Two-Step Chemical-Kinetic Descriptions for Detonation Studies

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Abstract

Theoretical [1–3] and numerical [4–6] studies on the structure and stability of detonations have often applied one-step approximations to model detonation chemistry. In order to study detonation properties [7] and evaluate pulse detonation engine performance [8], using multidimensional computational methods, it is desirable to have a simplified, realistic chemical-kinetic description for model fuels like acetylene and ethylene, and practical fuels like propane and JP-10. Detailed chemical-kinetic descriptions, consisting of 174 elementary steps among 36 chemical species, have been developed for ignition and detonation of acetylene, ethylene, and JP-10 fuels [9–11]. Induction times predicted using this mechanism for isobaric homogeneous ignition are in good agreement with induction-time data from shock tube studies. From this detailed mechanism, short mechanisms comprising only the most important elementary steps have been identified for acetylene [9] and ethylene [10]. Systematic reduction, using steady-state and partial-equilibrium approximations, has further yielded a seven-step mechanism for acetylene detonation for high temperatures. Further, it was found that the seven-step mechanism can be reduced by combining the first four steps which are important during induction stage into a one-step approximation. This one-step reaction leads to chain-branching thermal explosion releasing most of the heat. It is followed by a CO-oxidation and radical-recombination step that proceeds at the rate of the H, OH recombination reaction. The temperature histories from this resulting two-step mechanism are in excellent agreement with those from the detailed mechanism. Such a two-step description has also been developed for ethylene from a knowledge of the detailed chemistry. The detailed study of high-temperature acetylene detonations indicates that the identities and the concentrations of the intermediates and radicals at the end of the induction period, essentially, identifies the first step of the two-step mechanism. From simulations using detailed mechanism, such identities and concentrations have been established for ethylene [10]. The rate of the first step

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is approximated as a combination of an initiation and a chain-branching rate and the rate parameters are identified by comparing with ignition-time predictions using detailed mechanism. The second step is chosen to be the CO-oxidation and recombination reaction similar to acetylene. These two-step descriptions are summarized here and the rates of these global reactions are expressed in terms of the rate parameters of elementary reactions listed in Table 1.

- A two-step mechanism for high temperature acetylene-air detonations has been developed [9] and modified slightly to release more heat at the end of the induction stage. This mechanism can be written as

\[
\begin{align*}
\text{C}_2\text{H}_2 + \frac{3}{2}\text{O}_2 & \rightarrow 2\text{CO} + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{OH} + \frac{1}{2}\text{H}, \\
2\text{CO} + \frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{OH} + \frac{1}{2}\text{H} + \text{cO}_2 & \rightleftharpoons (2 - a)\text{CO}_2 + a\text{CO} + (1 - b)\text{H}_2\text{O} + 2b(\text{OH} + r\text{H})/(1 + r),
\end{align*}
\]

where \( r = [\text{H}]_\infty/[	ext{OH}]_\infty \), \( s = k_3/\text{k}_4[\text{H}_2\text{O}]_\infty \), and

\[
\begin{align*}
a & = \frac{2}{1 + k_{5\infty}/(rk_{6\infty})}, \\
b & = \frac{(1 + r)}{1 + r + 2\sqrt{rs}}, \\
c & = \frac{2 - a + b(1 - r)}{2(1 + r)}.
\end{align*}
\]

The rates for these two steps are given by

\[
\begin{align*}
\omega_1 & = 8(k_7k_8/k_1)\text{[M]}[\text{C}_2\text{H}_2] + 2pk_1[\text{H}][\text{O}_2]H\{[\text{C}_2\text{H}_2]\}, \\
\omega_{II} & = 2(k_3[M][H][OH] - k_4[M][\text{H}_2\text{O}]),
\end{align*}
\]

where \( H\{\} \) denotes the Heaviside step function, which is needed to turn off the fuel-consumption reaction after all of the fuel is consumed, because the reduced chemistry [9] relates the branching rate of the fuel-consumption process to the rate of elementary reaction 1 of Table 1. The subscript \( o \) signifies evaluation at the initial temperature \( T_o \), while factors without this subscript vary with temperature, for reasons explained previously [9]. The parameter \( p = k_1/(k_1 + k_2[M] + k_3) \) in Eq. (2) is a correction factor that accounts for the slowdown in the branching rate that occurs when the temperature decreases. This slowdown, which was not addressed in the previous [9] two-step approximation, arises because elementary step 2, as well as step 9, which is followed partially by \( \text{C}_2\text{H}_3 + \text{O}_2 \rightarrow \text{C}_2\text{H}_2 + \text{HO}_2 \), results in the formation of the relatively stable \( \text{HO}_2 \).

- Similar to acetylene, the following two-step mechanism has been identified for ethylene
detonations [10].

\[
C_2H_4 + 2O_2 \rightarrow 2CO + \frac{4}{3}H_2O + \frac{2}{3}OH + \frac{2}{3}H, \quad (I)
\]

\[
2CO + \frac{4}{3}H_2O + \frac{2}{3}H + \frac{2}{3}OH + cO_2 \rightleftharpoons (2 - a)CO_2 + aCO + (2 - b)H_2O + 2b(OH + rH)/(1 + r), \quad (II)
\]

where \( r \) and \( s \) have been defined above, while \( a \), \( b \) and \( c \) are as follows

\[
\begin{align*}
a &= \frac{2}{1 + k_{5\infty} / (r k_{6\infty})}, \\
b &= \frac{2(1 + r)}{1 + r + 2\sqrt{rs}}, \\
c &= \frac{(2 - a)}{2} + \frac{b(1 - r)}{2(1 + r)}. 
\end{align*}
\]

The rates of the global reactions are

\[
\begin{align*}
\omega_1 &= k_{10}[C_2H_4][O_2] + q k_1[H][O_2] H \{[C_2H_4]\}, \\
\omega_{II} &= \frac{3}{2} (k_3[M][H][OH] - k_4[M][H_2O]),
\end{align*}
\]

where the correction factor \( q = k_1/(k_1 + k_2[M] + t k_{11}) \), in which \( t = k_{12}[O_2]/(k_{12}[O_2] + k_{13}[M]) \) is introduced to extend the range of applicability of the two-step mechanism to lower temperatures, where the branching rate is slowed by the formation of HO_2. The factor \( q \) is analogous to the factor \( p \) for acetylene, the slowing for ethylene occurring through elementary reaction 2 in Table 1 and also through the reaction 11 followed by the reaction 12.

- Related two-step mechanisms have also been developed for propane and JP-10 fuels.

These studies reveal different ignition mechanisms for different fuels. For acetylene and ethylene, chain-branching thermal explosion theory has been applied to obtain a two-step mechanism for use in detonation calculations. For higher hydrocarbons, however, the choice of fuel-consumption criteria may lead to such simplified descriptions.
Figure 1: Comparison between the detailed and the two-step mechanism for ignition-times and temperature histories for isobaric homogeneous ignition of ethylene-air mixtures

Table 1: Relevant Elementary Reactions and Rate Parameters

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Reaction</th>
<th>$A^a$</th>
<th>$n^a$</th>
<th>$E^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H + O_2 \rightarrow OH + O$</td>
<td>3.52 x 10^{10}</td>
<td>-0.70</td>
<td>71.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$H + O_2 + M \rightarrow HO_2 + M$</td>
<td>2.60 x 10^{10}</td>
<td>-1.20</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$H + OH + M \rightarrow H_2O + M$</td>
<td>2.20 x 10^{12}</td>
<td>-2.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$H_2O + M \rightarrow H + OH + M$</td>
<td>2.18 x 10^{23}</td>
<td>-1.93</td>
<td>499.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$CO + OH \rightarrow CO_2 + H$</td>
<td>4.40 x 10^{6}</td>
<td>1.50</td>
<td>-3.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$CO_2 + H \rightarrow CO + OH$</td>
<td>4.97 x 10^{8}</td>
<td>1.50</td>
<td>89.7</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$C_2H_2 + O_2 \rightarrow CH_2O + CO$</td>
<td>4.60 x 10^{15}</td>
<td>-0.54</td>
<td>188.0</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$CH_2O + M \rightarrow CHO + H + M$</td>
<td>6.26 x 10^{16}</td>
<td>0.00</td>
<td>326.0</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$C_2H_2 + H + M \rightarrow C_2H_3 + M$</td>
<td>4.40 x 10^{14}</td>
<td>-0.10</td>
<td>-24.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_0$ 1.86 x 10^{10}</td>
<td>0.80</td>
<td>-3.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>$C_2H_4 + O_2 \rightarrow C_2H_3 + HO_2$</td>
<td>4.22 x 10^{13}</td>
<td>0.00</td>
<td>241.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$C_2H_4 + H + M \rightarrow C_2H_5 + M$</td>
<td>1.90 x 10^{15}</td>
<td>-5.57</td>
<td>21.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_0$ 1.08 x 10^{12}</td>
<td>0.45</td>
<td>7.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$</td>
<td>2.00 x 10^{12}</td>
<td>0.00</td>
<td>20.9</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>$C_2H_5 + M \rightarrow C_2H_4 + H + M$</td>
<td>3.99 x 10^{13}</td>
<td>-4.99</td>
<td>167.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_0$ 1.11 x 10^{10}</td>
<td>1.04</td>
<td>153.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Specific reaction-rate constant $k = AT^n e^{-E/RT}$; units mol, cm$^3$, s, K and kJ/mol.

*b* Chaperon efficiencies: CO, 0.75; CO$_2$, 1.5; H$_2$O, 7.0; O$_2$, 0.3; C$_2$H$_6$, 1.5; others, 1.0.

*c* Chaperon efficiencies: CO, 1.9; CO$_2$, 3.8; H$_2$, 2.5; H$_2$O, 12.0; others, 1.0.

*d* Chaperon efficiencies: CO, 1.9; CO$_2$, 3.8; H$_2$, 2.5; H$_2$O, 16.3; others, 1.0.

*e* Troe Falloff $F_e = 0.7$; Chaperon efficiencies: M = 1.0 for all species.

*f* Troe Falloff $F_e = 0.832 \times \exp(-T/1203.0)$; Chaperon efficiencies: M = 1.0 for all species.
References


