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Shock Tube Studies of the Oxidation of Acetylene in Fuel-Rich Mixtures

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The oxidation of C_2H_2 in fuel-rich mixtures was studied in the temperature range 1600—2500 K by a shock-tube technique combined with UV absorption spectroscopy. The absorption profile, attributed to both an increase of C_4H_2 and a decrease of C_2H_2, could be modeled with a reaction mechanism comprising 38 elementary reactions. The progress of the oxidation was found to be greatly influenced by the pyrolysis steps of C_2H_2.

The kinetics of C_2H_2 oxidation at high temperatures above 1000 K has been studied in shock waves and flames. The progress of the oxidation was monitored by various measuring techniques and the obtained results have been subjected to discussion concerning the reaction mechanism.

White and Gardiner[1] did a literature survey for C_2H_2 oxidation in shock waves and carried out extensive computer modeling for a reaction employing the reported experimental results. The reaction mechanism adopted was one devised by Olson and Gardiner[2,3] to model CH_4 oxidation in shock waves. The reaction mechanism includes various reaction steps involving the primary products of C_2H_2, C_2H_4, C_2H_6 and CH_2O appearing in CH_4 oxidation. Therefore, it was considered that the reaction mechanism devised for CH_4 oxidation could be applicable to C_2H_2 oxidation. The consequences were not satisfactory for C_2H_2 oxidation nor for other three species oxidations. A completely different reaction mechanism appropriate to each oxidation had to be devised.

Such a conclusion has also been derived from modeling studies of C_2H_2 oxidation in flames by Levy,[4] in which a modified reaction mechanism based on that by Olson and Gardiner[2] was used. One of difficulties in using their reaction mechanism is that the concentration of CH_4 is modeled too large in comparison with the measured value. To improve on these difficulties, he included ketene as an intermediate species produced by a reaction between C_2H_2 and OH,

$$C_2H_2 + OH = C_2H_2O + H \quad (7)$$

$$C_2H_2O + OH = CH_2O + CHO$$

instead of

$$C_2H_2 + OH = CH_3 + CO,$$

where the elementary reactions with numbers exhibit the reactions adopted in the present reaction mechanism of Table 1. His intention is that the two-step decay of C_2H_2 by OH does not give a CH_n group directly and the concentration of CH_4 given by computer modeling does not become as large as modeled above.

Recently, Gardiner's group[5] further studied C_2H_2 oxidation in shock waves by computer modeling for the reported data concerning the ignition delay, including their own data for a laser-schlieren experiment, and the exponential growth. In the derived reaction mechanism, ketene as well as the ketene radical were taken into account:

$$C_2H_2O + OH = C_2HO + H_2O. \quad (9)$$

The assumed product of this reaction is different from the above, i.e., the formyl groups are not produced.

All of the experimental results concerning C_2H_2 oxidation in shock waves reported so far are for fuel-lean mixtures. The role of pyrolysis steps in C_2H_2 oxidation must be small in these experiments. We carried out oxidation in rich mixtures and measured the concentration of C_4H_2 through UV absorption spectroscopy at 216 nm. The obtained absorption profile was subjected to computer modeling using the above-mentioned reaction mechanism. The applicability of the mechanism to the present case was examined.

Experimental

The rectangular shock-tube and optical set-up used were fully described in a previous paper.[6]

Briefly, the light from a D_2-lamp (Hanau, D200F) was detected by a photomultiplier (Hamamatsu, R208) with a monochromator (Jarrell-Ash, JE25) after passing through two shock-tube windows. The test gas compositions used were $C_2H_2/O_2/Ar$=3/1/96 and 5/1/94 prepared from 99.6% pure C_2H_2, 99.99% pure O_2 and 99.999% pure Ar. Hereafter, and in the figure captions, the former mixture is abbreviated as a 3/1 mixture and the latter as a 5/1 mixture. The shock velocity was measured with a universal counter (Takeda-Riken, TR5002) by detecting signals from 4 piezo-gauges (International Transducer,PK16-13) mounted on the shock-tube with a 10-cm spacing. The shock temperature was calculated from the measured shock velocity by assuming a full relaxation and no chemical reaction.

Results and Discussion

Figure 1 shows a representative oscillogram obtained in this study. It can be seen that absorption increases to a maximum value after showing shock front absorption by C_2H_2, and then decreases. The decrease was not observed for C_2H_2/Ar mixtures without O_2.[6] We estimated the absorption A from the oscillogram according to the equation $A=\ln(I_o/(I_o-\Delta I_t))$, where I_o is the incident light intensity and ΔI_t the absorbed

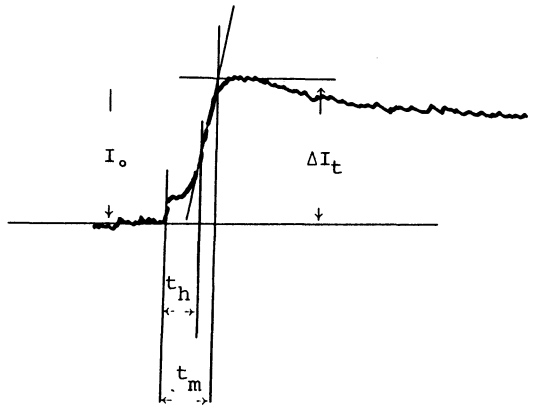

Fig. 1. A sample oscillogram for the 3/1 mixture. P_1=10 Torr and T_2=2114 K. Parameters t_h and t_m used in computer modeling are shown schematically.

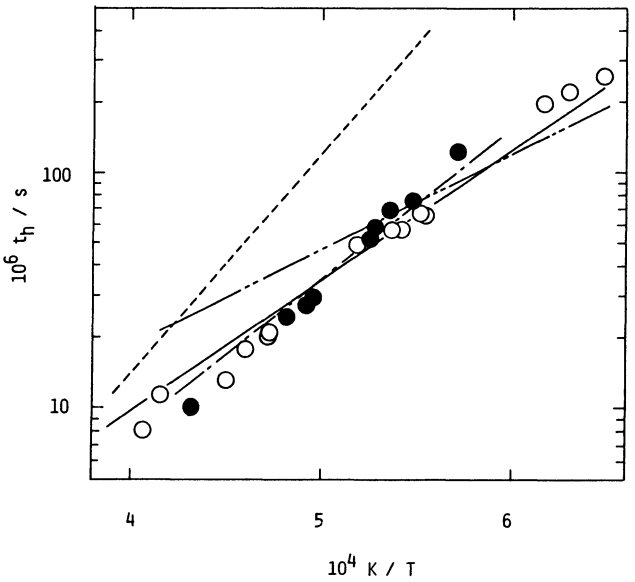

Fig. 2. Relation between t_h and $10^4/T$. Symbols used are: ○ for the 3/1 mixture. ● for the 5/1 mixture. Lines are by computer modeling: (——) for the 3/1 mixture, (-·-·-) for the 5/1 mixture, (----) for the C_2H_2/Ar mixture without O_2.[6] These three lines are modeled using Table 1 reaction mechanism. (-···-) for the 3/1 mixture. Ref. 5 reaction mechanism is used.

intensity at reaction time t (laboratory time). The parameter t_h used for computer modeling was derived from this A and defined to be the time when A reaches half of its maximum value. The maximum A are further divided by $[C_2H_2]_0$, the shock front concentration of C_2H_2, so as to be able to compare the values of A directly in different test gas mixtures. These values of t_h and A are plotted vs. $10^4/T$ in Figs. 2 and 3, respectively. In the figures, the values of t_h and A evaluated for the C_2H_2 mixture without O_2 (C_2H_2/Ar= 3.2/96.8) are shown for a comparison.[6] It can be seen that the A for a 3/1 mixture is smaller than that for a 5/1 mixture. This tendency can also be seen in the t_h value. The values for a C_2H_2 mixture without O_2 are

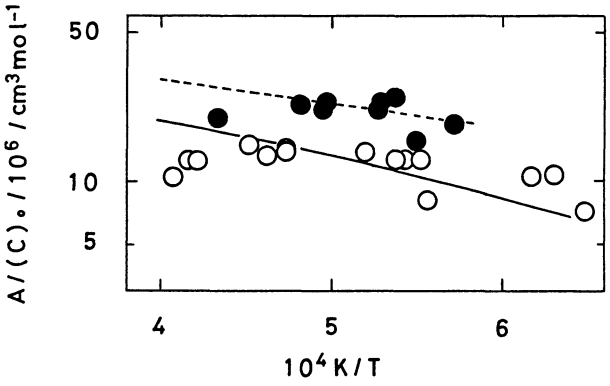

Fig. 3. Relation between A and $10^4/T$. Symbols and lines are the same as in Fig. 2. For the 5/1 mixture, the values are almost the same as those for the C_2H_2/Ar mixture.[6]

much larger than those for 3/1 and 5/1 mixtures.

We adopted computer modeling in order to interpret the measured profile of the absorption more quantitatively and to obtain a reasonable reaction mechanism. We tried it first using the reaction mechanism of Gardiner's group,[5] since the experiments were done under similar conditions to the present. Their mechanism is composed of 23 elementary reactions (Reactions 1—23 in Table 1); the only exception is that k_2 is 1/5 of that in Table 1.[8,9]

It is well-known that absorption is an aggregate by the species present in the reaction region. As for the species in C_2H_2 oxidation. C_2H_2, C_4H_2, CO_2, O_2, C_6H_2, and C_2H_2O are expected to absorb 216-nm light. The absorptions by C_6H_2 and C_2H_2O were, however, neglected in the computer modeling, since absorption data at such high temperatures as the present were not available for these two species. From a former study of C_2H_2 pyrolysis,[6] it is expected that $[C_6H_2]$ only reaches a value less than 1/10 of $[C_4H_2]$. As for the growth of C_2H_2O, it is expected to be small due to the rich mixtures investigated. Thus, ignoring absorptions by these two species does not seem to greatly influence the computer modeling results. The absorptivities of the first 4 species obtained by several workers[6,7] are shown vs. $10^4/T$ in Fig. 4. These absorptivities were incorporated into the present computer program[6] and computations were carried out. The absorption given by $A=\sum a_i[C_i]d$ was evaluated, where a_i and $[C_i]$ are the absorptivity and the concentration of species i, respectively,and d is the light-path length. From the absorption modeling, the two parameters corresponding to the above t_h and A were evaluated. Only the t_h values are plotted in Fig. 2, since the values of A are not very much dependent on the kinetic parameters. It was found that the t_h values by computer modeling are not in accordance with the experimental results.

It is important to determine whether a proposed reaction mechanism can reproduce other experimental results. We carried this out further using one mechanism by Levy[4] and another one by Miller et al.[10] in

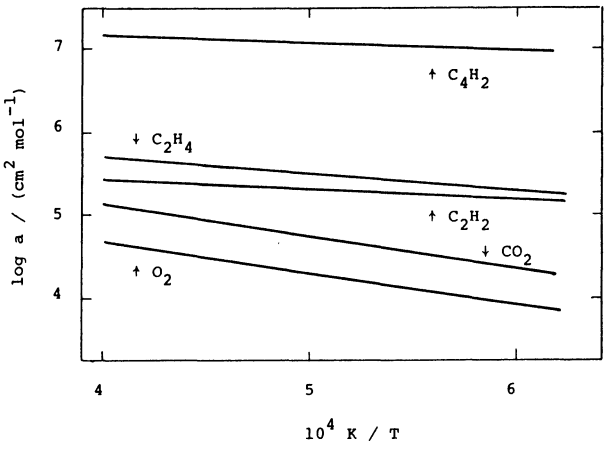

Fig. 4. Absorptivities used in computer modeling.

addition to that by Gardiner's group as above. All of the reaction mechanisms by these three groups include the chemistry of ketene groups. As for the case by Miller et al., they derived the reaction mechanism so as to be able to reproduce both of the experimental results by shock waves and flames. The shock-tube data investigated by them were, however, not adopted in the work by Gardiner's group. Thus, the present modeling plays roles in making up for such a deficiency. As for the modeling results, these two mechanisms by Levy and by Miller et al. were not appropriate for reproducing the present results. The t_h values by Levy's mechanism is larger, like the results by Gardiner's group, whereas the values by the mechanism by Miller et al. is smaller than that from the experiment.

There are two other mechanisms proposed by Jachimowski[11] and by Shaub and Bauer,[12] in which the chemistry of ketene groups is not included. These mechanisms were found not to be appropriate for reproducing the present experimental results.

One of the reasons of such failures in computer modeling could be given as follows. Acetylene in rich mixtures as in the present is expected to decay primarily through pyrolysis steps. Therefore, the k values of the reactions concerning such steps must be adopted with care. We showed in a previous paper[6] that the k_3 value largely depends on the absorption profile and proposed a smaller value than those previously reported. The k_3 value adopted in the three mechanisms by Jachimowski, by Shaub and Bauer and by Miller et al.[10] is the same as proposed by Browne et al.[14] This k_3 value is almost one order larger than the value accepted in the previous paper.[6]

As for the mechanisms by Gardiner's group and by Levy, a reasonable k_3 value is adopted. Therefore, the failure in computer modeling seems to be due to the absence of any important decaying processes of C_2H_2 necessary for rich mixtures. We added Reactions 24—38 to the reaction mechanism by Gardiner's group[5] so as to be appropriate to the present mixtures. This

Table 1. Reaction Mechanism and Rate Constants $k=A\exp(-E/RT)$ (mol, cm, s, and kcal units)

No.	Reaction	log A	E
1	$C_2H_2+M=C_2H+H+M$	16.62	107.00
2	$C_2H_2+C_2H_2=C_4H_3+H$	13.0	45.9
3	$C_2H+H_2=H+C_2H_2$	12.9	2.63
4	$C_2H_2+C_2H=C_4H_2+H$	13.6	0.0
5	$C_2H_2+O=CH_2+CO$	8.61+1.5 log T	1.7
6	$C_2H_2+O=C_2HO+H$	14.63	12.1
7	$C_2H_2+OH=C_2H_2O+H$	14.60	18.6
8	$C_2H_2O+M=CO+CH_2+M$	15.56	57.3
9	$C_2H_2O+OH=C_2HO+H_2O$	13.0	2.7
10	$C_2H_2O+H=C_2HO+H_2$	13.48	8.5
11	$C_2H+O_2=C_2HO+O$	13.0	0.0
12	$C_2HO+H=CH_2+CO$	13.48	0.0
13	$CH_2+O_2=CO_2+H+H$	13.48	1.5
14	$O+H_2=OH+H$	14.34	13.7
15	$OH+H_2=H_2O+H$	13.72	6.5
16	$H+O_2=OH+O$	17.08−0.9 log T	16.63
17	$H_2+M=H+H+M$	12.34+0.5 log T	92.6
18	$H+O_2+M=HO_2+M$	15.4	0.0
19	$HO_2+H=OH+OH$	14.4	1.9
20	$OH+OH=H_2O+O$	13.53	5.0
21	$HO_2+H=H_2+O_2$	13.4	0.7
22	$HO_2+OH=H_2O+O_2$	13.7	1.0
23	$CO+OH=CO_2+H$	12.6	8.0
24	$C_4H_2+O=C_3H_2+CO$	13.43	1.72
25	$C_4H_2+OH=C_3H_2+CHO$	13.48	0.0
26	$C_3H_2+O=C_2H+CHO$	13.83	0.0
27	$C_3H_2+OH=C_2H_2+CHO$	13.83	0.0
28	$C_4H_3+M=C_4H_2+H+M$	16.0	60.0
29	$C_4H_2+M=C_4H+H+M$	17.53	80.0
30	$C_2H_2+C_4H=C_6H_2+H$	13.6	0.0
31	$C_4H_2+C_2H=C_6H_2+H$	13.6	0.0
32	$C_6H_2+M=C_6H+H+M$	16.7	80.0
33	$H+C_4H_2=H_2+C_4H$	13.3	0.0
34	$H+C_6H_2=H_2+C_6H$	13.3	0.0
35	$C_2H_2+OH=C_2H+H_2O$	12.78	7.0
36	$C_2H_2+O=C_2H+OH$	15.5−0.6 log T	15.0
37	$C_4H_2+O=C_4H+OH$	13.0	0.0
38	$C_4H_2+OH=C_4H+H_2O$	13.0	0.0

extended mechanism is the final one determined in this study. By computer modeling with this reaction mechanism, we could reproduce the experimental t_h data shown in Fig. 2.

From the obtained oscillograms, parameters t_m, corresponding to the time when the absorption A reaches a maximum value, were also evaluated and are plotted in Fig. 5 vs. $10^4/T$. The t_m values found by modeling are also shown in the figure for a comparison. This value for t_m has been used as a parameter in previous modeling studies.[6,13] A good agreement between experiment and modeling could be obtained for a 3/1 mixture. For a 5/1 mixture, however, the values by modeling are larger than those by experiment. This incompatibility could not be diminished without greatly disordering the mechanism by Gardiner's group;[5] thus, the k_3 value had to be increased by more than two times. In this case, however, we could not reproduce the other parameter t_h and the t_m in the 3/1 mixture. Therefore, it can be said that the t_m in the 5/1 mixture does not accord with the reaction mechanism

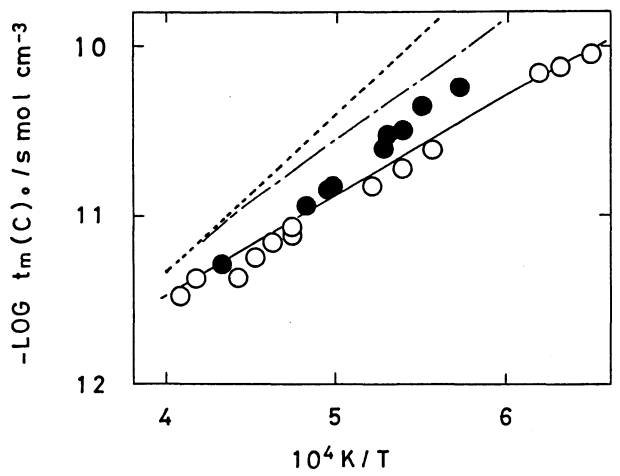

Fig. 5. Relation between t_m and $10^4/T$. Symbols and lines are the same as in Fig. 2.

in Table 1 and remains uninterpretable.

The features of the mechanism shown in Table 1, except for Reactions 1—23, can be described as follows. Reactions 24—27 show the degradation process of C_4H_2 by oxides to smaller hydrocarbons.[15] These reactions, as well as Reactions 37 and 38, seem to be concerned with a decrease in the absorption after exhibiting a maximum value. This can be an evidence to support the idea that the absorption measured in the C_2H_2 mixtures without O_2 did not show a decrease. There have been, however, only a few studies in which the oxidation of C_4H_2 were measured directly. We did not go into this point further and only adopted Reactions 24—27, 37, and 38 as such reactions for the decay of C_4H_2. Reactions 28—34 are concerned with polyacetylenes and polyacetylene radicals. Since the concentrations of these species are modeled to be large, these reactions must be important under the present fuel-rich conditions, as in the pyrolysis of C_2H_2. Abstraction reactions of H atom, 35—38, by an O atom and an OH radical produce acetylene radicals. The number of reaction channels to produce acetylene radicals is larger in the present experiment than that in C_2H_2 pyrolysis. Since the acetylene radicals play roles as chain carriers, the overall reaction rate is expected to become larger in the present experiment. This is in accordance with the measured results of the overall reaction rate given by the reciprocals of t_h and t_m in Figs. 2 and 5. Gardiner's group ignored these reactions as not being important.

As for the reaction mechanism of the oxidation of C_2H_2, Shaub and Bauer[12] referred to two important points differring from the present treatment. One is that the ketene and the ketene radical produced as intermediates were presumed to decompose via unimolecular steps very rapidly. Reactions of the ketene groups were not considered explicitely in their reaction mechanism. The mechanism shown in Table 1 includes not only such steps but also the H atom abstraction reactions by an O atom and an OH radical. The other different point is that they considered reactions involving the CH_2 radical to be unimportant. In Table 1, however, the reaction between CH_2 radical and O_2 was assumed to be the main route to produce CO_2.[5] Reaction 23 has been known as a primary step in producing CO_2 in hydrocarbon oxidation.

In conclusion, the present experimental results could be explained with an extended reaction mechanism based upon that by Gardiner's group.[5] All of the rate constants used were obtained from the existing literature.

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