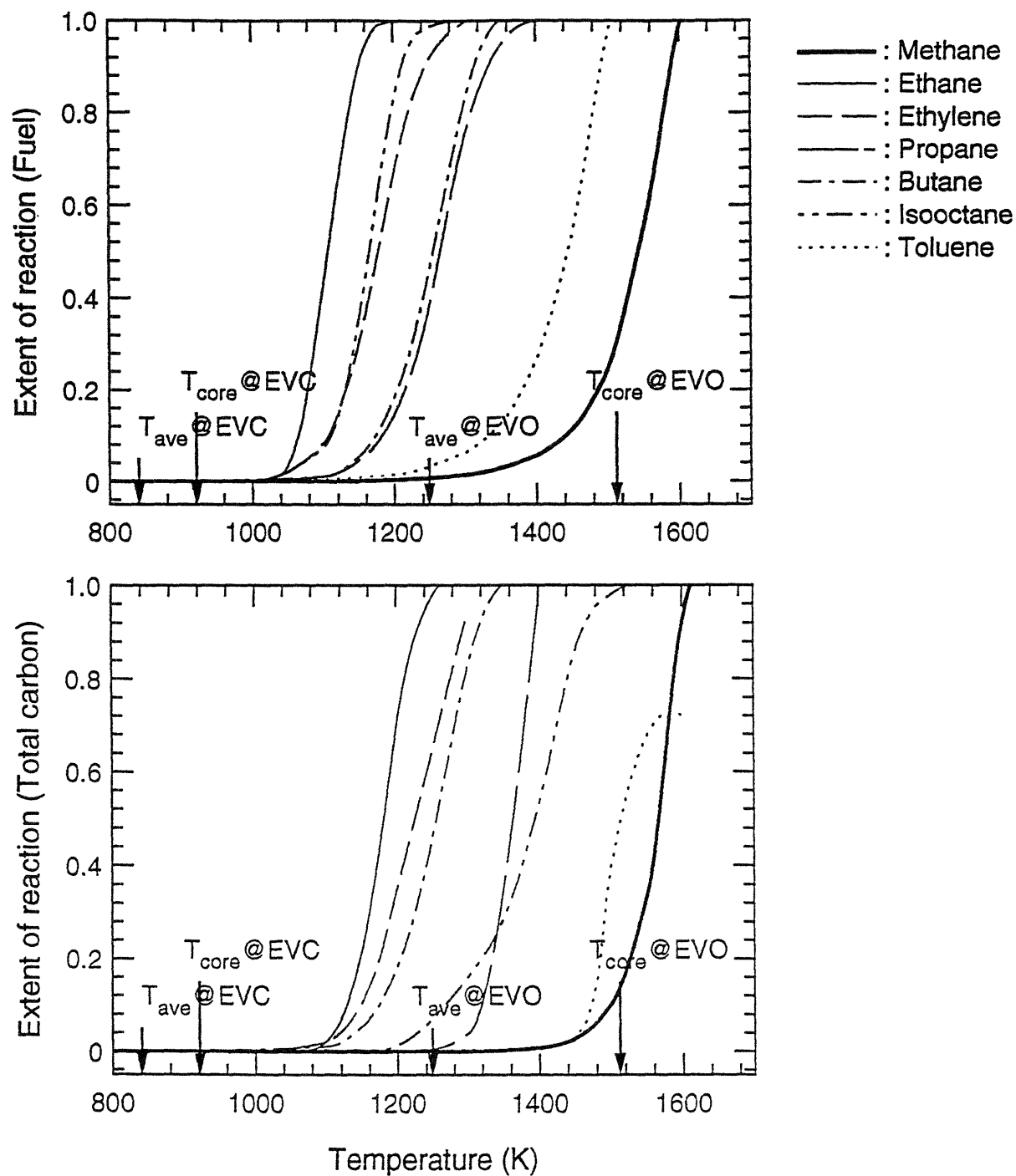


Figure 4.8: Calculated extent of (top) fuel destruction and (bottom) hydrocarbon conversion as a function of temperature at the residence time of 1 ms. ($P=1$ atm, $\Phi=0.9$, $X_{U}=1\%$).

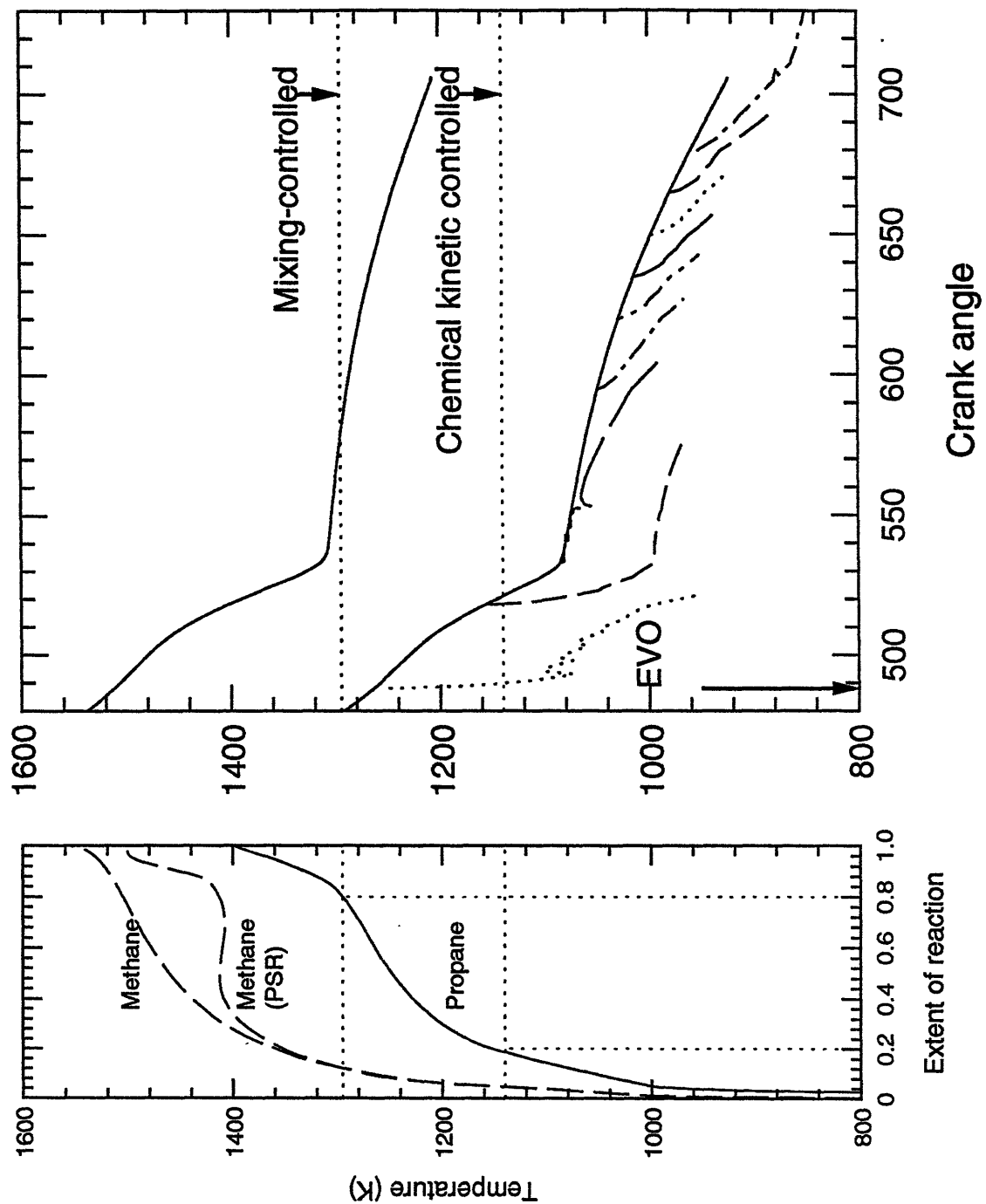


Figure 4.9: Calculated limits for mixing-controlled and kinetically controlled oxidation regions in the port for a residence time of 1 ms. Controlling limits shown for propane oxidation.

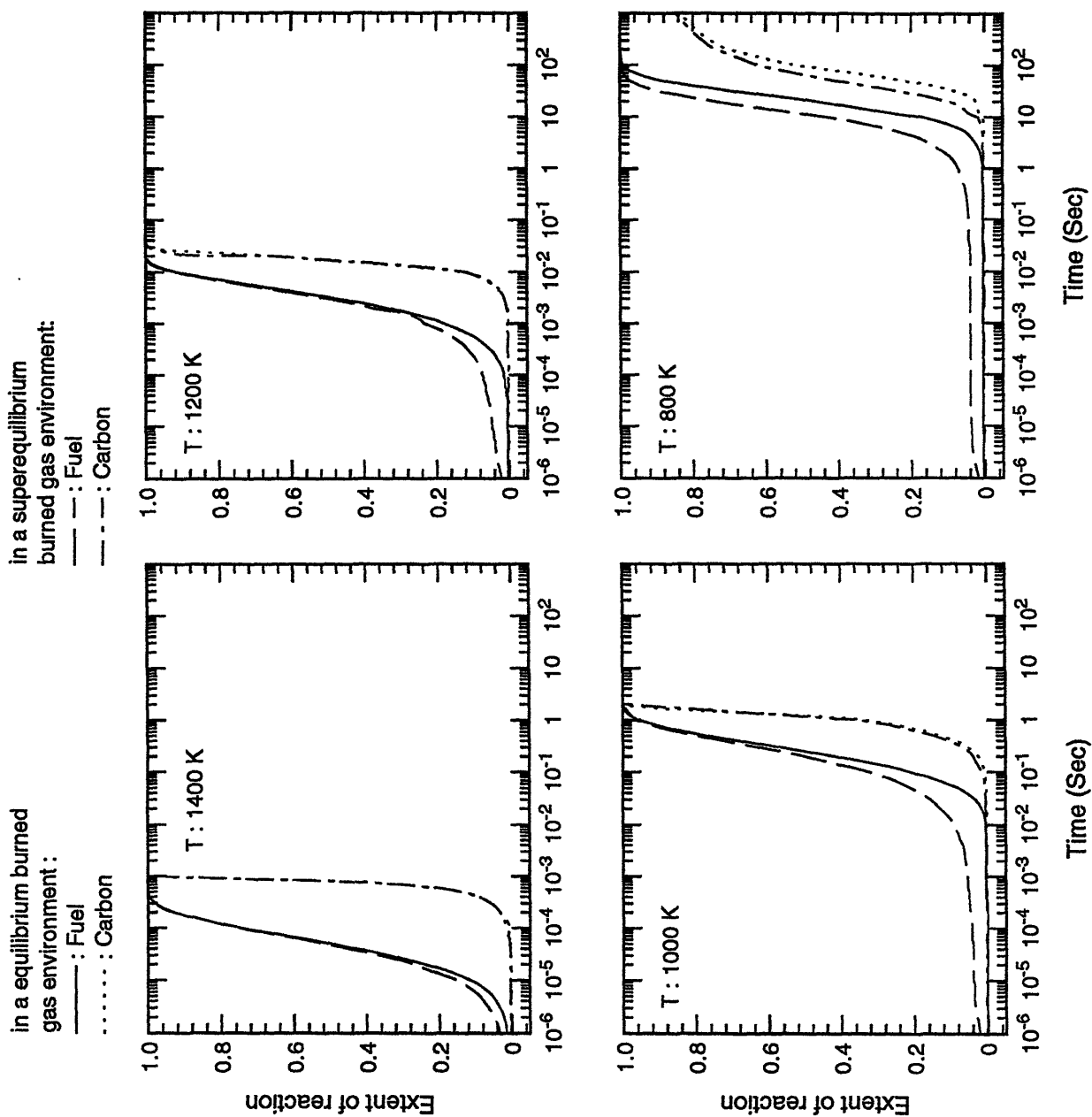


Figure 4.10: Comparisons of calculated extent of fuel and hydrocarbon reaction as a function of time in an equilibrium burned gas environment and in a non-equilibrium burned gas environment at 1400 K(top left), 1200 K(top right), 1000 K(bottom left) and 800 K(bottom right). Fuel : butane, ($P=1$ atm, $\Phi=0.9$, $X_{u}=10\%$)

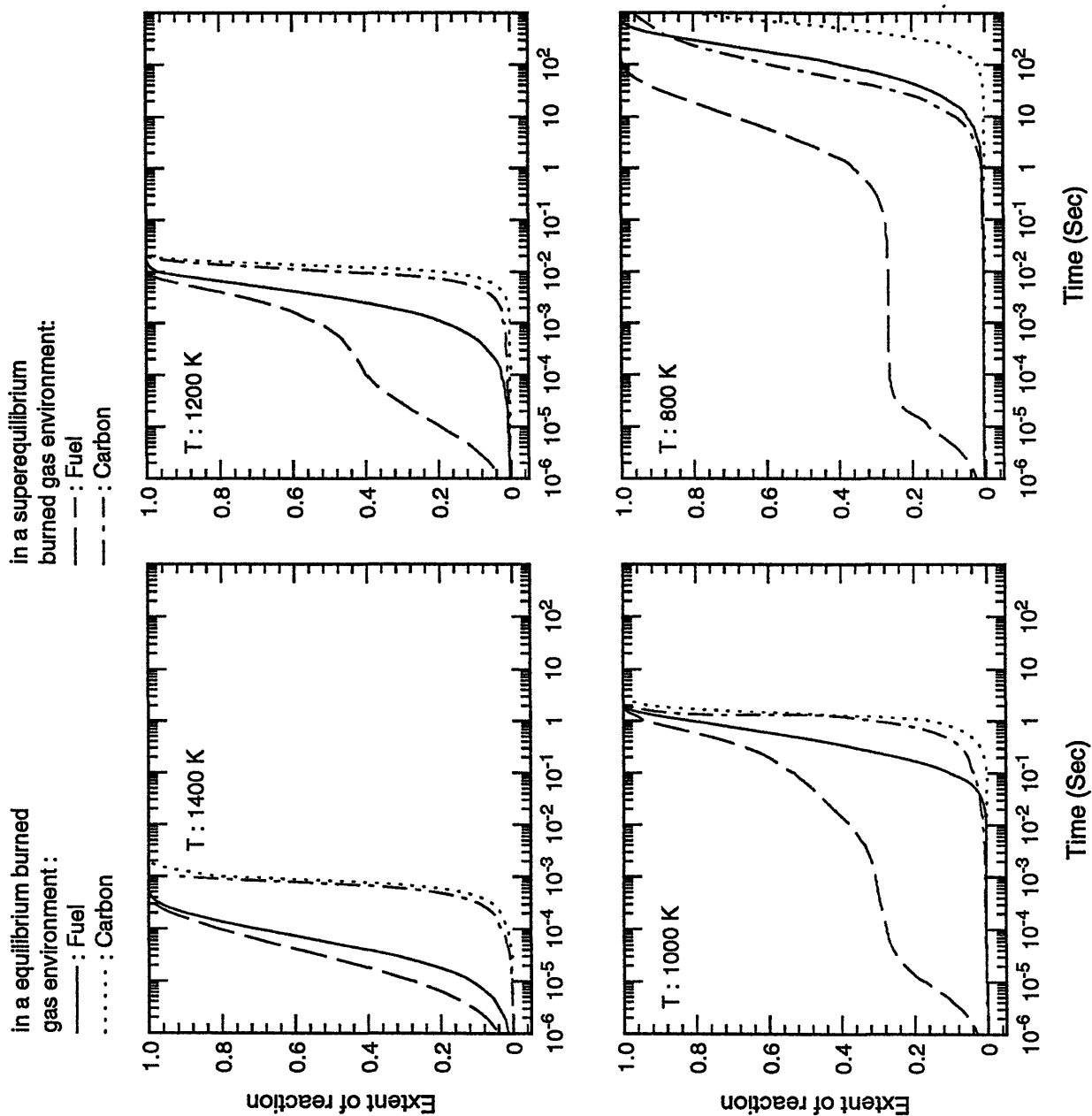


Figure 4.11: Comparisons of calculated extent of fuel and hydrocarbon reaction as a function of time in an equilibrium burned gas environment and in a non-equilibrium burned gas environment at 1400 K(top right), 1200 K (top left), and 1000 K(bottom left) and 800 K(bottom right). Fuel : butane, ($P=1$ atm, $\Phi=0.9$, $X_u=1\%$)

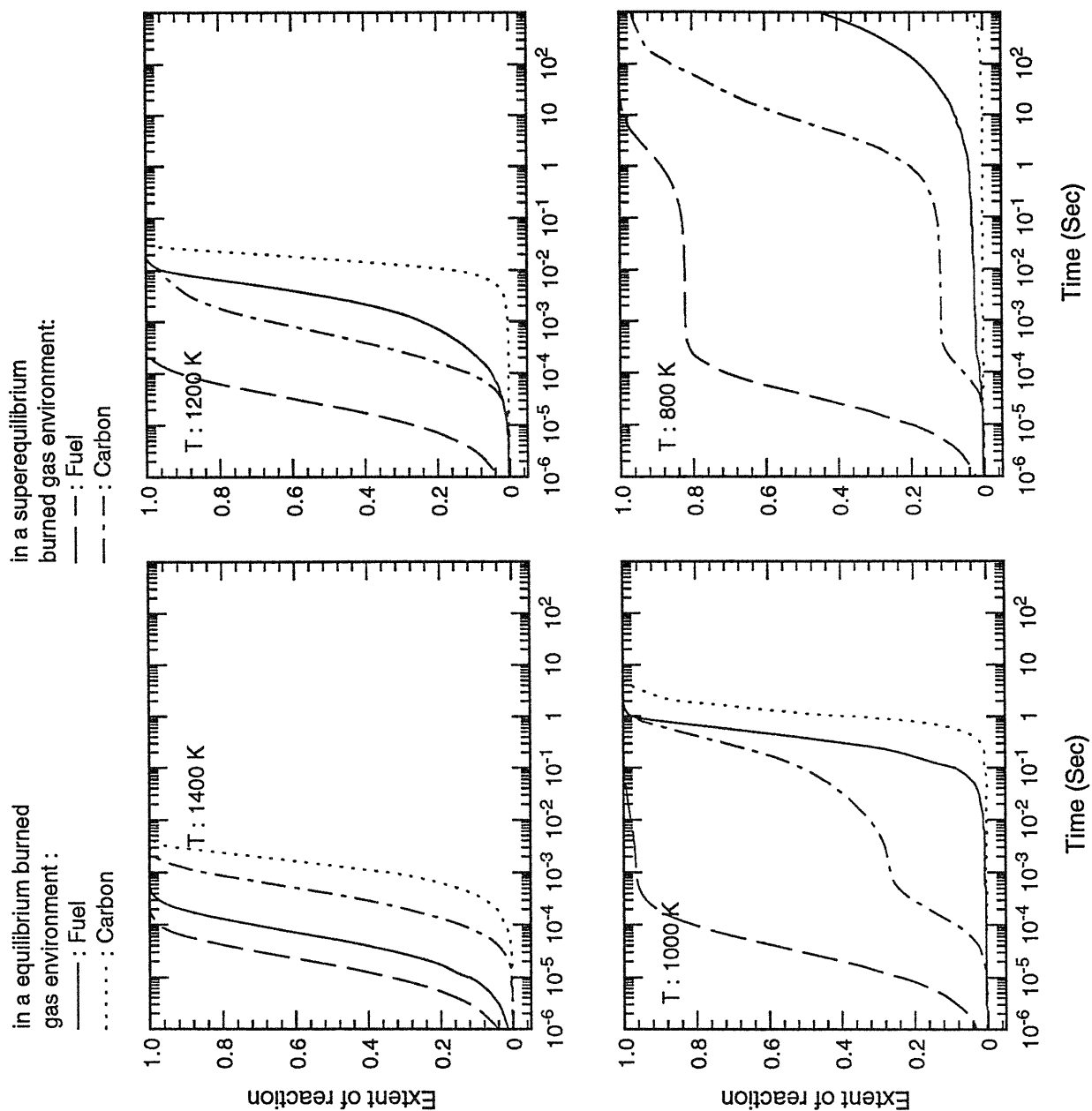


Figure 4.12: Comparisons of calculated extent of fuel and hydrocarbon reaction as a function of time in an equilibrium burned gas environment and in a non-equilibrium burned gas environment at 1400 K (top right), 1200 K (top left), and 1000 K (bottom left) and 800 K (bottom right). Fuel : butane, ($P=1$ atm, $\Phi=0.9$, $X_{U}=0.1\%$)

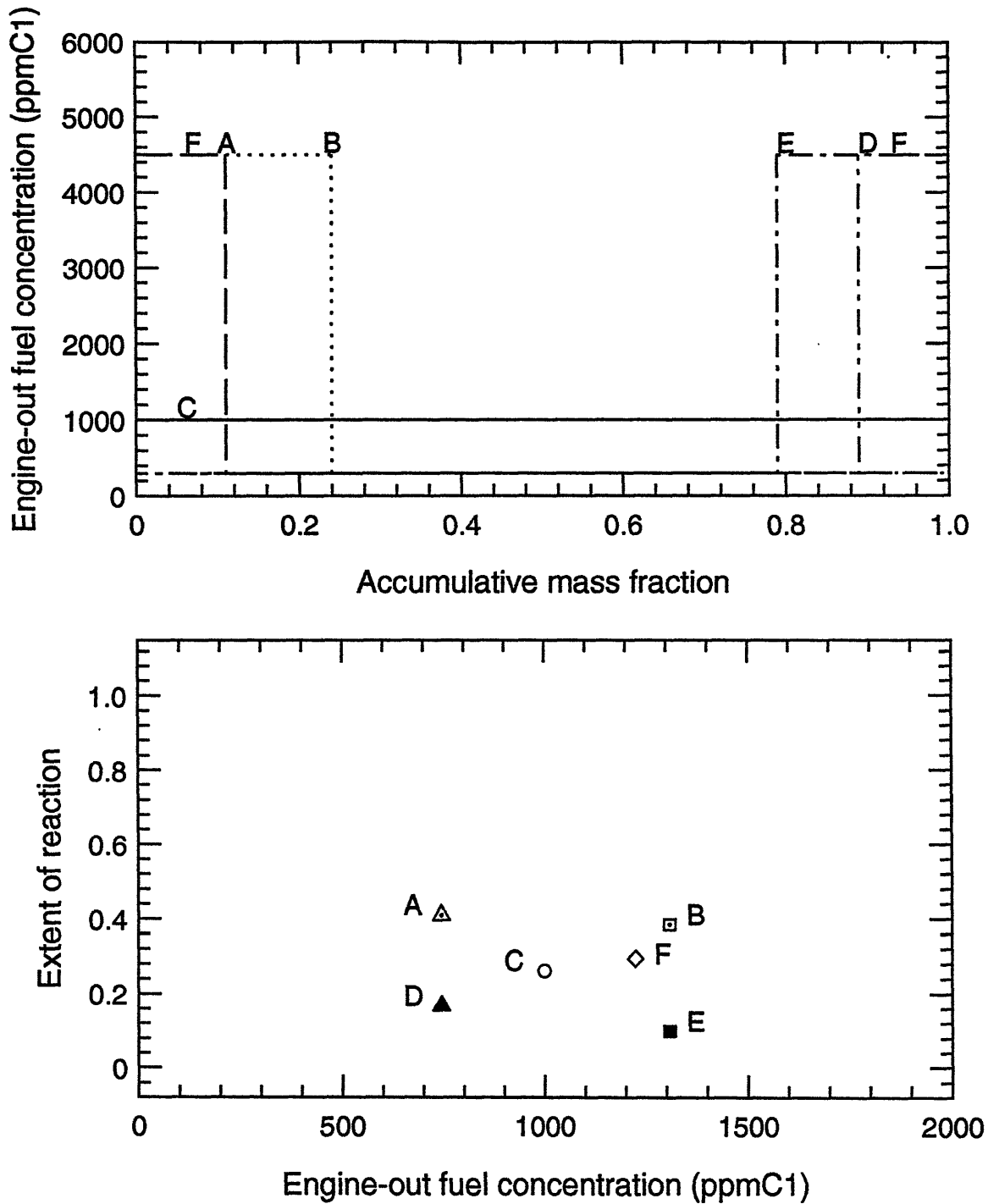


Figure 4.13: Comparisons of extent of reaction in the exhaust port for isooctane with different initial concentration profiles. Operating conditions : $\Phi=0.9$, 1500 rpm, 3.75 kpa IMEP, MBT spark timing. (all of profiles have only one 4500 ppmC1 high step just as shown in the top plot except for profile F, which has one peak at beginning as profile A and the other peak at the end as profile D)

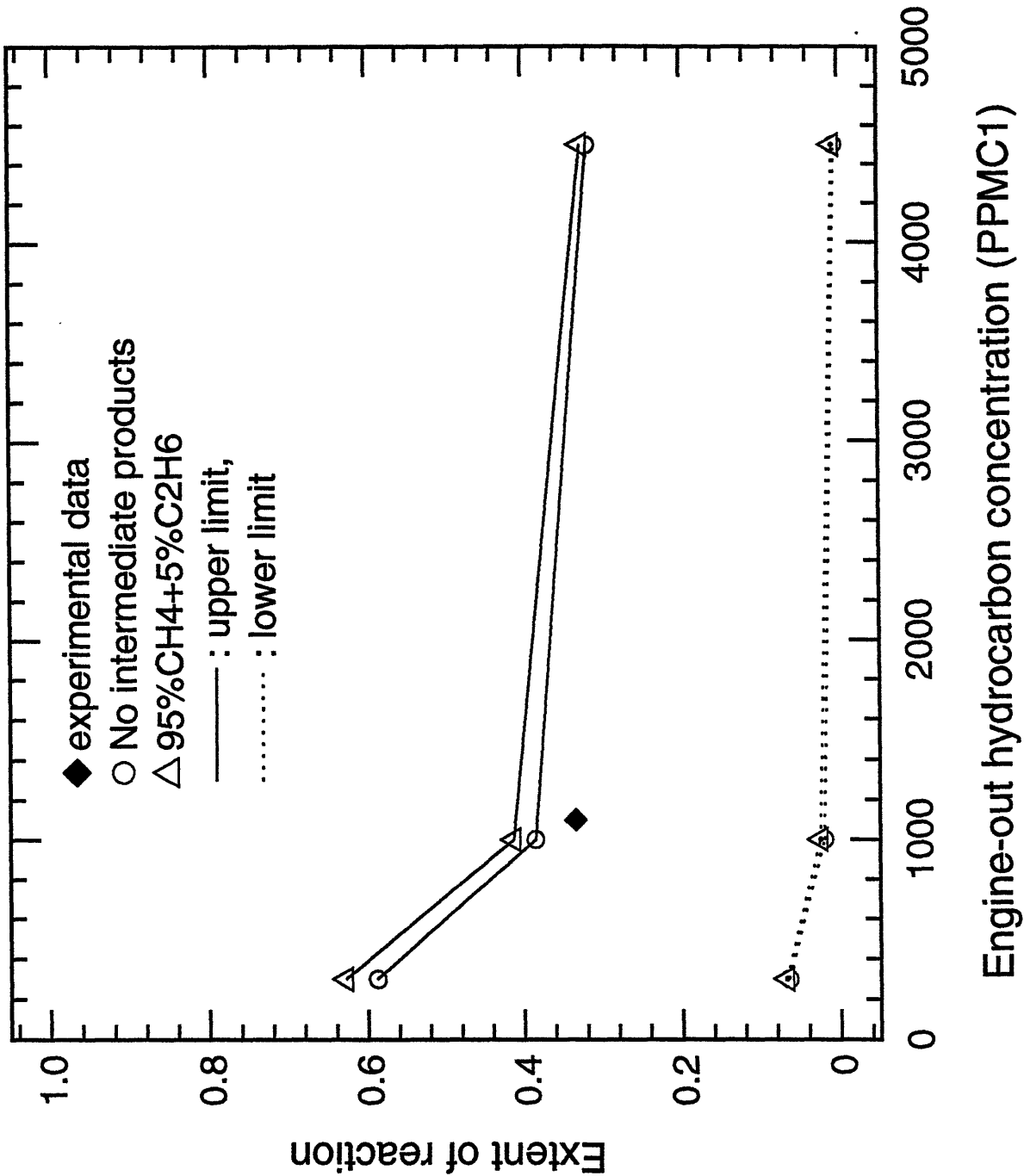


Figure 4.14: A comparison of calculated extent of reaction in the exhaust port for pure methane and the mixture of 95% methane plus 5% ethane. Solid lines are simulations performed with core temperatures (no heat loss to the exhaust walls), dashed lines are simulations with average temperatures. Symbols represent the experimental measurement values. Operating condition : $\Phi=0.9$, 1500rpm, 3.75 kpa IMEP, MBT spark timing.

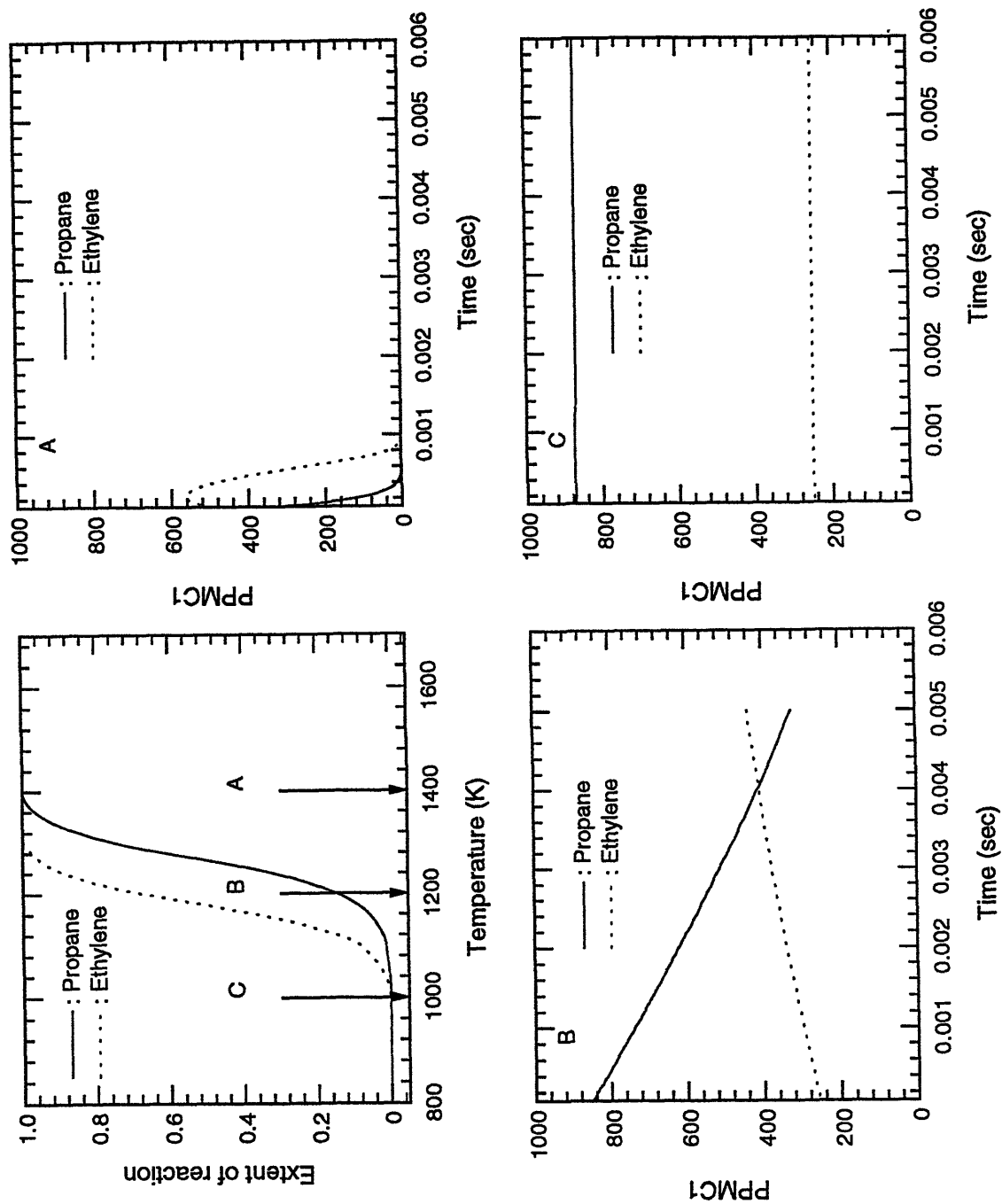


Figure 4.15: Calculated extent of fuel reaction as function of temperature at the residence time 1 ms for propane and ethylene. (top left) and the reaction profiles for the uniform mixture of propane and ethylene (propane : ethylene = 4 : 1) at (A) 1400 K (top right) (B) 1200 K (bottom left) (C) 1000 K (bottom right). ($P=1$ atm, $\Phi=0.9$)

CHAPTER 5

SUMMARY and CONCLUSIONS

Existing comprehensive detailed chemical kinetic mechanisms of oxidation of hydrocarbons have been applied to the hydrocarbon emissions problems using zero-dimensional modeling in this work. The parametric simulations presented in this work provide useful information on the behavior of different fuel components during oxidation under kinetically controlled conditions. Further correlations between characteristic reaction time scales, which are obtained from the parametric computations, and experimental data of total hydrocarbon emissions from the steady engine operations on single-component fuels show the practical use of the simple zero-dimensional approach. Furthermore, the extended study of the binary fuel using the detailed chemical kinetic models show how the two components interact in a binary fuel. Global expressions, which have been fitted from the numerical simulation data, can give reasonable predictions of fuel and hydrocarbon conversion times and can be used to combined with more complicated transport models. From the port oxidation study, the calculations show that the extent of oxidation of the remaining unburned fuel observed through the exhaust port cannot be reproduced by the simulations using the well mixed (average) temperatures in the exhaust, but that the experimental results can be bracketed by the average and upper limits on core temperatures. Most of the oxidation is shown to occur at the very early exhaust times, when temperatures in the exhaust port are in excess of 1200 K. For the fuels considered, it is suggested that oxidation is controlled by mixing rates at the initial stages of exhaust, where temperatures are high and the cold unburned mixture emerges from the wall layers into the hot core jet to oxidize, then controlled by slow chemical kinetics later. Appropriate mixing models will be required for further understanding this question and it will be the next phase of this work.

This work is an attempt to study the oxidation of hydrocarbon emissions in a view of chemical kinetics. More accurate comprehensive detailed chemical kinetic mechanisms will be expected in the future to provide precise predictions of hydrocarbon oxidation. Further exploration should also concentrate on reducing the necessary computational times by making reasonable simplifications.

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APPENDIX REACTIONS AND RATE COEFFICIENTS FOR DETAILED CHEMICAL KINETIC MECHANISMS

Appendix A.1 Ethane (ethylene, methane) chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T ^b exp(-E/RT))			Source/Modification
		A	b	E	
1	H+H+M=H ₂ +M	7.31E+17	-1	0	# All Reactions : Ref[13]
2	O+O+M=O ₂ +M	1.14E+17	-1	0	
3	O+H+M=OH+M	6.20E+16	-0.6	0	
4	H ₂ +O ₂ =OH+OH	1.70E+13	0	47780	
5	O+H ₂ =OH+H	3.87E+04	2.7	6260	
6	H+O ₂ =OH+O	1.90E+14	0	16812	
7	H+O ₂ +M=HO ₂ +M	8.00E+17	-0.8	0	
8	H+OH+M=H ₂ O+M	8.62E+21	-2	0	
9	H ₂ +OH=H ₂ O+H	2.16E+08	1.5	3430	
10	H ₂ O+O=OH+OH	1.50E+10	1.1	17260	
11	HO ₂ +OH=H ₂ O+O ₂	2.89E+13	0	-497	
12	HO ₂ +O=OH+O ₂	1.81E+13	0	-400	
13	H+HO ₂ =H ₂ +O ₂	4.22E+13	0	1411	
14	H+HO ₂ =OH+OH	4.95E+13	0	143	
15	H+HO ₂ =H ₂ O+O	1.18E+14	0	2730	
16	HO ₂ +HO ₂ =H ₂ O ₂ +O ₂	1.46E+13	0	5088	
17	OH+OH=H ₂ O ₂	1.56E+16	-1.5	149	
18	H ₂ O ₂ +OH=HO ₂ +H ₂ O	1.78E+12	0	326	
19	H ₂ O ₂ +H=HO ₂ +H ₂	1.70E+12	0	3750	
20	H ₂ O ₂ +H=H ₂ O+OH	1.00E+13	0	3590	
21	H ₂ O ₂ +O=HO ₂ +OH	2.80E+13	0	6400	
22	CO+HO ₂ =CO ₂ +OH	1.50E+14	0	23650	
23	CO+OH=CO ₂ +H	4.40E+06	1.5	-740	
24	CO+O+M=CO ₂ +M	2.83E+13	0	-4540	
25	CO+O ₂ =CO ₂ +O	2.53E+12	0	47700	
26	HCO+M=H+CO+M	1.85E+17	-1	17000	
27	HCO+OH=CO+H ₂ O	1.00E+14	0	0	
28	HCO+O=CO+OH	3.00E+13	0	0	
29	HCO+O=CO ₂ +H	3.00E+13	0	0	
30	HCO+H=CO+H ₂	7.22E+13	0	0	
31	HCO+O ₂ =CO+HO ₂	4.22E+12	0	0	
32	HCO+CH ₃ =CO+CH ₄	1.20E+14	0	0	
33	HCO+HO ₂ =CO ₂ +OH+H	3.00E+13	0	0	
34	HCO+C ₂ H ₆ =CH ₂ O+C ₂ H ₅	4.70E+04	2.7	18235	
35	HCO+HCO=CH ₂ O+CO	1.80E+13	0	0	
36	HCO+HCO=H ₂ +CO+CO	3.00E+12	0	0	
37	CH ₄ =CH ₃ +H	5.99E+30	-4.9	108553	

38	CH ₄ +HO ₂ =CH ₃ +H ₂ O ₂	1.12E+13	0	24641
39	CH ₄ +OH=CH ₃ +H ₂ O	1.55E+07	1.8	2774
40	CH ₄ +O=CH ₃ +OH	6.92E+08	1.6	8486
41	CH ₄ +H=CH ₃ +H ₂	8.58E+03	3.1	7941
42	CH ₄ +CH ₂ =CH ₃ +CH ₃	4.30E+12	0	10038
43	CH ₃ +M=CH ₂ +H+M	1.90E+16	0	91600
44	CH ₃ +HO ₂ =CH ₃ O+OH	4.00E+13	0	5000
45	CH ₄ +O ₂ =CH ₃ +HO ₂	7.63E+13	0	58590
46	CH ₃ +OH=CH ₂ OH+H	2.64E+19	-1.8	8068
47	CH ₃ +OH=CH ₃ O+H	5.74E+12	-0.2	13931
48	CH ₃ +OH=CH ₂ +H ₂ O	8.90E+18	-1.8	8067
49	CH ₃ +OH=CH ₂ O+H ₂	3.19E+12	-0.5	10810
50	CH ₃ +O=CH ₂ O+H	8.43E+13	0	0
51	CH ₃ +H=CH ₂ +H ₂	7.00E+13	0	15100
52	CH ₃ +O ₂ =CH ₃ O+O	6.00E+12	0	33700
53	CH ₃ +O ₂ =CH ₂ O+OH	3.05E+30	-4.7	36571
54	CH ₃ +CH ₃ =C ₂ H ₅ +H	3.01E+13	0	13513
55	CH ₃ +CH ₃ =C ₂ H ₆	2.39E+38	-7.6	11359
56	CH ₃ +CH ₃ O=CH ₄ +CH ₂ O	2.41E+13	0	0
57	CH ₃ +CH ₂ OH=CH ₄ +CH ₂ O	2.41E+12	0	0
58	CH ₂ +OH=CH+H ₂ O	1.13E+07	2	3000
59	CH ₂ +OH=CH ₂ O+H	2.50E+13	0	0
60	CH ₂ +O=CO+H+H	9.08E+13	0	656
61	CH ₂ +O=CO+H ₂	3.89E+13	0	-149
62	CH ₂ +H=CH+H ₂	5.52E+12	0	-2026
63	CH ₂ +O ₂ =HCO+OH	4.30E+10	0	-500
64	CH ₂ +O ₂ =CO ₂ +H ₂	6.90E+11	0	500
65	CH ₂ +O ₂ =CO ₂ +H+H	1.60E+12	0	1000
66	CH ₂ +O ₂ =CO+H ₂ O	1.87E+10	0	-1000
67	CH ₂ +O ₂ =CO+OH+H	8.64E+10	0	-500
68	CH ₂ +O ₂ =CH ₂ O+O	1.00E+14	0	4500
69	CH ₂ +CO ₂ =CH ₂ O+CO	1.10E+11	0	1000
70	CH ₂ +CH ₂ =C ₂ H ₂ +H ₂	3.20E+13	0	0
71	CH ₂ +CH ₃ =C ₂ H ₄ +H	4.00E+13	0	0
72	CH ₂ +CH=C ₂ H ₂ +H	4.00E+13	0	0
73	CH ₂ +C ₂ H ₂ =H+C ₃ H ₃	1.20E+13	0	6620
74	CH ₂ +C ₂ H ₄ =C ₃ H ₆	4.30E+12	0	10038
75	CH ₂ +C ₂ H ₆ =CH ₃ +C ₂ H ₅	6.50E+12	0	7911
76	CH ₂ +C ₃ H ₈ =CH ₃ +C ₃ H ₇	2.19E+12	0	6405
77	CH ₂ +C ₃ H ₈ =CH ₃ +NC ₃ H ₇	1.79E+12	0	6405
78	CH+OH=HCO+H	3.00E+13	0	0
79	CH+O=CO+H	1.00E+14	0	0
80	CH+O ₂ =HCO+O	3.30E+13	0	0
81	CH+O ₂ =CO+OH	2.00E+13	0	0
82	CH+CO ₂ =HCO+CO	3.40E+12	0	690
83	CH+CH ₄ =C ₂ H ₄ +H	6.00E+13	0	0
84	CH+CH ₃ =C ₂ H ₃ +H	3.00E+13	0	0
85	CH ₃ O+M=CH ₂ O+H+M	4.88E+15	0	22773
86	CH ₃ O+HO ₂ =CH ₂ O+H ₂ O ₂	3.00E+11	0	0
87	CH ₃ O+OH=CH ₂ O+H ₂ O	1.00E+13	0	0

88	CH3O+O=CH2O+OH	1.30E+13	0	0
89	CH3O+H=CH2O+H2	2.00E+13	0	0
90	CH3O+O2=CH2O+HO2	2.35E+10	0	1788
91	CH3O+CH2O=CH3OH+HCO	1.15E+11	0	1280
92	CH3O+CO=CH3+CO2	1.57E+13	0	2981
93	CH3O+HCO=CH3OH+CO	9.00E+13	0	0
94	CH3O+C2H5=CH2O+C2H6	2.41E+13	0	0
95	CH3O+C2H3=CH2O+C2H4	2.41E+13	0	0
96	CH3O+C2H4=CH2O+C2H5	1.20E+11	0	7000
97	CH2O+M=HCO+H+M	5.72E+16	0	76480
98	CH2O+HO2=HCO+H2O2	4.00E+12	0	11665
99	CH2O+OH=HCO+H2O	3.43E+09	1.2	-447
100	CH2O+O=HCO+OH	1.81E+13	0	3088
101	CH2O+H=HCO+H2	1.12E+08	1.7	2127
102	CH2O+O2=HCO+HO2	2.04E+13	0	39000
103	CH2O+CH3=HCO+CH4	8.91E-13	7.4	-960
104	C2H6=C2H5+H	2.08E+38	-7.1	106507
105	C2H6+HO2=C2H5+H2O2	1.21E+12	0	17600
106	C2H6+OH=C2H5+H2O	5.13E+06	2.1	860
107	C2H6+O=C2H5+OH	1.14E-07	6.5	274
108	C2H6+H=C2H5+H2	5.00E+02	3.5	5210
109	C2H6+O2=C2H5+HO2	1.00E+13	0	51000
110	C2H6+CH3O=C2H5+CH3OH	3.02E+11	0	7000
111	C2H6+CH3=C2H5+CH4	3.97E+05	2.5	17684
112	C2H5+HO2=C2H4+H2O2	3.00E+11	0	0
113	C2H5+HO2=>CH3+CH2O+OH	2.50E+13	0	0
114	C2H5+OH=C2H4+H2O	2.41E+13	0	0
115	C2H5+OH=>CH3+CH2O+H	2.41E+13	0	0
116	C2H5+O=CH2O+CH3	4.24E+13	0	0
117	C2H5+O=CH3CHO+H	5.30E+13	0	0
118	C2H5+O=C2H4+OH	3.05E+13	0	0
119	C2H5+H=C2H4+H2	1.25E+14	0	8000
120	C2H5+O2=C2H4+HO2	1.70E+10	0	-670
121	C2H5+CH3=C2H4+CH4	4.37E-04	5	8300
122	C2H5+C2H5=C2H4+C2H6	1.40E+12	0	0
123	C2H4+M=C2H2+H2+M	3.00E+17	0	79350
124	C2H4+M=C2H3+H+M	2.97E+17	0	96560
125	C2H4+HO2=>C2H4O+OH	6.22E+12	0	18962
126	C2H4+OH=C2H3+H2O	2.02E+13	0	5960
127	C2H4+O=CH3+HCO	1.08E+14	0	7432
128	C2H4+O=>CH2+HCO+H	5.66E+12	0	1488
129	C2H4+H=C2H3+H2	3.36E-07	6	1692
130	C2H4+H=C2H5	1.05E+14	-0.5	655
131	C2H4+O2=C2H3+HO2	4.00E+13	0	61500
132	C2H4+C2H4=C2H5+C2H3	5.00E+14	0	64700
133	C2H4+CH3=C2H3+CH4	3.97E+05	2.5	20000
134	C2H4O=CH4+CO	3.16E+14	0	57000
135	C2H3=C2H2+H	2.10E+44	-8.4	51106
136	C2H3+HO2=>CH3+CO+OH	3.00E+13	0	0
137	C2H3+OH=C2H2+H2O	3.00E+13	0	0

138	$\text{C}_2\text{H}_3 + \text{OH} = \text{CH}_3\text{CHO}$	3.00E+13	0	0
139	$\text{C}_2\text{H}_3 + \text{O} = \text{CH}_3 + \text{CO}$	3.00E+13	0	0
140	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	3.00E+13	0	0
141	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$	3.00E+12	0	-250
142	$\text{C}_2\text{H}_3 + \text{CH}_3 = \text{C}_2\text{H}_2 + \text{CH}_4$	4.37E-04	5	8300
143	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	1.50E+13	0	10000
144	$\text{C}_2\text{H}_3 + \text{HCO} = \text{C}_2\text{H}_4 + \text{CO}$	9.03E+13	0	0
145	$\text{C}_2\text{H}_3 + \text{CH}_2\text{O} = \text{C}_2\text{H}_4 + \text{HCO}$	5.42E+03	2.8	5862
146	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$	1.08E+13	0	0
147	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_4\text{H}_6$	4.94E+13	0	0
148	$\text{C}_2\text{H}_2 = \text{C}_2\text{H} + \text{H}$	2.37E+32	-5.3	130688
149	$\text{C}_2\text{H}_2 + \text{HO}_2 = \text{CH}_2\text{CO} + \text{OH}$	1.00E+13	0	18280
150	$\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$	3.39E+07	2	14000
151	$\text{C}_2\text{H}_2 + \text{OH} = \text{HCCOH} + \text{H}$	5.06E+05	2.3	13500
152	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	2.19E-04	4.5	-1000
153	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_3 + \text{CO}$	4.85E-04	4	-2000
154	$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$	6.02E+13	0	22257
155	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	1.52E+04	2.8	497
156	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	6.50E+03	2.8	497
157	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{OH}$	2.00E+08	1.5	30100
158	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{C}_2\text{H} + \text{HO}_2$	1.20E+13	0	74520
159	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{SC}_3\text{H}_5$	1.61E+40	-8.6	20331
160	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{PC}_3\text{H}_4 + \text{H}$	2.73E+17	-2	20592
161	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{AC}_3\text{H}_5$	2.61E+46	-9.8	36951
162	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{AC}_3\text{H}_4 + \text{H}$	6.74E+19	-2.1	31591
163	$\text{HCCOH} + \text{H} = \text{CH}_2\text{CO} + \text{H}$	1.00E+13	0	0
164	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0	0
165	$\text{C}_2\text{H} + \text{O} = \text{CO} + \text{CH}$	1.00E+13	0	0
166	$\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{CO} + \text{H}$	5.00E+13	0	1510
167	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	4.11E+15	0	59270
168	$\text{CH}_2\text{CO} + \text{O}_2 = \text{CH}_2\text{O} + \text{CO}_2$	1.00E+08	0	0
169	$\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$	7.50E+12	0	2000
170	$\text{CH}_2\text{CO} + \text{O} = \text{CH}_2 + \text{CO}_2$	1.76E+12	0	1349
171	$\text{CH}_2\text{CO} + \text{O} = \text{HCCO} + \text{OH}$	1.00E+13	0	8000
172	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	4.54E+09	1.3	3160
173	$\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$	5.00E+13	0	8000
174	$\text{HCCO} + \text{M} = \text{CH} + \text{CO} + \text{M}$	6.00E+15	0	58821
175	$\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00E+13	0	0
176	$\text{HCCO} + \text{O} = \text{CO} + \text{CO} + \text{H}$	1.93E+14	0	590
177	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	1.50E+14	0	0
178	$\text{HCCO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46E+12	0	2500
179	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H} + \text{CH}_2\text{O}$	1.00E+13	0	2000
180	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0
181	$\text{CH}_3\text{OH} = \text{CH}_3 + \text{OH}$	1.57E+46	-9.3	103522
182	$\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$	6.30E+12	0	19360
183	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	4.53E+11	0.3	1160
184	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	3.63E+11	0.7	5868
185	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$	1.00E+13	0	4690
186	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$	4.00E+13	0	6100
187	$\text{CH}_3\text{OH} + \text{CH}_2\text{O} = \text{CH}_3\text{O} + \text{CH}_3\text{O}$	1.55E+12	0	79570

188	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$	3.57E+11	0	8663
189	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$	4.68E+05	2.3	12764
190	$\text{CH}_2\text{OH} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$	1.00E+14	0	25100
191	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	3.00E+13	0	0
192	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	2.17E+14	0	4690
193	$\text{CH}_3\text{CHO} = \text{CH}_3 + \text{HCO}$	2.45E+16	0	84128
194	$\text{CH}_3\text{CHO} + \text{HO}_2 = \text{CH}_3\text{CO} + \text{H}_2\text{O}_2$	1.70E+12	0	10700
195	$\text{CH}_3\text{CHO} + \text{OH} = \text{CH}_3\text{CO} + \text{H}_2\text{O}$	1.00E+13	0	0
196	$\text{CH}_3\text{CHO} + \text{O} = \text{CH}_3\text{CO} + \text{OH}$	5.00E+12	0	1790
197	$\text{CH}_3\text{CHO} + \text{H} = \text{CH}_3\text{CO} + \text{H}_2$	4.00E+13	0	4210
198	$\text{CH}_3\text{CHO} + \text{O}_2 = \text{CH}_3\text{CO} + \text{HO}_2$	2.00E+13	0.5	42200
199	$\text{CH}_3\text{CHO} + \text{CH}_3 = \text{CH}_3\text{CO} + \text{CH}_4$	2.00E-06	5.6	2464
200	$\text{CH}_3\text{CO} + \text{M} = \text{CH}_3 + \text{CO} + \text{M}$	8.64E+15	0	14400

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.2 Propane (propene) chemical kinetic reaction mechanism

REACTIONS CONSIDERED	(k = A T ^a exp(-E/RT))			Source/Modification
	A	b	E	
1 H+H+M=H2+M	7.31E+17	-1	0	# All reactions : Ref[15]
2 O+O+M=O2+M	1.14E+17	-1	0	
3 O+H+M=OH+M	6.20E+16	-0.6	0	
4 H2+O2=OH+OH	1.70E+13	0	47780	
5 O+H2=OH+H	1.50E+07	2	7550	
6 H+O2=OH+O	1.20E+17	-0.9	16520	
7 H+O2+M=HO2+M	8.00E+17	-0.8	0	
8 H+O2+O2=HO2+O2	6.70E+19	-1.4	0	
9 H+OH+M=H2O+M	8.62E+21	-2	0	
10 H2+OH=H2O+H	1.00E+08	1.6	3300	
11 H2O+O=OH+OH	1.50E+10	1.1	17260	
12 HO2+OH=H2O+O2	5.00E+13	0	1000	
13 HO2+O=OH+O2	2.00E+13	0	0	
14 H+HO2=H2+O2	2.50E+13	0	690	
15 H+HO2=OH+OH	1.50E+14	0	1000	
16 HO2+HO2=H2O2+O2	2.80E+12	0	0	
17 H2O2+M=OH+OH+M	1.30E+17	0	45410	
18 H2O2+OH=HO2+H2O	7.00E+12	0	1430	
19 H2O2+H=H2O+OH	1.00E+13	0	3590	
20 H2O2+H=HO2+H2	1.70E+12	0	3750	
21 H2O2+O=HO2+OH	2.80E+13	0	6400	
22 CO+HO2=CO2+OH	4.57E+14	0	25240	
23 CO+OH=CO2+H	4.40E+06	1.5	-740	
24 CO+O+M=CO2+M	2.83E+13	0	-4540	
25 CO+O2=CO2+O	2.53E+12	0	47700	
26 HCO+M=H+CO+M	2.86E+14	0	16800	
27 HCO+OH=CO+H2O	5.00E+13	0	0	
28 HCO+O=CO+OH	3.00E+13	0	0	
29 HCO+O=CO2+H	3.00E+13	0	0	
30 HCO+H=CO+H2	7.22E+13	0	0	
31 HCO+O2=CO+HO2	3.31E+13	-0.3	0	
32 HCO+CH3=CO+CH4	3.00E+11	0.5	0	
33 CH4=CH3+H	1.00E+15	0	100380	
34 CH4+HO2=CH3+H2O2	4.00E+12	0	19360	
35 CH4+OH=CH3+H2O	1.09E+05	2.4	2110	
36 CH4+O=CH3+OH	1.40E+07	2.1	7620	
37 CH4+H=CH3+H2	2.60E+04	3	8750	
38 CH4+CH2=CH3+CH3	6.00E+14	0	14000	
39 CH3+M=CH2+H+M	1.90E+16	0	91600	
40 CH3+HO2=CH3O+OH	3.00E+13	0	1080	
41 CH3+HO2=CH4+O2	1.00E+12	0	400	
42 CH3+OH=CH2O+H2	4.00E+12	0	0	
43 CH3+OH=CH3O+H	9.00E+14	0	15400	

44	CH ₃ +OH=CH ₂ +H ₂ O	3.00E+13	0	3000
45	CH ₃ +O=CH ₂ O+H	6.00E+13	0	0
46	CH ₃ +O=CH ₂ +OH	5.00E+13	0	12000
47	CH ₃ +H=CH ₂ +H ₂	7.00E+13	0	15100
48	CH ₃ +O ₂ =CH ₃ O+O	2.24E+14	0	33700
49	CH ₃ +CH ₃ =C ₂ H ₅ +H	8.00E+14	0	26530
50	CH ₃ +CH ₃ =C ₂ H ₄ +H ₂	2.10E+14	0	19200
51	C ₂ H ₆ =CH ₃ +CH ₃	1.40E+16	0	87480
52	CH ₂ +OH=CH+H ₂ O	4.00E+13	0	0
53	CH ₂ +OH=CH ₂ O+H	2.00E+13	0	0
54	CH ₂ +O=CO+H+H	3.00E+13	0	0
55	CH ₂ +O=CO+H ₂	5.00E+13	0	0
56	CH ₂ +O=CH+OH	5.00E+13	0.7	12000
57	CH ₂ +O=HCO+H	5.00E+13	0	0
58	CH ₂ +H=CH+H ₂	4.00E+13	0	0
59	CH ₂ +O ₂ =HCO+OH	4.30E+10	0	-500
60	CH ₂ +O ₂ =CO ₂ +H ₂	6.90E+11	0	500
61	CH ₂ +O ₂ =CO ₂ +H+H	1.60E+12	0	1000
62	CH ₂ +O ₂ =CO+H ₂ O	1.87E+10	0	-1000
63	CH ₂ +O ₂ =CO+OH+H	8.64E+10	0	-500
64	CH ₂ +O ₂ =CH ₂ O+O	5.00E+13	0	9000
65	CH ₂ +CO ₂ =CH ₂ O+CO	1.10E+11	0	1000
66	CH ₂ +CH ₂ =C ₂ H ₂ +H ₂	3.20E+13	0	0
67	CH ₂ +CH ₃ =C ₂ H ₄ +H	4.00E+13	0	0
68	CH ₂ +CH=C ₂ H ₂ +H	4.00E+13	0	0
69	CH+OH=HCO+H	3.00E+13	0	0
70	CH+O=CO+H	4.00E+13	0	0
71	CH+O ₂ =HCO+O	3.30E+13	0	0
72	CH+O ₂ =CO+OH	2.00E+13	0	0
73	CH+CO ₂ =HCO+CO	3.40E+12	0	690
74	CH+CH ₄ =C ₂ H ₄ +H	6.00E+13	0	0
75	CH+CH ₃ =C ₂ H ₃ +H	3.00E+13	0	0
76	CH ₃ O+M=CH ₂ O+H+M	1.80E+14	0	25100
77	CH ₃ O+OH=CH ₂ O+H ₂ O	1.00E+13	0	0
78	CH ₃ O+O=CH ₂ O+OH	1.00E+13	0	0
79	CH ₃ O+H=CH ₂ O+H ₂	2.00E+13	0	0
80	CH ₃ O+O ₂ =CH ₂ O+HO ₂	1.50E+13	0	7170
81	CH ₃ O+CH ₂ O=CH ₃ OH+HCO	1.15E+11	0	1280
82	CH ₃ O+CH ₄ =CH ₃ OH+CH ₃	2.00E+11	0	7000
83	CH ₂ O+M=HCO+H+M	5.72E+16	0	76480
84	CH ₂ O+HO ₂ =HCO+H ₂ O ₂	1.00E+12	0	9600
85	CH ₂ O+OH=HCO+H ₂ O	7.00E+13	0	1250
86	CH ₂ O+O=HCO+OH	3.50E+13	0	3510
87	CH ₂ O+H=HCO+H ₂	2.50E+13	0	3990
88	CH ₂ O+O ₂ =HCO+HO ₂	2.04E+13	0	39000
89	CH ₂ O+CH ₃ =HCO+CH ₄	1.00E+11	0	6100
90	C ₂ H ₆ +HO ₂ =C ₂ H ₅ +H ₂ O ₂	1.69E+13	0	20460
91	C ₂ H ₆ +OH=C ₂ H ₅ +H ₂ O	5.13E+05	2.1	860
92	C ₂ H ₆ +O=C ₂ H ₅ +OH	4.40E+07	2	5120
93	C ₂ H ₆ +H=C ₂ H ₅ +H ₂	5.40E+02	3.5	5210

94	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	1.00E+13	0	51000
95	$\text{C}_2\text{H}_6 + \text{CH}_3\text{O} = \text{C}_2\text{H}_5 + \text{CH}_3\text{OH}$	3.02E+11	0	7000
96	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	5.50E-01	4	8290
97	$\text{C}_2\text{H}_5 + \text{O} = \text{CH}_3\text{CHO} + \text{H}$	5.00E+13	0	0
98	$\text{C}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_4 + \text{H}_2$	1.25E+14	0	8000
99	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	1.58E+10	0	-1900
100	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	1.40E+12	0	0
101	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	3.00E+17	0	79350
102	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_3 + \text{H} + \text{M}$	2.97E+17	0	96560
103	$\text{C}_2\text{H}_4 + \text{HO}_2 = \text{C}_2\text{H}_4\text{O} + \text{OH}$	1.00E+13	0	18280
104	$\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	4.90E+12	0	1230
105	$\text{C}_2\text{H}_4 + \text{OH} = \text{CH}_2\text{O} + \text{CH}_3$	1.50E+12	0	960
106	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{O} + \text{CH}_2$	4.00E+13	0	5000
107	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{HCO}$	2.20E+09	1.2	740
108	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	4.00E+06	2	6000
109	$\text{C}_2\text{H}_5 + \text{M} = \text{C}_2\text{H}_4 + \text{H} + \text{M}$	2.00E+15	0	30120
110	$\text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2$	4.00E+13	0	61500
111	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_3$	5.00E+14	0	64700
112	$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$	5.60E+11	0	11110
113	$\text{C}_2\text{H}_4\text{O} = \text{CH}_4 + \text{CO}$	2.00E+14	0	58000
114	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$	2.20E+14	0	38000
115	$\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	5.00E+12	0	0
116	$\text{C}_2\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{H}$	3.30E+13	0	0
117	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	2.50E+13	0	0
118	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$	3.20E+12	0	-350
119	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	1.50E+13	0	10000
120	$\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	4.57E+16	0	106840
121	$\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$	1.00E+13	0	7000
122	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	3.20E+10	0	200
123	$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$	6.00E+13	0	23660
124	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	4.10E+08	1.5	1700
125	$\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H} + \text{OH}$	3.20E+15	-0.6	15000
126	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	4.30E+14	0	12120
127	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{OH}$	2.00E+08	1.5	30100
128	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCO} + \text{HCO}$	4.00E+12	0	28000
129	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0	0
130	$\text{C}_2\text{H} + \text{O} = \text{CO} + \text{CH}$	1.00E+13	0	0
131	$\text{C}_2\text{H} + \text{O}_2 = \text{HCCO} + \text{O}$	5.00E+13	0	1500
132	$\text{C}_2\text{H} + \text{O}_2 = \text{HCO} + \text{CO}$	5.00E+13	0	1510
133	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	4.11E+15	0	59270
134	$\text{CH}_2\text{CO} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$	1.00E+13	0	0
135	$\text{CH}_2\text{CO} + \text{O} = \text{HCO} + \text{HCO}$	2.00E+13	0	2300
136	$\text{CH}_2\text{CO} + \text{O} = \text{CH}_2\text{O} + \text{CO}$	2.00E+13	0	0
137	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	7.00E+12	0	3010
138	$\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00E+13	0	0
139	$\text{HCCO} + \text{O} = \text{CO} + \text{CO} + \text{H}$	1.93E+14	0	590
140	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	3.00E+13	0	0
141	$\text{HCCO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46E+12	0	2500
142	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H} + \text{CH}_2\text{O}$	1.00E+13	0	2000
143	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0

144	$\text{CH}_3\text{OH}=\text{CH}_3+\text{OH}$	6.00E+16	0	91060
145	$\text{CH}_3\text{OH}+\text{HO}_2=\text{CH}_2\text{OH}+\text{H}_2\text{O}_2$	6.30E+12	0	19360
146	$\text{CH}_3\text{OH}+\text{OH}=\text{CH}_2\text{OH}+\text{H}_2\text{O}$	1.00E+13	0	1700
147	$\text{CH}_3\text{OH}+\text{O}=\text{CH}_2\text{OH}+\text{OH}$	1.00E+13	0	4690
148	$\text{CH}_3\text{OH}+\text{H}=\text{CH}_2\text{OH}+\text{H}_2$	4.00E+13	0	6100
149	$\text{CH}_3\text{OH}+\text{CH}_2\text{O}=\text{CH}_3\text{O}+\text{CH}_3\text{O}$	1.55E+12	0	79570
150	$\text{CH}_3\text{OH}+\text{CH}_3=\text{CH}_2\text{OH}+\text{CH}_4$	1.82E+11	0	9800
151	$\text{CH}_2\text{OH}+\text{M}=\text{CH}_2\text{O}+\text{H}+\text{M}$	1.00E+14	0	25100
152	$\text{CH}_2\text{OH}+\text{H}=\text{CH}_2\text{O}+\text{H}_2$	3.00E+13	0	0
153	$\text{CH}_2\text{OH}+\text{O}_2=\text{CH}_2\text{O}+\text{HO}_2$	1.00E+13	0	7170
154	$\text{CH}_3\text{CHO}=\text{CH}_3+\text{HCO}$	2.00E+15	0	79110
155	$\text{CH}_3\text{CHO}+\text{HO}_2=\text{CH}_3+\text{CO}+\text{H}_2\text{O}_2$	1.70E+12	0	10700
156	$\text{CH}_3\text{CHO}+\text{OH}=\text{CH}_3+\text{CO}+\text{H}_2\text{O}$	1.00E+13	0	0
157	$\text{CH}_3\text{CHO}+\text{O}=\text{CH}_3+\text{CO}+\text{OH}$	5.00E+12	0	1790
158	$\text{CH}_3\text{CHO}+\text{H}=\text{CH}_3+\text{CO}+\text{H}_2$	4.00E+13	0	4210
159	$\text{CH}_3\text{CHO}+\text{O}_2=\text{CH}_3+\text{CO}+\text{HO}_2$	2.00E+13	0.5	42200
160	$\text{CH}_3\text{CHO}+\text{CH}_3=\text{CH}_3+\text{CO}+\text{CH}_4$	8.50E+11	0	6000
161	$\text{C}_3\text{H}_8=\text{C}_2\text{H}_5+\text{CH}_3$	7.94E+16	0	85100
162	$\text{C}_3\text{H}_8+\text{HO}_2=\text{NC}_3\text{H}_7+\text{H}_2\text{O}_2$	4.50E+11	0	14900
163	$\text{C}_3\text{H}_8+\text{HO}_2=\text{IC}_3\text{H}_7+\text{H}_2\text{O}_2$	2.00E+11	0	12500
164	$\text{C}_3\text{H}_8+\text{OH}=\text{NC}_3\text{H}_7+\text{H}_2\text{O}$	4.71E+05	2.4	390
165	$\text{C}_3\text{H}_8+\text{OH}=\text{IC}_3\text{H}_7+\text{H}_2\text{O}$	3.58E+02	3.2	-1600
166	$\text{C}_3\text{H}_8+\text{O}=\text{NC}_3\text{H}_7+\text{OH}$	3.72E+06	2.4	1390
167	$\text{C}_3\text{H}_8+\text{O}=\text{IC}_3\text{H}_7+\text{OH}$	5.50E+05	2.5	790
168	$\text{C}_3\text{H}_8+\text{H}=\text{NC}_3\text{H}_7+\text{H}_2$	1.35E+14	0	9680
169	$\text{C}_3\text{H}_8+\text{H}=\text{IC}_3\text{H}_7+\text{H}_2$	2.00E+14	0	8300
170	$\text{C}_3\text{H}_8+\text{O}_2=\text{NC}_3\text{H}_7+\text{HO}_2$	4.00E+13	0	47500
171	$\text{C}_3\text{H}_8+\text{O}_2=\text{IC}_3\text{H}_7+\text{HO}_2$	4.00E+13	0	47500
172	$\text{C}_3\text{H}_8+\text{IC}_3\text{H}_7=\text{NC}_3\text{H}_7+\text{C}_3\text{H}_8$	1.00E+11	0	12900
173	$\text{C}_3\text{H}_8+\text{AC}_3\text{H}_5=\text{NC}_3\text{H}_7+\text{C}_3\text{H}_6$	7.94E+11	0	20500
174	$\text{C}_3\text{H}_8+\text{AC}_3\text{H}_5=\text{IC}_3\text{H}_7+\text{C}_3\text{H}_6$	7.94E+11	0	16200
175	$\text{C}_3\text{H}_8+\text{C}_2\text{H}_5=\text{NC}_3\text{H}_7+\text{C}_2\text{H}_6$	3.16E+11	0	12300
176	$\text{C}_3\text{H}_8+\text{C}_2\text{H}_5=\text{IC}_3\text{H}_7+\text{C}_2\text{H}_6$	5.01E+10	0	10400
177	$\text{C}_3\text{H}_8+\text{C}_2\text{H}_3=\text{NC}_3\text{H}_7+\text{C}_2\text{H}_4$	1.00E+11	0	10400
178	$\text{C}_3\text{H}_8+\text{C}_2\text{H}_3=\text{IC}_3\text{H}_7+\text{C}_2\text{H}_4$	1.00E+11	0	10400
179	$\text{C}_3\text{H}_8+\text{CH}_3\text{O}=\text{NC}_3\text{H}_7+\text{CH}_3\text{OH}$	3.18E+11	0	7050
180	$\text{C}_3\text{H}_8+\text{CH}_3\text{O}=\text{IC}_3\text{H}_7+\text{CH}_3\text{OH}$	7.20E+10	0	4470
181	$\text{C}_3\text{H}_8+\text{CH}_3=\text{NC}_3\text{H}_7+\text{CH}_4$	3.00E+12	0	11710
182	$\text{C}_3\text{H}_8+\text{CH}_3=\text{IC}_3\text{H}_7+\text{CH}_4$	8.07E+11	0	10110
183	$\text{NC}_3\text{H}_7=\text{C}_2\text{H}_4+\text{CH}_3$	3.00E+14	0	33220
184	$\text{NC}_3\text{H}_7=\text{C}_3\text{H}_6+\text{H}$	1.00E+14	0	37280
185	$\text{NC}_3\text{H}_7+\text{O}_2=\text{C}_3\text{H}_6+\text{HO}_2$	1.00E+12	0	5000
186	$\text{IC}_3\text{H}_7=\text{C}_2\text{H}_4+\text{CH}_3$	1.00E+14	0	45000
187	$\text{C}_3\text{H}_6+\text{H}=\text{IC}_3\text{H}_7$	3.00E+12	0	960
188	$\text{IC}_3\text{H}_7+\text{O}_2=\text{C}_3\text{H}_6+\text{HO}_2$	3.00E+12	0	3000
189	$\text{C}_3\text{H}_6=\text{AC}_3\text{H}_5+\text{H}$	1.00E+15	0	88040
190	$\text{C}_3\text{H}_6=\text{SC}_3\text{H}_5+\text{H}$	3.33E+14	0	88040
191	$\text{C}_3\text{H}_6=\text{C}_2\text{H}_3+\text{CH}_3$	7.00E+15	0	85800
192	$\text{C}_3\text{H}_6+\text{HO}_2=\text{C}_3\text{H}_6\text{O}+\text{OH}$	1.05E+12	0	14190
193	$\text{C}_3\text{H}_6+\text{HO}_2=\text{AC}_3\text{H}_5+\text{H}_2\text{O}_2$	1.50E+11	0	14190

194	$\text{C}_3\text{H}_6 + \text{HO}_2 = \text{SC}_3\text{H}_5 + \text{H}_2\text{O}_2$	7.50E+09	0	12570
195	$\text{C}_3\text{H}_6 + \text{HO}_2 = \text{TC}_3\text{H}_5 + \text{H}_2\text{O}_2$	3.00E+09	0	9930
196	$\text{C}_3\text{H}_6 + \text{OH} = \text{AC}_3\text{H}_5 + \text{H}_2\text{O}$	1.15E+13	0	600
197	$\text{C}_3\text{H}_6 + \text{OH} = \text{SC}_3\text{H}_5 + \text{H}_2\text{O}$	9.00E+13	0	6450
198	$\text{C}_3\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$	1.00E+13	0	0
199	$\text{C}_3\text{H}_6 + \text{OH} + \text{O}_2 = \text{CH}_3\text{CHO} + \text{CH}_2\text{O} + \text{OH}$	3.00E+10	0	-8230
200	$\text{C}_3\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{HCO}$	6.83E+04	2.6	-1130
201	$\text{C}_3\text{H}_6 + \text{O} = \text{C}_2\text{H}_4 + \text{CH}_2\text{O}$	6.83E+04	2.6	-1130
202	$\text{C}_3\text{H}_6 + \text{O} = \text{CH}_3 + \text{CH}_3 + \text{CO}$	6.83E+04	2.6	-1130
203	$\text{C}_3\text{H}_6 + \text{H} = \text{AC}_3\text{H}_5 + \text{H}_2$	2.50E+12	0	1100
204	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{SC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	47560
205	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{TC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	44000
206	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{AC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	50900
207	$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_5 = \text{AC}_3\text{H}_5 + \text{C}_2\text{H}_6$	1.00E+11	0	9800
208	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{AC}_3\text{H}_5 + \text{CH}_4$	1.40E+11	0	8800
209	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{SC}_3\text{H}_5 + \text{CH}_4$	6.60E+11	0	10110
210	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{TC}_3\text{H}_5 + \text{CH}_4$	2.40E+11	0	8030
211	$\text{C}_3\text{H}_6\text{O} = \text{C}_2\text{H}_6 + \text{CO}$	1.26E+14	0	58000
212	$\text{SC}_3\text{H}_5 = \text{C}_2\text{H}_2 + \text{CH}_3$	3.00E+10	0	36200
213	$\text{SC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CHO} + \text{HCO}$	3.00E+12	0	-250
214	$\text{SC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3 + \text{CO} + \text{CH}_2\text{O}$	2.00E+12	0	-250
215	$\text{AC}_3\text{H}_5 = \text{AC}_3\text{H}_4 + \text{H}$	8.91E+12	0	59000
216	$\text{AC}_3\text{H}_5 + \text{H} = \text{AC}_3\text{H}_4 + \text{H}_2$	3.33E+12	0	0
217	$\text{AC}_3\text{H}_5 + \text{CH}_3 = \text{AC}_3\text{H}_4 + \text{CH}_4$	5.00E+11	0	0
218	$\text{AC}_3\text{H}_5 + \text{O}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{CH}_2\text{O} + \text{CH}_2\text{O}$	1.50E+13	0	-250
219	$\text{TC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3 + \text{CO} + \text{CH}_2\text{O}$	3.20E+12	0	-250
220	$\text{AC}_3\text{H}_4 + \text{HO}_2 = \text{C}_2\text{H}_4 + \text{CO} + \text{OH}$	1.00E+12	0	14000
221	$\text{AC}_3\text{H}_4 + \text{HO}_2 = \text{C}_3\text{H}_3 + \text{H}_2\text{O}_2$	3.00E+13	0	14000
222	$\text{AC}_3\text{H}_4 + \text{OH} = \text{CH}_2\text{CO} + \text{CH}_3$	2.00E+12	0	860
223	$\text{AC}_3\text{H}_4 + \text{OH} = \text{C}_2\text{H}_4 + \text{HCO}$	1.00E+12	0	900
224	$\text{AC}_3\text{H}_4 + \text{O} = \text{CO} + \text{C}_2\text{H}_4$	7.80E+12	0	1600
225	$\text{AC}_3\text{H}_4 + \text{H} = \text{TC}_3\text{H}_5$	8.50E+12	0	2000
226	$\text{AC}_3\text{H}_4 + \text{H} = \text{SC}_3\text{H}_5$	4.00E+12	0	2700
227	$\text{PC}_3\text{H}_4 = \text{AC}_3\text{H}_4$	7.76E+11	0	55700
228	$\text{PC}_3\text{H}_4 + \text{OH} = \text{C}_3\text{H}_3 + \text{H}_2\text{O}$	1.85E+12	0	1650
229	$\text{PC}_3\text{H}_4 + \text{OH} = \text{CH}_2\text{CO} + \text{CH}_3$	4.50E+11	0	0
230	$\text{PC}_3\text{H}_4 + \text{O} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{CO}$	1.60E+13	0	2010
231	$\text{PC}_3\text{H}_4 + \text{H} = \text{TC}_3\text{H}_5$	6.63E+12	0	2000
232	$\text{PC}_3\text{H}_4 + \text{H} = \text{SC}_3\text{H}_5$	5.78E+12	0	3100
233	$\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$	1.80E+12	0	0
234	$\text{C}_2\text{H}_2 + \text{CH} = \text{C}_3\text{H}_3$	3.00E+13	0	0
235	$\text{C}_3\text{H}_3 + \text{H} = \text{PC}_3\text{H}_4$	2.00E+13	0	0
236	$\text{C}_3\text{H}_3 + \text{O} = \text{C}_2\text{H}_3 + \text{CO}$	3.80E+13	0	0
237	$\text{C}_3\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CO} + \text{HCO}$	3.01E+10	0	2870
238	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 = \text{C}_4\text{H}_6 + \text{H}$	1.00E+12	0	7300
239	$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 = \text{C}_4\text{H}_3 + \text{H}$	2.00E+12	0	45900
240	$\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{C}_4\text{H}_2 + \text{H}$	3.50E+13	0	0
241	$\text{C}_4\text{H}_3 + \text{M} = \text{C}_4\text{H}_2 + \text{H} + \text{M}$	1.00E+16	0	59700
242	$\text{C}_4\text{H}_2 + \text{M} = \text{C}_4\text{H} + \text{H} + \text{M}$	3.50E+17	0	80000
243	$\text{C}_4\text{H}_7 = \text{C}_4\text{H}_6 + \text{H}$	1.20E+14	0	49300

244	C4H7=C2H4+C2H3	1.00E+12	0	28000
245	C4H7+H=C4H6+H2	3.16E+13	0	0
246	C4H7+O2=C4H6+HO2	1.00E+11	0	0
247	C4H7+C2H3=C4H6+C2H4	4.00E+12	0	0
248	C4H7+C2H5=C4H6+C2H6	4.00E+12	0	0
249	C4H7+C2H5=PC4H8+C2H4	5.00E+11	0	0
250	C4H7+C2H5=TRAC4H8+C2H4	5.00E+11	0	0
251	C4H6=C2H3+C2H3	3.98E+19	-1	98150
252	C4H6+OH=C2H5+CH2CO	1.00E+12	0	0
253	C4H6+OH=SC3H5+CH2O	1.00E+12	0	0
254	C4H6+OH=CH3CHO+C2H3	1.00E+12	0	0
255	C4H6+O=C2H4+CH2CO	1.00E+12	0	0
256	C4H6+O=PC3H4+CH2O	1.00E+12	0	0
257	PC4H8=C4H7+H	4.08E+18	-1	97350
258	TRAC4H8=C4H7+H	4.07E+18	-1	97350
259	PC4H8+H=C4H7+H2	1.00E+14	0	3900
260	TRAC4H8+H=C4H7+H2	2.00E+14	0	3500
261	PC4H8+OH=C4H7+H2O	1.41E+13	0	3060
262	TRAC4H8+OH=C4H7+H2O	2.29E+13	0	3060
263	PC4H8+CH3=C4H7+CH4	1.00E+11	0	7300
264	TRAC4H8+CH3=C4H7+CH4	1.00E+11	0	8200
265	PC4H8+O=C3H6+CH2O	5.01E+12	0	0
266	TRAC4H8+O=IC3H7+HCO	6.03E+12	0	0
267	TRAC4H8+O=CH3CHO+C2H4	1.00E+12	0	0
268	PC4H8+OH=NC3H7+CH2O	1.51E+12	0	0
269	TRAC4H8+OH=CH3CHO+C2H5	3.02E+12	0	0
270	PC4H8=AC3H5+CH3	1.00E+16	0	73400
271	PC4H8=C2H3+C2H5	1.00E+19	-1	96770
272	PC4H8+O=CH3CHO+C2H4	1.50E+13	0	850
273	PC4H8+O=C2H5+CH3+CO	1.29E+13	0	850
274	PC4H8+OH=CH3CHO+C2H5	1.00E+11	0	0
275	PC4H8+OH=C2H6+CH3+CO	1.00E+10	0	0
276	C2H5+CH3=C2H4+CH4	4.37E-04	5	8300
277	C2H3+CH3=C2H2+CH4	4.37E-04	5	8300

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.3 Butane (1-butene) chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T**b exp(-E/RT))			Source/Modification
		A	b	E	
1	H+H+M=H2+M	7.31E+17	-1	0	#Reactions 1 - 237 : Ref[15]
2	O+O+M=O2+M	1.14E+17	-1	0	#Reactions 238 - 333 : Ref[16]
3	O+H+M=OH+M	6.20E+16	-0.6	0	
4	H2+O2=OH+OH	1.70E+13	0	47780	
5	O+H2=OH+H	1.50E+07	2	7550	
6	H+O2=OH+O	1.20E+17	-0.9	16520	
7	H+O2+M=HO2+M	8.00E+17	-0.8	0	
8	H+O2+O2=HO2+O2	6.70E+19	-1.4	0	
9	H+OH+M=H2O+M	8.62E+21	-2	0	
10	H2+OH=H2O+H	1.00E+08	1.6	3300	
11	H2O+O=OH+OH	1.50E+10	1.1	17260	
12	HO2+OH=H2O+O2	5.00E+13	0	1000	
13	HO2+O=OH+O2	2.00E+13	0	0	
14	H+HO2=H2+O2	2.50E+13	0	690	
15	H+HO2=OH+OH	1.50E+14	0	1000	
16	HO2+HO2=H2O2+O2	2.80E+12	0	0	
17	H2O2+M=OH+OH+M	1.30E+17	0	45410	
18	H2O2+OH=HO2+H2O	7.00E+12	0	1430	
19	H2O2+H=H2O+OH	1.00E+13	0	3590	
20	H2O2+H=HO2+H2	1.70E+12	0	3750	
21	H2O2+O=HO2+OH	2.80E+13	0	6400	
22	CO+HO2=CO2+OH	4.57E+14	0	25240	
23	CO+OH=CO2+H	4.40E+06	1.5	-740	
24	CO+O+M=CO2+M	2.83E+13	0	-4540	
25	CO+O2=CO2+O	2.53E+12	0	47700	
26	HCO+M=H+CO+M	2.86E+14	0	16800	
27	HCO+OH=CO+H2O	5.00E+13	0	0	
28	HCO+O=CO+OH	3.00E+13	0	0	
29	HCO+O=CO2+H	3.00E+13	0	0	
30	HCO+H=CO+H2	7.22E+13	0	0	
31	HCO+O2=CO+HO2	3.31E+13	-0.3	0	
32	HCO+CH3=CO+CH4	3.00E+11	0.5	0	
33	CH4=CH3+H	1.00E+15	0	100380	
34	CH4+HO2=CH3+H2O2	4.00E+12	0	19360	
35	CH4+OH=CH3+H2O	1.09E+05	2.4	2110	
36	CH4+O=CH3+OH	1.40E+07	2.1	7620	
37	CH4+H=CH3+H2	2.60E+04	3	8750	
38	CH4+CH2=CH3+CH3	6.00E+14	0	14000	
39	CH3+M=CH2+H+M	1.90E+16	0	91600	
40	CH3+HO2=CH3O+OH	3.00E+13	0	1080	
41	CH3+HO2=CH4+O2	1.00E+12	0	400	
42	CH3+OH=CH2O+H2	4.00E+12	0	0	
43	CH3+OH=CH3O+H	9.00E+14	0	15400	

44	CH ₃ +OH=CH ₂ +H ₂ O	3.00E+13	0	3000
45	CH ₃ +O=CH ₂ O+H	6.00E+13	0	0
46	CH ₃ +O=CH ₂ +OH	5.00E+13	0	12000
47	CH ₃ +H=CH ₂ +H ₂	7.00E+13	0	15100
48	CH ₃ +O ₂ =CH ₃ O+O	2.24E+14	0	33700
49	CH ₃ +CH ₃ =C ₂ H ₅ +H	8.00E+14	0	26530
50	CH ₃ +CH ₃ =C ₂ H ₄ +H ₂	2.10E+14	0	19200
51	C ₂ H ₆ =CH ₃ +CH ₃	1.40E+16	0	87480
52	CH ₂ +OH=CH+H ₂ O	4.00E+13	0	0
53	CH ₂ +OH=CH ₂ O+H	2.00E+13	0	0
54	CH ₂ +O=CO+H+H	3.00E+13	0	0
55	CH ₂ +O=CO+H ₂	5.00E+13	0	0
56	CH ₂ +O=CH+OH	5.00E+13	0.7	12000
57	CH ₂ +O=HCO+H	5.00E+13	0	0
58	CH ₂ +H=CH+H ₂	4.00E+13	0	0
59	CH ₂ +O ₂ =HCO+OH	4.30E+10	0	-500
60	CH ₂ +O ₂ =CO ₂ +H ₂	6.90E+11	0	500
61	CH ₂ +O ₂ =CO ₂ +H+H	1.60E+12	0	1000
62	CH ₂ +O ₂ =CO+H ₂ O	1.87E+10	0	-1000
63	CH ₂ +O ₂ =CO+OH+H	8.64E+10	0	-500
64	CH ₂ +O ₂ =CH ₂ O+O	5.00E+13	0	9000
65	CH ₂ +CO ₂ =CH ₂ O+CO	1.10E+11	0	1000
66	CH ₂ +CH ₂ =C ₂ H ₂ +H ₂	3.20E+13	0	0
67	CH ₂ +CH ₃ =C ₂ H ₄ +H	4.00E+13	0	0
68	CH ₂ +CH=C ₂ H ₂ +H	4.00E+13	0	0
69	CH+OH=HCO+H	3.00E+13	0	0
70	CH+O=CO+H	4.00E+13	0	0
71	CH+O ₂ =HCO+O	3.30E+13	0	0
72	CH+O ₂ =CO+OH	2.00E+13	0	0
73	CH+CO ₂ =HCO+CO	3.40E+12	0	690
74	CH+CH ₄ =C ₂ H ₄ +H	6.00E+13	0	0
75	CH+CH ₃ =C ₂ H ₃ +H	3.00E+13	0	0
76	CH ₃ O+M=CH ₂ O+H+M	1.80E+14	0	25100
77	CH ₃ O+OH=CH ₂ O+H ₂ O	1.00E+13	0	0
78	CH ₃ O+O=CH ₂ O+OH	1.00E+13	0	0
79	CH ₃ O+H=CH ₂ O+H ₂	2.00E+13	0	0
80	CH ₃ O+O ₂ =CH ₂ O+HO ₂	1.50E+13	0	7170
81	CH ₃ O+CH ₂ O=CH ₃ OH+HCO	1.15E+11	0	1280
82	CH ₃ O+CH ₄ =CH ₃ OH+CH ₃	2.00E+11	0	7000
83	CH ₂ O+M=HCO+H+M	5.72E+16	0	76480
84	CH ₂ O+HO ₂ =HCO+H ₂ O ₂	1.00E+12	0	9600
85	CH ₂ O+OH=HCO+H ₂ O	7.00E+13	0	1250
86	CH ₂ O+O=HCO+OH	3.50E+13	0	3510
87	CH ₂ O+H=HCO+H ₂	2.50E+13	0	3990
88	CH ₂ O+O ₂ =HCO+HO ₂	2.04E+13	0	39000
89	CH ₂ O+CH ₃ =HCO+CH ₄	1.00E+11	0	6100
90	C ₂ H ₆ +HO ₂ =C ₂ H ₅ +H ₂ O ₂	1.69E+13	0	20460
91	C ₂ H ₆ +OH=C ₂ H ₅ +H ₂ O	5.13E+05	2.1	860
92	C ₂ H ₆ +O=C ₂ H ₅ +OH	4.40E+07	2	5120
93	C ₂ H ₆ +H=C ₂ H ₅ +H ₂	5.40E+02	3.5	5210

94	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	1.00E+13	0	51000
95	$\text{C}_2\text{H}_6 + \text{CH}_3\text{O} = \text{C}_2\text{H}_5 + \text{CH}_3\text{OH}$	3.02E+11	0	7000
96	$\text{C}_2\text{H}_6 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{CH}_4$	5.50E-01	4	8290
97	$\text{C}_2\text{H}_5 + \text{O} = \text{CH}_3\text{CHO} + \text{H}$	5.00E+13	0	0
98	$\text{C}_2\text{H}_5 + \text{H} = \text{C}_2\text{H}_4 + \text{H}_2$	1.25E+14	0	8000
99	$\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$	1.58E+10	0	-1900
100	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$	1.40E+12	0	0
101	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	3.00E+17	0	79350
102	$\text{C}_2\text{H}_4 + \text{M} = \text{C}_2\text{H}_3 + \text{H} + \text{M}$	2.97E+17	0	96560
103	$\text{C}_2\text{H}_4 + \text{HO}_2 = \text{C}_2\text{H}_4\text{O} + \text{OH}$	1.00E+13	0	18280
104	$\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	4.90E+12	0	1230
105	$\text{C}_2\text{H}_4 + \text{OH} = \text{CH}_2\text{O} + \text{CH}_3$	1.50E+12	0	960
106	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_2\text{O} + \text{CH}_2$	4.00E+13	0	5000
107	$\text{C}_2\text{H}_4 + \text{O} = \text{CH}_3 + \text{HCO}$	2.20E+09	1.2	740
108	$\text{C}_2\text{H}_4 + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$	4.00E+06	2	6000
109	$\text{C}_2\text{H}_5 + \text{M} = \text{C}_2\text{H}_4 + \text{H} + \text{M}$	2.00E+15	0	30120
110	$\text{C}_2\text{H}_4 + \text{O}_2 = \text{C}_2\text{H}_3 + \text{HO}_2$	4.00E+13	0	61500
111	$\text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_3$	5.00E+14	0	64700
112	$\text{C}_2\text{H}_4 + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{CH}_4$	5.60E+11	0	11110
113	$\text{C}_2\text{H}_4\text{O} = \text{CH}_4 + \text{CO}$	2.00E+14	0	58000
114	$\text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{H}$	2.20E+14	0	38000
115	$\text{C}_2\text{H}_3 + \text{OH} = \text{C}_2\text{H}_2 + \text{H}_2\text{O}$	5.00E+12	0	0
116	$\text{C}_2\text{H}_3 + \text{O} = \text{CH}_2\text{CO} + \text{H}$	3.30E+13	0	0
117	$\text{C}_2\text{H}_3 + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$	2.50E+13	0	0
118	$\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$	3.20E+12	0	-350
119	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	1.50E+13	0	10000
120	$\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	4.57E+16	0	106840
121	$\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$	1.00E+13	0	7000
122	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	3.20E+10	0	200
123	$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$	6.00E+13	0	23660
124	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	4.10E+08	1.5	1700
125	$\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H} + \text{OH}$	3.20E+15	-0.6	15000
126	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	4.30E+14	0	12120
127	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{OH}$	2.00E+08	1.5	30100
128	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCO} + \text{HCO}$	4.00E+12	0	28000
129	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0	0
130	$\text{C}_2\text{H} + \text{O} = \text{CO} + \text{CH}$	1.00E+13	0	0
131	$\text{C}_2\text{H} + \text{O}_2 = \text{HCCO} + \text{O}$	5.00E+13	0	1500
132	$\text{C}_2\text{H} + \text{O}_2 = \text{HCO} + \text{CO}$	5.00E+13	0	1510
133	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	4.11E+15	0	59270
134	$\text{CH}_2\text{CO} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$	1.00E+13	0	0
135	$\text{CH}_2\text{CO} + \text{O} = \text{HCO} + \text{HCO}$	2.00E+13	0	2300
136	$\text{CH}_2\text{CO} + \text{O} = \text{CH}_2\text{O} + \text{CO}$	2.00E+13	0	0
137	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	7.00E+12	0	3010
138	$\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00E+13	0	0
139	$\text{HCCO} + \text{O} = \text{CO} + \text{CO} + \text{H}$	1.93E+14	0	590
140	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	3.00E+13	0	0
141	$\text{HCCO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46E+12	0	2500
142	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H} + \text{CH}_2\text{O}$	1.00E+13	0	2000
143	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0

144	CH3OH=CH3+OH	6.00E+16	0	91060
145	CH3OH+HO2=CH2OH+H2O2	6.30E+12	0	19360
146	CH3OH+OH=CH2OH+H2O	1.00E+13	0	1700
147	CH3OH+O=CH2OH+OH	1.00E+13	0	4690
148	CH3OH+H=CH2OH+H2	4.00E+13	0	6100
149	CH3OH+CH2O=CH3O+CH3O	1.55E+12	0	79570
150	CH3OH+CH3=CH2OH+CH4	1.82E+11	0	9800
151	CH2OH+M=CH2O+H+M	1.00E+14	0	25100
152	CH2OH+H=CH2O+H2	3.00E+13	0	0
153	CH2OH+O2=CH2O+HO2	1.00E+13	0	7170
154	CH3CHO=CH3+HCO	2.00E+15	0	79110
155	CH3CHO+HO2=CH3+CO+H2O2	1.70E+12	0	10700
156	CH3CHO+OH=CH3+CO+H2O	1.00E+13	0	0
157	CH3CHO+O=CH3+CO+OH	5.00E+12	0	1790
158	CH3CHO+H=CH3+CO+H2	4.00E+13	0	4210
159	CH3CHO+O2=CH3+CO+HO2	2.00E+13	0.5	42200
160	CH3CHO+CH3=CH3+CO+CH4	8.50E+11	0	6000
161	C3H8=C2H5+CH3	7.94E+16	0	85100
162	C3H8+HO2=NC3H7+H2O2	4.50E+11	0	14900
163	C3H8+HO2=IC3H7+H2O2	2.00E+11	0	12500
164	C3H8+OH=NC3H7+H2O	4.71E+05	2.4	390
165	C3H8+OH=IC3H7+H2O	3.58E+02	3.2	-1600
166	C3H8+O=NC3H7+OH	3.72E+06	2.4	1390
167	C3H8+O=IC3H7+OH	5.50E+05	2.5	790
168	C3H8+H=NC3H7+H2	1.35E+14	0	9680
169	C3H8+H=IC3H7+H2	2.00E+14	0	8300
170	C3H8+O2=NC3H7+HO2	4.00E+13	0	47500
171	C3H8+O2=IC3H7+HO2	4.00E+13	0	47500
172	C3H8+IC3H7=NC3H7+C3H8	1.00E+11	0	12900
173	C3H8+AC3H5=NC3H7+C3H8	7.94E+11	0	20500
174	C3H8+AC3H5=IC3H7+C3H8	7.94E+11	0	16200
175	C3H8+C2H5=NC3H7+C2H6	3.16E+11	0	12300
176	C3H8+C2H5=IC3H7+C2H6	5.01E+10	0	10400
177	C3H8+C2H3=NC3H7+C2H4	1.00E+11	0	10400
178	C3H8+C2H3=IC3H7+C2H4	1.00E+11	0	10400
179	C3H8+CH3O=NC3H7+CH3OH	3.18E+11	0	7050
180	C3H8+CH3O=IC3H7+CH3OH	7.20E+10	0	4470
181	C3H8+CH3=NC3H7+CH4	3.00E+12	0	11710
182	C3H8+CH3=IC3H7+CH4	8.07E+11	0	10110
183	NC3H7=C2H4+CH3	3.00E+14	0	33220
184	NC3H7=C3H6+H	1.00E+14	0	37280
185	NC3H7+O2=C3H6+HO2	1.00E+12	0	5000
186	IC3H7=C2H4+CH3	1.00E+14	0	45000
187	C3H6+H=IC3H7	3.00E+12	0	960
188	IC3H7+O2=C3H6+HO2	3.00E+12	0	3000
189	C3H6=AC3H5+H	1.00E+15	0	88040
190	C3H6=SC3H5+H	3.33E+14	0	88040
191	C3H6=C2H3+CH3	7.00E+15	0	85800
192	C3H6+HO2=C3H6O+OH	1.05E+12	0	14190
193	C3H6+HO2=AC3H5+H2O2	1.50E+11	0	14190

194	$\text{C}_3\text{H}_6 + \text{HO}_2 = \text{SC}_3\text{H}_5 + \text{H}_2\text{O}_2$	7.50E+09	0	12570
195	$\text{C}_3\text{H}_6 + \text{HO}_2 = \text{TC}_3\text{H}_5 + \text{H}_2\text{O}_2$	3.00E+09	0	9930
196	$\text{C}_3\text{H}_6 + \text{OH} = \text{AC}_3\text{H}_5 + \text{H}_2\text{O}$	1.15E+13	0	600
197	$\text{C}_3\text{H}_6 + \text{OH} = \text{SC}_3\text{H}_5 + \text{H}_2\text{O}$	9.00E+13	0	6450
198	$\text{C}_3\text{H}_6 + \text{OH} = \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$	1.00E+13	0	0
199	$\text{C}_3\text{H}_6 + \text{OH} + \text{O}_2 = \text{CH}_3\text{CHO} + \text{CH}_2\text{O} + \text{OH}$	3.00E+10	0	-8230
200	$\text{C}_3\text{H}_6 + \text{O} = \text{C}_2\text{H}_5 + \text{HCO}$	6.83E+04	2.6	-1130
201	$\text{C}_3\text{H}_6 + \text{O} = \text{C}_2\text{H}_4 + \text{CH}_2\text{O}$	6.83E+04	2.6	-1130
202	$\text{C}_3\text{H}_6 + \text{O} = \text{CH}_3 + \text{CH}_3 + \text{CO}$	6.83E+04	2.6	-1130
203	$\text{C}_3\text{H}_6 + \text{H} = \text{AC}_3\text{H}_5 + \text{H}_2$	2.50E+12	0	1100
204	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{SC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	47560
205	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{TC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	44000
206	$\text{C}_3\text{H}_6 + \text{O}_2 = \text{AC}_3\text{H}_5 + \text{HO}_2$	4.00E+13	0	50900
207	$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_5 = \text{AC}_3\text{H}_5 + \text{C}_2\text{H}_6$	1.00E+11	0	9800
208	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{AC}_3\text{H}_5 + \text{CH}_4$	1.40E+11	0	8800
209	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{SC}_3\text{H}_5 + \text{CH}_4$	6.60E+11	0	10110
210	$\text{C}_3\text{H}_6 + \text{CH}_3 = \text{TC}_3\text{H}_5 + \text{CH}_4$	2.40E+11	0	8030
211	$\text{C}_3\text{H}_6\text{O} = \text{C}_2\text{H}_6 + \text{CO}$	1.26E+14	0	58000
212	$\text{SC}_3\text{H}_5 = \text{C}_2\text{H}_2 + \text{CH}_3$	3.00E+10	0	36200
213	$\text{SC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CHO} + \text{HCO}$	3.00E+12	0	-250
214	$\text{SC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3 + \text{CO} + \text{CH}_2\text{O}$	2.00E+12	0	-250
215	$\text{AC}_3\text{H}_5 = \text{AC}_3\text{H}_4 + \text{H}$	8.91E+12	0	59000
216	$\text{AC}_3\text{H}_5 + \text{H} = \text{AC}_3\text{H}_4 + \text{H}_2$	3.33E+12	0	0
217	$\text{AC}_3\text{H}_5 + \text{CH}_3 = \text{AC}_3\text{H}_4 + \text{CH}_4$	5.00E+11	0	0
218	$\text{AC}_3\text{H}_5 + \text{O}_2 + \text{O}_2 \Rightarrow \text{CO} + \text{OH} + \text{CH}_2\text{O} + \text{CH}_2\text{O}$	1.50E+13	0	-250
219	$\text{TC}_3\text{H}_5 + \text{O}_2 = \text{CH}_3 + \text{CO} + \text{CH}_2\text{O}$	3.20E+12	0	-250
220	$\text{AC}_3\text{H}_4 + \text{HO}_2 = \text{C}_2\text{H}_4 + \text{CO} + \text{OH}$	1.00E+12	0	14000
221	$\text{AC}_3\text{H}_4 + \text{HO}_2 = \text{C}_3\text{H}_3 + \text{H}_2\text{O}_2$	3.00E+13	0	14000
222	$\text{AC}_3\text{H}_4 + \text{OH} = \text{CH}_2\text{CO} + \text{CH}_3$	2.00E+12	0	860
223	$\text{AC}_3\text{H}_4 + \text{OH} = \text{C}_2\text{H}_4 + \text{HCO}$	1.00E+12	0	900
224	$\text{AC}_3\text{H}_4 + \text{O} = \text{CO} + \text{C}_2\text{H}_4$	7.80E+12	0	1600
225	$\text{AC}_3\text{H}_4 + \text{H} = \text{TC}_3\text{H}_5$	8.50E+12	0	2000
226	$\text{AC}_3\text{H}_4 + \text{H} = \text{SC}_3\text{H}_5$	4.00E+12	0	2700
227	$\text{PC}_3\text{H}_4 = \text{AC}_3\text{H}_4$	7.76E+11	0	55700
228	$\text{PC}_3\text{H}_4 + \text{OH} = \text{C}_3\text{H}_3 + \text{H}_2\text{O}$	1.85E+12	0	1650
229	$\text{PC}_3\text{H}_4 + \text{OH} = \text{CH}_2\text{CO} + \text{CH}_3$	4.50E+11	0	0
230	$\text{PC}_3\text{H}_4 + \text{O} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{CO}$	1.60E+13	0	2010
231	$\text{PC}_3\text{H}_4 + \text{H} = \text{TC}_3\text{H}_5$	6.63E+12	0	2000
232	$\text{PC}_3\text{H}_4 + \text{H} = \text{SC}_3\text{H}_5$	5.78E+12	0	3100
233	$\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$	1.80E+12	0	0
234	$\text{C}_2\text{H}_2 + \text{CH} = \text{C}_3\text{H}_3$	3.00E+13	0	0
235	$\text{C}_3\text{H}_3 + \text{H} = \text{PC}_3\text{H}_4$	2.00E+13	0	0
236	$\text{C}_3\text{H}_3 + \text{O} = \text{C}_2\text{H}_3 + \text{CO}$	3.80E+13	0	0
237	$\text{C}_3\text{H}_3 + \text{O}_2 = \text{CH}_2\text{CO} + \text{HCO}$	3.01E+10	0	2870
238	$\text{C}_4\text{H}_{10} = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$	1.00E+16	0	81300
239	$\text{C}_4\text{H}_{10} = \text{NC}_3\text{H}_7 + \text{CH}_3$	1.00E+17	0	85400
240	$\text{C}_4\text{H}_{10} + \text{O}_2 = \text{PC}_4\text{H}_9 + \text{HO}_2$	2.51E+13	0	49000
241	$\text{C}_4\text{H}_{10} + \text{O}_2 = \text{SC}_4\text{H}_9 + \text{HO}_2$	3.98E+13	0	47600
242	$\text{C}_4\text{H}_{10} + \text{H} = \text{PC}_4\text{H}_9 + \text{H}_2$	1.12E+08	2	7700
243	$\text{C}_4\text{H}_{10} + \text{H} = \text{SC}_4\text{H}_9 + \text{H}_2$	2.00E+07	2	5000

244	C4H10+OH=PC4H9+H2O	8.72E+09	1.1	1810
245	C4H10+OH=SC4H9+H2O	4.00E+09	1.3	700
246	C4H10+O=PC4H9+OH	4.89E+06	2.4	5540
247	C4H10+O=SC4H9+OH	9.00E+05	2.6	2600
248	C4H10+CH3=PC4H9+CH4	2.60E+12	0	11600
249	C4H10+CH3=SC4H9+CH4	4.01E+11	0	9600
250	C4H10+C2H3=PC4H9+C2H4	1.00E+12	0	18000
251	C4H10+C2H3=SC4H9+C2H4	7.94E+11	0	16800
252	C4H10+C2H5=PC4H9+C2H6	1.00E+11	0	13400
253	C4H10+C2H5=SC4H9+C2H6	1.00E+11	0	10400
254	C4H10+AC3H5=PC4H9+C3H6	7.94E+11	0	20500
255	C4H10+SC3H5=SC4H9+C3H6	3.16E+11	0	16400
256	C4H10+HO2=PC4H9+H2O2	2.24E+13	0	19400
257	C4H10+HO2=SC4H9+H2O2	1.35E+13	0	17000
258	C4H10+CH3O=PC4H9+CH3OH	3.02E+11	0	7000
259	C4H10+CH3O=SC4H9+CH3OH	6.03E+11	0	7000
260	PC4H9=C2H5+C2H4	2.51E+13	0	28800
261	PC4H9=PC4H8+H	1.30E+13	0	39000
262	PC4H9+O2=PC4H8+HO2	1.00E+12	0	2000
263	SC4H9=PC4H8+H	2.00E+13	0	40400
264	SC4H9=TRAC4H8+H	5.00E+13	0	37900
265	SC4H9=CISC4H8+H	5.00E+14	0	37900
266	SC4H9=C3H6+CH3	4.00E+14	0	33200
267	SC4H9+O2=PC4H8+HO2	2.00E+12	0	4500
268	SC4H9+O2=TRAC4H8+HO2	2.00E+13	0	4250
269	SC4H9+O2=CISC4H8+HO2	2.00E+13	0	4250
270	PC4H8=SC4H7+H	4.08E+18	-1	97350
271	PC4H8=AC3H5+CH3	8.00E+16	0	74000
272	PC4H8+O2=SC4H7+HO2	4.00E+12	0	40000
273	PC4H8=C2H3+C2H5	2.00E+18	-1	96770
274	PC4H8+H=SC4H7+H2	5.00E+13	0	3900
275	PC4H8+OH=NC3H7+CH2O	6.50E+12	0	0
276	PC4H8+OH=CH3CHO+C2H5	1.00E+11	0	0
277	PC4H8+OH=C2H6+CH3+CO	1.00E+10	0	0
278	PC4H8+OH=SC4H7+H2O	1.75E+13	0	3060
279	PC4H8+O=C3H6+CH2O	2.51E+12	0	0
280	PC4H8+O=CH3CHO+C2H4	1.25E+12	0	850
281	PC4H8+O=C2H5+CH3+CO	1.63E+13	0	850
282	PC4H8+O=SC4H7+OH	1.30E+13	0	4500
283	PC4H8+HO2=SC4H7+H2O2	1.00E+11	0	17060
284	PC4H8+CH3=SC4H7+CH4	1.00E+11	0	7300
285	PC4H8+C2H5=SC4H7+C2H6	1.00E+11	0	8000
286	PC4H8+AC3H5=SC4H7+C3H6	8.00E+10	0	12400
287	PC4H8+SC3H5=SC4H7+C3H6	8.00E+10	0	12400
288	PC4H8+TC3H5=SC4H7+C3H6	8.00E+10	0	12400
289	PC4H8+SC4H7=SC4H7+CISC4H8	3.98E+10	0	12400
290	PC4H8+SC4H7=SC4H7+TRAC4H8	3.98E+10	0	12400
291	CISC4H8=TRAC4H8	1.00E+13	0	62000
292	CISC4H8=C4H6+H2	1.00E+13	0	65500
293	TRAC4H8=SC4H7+H	4.07E+18	-1	97350

294	CISC4H8=SC4H7+H	4.07E+18	-1	97350
295	TRAC4H8+H=SC4H7+H2	5.00E+12	0	3500
296	CISC4H8+H=SC4H7+H2	1.00E+12	0	3500
297	TRAC4H8+OH=SC4H7+H2O	1.01E+14	0	3060
298	CISC4H8+OH=SC4H7+H2O	1.26E+14	0	3060
299	TRAC4H8+CH3=SC4H7+CH4	1.00E+11	0	8200
300	CISC4H8+CH3=SC4H7+CH4	1.00E+11	0	8200
301	TRAC4H8+O=IC3H7+HCO	6.03E+12	0	0
302	CISC4H8+O=IC3H7+HCO	6.03E+12	0	0
303	TRAC4H8+O=CH3CHO+C2H4	1.00E+12	0	0
304	CISC4H8+O=CH3CHO+C2H4	1.00E+12	0	0
305	TRAC4H8+OH=CH3CHO+C2H5	1.51E+13	0	0
306	CISC4H8+OH=CH3CHO+C2H5	1.40E+13	0	0
307	CISC4H8=SC3H5+CH3	1.25E+15	0	71300
308	TRAC4H8=SC3H5+CH3	6.50E+14	0	71300
309	SC4H7=C4H6+H	1.20E+14	0	49300
310	SC4H7=C2H4+C2H3	1.00E+11	0	37000
311	SC4H7+H=C4H6+H2	3.16E+12	0	0
312	SC4H7+O2=C4H6+HO2	1.00E+11	0	0
313	SC4H7+C2H3=C4H6+C2H4	4.00E+12	0	0
314	SC4H7+C2H5=C4H6+C2H6	4.00E+12	0	0
315	SC4H7+C2H5=PC4H8+C2H4	5.00E+11	0	0
316	SC4H7+C2H5=TRAC4H8+C2H4	5.00E+11	0	0
317	SC4H7+C2H5=CISC4H8+C2H4	5.00E+11	0	0
318	SC4H7+AC3H5=C4H6+C3H6	4.00E+13	0	0
319	SC4H7+CH3=C4H6+CH4	1.00E+13	0	0
320	SC4H7+SC4H7=C4H6+PC4H8	3.16E+12	0	0
321	C4H6=C2H3+C2H3	3.98E+19	-1	98150
322	C4H6+OH=C2H5+CH2CO	1.00E+12	0	0
323	C4H6+OH=SC3H5+CH2O	2.00E+12	0	0
324	C4H6+OH=CH3CHO+C2H3	5.00E+12	0	0
325	C4H6+O=C2H4+CH2CO	1.00E+12	0	0
326	C4H6+O=PC3H4+CH2O	1.00E+12	0	0
327	C2H5+CH3=C2H4+CH4	4.37E-04	5	8300
328	C2H3+CH3=C2H2+CH4	4.37E-04	5	8300
329	C2H3+C2H4=C4H6+H	1.00E+11	0	7300
330	C2H2+C2H2=C4H3+H	2.00E+12	0	45900
331	C2H2+C2H=C4H2+H	3.50E+13	0	0
332	C4H3+M=C4H2+H+M	1.00E+16	0	59700
333	C4H2+M=C4H+H+M	3.50E+17	0	80000

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.4 Isooctane chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T**b exp(-E/RT))			Source/Modification
		A	b	E	
1	H+O2=O+OH	5.13E+16	-0.8	16510	# All reactions : Ref[17]
2	H2+O=H+OH	1.82E+10	1	8900	#(Reactions 351 - 455
3	H2O+O=OH+OH	6.76E+13	0	18350	# are reverse reactions
4	H2O+H=H2+OH	9.55E+13	0	20300	# for reactions 244 - 350)
5	H2O2+OH=H2O+HO2	1.00E+13	0	1800	
6	H2O+M=H+OH+M	2.19E+16	0	105000	
	H2O Enhanced by	2.000E+01			
7	H+O2+M=HO2+M	1.66E+15	0	-1000	
	H2O Enhanced by	2.100E+01			
	CO2 Enhanced by	5.000E+00			
	CO Enhanced by	2.000E+00			
	H2 Enhanced by	3.300E+00			
8	HO2+O=OH+O2	5.01E+13	0	1000	
9	HO2+H=OH+OH	2.51E+14	0	1900	
10	HO2+H=H2+O2	2.51E+13	0	700	
11	HO2+OH=H2O+O2	5.01E+13	0	1000	
12	H2O2+O2=HO2+HO2	3.98E+13	0	42640	
13	H2O2+M=OH+OH+M	1.20E+17	0	45500	
	H2O Enhanced by	6.000E+00			
	O2 Enhanced by	7.800E-01			
	H2O2 Enhanced by	6.600E+00			
14	H2O2+H=HO2+H2	1.70E+12	0	3750	
15	O+H+M=OH+M	1.00E+16	0	0	
16	O2+M=O+O+M	5.13E+15	0	115000	
17	H2+M=H+H+M	2.19E+14	0	96000	
	H2O Enhanced by	6.000E+00			
	H Enhanced by	2.000E+00			
	H2 Enhanced by	3.000E+00			
18	CO+OH=CO2+H	1.51E+07	1.3	-770	
19	CO+HO2=CO2+OH	1.51E+14	0	23650	
20	CO+O+M=CO2+M	5.89E+15	0	4100	
21	CO2+O=CO+O2	2.75E+12	0	43830	
22	HCO+OH=CO+H2O	1.00E+14	0	0	
23	HCO+M=H+CO+M	1.45E+14	0	19000	
24	HCO+H=CO+H2	2.00E+14	0	0	
25	HCO+O=CO+OH	1.00E+14	0	0	
26	HCO+HO2=CH2O+O2	1.00E+14	0	3000	
27	HCO+O2=CO+HO2	3.98E+12	0	0	
28	CH2O+M=HCO+H+M	3.31E+16	0	81000	
29	CH2O+OH=HCO+H2O	7.59E+12	0	170	
30	CH2O+H=HCO+H2	3.31E+14	0	10500	
31	CH2O+O=HCO+OH	5.01E+13	0	4600	
32	CH2O+HO2=HCO+H2O2	2.00E+11	0	8000	

33	CH4+M=CH3+H+M	1.41E+17	0	88400
34	CH4+H=CH3+H2	1.26E+14	0	11900
35	CH4+OH=CH3+H2O	3.47E+03	3.1	2000
36	CH4+O=CH3+OH	2.14E+06	2.2	6480
37	CH4+HO2=CH3+H2O2	2.00E+13	0	18000
38	CH3+HO2=CH3O+OH	3.24E+13	0	0
39	CH3+OH=CH2O+H2	3.98E+12	0	0
40	CH3+O=CH2O+H	1.29E+14	0	2000
41	CH3+O2=CH3O+O	4.79E+13	0	29000
42	CH2O+CH3=CH4+HCO	1.00E+10	0.5	6000
43	CH3+HCO=CH4+CO	3.02E+11	0.5	0
44	CH3+HO2=CH4+O2	1.00E+12	0	400
45	CH3O+M=CH2O+H+M	5.01E+13	0	21000
46	CH3O+O2=CH2O+HO2	7.59E+10	0	2700
47	C2H6=CH3+CH3	2.24E+19	-1	88310
48	C2H6+CH3=C2H5+CH4	5.50E-01	4	8280
49	C2H6+H=C2H5+H2	5.37E+02	3.5	5200
50	C2H6+OH=C2H5+H2O	8.71E+09	1.1	1810
51	C2H6+O=C2H5+OH	1.12E+14	0	7850
52	C2H5+M=C2H4+H+M	2.00E+15	0	30000
53	C2H5+O2=C2H4+HO2	1.00E+12	0	5000
54	C2H4+C2H4=C2H5+C2H3	5.01E+14	0	64700
55	C2H4+M=C2H2+H2	9.33E+16	0	77200
56	C2H4+M=C2H3+H+M	6.31E+18	0	108720
57	C2H4+O=CH3+HCO	3.31E+12	0	1130
58	C2H4+O=CH2O+CH2	2.51E+13	0	5000
59	C2H4+H=C2H3+H2	1.51E+07	2	6000
60	C2H4+OH=C2H3+H2O	4.79E+12	0	1230
61	C2H4+OH=CH3+CH2O	2.00E+12	0	960
62	C2H3+M=C2H2+H+M	7.94E+14	0	31500
63	C2H3+O2=C2H2+HO2	1.00E+12	0	10000
64	C2H2+M=C2H+H+M	1.00E+14	0	114000
65	C2H2+O2=HCO+HCO	3.98E+12	0	28000
66	C2H2+H=C2H+H2	2.00E+14	0	19000
67	C2H2+OH=C2H+H2O	6.03E+12	0	7000
68	C2H2+OH=CH2CO+H	3.24E+11	0	200
69	C2H2+O=C2H+OH	3.24E+15	-0.6	17000
70	C2H2+O=CH2+CO	6.76E+13	0	4000
71	C2H+O2=HCO+CO	1.00E+13	0	7000
72	C2H+O=CO+CH	5.01E+13	0	0
73	CH2+O2=HCO+OH	1.00E+14	0	3700
74	CH2+O=CH+OH	1.91E+11	0.7	25000
75	CH2+H=CH+H2	2.69E+11	0.7	25700
76	CH2+OH=CH+H2O	2.69E+11	0.7	25700
77	CH+O2=CO+OH	1.35E+11	0.7	25700
78	CH+O2=HCO+O	1.00E+13	0	0
79	CH3OH+M=CH3+OH+M	3.02E+18	0	80000
80	CH3OH+OH=CH2OH+H2O	3.98E+12	0	1370
81	CH3OH+O=CH2OH+OH	1.70E+12	0	2290
82	CH3OH+H=CH2OH+H2	3.02E+13	0	7000

83	CH3OH+H=CH3+H2O	5.25E+12	0	5340
84	CH3OH+CH3=CH2OH+CH4	1.82E+11	0	9800
85	CH3OH+HO2=CH2OH+H2O2	6.31E+12	0	19360
86	CH2OH+M=CH2O+H+M	2.51E+13	0	29000
87	CH2OH+O2=CH2O+HO2	8.31E+11	0	0
88	C2H2+C2H2=C4H3+H	1.00E+13	0	45000
89	C4H3+M=C4H2+H+M	1.00E+16	0	60000
90	C2H2+C2H=C4H2+H	3.98E+13	0	0
91	C4H2+M=C4H+H+M	3.47E+17	0	80000
92	C2H3+H=C2H2+H2	2.00E+13	0	2500
93	C3H8=CH3+C2H5	1.70E+16	0	84840
94	CH3+C3H8=CH4+IC3H7	1.10E+15	0	25140
95	CH3+C3H8=CH4+NC3H7	1.10E+15	0	25140
96	H+C3H8=H2+IC3H7	8.71E+06	2	5000
97	H+C3H8=H2+NC3H7	5.62E+07	2	7700
98	IC3H7=H+C3H6	6.31E+13	0	36900
99	IC3H7=CH3+C2H4	2.00E+10	0	29500
100	NC3H7=CH3+C2H4	9.55E+13	0	31000
101	NC3H7=H+C3H6	1.26E+14	0	37000
102	IC3H7+C3H8=NC3H7+C3H8	3.02E+10	0	12900
103	C2H3+C3H8=C2H4+IC3H7	1.00E+11	0	10400
104	C2H3+C3H8=C2H4+NC3H7	1.00E+11	0	10400
105	C2H5+C3H8=C2H6+IC3H7	1.00E+11	0	10400
106	C2H5+C3H8=C2H6+NC3H7	1.00E+11	0	10400
107	C3H8+O=IC3H7+OH	2.81E+13	0	5200
108	C3H8+O=NC3H7+OH	1.12E+14	0	7850
109	C3H8+OH=IC3H7+H2O	4.79E+08	1.4	850
110	C3H8+OH=NC3H7+H2O	5.75E+08	1.4	850
111	C3H8+HO2=IC3H7+H2O2	3.39E+12	0	17000
112	C3H8+HO2=NC3H7+H2O2	1.12E+13	0	19400
113	C3H6+O=C2H4+CH2O	6.76E+04	2.6	-1130
114	IC3H7+O2=C3H6+HO2	1.00E+12	0	5000
115	NC3H7+O2=C3H6+HO2	1.00E+12	0	5000
116	C3H8+O2=IC3H7+HO2	3.98E+13	0	47500
117	C3H8+O2=NC3H7+HO2	3.98E+13	0	47500
118	C3H6+OH=C2H5+CH2O	1.00E+12	0	0
119	C3H6+O=C2H5+HCO	6.76E+04	2.6	-1130
120	C3H6+OH=CH3+CH3CHO	1.00E+12	0	0
121	C3H6+O=CH3+CH3CO	6.67E+04	2.6	-1130
122	CH3CHO+H=CH3CO+H2	3.98E+13	0	4200
123	CH3CHO+OH=CH3CO+H2O	1.00E+13	0	0
124	CH3CHO+O=CH3CO+OH	5.01E+12	0	1790
125	CH3CHO+CH3=CH3CO+CH4	1.73E+12	0	8440
126	CH3CHO+HO2=CH3CO+H2O2	1.70E+12	0	10700
127	CH3CHO=CH3+HCO	7.08E+15	0	81780
128	CH3CHO+O2=CH3CO+HO2	2.00E+13	0.5	42200
129	CH3CO+M=CH3+CO+M	4.37E+15	0	10500
130	C3H6+H=C3H5+H2	5.01E+12	0	1500
131	C3H6+CH3=C3H5+CH4	1.58E+12	0	8800
132	C3H6+C2H5=C3H5+C2H6	1.00E+11	0	9800

133	$\text{C}_3\text{H}_6 + \text{OH} = \text{C}_3\text{H}_5 + \text{H}_2\text{O}$	1.00E+13	0	3060
134	$\text{C}_3\text{H}_8 + \text{C}_3\text{H}_5 = \text{IC}_3\text{H}_7 + \text{C}_3\text{H}_6$	2.00E+11	0	16100
135	$\text{C}_3\text{H}_8 + \text{C}_3\text{H}_5 = \text{NC}_3\text{H}_7 + \text{C}_3\text{H}_6$	7.94E+11	0	20500
136	$\text{C}_3\text{H}_5 = \text{C}_3\text{H}_4 + \text{H}$	3.98E+13	0	70000
137	$\text{C}_3\text{H}_5 + \text{O}_2 = \text{C}_3\text{H}_4 + \text{HO}_2$	6.03E+11	0	10000
138	$\text{PC}_4\text{H}_8 = \text{C}_3\text{H}_5 + \text{CH}_3$	1.51E+19	-1	73400
139	$\text{PC}_4\text{H}_8 = \text{C}_2\text{H}_3 + \text{C}_2\text{H}_5$	1.00E+19	-1	96770
140	$\text{PC}_4\text{H}_8 + \text{O} = \text{CH}_3\text{CHO} + \text{C}_2\text{H}_4$	1.29E+13	0	850
141	$\text{PC}_4\text{H}_8 + \text{O} = \text{CH}_3\text{CO} + \text{C}_2\text{H}_5$	1.29E+13	0	850
142	$\text{PC}_4\text{H}_8 + \text{OH} = \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5$	1.00E+11	0	0
143	$\text{PC}_4\text{H}_8 + \text{OH} = \text{CH}_3\text{CO} + \text{C}_2\text{H}_6$	1.00E+10	0	0
144	$\text{C}_3\text{H}_4 + \text{O} = \text{CH}_2\text{O} + \text{C}_2\text{H}_2$	1.00E+12	0	0
145	$\text{C}_3\text{H}_4 + \text{O} = \text{HCO} + \text{C}_2\text{H}_3$	1.00E+12	0	0
146	$\text{C}_3\text{H}_4 + \text{OH} = \text{CH}_2\text{O} + \text{C}_2\text{H}_3$	1.00E+12	0	0
147	$\text{C}_3\text{H}_4 + \text{OH} = \text{HCO} + \text{C}_2\text{H}_4$	1.00E+12	0	0
148	$\text{C}_3\text{H}_6 = \text{C}_3\text{H}_5 + \text{H}$	1.00E+13	0	78000
149	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	3.55E+04	2.7	1390
150	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	1.10E+13	0	3400
151	$\text{CH}_2\text{CO} + \text{O} = \text{HCO} + \text{HCO}$	1.00E+13	0	2400
152	$\text{CH}_2\text{CO} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$	2.82E+13	0	0
153	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	2.00E+16	0	60000
154	$\text{CH}_2\text{CO} + \text{O} = \text{HCCO} + \text{OH}$	5.01E+13	0	8000
155	$\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$	7.59E+12	0	3000
156	$\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$	7.59E+13	0	8000
157	$\text{HCCO} + \text{OH} = \text{HCO} + \text{HCO}$	1.00E+13	0	0
158	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	5.01E+13	0	0
159	$\text{HCCO} + \text{O} = \text{HCO} + \text{CO}$	3.39E+13	0	2000
160	$\text{C}_3\text{H}_6 = \text{C}_2\text{H}_3 + \text{CH}_3$	6.31E+15	0	85800
161	$\text{C}_3\text{H}_5 + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$	1.00E+13	0	0
162	$\text{C}_3\text{H}_5 + \text{CH}_3 = \text{C}_3\text{H}_4 + \text{CH}_4$	1.00E+12	0	0
163	$\text{C}_2\text{H}_6 + \text{O}_2 = \text{C}_2\text{H}_5 + \text{HO}_2$	1.00E+13	0	51000
164	$\text{C}_2\text{H}_6 + \text{HO}_2 = \text{C}_2\text{H}_5 + \text{H}_2\text{O}_2$	1.12E+13	0	19400
165	$\text{CH}_3 + \text{C}_2\text{H}_3 = \text{CH}_4 + \text{C}_2\text{H}_2$	1.00E+12	0	0
166	$\text{CH}_3 + \text{C}_2\text{H}_5 = \text{CH}_4 + \text{C}_2\text{H}_4$	7.94E+11	0	0
167	$\text{C}_2\text{H}_5 + \text{C}_3\text{H}_5 = \text{C}_3\text{H}_6 + \text{C}_2\text{H}_4$	1.26E+12	0	0
168	$\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 = \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4$	5.01E+11	0	0
169	$\text{CH}_3\text{OH} + \text{CH}_2\text{O} = \text{CH}_3\text{O} + \text{CH}_3\text{O}$	1.55E+12	0	79570
170	$\text{CH}_2\text{O} + \text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{HCO}$	6.03E+11	0	3300
171	$\text{CH}_4 + \text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{CH}_3$	2.00E+11	0	7000
172	$\text{C}_2\text{H}_6 + \text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{C}_2\text{H}_5$	3.02E+11	0	7000
173	$\text{C}_3\text{H}_8 + \text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{IC}_3\text{H}_7$	3.02E+11	0	7000
174	$\text{C}_3\text{H}_8 + \text{CH}_3\text{O} = \text{CH}_3\text{OH} + \text{NC}_3\text{H}_7$	3.02E+11	0	7000
175	$\text{C}_4\text{H}_{10} = \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$	2.00E+16	0	81300
176	$\text{C}_4\text{H}_{10} = \text{NC}_3\text{H}_7 + \text{CH}_3$	1.00E+17	0	85400
177	$\text{C}_4\text{H}_{10} + \text{O}_2 = \text{PC}_4\text{H}_9 + \text{HO}_2$	2.51E+13	0	49000
178	$\text{C}_4\text{H}_{10} + \text{O}_2 = \text{SC}_4\text{H}_9 + \text{HO}_2$	3.98E+13	0	47600
179	$\text{C}_4\text{H}_{10} + \text{H} = \text{PC}_4\text{H}_9 + \text{H}_2$	5.62E+07	2	7700
180	$\text{C}_4\text{H}_{10} + \text{H} = \text{SC}_4\text{H}_9 + \text{H}_2$	1.74E+07	2	5000
181	$\text{C}_4\text{H}_{10} + \text{OH} = \text{PC}_4\text{H}_9 + \text{H}_2\text{O}$	8.71E+09	1.1	1810
182	$\text{C}_4\text{H}_{10} + \text{OH} = \text{SC}_4\text{H}_9 + \text{H}_2\text{O}$	2.57E+09	1.3	700

183	C4H10+O=PC4H9+OH	1.12E+14	0	7850
184	C4H10+O=SC4H9+OH	5.62E+13	0	5200
185	C4H10+CH3=PC4H9+CH4	1.29E+12	0	11600
186	C4H10+CH3=SC4H9+CH4	7.94E+11	0	9500
187	C4H10+C2H3=PC4H9+C2H4	1.00E+12	0	18000
188	C4H10+C2H3=SC4H9+C2H4	7.94E+11	0	16800
189	C4H10+C2H5=PC4H9+C2H6	1.00E+11	0	13400
190	C4H10+C2H5=SC4H9+C2H6	1.00E+11	0	10400
191	C4H10+C3H5=PC4H9+C3H6	7.94E+11	0	20500
192	C4H10+C3H5=SC4H9+C3H6	3.16E+11	0	16400
193	C4H10+HO2=PC4H9+H2O2	1.12E+13	0	19400
194	C4H10+HO2=SC4H9+H2O2	6.76E+12	0	17000
195	C4H10+CH3O=PC4H9+CH3OH	3.02E+11	0	7000
196	C4H10+CH3O=SC4H9+CH3OH	6.03E+11	0	7000
197	PC4H9=C2H5+C2H4	2.51E+13	0	28800
198	PC4H9=PC4H8+H	1.26E+13	0	38600
199	PC4H9+O2=PC4H8+HO2	1.00E+12	0	2000
200	SC4H9=SC4H8+H	5.01E+12	0	37900
201	SC4H9=PC4H8+H	2.00E+13	0	40400
202	SC4H9=C3H6+CH3	2.00E+14	0	33200
203	SC4H9+O2=PC4H8+HO2	1.00E+12	0	4500
204	SC4H9+O2=SC4H8+HO2	2.00E+12	0	4250
205	PC4H8=C4H7+H	4.07E+18	-1	97350
206	SC4H8=C4H7+H	4.07E+18	-1	97350
207	PC4H8+H=C4H7+H2	5.01E+13	0	3900
208	SC4H8+H=C4H7+H2	5.01E+13	0	3800
209	PC4H8+OH=C4H7+H2O	1.41E+13	0	3060
210	SC4H8+OH=C4H7+H2O	2.29E+13	0	3060
211	PC4H8+CH3=C4H7+CH4	1.00E+11	0	7300
212	SC4H8+CH3=C4H7+CH4	1.00E+11	0	8200
213	PC4H8+O=C3H6+CH2O	5.01E+12	0	0
214	SC4H8+O=IC3H7+HCO	6.03E+12	0	0
215	SC4H8+O=C2H4+CH3CHO	1.00E+12	0	0
216	PC4H8+OH=NC3H7+CH2O	1.51E+12	0	0
217	SC4H8+OH=C2H5+CH3CHO	3.02E+12	0	0
218	C4H7=C4H6+H	1.20E+14	0	49300
219	C4H7=C2H4+C2H3	1.00E+11	0	37000
220	C4H7+O2=C4H6+HO2	1.00E+11	0	0
221	C4H7+H=C4H6+H2	3.16E+13	0	0
222	C4H7+C2H3=C4H6+C2H4	3.98E+12	0	0
223	C4H7+C2H5=C4H6+C2H6	3.98E+12	0	0
224	C4H7+C2H5=PC4H8+C2H4	5.01E+11	0	0
225	C4H7+C2H5=SC4H8+C2H4	5.01E+11	0	0
226	C4H7+C3H5=C4H6+C3H6	6.31E+12	0	0
227	C4H6=C2H3+C2H3	3.98E+19	-1	98150
228	C4H6+OH=C2H5+CH2CO	1.00E+12	0	0
229	C4H6+OH=C3H5+CH2O	1.00E+12	0	0
230	C4H6+OH=C2H3+CH3CHO	1.00E+12	0	0
231	C4H6+O=C2H4+CH2CO	1.00E+12	0	0
232	C4H6+O=C3H4+CH2O	1.00E+12	0	0

233	$C_2H_3 + C_2H_4 = C_4H_6 + H$	5.01E+11	0	7300
234	$C_5H_{10} = CH_3 + C_4H_7$	1.00E+19	-1	81550
235	$C_5H_{10} + O = PC_4H_8 + CH_2O$	8.51E+12	0	0
236	$C_5H_{10} + O = C_3H_6 + CH_3CHO$	8.51E+12	0	0
237	$C_5H_{10} + OH = PC_4H_9 + CH_2O$	1.00E+12	0	0
238	$C_5H_{10} + OH = NC_3H_7 + CH_3CHO$	1.00E+12	0	0
239	$C_2H_5 + H = CH_3 + CH_3$	3.16E+13	0	0
240	$CH_3OH + O_2 = CH_2OH + HO_2$	3.98E+13	0	50900
241	$C_2H_4 + O_2 = C_2H_3 + HO_2$	3.98E+13	0	61500
242	$C_2H_4 + CH_3 = C_2H_3 + CH_4$	1.00E+13	0	13000
243	$C_3H_6 + O_2 = C_3H_5 + HO_2$	1.00E+14	0	39000
244	$IC_8H_{18} \Rightarrow TC_4H_9 + IC_4H_9$	2.00E+16	0	78000
245	$IC_8H_{18} \Rightarrow IC_3H_7 + NEOC_5H_{11}$	2.00E+16	0	78000
246	$IC_8H_{18} + H \Rightarrow AC_8H_{17} + H_2$	8.51E+07	2	7700
247	$IC_8H_{18} + H \Rightarrow BC_8H_{17} + H_2$	8.91E+06	2	5000
248	$IC_8H_{18} + H \Rightarrow CC_8H_{17} + H_2$	1.26E+13	0	7300
249	$IC_8H_{18} + H \Rightarrow DC_8H_{17} + H_2$	5.62E+07	2	7700
250	$IC_8H_{18} + O \Rightarrow AC_8H_{17} + OH$	1.51E+14	0	7850
251	$IC_8H_{18} + O \Rightarrow BC_8H_{17} + OH$	2.82E+13	0	5200
252	$IC_8H_{18} + O \Rightarrow CC_8H_{17} + OH$	1.00E+13	0	3280
253	$IC_8H_{18} + O \Rightarrow DC_8H_{17} + OH$	1.00E+14	0	7850
254	$IC_8H_{18} + OH \Rightarrow AC_8H_{17} + H_2O$	1.29E+10	1.1	1810
255	$IC_8H_{18} + OH \Rightarrow BC_8H_{17} + H_2O$	1.29E+09	1.3	700
256	$IC_8H_{18} + OH \Rightarrow CC_8H_{17} + H_2O$	1.95E+12	0	440
257	$IC_8H_{18} + OH \Rightarrow DC_8H_{17} + H_2O$	8.71E+09	1.1	1810
258	$IC_8H_{18} + O_2 \Rightarrow AC_8H_{17} + HO_2$	3.72E+13	0	49000
259	$IC_8H_{18} + O_2 \Rightarrow BC_8H_{17} + HO_2$	2.00E+13	0	48000
260	$IC_8H_{18} + O_2 \Rightarrow CC_8H_{17} + HO_2$	2.00E+12	0	46000
261	$IC_8H_{18} + O_2 \Rightarrow DC_8H_{17} + HO_2$	2.51E+13	0	49000
262	$IC_8H_{18} + HO_2 \Rightarrow AC_8H_{17} + H_2O_2$	1.70E+13	0	19400
263	$IC_8H_{18} + HO_2 \Rightarrow BC_8H_{17} + H_2O_2$	3.39E+12	0	17000
264	$IC_8H_{18} + HO_2 \Rightarrow CC_8H_{17} + H_2O_2$	3.02E+12	0	14400
265	$IC_8H_{18} + HO_2 \Rightarrow DC_8H_{17} + H_2O_2$	1.12E+13	0	19400
266	$IC_8H_{18} + CH_3 \Rightarrow AC_8H_{17} + CH_4$	1.17E+13	0	11600
267	$IC_8H_{18} + CH_3 \Rightarrow BC_8H_{17} + CH_4$	2.40E+12	0	9500
268	$IC_8H_{18} + CH_3 \Rightarrow CC_8H_{17} + CH_4$	2.00E+11	0	7900
269	$IC_8H_{18} + CH_3 \Rightarrow DC_8H_{17} + CH_4$	7.76E+12	0	11600
270	$AC_8H_{17} \Rightarrow AC_7H_{14} + CH_3$	1.00E+10	0	26000
271	$AC_8H_{17} \Rightarrow IC_4H_8 + IC_4H_9$	1.29E+13	0	29500
272	$BC_8H_{17} \Rightarrow CC_7H_{14} + CH_3$	1.00E+13	0	26000
273	$CC_8H_{17} \Rightarrow IC_4H_8 + IC_4H_9$	5.01E+12	0	29000
274	$CC_8H_{17} \Rightarrow IC_8H_{16} + H$	1.00E+13	0	38000
275	$DC_8H_{17} \Rightarrow AC_7H_{14} + CH_3$	1.26E+13	0	32800
276	$DC_8H_{17} \Rightarrow C_3H_6 + NEOC_5H_{11}$	1.29E+13	0	29500
277	$DC_8H_{17} \Rightarrow IC_8H_{16} + H$	3.31E+13	0	36000
278	$AC_8H_{17} + O_2 \Rightarrow IC_8H_{16} + HO_2$	1.51E+10	0	10000
279	$BC_8H_{17} + O_2 \Rightarrow IC_8H_{16} + HO_2$	1.00E+10	0	10000
280	$CC_8H_{17} + O_2 \Rightarrow IC_8H_{16} + HO_2$	1.00E+10	0	10000
281	$DC_8H_{17} + O_2 \Rightarrow IC_8H_{16} + HO_2$	1.00E+10	0	10000
282	$IC_8H_{16} + O \Rightarrow IC_4H_8 + IC_4H_7 + OH$	2.82E+13	0	5200 # no reverse reacton

283	IC8H16+OH=>IC4H8+IC4H7+H2O	1.29E+09	1.3	700 # no reverse reacton
284	IC8H16+O=>IC7H15+HCO	1.00E+11	0	0
285	IC7H15=>IC4H8+IC3H7	2.51E+13	0	28000
286	IC7H15=>AC7H14+H	3.98E+13	0	40000
287	IC7H15=>TC4H9+C3H6	2.51E+13	0	28200
288	IC7H15=>CC7H14+H	3.98E+13	0	40400
289	AC7H14+H=>IC7H13+H2	2.82E+13	0	4000
290	CC7H14+H=>IC7H13+H2	5.62E+13	0	4000
291	AC7H14+O=>IC7H13+OH	5.13E+05	2.6	-1100
292	CC7H14+O=>IC7H13+OH	5.13E+05	2.6	-1100
293	AC7H14+OH=>IC7H13+H2O	1.35E+14	0	3100
294	CC7H14+OH=>IC7H13+H2O	1.35E+14	0	3100
295	AC7H14+O=>IC6H13+HCO	2.00E+11	0	0
296	CC7H14+O=>NEOC5H11+CH3CO	1.00E+11	0	0
297	AC7H14+OH=>IC6H13+CH2O	1.00E+11	0	0
298	CC7H14+OH=>NEOC5H11+CH3CHO	1.00E+11	0	0
299	IC8H16=>IC4H7+TC4H9	2.51E+16	0	71000
300	IC8H16=>C6H11+C2H5	2.51E+16	0	71000
301	AC7H14=>IC4H7+IC3H7	5.01E+16	0	71000
302	AC7H14=>TC4H9+C3H5	2.51E+16	0	71000
303	CC7H14=>C6H11+CH3	2.51E+16	0	71000
304	IC8H16+OH=>IC7H15+CH2O	1.00E+11	0	0
305	IC7H13=>IC4H8+C3H5	5.01E+13	0	30000
306	IC7H13=>IC4H7+C3H6	5.01E+13	0	30000
307	IC7H13=>C6H10+CH3	2.00E+14	0	32800
308	IC6H13=>IC3H7+C3H6	2.51E+13	0	28200
309	IC6H13=>TC4H9+C2H4	2.51E+13	0	28800
310	IC6H13=>IC4H9+C2H4	2.51E+13	0	28800
311	C6H11=>C3H5+C3H6	2.51E+13	0	30000
312	C6H11=>C6H10+H	1.26E+14	0	49300
313	C6H11+O2=>C6H10+HO2	1.00E+11	0	0
314	C6H10=>C3H5+C3H5	2.51E+14	0	5940
315	NEOC5H11=>IC4H8+CH3	1.00E+11	0	26000
316	IC4H10=>IC3H7+CH3	2.00E+17	0	83400
317	IC4H10=>TC4H9+H	1.00E+15	0	83400
318	IC4H10=>IC4H9+H	1.00E+15	0	83400
319	IC4H10+H=>TC4H9+H2	1.26E+14	0	7300
320	IC4H10+H=>IC4H9+H2	1.00E+14	0	8400
321	IC4H10+OH=>TC4H9+H2O	1.95E+12	0	440
322	IC4H10+OH=>IC4H9+H2O	4.90E+03	3	-700
323	IC4H10+O=>TC4H9+OH	1.10E+13	0	3280
324	IC4H10+O=>IC4H9+OH	3.16E+13	0	5760
325	IC4H10+CH3=>TC4H9+CH4	1.00E+11	0	7900
326	IC4H10+CH3=>IC4H9+CH4	8.91E+11	0	10340
327	IC4H10+HO2=>TC4H9+H2O2	3.16E+12	0	14400
328	IC4H10+HO2=>IC4H9+H2O2	1.70E+13	0	19400
329	IC4H10+O2=>TC4H9+HO2	2.00E+12	0	46000
330	IC4H10+O2=>IC4H9+HO2	3.72E+13	0	49000
331	IC4H10+C2H5=>TC4H9+C2H6	1.00E+11	0	7900
332	IC4H10+C2H5=>IC4H9+C2H6	1.51E+12	0	10400

333	IC4H9=>C3H6+CH3	1.00E+14	0	32800
334	IC4H9=>IC4H8+H	3.31E+14	0	36000
335	TC4H9=>IC4H8+H	1.00E+15	0	43600
336	TC4H9=>C3H6+CH3	1.58E+15	0	46300
337	TC4H9+O2=>IC4H8+HO2	1.00E+12	0	5000
338	IC4H9+O2=>IC4H8+HO2	1.00E+12	0	5000
339	IC4H8=>C3H5+CH3	1.51E+19	-1	73400
340	IC4H8=>IC4H7+H	1.00E+17	0	88000
341	IC4H8+H=>IC4H7+H2	1.00E+13	0	3800
342	IC4H8+O=>IC4H7+OH	2.51E+05	2.6	-1130
343	IC4H8+OH=>IC4H7+H2O	1.91E+12	0	1230
344	IC4H8+O=>IC3H7+HCO	7.24E+05	2.3	-1050
345	IC4H8+OH=>IC3H7+CH2O	1.51E+12	0	0
346	IC4H8+CH3=>IC4H7+CH4	6.03E+11	0	8900
347	IC4H7=>C3H4+CH3	1.00E+13	0	32600
348	C2H3+O2=>CH2O+HCO	3.98E+12	0	-250
349	AC8H17=>DC8H17	6.03E+11	0	14100
350	AC8H17=>CC8H17	1.00E+11	0	16100
351	TC4H9+IC4H9=>IC8H18	1.00E+12	0	0
352	IC3H7+NEOC5H11=>IC8H18	1.00E+12	0	0
353	AC8H17+H2=>IC8H18+H	1.00E+12	0	30000
354	BC8H17+H2=>IC8H18+H	1.00E+12	0	30000
355	CC8H17+H2=>IC8H18+H	1.00E+12	0	30000
356	DC8H17+H2=>IC8H18+H	1.00E+12	0	30000
357	AC8H17+OH=>IC8H18+O	1.00E+12	0	30000
358	BC8H17+OH=>IC8H18+O	1.00E+12	0	30000
359	CC8H17+OH=>IC8H18+O	1.00E+12	0	30000
360	DC8H17+OH=>IC8H18+O	1.00E+12	0	30000
361	AC8H17+H2O=>IC8H18+OH	1.00E+12	0	30000
362	BC8H17+H2O=>IC8H18+OH	1.00E+12	0	30000
363	CC8H17+H2O=>IC8H18+OH	1.00E+12	0	30000
364	DC8H17+H2O=>IC8H18+OH	1.00E+12	0	30000
365	AC8H17+HO2=>IC8H18+O2	2.00E+12	0	30000
366	BC8H17+HO2=>IC8H18+O2	5.01E+12	0	30000
367	CC8H17+HO2=>IC8H18+O2	2.00E+12	0	30000
368	DC8H17+HO2=>IC8H18+O2	2.00E+12	0	30000
369	AC8H17+H2O2=>IC8H18+HO2	1.00E+12	0	30000
370	BC8H17+H2O2=>IC8H18+HO2	1.00E+12	0	30000
371	CC8H17+H2O2=>IC8H18+HO2	1.00E+12	0	30000
372	DC8H17+H2O2=>IC8H18+HO2	1.00E+12	0	30000
373	AC8H17+CH4=>IC8H18+CH3	1.00E+12	0	30000
374	BC8H17+CH4=>IC8H18+CH3	1.00E+12	0	30000
375	CC8H17+CH4=>IC8H18+CH3	1.00E+12	0	30000
376	DC8H17+CH4=>IC8H18+CH3	1.00E+12	0	30000
377	AC7H14+CH3=>AC8H17	6.31E+09	0	7000
378	IC4H8+IC4H9=>AC8H17	1.00E+11	0	8000
379	CC7H14+CH3=>BC8H17	6.31E+10	0	7000
380	IC4H8+IC4H9=>CC8H17	6.03E+10	0	7000
381	IC8H16+H=>CC8H17	1.00E+10	0	1500
382	AC7H14+CH3=>DC8H17	1.58E+10	0	7000

383	C3H6+NEOC5H11=>DC8H17	1.00E+10	0	7000
384	IC8H16+H=>DC8H17	1.00E+09	0	1200
385	IC8H16+HO2=>AC8H17+O2	2.00E+11	0	20000
386	IC8H16+HO2=>BC8H17+O2	2.00E+11	0	20000
387	IC8H16+HO2=>CC8H17+O2	2.00E+11	0	20000
388	IC8H16+HO2=>DC8H17+O2	2.00E+11	0	20500
389	IC7H15+HCO=>IC8H16+O	1.00E+10	0	30000
390	IC4H8+IC3H7=>IC7H15	3.98E+10	0	6900
391	AC7H14+H=>IC7H15	1.58E+13	0	1200
392	TC4H9+C3H6=>IC7H15	1.20E+11	0	8000
393	CC7H14+H=>IC7H15	1.58E+13	0	1200
394	IC7H13+H2=>AC7H14+H	1.00E+12	0	14000
395	IC7H13+H2=>CC7H14+H	2.00E+12	0	14000
396	IC7H13+OH=>AC7H14+O	1.41E+12	0	30000
397	IC7H13+OH=>CC7H14+O	1.41E+12	0	30000
398	IC7H13+H2O=>AC7H14+OH	1.00E+13	0	27000
399	IC7H13+H2O=>CC7H14+OH	1.00E+13	0	27000
400	IC6H13+HCO=>AC7H14+O	1.00E+12	0	30000
401	NEOC5H11+CH3CO=>CC7H14+O	1.00E+12	0	30000
402	IC6H13+CH2O=>AC7H14+OH	5.01E+12	0	27000
403	NEOC5H11+CH3CHO=>CC7H14+OH	1.00E+12	0	27000
404	IC4H7+TC4H9=>IC8H16	1.00E+13	0	0
405	C6H11+C2H5=>IC8H16	1.00E+13	0	0
406	IC4H7+IC3H7=>AC7H14	1.00E+13	0	0
407	TC4H9+C3H5=>AC7H14	1.00E+13	0	0
408	C6H11+CH3=>CC7H14	1.00E+13	0	0
409	IC7H15+CH2O=>IC8H16+OH	1.00E+12	0	0
410	IC4H8+C3H5=>IC7H13	1.26E+11	0	17000
411	IC4H7+C3H6=>IC7H13	1.26E+11	0	17000
412	C6H10+CH3=>IC7H13	6.46E+11	0	9100
413	IC3H7+C3H6=>IC6H13	3.98E+10	0	6900
414	TC4H9+C2H4=>IC6H13	3.98E+10	0	6900
415	IC4H9+C2H4=>IC6H13	3.98E+10	0	6900
416	C3H5+C3H6=>C6H11	6.31E+10	0	17000
417	C6H10+H=>C6H11	7.94E+12	0	1200
418	C6H10+HO2=>C6H11+O2	1.00E+11	0	17000
419	C3H5+C3H5=>C6H10	6.31E+12	0	0
420	IC4H8+CH3=>NEOC5H11	1.00E+11	0	7200
421	IC3H7+CH3=>IC4H10	1.58E+13	0	0
422	TC4H9+H=>IC4H10	1.00E+11	0	0
423	IC4H9+H=>IC4H10	1.00E+11	0	0
424	TC4H9+H2=>IC4H10+H	1.00E+12	0	16000
425	IC4H9+H2=>IC4H10+H	3.16E+12	0	15700
426	TC4H9+H2O=>IC4H10+OH	3.98E+12	0	22000
427	IC4H9+H2O=>IC4H10+OH	8.91E+03	3	20800
428	TC4H9+OH=>IC4H10+O	2.00E+12	0	9600
429	IC4H9+OH=>IC4H10+O	2.00E+12	0	9600
430	TC4H9+CH4=>IC4H10+CH3	2.00E+11	0	21000
431	IC4H9+CH4=>IC4H10+CH3	2.00E+11	0	15000
432	TC4H9+H2O2=>IC4H10+HO2	3.16E+12	0	7400

433	IC4H9+H2O2=>IC4H10+HO2	3.16E+12	0	7400
434	TC4H9+HO2=>IC4H10+O2	2.00E+12	0	2000
435	IC4H9+HO2=>IC4H10+O2	2.00E+12	0	2000
436	TC4H9+C2H6=>IC4H10+C2H5	3.02E+11	0	21000
437	IC4H9+C2H6=>IC4H10+C2H5	3.16E+11	0	12300
438	C3H6+CH3=>IC4H9	3.16E+11	0	9100
439	IC4H8+H=>IC4H9	1.00E+13	0	1200
440	IC4H8+H=>TC4H9	3.16E+13	0	1500
441	C3H6+CH3=>TC4H9	1.00E+11	0	7000
442	IC4H8+HO2=>TC4H9+O2	2.00E+11	0	17500
443	IC4H8+HO2=>IC4H9+O2	2.00E+11	0	17500
444	C3H5+CH3=>IC4H8	3.98E+12	0	0
445	IC4H7+H=>IC4H8	2.00E+13	0	0
446	IC4H7+H2=>IC4H8+H	3.02E+13	0	25000
447	IC4H7+OH=>IC4H8+O	7.08E+11	0	29900
448	IC4H7+H2O=>IC4H8+OH	4.79E+12	0	26470
449	IC3H7+HCO=>IC4H8+O	2.00E+05	2.3	80280
450	IC3H7+CH2O=>IC4H8+OH	1.95E+13	0	13230
451	IC4H7+CH4=>IC4H8+CH3	6.03E+11	0	29900
452	C3H4+CH3=>IC4H7	2.00E+11	0	7500
453	CH2O+HCO=>C2H3+O2	3.98E+12	0	86300
454	DC8H17=>AC8H17	8.91E+11	0	14100
455	CC8H17=>AC8H17	8.91E+11	0	21100

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.5 Toluene chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T**b exp(-E/RT))			Source/Modification
		A	b	E	
1	C6H6+O2=>C6H5+HO2	6.30E+13	0	60000	#Reactions 1 - 142 : Ref[20]
2	C6H5OH+O=>C6H5O+OH	2.81E+13	0	7352	#Reactions 143 - 262 : Ref[20]
3	C2H3+C6H5OH=>C2H4+C6H5O	6.00E+12	0	0	#(Reactions 72 - 142 are the
4	C4H5+C6H5OH=>C4H6+C6H5O	6.00E+12	0	0	# reverse reactions for
5	C6H5+C6H5OH=>C6H6+C6H5O	4.91E+12	0	4400	# reactions 1 - 71)
6	C5H5+O=>C4H5+CO	1.00E+14	0	0	
7	C5H6+O2=>C5H5+HO2	2.00E+13	0	25000	
8	C5H6+HO2=>C5H5+H2O2	1.99E+12	0	11660	
9	C5H6+OH=>C5H5+H2O	3.43E+09	1.2	-447	
10	C5H6+H=>C5H5+H2	2.19E+08	1.8	3000	
11	C5H6+O=>C5H5+OH	1.81E+13	0	3080	
12	C5H6+C2H3=>C5H5+C2H4	6.00E+12	0	0	
13	C5H6+C4H5=>C5H5+C4H6	6.00E+12	0	0	
14	C5H4OH=>C5H4O+H	2.10E+13	0	48000	
15	C5H4O=>CO+C2H2+C2H2	1.00E+15	0	78000	
16	C4H5+M=>C4H4+H+M	2.98E+33	-5	44320	
17	C4H5+O2=>C4H4+HO2	1.20E+11	0	0	
18	C2H3+O2=>C2H2+HO2	1.20E+11	0	0	
19	C2H2+O=>HCCO+H	5.80E+06	2.1	1562	
20	CH2+O2=>H+OH+CO	6.02E+11	0	0	
21	CH2+O2=>CO+H2O	2.41E+11	0	0	
22	HCCO+O2=>OH+CO+CO	1.46E+12	0	2500	
23	H2O2+O=>OH+HO2	9.55E+06	2	3970	
24	C6H5CH2+H=>C6H5CH3	1.80E+14	0	0	
25	C6H5CH3=>C6H5+CH3	1.40E+16	0	99800	
26	C6H5CH3+O2=>C6H5CH2+HO2	3.00E+14	0	41400	
27	C6H5CH3+OH=>C6H5CH2+H2O	1.26E+13	0	2583	
28	C6H5CH3+H=>C6H5CH2+H2	1.20E+14	0	8235	
29	C6H5CH3+H=>C6H6+CH3	1.20E+13	0	5148	
30	C6H5CH3+O=>OC6H4CH3+H	1.63E+13	0	3418	
31	CH3+C6H5CH3=>CH4+C6H5CH2	3.16E+11	0	9500	
32	C6H5+C6H5CH3=>C6H6+C6H5CH2	2.10E+12	0	4400	
33	C6H5OH+C6H5CH2=>C6H5O+C6H5CH3	1.05E+11	0	9500	
34	CRESOLS+C6H5CH2=>OC6H4CH3+C6H5CH3	1.05E+11	0	9500	
35	C6H5CH2+O=>C6H5CHO+H	2.50E+14	0	0	
36	C6H5CH2+O=>C6H5+CH2O	8.00E+13	0	0	
37	C6H5CH2+HO2=>C6H5CHO+H+OH	2.50E+14	0	0	
38	C6H5CH2+HO2=>C6H5+CH2O+OH	8.00E+13	0	0	
39	C6H5CH2+C6H5CH2=>BIBENZYL	2.51E+11	0.4	0	
40	C6H5C2H5=>C6H5CH2+CH3	2.00E+15	0	72700	
41	C6H5CH2+OH=>BENZOL	6.00E+13	0	0	
42	BENZOL+O2=>C6H5CHO+HO2+H	2.00E+14	0	41400	
43	BENZOL+OH=>C6H5CHO+H2O+H	8.43E+12	0	2583	

44	BENZOL+H=>C6H5CHO+H2+H	8.00E+13	0	8235
45	BENZOL+H=>C6H6+CH2OH	1.20E+13	0	5148
46	BENZOL+C6H5CH2=>C6H5CHO+C6H5CH3+H	2.11E+11	0	9500
47	BENZOL+C6H5=>C6H5CHO+C6H6+H	1.40E+12	0	4400
48	C6H5CHO+O2=>C6H5CO+HO2	1.02E+13	0	38950
49	C6H5CHO+OH=>C6H5CO+H2O	1.71E+09	1.2	-447
50	C6H5CHO+H=>C6H5CO+H2	5.00E+13	0	4928
51	C6H5CHO+H=>C6H6+HCO	1.20E+13	0	5148
52	C6H5CHO+O=>C6H5CO+OH	9.04E+12	0	3080
53	C6H5CH2+C6H5CHO=>C6H5CH3+C6H5CO	2.77E+03	2.8	5773
54	CH3+C6H5CHO=>CH4+C6H5CO	2.77E+03	2.8	5773
55	C6H5+C6H5CHO=>C6H6+C6H5CO	7.01E+11	0	4400
56	C6H5C2H5+OH=>C6H5C2H3+H2O+H	8.43E+12	0	2583
57	C6H5C2H5+H=>C6H5C2H3+H2+H	8.00E+13	0	8235
58	C6H5C2H5+O2=>C6H5C2H3+HO2+H	2.00E+14	0	41400
59	OC6H4CH3+H=>CRESOLS	2.50E+14	0	0
60	OC6H4CH3=>C6H6+H+CO	2.51E+11	0	43900
61	CRESOLS+OH=>OC6H4CH3+H2O	6.00E+12	0	0
62	CRESOLS+H=>OC6H4CH3+H2	1.15E+14	0	12400
63	CRESOLS+H=>C6H5CH3+OH	2.21E+13	0	7910
64	CRESOLS+H=>C6H5OH+CH3	1.20E+13	0	5148
65	C6H5CO=>C6H5+CO	3.98E+14	0	29400
66	CH4=>CH3+H	6.14E+14	0	103800
67	CH4+HO2=>CH3+H2O2	1.81E+11	0	18580
68	CH3+OH=>CH2OH+H	1.09E+11	0.4	-708
69	CH2OH+O2=>CH2O+HO2	2.41E+14	0	5000
70	CH2OH+M=>CH2O+H+M	1.67E+24	-2.5	34190
71	CH2O+HO2=>HCO+H2O2	1.99E+12	0	11660
72	C6H5+HO2=>C6H6+O2	1.27E+09	0.8	-2740
73	C6H5O+OH=>C6H5OH+O	1.22E+11	0.5	22782
74	C2H4+C6H5O=>C2H3+C6H5OH	6.79E+14	-0.1	20600
75	C4H6+C6H5O=>C4H5+C6H5OH	4.48E+14	-0.1	20430
76	C6H6+C6H5O=>C6H5+C6H5OH	1.51E+16	-0.6	29850
77	C4H5+CO=>C5H5+O	3.08E+04	1.8	57320
78	HO2+C5H5=>C5H6+O2	1.64E+14	-0.7	-440
79	C5H5+H2O2=>C5H6+HO2	2.54E+15	-1.1	24980
80	C5H5+H2O=>C5H6+OH	6.44E+10	0.7	44213
81	C5H5+H2=>C5H6+H	1.88E+08	1.5	32030
82	C5H5+OH=>C5H6+O	1.05E+13	-0.3	30360
83	C5H5+C2H4=>C2H3+C5H6	9.02E+16	-0.9	32440
84	C5H5+C4H6=>C5H6+C4H5	5.96E+16	-1	32280
85	C5H4O+H=>C5H4OH	4.03E+12	0.4	4860
86	CO+C2H2+C2H2=>C5H4O	7.14E-05	3.6	-4360
87	C4H4+H+M=>C4H5+M	1.48E+31	-4.5	-1470
88	C4H4+HO2=>C4H5+O2	1.81E+09	0.4	3350
89	C2H2+HO2=>C2H3+O2	8.90E+11	-0.1	8995
90	HCCO+H=>C2H2+O	4.34E+06	1.9	20422
91	H+OH+CO=>CH2+O2	1.39E+10	0.4	57090
92	CO+H2O=>CH2+O2	3.87E+10	0.5	176300
93	OH+CO+CO=>HCCO+O2	4.02E+04	2	87150

94	OH+HO2=>H2O2+O	4.33E+03	2.8	17920
95	C6H5CH3=>C6H5CH2+H	8.79E+14	0.4	90840
96	C6H5+CH3=>C6H5CH3	1.17E+06	2	-3700
97	C6H5CH2+HO2=>C6H5CH3+O2	1.86E+14	-0.5	-300
98	C6H5CH2+H2O=>C6H5CH3+OH	6.95E+12	0	33300
99	C6H5CH2+H2=>C6H5CH3+H	1.31E+12	0.3	23070
100	C6H6+CH3=>C6H5CH3+H	1.20E+12	0	15970
101	OC6H4CH3+H=>C6H5CH3+O	7.49E+17	-1	19060
102	CH4+C6H5CH2=>CH3+C6H5CH3	3.10E+13	-0.4	27000
103	C6H6+C6H5CH2=>C6H5+C6H5CH3	4.09E+16	-1.1	27910
104	C6H5O+C6H5CH3=>C6H5OH+C6H5CH2	1.04E+10	0.6	13912
105	OC6H4CH3+C6H5CH3=>CRESOLS+C6H5CH2	8.47E+10	0.6	13650
106	C6H5CHO+H=>C6H5CH2+O	5.59E+14	0.2	66600
107	C6H5+CH2O=>C6H5CH2+O	8.79E+06	2	58100
108	C6H5CHO+H+OH=>C6H5CH2+HO2	2.72E+11	0.8	104
109	C6H5+CH2O+OH=>C6H5CH2+HO2	4.28E+03	2.5	-8399
110	BIBENZYL=>C6H5CH2+C6H5CH2	1.38E+18	-0.5	67170
111	C6H5CH2+CH3=>C6H5C2H5	9.05E+06	1.5	-7160
112	BENZOL=>C6H5CH2+OH	3.77E+18	-0.6	84820
113	C6H5CHO+HO2+H=>BENZOL+O2	1.01E+11	0.5	-29540
114	C6H5CHO+H2O+H=>BENZOL+OH	9.73E+09	0.7	1748
115	C6H5CHO+H2+H=>BENZOL+H	4.22E+09	0.9	-8225
116	C6H6+CH2OH=>BENZOL+H	1.95E+08	1	16640
117	C6H5CHO+C6H5CH3+H=>BENZOL+C6H5CH2	2.72E+08	0.8	-22210
118	C6H5CHO+C6H6+H=>BENZOL+C6H5	3.51E+13	-0.3	-3800
119	C6H5CO+HO2=>C6H5CHO+O2	3.39E+10	0.2	900
120	C6H5CO+H2O=>C6H5CHO+OH	1.25E+07	1.6	31080
121	C6H5CO+H2=>C6H5CHO+H	1.67E+10	0.6	20840
122	C6H6+HCO=>C6H5CHO+H	1.08E+08	1.2	17550
123	C6H5CO+OH=>C6H5CHO+O	2.04E+09	0.6	17230
124	C6H5CO+C6H5CH3=>C6H5CH2+C6H5CHO	2.26E+01	3.4	6437
125	CH4+C6H5CO=>CH3+C6H5CHO	2.22E+03	2.9	23930
126	C6H6+C6H5CO=>C6H5+C6H5CHO	1.11E+14	-0.5	28570
127	C6H5C2H3+H2O+H=>C6H5C2H5+OH	2.21E+09	0.8	-11850
128	C6H5C2H3+H2+H=>C6H5C2H5+H	9.57E+08	1	-21820
129	C6H5C2H3+HO2+H=>C6H5C2H5+O2	2.28E+10	0.6	-43140
130	CRESOLS=>OC6H4CH3+H	1.51E+15	-0.2	86690
131	C6H6+H+CO=>OC6H4CH3	1.55E+00	2.4	760
132	OC6H4CH3+H2O=>CRESOLS+OH	6.88E+12	0.4	32550
133	OC6H4CH3+H2=>CRESOLS+H	6.03E+12	0.6	29330
134	C6H5CH3+OH=>CRESOLS+H	1.70E+07	1.5	7438
135	C6H5OH+CH3=>CRESOLS+H	7.27E+05	1.6	13090
136	C6H5+CO=>C6H5CO	1.45E+06	2.1	1970
137	CH3+H=>CH4	5.35E+12	0	-1187
138	CH3+H2O2=>CH4+HO2	2.43E+12	-0.7	1003
139	CH2OH+H=>CH3+OH	9.48E+14	-0.6	-3772
140	CH2O+HO2=>CH2OH+O2	7.85E+12	0.6	25860
141	CH2O+H+M=>CH2OH+M	1.27E+23	-2	5990
142	HCO+H2O2=>CH2O+HO2	7.96E+12	-0.4	8659
143	C6H6+O2=C6H5O+OH	4.00E+13	0	34000

144	C6H6+C6H5=BIPHENYL+H	4.00E+11	0	4000
145	C6H6=C6H5+H	5.00E+15	0	108000
146	C6H6+H=C6H5+H2	2.50E+14	0	16000
147	C6H6+O=C6H5O+H	2.78E+13	0	4910
148	C6H6+OH=C6H5+H2O	2.13E+13	0	4580
149	C4H3+M=C4H2+H+M	1.00E+16	0	60000
150	C6H5O=C5H5+CO	2.51E+11	0	43900
151	C6H5+O2=C6H5O+O	2.10E+12	0	7470
152	C6H5+HO2=C6H5O+OH	5.00E+13	0	1000
153	C6H5=C4H3+C2H2	4.50E+13	0	72530
154	C6H5OH=C6H5O+H	2.00E+16	0	88000
155	C6H5OH+H=C6H6+OH	2.20E+13	0	7910
156	C6H5OH+H=C6H5O+H2	1.15E+14	0	12400
157	C6H5OH+C5H5=C6H5O+C5H6	2.67E+14	0	25200
158	C5H6=C5H5+H	8.13E+24	-3	78682
159	C5H6+O2=C5H5O+OH	1.00E+13	0	20712
160	C6H5OH+OH=C6H5O+H2O	3.00E+13	0	0
161	C6H5OH+HO2=C6H5O+H2O2	3.00E+13	0	15000
162	C5H5O=C4H5+CO	3.00E+16	0	15000
163	C5H5+O=C5H5O	1.00E+13	0	0
164	C5H5+OH=C5H4OH+H	1.00E+13	0	0
165	C5H4OH=C4H4+HCO	1.00E+15	0	0
166	C5H5+HO2=C5H5O+OH	2.00E+13	0	0
167	C6H5+C6H5=BIPHENYL	3.10E+12	0	0
168	C4H5=C2H3+C2H2	1.40E+13	0	32900
169	C4H2+O=C2HO+C2H	1.00E+13	0	0
170	C4H2+O=CO+C3H2	1.20E+12	0	0
171	C4H2+OH=HCO+C3H2	3.00E+13	0	0
172	C2H4+M=C2H2+H2	9.33E+16	0	77200
173	C2H4+OH=C2H3+H2O	4.79E+12	0	1230
174	C2H4+O=CH3+HCO	3.31E+12	0	1130
175	C2H4+O=CH2O+CH2	2.51E+13	0	5000
176	C2H4+OH=CH3+CH2O	2.00E+12	0	960
177	C2H3+M=C2H2+H+M	3.00E+15	0	32000
178	C2H3+O2=CH2O+HCO	3.98E+12	0	-250
179	C2H3+H=C2H2+H2	6.00E+12	0	0
180	C2H3+OH=C2H2+H2O	5.00E+12	0	0
181	C2H3+CH2=C2H2+CH3	3.00E+13	0	0
182	C2H3+C2H=C2H2+C2H2	3.00E+13	0	0
183	C2H3+O=C2H2O+H	3.30E+13	0	0
184	CH2+CH2=C2H2+H2	4.00E+13	0	0
185	CH2+CH2=C2H3+H	5.00E+12	0	0
186	CH2+OH=CH+H2O	2.51E+11	0.7	25700
187	CH2+O=CH+OH	2.00E+11	0.7	25000
188	CH2+O2=CO2+H+H	1.59E+12	0	1000
189	C2H2+M=C2H+H	4.17E+16	0	107000
190	C2H2+C2H2=C4H3+H	2.00E+12	0	45900
191	C2H2+O=CH2+CO	1.60E+14	0	9890
192	C2H2+O=C2HO+H	4.00E+14	0	10660
193	C2H2+OH=C2H+H2O	6.31E+12	0	7000

194	$\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H}_2\text{O} + \text{H}$	3.20E+11	0	200
195	$\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{C}_4\text{H}_2 + \text{H}$	3.00E+13	0	0
196	$\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$	1.20E+13	0	6600
197	$\text{C}_3\text{H}_4 + \text{M} = \text{C}_3\text{H}_3 + \text{H} + \text{M}$	2.00E+17	0	65000
198	$\text{C}_2\text{H}_2\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{HCO}$	2.80E+13	0	0
199	$\text{C}_2\text{H}_2\text{O} + \text{OH} = \text{C}_2\text{HO} + \text{H}_2\text{O}$	7.50E+12	0	3000
200	$\text{C}_2\text{H}_2\text{O} + \text{H} = \text{CH}_3 + \text{CO}$	1.13E+13	0	3428
201	$\text{C}_2\text{H}_2\text{O} + \text{H} = \text{C}_2\text{HO} + \text{H}_2$	7.50E+13	0	8000
202	$\text{C}_2\text{H}_2\text{O} + \text{O} = \text{C}_2\text{HO} + \text{OH}$	5.00E+13	0	8000
203	$\text{C}_2\text{H}_2\text{O} + \text{O} = \text{CH}_2\text{O} + \text{CO}$	2.00E+13	0	0
204	$\text{C}_2\text{H}_2\text{O} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	2.00E+16	0	60000
205	$\text{C}_2\text{HO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46E+12	0	2500
206	$\text{C}_2\text{HO} + \text{O} = \text{CO} + \text{CO} + \text{H}$	1.20E+12	0	0
207	$\text{C}_2\text{HO} + \text{OH} = \text{HCO} + \text{HCO}$	1.00E+13	0	0
208	$\text{C}_2\text{HO} + \text{H} = \text{CH}_2 + \text{CO}$	5.00E+13	0	0
209	$\text{C}_2\text{HO} + \text{CH}_2 = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0
210	$\text{C}_2\text{HO} + \text{CH}_2 = \text{CH}_2\text{O} + \text{C}_2\text{H}$	1.00E+13	0	2000
211	$\text{C}_2\text{HO} + \text{C}_2\text{HO} = \text{C}_2\text{H}_2 + \text{CO} + \text{CO}$	1.00E+13	0	0
212	$\text{C}_2\text{H} + \text{OH} = \text{C}_2\text{HO} + \text{H}$	2.00E+13	0	0
213	$\text{C}_2\text{H} + \text{O}_2 = \text{C}_2\text{HO} + \text{O}$	5.00E+13	0	1500
214	$\text{C}_2\text{H} + \text{O} = \text{CO} + \text{CH}$	5.00E+13	0	0
215	$\text{CH}_4 + \text{M} = \text{CH}_3 + \text{H} + \text{M}$	2.00E+17	0	88000
216	$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	7.94E+13	0	56000
217	$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$	1.26E+14	0	11900
218	$\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$	2.50E+13	0	5010
219	$\text{CH}_4 + \text{O} = \text{CH}_3 + \text{OH}$	1.90E+14	0	11720
220	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$	4.79E+13	0	29000
221	$\text{CH}_3 + \text{OH} = \text{CH}_3\text{O} + \text{H}$	6.30E+12	0	0
222	$\text{CH}_3\text{O} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$	5.00E+13	0	21000
223	$\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	1.00E+12	0	6000
224	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	2.00E+13	0	0
225	$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}_2$	1.00E+16	0	32000
226	$\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	1.29E+14	0	2000
227	$\text{CH}_3 + \text{CH}_2\text{O} = \text{CH}_4 + \text{HCO}$	1.00E+10	0.5	6000
228	$\text{CH}_3 + \text{HCO} = \text{CH}_4 + \text{CO}$	3.00E+11	0.5	0
229	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	2.00E+13	0	0
230	$\text{CH}_2\text{O} + \text{M} = \text{HCO} + \text{H} + \text{M}$	5.00E+16	0	76500
231	$\text{CH}_2\text{O} + \text{OH} = \text{HCO} + \text{H}_2\text{O}$	3.00E+13	0	1200
232	$\text{CH}_2\text{O} + \text{H} = \text{HCO} + \text{H}_2$	2.50E+13	0	3900
233	$\text{CH}_2\text{O} + \text{O} = \text{HCO} + \text{OH}$	3.50E+13	0	3510
234	$\text{HCO} + \text{HO}_2 = \text{CH}_2\text{O} + \text{O}_2$	1.00E+14	0	3000
235	$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}$	2.94E+14	0	15570
236	$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	3.31E+12	0	7000
237	$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	1.00E+14	0	0
238	$\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	2.00E+14	0	0
239	$\text{HCO} + \text{O} = \text{CO} + \text{OH}$	1.00E+14	0	0
240	$\text{CH} + \text{O}_2 = \text{HCO} + \text{O}$	1.00E+13	0	0
241	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	5.90E+15	0	4100
242	$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	2.50E+12	0	47690
243	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	4.17E+11	0	1000

244	CO+HO2=CO2+OH		5.75E+13	0	22930
245	O+H2O=OH+OH		6.80E+13	0	18365
246	H+O2=OH+O		1.89E+14	0	16400
247	O+H2=OH+H		4.20E+14	0	13750
248	H+HO2=H2+O2		7.28E+13	0	2126
249	O+HO2=OH+O2		5.00E+13	0	1000
250	HO2+OH=H2O+O2		8.00E+12	0	0
251	H+HO2=OH+OH		1.34E+14	0	1070
252	H2+HO2=H2O2+H		7.91E+13	0	25000
253	OH+H2O2=H2O+HO2		6.10E+12	0	1430
254	HO2+HO2=H2O2+O2		1.80E+12	0	0
255	H+H2O2=OH+H2O		7.80E+11	0	0
256	H2O2+M=OH+OH+M		1.44E+17	0	45510
	H2	Enhanced by	2.300E+00		
	O2	Enhanced by	7.800E-01		
	H2O	Enhanced by	6.000E+00		
	H2O2	Enhanced by	6.600E+00		
257	H2+OH=H2O+H		4.74E+13	0	6098
258	H+O2+M=HO2+M		1.46E+15	0	-1000
	H2	Enhanced by	3.000E+00	0	
	O2	Enhanced by	1.300E+00	0	
	H2O	Enhanced by	2.130E+01	1	
	N2	Enhanced by	1.300E+00	0	
	CO2	Enhanced by	7.000E+00	0	
	C6H6	Enhanced by	2.000E+01	1	
	CH4	Enhanced by	5.000E+00	0	
259	H2O+M=H+OH+M		1.30E+15	0	105140
	H2	Enhanced by	4.000E+00		
	O2	Enhanced by	1.500E+00		
	H2O	Enhanced by	2.000E+01		
	N2	Enhanced by	1.500E+00		
	CO2	Enhanced by	4.000E+00		
	C6H6	Enhanced by	2.000E+01		
260	H+O+M=OH+M		7.10E+18	-1	0
261	H2+M=H+H+M		2.20E+14	0	96000
	H2	Enhanced by	4.100E+00		
	O2	Enhanced by	2.000E+00		
	H2O	Enhanced by	1.500E+01		
	N2	Enhanced by	2.000E+00		
262	O2+M=O+O+M		1.80E+18	-1	118000

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.6 Methanol chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T**b exp(-E/RT))			Source/Modification
		A	b	E	
1	CH2O+M=HCO+H+M	2.64E+32	-4.1	92550	# All reactions : Ref[23,25]
2	CH2O+M=H2+CO+M	8.25E+15	0	69540	
3	CH2O+O2=HCO+HO2	2.05E+13	0	38920	
4	CH2O+H=HCO+H2	1.00E+14	0	4928	
5	CH2O+O=HCO+OH	1.81E+13	0	3078	
6	CH2O+OH=HCO+H2O	3.43E+09	1.2	-447	
7	CH2O+HO2=HCO+H2O2	1.99E+12	0	11660	
8	HCO+M=H+CO+M	1.85E+17	-1	17000	
9	HCO+O2=CO+HO2	4.22E+12	0	0	
10	HCO+H=CO+H2	7.23E+13	0	0	
11	HCO+O=CO+OH	3.00E+13	0	0	
12	HCO+O=CO2+H	3.00E+13	0	0	
13	HCO+OH=CO+H2O	5.00E+13	0	0	
14	HCO+HO2=CO2+OH+H	3.00E+13	0	0	
15	CO+OH=CO2+H	1.10E+03	2.5	-3283	
16	CO+HO2=CO2+OH	6.63E+13	0	22950	
17	CO+O+M=CO2+M	4.00E+13	0	-4540	
18	CO+O2=CO2+O	2.53E+12	0	47690	
19	H+O2=OH+O	1.92E+14	0	16440	
20	H2+O=OH+H	5.08E+04	2.7	6292	
21	OH+OH=H2O+O	2.88E+00	3.7	-4313	
22	OH+H2=H2O+H	2.16E+08	1.5	3430	
23	H2O2+OH=H2O+HO2	7.00E+12	0	1430	
24	H2O2+H=H2O+OH	1.00E+13	0	3590	
25	HO2+HO2=H2O2+O2	3.00E+12	0	1387	
26	H+HO2=OH+OH	1.69E+14	0	874	
27	H+HO2=H2+O2	6.63E+13	0	2126	
28	HO2+OH=H2O+O2	1.45E+16	-1	0	
29	HO2+O=O2+OH	1.81E+13	0	-397	
30	H2O2+H=H2+HO2	4.82E+13	0	7948	
31	O+O+M=O2+M	6.17E+15	-0.5	0	
32	H2+M=H+H+M	4.58E+19	-1.4	104400	
33	H+OH+M=H2O+M	2.25E+22	-2	0	
34	H2O2+M=OH+OH+M	1.20E+17	0	45500	
35	O+H+M=OH+M	4.72E+18	-1	0	
36	H+O2+M=HO2+M	2.00E+15	0	-1000	
37	CH3OH=CH3+OH	3.80E+15	0	91780	
38	CH3OH=CH2OH+H	3.70E+15	0	96790	
39	CH3OH+O2=CH2OH+HO2	2.05E+13	0	44910	
40	CH3OH+H=CH2OH+H2	3.20E+13	0	6095	
41	CH3OH+H=CH3O+H2	8.00E+12	0	6095	
42	CH3OH+O=CH2OH+OH	3.88E+05	0	3080	
43	CH3OH+OH=CH2OH+H2O	1.77E+04	2.7	-883	

44	CH3OH+OH=CH3O+H2O	1.77E+04	2.7	-883
45	CH3OH+HO2=CH2OH+H2O2	3.98E+13	0	19400
46	CH3OH+CH3=CH2OH+CH4	3.19E+01	3.2	7172
47	CH3OH+CH3=CH3O+CH4	1.45E+01	3.1	6935
48	CH2OH+M=CH2O+H+M	2.44E+24	-2.5	34200
49	CH2OH+O2=CH2O+HO2	2.41E+14	0	5000
50	CH2OH+H=CH2O+H2	3.00E+13	0	0
51	CH2OH+HO2=CH2O+H2O2	1.20E+13	0	0
52	CH2OH+CH2OH=CH3OH+CH2O	1.20E+13	0	0
53	CH2OH+HCO=CH3OH+CO	1.20E+14	0	0
54	CH2OH+CH2O=CH3OH+HCO	5.54E+03	2.8	5862
55	CH3O+M=CH2O+H+M	1.36E+25	-2.7	30600
56	CH3O+O2=CH2O+HO2	6.30E+10	0	2600
57	CH3O+CO=CH3+CO2	1.57E+13	0	11800
58	CH3O+H=CH2O+H2	2.00E+13	0	0
59	CH3O+HO2=CH2O+H2O2	1.20E+13	0	0
60	CH4=CH3+H	6.90E+14	0	103800
61	CH4+H=CH3+H2	5.47E+07	2	11210
62	CH4+O=CH3+OH	6.93E+08	1.6	8484
63	CH4+OH=CH3+H2O	5.72E+06	2	2639
64	CH3+O2=CH3O+O	1.99E+18	-1.6	29230
65	CH3+HO2=CH3O+OH	2.00E+13	0	1076
66	CH3+HO2=CH4+O2	3.61E+12	0	0
67	CH3+OH=CH2OH+H	6.67E+10	0.4	-707.9
68	CH3+OH=CH3O+H	5.74E+12	-0.2	13930
69	CH3+O=CH2O+H	8.43E+13	0	0
70	CH3+CH3=C2H6	5.88E+15	-0.9	705.1
71	CH3+CH3=C2H4+H2	1.00E+16	0	32030
72	CH3+CH3=C2H5+H	2.80E+13	0	13600
73	CH3+CH2OH=C2H5+OH	1.37E+14	-0.4	6589
74	CH3+CH2O=HCO+CH4	5.54E+03	2.8	5862
75	C2H6+H=C2H5+H2	5.37E+02	3.5	5200
76	C2H6+OH=C2H5+H2O	5.13E+06	2.1	855
77	C2H5=C2H4+H	1.23E+09	1.2	37190
78	C2H5+O2=C2H4+HO2	8.43E+11	0	3874
79	C2H5+C2H3=C2H4+C2H4	4.82E+11	0	0
80	C2H4=C2H2+H2	6.39E+12	0.4	88770
81	C2H4+H=C2H3+H2	1.32E+06	2.5	12240
82	C2H4+O=CH2O+CH2	2.50E+13	1	5000
83	C2H4+OH=C2H3+H2O	2.02E+13	0	5955
84	C2H3+M=C2H2+H+M	4.81E+29	-4	43140
85	C2H3+H=C2H2+H2	3.00E+13	0	0
86	C2H2+M=C2H+H+M	6.66E+30	-3.7	127100
87	C2H2+O2=HCO+HCO	4.00E+12	0	28010
88	C2H2+H=C2H+H2	6.02E+13	0	22250
89	C2H2+OH=C2H+H2O	1.45E+04	2.7	12040
90	C2H2+O=C2H+OH	3.20E+15	-0.6	17000
91	C2H2+O=CH2+CO	1.75E+13	0	3179
92	C2H+O2=HCO+CO	2.41E+12	0	0
93	C2H+O=CO+CH	1.81E+13	0	0

94	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	$1.57\text{E}+13$	0	0
95	$\text{CH}_2 + \text{O} = \text{CO} + \text{H} + \text{H}$	$1.05\text{E}+13$	0	0
96	$\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$	$9.64\text{E}+13$	0	0
97	$\text{CH}_2 + \text{OH} = \text{CH}_2\text{O} + \text{H}$	$2.41\text{E}+13$	0	0
98	$\text{CH} + \text{O}_2 = \text{CO} + \text{OH}$	$1.35\text{E}+11$	0.7	25690
99	$\text{CH} + \text{O}_2 = \text{HCO} + \text{O}$	$1.00\text{E}+13$	0	0

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

Appendix A.7 MTBE chemical kinetic reaction mechanism

REACTIONS CONSIDERED		(k = A T**b exp(-E/RT))			Source/Modification
		A	b	E	
1	H+H+M=H2+M	7.31E+17	-1	0	#Reaction 1 - 393 : Ref[15]
2	O+O+M=O2+M	1.14E+17	-1	0	#Reaction 394 - 459 :Ref[39]
3	O+H+M=OH+M	6.20E+16	-0.6	0	#Reaction 460 - 482 : Ref[24]
4	H2+O2=OH+OH	1.70E+13	0	47780	#Reaction 483 - 484 : Ref[25]
5	O+H2=OH+H	3.87E+04	2.7	6260	
6	H+O2=OH+O	1.90E+14	0	16812	
7	H+O2+M=HO2+M	8.00E+17	-0.8	0	
8	H+OH+M=H2O+M	8.62E+21	-2	0	
9	H2+OH=H2O+H	2.16E+08	1.5	3430	
10	H2O+O=OH+OH	1.50E+10	1.1	17260	
11	HO2+OH=H2O+O2	2.89E+13	0	-497	
12	HO2+O=OH+O2	1.81E+13	0	-400	
13	H+HO2=H2+O2	4.22E+13	0	1411	
14	H+HO2=OH+OH	4.95E+13	0	143	
15	H+HO2=H2O+O	1.18E+14	0	2730	
16	HO2+HO2=H2O2+O2	4.08E+02	3.3	996	
17	OH+OH=H2O2	1.56E+16	-1.5	149	
18	H2O2+OH=HO2+H2O	1.78E+12	0	326	
19	H2O2+H=HO2+H2	1.70E+12	0	3750	
20	H2O2+H=H2O+OH	1.00E+13	0	3590	
21	H2O2+O=HO2+OH	2.80E+13	0	6400	
22	CO+HO2=CO2+OH	1.50E+14	0	23650	
23	CO+OH=CO2+H	4.40E+06	1.5	-740	
24	CO+O+M=CO2+M	2.83E+13	0	-4540	
25	CO+O2=CO2+O	2.53E+12	0	47700	
26	HCO+M=H+CO+M	1.85E+17	-1	17000	
27	HCO+OH=CO+H2O	1.00E+14	0	0	
28	HCO+O=CO+OH	3.00E+13	0	0	
29	HCO+O=CO2+H	3.00E+13	0	0	
30	HCO+H=CO+H2	7.22E+13	0	0	
31	HCO+O2=CO+HO2	1.18E+09	1.2	-288	
32	HCO+CH3=CO+CH4	1.20E+14	0	0	
33	HCO+HO2=CO2+OH+H	3.00E+13	0	0	
34	HCO+C2H6=CH2O+C2H5	4.70E+04	2.7	18235	
35	HCO+HCO=CH2O+CO	1.80E+13	0	0	
36	HCO+HCO=H2+CO+CO	3.00E+12	0	0	
37	CH4=CH3+H	5.99E+30	-4.9	108553	
38	CH4+HO2=CH3+H2O2	1.12E+13	0	24641	
39	CH4+OH=CH3+H2O	1.55E+07	1.8	2774	
40	CH4+O=CH3+OH	6.92E+08	1.6	8486	
41	CH4+H=CH3+H2	8.58E+03	3.1	7941	
42	CH4+CH2=CH3+CH3	4.30E+12	0	10038	
43	CH3+M=CH2+H+M	1.90E+16	0	91600	

44	$\text{CH}_3 + \text{HO}_2 = \text{CH}_3\text{O} + \text{OH}$	4.00E+13	0	5000
45	$\text{CH}_4 + \text{O}_2 = \text{CH}_3 + \text{HO}_2$	7.63E+13	0	58590
46	$\text{CH}_3 + \text{OH} = \text{CH}_2\text{OH} + \text{H}$	2.64E+19	-1.8	8068
47	$\text{CH}_3 + \text{OH} = \text{CH}_3\text{O} + \text{H}$	5.74E+12	-0.2	13931
48	$\text{CH}_3 + \text{OH} = \text{CH}_2 + \text{H}_2\text{O}$	8.90E+18	-1.8	8067
49	$\text{CH}_3 + \text{OH} = \text{CH}_2\text{O} + \text{H}_2$	3.19E+12	-0.5	10810
50	$\text{CH}_3 + \text{O} = \text{CH}_2\text{O} + \text{H}$	8.43E+13	0	0
51	$\text{CH}_3 + \text{H} = \text{CH}_2 + \text{H}_2$	7.00E+13	0	15100
52	$\text{CH}_3 + \text{O}_2 = \text{CH}_3\text{O} + \text{O}$	6.00E+12	0	33700
53	$\text{CH}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{OH}$	3.05E+30	-4.7	36571
54	$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_5 + \text{H}$	3.01E+13	0	13513
55	$\text{CH}_3 + \text{CH}_3 = \text{C}_2\text{H}_6$	2.39E+38	-7.6	11359
56	$\text{CH}_3 + \text{CH}_3\text{O} = \text{CH}_4 + \text{CH}_2\text{O}$	2.41E+13	0	0
57	$\text{CH}_3 + \text{CH}_2\text{OH} = \text{CH}_4 + \text{CH}_2\text{O}$	2.41E+12	0	0
58	$\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$	1.13E+07	2	3000
59	$\text{CH}_2 + \text{OH} = \text{CH}_2\text{O} + \text{H}$	2.50E+13	0	0
60	$\text{CH}_2 + \text{O} = \text{CO} + \text{H} + \text{H}$	9.08E+13	0	656
61	$\text{CH}_2 + \text{O} = \text{CO} + \text{H}_2$	3.89E+13	0	-149
62	$\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$	5.52E+12	0	-2026
63	$\text{CH}_2 + \text{O}_2 = \text{HCO} + \text{OH}$	4.30E+10	0	-500
64	$\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H}_2$	6.90E+11	0	500
65	$\text{CH}_2 + \text{O}_2 = \text{CO}_2 + \text{H} + \text{H}$	1.60E+12	0	1000
66	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{H}_2\text{O}$	1.87E+10	0	-1000
67	$\text{CH}_2 + \text{O}_2 = \text{CO} + \text{OH} + \text{H}$	8.64E+10	0	-500
68	$\text{CH}_2 + \text{O}_2 = \text{CH}_2\text{O} + \text{O}$	1.00E+14	0	4500
69	$\text{CH}_2 + \text{CO}_2 = \text{CH}_2\text{O} + \text{CO}$	1.10E+11	0	1000
70	$\text{CH}_2 + \text{CH}_2 = \text{C}_2\text{H}_2 + \text{H}_2$	3.20E+13	0	0
71	$\text{CH}_2 + \text{CH}_3 = \text{C}_2\text{H}_4 + \text{H}$	4.00E+13	0	0
72	$\text{CH}_2 + \text{CH} = \text{C}_2\text{H}_2 + \text{H}$	4.00E+13	0	0
73	$\text{CH}_2 + \text{C}_2\text{H}_2 = \text{H} + \text{C}_3\text{H}_3$	1.20E+13	0	6620
74	$\text{CH}_2 + \text{C}_2\text{H}_4 = \text{C}_3\text{H}_6$	4.30E+12	0	10038
75	$\text{CH}_2 + \text{C}_2\text{H}_6 = \text{CH}_3 + \text{C}_2\text{H}_5$	6.50E+12	0	7911
76	$\text{CH}_2 + \text{C}_3\text{H}_8 = \text{CH}_3 + \text{C}_3\text{H}_7$	2.19E+12	0	6405
77	$\text{CH}_2 + \text{C}_3\text{H}_8 = \text{CH}_3 + \text{NC}_3\text{H}_7$	1.79E+12	0	6405
78	$\text{CH} + \text{OH} = \text{HCO} + \text{H}$	3.00E+13	0	0
79	$\text{CH} + \text{O} = \text{CO} + \text{H}$	1.00E+14	0	0
80	$\text{CH} + \text{O}_2 = \text{HCO} + \text{O}$	3.30E+13	0	0
81	$\text{CH} + \text{O}_2 = \text{CO} + \text{OH}$	2.00E+13	0	0
82	$\text{CH} + \text{CO}_2 = \text{HCO} + \text{CO}$	3.40E+12	0	690
83	$\text{CH} + \text{CH}_4 = \text{C}_2\text{H}_4 + \text{H}$	6.00E+13	0	0
84	$\text{CH} + \text{CH}_3 = \text{C}_2\text{H}_3 + \text{H}$	3.00E+13	0	0
85	$\text{CH}_3\text{O} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$	4.88E+15	0	22773
86	$\text{CH}_3\text{O} + \text{HO}_2 = \text{CH}_2\text{O} + \text{H}_2\text{O}_2$	3.00E+11	0	0
87	$\text{CH}_3\text{O} + \text{OH} = \text{CH}_2\text{O} + \text{H}_2\text{O}$	1.00E+13	0	0
88	$\text{CH}_3\text{O} + \text{O} = \text{CH}_2\text{O} + \text{OH}$	1.30E+13	0	0
89	$\text{CH}_3\text{O} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	2.00E+13	0	0
90	$\text{CH}_3\text{O} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	2.35E+10	0	1788
91	$\text{CH}_3\text{O} + \text{CH}_2\text{O} = \text{CH}_3\text{OH} + \text{HCO}$	1.15E+11	0	1280
92	$\text{CH}_3\text{O} + \text{CO} = \text{CH}_3 + \text{CO}_2$	1.57E+13	0	2981
93	$\text{CH}_3\text{O} + \text{HCO} = \text{CH}_3\text{OH} + \text{CO}$	9.00E+13	0	0

94	CH3O+C2H5=CH2O+C2H6	2.41E+13	0	0
95	CH3O+C2H3=CH2O+C2H4	2.41E+13	0	0
96	CH3O+C2H4=CH2O+C2H5	1.20E+11	0	7000
97	CH2O+M=HCO+H+M	5.72E+16	0	76480
98	CH2O+HO2=HCO+H2O2	4.00E+12	0	11665
99	CH2O+OH=HCO+H2O	3.43E+09	1.2	-447
100	CH2O+O=HCO+OH	1.81E+13	0	3088
101	CH2O+H=HCO+H2	1.12E+08	1.7	2127
102	CH2O+O2=HCO+HO2	2.04E+13	0	39000
103	CH2O+CH3=HCO+CH4	8.91E-13	7.4	-960
104	C2H6=C2H5+H	2.08E+38	-7.1	106507
105	C2H6+HO2=C2H5+H2O2	1.21E+12	0	17600
106	C2H6+OH=C2H5+H2O	5.13E+06	2.1	860
107	C2H6+O=C2H5+OH	1.14E-07	6.5	274
108	C2H6+H=C2H5+H2	5.00E+02	3.5	5210
109	C2H6+O2=C2H5+HO2	1.00E+13	0	51000
110	C2H6+CH3O=C2H5+CH3OH	3.02E+11	0	7000
111	C2H6+CH3=C2H5+CH4	3.97E+05	2.5	17684
112	C2H5+HO2=C2H4+H2O2	3.00E+11	0	0
113	C2H5+HO2=>CH3+CH2O+OH	2.50E+13	0	0
114	C2H5+OH=C2H4+H2O	2.41E+13	0	0
115	C2H5+OH=>CH3+CH2O+H	2.41E+13	0	0
116	C2H5+O=CH2O+CH3	4.24E+13	0	0
117	C2H5+O=CH3CHO+H	5.30E+13	0	0
118	C2H5+O=C2H4+OH	3.05E+13	0	0
119	C2H5+H=C2H4+H2	1.25E+14	0	8000
120	C2H5+O2=C2H4+HO2	1.70E+10	0	-670
121	C2H5+CH3=C2H4+CH4	4.37E-04	5	8300
122	C2H5+C2H5=C2H4+C2H6	1.40E+12	0	0
123	C2H4+M=C2H2+H2+M	3.00E+17	0	79350
124	C2H4+M=C2H3+H+M	2.97E+17	0	96560
125	C2H4+HO2=>C2H4O+OH	6.22E+12	0	18962
126	C2H4+OH=C2H3+H2O	2.02E+13	0	5960
127	C2H4+O=CH3+HCO	1.08E+14	0	7432
128	C2H4+O=>CH2+HCO+H	5.66E+12	0	1488
129	C2H4+H=C2H3+H2	3.36E-07	6	1692
130	C2H4+H=C2H5	1.05E+14	-0.5	655
131	C2H4+O2=C2H3+HO2	4.00E+13	0	61500
132	C2H4+C2H4=C2H5+C2H3	5.00E+14	0	64700
133	C2H4+CH3=C2H3+CH4	3.97E+05	2.5	20000
134	C2H4O=CH4+CO	3.16E+14	0	57000
135	C2H3=C2H2+H	2.10E+44	-8.4	51106
136	C2H3+HO2=>CH3+CO+OH	3.00E+13	0	0
137	C2H3+OH=C2H2+H2O	3.00E+13	0	0
138	C2H3+OH=CH3CHO	3.00E+13	0	0
139	C2H3+O=CH3+CO	3.00E+13	0	0
140	C2H3+H=C2H2+H2	3.00E+13	0	0
141	C2H3+O2=CH2O+HCO	3.00E+12	0	-250
142	C2H3+CH3=C2H2+CH4	4.37E-04	5	8300
143	C2H3+C2H6=C2H4+C2H5	1.50E+13	0	10000

144	$\text{C}_2\text{H}_3 + \text{HCO} = \text{C}_2\text{H}_4 + \text{CO}$	9.03E+13	0	0
145	$\text{C}_2\text{H}_3 + \text{CH}_2\text{O} = \text{C}_2\text{H}_4 + \text{HCO}$	5.42E+03	2.8	5862
146	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$	1.08E+13	0	0
147	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 = \text{C}_4\text{H}_6$	4.94E+13	0	0
148	$\text{C}_2\text{H}_2 = \text{C}_2\text{H} + \text{H}$	2.37E+32	-5.3	130688
149	$\text{C}_2\text{H}_2 + \text{HO}_2 = \text{CH}_2\text{CO} + \text{OH}$	1.00E+13	0	18280
150	$\text{C}_2\text{H}_2 + \text{OH} = \text{C}_2\text{H} + \text{H}_2\text{O}$	3.39E+07	2	14000
151	$\text{C}_2\text{H}_2 + \text{OH} = \text{HCCOH} + \text{H}$	5.06E+05	2.3	13500
152	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	2.19E-04	4.5	-1000
153	$\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_3 + \text{CO}$	4.85E-04	4	-2000
154	$\text{C}_2\text{H}_2 + \text{H} = \text{C}_2\text{H} + \text{H}_2$	6.02E+13	0	22257
155	$\text{C}_2\text{H}_2 + \text{O} = \text{CH}_2 + \text{CO}$	1.52E+04	2.8	497
156	$\text{C}_2\text{H}_2 + \text{O} = \text{HCCO} + \text{H}$	6.50E+03	2.8	497
157	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCCO} + \text{OH}$	2.00E+08	1.5	30100
158	$\text{C}_2\text{H}_2 + \text{O}_2 = \text{C}_2\text{H} + \text{HO}_2$	1.20E+13	0	74520
159	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{SC}_3\text{H}_5$	1.61E+40	-8.6	20331
160	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{PC}_3\text{H}_4 + \text{H}$	2.73E+17	-2	20592
161	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{AC}_3\text{H}_5$	2.61E+46	-9.8	36951
162	$\text{C}_2\text{H}_2 + \text{CH}_3 = \text{AC}_3\text{H}_4 + \text{H}$	6.74E+19	-2.1	31591
163	$\text{HCCOH} + \text{H} = \text{CH}_2\text{CO} + \text{H}$	1.00E+13	0	0
164	$\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00E+13	0	0
165	$\text{C}_2\text{H} + \text{O} = \text{CO} + \text{CH}$	1.00E+13	0	0
166	$\text{C}_2\text{H} + \text{O}_2 = \text{CO} + \text{CO} + \text{H}$	5.00E+13	0	1510
167	$\text{CH}_2\text{CO} + \text{M} = \text{CH}_2 + \text{CO} + \text{M}$	4.11E+15	0	59270
168	$\text{CH}_2\text{CO} + \text{O}_2 = \text{CH}_2\text{O} + \text{CO}_2$	2.00E+13	0	61500
169	$\text{CH}_2\text{CO} + \text{HO}_2 \Rightarrow \text{CH}_2\text{O} + \text{CO} + \text{OH}$	6.00E+11	0	12738
170	$\text{CH}_2\text{CO} + \text{OH} = \text{HCCO} + \text{H}_2\text{O}$	7.50E+12	0	2000
171	$\text{CH}_2\text{CO} + \text{O} = \text{CH}_2 + \text{CO}_2$	1.76E+12	0	1349
172	$\text{CH}_2\text{CO} + \text{O} = \text{HCCO} + \text{OH}$	1.00E+13	0	8000
173	$\text{CH}_2\text{CO} + \text{H} = \text{CH}_3 + \text{CO}$	1.50E+04	2.8	673
174	$\text{CH}_2\text{CO} + \text{H} = \text{HCCO} + \text{H}_2$	5.00E+13	0	8000
175	$\text{HCCO} + \text{M} = \text{CH} + \text{CO} + \text{M}$	6.00E+15	0	58821
176	$\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00E+13	0	0
177	$\text{HCCO} + \text{O} = \text{CO} + \text{CO} + \text{H}$	1.93E+14	0	590
178	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	1.50E+14	0	0
179	$\text{HCCO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46E+12	0	2500
180	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H} + \text{CH}_2\text{O}$	1.00E+13	0	2000
181	$\text{HCCO} + \text{CH}_2 = \text{C}_2\text{H}_3 + \text{CO}$	3.00E+13	0	0
182	$\text{CH}_3\text{OH} = \text{CH}_3 + \text{OH}$	1.90E+16	0	91780
183	$\text{CH}_3\text{OH} + \text{HO}_2 = \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$	3.98E+13	0	19400
184	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2\text{O}$	1.77E+04	2.7	-883
185	$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{H}_2\text{O}$	1.77E+04	2.7	-883
186	$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$	3.88E+05	2.5	3080
187	$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$	3.20E+13	0	6095
188	$\text{CH}_3\text{OH} + \text{CH}_2\text{O} = \text{CH}_3\text{O} + \text{CH}_3\text{O}$	1.55E+12	0	79570
189	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_2\text{OH} + \text{CH}_4$	3.19E+01	3.2	7172
190	$\text{CH}_3\text{OH} + \text{CH}_3 = \text{CH}_3\text{O} + \text{CH}_4$	1.45E+01	3.1	6935
191	$\text{CH}_2\text{OH} + \text{M} = \text{CH}_2\text{O} + \text{H} + \text{M}$	1.00E+14	0	25100
192	$\text{CH}_2\text{OH} + \text{H} = \text{CH}_2\text{O} + \text{H}_2$	3.00E+13	0	0
193	$\text{CH}_2\text{OH} + \text{O}_2 = \text{CH}_2\text{O} + \text{HO}_2$	2.17E+14	0	4690

194	CH3CHO=CH3+HCO	2.45E+16	0	84128
195	CH3CHO+HO2=CH3CO+H2O2	1.70E+12	0	10700
196	CH3CHO+OH=CH3CO+H2O	1.00E+13	0	0
197	CH3CHO+O=CH3CO+OH	5.00E+12	0	1790
198	CH3CHO+H=CH3CO+H2	4.00E+13	0	4210
199	CH3CHO+O2=CH3CO+HO2	2.00E+13	0.5	42200
200	CH3CHO+CH3=CH3CO+CH4	2.00E-06	5.6	2464
201	CH3CO+M=CH3+CO+M	8.64E+15	0	14400
202	C3H8=C2H5+CH3	6.03E+94	-22.7	130427
203	C3H8+O2=NC3H7+HO2	4.00E+13	0	47500
204	C3H8+O2=IC3H7+HO2	4.00E+13	0	47500
205	C3H8+HO2=NC3H7+H2O2	4.76E+04	2.5	16494
206	C3H8+HO2=IC3H7+H2O2	9.64E+03	2.6	13910
207	C3H8+OH=NC3H7+H2O	4.16E+07	1.7	540
208	C3H8+OH=IC3H7+H2O	1.84E+05	2.4	-573
209	C3H8+O=NC3H7+OH	3.72E+06	2.4	5505
210	C3H8+O=IC3H7+OH	5.50E+05	2.5	3140
211	C3H8+H=NC3H7+H2	2.00E+14	0	9959
212	C3H8+H=IC3H7+H2	1.30E+13	0	5638
213	C3H8+CH3=NC3H7+CH4	3.00E+12	0	11710
214	C3H8+CH3=IC3H7+CH4	8.07E+11	0	10110
215	C3H8+C2H5=NC3H7+C2H6	3.16E+11	0	12300
216	C3H8+C2H5=IC3H7+C2H6	5.01E+10	0	10400
217	C3H8+C2H3=NC3H7+C2H4	6.00E+02	3.3	10502
218	C3H8+C2H3=IC3H7+C2H4	1.00E+03	3.1	8829
219	C3H8+IC3H7=NC3H7+C3H8	1.00E+11	0	12900
220	C3H8+AC3H5=NC3H7+C3H6	7.94E+11	0	20500
221	C3H8+AC3H5=IC3H7+C3H6	7.94E+11	0	16200
222	C3H8+CH3O=NC3H7+CH3OH	3.18E+11	0	7050
223	C3H8+CH3O=IC3H7+CH3OH	7.20E+10	0	4470
224	NC3H7=C2H4+CH3	4.07E+12	0	29580
225	NC3H7+O2=C3H6+HO2	3.58E+09	0	-3532
226	IC3H7=C2H4+CH3	1.00E+14	0	45000
227	IC3H7+O2=C3H6+HO2	1.84E+10	0	-2151
228	C3H6=AC3H5+H	4.57E+14	0	88900
229	C3H6=SC3H5+H	7.59E+14	0	101300
230	C3H6=TC3H5+H	1.45E+15	0	98060
231	C3H6=C2H3+CH3	7.10E+15	0	87240
232	C3H6+HO2=C3H6O+OH	1.02E+12	0	14964
233	C3H6+HO2=AC3H5+H2O2	1.50E+11	0	14190
234	C3H6+HO2=SC3H5+H2O2	7.50E+09	0	12570
235	C3H6+HO2=TC3H5+H2O2	3.00E+09	0	9930
236	C3H6+OH=AC3H5+H2O	7.70E+05	2.2	622
237	C3H6+OH=SC3H5+H2O	1.01E+13	0	5960
238	C3H6+OH=TC3H5+H2O	1.17E+09	1	-424
239	C3H6+OH=C2H5+CH2O	3.91+145	-40	65733
240	C3H6+OH+O2=>CH3CHO+CH2O+OH	3.00E+10	0	-8280
241	C3H6+O=C2H5+HCO	5.22E+07	1.6	-628
242	C3H6+O=CH3+CH3+CO	6.96E+07	1.6	-628
243	C3H6+O=C2H4+CH2O	3.48E+07	1.6	-628

244	NC3H7=C3H6+H	6.30E+13	0	36807
245	C3H6+H=IC3H7	3.00E+12	0	960
246	C3H6+H=AC3H5+H2	6.46E+12	0	4445
247	C3H6+H=SC3H5+H2	3.25E+11	0	4445
248	C3H6+O2=SC3H5+HO2	2.00E+13	0	47600
249	C3H6+O2=TC3H5+HO2	2.00E+13	0	44000
250	C3H6+O2=AC3H5+HO2	1.95E+12	0	39000
251	C3H6+CH3=AC3H5+CH4	1.60E+11	0	8800
252	C3H6+CH3=SC3H5+CH4	3.30E+11	0	10110
253	C3H6+CH3=TC3H5+CH4	5.00E+10	0	8030
254	C3H6+C2H5=AC3H5+C2H6	1.00E+11	0	9800
255	C3H6O=>C2H5+HCO	1.26E+14	0	58000
256	AC3H5+O2=>CH2O+CH2O+CH	6.31E+11	0	17210
257	AC3H5+HO2=>C2H3+CH2O+OH	4.50E+12	0	0
258	AC3H5+H=AC3H4+H2	3.33E+12	0	0
259	AC3H5+O=>C2H4+CO+H	1.81E+14	0	0
260	AC3H5+CH3=AC3H4+CH4	1.00E+11	0	0
261	AC3H5+C2H5=AC3H4+C2H6	4.00E+11	0	0
262	AC3H5+C2H3=AC3H4+C2H4	1.00E+12	0	0
263	SC3H5+O2=CH3CHO+HCO	4.34E+12	0	0
264	SC3H5+HO2=>CH2CO+CH3+OH	4.50E+12	0	0
265	SC3H5+H=AC3H4+H2	3.33E+12	0	0
266	SC3H5+O=>CH2CO+CH3	1.81E+14	0	0
267	SC3H5+CH3=AC3H4+CH4	1.00E+11	0	0
268	SC3H5+C2H5=AC3H4+C2H6	1.00E+11	0	0
269	SC3H5+C2H3=AC3H4+C2H4	1.00E+11	0	0
270	TC3H5+O2=CH3CO+CH2O	4.34E+11	0	0
271	TC3H5+HO2=>CH2CO+CH3+OH	4.50E+12	0	0
272	TC3H5+H=AC3H4+H2	3.33E+12	0	0
273	TC3H5+O=>HCCO+CH3+H	1.81E+14	0	0
274	TC3H5+CH3=AC3H4+CH4	1.00E+11	0	0
275	TC3H5+C2H5=AC3H4+C2H6	1.00E+11	0	0
276	TC3H5+C2H3=AC3H4+C2H4	1.00E+11	0	0
277	AC3H4+M=C3H3+H+M	2.00E+18	0	80000
278	AC3H4+AC3H4=AC3H5+C3H3	5.00E+14	0	64700
279	AC3H4=PC3H4	1.20E+15	0	92400
280	AC3H4+O2=C3H3+HO2	4.00E+13	0	61500
281	AC3H4+HO2=>CH2CO+CH2+OH	8.00E+12	0	19000
282	AC3H4+OH=CH2CO+CH3	3.12E+12	0	-397
283	AC3H4+OH=C3H3+H2O	1.45E+13	0	4173
284	AC3H4+O=C2H3+HCO	1.10E-02	4.6	-4243
285	AC3H4+H=AC3H5	2.00E+12	0	2700
286	AC3H4+H=TC3H5	6.50E+12	0	2000
287	AC3H4+H=C3H3+H2	1.00E+12	0	1500
288	AC3H4+CH3=C3H3+CH4	2.00E+12	0	7700
289	AC3H4+AC3H5=C3H3+C3H6	2.00E+12	0	7700
290	AC3H4+C2H=C3H3+C2H2	1.00E+13	0	0
291	PC3H4+M=C3H3+H+M	4.70E+18	0	80000
292	PC3H4=C2H+CH3	4.20E+16	0	100000
293	CC3H4=AC3H4	1.51E+14	0	50400

294	CC3H4=PC3H4	7.08E+13	0	43700
295	PC3H4+O2=>HCCO+OH+CH2	2.00E+08	1.5	30100
296	PC3H4+O2=C3H3+HO2	5.00E+12	0	51000
297	PC3H4+HO2=>C2H4+CO+OH	3.00E+12	0	19000
298	PC3H4+OH=C3H3+H2O	3.00E+03	3	200
299	PC3H4+OH=CH2CO+CH3	5.00E-04	4.5	-1000
300	PC3H4+O=CH2CO+CH2	6.40E+12	0	2010
301	PC3H4+O=C2H3+HCO	3.20E+12	0	2010
302	PC3H4+O=HCCO+CH3	6.30E+12	0	2010
303	PC3H4+O=>HCCO+CH2+H	3.20E+11	0	2010
304	PC3H4+H=TC3H5	6.50E+12	0	2000
305	PC3H4+H=C3H3+H2	1.00E+12	0	1500
306	PC3H4+CH3=C3H3+CH4	2.00E+12	0	7700
307	PC3H4+C2H=C3H3+C2H2	1.00E+12	0	0
308	PC3H4+C2H3=C3H3+C2H4	1.00E+12	0	7700
309	PC3H4+AC3H5=C3H3+C3H6	2.00E+12	0	7700
310	C3H3+H=C3H2+H2	1.60E+14	0	0
311	C3H3+O=>C2H+HCO+H	1.39E+14	0	0
312	C3H3+O=>C2H2+CO+H	1.40E+14	0	0
313	C3H3+OH=C3H2+H2O	1.06E+13	0	0
314	C3H3+O2=CH2CO+HCO	3.01E+10	0	2870
315	C3H3+CH3=C2H5+C2H	1.00E+13	0	37500
316	C3H3+CH3=C4H6	1.00E+12	0	0
317	CH+C2H2=C3H2+H	1.00E+14	0	0
318	C3H2+O2=HCO+HCCO	1.00E+13	0	0
319	C2H3+C2H4=C4H6+H	1.00E+12	0	7300
320	C2H2+C2H2=C4H3+H	2.00E+12	0	45900
321	C2H2+C2H=C4H2+H	3.50E+13	0	0
322	C4H3+M=C4H2+H+M	1.00E+16	0	59700
323	C4H2+OH=C3H2+HCO	6.66E+12	0	-410
324	C4H2+O=C3H2+CO	1.20E+12	0	0
325	SC4H7=C4H6+H	1.20E+14	0	49300
326	SC4H7=C2H4+C2H3	1.00E+11	0	37000
327	SC4H7+H=C4H6+H2	3.16E+12	0	0
328	SC4H7+O2=C4H6+HO2	1.00E+11	0	0
329	SC4H7+CH3=C4H6+CH4	1.00E+13	0	0
330	SC4H7+C2H3=C4H6+C2H4	4.00E+12	0	0
331	SC4H7+C2H5=C4H6+C2H6	4.00E+12	0	0
332	SC4H7+C2H5=PC4H8+C2H4	5.00E+11	0	0
333	SC4H7+C2H5=TRAC4H8+C2H4	5.00E+11	0	0
334	SC4H7+C2H5=CISC4H8+C2H4	5.00E+11	0	0
335	SC4H7+AC3H5=C4H6+C3H6	4.00E+13	0	0
336	SC4H7+SC4H7=C4H6+PC4H8	3.16E+12	0	0
337	C4H6+OH=AC3H5+CH2O	7.23E+12	0	-994
338	C4H6+OH=C4H5+H2O	2.17E+13	0	4173
339	C4H6+O=C2H4+CH2CO	1.00E+12	0	0
340	C4H6+O=PC3H4+CH2O	1.00E+12	0	0
341	PC4H8=SC4H7+H	4.08E+18	-1	97350
342	PC4H8=CISC4H8	4.00E+11	0	60000
343	PC4H8=TRAC4H8	4.00E+11	0	60000

344	PC4H8=AC3H5+CH3	8.00E+16	0	74000
345	PC4H8=C2H3+C2H5	2.00E+18	-1	96770
346	PC4H8+O2=SC4H7+HO2	4.00E+12	0	40000
347	PC4H8+HO2=SC4H7+H2O2	1.00E+11	0	17060
348	PC4H8+OH=NC3H7+CH2O	6.50E+12	0	0
349	PC4H8+OH=CH3CHO+C2H5	1.00E+11	0	0
350	PC4H8+OH=C2H6+CH3+CO	1.00E+10	0	0
351	PC4H8+OH=SC4H7+H2O	1.75E+13	0	3060
352	PC4H8+O=C3H6+CH2O	2.51E+12	0	0
353	PC4H8+O=CH3CHO+C2H4	1.25E+12	0	850
354	PC4H8+O=C2H5+CH3+CO	1.63E+13	0	850
355	PC4H8+O=SC4H7+OH	1.30E+13	0	4500
356	PC4H8+H=SC4H7+H2	5.00E+13	0	3900
357	PC4H8+CH3=SC4H7+CH4	1.00E+11	0	7300
358	PC4H8+C2H5=SC4H7+C2H6	1.00E+11	0	8000
359	PC4H8+AC3H5=SC4H7+C3H6	8.00E+10	0	12400
360	PC4H8+SC3H5=SC4H7+C3H6	8.00E+10	0	12400
361	PC4H8+TC3H5=SC4H7+C3H6	8.00E+10	0	12400
362	PC4H8+SC4H7=SC4H7+CISC4H8	3.98E+10	0	12400
363	PC4H8+SC4H7=SC4H7+TRAC4H8	3.98E+10	0	12400
364	CISC4H8=TRAC4H8	1.72E+14	0	64280
365	CISC4H8=C4H6+H2	1.00E+13	0	65500
366	CISC4H8=SC4H7+H	4.07E+18	-1	97350
367	CISC4H8=SC3H5+CH3	2.00E+16	0	71300
368	CISC4H8+OH=SC4H7+H2O	1.26E+14	0	3060
369	CISC4H8+OH=CH3CHO+C2H5	1.40E+13	0	0
370	CISC4H8+O=IC3H7+HCO	6.03E+12	0	0
371	CISC4H8+O=CH3CHO+C2H4	1.00E+12	0	0
372	CISC4H8+H=SC4H7+H2	1.00E+12	0	3500
373	CISC4H8+CH3=SC4H7+CH4	1.00E+11	0	8200
374	TRAC4H8=SC4H7+H	4.07E+18	-1	97350
375	TRAC4H8=SC3H5+CH3	2.00E+16	0	71300
376	TRAC4H8+OH=SC4H7+H2O	1.00E+14	0	3060
377	TRAC4H8+OH=CH3CHO+C2H5	1.50E+13	0	0
378	TRAC4H8+O=IC3H7+HCO	6.03E+12	0	0
379	TRAC4H8+O=CH3CHO+C2H4	1.00E+12	0	0
380	TRAC4H8+H=SC4H7+H2	5.00E+12	0	3500
381	TRAC4H8+CH3=SC4H7+CH4	1.00E+11	0	8200
382	CISC4H8+HO2=SC4H7+H2O2	3.20E+12	0	14900
383	TRAC4H8+HO2=SC4H7+H2O2	3.20E+12	0	14900
384	C4H2+M=C4H+H+M	3.50E+17	0	80000
385	C3H3+C3H3=C6H6	3.00E+11	0	0
386	C3H3+AC3H4=>C6H6+H	1.40E+12	0	10000
387	AC3H5+AC3H5=C6H10	1.02E+13	0	-263
388	C6H10=>C6H9+H	1.00E+16	0	85000
389	C6H10+OH=>C6H9+H2O	3.70E+13	0	0
390	C6H9=C2H3+C4H6	5.00E+13	0	38000
391	CH2CO+CH3=C2H5+CO	1.00E+12	0	3000
392	CH2CO+C2H3=AC3H5+CO	1.00E+12	0	3000
393	CH2CO+CH2=C2H4+CO	2.00E+12	0	3000

394	C4H10=C2H5+C2H5	2.00E+16	0	81300
395	C4H10=NC3H7+CH3	1.74E+17	0	85400
396	C4H10=PC4H9+H	1.00E+14	0	100000
397	C4H10=SC4H9+H	1.00E+14	0	100000
398	C4H10+O2=PC4H9+HO2	2.50E+13	0	49000
399	C4H10+O2=SC4H9+HO2	4.00E+13	0	47600
400	C4H10+H=PC4H9+H2	5.63E+07	2	7700
401	C4H10+H=SC4H9+H2	1.76E+07	2	5000
402	C4H10+OH=PC4H9+H2O	4.13E+07	1.7	753
403	C4H10+OH=SC4H9+H2O	7.23E+07	1.6	-247
404	C4H10+O=PC4H9+OH	1.13E+14	0	7850
405	C4H10+O=SC4H9+OH	5.62E+13	0	5200
406	C4H10+CH3=PC4H9+CH4	2.19E+11	0	11400
407	C4H10+CH3=SC4H9+CH4	2.19E+11	0	9600
408	C4H10+C2H3=PC4H9+C2H4	1.00E+12	0	18000
409	C4H10+C2H3=SC4H9+C2H4	8.00E+11	0	16800
410	C4H10+C2H5=PC4H9+C2H6	1.58E+11	0	12300
411	C4H10+C2H5=SC4H9+C2H6	1.00E+11	0	10400
412	C4H10+AC3H5=PC4H9+C3H6	7.94E+11	0	20500
413	C4H10+SC3H5=SC4H9+C3H6	3.16E+11	0	16400
414	C4H10+HO2=PC4H9+H2O2	1.70E+13	0	20460
415	C4H10+HO2=SC4H9+H2O2	1.12E+13	0	17700
416	C4H10+CH3O=PC4H9+CH3OH	3.00E+11	0	7000
417	C4H10+CH3O=SC4H9+CH3OH	6.00E+11	0	7000
418	PC4H9=C2H5+C2H4	2.50E+13	0	28800
419	PC4H9=PC4H8+H	1.26E+13	0	38600
420	SC4H9=PC4H8+H	2.00E+13	0	40400
421	SC4H9=TRAC4H8+H	5.00E+12	0	37900
422	SC4H9=CISC4H8+H	5.00E+12	0	37900
423	SC4H9=C3H6+CH3	2.00E+14	0	33200
424	IC4H7=AC3H4+CH3	1.00E+13	0	51000
425	IC4H8=TC3H5+CH3	1.00E+16	0	87000
426	IC4H8=IC4H7+H	1.00E+17	0	88000
427	IC4H8+O2=IC4H7+HO2	1.20E+14	0	45900
428	IC4H8+O=C3H6+CH2O	4.70E+12	0	0
429	IC4H8+O=IC3H7+HCO	7.24E+05	2.3	-1050
430	IC4H10=IC3H7+CH3	2.00E+17	0	83400
431	IC4H10=TC4H9+H	1.00E+15	0	93300
432	IC4H10=IC4H9+H	1.00E+15	0	98000
433	IC4H10+H=TC4H9+H2	1.26E+14	0	7300
434	IC4H10+H=IC4H9+H2	1.00E+14	0	8400
435	IC4H10+OH=TC4H9+H2O	5.73E+10	0.5	63
436	IC4H10+OH=IC4H9+H2O	2.29E+08	1.5	776
437	IC4H10+O=TC4H9+OH	1.10E+13	0	3280
438	IC4H10+O=IC4H9+OH	3.20E+13	0	5760
439	IC4H10+CH3=TC4H9+CH4	1.00E+11	0	7900
440	IC4H10+CH3=IC4H9+CH4	8.20E+12	0	14200
441	IC4H10+HO2=TC4H9+H2O2	2.80E+12	0	16000
442	IC4H10+HO2=IC4H9+H2O2	2.55E+13	0	20460
443	IC4H10+O2=TC4H9+HO2	2.04E+13	0	41350

444	IC4H10+O2=IC4H9+HO2	1.80E+14	0	46000
445	IC4H10+C2H5=TC4H9+C2H6	1.00E+11	0	7900
446	IC4H10+C2H5=IC4H9+C2H6	1.51E+12	0	10400
447	IC4H10+CH3O=TC4H9+CH3OH	1.90E+10	0	2800
448	IC4H10+CH3O=IC4H9+CH3OH	4.80E+11	0	7000
449	IC4H9=C3H6+CH3	2.00E+13	0	29950
450	IC4H9=IC4H8+H	4.00E+12	0	32800
451	TC4H9=IC4H8+H	8.30E+13	0	38150
452	TC4H9=C3H6+CH3	2.50E+12	0	38150
453	TC4H9+O2=IC4H8+HO2	1.00E+12	0	5000
454	IC4H9+O2=IC4H8+HO2	1.00E+12	0	5000
455	IC4H8+CH3=IC4H7+CH4	8.91E+00	3.5	4420
456	IC4H8+HO2=IC4H7+H2O2	1.95E+04	2.6	13900
457	IC4H8+H=IC4H7+H2	3.47E+05	2.5	2490
458	IC4H8+O=IC4H7+OH	3.47E+11	0	5880
459	IC4H8+OH=IC4H7+H2O	6.31E+06	2	-298
460	TC4H9OCH3=IC4H8+CH3OH	8.00E+13	0	59000 * Original A=4.00E+13
461	TC4H8OCH3=IC4H8+CH3O	5.00E+14	0	24800
462	TC4H9OCH2=CH2O+TC4H9	2.50E+14	0	19800
463	TC4H8OCH3=TC4H9OCH2	3.00E+12	0	15800
464	TC4H9OCH3+H=TC4H8OCH3+H2	8.40E+07	2	7700
465	TC4H9OCH3+H=TC4H9OCH2+H2	1.32E+08	2	5000 * Original A=1.32E+07
466	TC4H9OCH3+CH3=TC4H8OCH3+CH4	1.95E+12	0	11600
467	TC4H9OCH3+CH3=TC4H9OCH2+CH4	6.03E+12	0	9500 * Original A=6.03E+11
468	TC4H9OCH3+C2H5=TC4H8OCH3+C2H6	1.50E+11	0	13400
469	TC4H9OCH3+C2H5=TC4H9OCH2+C2H6	5.00E+11	0	9400 * Original A=5.00E+10
470	TC4H9OCH3+C2H3=TC4H8OCH3+C2H4	1.50E+12	0	18000
471	TC4H9OCH3+C2H3=TC4H9OCH2+C2H4	5.00E+12	0	14000 * Original A=5.00E+11
472	TC4H9OCH3+O=TC4H8OCH3+OH	6.54E+06	2.4	5500
473	TC4H9OCH3+O=TC4H9OCH2+OH	4.17E+14	0	5200 * Original A=4.17E+13
474	TC4H9OCH3+OH=TC4H8OCH3+H2O	1.56E+10	1	1590
475	TC4H9OCH3+OH=TC4H9OCH2+H2O	3.16E+14	0	739 * Original A=3.16E+13
476	TC4H9OCH3+HO2=TC4H8OCH3+H2O2	1.20E+13	0	19400
477	TC4H9OCH3+HO2=TC4H9OCH2+H2O2	8.32E+13	0	17700 * Original A=8.32E+12
478	TC4H9OCH3+CH3O=TC4H8OCH3+CH3OH	4.80E+11	0	7000
479	TC4H9OCH3+CH3O=TC4H9OCH2+CH3OH	1.60E+12	0	3000 * Original A=1.60E+11
480	TC4H9OCH3+O2=TC4H8OCH3+HO2	3.75E+13	0	49000
481	TC4H9OCH3+O2=TC4H9OCH2+HO2	1.25E+13	0	45000
482	TC4H9OCH3+TC4H8OCH3=TC4H9OCH2+TC4H9OCH3	7.50E+10	0	12300
483	CH3OH=CH2OH+H	1.54E+16	0	96790
484	CH3OH+H=CH3O+H2	8.00E+12	0	6095

NOTE : A units mole-cm-sec-K, E units cal/mole

= : reversible reaction

=> : irreversible reaction

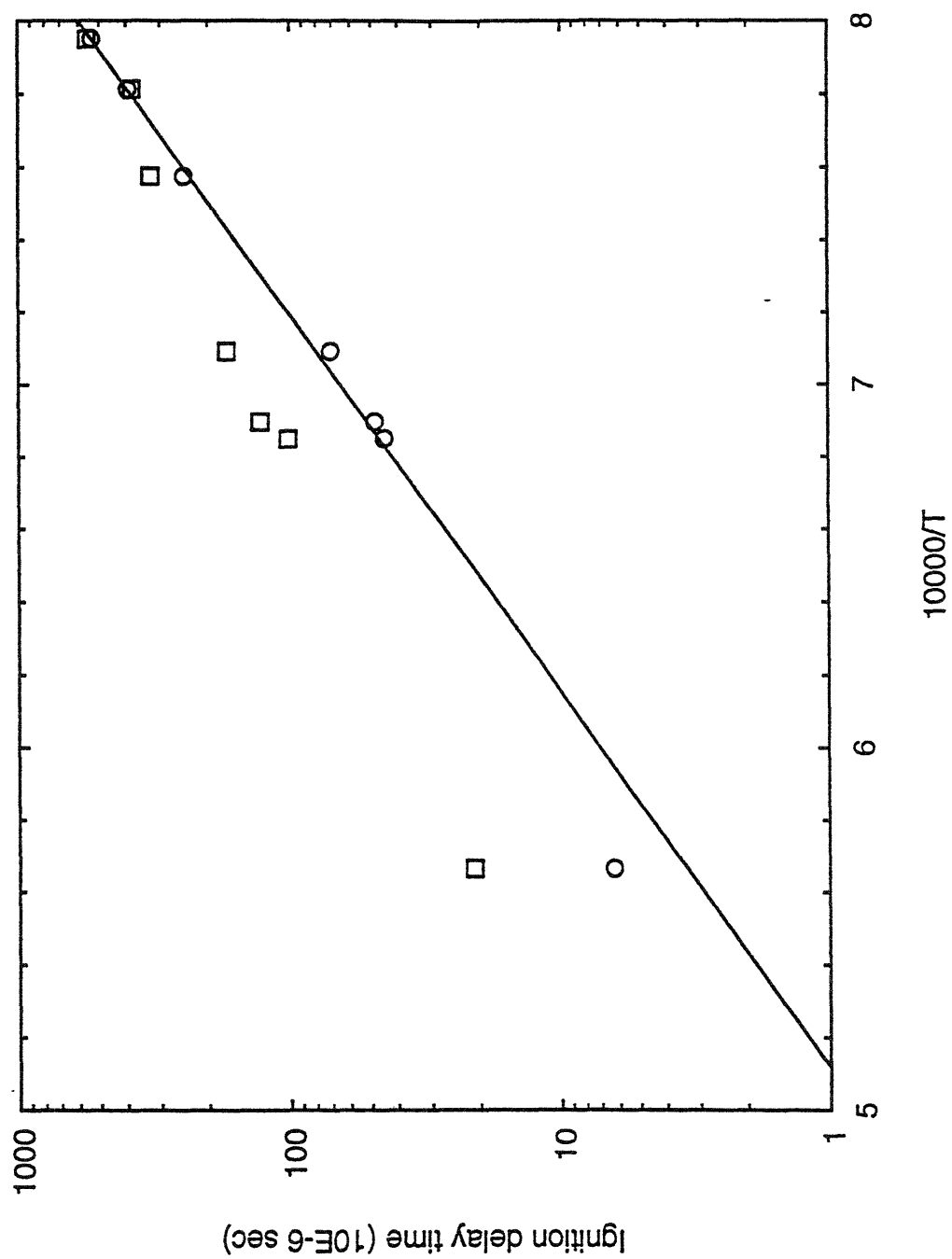


Figure A.1: A comparison of experimental results [19](square symbol) and computed results (circle-line) of ignition delay times for mixture of isooctane, oxygen, and argon. All mixtures contain stoichiometric amount of isooctane and oxygen at approximate 2 atm pressure, with 70% argon diluent.

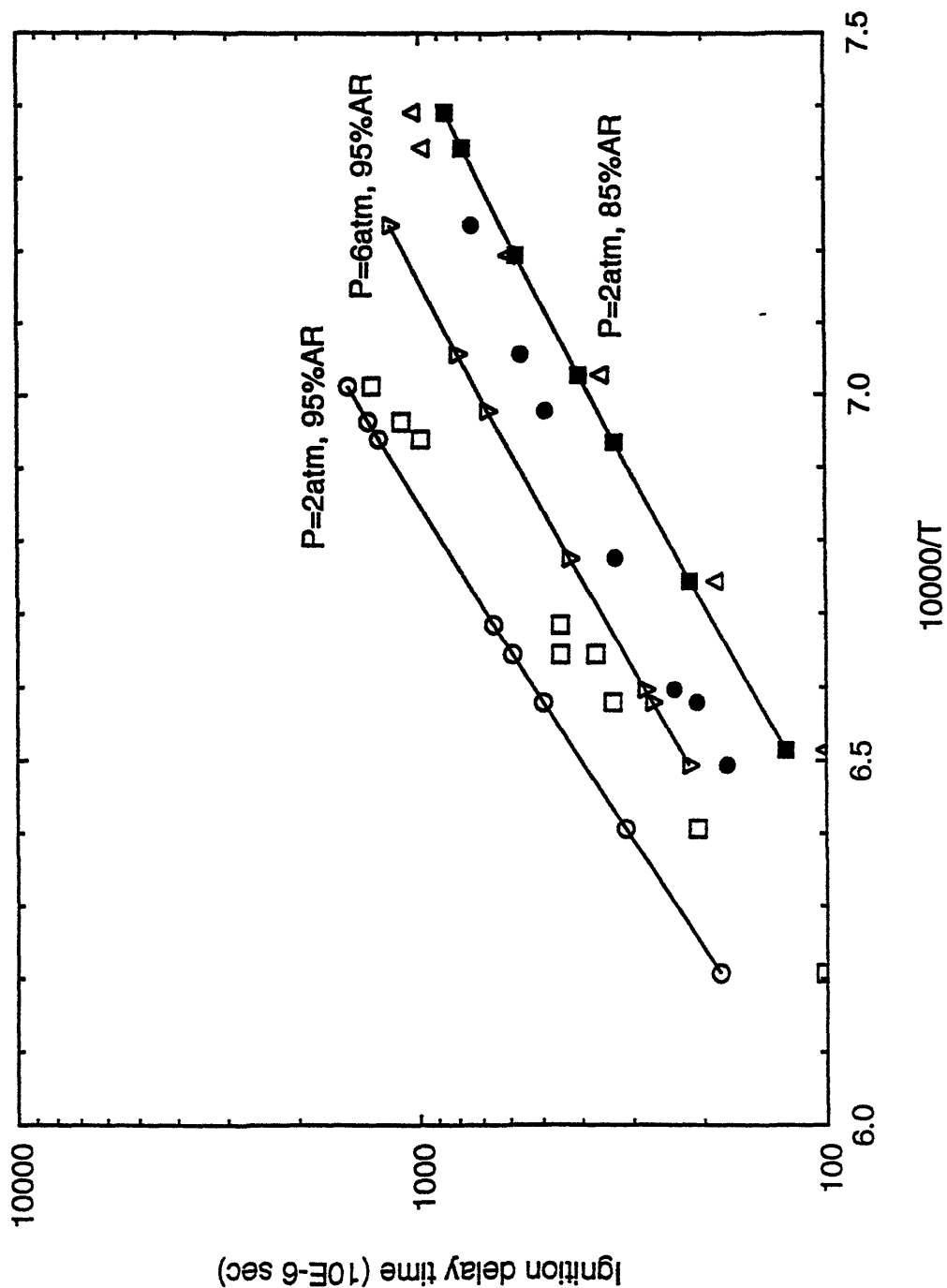


Figure A.2: Comparisons of experimental results [22](symbols) and computed results (lines) of ignition delay times for mixture of toluene, oxygen, and argon. All mixtures contain stoichiometric amount of toluene and oxygen at 2 atm pressure, with 95% argon diluent. (square symbols, circle-line), 6 atm pressure, with 95% argon diluent. (circle symbols, triangle-line), and 2 atm pressure, with 85% argon diluent. (triangle symbols, square-line), respectively.

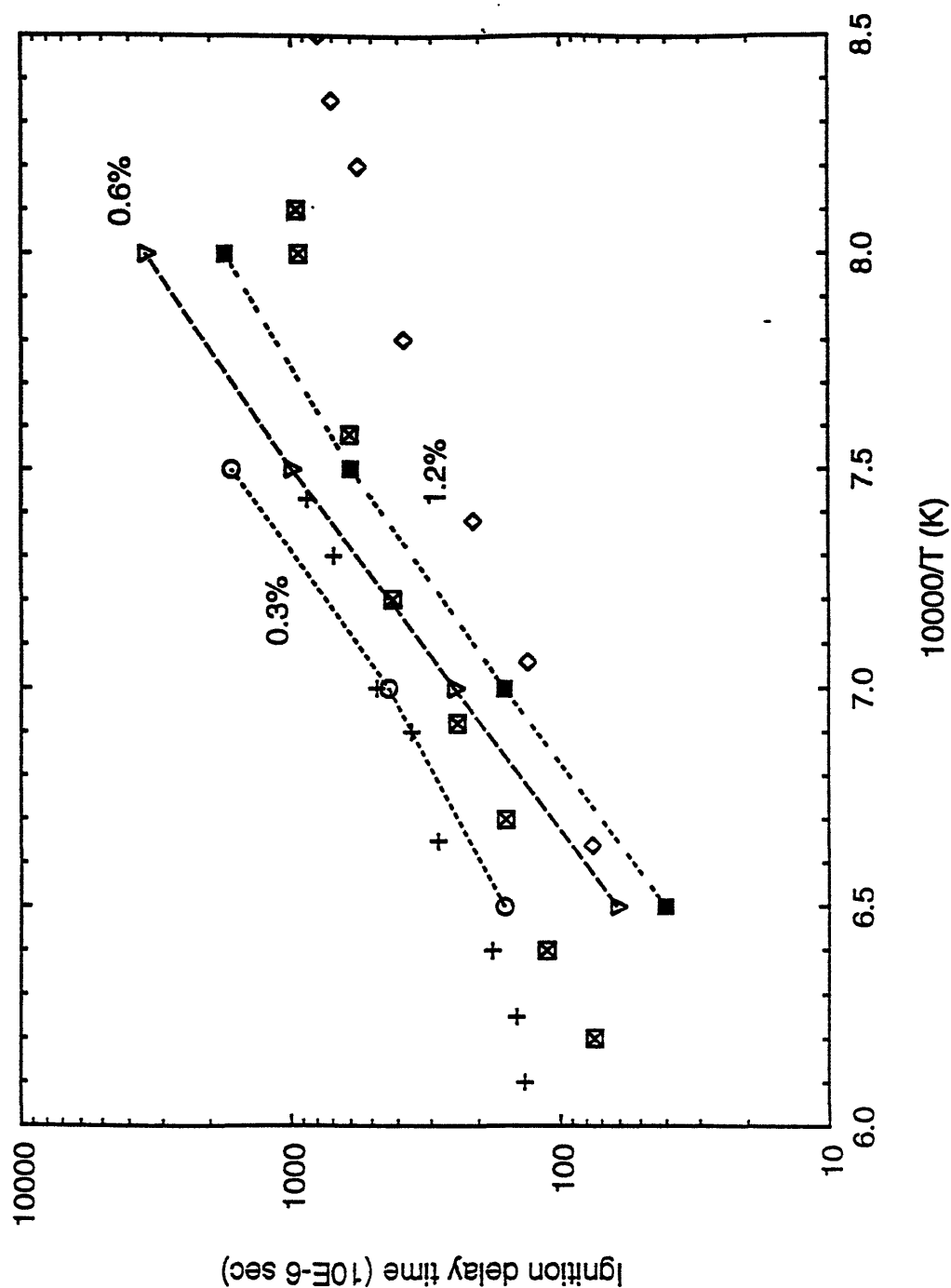


Figure A.3: Comparisons of experimental results [24](symbols) and computed results (lines) of ignition delay times for mixture MTBE, oxygen and argon. All mixtures contain stoichiometric amount of MTBE and oxygen at 3.5 bar pressure, with initial compositions of MTBE/O₂/Ar in the ratios 0.3/2.25/97.45 (cross symbols and circle-line), 0.6/4.5/94.9 (square symbols and triangle-line), and 1.2/9.0/89.8 (diamond symbols and square-line), respectively.