A Progress Report

on

A Comprehensive Kinetic Model of Ethylene and Acetylene Oxidation at High Temperatures

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1. Introduction

The objective of the present study is to develop a comprehensive kinetic model for the combustion of a wide variety of practical fuels. The starting point of such a model is naturally the combustion mechanism of the major intermediates of all hydrocarbon combustion, namely ethylene and acetylene. This is because the initial reaction during the combustion of higher-alkane and alkene compounds are dominated by the $\beta$-scission process, which leads to the production of ethylene. While a substantial amount of ethylene is oxidized to $C_1$ species and formaldehyde, acetylene may form as a result of pyrolytic reactions of ethylene. For stoichiometric to fuel rich flames, acetylene is the dominate intermediate.

A reliable fundamental model should not only be self-consistent and physically justifiable, it should also be predictive for a variety of combustion problems, ranging from ignition, laminar flame propagation, to major and minor species concentrations in flames. There have been several comprehensive kinetic models reported in the literature for the combustion of acetylene and/or ethylene (e.g., Warnatz 1981; Miller et al., 1982; Westbrook and Dryer, 1984; Dagaut et al., 1990). A variety of combustion properties have been successfully predicted by these models. However, recent progresses in the fundamental reaction kinetics and noticeably in the reaction kinetics of the vinyl radical have brought with significant changes to the kinetic rates and pathways during the oxidation of acetylene and ethylene. In addition to the kinetics of the vinyl radical, comprehensive reviews of the kinetic data relevant to acetylene and ethylene combustion are also available and continuously being updated (e.g., Tsang and Hampson, 1986; Baulch et al., 1992, 1994; Frenklach et al., 1995). These factors, along with the critical importance of the acetylene and ethylene chemistry in high-hydrocarbon combustion, warrant a re-examination of the kinetic mechanisms of acetylene and ethylene combustion.

In the present study, we (a) undertook a critical review of the fundamental data of ethylene and acetylene combustion, (b) compiled a detailed kinetic model through a critical review of
relevant kinetic data and through quantum mechanical/RRKM calculations, and (c) performed extensive verification tests of the model against the compiled combustion data. Here, we shall report the results obtained from this phase of study.

2. Critical Survey of Literature Combustion Data

The main purposes of the literature survey are (a) to examine the consistency of the literature data and (b) to compile reliable data for model verification. Review of literature data has been carried out for the shock tube ignition and the detailed structures for burner-stabilized premixed flames of ethylene and acetylene. In the following, we shall present the results of literature survey and data comparison.

2.1. Shock-Tube Ignition

Experimental data for ethylene ignition in shock tubes are limited to the studies by Homer and Kistiakowsky (1967), Baker and Skinner (1972), and Jachimowski (1977). The experimental conditions and methods employed in these studies are summarized in Table 1. These experiments are designated as shock mixtures 1-14.

Data comparison is complicated by the differences in the ignition detection method and definition, and the type of shock waves employed in these studies, as indicated in Table 1. A summary of the data is shown in Figure 1, where the ignition delay times are plotted in the form of $\tau(\mu s) / \left[ [C_2H_4]_o^\alpha [O_2]_o^\beta [Ar]_o^\gamma \right]$, where $[]_o$ denotes the initial reactant concentration (mol/cm$^3$), and $\alpha$, $\beta$, and $\gamma$ empirical parameters to be discussed later. Baker and Skinner (1972) reported only $\tau$-versus-$T_5$ correlations for individual mixtures. The data shown in Figure 1 were generated from their correlations at an approximate temperature interval of 50 K. The experiments of Jachimowski were conducted in incident shock waves. The time elapse between the passage of the shock and the instant of maximum IR emission was scaled from the laboratory times to gas times (Gardiner et al., 1981), and the resulting gas times are plotted in the figure.
Baker and Skinner (1972) presented the correlation equation,
\[ \tau(\mu s) = 10^{-5.9} e^{17200/T} [C_2H_4]_0^{0.3}[O_2]_0^{-1.1}[Ar]_0^{0.4}, \]
on the basis of a least-square fit of their own data. We have derived a more comprehensive correlation equation
\[ \tau(\mu s) = 10^{-57.97} T^{14.854} e^{35900/T} [C_2H_4]_0^{0.230}[O_2]_0^{-0.839}[Ar]_0^{0.247}, \]
which combines the data of Baker and Skinner (1972) and those of the two other studies. A comparison of the data and the correlation equation is presented in Figure 1. The uncertainty factor of the experimental data shown in Figure 1 is estimated to be 2, as judged by the scatter around the line given by the correlation equation.

The level-off of the correlation-equation curve at temperatures higher than 2000 K may be artificial because it is strongly influenced by the data of Jachimowski (1977), who determined the ignition delay as the time elapse between the shock passage and the post-ignition instant of maximum IR emission.

Our correlation equation is qualitatively the same as that of Baker and Skinner (1972). Specifically, an increase in the initial fuel concentration retards ignition, while a similar increase in oxygen concentration strongly promotes ignition. An increase in pressure tends to slow down the ignition process, as indicated by the positive exponent of the diluent argon concentration.

A similar data analysis was carried out for acetylene ignition in shock tubes. The experimental data are summarized in Table 2. These experiments are designated as shock mixtures 15-33. The data can be plotted in a fashion similar to the ethylene plot, as shown in Figure 2. A correlation equation was obtained as
\[ \tau(\mu s) = 10^{-7.035} e^{9770/T} [C_2H_2]_0^{-0.236}[O_2]_0^{-0.701}[Ar]_0^{0.015}, \]
by fitting the data of shock mixtures 16 through 33, but excluding mixtures 17, 22, 23, and 24. It is seen that most of the data fall within a factor of 2 from the fitted line, with the exception of mixture 17 (Bradley and Kistiakowsky, 1961) and mixture 23 (Jachimowski, 1977). In particular, the data of mixture 17 lie significantly lower than the fit, suggesting that
impurity may be responsible for the small ignition delay times observed in the experiments. The data of mixture 23 lie above the fit, which can be well explained by the fact that the induction times were determined as the post-ignition instant of maximum IR emission. The uncertainty factor in the data is estimated to be 2, as judged by the scatter around the fit.

Unlike the ignition of ethylene, increases in the concentrations of acetylene and oxygen generally facilitate the ignition of the mixture. On the other hand, an increase in the total pressure has a very small effect on the ignition delay times.

2.2. Laminar Burning Velocity

There have been several experimental studies reported for the measurement of the laminar burning velocity of ethylene and acetylene in air at the atmospheric pressure. A review of the literature data is given by Egolfopoulos et al. (1990a). In the present study, we adopted the burning velocity data collected in the Princeton counterflow flames (Egolfopoulos et al., 1990b). These data were obtained with a linear extrapolation technique (Wu and Law, 1984), and were re-analyzed using a nonlinear extrapolation technique (Tien and Matalon, 1991) in the work of Sun et al. (1997). Both linearly and nonlinearly extrapolated data will be used for comparison with model calculations.

There are only limit amount of burning velocity data of ethylene and acetylene at variable pressures. Egolfopoulos et al. (1990) reported the burning velocity data of ethylene in nitrogen diluted air (18% O₂/82% N₂) as a function of the equivalence ratio and at the pressures of 0.5, 1, and 2 atm. In addition, the burning velocities were also determined for a stoichiometric mixture at the additional pressures of 0.25 and 3 atm. Similar data were reported for acetylene burning in a nitrogen diluted air (13%O₂/87%N₂) at the pressures of 0.5 and 1 atm with varying equivalence ratios, along with a single point measurement for a stoichiometric mixture at 0.25 atm. These pressure-dependence data have also been included for the purpose of model verification.
2.3. Burner-Stabilized Flames

The major and minor species profiles determined in burner-stabilized premixed flames offer the possibility of model verification on a level more detailed than that based on the global combustion behavior. However, the species profiles are often collected with the intrusive molecular beam mass spectrometric technique, and are expected to be less certain than the burning velocity and ignition delay. Nonetheless, we have included four burner-stabilized flames for the purpose of model verification. The conditions of these flames are summarized in Table 3. For each fuel, we tested our model against the flame structures for a fuel-lean mixture and a fuel rich mixture. There are additional reliable data on sooting acetylene and ethylene flames. Because the current model includes only species with size up to C$_4$H$_4$, these data are not included in the model verification in the current phase of study.

3. Quantum Mechanical and RRKM calculations

3.1. Computational Methodologies

Quantum mechanical calculations were performed with the Gaussian94 program (Frisch et al. 1995). Two different methods were employed in the calculation. In the first method, geometries were optimized with the Density Functional Theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) with the B3LYP functional (Becke, 1993; Lee et al., 1988) and the 6-31G(d) basis set. For energy calculations, we employed the G2 procedure (Curtiss et al., 1991) at the B3LYP/6-31G(d) geometry. This computational procedure is referred to as the G2(B3LYP) method. In the second method, geometry optimization was carried out using the Complete Active Space Multireference Configuration Interaction (CASSCF) method (Eade and Robb, 1981) with the same basis set. The CASSCF energy was corrected by an MP2-level electron correlation.

Thermal rate coefficients were calculated from the microcanonical rate constants obtained from the RRKM theory (Holbrook et al., 1996; Gilbert and Smith, 1990)
\[ k(E) = l_a \frac{Q_r^{\dagger} W(E^{\dagger})}{Q_r \rho(E)}, \]

where \( l_a \) is the reaction path degeneracy; \( Q_r^{\dagger} \) and \( Q_r \) are respectively the partition functions for inactive rotational degrees of freedom of the transition state and the reactant molecule; \( W(E^{\dagger}) \) is the sum of rovibrational energy states of the transition state at energy level \( E^{\dagger} \), \( \rho(E) \) is the density of states of the stable species at energy level \( E = E^{\dagger} + E_o \); \( E_o \) is the energy barrier; and \( h \) is the Planck constant. The direct-count algorithm of Beyer and Swinehart (1973) was used to calculate the sums of energy states, while the densities of states were calculated using the Whitten–Rabinovitch approximation (Whitten and Rabinovitch, 1963; 1964). Active rotations were accommodated using the method of Astholz et al. (1979). The thermal rate coefficients were obtained by assuming a steady state for each of the energized species and by implementing weak collision stabilization.

### 3.2. \( \text{C}_2\text{H}_2 + \text{O}_2 \) Reactions

For acetylene oxidation behind shock waves, the radical-chain process was originally thought to be initiated via two possible steps: (a) the C-H bond fission in acetylene and/or (b) the molecular reaction of acetylene with \( \text{O}_2 \), with the following reaction pathways being previously considered (Gardiner and Walker, 1968; Jachimowski, 1977; Miller et al, 1982),

\[
\begin{align*}
\text{C}_2\text{H}_2 + \text{O}_2 & \rightarrow 2\text{CO} + 2\text{H} & \Delta H = -3.1 \text{ kcal/mol} & (176a) \\
\text{C}_2\text{H}_2 + \text{O}_2 & \rightarrow \text{CHO} + \text{CHO} & \Delta H = -34.5 \text{ kcal/mol} & (176b) \\
\text{C}_2\text{H}_2 + \text{O}_2 & \rightarrow \text{CHCO} + \text{OH} & \Delta H = -2.7 \text{ kcal/mol} & (176c) \\
\text{C}_2\text{H}_2 + \text{O}_2 & \rightarrow \text{CH}_2\text{CO} + \text{O} & \Delta H = -6.3 \text{ kcal/mol} & (176d)
\end{align*}
\]

Recent theoretical (Bauschlicher and Langhoff, 1991) and experimental (Ervin et al., 1990) results placed the C-H bond energy (BDE) of acetylene in the 133 - 134 kcal/mol range. Such a BDE value essentially rules out the C-H bond fission as the most efficient initiation step. Hidaka et al. (1996) recently showed in their shock tube study at temperatures between 1050 and 1600 K that acetylene ignition cannot be adequately predicted without the molecular
reaction 176. Such a conclusion was also reached in an early work of Miller et al. (1982). It was shown that the ignition delay times can be predicted if channel 176a was included in the kinetic scheme with a rate expression of 

\[ k_{176a} = 1 \times 10^{12} \exp[-28(\text{kcal/mol})/RT] \text{ (cm}^3\text{mol}^{-1}\text{s}^{-1}) \]

(Hidaka et al., 1996). We note that this rate expression remains to be a fit to the experimental data. The small activation energy associated with such a molecular reaction is yet to be understood from fundamental consideration of potential energy surfaces. In addition, it was concluded from previous studies (Miller et al., 1982; Hidaka et al. 1996) that specific reaction channel(s) for the molecular reaction cannot be distinguished by kinetic modeling, in that any channel (176a-d) with an appropriately chosen rate coefficient can reproduce the experimental ignition delay data. This situation further demonstrates the need to examine the relevant reaction pathway on the basis of fundamental consideration of reaction energetics.

We considered two possible pathways for the reaction of acetylene with molecular oxygen. The first pathway is the direct attack of O\(_2\) on the triple C≡C bond, forming a hot adduct, which may isomerize to a number of isomers, as depicted in Figure 3. The dissociation of the hot isomers leads to the products consistent with reactions 176b-c. The energy barrier of O\(_2\) attachment to the \(\pi\) bond in acetylene, leading to the H\(\dot{C}\)=CH–O–\(\dot{O}\) biradical, was examined at the G2(B3LYP) and CASSCF levels of theory. Both methods yielded 55 kcal/mol for the energy barrier. We note that Sheng and Bozzelli (1998) reported the results of \textit{ab initio} calculations for the same reaction. At the B3LYP/6-31G(d) and BHANDH/6-31G(d) levels of theory without considering the configuration interaction and basis set extension for energy calculations, the C\(_2\)H\(_2\)-to-O\(_2\) addition energy barrier was found to be 30-35 kcal/mol. Despite of the lower energy barrier for the entrance channel reported by Sheng and Bozzelli (1998), the maximal energy barriers along their proposed pathways, leading to the final dissociated products, were still between 51 and 66 kcal/mol. Thus, it is reasonable to conclude on the basis of the two studies that the energy barrier along the first pathway is close to or greater than 55 kcal/mol.
Recognizing that the energy barrier reported in the literature (Kiefer and Von Drasek, 1990; Smith et al. 1992) for the isomerization of acetylene to vinylidene is 41-45 kcal/mol, and the resulting singlet vinylidene could react with O₂ without an appreciable energy barrier, we examine this second possibility. Figure 4 presents the energy diagram, computed at the G2(B3LYP) level of theory. It is seen that the mechanism depicted in the figure can be viewed as an analog of acetylene dimerization via vinylidene formation and its further reaction but the overall reaction of C₂H₂ with O₂ leading to dissociated products is significantly more exothermic. The addition of H₂CC to O₂ leads to the formation of the biradical adduct with an exothermicity of 63 kcal/mol. The biradical may isomerize to a number of isomers or it may dissociate to CH₂ + CO₂ and CH₂CO + O. The isomers may also dissociate to HCO + HCO, CH₂O + CO, HCO + H + CO. All of the dissociative reactions are chemically activated and highly exothermic, as such the reaction of acetylene and molecule oxygen should lead to

\[ \text{C}_2\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{CC} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{CO} \]

\[ \rightarrow \text{HCO} + \text{H} + \text{CO} \]

\[ \rightarrow \text{HCO} + \text{HCO} \]

\[ \rightarrow \text{CH}_2 + \text{CO}_2 \]

\[ \rightarrow \text{CH}_2\text{CO} + \text{O} \]

The first four product channels can be inferred (Baulch et al. 1992) from the experimental measurements for the reaction

\[ \text{CH}_2\text{CO} + \text{O} \rightarrow \text{products} \]

where CH₂O, CO, CO₂, OH, and H were measured as the products. Based on the analysis described above, the vinylidene pathway should have an overall energy barrier equal to that of the C₂H₂-to-H₂CC: isomerization, which is considerably lower than that of the oxygen attachment to acetylene previously discussed. It follows that the preferred initiation reactions in acetylene oxidation is

\[ \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{H}_2\text{CC} + \text{M} \] (175)

\[ \text{H}_2\text{CC} + \text{O}_2 \rightarrow \text{products} \] (176e)
Because reaction 175 is always in close equilibrium, an overall rate coefficient can be written as
\[
\text{C}_2\text{H}_2 + \text{O}_2 \rightarrow \text{products} \quad (176)
\]
with its rate coefficient given by
\[
k = K_{175} \times k_{176e} = 4.6 \times 10^{15} T^{-0.54} \exp[-45 \text{ (kcal/mol)}/RT] \text{ cm}^3\text{mol}^{-1}\text{s}^{-1}
\]
where \( K_{175} \) is the equilibrium constant of reaction 175, and \( k_{176e} = 1 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \), based on the analogous reaction of singlet methylene with molecular oxygen. The branching ratio to various products cannot be accurately determined from the present study, but this is not critical for the problem of acetylene ignition because any radical produced from reaction 176 (with the exception of \( \text{CH}_2\text{O} + \text{CO} \)) will quickly induce the growth of a radical pool by their subsequent chain-branching reactions. In this present study, we used the \( \text{CH}_2 + \text{CO}_2 \) channel as the product channel.

3.3. CH\(_3\)CO System

The reactions considered involves the bimolecular combination and the chemically activated reactions of \( \text{CH}_2\text{CO} + \text{H} \) and \( \text{CH}_3 + \text{CO} \), i.e.,

\[
\begin{align*}
\text{CH}_2\text{CO} + \text{H} & \quad \Rightarrow \quad \text{[CH}_3\text{CO]}^* \\
\text{[CH}_2\text{CHO]}^* & \quad \Leftrightarrow \quad \text{CH}_2\text{CHO} \\
\text{CH}_3 + \text{CO} & \quad \Leftrightarrow \quad \text{CH}_3\text{CO}
\end{align*}
\]

The vinoxy (\( \text{CH}_2\text{CHO} \)) radical is one of the major intermediate during ethylene and acetylene oxidation. Specifically, vinoxy is produced from the reaction between vinyl (\( \text{C}_2\text{H}_3 \)) and molecular oxygen,
\[
\text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{CH}_2\text{CHO} + \text{H}, \quad (192)
\]
and decomposes quickly to \( \text{CH}_3 + \text{CO} \) and \( \text{CH}_2\text{CO} + \text{H} \),
\[
\text{CH}_2\text{CHO} (+\text{M}) \rightarrow \text{CH}_3 + \text{CO} (+\text{M}) \quad (201)
\]
\[
\text{CH}_2\text{CHO} (+\text{M}) \rightarrow \text{CH}_2\text{CO} + \text{H} (+\text{M}) . \quad (-178)
\]

Because the second decomposition reaction releases the H atom, which is much more reactive than the CH\textsubscript{3} radical, the branching ratio may influence the prediction of the global and detailed combustion characteristics for ethylene and acetylene combustion. There have not been any experimental measurements for this branching ratio, other than some evidence that the first reaction is significantly faster than the second. Tsang (1986) evaluated the rate coefficients of CH\textsubscript{3} + CO recombination, but two new measurements (Baldwin \textit{et al.}, 1987; Bencsura \textit{et al.}, 1992) have emerged since then. The European kinetic data compilation (Baulch \textit{et al.}, 1994) did include the two new studies in their kinetic data evaluation, but the recommendation for the limiting-pressure rate coefficients and the fall-off broadening factor are valid only up to 500 K. In the present study, we extrapolated the low temperature data to high temperatures with RRKM calculations.

Figure 5 presents the potential energy diagram of the reaction. The initial energies are computed at the G2(B3LYP) level of theory. The values are shown in the parentheses in Figure 5. The computed energies were then compared to the enthalpies of formation found in the compilation of Burcat (1996). Minor corrections were made to the stable geometries. The transition-state energies were also slightly adjusted to fit the RRKM rate coefficients to the experimental data. Using the RRKM parameters shown in Table 4 and the potential energies shown in Figure 5, we computed the second-order rate coefficient of CH\textsubscript{3} + CO combination, and compare the theoretical results with selected experimental data of Bencsura \textit{et al.} (1992) and Baldwin \textit{et al.} (1987), as shown in Figure 6. A \(\langle \Delta E \rangle_{\text{down}}\) value of 260 cm\(^{-1}\) was used for helium to fit the data of Bencsura \textit{et al.} (1992), and the data of Baldwin \textit{et al.} (1987) were fitted with \(\langle \Delta E \rangle_{\text{down}} = 100\) cm\(^{-1}\) for argon. The pressure dependent rate coefficients were fitted in Troe's formula (Gilbert \textit{et al.} 1982) and shown in Appendix A.

The rate coefficient was also computed for the chemically activated reaction
\[
\text{CH}_2\text{CO} + \text{H} \rightarrow \text{CH}_3 + \text{CO} . \quad (180)
\]
Comparison with the experimental data is shown in Figure 7. RRKM calculations reveal that the pressure has little influence on the rate coefficient of this reaction. Unlike the recommendation of Baulch et al. (1992), which is based on an extrapolation of the low-temperature data, our RRKM results show a significant upward curvature on an Arrhenius plot at high temperatures, and support the high-temperature data of Frank et al. (1986). The RRKM results can be represented by a modified Arrhenius equation as

\[ k = 1.5 \times 10^9 T^{1.43} \exp(-1350/T) \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \text{ over range 200 - 2500 K} \]

3.4. C\textsubscript{3}H\textsubscript{4} and C\textsubscript{3}H\textsubscript{5} Systems

The reactions of propyne and allene mutual isomerization and of propyne + H, allene + H, and CH\textsubscript{3} + C\textsubscript{2}H\textsubscript{2} were studied with quantum mechanical and RRKM calculations. The quantum mechanical calculations were performed at the G2(B3LYP) level of theory. The results have been reported in a journal article (Davis et al. 1999), which is attached as Appendix B.

4. Detailed Kinetic Model

The detailed kinetic model compiled in the present study consists of 52 species and 367 elementary reactions. This model was compiled for ethylene and acetylene combustion and is based on a series of works reported in the past (Sun et al. 1996, Wang et al., 1996, Davis et al. 1998b, Wang and Frenklach, 1997). The small-species chemistry is largely based on the GRI-Mech (Frenklach et al. 1995). Whenever possible, we used Troe’s fall-off formalism (Gilbert et al., 1983) to describe the pressure dependence of the rate coefficients for unimolecular dissociation and bimolecular combination reactions. The kinetic model retains a reasonable number of C\textsubscript{3} and C\textsubscript{4} species to ensure proper simulation under the fuel-rich conditions and to make it possible for expansion of the kinetic model to include large hydrocarbon chemistry.
4.1. $\text{H}_2/\text{O}_2$ Chemistry

The H/O chemistry was taken from the GRIMech (Frenklach et al. 1995), with the exception of the reactions

$$\text{HO}_2 + \text{H} \rightarrow \text{OH} + \text{OH}$$

$$\text{HO}_2 + \text{H} \rightarrow \text{H}_2 + \text{O}_2,$$

whose rate coefficients were taken from the recent work of Mueller et al. (1998).

4.2. $\text{C}_1$ Chemistry

The C$_1$ chemistry is largely based on the GRIMech. The reaction of triplet methylene with molecular oxygen was found to exert a large influence on the ignition characteristics of acetylene. Two product channels were considered, including

$$\text{CH}_2 + \text{O}_2 \rightarrow \text{HCO} + \text{OH} \quad (55)$$

$$\text{CH}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H} + \text{H} \quad (56)$$

We adopted the total rate coefficient from the GRIMech compilation (Frenklach et al. 1995), and assigned the branching ratio $k_{55}/(k_{55}+k_{56}) = 0.8$, based on the CO-to-CO$_2$ ratio detected in the work of Bley et al. (1992) and Dombrowsky and Wagner (1992).

The bimolecular combination and chemically activated reactions of CH$_3$ and HCO were included in the kinetic model, with their rate coefficients derived from an RRKM analysis. These reactions are

$$\text{CH}_3 + \text{HCO} (+\text{M}) \rightarrow \text{CH}_3\text{CHO} (+\text{M}) \quad (99)$$

$$\text{CH}_3\text{CO} + \text{H} (+\text{M}) \rightarrow \text{CH}_3\text{CHO} (+\text{M}) \quad (211)$$

$$\text{CH}_2\text{CHO} + \text{H} (+\text{M}) \rightarrow \text{CH}_3\text{CHO} (+\text{M}) \quad (202)$$

$$\text{CH}_3\text{CO} + \text{H} \rightarrow \text{CH}_3 + \text{HCO} \quad (212)$$

$$\text{CH}_2\text{CHO} + \text{H} \rightarrow \text{CH}_3 + \text{HCO} \quad (204)$$

$$\text{CH}_2\text{CHO} + \text{H} \rightarrow \text{CH}_3\text{CO} + \text{H} \quad (203)$$

The motivation for this RRKM analysis is again the need to consider the destruction reactions of vinoxy (CH$_2$CHO), a product of vinyl oxidation by molecular oxygen.
4.3. C₂ Chemistry

Among reactions pertinent to ethylene and acetylene oxidation, the sum of the rate coefficients of the reaction

\[
\begin{align*}
C_2H_2 + O & \rightarrow HCCO + H \\
C_2H_2 + O & \rightarrow CH_2 + CO
\end{align*}
\]

was taken from the GRIMech compilation, but the branching ratio was assigned to be \( k_{155}/(k_{155}+k_{156}) = 0.8 \), based on the work of Michael and Wagner (1990). The reaction of vinyl + O was split into two channels,

\[
\begin{align*}
C_2H_3 + O & \rightarrow CH_2CO + H \\
C_2H_3 + O & \rightarrow CH_3 + CO
\end{align*}
\]

based on Donaldson et al. (1995). The total rate coefficient of \( 9.6 \times 10^{13} \text{ cm}^3\text{mol}^{-1}\text{s}^{-1} \) was adopted from the compilation of Tsang and Hampson (1996).

The reaction between vinyl and molecular oxygen influences very significantly the combustion characteristics of ethylene. Slagle et al. (1984) determined the mechanism of the reaction to be

\[
C_2H_3 + O_2 \rightarrow HCO + CH_2O
\]

at 298 and 600 K. Westmoreland (1996) and Bozzelli and Dear (1993) employed the QRRK technique to calculate the branching ratios of the reaction and reported that vinoxy + H may be a significant product channel. Since these two studies, a new mechanism has been proposed by Carpenter (1993, 1995). This mechanism involves the cyclization of the \( \text{C}_2\text{H}_3\text{O}_2 \) adduct radical to a three-member-ring dioxiranyl radical. Recently, Mebel et al. (1996) performed \textit{ab initio} and RRKM calculations for the multichannel rate coefficients of the \( \text{C}_2\text{H}_3 + \text{O}_2 \) reactions, and concluded that the HCO + CH₂O channel has the highest rate constant, and at \( T > 900 \text{ K} \), the CH₂CHO + O are the major products. At very high temperatures, the channel producing \( \text{C}_2\text{H}_2 + \text{HO}_2 \) becomes competitive. Based on this latter study, we specified the following reactions for the reaction of vinyl + \( \text{O}_2 \),

\[
\begin{align*}
C_2H_3 + O_2 & \rightarrow HCO + CH_2O
\end{align*}
\]
\[
\begin{align*}
C_2H_3 + O_2 & \rightarrow C_2H_2 + HO_2 \quad \text{(191)} \\
C_2H_3 + O_2 & \rightarrow CH_2CHO + O \quad \text{(192)} \\
C_2H_3 + O_2 & \rightarrow HCO + CH_2O , \quad \text{(193)}
\end{align*}
\]

and adopted the RRKM rate parameters of Mebel et al. (1996).

The kinetics of CH$_3$CO and CH$_3$CHO was included in the kinetic model. The rate parameters were taken mainly from Tsang and Hampson (1986) for CH$_3$CO and from Baulch et al. (1994) for CH$_3$CHO.

The rate parameters of the H-abstraction of ethylene by the H atom

\[
C_2H_4 + H \rightarrow C_2H_3 + H_2 \quad \text{(226)}
\]

were updated, based on the recent work of Knyazev et al. (1996), who experimentally determined $k_{226}$ in the temperature range 499-947 K and performed \textit{ab initio} studies and transition state calculations. Their rate expression yields a rate constant at 1200 K which is about a factor of 2 lower than the compilation of the GRI-Mech.

### 4.4. C$_3$ and C$_4$ Chemistry

The C$_3$ and C$_4$ chemistry becomes relevant for fuel rich combustion. In the present model, we included the chemistry of propyne, allene and propene, and incorporated the results of Davis et al. (1998a, 1998b), who studied the pyrolysis and oxidation kinetics of propyne and propene in laminar flames and in a flow reactor. The chemistry of C$_4$H$_2$ and C$_4$H$_4$ is also included in the kinetic model. The rate parameters for the relevant reactions were taken from Wang and Frenklach (1997). The inclusion of the C$_3$ and C$_4$ chemistry not only ensures the fuel-rich chemistry is adequately accounted for by the present model, it also provides an easy extension of the kinetic model to include the chemistry of higher hydrocarbons.
5. Simulation of Shock-Tube Experiments

5.1. Ethylene Oxidation in Shock Tubes

The shock tube simulation was performed using the Sandia Chemkin-II codes (Kee et al., 1989) with a constant-density model for experiments conducted behind reflected shock waves and with the Sandia Shock code (Mitchell and Kee, 1982) for incident shock waves. When possible, the computational ignition was defined in the same fashion as the experiment.

Figures 8-11 presents the experimental data and computational results for ethylene oxidation in shock tubes. A total 13 mixtures were used for data comparison, covering a wide range of equivalence ratio, pressure, and temperature. The ignition delay data shown in Figure 11 are derived from the correlation equations reported by Baker and Skinner (1972), and are not the actually data points. In addition, the experimental ignition delay data with values greater than 2000 µs are not shown in the figure. Excessively long induction-time data are expected to be inaccurate because of the growth of non-ideality and the decay of shock wave at long reaction time after shock passage.

In general, the shock-tube ignition delay times were reasonably well predicted, keeping in mind that the uncertainty factor in the experimental data is a factor of 2. The experimental data of Jachimowski (1977) were collected in incident shock waves under the condition of extremely short induction times, ~10 µs. Although measurements with such short induction times are extremely difficult, the agreement is surprisingly good between experiment and simulation (see Figure 9).

Jachimowski (1977) also reported the maximum of concentration product, [CO][O], based on the ultraviolet emission intensity at 0.37 µm due to CO + O → CO₂ + hv. These data provide a more unambiguous and stringent test for the kinetic model. Figure 10 presents the comparison of the experimental and computed maximum [CO][O]. It is seen that the experimental data are nicely predicted by the current model.

The current kinetic model does not predict well the ignition delay times of shock mixtures 6 and 7 reported by Baker and Skinner (1972). Both mixtures are fuel-rich with the
equivalence ratio equal to 2. It is conceivable that the kinetic model is inadequate in predicting
the ignition of fuel-rich ethylene mixtures. At the same time, one should recognize that
experimental ignition point may be difficult to define, as it is based on the maximum intensity
of light emission after shock passage. The detailed temporal profiles computed for these two
mixtures reveal that the oxidation appears to be a slow process, and thus it is difficult to
pinpoint the ignition point experimentally.

Because the experimental data for ethylene ignition are rather old and scarce, the current
modeling effort suggests the need for additional data especially in the middle temperature range
of 1200 - 1800 K, where only one series of study was reported.

5.2. Acetylene Oxidation in Shock Tubes

Figures 12-20 presents comparisons of experimental data and computational results for
acetylene oxidation in shock tubes. Some 17 mixtures were included for the purpose of model
verification. Again, the predictions for ignition delay times are generally very good, both
qualitatively and quantitatively. In almost all cases, the prediction is well within the uncertainty
of the data reported for these mixtures.

In addition to the ignition delay, more stringent tests for the model were carried by
comparing the experimental data with the numerical predictions for species concentrations
during the oxidation of acetylene. Figure 15 shows the experimental and computed maximum
\([O][CO]\) for two mixtures reported by Jachimowski (1977). It is seen that the experimental
data are well predicted by the current model. On the other hand, the prediction is not
satisfactory for the temporary CO\(_2\) concentration profiles reported by Hidaka et al. (1996), as
seen in Figure 20.

We also compared the model predictions for the laser Schlieren profiles measured prior to
the ignition of acetylene, as seen in Figure 18. These profiles characterize the induction-zone
exothermicity during acetylene oxidation in shock tubes.
5.3. Mechanisms of Acetylene and Ethylene Oxidation in Shock Tubes

The mechanistic feature of the oxidation of hydrocarbons in shock tube is that upon shock heating of the fuel-oxygen-diluent mixture, the initiation reactions generate an initial radical pool. Over a finite period of reaction, the radical pool, albeit small, grows exponentially in size via a chain reaction mechanism, although at this stage the consumption of the fuel is insignificant. The chain mechanism eventually causes the mixture to ignite, during and after which the fuel is quickly consumed, products are formed, and heat is released over a reaction time considerably shorter than the time to ignition.

The radical-chain initiation reaction is an essential part in our understanding of the mechanism of spontaneous ignition of fuel-oxygen mixtures. Two types of initiation reactions have been previously considered, namely, the H-abstraction of fuel by molecular oxygen and the unimolecular dissociation of the fuel. Here, we uncover a third possible initiation reaction mechanism. This mechanism is dominated by the production of vinylidene, followed by the oxidation of vinylidene by molecular oxygen. The theoretical justification for the mechanism of the initial radical production in acetylene oxidation has been discussed in section 3.2. The agreement between experimental data and theoretical prediction seen in Figures 12-20 further confirms that the reaction sequence given by (175) and (176) is responsible for the production of the initial radical pool. Thus, like the dimerization mechanism of acetylene pyrolysis below 1800 K (Kiefer and Von Drasek, 1990) acetylene oxidation in shock tubes is initiated by the isomerization of acetylene to vinylidene. The initial radical pool is then established via the reaction of vinylidene and molecular oxygen.

For ethylene oxidation in shock tubes, we identified the following reaction sequence, again involving vinylidene formation via 1,1-elimination in ethylene, followed by the reaction of vinylidene with molecular oxygen, as the process which leads to the production of initial free radicals,

\[
\begin{align*}
C_2H_4 (+M) &\rightarrow H_2CC + H_2 \\
H_2CC + O_2 &\rightarrow \text{radical products}
\end{align*}
\]
An additional issue relevant to acetylene ignition concerns the reaction between methylene and molecular oxygen. Hidaka *et al.* (1996) concluded that in order to predict the early production of CO$_2$ in their experiments, the products must be assigned as CO$_2$ + 2H• for the reaction of the triplet methylene with O$_2$. This conclusion is in an apparent disagreement with the LS experiments of Hwang *et al.* (1987), who concluded on the basis of computer modeling of LS profiles that CO$_2$ could not be the major product of the :CH$_2$ + O$_2$ reaction. This conclusion was supported later by the direct experimental investigations (Dombrowsky and Wagner, 1992; Bley *et al.*, 1992) of the same reaction. Our computer simulation results indicate that Hidaka *et al.*’s data can be well predicted with •CHO + •OH as the only channel of the :CH$_2$ + O$_2$ reaction, without having to consider CO$_2$ + 2H• as the products.

6. Simulation of Laminar Burning Velocity

Figure 21 presents the comparison between experimental and computed laminar burning velocity of ethylene and acetylene in air at atmospheric pressure. The current model predicts the ethylene data much better than our previous version (Sun *et al.*, 1996). The model still predicts lower burning velocities than the experimental data for moderately fuel-rich acetylene-air mixtures, although the data on the fuel-lean side of stoichiometry are well accounted for by the kinetic model.

Burning velocities at reduced and elevated pressures were also included for model comparison. Figure 22 shows the variation of burning velocity as a function of pressure and equivalence ratio for mixtures of ethylene in a N$_2$ diluted air (O$_2$/N$_2$ = 18/82). It is seen that agreement between experiment and model is quite good. Figure 23 presents the variation of the experimental and computational burning velocity as a function of pressure for a stoichiometric mixture of ethylene in the N$_2$ diluted air. It is seen that the pressure dependence is well captured by simulation, although the predicted burning velocities are higher than the experimental data by ~2-3 cm/s for pressure greater or equal than 0.5 atm.
Figures 24 and 25 present the similar plots for the pressure dependence of the burning velocity of acetylene in an N$_2$ diluted mixture (O$_2$/N$_2$ = 13/87). For stoichiometric and fuel-rich mixtures, the model predictions are larger than the experimental data, which is opposite to the trend observed for the acetylene-air mixtures shown in Figure 21, where the predictions are seen to be smaller than the experimental data for the fuel-rich conditions. A first order sensitivity analysis does not show that for burning velocity predictions the influential reactions are different between the acetylene-air and acetylene-N$_2$-diluted air mixtures. It is likely that a further improvement of the kinetic mechanism cannot be achieved before the acetylene data are re-examined.

7. Simulation of Burner-Stabilized Flames

For the simulation of Flames 1 and 2, we followed the suggestion of Bhargava and Westmoreland (1998a, b) and lowered the measured flame temperature by 100 K to account for the probe effect. In addition, the temperature profile was shifted downstream by 0.05 cm to account for perturbation caused by the thermocouple, and the species profiles were moved 0.09 cm toward the burner surface to account for the quartz probe effect.

Figure 26 presents the mole fraction profiles of the major species in Flame 1, a fuel-rich ethylene flame reported by Bhargava and Westmoreland (1998a). It is seen that the kinetic model predicts the species profiles very well. Figure 27 shows the experimental and computed mole fraction profiles of H and OH. The agreement is better than 40%. Figures 28 and 29 present the comparison of model and experiment for 16 minor species. It is seen that peak concentrations of most species are predicted to within a factor of 2. The width and the shapes of the mole fraction profiles are also reasonably well predicted.

Figure 30 presents the mole fraction profiles of major species in Flame 2 (Bhargava and Westmoreland, 1998b). It is seen that the agreement between model and experiment worsen for this fuel-lean ethylene flame. In particular, the model underpredicts quite significantly CO$_2$ concentrations in the post flame zone. It is likely that this difference is caused by the
discrepancy between model and experiment for the concentrations of the major radical species, as shown in Figure 31. The present model predicts the peak mole fractions of O and H to be 2 times higher than the experimental counterparts. In addition, the peak OH concentration was also over-predicted by about 50%. First order sensitivity tests show that the differences between model and experiment cannot be easily accounted for by adjusting the rate parameters in the kinetic model within the uncertainty of these parameters. Figures 32 and 33 show the comparison for 12 minor species measured in Flame 2.

For the two acetylene flames (Flames 3 and 4), the agreement between model and experiment is generally good, as seen in Figures 34 through 37. For Flame 3, most of the minor species concentrations were predicted to within the experimental uncertainties. Overpredictions for C\textsubscript{3}H\textsubscript{3} and C\textsubscript{4}H\textsubscript{2} are likely to be caused by the lack of molecular mass growth processes in the present kinetic model. The discrepancy between model and experiment for CH\textsubscript{4} at distances close to the burner is likely to be caused by the recombination of methyl and the H atom on the burner surface. Such an effect is not account for by the numerical simulation.

8. Summary

In this work, we proposed a comprehensive kinetic model for acetylene and ethylene combustion. The kinetic model has been compiled on basis of both critical review of the recent literature kinetic data and theoretical calculations using modern quantum mechanical tools and the RRKM method. The kinetic parameters were taken from experimental/theoretical sources without invoking ad hoc adjustments. The comprehensiveness of the model is demonstrated by extensive verification tests against a variety of combustion data, including ignition behaviors, laminar flame propagation, and detailed structure of burner stabilized flames. It is shown that most of the reliable combustion data are well predicted by the kinetic model.

Through this study, we have concluded that the source of the initial radical pool in ethylene and acetylene oxidation in shock tubes originate from reaction pathways of vinylidene.
In the case of acetylene oxidation, the initiation reactions involves the isomerization of acetylene to vinylidene, followed by the reaction of vinylidene and molecular oxygen to produce the initial radical pool. For ethylene oxidation, the initiation steps are vinylidene formation via 1,1-elimination of H₂ in ethylene, followed again by the reaction between vinylidene and molecular oxygen. This is a significant finding as we have expanded the two previously understood initiation mechanisms of radical chain reactions, namely, unimolecular dissociation of the parent fuel and the H-abstraction of the fuel by molecular oxygen, to three possible mechanisms. Based on preliminary analysis of reaction energetics, it is likely that the new mechanism involving vinylidene and other carbene species dominates the initiation reactions for a large body of alkene compounds.
9. References


Table 1. Shock-Tube Ignition Delay of Ethylene-Oxygen-Argon Mixtures.

<table>
<thead>
<tr>
<th>No.</th>
<th>φ</th>
<th>Mole Percent</th>
<th>$P_5$ or $P_2$</th>
<th>$T_5$ or $T_2$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.5</td>
<td>3.0</td>
<td>0.6-0.8</td>
<td>1505-2225</td>
<td>Reflected shock wave</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>0.5</td>
<td>1.0</td>
<td>0.6-0.7</td>
<td>1540-2325</td>
<td>IR emission from CO</td>
</tr>
</tbody>
</table>
<pre><code>                      |     |              |                |                |                                |                                 |
</code></pre>
<p>| 3   | 1.0 | 1.0          | 3.0            | 3              | 1112-1556                      | Reflected shock wave            |
| 4   | 0.5 | 0.5          | 3.0            | 3              | 1118-1430                      | Maximum light emission          |
| 5   | 1.0 | 0.25         | 0.75           | 12             | 1176-1531                      | (maximum point close to        |
| 6   | 2.0 | 2.0          | 3.0            | 3              | 1117-1616                      | that of a rapid pressure        |
| 7   | 2.0 | 1.0          | 1.5            | 3              | 1155-1747                      | rise)                           |
| 8   | 0.5 | 1.0          | 6.0            | 3              | 1080-1440                      |                                 |
| 9   | 0.13| 0.25         | 6              | 3              | 1058-1418                      |                                 |
| 10  | 0.5 | 0.25         | 1.5            | 3              | 1100-1628                      |                                 |
| 11  | 2.0 | 0.5          | 0.75           | 3              | 1166-1876                      |                                 |
| 12  | 0.5 | 1            | 6              | 1.2-1.6        | 1800-2301                      | Incident shock wave            |
| 13  | 1.0 | 2            | 6              | 1.2-1.7        | 1815-2339                      | Maximum IR                      |
| 14  | 1.5 | 3            | 6              | 1.3-1.7        | 1868-2311                      | emission due to CO + O → CO₂ + hv |</p>
Table 2. Shock-Tube Ignition Delay of Acetylene-Oxygen-Argon Mixtures.

<table>
<thead>
<tr>
<th>Shock No.</th>
<th>φ (Mole Percent)</th>
<th>P5 or P2 (atm)</th>
<th>T5 or T2 (K)</th>
<th>Method</th>
<th>Reference</th>
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<tbody>
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<td>15</td>
<td>0.78</td>
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<td>3.2</td>
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<td>1370-2455 Incident shock wave</td>
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<td></td>
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<td></td>
<td></td>
<td>UV emission from OH</td>
<td>Stubbeman &amp; Gardiner (1961)</td>
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<tr>
<td>16</td>
<td>1.65</td>
<td>1.35</td>
<td>2.04</td>
<td>0.09-0.16</td>
<td>1610-2050 Incident shock wave</td>
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<td></td>
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<td>X-ray densitometry</td>
<td>Gardiner (1961)</td>
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<td>17</td>
<td>3.21</td>
<td>10.8</td>
<td>8.4</td>
<td>0.19-0.28</td>
<td>954-1090 Reflected shock wave</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>Onset of CO &amp; H2O production (TOF mass spec.)</td>
<td>Bradley &amp; Kistiakowsky (1961)</td>
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<tr>
<td>18</td>
<td>0.32</td>
<td>0.57</td>
<td>4.43</td>
<td>0.06-0.12</td>
<td>1293-1994 Reflected shock wave</td>
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<td></td>
<td></td>
<td>Kistiakowsky &amp; Richards (1962)</td>
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<td>19</td>
<td>3.45</td>
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<td>2.1</td>
<td>0.09-0.13</td>
<td>1694-2049 Onset of vacuum UV radiation</td>
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<tr>
<td>20</td>
<td>1.67</td>
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<td>3.0</td>
<td>0.07-0.16</td>
<td>1391-2371 Reflected shock wave</td>
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<tr>
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<td>IR emission from CO &amp; CO2 (10% maximum value)</td>
<td>Homer &amp; Kistiakowsky (1967)</td>
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<tr>
<td>21</td>
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<td>0.8</td>
<td>0.6-0.76</td>
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<td></td>
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<td>IR emission due to CO + O → CO2 + hv</td>
<td>Homer &amp; Kistiakowsky (1967)</td>
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<tr>
<td>22</td>
<td>0.67</td>
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<td>3.75</td>
<td>1.2-1.5</td>
<td>1823-2322 Reflected shock wave</td>
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<tr>
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<td>Maximum IR emission due to CO + O → CO2 + hv</td>
<td>Jachimowski (1977)</td>
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<tr>
<td>24</td>
<td>-</td>
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<td>1.3-1.6</td>
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<tr>
<td></td>
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<td>due to CO + O → CO2 + hv</td>
<td>Hidaka et al. (1981)</td>
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<tr>
<td>25</td>
<td>2.0</td>
<td>2.0</td>
<td>2.5</td>
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<td>1171-1705 Reflected shock wave</td>
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<tr>
<td>26</td>
<td>0.71</td>
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<td>27</td>
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<td>28</td>
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<td>1.25</td>
<td>0.22-0.34</td>
<td>1528-2173 Incident shock wave</td>
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<td>Maximum LS density gradients</td>
<td>Hidaka et al. (1984)</td>
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<td>29</td>
<td>0.25</td>
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<td>5.0</td>
<td>0.19-0.30</td>
<td>1346-1949 Incident shock wave</td>
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<td>Hidaka et al. (1984)</td>
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<td>30</td>
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<td>1.1-2.0</td>
<td>1092-1565 Reflected shock wave</td>
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<td>31</td>
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<td>1.0</td>
<td>5.0</td>
<td>1.1-1.7</td>
<td>1051-1393 Onset of IR emission from CO2</td>
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<tr>
<td>32</td>
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<td>1.3-2.1</td>
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<td>1.0</td>
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<td>1.2-1.8</td>
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<tr>
<td>34</td>
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<td>2.0</td>
<td>2.5</td>
<td>1.3-1.9</td>
<td>1177-1467 Onset of IR emission from CO2</td>
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* With an additional 0.5% H2.  
* with an additional 1% C2H4.
Table 3. Laminar Premixed Flat Flames for Model Verification

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<th>No.</th>
<th>Reactants</th>
<th>$\phi$</th>
<th>$p$</th>
<th>$v_0$</th>
<th>$T_{\text{max}}$</th>
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<td>1</td>
<td>$0.194\text{C}_2\text{H}_4-0.306\text{O}_2-0.5\text{Ar}$</td>
<td>1.9</td>
<td>20</td>
<td>62.5</td>
<td>2090</td>
<td>Bhargava and Westmoreland, 1998a</td>
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<td>2</td>
<td>$0.086\text{C}_2\text{H}_4-0.345\text{O}_2-0.569\text{Ar}$</td>
<td>0.75</td>
<td>30</td>
<td>30</td>
<td>1925</td>
<td>Bhargava and Westmoreland, 1998b</td>
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<tr>
<td>3</td>
<td>$0.465\text{C}_2\text{H}_2-0.485\text{O}_2-0.05\text{Ar}$</td>
<td>2.4</td>
<td>20</td>
<td>50</td>
<td>1900</td>
<td>Westmoreland et al., 1986</td>
</tr>
<tr>
<td>4</td>
<td>$0.03\text{C}_2\text{H}_2-0.97\text{O}_2$</td>
<td>0.077</td>
<td>76</td>
<td>57</td>
<td>$&gt;1300$</td>
<td>Eberius et al. 1973</td>
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Table 4. RRKM Parameters for the Reaction of CH$_3$CO.

<table>
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<tr>
<th>Compound</th>
<th>Freq (cm$^{-1}$)</th>
<th>$B_0$ (cm$^{-1}$)</th>
<th>Path deg.</th>
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<tr>
<td>CH$_3$CO</td>
<td>454.6 839.3 943.7 1038.0 1355.0 1458.3 1898.9 2982.9 3070.7 3073.7</td>
<td>0.321(1,2) - inactive 6.433(3,1) - active 2.761(1,1) - active</td>
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</tr>
<tr>
<td></td>
<td>$\sigma$ = 3.97 Å, $\epsilon/k_B$ = 436 K</td>
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<tr>
<td>TS1</td>
<td>250.7 399.5 449.9 529.3 690.4 991.8 1137.7 1399.2 2184.3 3144.3 3232.2</td>
<td>0.299(1,2) - inactive 2.962(1,1) - active</td>
<td>1</td>
</tr>
<tr>
<td>TS2</td>
<td>219.7 434.7 458.1 766.0 1408.7 1412.8 2066.3 3071.2 3231.6 3240.7</td>
<td>0.211(1,2) - inactive 5.780(3,1) - active 1.891(1,1) - active</td>
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</tr>
<tr>
<td>TS3</td>
<td>421.2 622.6 834.6 1021.8 1114.3 1224.4 1452.9 1805.4 1867.3 3014.3 3189.7</td>
<td>0.329(1,2) - inactive 3.328(1,1) - active</td>
<td>2</td>
</tr>
<tr>
<td>CH$_2$CHO</td>
<td>450.1 494.8 737.4 956.8 965.0 1144.5 1387.4 1465.6 1541.2 2906.1 3110.4 3218.8</td>
<td>0.351(1,2) - inactive 2.235(1,1) - active</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>$\sigma$ = 3.97 Å, $\epsilon/k_B$ = 436 K</td>
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</tr>
<tr>
<td>TS4</td>
<td>321.0 483.5 522.3 575.7 621.5 989.8 1128.1 1405.8 2109.3 3132.8 3243.2</td>
<td>0.320(1,2) - inactive 2.887(1,1) - active</td>
<td>1</td>
</tr>
</tbody>
</table>

Equilibrium constants

CH$_2$CO + H = CH$_3$ + CO $K_{eq} = 3.04 \times 10^1 T^{-0.53} \exp(21400/T)$

CH$_3$ + CO = CH$_3$CO $K_{eq} = 1.55 \times 10^{-5} T^{0.97} \exp(5810/T)$
\[ \tau \cdot \left( \frac{[\text{C}_2\text{H}_4]^{0.230}}{[\text{O}_2]^{-0.839}} [\text{Ar}]^{0.247}} \right) = 10^{-57.97} T^{14.854} \exp \left( \frac{35900}{T} \right) \]

Figure 1. Literature shock-tube ignition data of ethylene-oxygen-argon mixtures. Symbols are experimental data, line is the correlation equation given in the panel. See Table 1 for reference sources and mixture conditions.
Figure 2. Literature shock-tube ignition data of acetylene-oxygen-argon mixtures. Symbols are experimental data, line is the correlation equation given in the panel. See Table 2 for reference sources and mixture conditions.
Figure 3. Reaction pathways following molecular oxygen attack on the π bond in acetylene. The bracket denotes that the species is a rovibrationally excited adduct.
**Figure 5.** Potential energy diagram of the CH$_3$CO reactions. The energy values in parentheses are obtained at the G2(B3LYP) level of theory.
Figure 6. Comparison of theoretical prediction and experimental data for the pressure fall-off of the rate coefficients of CH$_3$CO $\rightarrow$ CH$_3$ + CO.
Figure 7. Comparison of theoretical prediction and experimental data for the rate coefficient of CH$_2$CO + H $\rightarrow$ CH$_3$ + CO.
Figure 8. Comparison of experimental (symbols, Homer and Kistiakowsky, 1967) and computed (lines) ignition delay times behind reflected shock waves for the mixtures of (a) 0.5%C₂H₄-3%O₂ (shock mixture 1, see Table 1) and (b) 0.5%C₂H₄-1%O₂ (shock mixture 2, see Table 1) in argon. The computational ignition delay was determined as the time corresponding to [CO] + [CO₂] equal to 10% of its final value.
Figure 9. Comparison of experimental (symbols, Jachimowski 1977) and computed (lines) ignition delay times in incident shock waves for the mixtures of (a) 1%C$_2$H$_4$-6%O$_2$, (b) 2%C$_2$H$_4$-6%O$_2$, and (c) 3%C$_2$H$_4$-6%O$_2$ in argon. Other shock conditions can found in Table 1. The computational ignition delay was determined as the laboratory time corresponding to maximum [O][CO].
**Figure 10.** Comparison of experimental (symbols, Jachimowski 1977) and computed (lines) maximum $[\text{CO}][\text{O}]$ in incident shock waves for the mixtures of (a) 1%C$_2$H$_4$-6%O$_2$, (b) 2%C$_2$H$_4$-6%O$_2$, and (c) 3%C$_2$H$_4$-6%O$_2$ in argon. Other shock conditions can be found in Table 1.
Figure 11. Comparison of experimental (symbols, Baker and Skinner, 1972) and computed (lines) ignition delay times behind reflected shock waves. The computational ignition was determined by the maximum pressure gradient. Shock mixtures (in argon): (3) 1%C2H4-3%O2, (4) 0.5%C2H4-3%O2, (5) 0.25%C2H4-0.75%O2, (6) 2%C2H4-3%O2, (7) 1%C2H4-1.5%O2, (8) 1%C2H4-6%O2, (9) 0.25%C2H4-6%O2, (10) 0.5%C2H4-1.5%O2. The initial pressure for all but one shock mixtures is 3 atm. The pressure of mixture 5 is 12 atm.
Figure 12. Comparison of experimental (symbols, Kistiakowsky and Richards, 1962) and computed (lines) ignition delay times behind reflected shock waves. The computational ignition was determined by the maximum pressure gradient. Mixture compositions (in argon): (a) 0.57%C2H2-4.43%O2 (shock mixture 18), (b) 2.9%C2H2-2.1%O2 (shock mixture 19), and (c) 2%C2H2-3%O2 (shock mixture 20). See Table 2 for additional experimental conditions.
Figure 13. Comparison of experimental (symbols, Homer and Kistiakowsky, 1967) and computed (lines) ignition delay times behind reflected shock waves. The computational ignition delay was determined as the time corresponding to [CO] + [CO₂] equal to 10% of its final value. Mixture compositions (in argon): (a) 0.5%C₂H₂-0.8%O₂ (shock 21), and (b) 0.5%C₂H₂-1.0%O₂-0.5%H₂ (shock 22). See Table 2 for additional experimental conditions.
Figure 14. Comparison of experimental (symbols, Jachimowski, 1977) and computed (lines) ignition delay times in incident shock waves. The computational ignition delay was determined as the time corresponding to maximum [O][CO]. Mixture compositions (in argon): (a) 1%C\textsubscript{2}H\textsubscript{2}-3.75%O\textsubscript{2} (shock mixture 23), and (b) 1%C\textsubscript{2}H\textsubscript{2}-1%C\textsubscript{2}H\textsubscript{4}-5.5%O\textsubscript{2} (shock mixture 24). See Table 2 for additional experimental conditions.
Figure 15. Comparison of experimental (symbols, Jachimowski, 1977) and computed (lines) maximum $[O][CO]$. Mixture compositions (in argon): (a) 1%C$_2$H$_2$-3.75%O$_2$ (shock mixture 23), and (b) 1%C$_2$H$_2$-1%C$_2$H$_4$-5.5%O$_2$ (shock mixture 24). See Table 2 for additional experimental conditions.
Figure 16. Comparison of experimental (symbols, Hidaka et al., 1981) and computed (lines) ignition delay times behind reflected shock waves. The computational ignition delay was determined by the maximum pressure gradient. Mixture compositions (in argon): (a) 2%C₂H₂-2.5%O₂ (shock mixture 25), (b) 1%C₂H₂-3.5%O₂ (shock 26), and (c) 1%C₂H₂-2.5%O₂ (shock mixture 27). An estimated value of 0.6 atm was used for pressure in the simulation.
Figure 17. Comparison of experimental (symbols, Hidaka et al. 1984) and computed (lines) maximum ignition delay times in incident shock waves. The experimental and computational ignition were determined by the maximum laser-Schlieren density gradient. Shock mixtures (in argon): (28) 0.5%C$_2$H$_2$-1.25%O$_2$ and (29) 0.5%C$_2$H$_2$-5%O$_2$. See Table 2 for additional experimental conditions.
Figure 18. Comparison of experimental (symbols, Hwang et al. 1986) and computed (lines) (a) depth of refractive index gradients and (b) full width at half-depth of the refractive index gradient. Shock mixtures (in argon): (28) 0.5%C$_2$H$_2$-1.25%O$_2$ and (29) 0.5%C$_2$H$_2$-5%O$_2$. See Table 2 for additional experimental conditions.
Figure 19. Comparison of experimental (symbols, Hidaka et al. 1996) and computed (lines) maximum ignition delay times behind reflected shock waves. The computational ignition was determined by the onset of CO2 concentration rise. Shock mixtures (in argon): (30) 0.5%C2H2-2.54%O2, (31) 1%C2H2-5%O2, (32) 0.5%C2H2-1.25%O2, (33) 1%C2H2-2.5%O2, and (34) 2%C2H2-2.5%O2. See Table 2 for additional experimental conditions.
Figure 20. Comparison of experimental (symbols, Hidaka et al. 1996) and computed (lines) CO$_2$ profiles in three shock mixtures.
Figure 21. Comparison of measured (symbols, Egolfopoulos et al. 1990b) and computed (lines) laminar burning velocity of ethylene and acetylene in air at atmospheric pressure. Filled symbols: linearly extrapolated data, open symbols: nonlinearly extrapolated data.
Figure 22. Comparison of measured (symbols, Egolfopoulos et al. 1990b) and computed (lines) laminar burning velocity of ethylene in a nitrogen diluted air (O₂/N₂=18/82).
Figure 23. Comparison of measured (symbols, Egolfopoulos et al. 1990b) and computed (line) pressure variation of the laminar burning velocity of a stoichiometric mixture of ethylene in a nitrogen diluted air (O$_2$/N$_2$=18/82).
Figure 24. Comparison of measured (symbols, Egolfopoulos et al. 1990b) and computed (lines) laminar burning velocity of acetylene in a nitrogen diluted air (O$_2$/N$_2$=18/82).
Figure 25. Comparison of measured (symbols, Egolfopoulos et al. 1990b) and computed (line) pressure variation of the laminar burning velocity of a stoichiometric mixture of acetylene in a nitrogen diluted air (O$_2$/N$_2$=18/82).
Figure 26. Experimental (Bhargava and Westmoreland, 1998a) and computed major species profiles of Flame 1 \( (p = 20 \text{ Torr, } \text{C}_2\text{H}_4/\text{O}_2/50\%\text{Ar, } \phi = 1.9) \).
Figure 27. Experimental (Bhargava and Westmoreland, 1998a) and computed H and OH mole fraction profiles of Flame 1 ($p = 20$ Torr, $C_2H_4/O_2/50\%$Ar, $\phi = 1.9$).
Figure 28. Experimental (Bhargava and Westmoreland, 1998a) and computed minor-species mole fraction profiles of Flame 1 \((p = 20 \text{Torr}, \text{C}_2\text{H}_4/\text{O}_2/50\% \text{Ar}, \phi = 1.9)\).
Figure 29. Experimental (Bhargava and Westmoreland, 1998a) and computed minor-species mole fraction profiles of Flame 1 ($p = 20$ Torr, $C_2H_4/O_2/50\% Ar$, $\phi = 1.9$).
Figure 30. Experimental (Bhargava and Westmoreland, 1998b) and computed major species profiles of Flame 2 ($p = 30$ Torr, C$_2$H$_4$/O$_2$/56.9%Ar, $\phi = 0.75$).
Figure 31. Experimental (Bhargava and Westmoreland, 1998b) and computed minor-species mole fraction profiles of Flame 2 ($p = 30$ Torr, $C_2H_4/O_2/56.9\%Ar$, $\phi = 0.75$).
Figure 32. Experimental (Bhargava and Westmoreland, 1998b) and computed minor-species mole fraction profiles of Flame 2 ($p = 30$ Torr, $C_2H_4/O_2/56.9\%Ar$, $\phi = 0.75$).
Figure 33. Experimental (Bhargava and Westmoreland, 1998b) and computed minor-species mole fraction profiles of Flame 2 ($p = 30$ Torr, $C_2H_4/O_2/56.9\% Ar$, $\phi = 0.75$).
Figure 34. Experimental (Westmoreland et al., 1986) and computed major species profiles of Flame 3 ($p = 20$ Torr, $C_2H_2/O_2/5\%Ar$, $\phi = 2.4$).
Figure 35. Experimental (Westmoreland et al., 1986) and computed minor-species mole fraction profiles of Flame 3 ($p = 20$ Torr, $C_2H_2/O_2/5\%Ar$, $\phi = 2.4$).
Figure 36. Experimental (Westmoreland et al., 1986) and computed minor-species mole fraction profiles of Flame 3 ($p = 20$ Torr, $C_2H_2/O_2/5\%Ar$, $\phi = 2.4$).
Figure 37. Experimental (Eberius et al. 73) and computed species mole fraction profiles of Flame 4 ($p = 76$ Torr, $3\%$C$_2$H$_2$/97$\%$O$_2$).
Appendix A. A Comprehensive and Detailed Kinetic Model of Ethylene and Acetylene Oxidation at High Temperatures

**SPECIES CONSIDERED**

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**REACTIONS CONSIDERED**

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<td>3. OH+H2=H+H2O</td>
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<td>4. OH+OH=H2O+H2</td>
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<td>5. H+H+M=H2+M</td>
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<tr>
<td>6. H+H+H2=H2+H2</td>
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<td>7. H+H+H2O=H2+H2O</td>
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<tr>
<td>8. H+H+CO2=H2+CO2</td>
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<tr>
<td>9. H+OH+M=H2O+M</td>
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Enhanced by 0.000E+00
Enhanced by 2.000E+00
Enhanced by 3.000E+00
Enhanced by 6.300E-01

**Units are in cal, mol, s, and cm.**
CO2  Enhanced by  2.000E+00
C2H6 Enhanced by  3.000E+00
AR Enhanced by  7.000E-01
C2H2 Enhanced by  3.000E+00
C2H4 Enhanced by  3.000E+00
11. O+O+M=O2+M 1.20E+17  -1.0  0.0
H2  Enhanced by  2.400E+00
H2O Enhanced by  1.540E+01
CH4 Enhanced by  2.000E+00
CO Enhanced by  1.750E+00
CO2 Enhanced by  3.600E+00
C2H6 Enhanced by  3.000E+00
AR Enhanced by  8.300E-01
C2H2 Enhanced by  3.000E+00
C2H4 Enhanced by  3.000E+00
12. H+O2+M=HO2+M 2.80E+18  -0.9  0.0
O2 Enhanced by  0.000E+00
H2O Enhanced by  0.000E+00
CO Enhanced by  7.500E-01
CO2 Enhanced by  1.500E+00
C2H6 Enhanced by  1.500E+00
N2 Enhanced by  0.000E+00
AR Enhanced by  0.000E+00
C2H2 Enhanced by  3.000E+00
C2H4 Enhanced by  3.000E+00
13. H+O2+O2=HO2+O2  3.00E+20  -1.7  0.0
14. H+O2+H2O=HO2+H2O 1.65E+19  -0.8  0.0
15. H+O2+N2=H2O+N2 2.60E+19  -1.2  0.0
16. H+O2+AR=HO2+AR  7.00E+17  -0.8  0.0
17. OH+OH(+M)=H2O2(+M)  7.40E+13  -0.4  0.0
Low pressure limit:  0.23000E+19 -0.90000E+00 -0.17000E+04
TROE centering:  0.73460E+00  0.94000E+02  0.17560E+04  0.51820E+04
H2 Enhanced by  2.000E+00
H2O Enhanced by  6.000E+00
CH4 Enhanced by  2.000E+00
CO Enhanced by  1.500E+00
CO2 Enhanced by  2.000E+00
C2H6 Enhanced by  3.000E+00
AR Enhanced by  7.000E-01
C2H2 Enhanced by  3.000E+00
C2H4 Enhanced by  3.000E+00
18. HO2+H=O+H2O  3.97E+12  0.0  671.0
19. HO2+H=O2+H2  1.66E+13  0.0  820.0
20. HO2+OH=OH  7.08E+13  0.0  300.0
21. HO2+O=OH+O2  2.00E+13  0.0  0.0
22. HO2+OH=O2+H2O  4.64E+13  0.0  500.0
23. HO2+HO2=O2+H2O  1.30E+11  0.0  -1630.0
Declared duplicate reaction...
24. HO2+HO2=O2+H2O  4.20E+14  0.0  12000.0
Declared duplicate reaction...
25. H2O2+H=H2+H2  1.21E+07  2.0  5200.0
26. H2O2+H=OH+H2O  1.00E+13  0.0  3600.0
27. H2O2+O=OH+H2O  9.63E+06  2.0  4000.0
28. H2O2+OH=H2+H2O  1.75E+12  0.0  320.0
Declared duplicate reaction...
29. H2O2+OH=H2+H2O  5.80E+14  0.0  9560.0
Declared duplicate reaction...
30. CO+O+M=CO2+M  6.02E+14  0.0  3000.0
H2 Enhanced by  2.000E+00
O2 Enhanced by  6.000E+00
H2O Enhanced by  6.000E+00
CH4 Enhanced by  2.000E+00
CO Enhanced by  1.500E+00
CO2 Enhanced by  3.500E+00
C2H6       Enhanced by    3.000E+00
AR         Enhanced by    5.000E-01
C2H2       Enhanced by    3.000E+00
C2H4       Enhanced by    3.000E+00
31. CO+CH=CO2+H                        4.76E+07  1.2    70.0
32. CO+H2 (+M) = CH2O (+M)             4.30E+07  1.5  79600.0
Low pressure limit:  0.50700E+28 -0.34200E+01  0.84350E+05
TROE centering:      0.93200E+00  0.19700E+03  0.15400E+04  0.10300E+05
H2          Enhanced by    2.000E+00
H2O         Enhanced by    6.000E+00
CH4         Enhanced by    2.000E+00
CO          Enhanced by    1.500E+00
CO2         Enhanced by    2.000E+00
C2H6        Enhanced by    3.000E+00
AR          Enhanced by    7.000E-01
C2H2        Enhanced by    3.000E+00
C2H4        Enhanced by    3.000E+00
33. CO+O2=CO2+O                        2.50E+12  0.0    47800.0
34. CO+H2O=CO2+OH                     1.50E+14  0.0    23600.0
35. C+OH=CO+H                         5.00E+13  0.0    1.8000
36. C+O2=CO+O                         5.80E+13  0.0    576.0
37. CH+H=CH2                          1.10E+14  0.0    0.0
38. CH+O=CO+H                         5.70E+13  0.0    0.0
39. CH+OH=HCO+H                       3.00E+13  0.0    0.0
40. CH+H2=CH2+H                       1.11E+12  1.8   1670.0
41. CH+H2O=CH2O+H                     5.71E+12  -0.5 -755.0
42. CH+O2=HCO+O                       3.30E+13  0.0    0.0
43. CH+CO (+M) = HCCO (+M)             5.00E+13  0.0    0.0
Low pressure limit:  0.26900E+29 -0.37400E+01  0.19360E+04
TROE centering:      0.57570E+00  0.23700E+03  0.16520E+04  0.50690E+04
H2          Enhanced by    2.000E+00
H2O         Enhanced by    6.000E+00
CH4         Enhanced by    2.000E+00
CO          Enhanced by    1.500E+00
CO2         Enhanced by    2.000E+00
C2H6        Enhanced by    3.000E+00
AR          Enhanced by    7.000E-01
C2H2        Enhanced by    3.000E+00
C2H4        Enhanced by    3.000E+00
44. CH+CO2=HCO+CO                     3.40E+12  0.0    690.0
45. HCO+H (+M) = CH2O (+M)             1.09E+12  0.5   260.0
Low pressure limit:  0.13500E+25 -0.25700E+01  0.14250E+04
TROE centering:      0.78240E+00  0.27100E+03  0.27550E+04  0.65700E+04
H2          Enhanced by    2.000E+00
H2O         Enhanced by    6.000E+00
CH4         Enhanced by    2.000E+00
CO          Enhanced by    1.500E+00
CO2         Enhanced by    2.000E+00
C2H6        Enhanced by    3.000E+00
AR          Enhanced by    7.000E-01
C2H2        Enhanced by    3.000E+00
C2H4        Enhanced by    3.000E+00
46. HCO+H2+CO+H2                      7.34E+13  0.0    0.0
47. HCO+O+CO+OH                       3.00E+13  0.0    0.0
48. HCO+O+CO2+H                       3.00E+13  0.0    0.0
49. HCO+OH+CO+H2O                     5.00E+13  0.0    0.0
50. HCO+M=CO+H                        1.87E+17  -1.0  17000.0
H2          Enhanced by    2.000E+00
H2O         Enhanced by    6.000E+00
CH4         Enhanced by    2.000E+00
CO          Enhanced by    1.500E+00
CO2         Enhanced by    2.000E+00
C2H6        Enhanced by    3.000E+00
C2H2        Enhanced by    3.000E+00
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Enhanced by</th>
<th>Rate Constant</th>
<th>A</th>
<th>B</th>
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<tr>
<td>HCO + O₂ → CO + HO₂</td>
<td>7.60E+12</td>
<td>0.0</td>
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<tr>
<td>CH₂ + H (+M) → CH₃ (+M)</td>
<td>2.50E+16</td>
<td>-0.8</td>
<td>0.0</td>
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<tr>
<td>H₂</td>
<td>Enhanced by</td>
<td>2.00E+00</td>
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<tr>
<td>H₂O</td>
<td>Enhanced by</td>
<td>6.00E+00</td>
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<tr>
<td>CH₄</td>
<td>Enhanced by</td>
<td>2.00E+00</td>
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<tr>
<td>CO</td>
<td>Enhanced by</td>
<td>1.50E+00</td>
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<td>CO₂</td>
<td>Enhanced by</td>
<td>2.00E+00</td>
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<tr>
<td>C₂H₆</td>
<td>Enhanced by</td>
<td>3.00E+00</td>
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</tr>
<tr>
<td>AR</td>
<td>Enhanced by</td>
<td>7.00E-01</td>
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<tr>
<td>C₂H₄</td>
<td>Enhanced by</td>
<td>3.00E+00</td>
<td></td>
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<tr>
<td>CH₂ + H₂ → H + CH₃</td>
<td>5.00E+05</td>
<td>2.0</td>
<td>7230.0</td>
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<tr>
<td>CH₂ + O → HCO + H</td>
<td>8.00E+13</td>
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<tr>
<td>CH₂ + O₂ → HCO + OH</td>
<td>1.06E+13</td>
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<tr>
<td>CH₂ + O₂ → CO + H + H</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + O₂ → H₂ + H₂O</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + H₂O → CH₂O + H</td>
<td>3.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + CO (+M) → CH₂CO (+M)</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>CH₂ + H₂O = CH₂ + H₂O</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
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</tr>
<tr>
<td>CH₂ + CO = CH₂ + CO</td>
<td>9.00E+12</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>CH₂ + CO₂ = CH₂ + CO₂</td>
<td>7.00E+12</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>CH₂O + H (+M) = CH₂OH (+M)</td>
<td>5.40E+11</td>
<td>0.5</td>
<td>3600.0</td>
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<tr>
<td>CH₂ + H₂O + H → CH₂ + HO₂</td>
<td>7.00E+00</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + O₂ + CO → CH₂ + CO₂</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + CO + H₂O → CH₂ + CO₂ + H₂O</td>
<td>1.20E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + H₂O (+M) = CH₃OH (+M)</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + H₂O = CH₂ + H₂O</td>
<td>2.00E+13</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + CO = CH₂ + CO</td>
<td>9.00E+12</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂ + CO₂ = CH₂ + CO₂</td>
<td>7.00E+12</td>
<td>0.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>CH₂O + H (+M) = CH₂OH (+M)</td>
<td>5.40E+11</td>
<td>0.5</td>
<td>3600.0</td>
<td></td>
</tr>
</tbody>
</table>
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H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
CO2 Enhanced by 2.000E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

79. CH2O+H(+M)=CH3O(+M) 5.40E+11 0.5 2600.0
Low pressure limit: 0.22000E+31 -0.48000E+01 0.55600E+04
TROE centering: 0.75800E+00 0.94000E+02 0.15550E+04 0.42000E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

80. CH2O+H=HCO+H2 2.30E+10 1.1 3275.0
81. CH2O+O=HCO+OH 3.90E+13 0.0 3540.0
82. CH2O+OH=HCO+H2O 3.43E+09 1.2 -447.0
83. CH2O+O2=HCO+HO2 1.00E+14 0.0 40000.0
84. CH2O+HO2=HCO+H2O2 1.00E+12 0.0 8000.0
85. CH2O+CH=CH2CO+H 9.46E+13 0.0 -515.0
Low pressure limit: 0.24770E+34 -0.47600E+01 0.24400E+04
TROE centering: 0.78300E+00 0.74000E+02 0.29410E+04 0.69640E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

86. CH3+H(+M)=CH4(+M) 1.27E+16 -0.6 383.0
Low pressure limit: 0.24770E+34 -0.47600E+01 0.24400E+04
TROE centering: 0.78300E+00 0.74000E+02 0.29410E+04 0.69640E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

87. CH3+O=CH2O+H 8.43E+13 0.0 0.0
88. CH3+OH(+M)=CH3OH(+M) 6.30E+13 0.0 0.0
Low pressure limit: 0.27000E+39 -0.63000E+01 0.31000E+04
TROE centering: 0.21050E+00 0.83500E+02 0.53900E+04 0.83700E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

89. CH3+OH=CH2+H2O 5.60E+07 1.6 5420.0
90. CH3+OH=CH2+H2O 2.50E+13 0.0 0.0
91. CH3+O2=O+CH3O 3.08E+13 0.0 2880.0
92. CH3+O2=OH+CH2O 3.60E+10 0.0 8940.0
93. CH3+HO2=CH4+O2 1.00E+12 0.0 0.0
94. CH3+HO2=CH3O+OH 1.34E+13 0.0 0.0
95. CH3+H2O2=CH4+HO2 2.45E+04 2.5 5180.0
96. CH3+C=CH2H+ 5.00E+13 0.0 0.0
97. CH3+CH=CH2H+ 3.00E+13 0.0 0.0
98. CH3+HCO=CH4+CO 8.48E+12 0.0 0.0
99. CH3+HCO(+M)=CH3CHO(+M) 1.80E+13 0.0 0.0
Low pressure limit: 0.22000E+49 -0.95880E+01 0.51000E+04
TROE centering: 0.61730E+00 0.13076E+02 0.20780E+04 0.50930E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO       Enhanced by    1.500E+00
CO2      Enhanced by    2.000E+00
C2H6     Enhanced by    3.000E+00
C2H2     Enhanced by    3.000E+00
C2H4     Enhanced by    3.000E+00

100. CH3+CH2O=CH4+HCO                              3.32E+03    2.8     5860.0
101. CH3+CH2=C2H4+H                                4.00E+13    0.0        0.0
102. CH3+CH2*=C2H4+H                               1.20E+13    0.0     -570.0
103. CH3+CH3(+M)=C2H6(+M)                          2.12E+16   -1.0      620.0

Low pressure limit:  0.17700E+51 -0.96700E+01  0.62200E+04
TROE centering:      0.53250E+00  0.15100E+03  0.10380E+04  0.49700E+04

H2       Enhanced by    2.000E+00
H2O      Enhanced by    6.000E+00
CH4      Enhanced by    2.000E+00
CO       Enhanced by    1.500E+00
CO2      Enhanced by    2.000E+00
C2H6     Enhanced by    3.000E+00
AR       Enhanced by    7.000E-01
C2H2     Enhanced by    3.000E+00
C2H4     Enhanced by    3.000E+00

104. CH3+CH3=H+C2H5                                4.99E+12    0.1    10600.0
105. CH3+HCCO=C2H4+CO                              5.00E+13    0.0        0.0
106. CH3+C2H=C3H3+H                                2.41E+13    0.0        0.0
107. CH3O+H(+M)=CH3OH(+M)                          5.00E+13    0.0        0.0

Low pressure limit:  0.86000E+29 -0.40000E+01  0.30250E+04
TROE centering:      0.89020E+00  0.14400E+03  0.28380E+04  0.45569E+05

H2       Enhanced by    2.000E+00
H2O      Enhanced by    6.000E+00
CH4      Enhanced by    2.000E+00
CO       Enhanced by    1.500E+00
CO2      Enhanced by    2.000E+00
C2H6     Enhanced by    3.000E+00
C2H2     Enhanced by    3.000E+00
C2H4     Enhanced by    3.000E+00

108. CH3O+H=CH2OH+H                                3.40E+06    1.6     0.0
109. CH3O+H=CH2O+H2                               2.00E+13    0.0        0.0
110. CH3O+H=CH3+OH                                3.20E+13    0.0        0.0
111. CH3O+H=CH2*+H2O                              1.60E+13    0.0        0.0
112. CH3O+O=CH2O+OH                                1.00E+13    0.0        0.0
113. CH3O+OH=CH2O+H2O                              5.00E+12    0.0        0.0
114. CH3O+O2=CH2O+HO2                              4.28E-13    7.6    -3530.0
115. CH2OH+H(+M)=CH3OH(+M)                        5.00E+13    0.0        0.0

Low pressure limit:  0.30000E+32 -0.48000E+01  0.33000E+04
TROE centering:      0.76790E+00  0.33800E+03  0.18120E+04  0.50810E+04

H2       Enhanced by    2.000E+00
H2O      Enhanced by    6.000E+00
CH4      Enhanced by    2.000E+00
CO       Enhanced by    1.500E+00
CO2      Enhanced by    2.000E+00
C2H6     Enhanced by    3.000E+00
C2H2     Enhanced by    3.000E+00
C2H4     Enhanced by    3.000E+00

116. CH2OH+H=CH2O+H2                               2.00E+13    0.0        0.0
117. CH2OH+H=CH3+OH                                1.20E+13    0.0        0.0
118. CH2OH+H=CH2*+H2O                              6.00E+12    0.0        0.0
119. CH2OH+O=CH2O+OH                                1.00E+13    0.0        0.0
120. CH2OH+OH=CH2O+H2O                              5.00E+12    0.0        0.0
121. CH2OH+O2=CH2O+HO2                              1.80E+13    0.0     900.0
122. CH4+H=CH3+H2                                  6.60E+08    1.6    10840.0
123. CH4+O=CH3+OH                                  1.02E+09    1.5     8600.0
124. CH4+OH=CH3+H2                                 1.00E+08    1.6     3120.0
125. CH4+CH=CH2+H                                 6.00E+13    0.0        0.0
126. CH4+CH2=CH3+CH3                               2.46E+06    2.0     8270.0
127. CH4+CH2*=CH3+CH3                              1.60E+13    0.0     -570.0
<table>
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<tr>
<th>Reaction</th>
<th>$k$ (s$^{-1}$)</th>
<th>$\Delta H$ (kJ/mol)</th>
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<tbody>
<tr>
<td>$\text{CH}_3\text{OH} + \text{H} = \text{CH}_2\text{OH} + \text{H}_2$</td>
<td>$1.70 \times 10^7$</td>
<td>4870.0</td>
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<tr>
<td>$\text{CH}_3\text{OH} + \text{H} = \text{CH}_3\text{O} + \text{H}_2$</td>
<td>$4.20 \times 10^6$</td>
<td>4870.0</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} = \text{CH}_2\text{OH} + \text{OH}$</td>
<td>$3.88 \times 10^5$</td>
<td>3100.0</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{O} = \text{CH}_3\text{O} + \text{OH}$</td>
<td>$1.30 \times 10^5$</td>
<td>5000.0</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_2\text{OH} + \text{H}_2$</td>
<td>$6.30 \times 10^6$</td>
<td>1500.0</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH} + \text{OH} = \text{CH}_3\text{O} + \text{CH}_4$</td>
<td>$3.00 \times 10^7$</td>
<td>9940.0</td>
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<tr>
<td>$\text{C}_2\text{H} + \text{H} (+\text{M}) = \text{C}_2\text{H}_2 (+\text{M})$</td>
<td>$1.00 \times 10^{17}$</td>
<td>0.0</td>
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</table>

**Low pressure limit:** $0.37500 \times 10^3 - 0.48000 \times 10^1$  
**TROE centering:** $0.64640 \times 10^0$  

Enhanced by: $\text{H}_2$ $2.00 \times 10^0$  
$\text{H}_2\text{O}$ $6.00 \times 10^0$  
$\text{CH}_4$ $2.00 \times 10^0$  
$\text{CO}$ $1.50 \times 10^0$  
$\text{CO}_2$ $2.00 \times 10^0$  
$\text{C}_2\text{H}_6$ $3.00 \times 10^0$  
$\text{AR}$ $7.00 \times 10^{-1}$  
$\text{C}_2\text{H}_2$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_4$ $3.00 \times 10^0$  

137. $\text{C}_2\text{H}_4 + \text{O} = \text{C}_2\text{H}_3 \text{OH}$ 
$5.00 \times 10^7$  

**Low pressure limit:** $0.24500 \times 10^{28} - 0.34000 \times 10^1$  
**TROE centering:** $0.19816 \times 10^1$  

Enhanced by: $\text{H}_2$ $2.00 \times 10^0$  
$\text{H}_2\text{O}$ $6.00 \times 10^0$  
$\text{CH}_4$ $2.00 \times 10^0$  
$\text{CO}$ $1.50 \times 10^0$  
$\text{CO}_2$ $2.00 \times 10^0$  
$\text{C}_2\text{H}_6$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_2$ $2.50 \times 10^0$  
$\text{C}_2\text{H}_4$ $2.50 \times 10^0$  

153. $\text{C}_2\text{H}_3 (+\text{M}) = \text{C}_2\text{H}_2 + \text{H} (+\text{M})$ 
$3.86 \times 10^8$  

**Low pressure limit:** $0.25650 \times 10^28 - 0.34000 \times 10^1$  
**TROE centering:** $0.19816 \times 10^0$  

Enhanced by: $\text{H}_2$ $2.00 \times 10^0$  
$\text{H}_2\text{O}$ $6.00 \times 10^0$  
$\text{CH}_4$ $2.00 \times 10^0$  
$\text{CO}$ $1.50 \times 10^0$  
$\text{CO}_2$ $2.00 \times 10^0$  
$\text{C}_2\text{H}_6$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_2$ $2.50 \times 10^0$  
$\text{C}_2\text{H}_4$ $2.50 \times 10^0$  

154. $\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H}_2 \text{OH}$ 
$4.60 \times 10^1$  

Enhanced by: $\text{H}_2$ $2.00 \times 10^0$  
$\text{H}_2\text{O}$ $6.00 \times 10^0$  
$\text{CH}_4$ $2.00 \times 10^0$  
$\text{CO}$ $1.50 \times 10^0$  
$\text{CO}_2$ $2.00 \times 10^0$  
$\text{C}_2\text{H}_6$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_2$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_4$ $3.00 \times 10^0$  

160. $\text{C}_2\text{H}_2 + \text{O} = \text{C}_2\text{H}_3 + \text{CO}$ 
$4.83 \times 10^1$  

Enhanced by: $\text{H}_2$ $2.00 \times 10^0$  
$\text{H}_2\text{O}$ $6.00 \times 10^0$  
$\text{CH}_4$ $2.00 \times 10^0$  
$\text{CO}$ $1.50 \times 10^0$  
$\text{CO}_2$ $2.00 \times 10^0$  
$\text{C}_2\text{H}_6$ $3.00 \times 10^0$  
$\text{C}_2\text{H}_2$ $2.50 \times 10^0$  
$\text{C}_2\text{H}_4$ $2.50 \times 10^0$
161. $\text{C}_2\text{H}_2 + \text{HCO} = \text{C}_2\text{H}_3 + \text{CO}$

162. $\text{C}_2\text{H}_2 + \text{CH} = \text{C}_2\text{H}_2 + \text{H}$

163. $\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$

164. $\text{C}_2\text{H}_2 + \text{CH}_2 = \text{C}_3\text{H}_3 + \text{H}$

165. $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 = \text{C}_4\text{H}_2 + \text{H}$

166. $\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{n-C}_4\text{H}_3 + \text{H}$

Low pressure limit: $0.12400\times10^32 - 0.47180\times10^1 0.18710\times10^4$

TROE centering: $0.10000\times10^1 0.10000\times10^3 0.56130\times10^4 0.13387\times10^5$

167. $\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{i-C}_4\text{H}_3 + \text{H}$

Low pressure limit: $0.12400\times10^32 - 0.47180\times10^1 0.18710\times10^4$

TROE centering: $0.10000\times10^1 0.10000\times10^3 0.56130\times10^4 0.13387\times10^5$

168. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_3 + \text{H}_2$

169. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

170. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

171. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

172. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

173. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

174. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

175. $\text{CH}_2\text{CO} + \text{H} = \text{C}_3\text{H}_4 + \text{H}_2$

176. $\text{C}_2\text{H}_2 + \text{H}_2 = \text{C}_4\text{H}_4 + \text{H}$

177. $\text{C}_2\text{H}_2 + \text{H}_2 = \text{C}_4\text{H}_4 + \text{H}$

178. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$

179. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$

180. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$

181. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$

182. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$

183. $\text{CH}_2\text{CO} + \text{H} = \text{C}_2\text{H}_2 + \text{H}_2$
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<th>Temperature</th>
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<tr>
<td>184. HCCOH+H=CH2CO+H</td>
<td>1.00E+13</td>
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<td>185. C2H3+H(+M)=C2H4(+M)</td>
<td>6.08E+12</td>
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<tr>
<td><strong>Low pressure limit:</strong></td>
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<td>0.33200E+04</td>
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<tr>
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<td>CH4 Enhanced by</td>
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<tr>
<td>CO Enhanced by</td>
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<td>CO2 Enhanced by</td>
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<td>C2H6 Enhanced by</td>
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<td>AR Enhanced by</td>
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<td>C2H2 Enhanced by</td>
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<td>C2H4 Enhanced by</td>
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<td>186. C2H3+H=C2H2+H2</td>
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<tr>
<td>187. C2H3+H=H2CC+H2</td>
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<td>C2H6 Enhanced by</td>
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<td>C2H2 Enhanced by</td>
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<td>C2H4 Enhanced by</td>
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<tr>
<td>196. C2H3+H2O2=C2H4+HO2</td>
<td>1.21E+10</td>
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<tr>
<td>197. C2H3+CH3=C2H2+CH4</td>
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<tr>
<td><strong>Low pressure limit:</strong></td>
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<tr>
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<td>0.25800E+00</td>
<td>0.59800E+03</td>
<td>0.21002E+05</td>
</tr>
</tbody>
</table>

*Rate parameters are only applicable to a pressure of 1 atm.*
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
CO2 Enhanced by 2.000E+00
C2H6 Enhanced by 3.000E+00
AR Enhanced by 7.000E-01
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

211. CH3CO+H(+M)=CH3CHO(+M) 9.60E+13 0.0 0.0
Low pressure limit:  0.38500E+45 -0.85690E+01  0.55000E+04
TROE centering:      0.10000E+01  0.29000E+04  0.29000E+04  0.51320E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
CO2 Enhanced by 2.000E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

212. CH3CO+H=CH3+HCO 8.00E+13 0.0 0.0
213. CH3CO+O=CH2CO+OH 3.90E+13 0.0 0.0
214. CH3CO+O=CH3+CO2 3.00E+13 0.0 0.0
215. CH3CO+O=CH2CO+H2O 1.20E+13 0.0 0.0
216. CH3CO+OH=CH3+CO+OH 1.80E+13 0.0 0.0
217. CH3CO+HO2=CH3+CO2+OH 1.20E+13 0.0 0.0
218. CH3CO+H=CH3+HCO 3.00E+13 0.0 0.0
219. CH3CO+O=CH3+COH2 3.00E+13 0.0 0.0
220. CH3CO+O=CH3+CO2+OH 2.50E+13 0.7 -1110.0
221. CH3CO+H2O=CH3CHO+H2O 4.10E+09 1.2 2400.0
222. CH3CO+OH=CH3+CO+OH 5.80E+12 0.0 1800.0
223. CH3CO+O=OH=CH3CO+HCO 3.00E+13 0.0 0.0
224. C2H4 (+M) +H2+H2CC(+M) 8.00E+12 0.4 88770.0
Low pressure limit:  0.70000E+51 -0.93100E+01  0.99860E+05
TROE centering:      0.73450E+00  0.18000E+03  0.10350E+04  0.54170E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
CO2 Enhanced by 2.000E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

225. C2H4+H(+M)=C2H5(+M) 1.08E+12 0.5 1820.0
Low pressure limit:  0.12000E+43 -0.76200E+01  0.69700E+04
TROE centering:      0.97530E+00  0.21000E+03  0.98400E+03  0.43740E+04
H2 Enhanced by 2.000E+00
H2O Enhanced by 6.000E+00
CH4 Enhanced by 2.000E+00
CO Enhanced by 1.500E+00
CO2 Enhanced by 2.000E+00
C2H6 Enhanced by 3.000E+00
C2H2 Enhanced by 3.000E+00
C2H4 Enhanced by 3.000E+00

226. C2H4+H=C2H3+H2 5.07E+07 1.9 12950.0
227. C2H4+O=OH=C2H3 1.51E+07 1.9 3740.0
228. C2H4+O=CH3+HCO 1.92E+07 1.8 220.0
229. C2H4+O=CH2+H2O 3.84E+05 1.8 220.0
230. C2H4+OH=C2H3+H2O 3.60E+06 2.0 2500.0
231. C2H4+O=H2=CH3+HCO 4.22E+13 0.0 60800.0
232. C2H4+HCO=C2H5+CO 1.00E+07 2.0 8000.0
233. C2H4+CH=CH3+H4 3.00E+13 0.0 0.0
234. C2H4+CH=pCH4+H 3.00E+13 0.0 0.0
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<tr>
<th>Reaction</th>
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<th>E0</th>
<th>Tเทคโนโลยี</th>
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<td>235. C2H4+CH2=aC3H5+H</td>
<td>2.00E+13</td>
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<td>236. C2H4+CH2*=H2CC*+CH4</td>
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<td>237. C2H4+CH2*=aC3H5+H</td>
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<td>238. C2H4+CH2*=H2CC+CH4</td>
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<td>239. C2H4+C2H=C4H4+H</td>
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<td>240. C2H5+H(+M)=C2H6 (+M)</td>
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<tr>
<td>253. C2H6+H=CH2H5+H2O</td>
<td>4.00E+13</td>
<td>0.0</td>
<td>-550.0</td>
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<td>254. C2H6+H=CH2H5+CH4</td>
<td>6.14E+06</td>
<td>1.7</td>
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<td>255. C3H2+O=C2H+HCO</td>
<td>1.00E+13</td>
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<td>256. C3H2+H=C3H3</td>
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<td>257. C3H2+OH=HCO+C2H2</td>
<td>6.80E+13</td>
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<td>258. C3H2+O2=HCO+H+CO</td>
<td>2.00E+12</td>
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<td>259. C3H2+CH=C4H2+H</td>
<td>5.00E+13</td>
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<td>260. C3H2+CH=H+C4H3+H</td>
<td>5.00E+13</td>
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<td>261. C3H2+CH=H+C4H3+H</td>
<td>5.00E+12</td>
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<td>262. C3H2+CH=H+C4H3+H</td>
<td>5.00E+12</td>
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<td>263. C3H2+H(+M)=aC3H4(+M)</td>
<td>2.00E+13</td>
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<td>TROE Centering: 0.23400E00 0.33000E03 0.48080E04 0.72620E04</td>
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<td>H2 Enhanced by 2.000E00</td>
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<td>H2O Enhanced by 6.000E00</td>
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<td>CH4 Enhanced by 2.000E00</td>
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<td>CO Enhanced by 1.500E00</td>
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<td>CO2 Enhanced by 2.000E00</td>
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<td>C2H6 Enhanced by 3.000E00</td>
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<td>C2H4 Enhanced by 3.000E00</td>
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<tr>
<td>264. C3H3+H(+M)=pC3H4 (+M)</td>
<td>3.00E+13</td>
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<td>Low pressure limit: 0.16000E+58 -0.12590E02 0.83760E04</td>
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<td>TROE Centering: 0.24500E00 0.33000E03 0.37060E04 0.67770E04</td>
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<td>H2O Enhanced by 6.000E00</td>
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<td>CH4 Enhanced by 2.000E00</td>
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<td>CO Enhanced by 1.500E00</td>
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<td>CO2 Enhanced by 2.000E00</td>
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<td>C2H6 Enhanced by 3.000E00</td>
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<td>AR Enhanced by 7.000E-01</td>
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<td>C2H2 Enhanced by 3.000E00</td>
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<td>C2H4 Enhanced by 3.000E00</td>
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<tr>
<td>265. C3H3+H=C3H2+H2</td>
<td>5.00E+13</td>
<td>0.0</td>
<td>1000.0</td>
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</table>
266. $C_3H_3 + O = CH_2O + C_2H$  \[2.00 \times 10^{13}\] 0.0 0.0
267. $C_3H_3 + OH = C_3H_2 + H_2O$  \[2.00 \times 10^{13}\] 0.0 0.0
268. $C_3H_3 + OH = C_2H_3 + HCO$  \[4.00 \times 10^{13}\] 0.0 0.0
269. $C_3H_3 + O_2 = CH_2CO + HCO$  \[3.00 \times 10^{10}\] 0.0 2868.0
270. $C_3H_3 + HO_2 = OH + CO + C_2H_3$  \[8.00 \times 10^{11}\] 0.0 0.0
271. $C_3H_3 + HO_2 = aC_3H_4 + CO$  \[1.90 \times 10^{12}\] 0.0 0.0
272. $C_3H_3 + HO_2 = pC_3H_4 + CO$  \[2.50 \times 10^{12}\] 0.0 0.0
273. $C_3H_3 + HCO = aC_3H_4 + CO$  \[2.50 \times 10^{13}\] 0.0 0.0
274. $C_3H_3 + HCO = pC_3H_4 + CO$  \[2.50 \times 10^{13}\] 0.0 0.0
275. $C_3H_3 + CH = i-C_4H_3 + H$  \[5.00 \times 10^{13}\] 0.0 0.0
276. $C_3H_3 + CH_2 = C_4H_4 + H$  \[5.00 \times 10^{13}\] 0.0 0.0
277. $C_3H_3 + CH_2 = C_4H_4 + H$  \[5.00 \times 10^{13}\] 0.0 0.0
278. $pC_3H_4 (+M) = cC_3H_4 (+M)$  \[1.80 \times 10^{12}\] 0.3 60000.0

Low pressure limit:  $0.18900 \times 10^{46} - 0.88710 \times 10^1$  $0.64200 \times 10^5$
TROE centering:  $0.17400 \times 10^0$  $0.10840 \times 10^4$  $0.20000 \times 10^5$  $0.42670 \times 10^4$

H_2  Enhanced by  $2.000 \times 10^0$
H_2O  Enhanced by  $6.000 \times 10^0$
CH_4  Enhanced by  $2.000 \times 10^0$
CO  Enhanced by  $1.500 \times 10^0$
CO_2  Enhanced by  $2.000 \times 10^0$
C_2H_6  Enhanced by  $3.000 \times 10^0$
C_2H_2  Enhanced by  $3.000 \times 10^0$
C_2H_4  Enhanced by  $3.000 \times 10^0$

279. $cC_3H_4 (+M) = aC_3H_4 (+M)$  \[1.80 \times 10^{12}\] 0.6 42200.0

Low pressure limit:  $0.40000 \times 10^{47} - 0.91120 \times 10^1$  $0.46900 \times 10^5$
TROE centering:  $0.00000 \times 10^0$  $0.23600 \times 10^3$  $0.20000 \times 10^4$  $0.15940 \times 10^4$

H_2  Enhanced by  $2.000 \times 10^0$
H_2O  Enhanced by  $6.000 \times 10^0$
CH_4  Enhanced by  $2.000 \times 10^0$
CO  Enhanced by  $1.500 \times 10^0$
CO_2  Enhanced by  $2.000 \times 10^0$
C_2H_6  Enhanced by  $3.000 \times 10^0$
C_2H_2  Enhanced by  $3.000 \times 10^0$
C_2H_4  Enhanced by  $3.000 \times 10^0$

*Rate parameters are only applicable to a pressure of 1 atm.*
290. \( pC_3H_4 + H = aC_3H_5 \)  
   \[ 2.07E+57 \quad -13.4 \quad 29212.9 \]

291. \( pC_3H_4 + H = C_3H_3 + H_2 \)  
   \[ 1.30E+06 \quad 2.0 \quad 5500.0 \]

292. \( pC_3H_4 + O = HCCO + CH_3 \)  
   \[ 3.45E+12 \quad 0.0 \quad 2250.0 \]

293. \( pC_3H_4 + O = C_2H_4 + CO \)  
   \[ 1.00E+13 \quad 0.0 \quad 2250.0 \]

294. \( pC_3H_4 + OH + C_3H_3 + H_2O \)  
   \[ 1.00E+06 \quad 2.0 \quad 100.0 \]

295. \( pC_3H_4 + O = C_3H_3 + CH_4 \)  
   \[ 2.00E+12 \quad 0.0 \quad 7700.0 \]

296. \( pC_3H_4 + CH_3 = C_3H_3 + CH_4 \)  
   \[ 2.00E+12 \quad 0.0 \quad 29212.9 \]

297. \( pC_3H_4 + CH_3 = C_3H_3 + CH_4 \)  
   \[ 1.00E+13 \quad 0.0 \quad 0.0 \]

298. \( aC_3H_5 + H(+M) = C_3H_6(+M) \)  
   \[ 1.80E+13 \quad 0.0 \quad 0.0 \]

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* Rate parameters are only applicable to a pressure of 1 atm.

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* Rate parameters are only applicable to a pressure of 1 atm.
H2    Enhanced by    2.000E+00
H2O   Enhanced by    6.000E+00
CH4   Enhanced by    2.000E+00
CO    Enhanced by    1.500E+00
CO2   Enhanced by    2.000E+00
C2H6  Enhanced by    3.000E+00
AR    Enhanced by    7.000E-01
C2H2  Enhanced by    3.000E+00
C2H4  Enhanced by    3.000E+00

338. C4H+O=C2H+C2O     5.00E+13  0.0  0.0
339. C4H+O2=HCCO+C2O   5.00E+13  0.0  1500.0
340. C4H2+H=C4H2       1.55E+10  0.9  954.0

Low pressure limit:  0.47000E+48 -0.93690E+01  0.40900E+04
TROE centering:      0.20200E+00  0.44700E+03  0.11620E+04  0.26350E+04

H2    Enhanced by    2.000E+00
H2O   Enhanced by    6.000E+00
CH4   Enhanced by    2.000E+00
CO    Enhanced by    1.500E+00
CO2   Enhanced by    2.000E+00
C2H6  Enhanced by    3.000E+00
C2H2  Enhanced by    3.000E+00
C2H4  Enhanced by    3.000E+00

341. C4H2+H(+M)=n-C4H3(+M)  2.20E+10  0.9  164.0

Low pressure limit:  0.11000E+53 -0.10251E+02  0.46000E+04
TROE centering:      0.10000E+01  0.51500E+03  0.51500E+03  0.25500E+04

H2    Enhanced by    2.000E+00
H2O   Enhanced by    6.000E+00
CH4   Enhanced by    2.000E+00
CO    Enhanced by    1.500E+00
CO2   Enhanced by    2.000E+00
C2H6  Enhanced by    3.000E+00
C2H2  Enhanced by    3.000E+00
C2H4  Enhanced by    3.000E+00

342. C4H2+H(+M)=i-C4H3(+M)  2.46E+45  -10.5  50149.5

Low pressure limit:  0.17000E+49 -0.94370E+01  0.74800E+04
TROE centering:      0.62000E+00  0.65900E+04  0.27520E+04

H2    Enhanced by    2.000E+00
H2O   Enhanced by    6.000E+00
CH4   Enhanced by    2.000E+00
CO    Enhanced by    1.500E+00
CO2   Enhanced by    2.000E+00
C2H6  Enhanced by    3.000E+00
C2H2  Enhanced by    3.000E+00
C2H4  Enhanced by    3.000E+00

* Rate parameters are only applicable to a pressure of 1 atm.

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<tr>
<td>H₂O</td>
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<td>CH₄</td>
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<td>CO</td>
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<tr>
<td>355. n-C₄H₃+H=C₄H₂+H₂</td>
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<td>356. i-C₄H₃+H=C₄H₂+H₂</td>
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<td>357. n-C₄H₃+OH=C₄H₂+H₂O</td>
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<td>358. i-C₄H₃+OH=C₄H₂+H₂O</td>
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<td>361. C₄H₄+H=i-C₄H₃+H₂</td>
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<td>367. C₄H₄+C₂H=i-C₄H₃+C₂H₂</td>
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