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 chemicalkinetic 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 chainbranching 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

$$C_2H_2 + \frac{3}{2}O_2 \rightarrow 2CO + \frac{1}{2}H_2O + \frac{1}{2}OH + \frac{1}{2}H,$$
 (I)

$$2CO + \frac{1}{2}H_2O + \frac{1}{2}OH + \frac{1}{2}H + cO_2 \iff (2-a)CO_2 + aCO + (1-b)H_2O + 2b(OH + rH)/(1+r),$$
(II)

where $r \equiv [\mathrm{H}]_{\infty}/[\mathrm{OH}]_{\infty}, s \equiv k_{3\infty}/k_{4\infty}[\mathrm{H}_2\mathrm{O}]_{\infty}$ and

$$a = \frac{2}{1 + k_{5\infty}/(rk_{6\infty})},$$

$$b = \frac{(1+r)}{1 + r + 2\sqrt{rs}},$$

$$c = \frac{2-a}{2} + \frac{b(1-r)}{2(1+r)}.$$
(1)

The rates for these two steps are given by

$$\omega_{\rm I} = 8(k_7k_8/k_1)_o[{\rm M}][{\rm C}_2{\rm H}_2] + 2pk_1[{\rm H}][{\rm O}_2]H\{[{\rm C}_2{\rm H}_2]\},
\omega_{\rm II} = 2(k_3[{\rm M}][{\rm H}][{\rm OH}] - k_4[{\rm M}][{\rm H}_2{\rm O}]),$$
(2)

where $H\{ \}$ denotes the Heaviside step function, which is needed to turn off the fuelconsumption 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 $p = k_1/(k_1 + k_2[M] + k_9)$ 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 $C_2H_3 + O_2 \rightarrow C_2H_2 + HO_2$, results in the formation of the relatively stable HO₂.

• Similar to acetylene, the following two-step mechanism has been identified for ethylene

detonations [10].

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

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

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

$$a = \frac{2}{1 + k_{5\infty}/(rk_{6\infty})},$$

$$b = \frac{2(1+r)}{1 + r + 2\sqrt{rs}},$$

$$c = \frac{(2-a)}{2} + \frac{b(1-r)}{2(1+r)}.$$
(3)

The rates of the global reactions are

$$\omega_{\rm I} = k_{10} [\rm C_2 H_4] [\rm O_2] + q \ k_1 [\rm H] [\rm O_2] H \{[\rm C_2 H_4]\}, \\ \omega_{\rm II} = \frac{3}{2} (k_3 [\rm M] [\rm H] [\rm OH] - k_4 [\rm M] [\rm H_2 O]), \end{cases}$$

$$(4)$$

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 HO₂. 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

No.	Reaction				\mathbf{A}^{a}	\mathbf{n}^{a}	${ m E}^{ m a}$
1	$H + O_2$	\rightarrow	OH + O		3.52×10^{16}	-0.70	71.4
2^{b}	$H + O_2 + M$	\rightarrow	$HO_2 + M$		$2.60 imes 10^{19}$	-1.20	0.0
3^{c}	H + OH + M	\rightarrow	$H_2O + M$		$2.20\! imes\!10^{22}$	-2.00	0.0
$4^{\rm c}$	$H_2O + M$	\rightarrow	H + OH + M		$2.18\! imes\!10^{23}$	-1.93	499.0
5	CO + OH	\rightarrow	$CO_2 + H$		4.40×10^{6}	1.50	-3.1
6	$\rm CO_2$ + H	\rightarrow	CO + OH		4.97×10^{8}	1.50	89.7
7	$C_2H_2 + O_2$	\rightarrow	$CH_2O + CO$		$4.60\! imes\!10^{15}$	-0.54	188.0
8 ^d	$CH_2O + M$	\rightarrow	CHO + H + M		$6.26\! imes\!10^{16}$	0.00	326.0
9^{e}	$C_2H_2 + H + M$		$C_2H_3 + M$	k_0	$4.40 imes 10^{14}$	-0.10	-24.05
				k_{∞}	$1.86\! imes\!10^{10}$	0.80	-3.38
10	$C_2H_4 + O_2$	\rightarrow	$C_2H_3 + HO_2$		4.22×10^{13}	0.00	241.0
11 ^f	$C_2H_4 + H + M$	\rightarrow	$C_2H_5 + M$	k_0	$1.90\! imes\!10^{35}$	-5.57	21.1
				k_{∞}	$1.08\! imes\!10^{12}$	0.45	7.6
12	$C_2H_5 + O_2$	\rightarrow	$C_2H_4 + HO_2$		$2.00\! imes\!10^{12}$	0.00	20.9
13 ^f	$C_2H_5 + M$	\rightarrow	$C_2H_4 + H + M$	k_0	$3.99\! imes\!10^{33}$	-4.99	167.4
				k_{∞}	1.11×10^{10}	1.04	153.8

 Table 1: Relevant Elementary Reactions and Rate Parameters

^aSpecific reaction-rate constant $k = AT^n e^{-E/RT}$; units mol, cm³, s, K and kJ/mol.

^bChaperon efficiencies: CO, 0.75; CO₂, 1.5; H₂O, 7.0; O₂, 0.3; C₂H₆, 1.5; others, 1.0.

^cChaperon efficiencies: CO, 1.9; CO₂, 3.8; H₂, 2.5; H₂O, 12.0; others, 1.0.

 $[^]d {\rm Chaperon}$ efficiencies: CO, 1.9; CO₂, 3.8; H₂, 2.5; H₂O, 16.3; others, 1.0.

^eTroe Falloff $F_c = 0.7$; Chaperon efficiencies: M = 1.0 for all species.

^fTroe Falloff $F_c = 0.832 \times \exp(-T/1203.0)$; Chaperon efficiencies: M = 1.0 for all species.

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