

Ignition Delay Times in C₂H₂-O₂-Ar Mixture behind a Reflected Shock Wave

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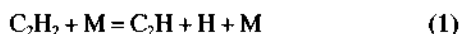
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Received May 8, 1997

Detonation characteristics of acetylene were studied behind reflected shock waves in the temperature range 800–1350 K by monitoring OH emission and pressure profiles. For a comprehensive measurement of ignition delay time, the mixture composition was varied in a wide range of Ar mole % was varied from 0.625 to 2.5 in stoichiometric ratio of C₂H₂-O₂-Ar. A computer simulation study was also performed to elucidate the important elementary steps determining ignition behavior. The 33-reaction mechanism provides a good agreement in delay time between the observed and the calculated ones.

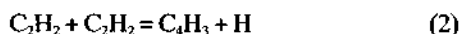
Introduction

Acetylene oxidation has been extensively studied by many workers with various techniques in order to understand the reaction mechanism of C₂H₂ combustion.^{1–4} Jachimowski² monitored the progress of the oxidation reaction by measuring radiation from the reaction O+CO→CO₂+hν over the temperature range 1815–2326 K. On the basis of the fit of the observed concentrations of CO and CO₂, he proposed the dissociation of acetylene and the reaction with oxygen molecule as the initiation steps,

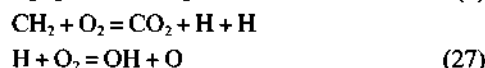
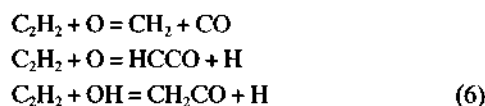


which are followed by subsequent chain-propagation steps via C₂H, CH₂ and HCO.

Hidaka and co-workers³ measured the ignition delay times in C₂H₂-O₂-Ar behind incident shock waves in the temperature range 1300–2200 K with laser schlieren techniques. They proposed reaction (1) and the dimerization of acetylene as initiation steps



They suggested the following reactions as key steps in determining ignition delay times:



Although their mechanism shows good agreement between the observed and their calculated ignition delay times, they found adjustment of their mechanism to suppress appearance of OH and CO₂ to be necessary.

Most work on acetylene oxidation has been focused on highly diluted and fuel-lean acetylene-oxygen mixture in Ar. The proposed mechanisms based on analysis of data observed for those experimental conditions may be doubtful for other concentration conditions. In this work, ignition de-

lay times in C₂H₂-O₂-Ar mixtures were monitored by measuring pressure profiles and emission profiles from OH radical. It is very difficult to determine individual rate constants. However, it is very useful in modeling complex processes if some kinetic data are available. The goal of this study is to propose a reliable kinetic scheme for describing the ignition mechanism of detonation of acetylene with various concentrations in Ar diluent.

Experimentals

The driven section of a single-pulse shock tube with 24.3 mm i.d., used previously,⁵ was extended by 40 cm to install a quartz window for optical measurements. The 306.4 nm emission from OH radical, attributed to transitions A²Δ→X²Π, was monitored with a Hamamatsu R-955 photomultiplier tube after passing through a Jobin-Yvon H-20 double-monochromator located behind the quartz window. The detected signal was fed into a Pacific Amplifier/Discriminator and recorded by a LeCroy 9450 digital oscilloscope.

Test gas mixtures were prepared by mixing acetylene (99.6% pure with 0.4% hydrocarbon impurity), oxygen (99.9% pure) and argon (99.999% pure) manometrically (within an error of ±0.1 torr) and allowed to mix for 24 h before use. The driver gas was pure grade helium (99.999%). Ten different mixtures, listed in Table 1, were prepared, including

Table 1. Experimental conditions for C₂H₂-O₂-Ar mixtures behind a reflected shock (P_i=100 torr)

Mixture (Φ)	C ₂ H ₂ %	O ₂ %	Ar %	T _s (K)	τ (μs)
A (1.0)	4	10	86	892-1112	168-1200
B (1.5)	6	10	84	869-1063	312-1244
C (2.5)	8	8	84	832-1084	216-1244
D (1.0)	2	5	93	978-1354	136-1204
E (0.63)	2	8	90	1020-1331	48-700
F (1.79)	10	14	76	840-1029	208-1276
G (0.83)	6	18	76	836-977	259-1900
H (0.63)	8	32	60	789-846	963-1950
I (1.0)	8	20	72	813-935	363-1930
J (0.9)	9	25	66	810-888	616-1324

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various concentrations of argon so that its effect on the reaction rate of ignition could be evaluated. The initial test gas pressure was fixed at 100 torr for all experiments.

The simulation of ignition delay time was performed with an aid of computer modeling using the assumption of constant-volume reaction at the reflected shock conditions. The reflected shock conditions (T_5 and P_5) were computed from the incident shock speed and the shock-tube diameter, assuming that the composition of the mixture remained frozen, *i.e.*, is assumed to be fixed in any thermodynamic process from the initial condition to the shocked. The program, originally written by Kee *et al.*,⁶ has been modified to run on a PC computer.

Results and Discussion

Ignition Delay Time. Figure 1 shows pressure and OH emission profiles measured simultaneously at the end of the driven section. The arrival of the reflected shock induces a weak pressure rise. The duration of relatively con-

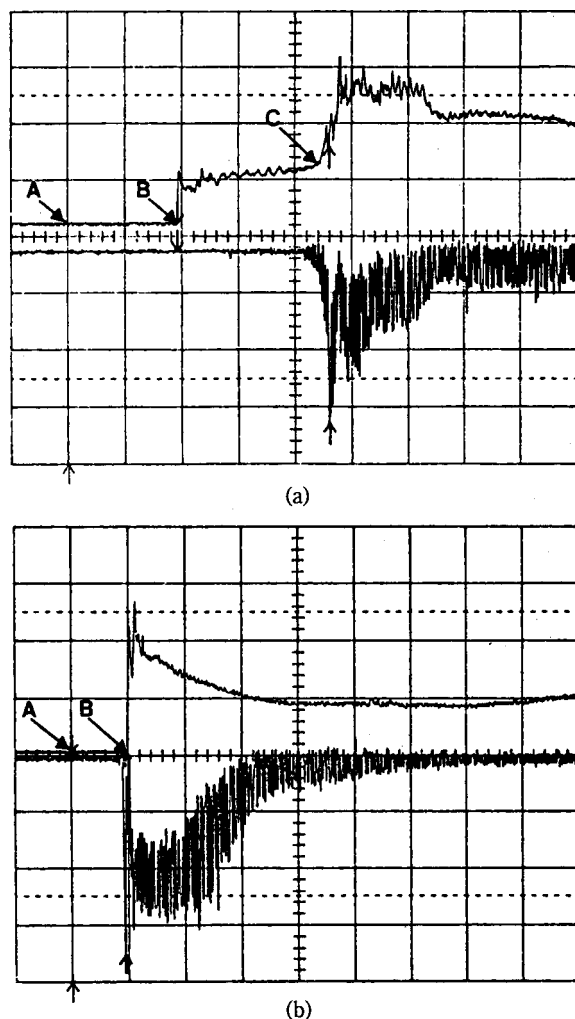


Figure 1. Typical oscillograms of pressure (upper) and OH emission (lower) profiles in $C_2H_2-O_2-Ar$ mixture behind reflected shocks (sweep speed: 0.2 ms/div): A; triggered point, B; arrival of a reflected shock and C; onset of detonation. Incident shock speeds are 667.5 m/s (a) and 1416 m/s (b).

stant pressure is dependent on the strength of the incident shock. This is followed by a strong pressure spike showing onset of detonation. At the same time a sudden increase in the OH emission is observed. The ignition delay time is defined from the OH emission as the time interval between the arrival of the reflected shock and maximum OH emission intensity associated with the von Neuman pressure spike. In some cases, when the strong incident shock passed through acetylene mixtures in the driven section, a sudden increase in pressure and OH emission appeared without delay. In this work, we focused our attention on a systematic study of ignition delay times.

The ranges of observed ignition delay time, τ , and calculated reflected-shock temperature, T_5 , for each mixture are also listed in Table 1. The plot of logarithm τ with respect to $1/T_5$ is very useful in thermodynamical basis for formulating observed ignition delay times, although P_5 is found to be proportional to T_5 . Figure 2(a) shows the results for mixtures A, D and I, for which $\Phi=1$. One sees that with increasing the Ar concentration the ignition delay becomes longer and longer. Figures 2(b) and 2(c) show the results for fuel-rich and fuel-lean mixtures, respectively. It can be also found from these figures that the ignition delay for acetylene detonation is nearly unaffected by equivalence ratio, but is very dependent on the Ar content.

Since $\ln \tau$ increases linearly with $1/T_5$, the observed ignition delay times can be fitted to an Arrhenius form

$$\tau = A \exp(E/RT) [C_2H_2]^a [O_2]^b [Ar]^c$$

where A is the pre-exponential factor, E is the activation energy, T is the reflected shock temperature, and a , b , and c are reaction orders. Multiple regression analysis was employed to obtain best-fit parameters. The final results are

$$\begin{aligned} \tau &= 5.97 \exp(E/RT) [C_2H_2]^{-0.5} [O_2]^{-0.06} [Ar]^{1.33} \\ E &= 14.7 (\pm 0.36) \text{ kcal/mol} \end{aligned}$$

where delay time and concentration are given in s and mol·dm⁻³, respectively. The reliability of these results can be proved by plotting all ignition delay time data as $\ln \{\tau/(5.97 [C_2H_2]^{-0.5} [O_2]^{-0.06} [Ar]^{1.33})\}$ versus $1/T$. As shown in Figure 3, it all lies close to a single line that represents calculated values. Previously, White⁷ reported an activation energy of 18 kcal·mol⁻¹ in $C_2H_2-O_2-Ar$ mixtures, not very different from our value. The difference can be found in reaction order of Ar. Contrary to his result, in this work the behavior of Ar was found to give rise to a retarding effect on the delay time. The role of Ar as an effective heat sink has been also observed in the detonation of ethylene oxide.⁵

Modeling of Ignition Delay Time. Reaction mechanisms for acetylene oxidation have been proposed by several workers.²⁻⁴ In the present work, we focused our attention on revealing key steps in ignition of acetylene-oxygen mixtures with various concentrations in Ar diluent. Assuming that the electronically excited OH may be proportional to the ground OH, we first started the calculation of ignition delay time with the mechanism proposed by Hidaka *et al.*³ For the mixture in which mole % of Ar is more than 90 and $T > 900$ K, their mechanism shows an agreement to a certain extent between the calculated and the observed values. When the content of Ar is below 90%, however, the discrepancy increases with decreasing Ar concentration. It should be not-

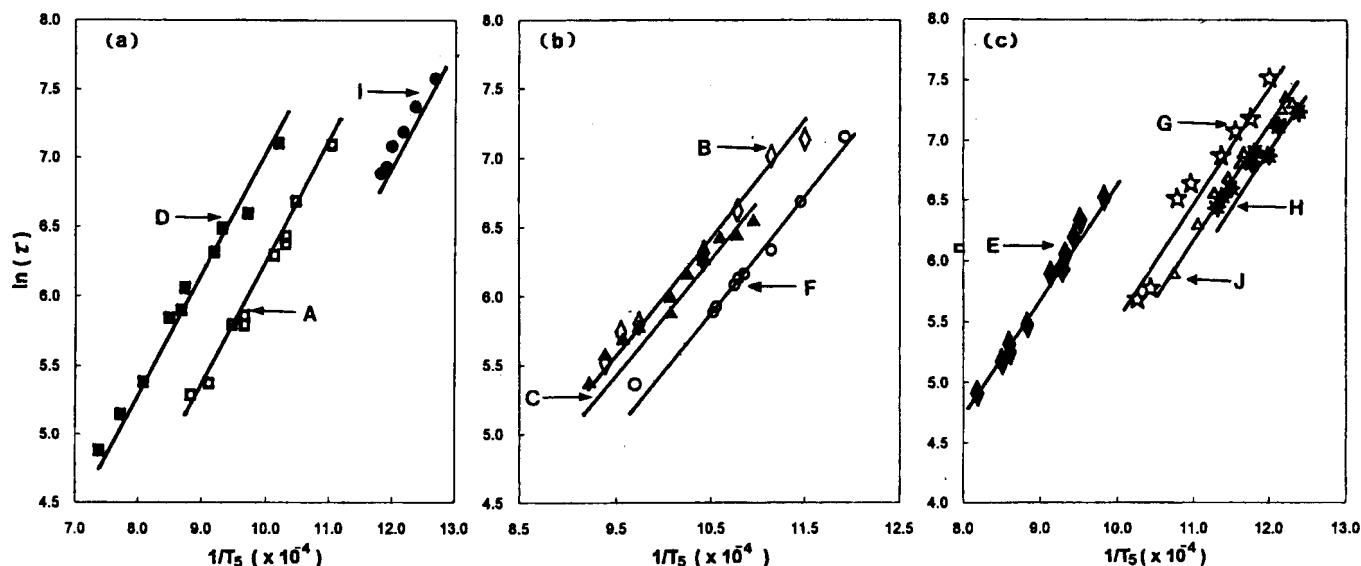
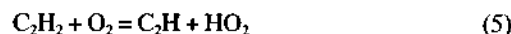


Figure 2. Plot of $\ln \tau$ vs. $1/T$ for $C_2H_2-O_2-Ar$ mixture: (a) A (\square , 4:10:86), D (\blacksquare , 2:5:93) and I (\bullet , 8:20:72), (b) B (\diamond , 6:10:84), C (\blacktriangle , 8:8:84) and F (\circ , 10:14:76), and (c) E (\blacklozenge , 2:8:90), G (\star , 6:18:76), H (\star , 8:32:60) and J (\triangle , 9:25:66). The solid lines represent calculated values for the corresponding mixtures.

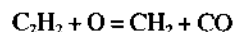
ed that for mixtures with less than 80% Ar their mechanism does not give rise to a maximum of OH concentration. We also calculated the ignition delay time using the mechanism proposed by Jachimowski.² His mechanism does not agree with our observed data at all.

We have modified the mechanism proposed by Hidaka *et al.* to develop a more reliable kinetic scheme for our ob-

served ignition delay time measurements. We added some possible chain-branching steps in which HCCO, CH_2 , CH and C radicals participate. Those steps, however, resulted in unchanged ignition delay time. This indicates that decomposition and dimerization of acetylene may not drive subsequent propagation-reactions sufficiently to produce OH concentrations satisfying the observed ignition delay time in mixtures of less than 90% Ar. The following reactions of acetylene with oxygen are important in our kinetic scheme.



Reaction (4), with $k=1.0 \times 10 \exp(-38 \text{ kcal mol}^{-1}/RT)$, which was introduced by Gardiner and Walker,⁸ has been taken into account in acetylene oxidation by Jachimowski² and detonation of LNG by Westbrook and Dryer.⁹ Reaction (5), with $k=1.2 \times 10 \exp(-74.52 \text{ kcal mol}^{-1}/RT)$, was included in a kinetic scheme for methane oxidation by Dagaut *et al.*¹⁰ Comparison of those rate constant suggests that reaction (4) is more significant in acetylene oxidation than reaction (5). Inclusion of these initiation steps in the kinetic scheme resulted in calculated values somewhat closed to experimental values observed in the low-temperature region for mixture A. However, above $T=1100$ K the ignition delay time decreases suddenly with increasing temperature. Among the chain branching steps, attack of oxygen atom on acetylene is very sensitive to temperature.



This step of $k=4.1 \times 10 T^{1.5} \exp(-1.7 \text{ kcal mol}^{-1}/RT)^3$ will become the predominant reaction between C_2H_2 and O in the high-temperature region. The methylene formation and its subsequent reactions gave rise to longer than observed ignition delay times. It suggests that the onset of detonation in acetylene mixture may be established before substantial quantities of fundamental radicals giving rise to propagation

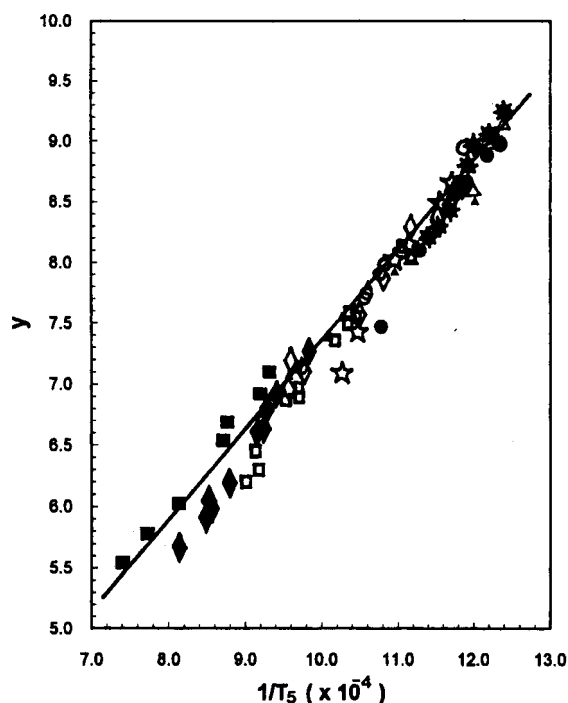


Figure 3. Plot of y vs. $1/T$ for $C_2H_2-O_2-Ar$ mixture: A (\square , 4:10:86), B (\diamond , 6:10:84), C (\blacktriangle , 8:8:84), D (\blacksquare , 2:5:93), E (\blacklozenge , 2:8:90), F (\circ , 10:14:76), G (\star , 6:18:76), H (\star , 8:32:60), I (\bullet , 8:20:72) and J (\triangle , 9:25:66), where $y = \ln \tau / \{5.97 [C_2H_2]^{0.5} [O_2]^{0.06} [Ar]^{1.33}\}$.

steps, such as O, OH and H, will be present. Exclusion of those processes implies calculated values very close in the low temperature region, but still discrepancy in the high temperature region.

Decomposition of HCO occurring subsequently after reaction (4)



will in part supply H radical in the high-temperature region to promote the product of OH.⁴ Consequently, in aid of this reaction we could obtain the temperature dependency of $\ln \tau$ with respect to $1/T$ similar to that of mixture A in Figure 2(a). For a precise match, elementary steps for HCCO and

Table 2. Reaction scheme and rate coefficient expressions for $\text{C}_2\text{H}_2\text{-O}_2\text{-Ar}$ mixtures behind a reflected shock. Rate coefficients are expressed in the form $k=AT^m \exp(-E/RT)$ where units are s^{-1} for unimolecular, $\text{cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ for bimolecular rate constants

Reaction	A	m	E	Ref
(1) $\text{C}_2\text{H}_2 + \text{M} = \text{C}_2\text{H} + \text{H} + \text{M}$	4.42×10^{16}		107300	[13]
(2) $\text{C}_2\text{H}_2 + \text{C}_2\text{H}_2 = \text{C}_4\text{H}_2 + \text{H}$	2.00×10^{12}		46080	[4]
(3) $\text{C}_2\text{H}_2 + \text{C}_2\text{H} = \text{C}_4\text{H}_3 + \text{H}$	3.50×10^{13}		0	[4]
(4) $\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCO} + \text{HCO}$	1.60×10^{13}		37900	this work
(5) $\text{C}_2\text{H}_2 + \text{O}_2 = \text{C}_2\text{H} + \text{HO}_2$	1.20×10^{13}		74520	[12]
(6) $\text{C}_2\text{H}_2 + \text{OH} = \text{CH}_2\text{CO} + \text{H}$	1.00×10^{10}		11520	this work
(7) $\text{CH}_2\text{CO} + \text{O} = \text{HCO} + \text{HCO}$	1.50×10^{13}		5000	this work
(8) $\text{C}_2\text{H} + \text{O}_2 = \text{HCCO} + \text{O}$	5.00×10^{13}		1440	[4]
(9) $\text{C}_2\text{H} + \text{OH} = \text{HCCO} + \text{H}$	2.00×10^{13}		0	[12]
(10) $\text{C}_2\text{H} + \text{O}_2 = \text{HCO} + \text{CO}$	1.00×10^{13}		6902	[3]
(11) $\text{HCCO} + \text{O}_2 = \text{CO} + \text{CO} + \text{OH}$	1.46×10^{12}		2500	[12]
(12) $\text{HCCO} + \text{OH} = \text{HCO} + \text{CO} + \text{H}$	1.00×10^{13}		0	[12]
(13) $\text{HCCO} + \text{M} = \text{CH} + \text{CO} + \text{M}$	6.00×10^{15}		58821	[12]
(14) $\text{HCCO} + \text{O} = \text{HCO} + \text{CO}$	1.20×10^{12}		0	[4]
(15) $\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	5.10×10^{10}		1700	[14]
(16) $\text{HCO} + \text{HO}_2 = \text{CO}_2 + \text{OH} + \text{H}$	3.16×10^{15}		0	[14]
(17) $\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	5.00×10^{13}		0	[14]
(18) $\text{HCO} + \text{M} = \text{CO} + \text{M} + \text{H}$	2.50×10^{14}		16812	[13]
(19) $\text{HCO} + \text{O} = \text{CO}_2 + \text{H}$	3.16×10^{13}		0	[14]
(20) $\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	2.16×10^{14}		0	[14]
(21) $\text{CH} + \text{O}_2 = \text{CO} + \text{OH}$	2.00×10^{13}		0	[4]
(22) $\text{CH} + \text{O} = \text{CO} + \text{H}$	4.00×10^{13}		0	[4]
(23) $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	4.00×10^{12}		7887	[3]
(24) $\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$	2.50×10^{13}		717	[4]
(25) $\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$	2.50×10^{14}		1912	[3]
(26) $\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	5.00×10^{13}		0	[3]
(27) $\text{H} + \text{O}_2 = \text{OH} + \text{O}$	1.20×10^{17}	-0.9	16490	[3]
(28) $\text{O} + \text{H}_2 = \text{OH} + \text{H}$	2.20×10^{14}		13623	[3]
(29) $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	5.20×10^{13}		6453	[3]
(30) $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	2.50×10^{15}		0	[3]
(31) $\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$	2.20×10^{12}	0.5	92491	[3]
(32) $\text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M}$	1.80×10^{11}	0.5	95700	[3]
(33) $\text{OH} + \text{OH} = \text{H}_2\text{O} + \text{O}$	1.00×10^8	1.6	3360	[3]

*Reversed reactions were automatically included in the computer program through equilibrium constants computed from polynomial fits to JANAF thermodynamical data.¹⁵

CH intermediates were taken into account. The addition of oxidation reactions of these species allowed us to obtain the kinetic mechanism for acetylene ignition that matched well to our data over the whole range of Ar content.

For a more precise fit of observed ignition time, elementary steps for the chemiluminescence of OH radical would be involved in the mechanism. Reactions forming electronically excited species have been more or less found in premixed flames. The strong OH emission from the reaction zone of hydrocarbon flame which has been considered to be associated with CH oxidation¹⁰



could be very important also in the detonation. This reaction is very exothermic ($\Delta H = -159.3$ kcal at 1000 K) and assumed to give sufficient energy for electronic excitation ($\Delta U = 92.8$ kcal/mol). In the hydrogen-oxygen reaction in shock tube, the OH was found to be formed mainly by the reaction



below 2000 K ($\Delta H = -104.3$ kcal at 1000 K). Hidaka *et al.*¹¹ determined the rate constant of this reaction from the ignition delay time and also proposed the deexcitation of OH radical giving rise to the emission from OH in the $\text{H}_2\text{-O}_2$ oxidation diluted highly in Ar.



The excitation and deexcitation steps were examined in the mechanism scheme in this work. Those steps resulted in the recursion problem in the OH^* concentration and the long

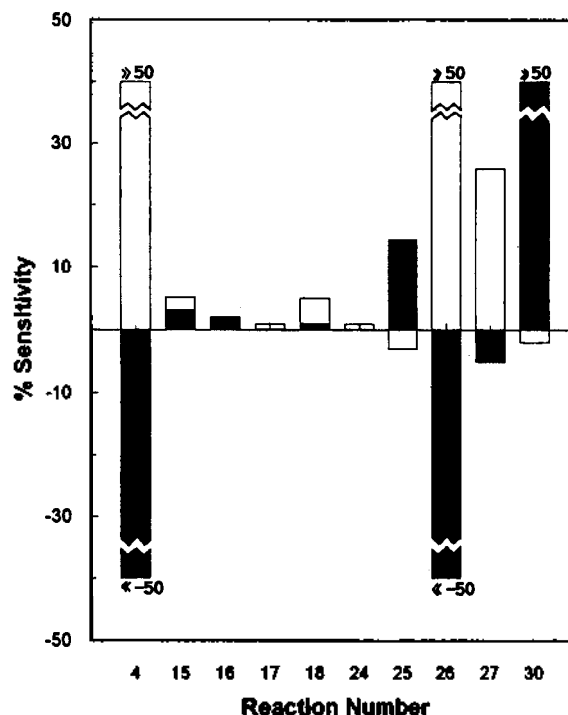


Figure 4. Sensitivity spectra of ignition delay time in mixture A at $T_3 = 1034$ K. The open and solid bars represent the results of multiplying the indicated rate constants by 1/5 and 5, respectively. The numbers indicate the reaction number in Table 2.

delayed appearance of $h\nu$. The chemiluminescence in the detonation may be much different from that in the flame, due to the higher temperature and pressure in the detonation and likely due to different propagation mechanism.

The final reaction scheme and rate coefficients for ignition of acetylene-oxygen mixtures diluted in Ar is listed Table 2. In this scheme, pre-exponential factors of reactions (4) and (6) were slightly changed. Simulation of ignition delay times was done with an assumption that the profile of OH emission is proportion to the concentration of OH species. The calculated values of ignition delay times for all mixtures studied in this work are shown as solid lines in the corresponding figures. As shown in Figure 2, the calculated values coincide with the observed ones for mixtures with various equivalence ratios and various mole percents of Ar.

A sensitivity analysis of ignition delay time was performed to validate the proposed mechanism for acetylene ignition. The sensitivity analysis was done for mixture A at 1034 K by multiplying reference rate constants from Table 2 by 5 or 1/5. The sensitivity spectra are shown in Figure 4. The sensitivity confirms that the ignition mechanism of detonation of acetylene is essentially governed by bimolecular reaction between acetylene and oxygen molecules to form 2 moles of CHO, rather than decomposition of acetylene molecule to form C_2H and H. The chain reaction is promoted by the further decomposition of CHO to generate H atom and continued by attack of H on O to form HO_2 . Additional reactions associated with CH, HCCO and CH are nearly insensitive to ignition delay time. The sensitivity will be slightly changed, depending on mixture and temperature.

Conclusions

The OH emission profiles in the shock-initiated ignition of $C_2H_2-O_2-Ar$ mixtures provide understanding of the ignition kinetics of acetylene. The experimental data could be well matched using a mechanism with 33 elementary steps. Contrary to the case of the combustion of acetylene diluted highly in Ar, reaction of acetylene with oxygen molecule to

form formyl radical and its subsequent reactions plays a key role in initiation of detonation.

Acknowledgments. This work was financially supported in part by the Basic Science Research Institute Program of the Ministry of Education, 1995-1996 Project No. BSRI-95-3432. Additional support was provided by the Agency for Defense Development.

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