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Shock Tube Studies of the H_2-O_2-CO Reaction by Atomic Resonance Absorption Spectroscopy

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The atomic resonance absorptions of O- and H-atoms in the reaction of shock-heated $H_2/O_2/CO/Ar(1/1/1/97$ and $0.2/1/1/97.8)$ mixtures were observed over a relatively low temperature range from 1000 to 1400 K. The induction times, determined from the absorptions, were investigated by means of computer modeling which included a sensitivity test. The rate constant for the important initiation reaction, $CO+O_2=CO_2+O$, was evaluated to be $k_{13}=10^{13.1\pm0.6}\exp(-196.9\pm14.9\ \mathrm{kJ}/RT)\ \mathrm{cm^3\,mol^{-1}\,s^{-1}}$, which may supplement the lack of reported rate constants in the low-temperature region.

The reaction

$$CO+O_2=CO_2+O \quad (13)$$

is a radical-producing step which initiates CO oxidation and has drawn the attention of many researchers, where the reaction number is in accordance with that given in Table 1. Recently, Thielen and Roth[1] studied CO oxidation in a shock-heated CO/O_2 system employing atomic resonance absorption spectroscopies (ARAS) of O-atoms. In a CO–O_2 mixture, the overall oxidation reaction is not so fast that it requires a high-temperature environment to observe the progress of the reaction within the restricted observation time of the shock-tube system. They determined the k_{13} value in the high-temperature region of 1700—3500 K.

Gardiner et al.[2] studied the reaction in both H_2/O_2 and $H_2/O_2/CO$ systems by means of UV absorption spectroscopy of the ground-state OH-radicals at temperatures of 1400—2500 K. They compared the induction times of OH absorption in the $H_2/O_2/CO$ system with those in the H_2/O_2 system and obtained k_{13} in the lower temperature region by computer modeling.

Reviews concerning elementary reactions in $H_2/O_2/CO$ system were given in detail by a group at the University of Leeds,[3] and more recently by Warnatz.[4] These two groups proposed the same k_{13} value in the temperature range 1500—3000 K.[3,4]

We have also adopted the $H_2/O_2/CO$ system and have observed the growth rates of O- and H-atoms directly by ARAS and have determined the k_{13} value in a low-temperature region in order to supplement the lack of reported rate constants.

Experimental

Since details concerning the incident shock-tube and the ARAS optical system were given in a previous paper,[5] we discuss them here only briefly.

The ARAS system comprises a light source and a detector. Gas mixtures of H_2 or O_2 diluted in He (by 1% flowing at 2 Torr through a quartz tube, 1 Torr=133.322 Pa) were excited by a microwave generator (Raytheon, PGM10X1); the accompanied emissions were used for the light source. A combination of a vacuum-UV-monochromator (Minuteman, 302-VM dispersion=40 nm/mm), of which wavelength was centered at 121.6 nm of the Lyman-α line by H-atoms or at 130.5 nm of the O-triplet line by O-atoms, and a solar blind photomultiplier (Hamamatsu, R-1459) was used as the detector. The signals of the absorption time profiles were recorded on a digital oscilloscope (Iwatsu, DS-6121) combined with an XY-recorder.

The test section of the shock tube was evacuated to less than 10^{-5} Torr before each run. The leak rate was ca. 10^{-5} Torr min^{-1}, and the shock waves were actuated within 3 min after closing all valves of the shock-tube.

Gases for the test gases ($H_2/O_2/CO/Ar=1/1/1/97$ and $0.2/1/1/97.8$) were 99.99999% pure H_2, 99.999% pure O_2, 99.6% pure CO and 99.999% pure Ar and were used without further purification.

Results and Discussion

Figure 1 is a sample oscillogram of the absorption history at 121.6 nm for the 1/1/1 ($H_2/O_2/CO$) mixture; it shows the slight rise at the shock front, a low plateau,

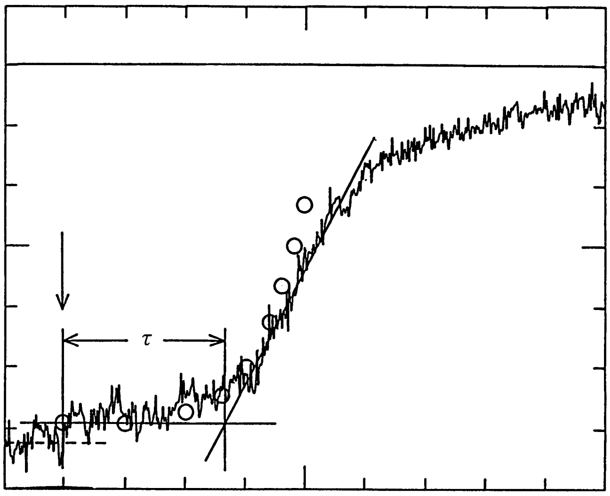

Fig. 1. A sample oscillogram of the absorption profile at 121.6 nm.
Test gas: $H_2/O_2/CO/Ar=1/1/1/97$,
$P_1=20$ Torr, $T_2=1173$ K.
The time-scale is 50 μs/div. The upper line shows the zero-level of the incident light intensity. The arrow shows the shock front. The induction time, τ, was evaluated as in the figure. The circles show the results by computer modeling with the reaction mechanism in Table 1.

and an exponential increase. Such a time profile was also obtained for absorption at 130.5 nm. Since the absorption by H_2 for the two light sources are smaller than those by O_2 and CO,[1,5,6] the absorption time profiles are not so different between the two mixtures. From the oscillograms, the induction times, τ, defined as the time interval between the shock arrival at the observation window and the foot of the exponential absorption rise, were evaluated on the laboratory base. As is shown in Fig. 1, the foot is the intersection of the low plateau and the extrapolated line of the absorption increase. The low plateau of the absorption after the shock front can be attributed to absorption by O_2 and CO.[1,5,6] Since the total absorption is the summation of each absorption of the contributing species, this revised definition of τ must be more reasonable than those adopted in a previous study.[5]

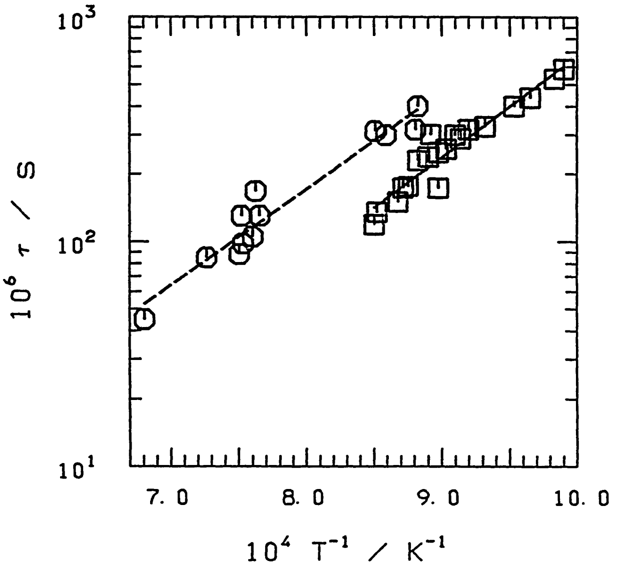

Fig. 2. Induction times, τ, at 121.6 nm vs. $10^4/T$.
Squares: for the 1/1/1 (H_2/O_2/CO) mixture,
Octagonals: for the 0.2/1/1 mixture.
The lines show the least-squares fits for the data points.

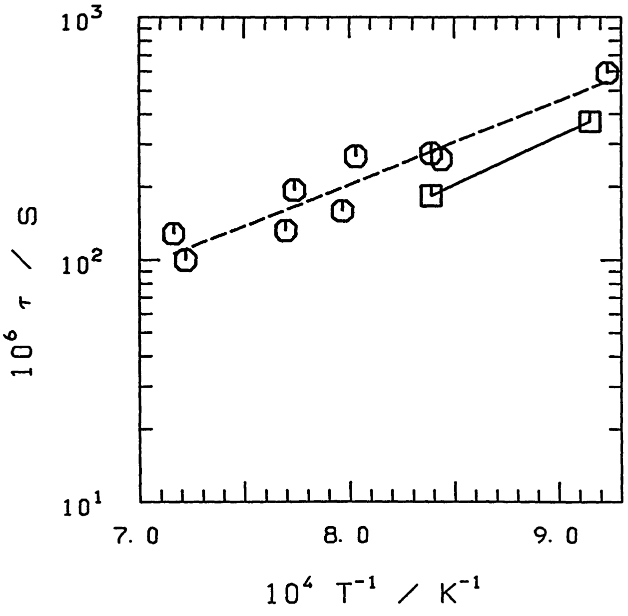

Fig. 3. Induction times, τ, at 130.5 nm vs. $10^4/T$.
Squares: for the 1/1/1 mixture,
Octagonals: for the 0.2/1/1 mixture.
The lines show the least-squares fits for the data points.

The data points of the experimental τ values obtained from the 121.6 and 130.5 nm absorption profiles are shown in Figs. 2 and 3, respectively. Each line exhibits a least-squares result for the data points. The temperature dependences of both lines are almost equal and the τ values in the 1/1/1 mixture are smaller than those in the 0.2/1/1 mixture.

These results were subjected to interpretation by computer modeling. The induction time for the modeling is defined as being the time interval between shock arrival and the attainment of certain values of the

Table 1. Reaction Mechanism and Rate Constant
$k=AT^n\exp(-E/RT)$ (mol, cm, s, and J units)

Reaction		A	n	E	Ref.
1)	$H_2+O_2=H+HO_2$	2.8+15[a]	0.	2.60+5	See Text
2)	$H_2+AR=H+H+Ar$	2.2+14	0.	3.77+5	4
3)	$O_2+AR=O+O+Ar$	1.2+14	0.	4.51+5	4
4)	$H+O_2=OH+O$	1.22+17	−0.91	6.91+4	4
5)	$O+H_2=OH+H$	1.5+7	2.0	3.16+4	4
6)	$OH+H_2=H_2O+H$	1. +8	1.6	1.38+4	4
7)	$H+O_2+AR=HO_2+Ar$	7. +17	−0.8	0.	4
8)	$OH+OH=H_2O+O$	1.5+9	1.14	0.	4
9)	$H+HO_2=OH+OH$	1.5+14	0.	4.18+3	4
10)	$OH+HO_2=H_2O+O_2$	2. +13	0.	0.	4
11)	$O+HO_2=OH+O_2$	2. +13	0.	0.	4
12)	$CO+OH=CO_2+H$	4.4+6	1.5	−3.1+3	4
13)	$CO+O_2=CO_2+O$	1.3+13	0.	1.97+5	This Work
14)	$CO+O+AR=CO_2+AR$	5.3+13	0.	−1.9+4	4

a) The number after + exhibits an index for 10.

radical concentrations. These concentrations for H- and O-atoms were assumed to be 8.3×10^{-13} and 1.66×10^{-12} mol cm^{-3}, respectively.[5,6] These are almost in accord with the detection limit of the present ARAS system; the induction times, thus defined, in computer modeling are considered to be compatible with the induction times obtained from an oscillogram of the absorption profile.[5]

The reaction mechanism used in the computer modeling of the present study is shown in Table 1. This mechanism comprises H_2–O_2 reaction steps of Reactions (1)—(11),[4] derived in a former study,[5] and CO steps to form CO_2, Reactions (12)—(14). Excepting the k_1 and k_{13} values, the k values are those recently recommended by Warnatz.[4] He re-evaluated the values by Baulch et al.[3] as well as those by other groups that have appeared after Baulch's review.

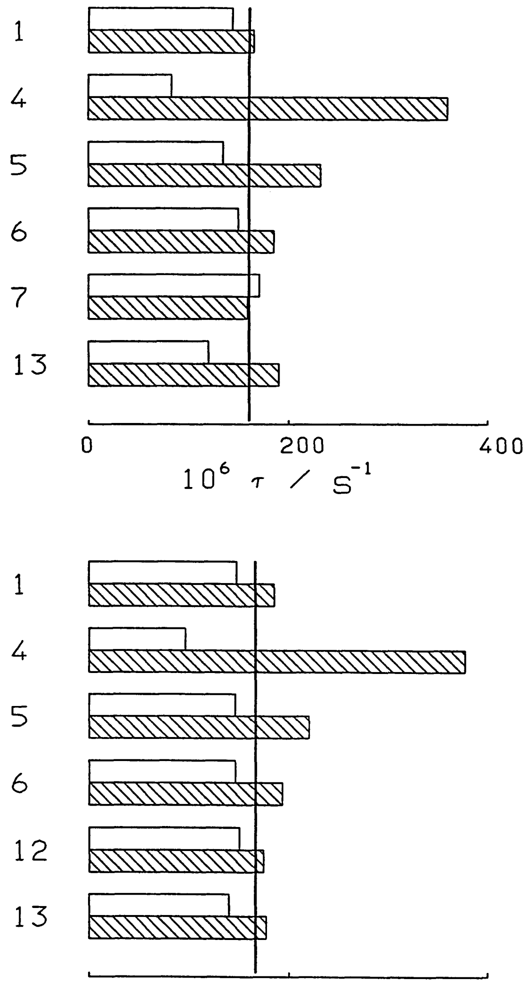

Fig. 4. Sensitivity calculation for τ.
Upper: for the result of Fig. 1 by H-atoms.
The numbers at the left hand side show the elementary reactions in Table 1. The above bar for each number shows the τ value obtained by computer modeling when each rate constant was multiplied by a factor of 5. The lower hatched bar was obtained by using the rate constant divided by the same factor. The elementary reactions giving small variations of τ are not shown in the figure. The vertical line through the bars shows the standard value of τ given by using the reaction parameters in Table 1.
Lower: for the 0.2/1/1 mixture at 1385 K by O-atoms. The numbers, the bars and the vertial line have the same meaning as those above.

In order to comprehend the roles of each reaction in the progress of the H_2–O_2–CO reaction, we carried out a sensitivity test for the reaction mechanism shown in Table 1 by changing each rate constant by factors of five and one-fifth. Figure 4 shows the results of the sensitivity test. The variations of the τ values are dominant for the sensitivity tests for Reactions (1), (4), (5), (6), and (13). A similar tendency of the variations was obtained for the two 1/1/1 and 0.2/1/1 mixtures.

Reaction (1) was found to be an important initiation in the H_2–O_2 reaction; we[5] thus had derived the k_1 value by means of ARAS and computer modeling which included a sensitivity test. The k_1 value in Table 1 is, however, that re-evaluated from the revised τ, as obtained above for the H_2/O_2 mixture. In the present system of the $H_2/O_2/CO$ mixture, Reaction (1) has a smaller effect on the variation of the τ values. Reactions (4)—(6) are bi-molecular reactions which include one radical; they are representative reaction steps in the H_2/O_2 reaction system. The rate constants for those steps had been well established in studies of the H_2/O_2 system. Reaction (13) is a radical-producing step to initiate CO oxidation, as is emphasized in the introduction; it is the most influential reaction on the τ values

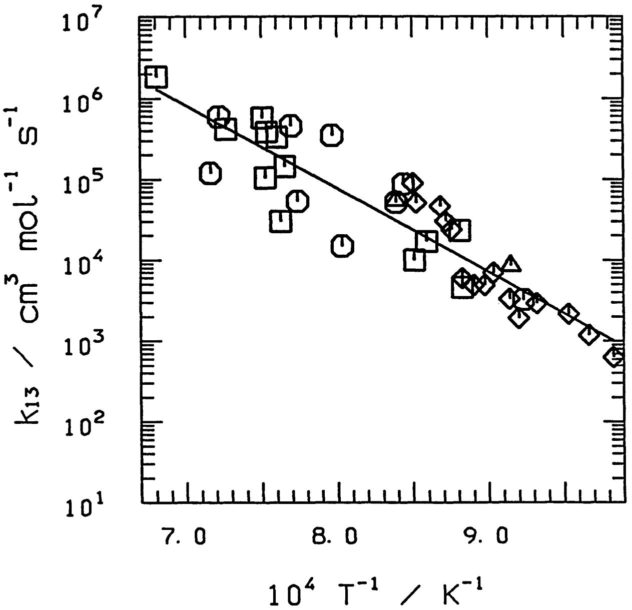

Fig. 5. Arrhenius plots of derived k_{13}.
Squares: for the 0.2/1/1 mixture at 121.6 nm,
Octagonals: for the 0.2/1/1 mixture at 130.5 nm,
Diamonds: for the 1/1/1 mixture at 121.6 nm,
Triangles: for the 1/1/1 mixture at 130.5 nm.
The line shows the least-squares fit for the data points.

among the CO participating reaction steps.

In the present study, we fit the τ values by computer modeling to the experimental τ values given in Figs. 2 and 3 by adjusting the k_{13} value. The k_{13} values, thus determined, are shown vs. $10^4/T$ in Fig. 5. We see no distinctive dependences of the k_{13} values on the test gas mixtures, as well as the species, H- or O-atoms, observed. The line shows the result of least-squares fitting for the k_{13} values and following Arrhenius expression could be derived:

$$k_{13}=10^{13.1\pm0.6}\exp(-196.9\pm14.9\text{ kJ}/RT)\text{ cm}^3\text{ mol}^{-1}\text{ s}^{-1},$$

where the values with ± exhibit one standard deviation.

Computer modeling with the reaction mechanism given in Table 1 was also carried out for the absorption time profile given in Fig. 1. The absorptivity of H-atoms used in the computer modeling was 5×10^{10} $\text{cm}^2\text{ mol}^{-1}$, which was determined in a study of the H_2O pyrolysis at temperatures above 2000 K (described later). The agreement of the absorption profile between the experiment and computer modeling is good for the early period of the reaction. At later stages, however, the absorption determined by modeling is larger than that found by experiment. These modeling results are due to the fact that the absorptivity of H-atoms becomes smaller at higher concentrations;[1,6] such effects were not taken into account in the computer modeling.

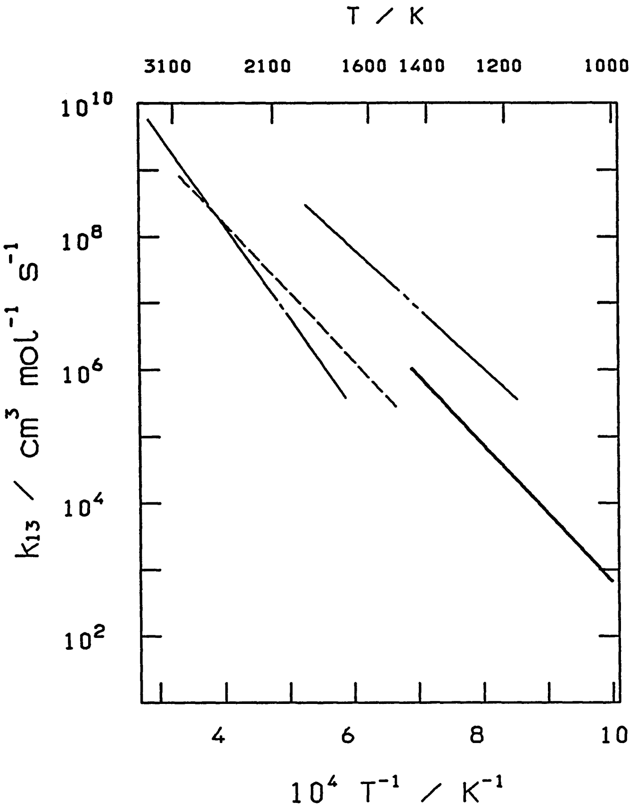

Fig. 6. Arrhenius expression of k_{13}.
Solid line: This work.
Chain line: by Thielen and Roth.[1]
Broken line: by Baulch et al.[3]
Chain-broken line: by Brabbs et al.[7]

Figure 6 shows an Arrhenius expressions for k_{13} from different sources by Thielen and Roth,[1] Baulch et al. (the same one by Warnatz)[3,4] and Brabbs et al.,[7] along with our value. Baulch et al.[3] took into account the expression by Gardiner et al.[2] in recommending their k_{13} value. Thus, the value given by Gardiner et al.[2] can be considered to be the data reviewed by Baulch et al.[3] and is not shown in the figure.

As shown in Fig. 6, most of these reported k_{13} values were obtained at higher temperatures than ours. The value by Brabbs et al.[7] was obtained in a temperature region close to the present study, but is larger than ours. Their value is also larger than the extrapolated values of Thielen and Roth[1] as well as Baulch et al.[3] by almost one order of magnitude. The discrepancies were so large that Gardiner et al.[2] examined the results by Brabbs et al.[7] by taking into account such view points as 1) the purities of the test gas mixtures used, 2) the difference of the vibrational relaxation times of CO depending on the compositions of the test gas mixtures used, and 3) a few uncertainties concerning the emission spectroscopy adopted.

Although Gardiner et al.[2] were not successful in explaining the larger value of k_{13} by Brabbs et al.,[7] their points[2] seem to cover most of the important criterions necessarily to consider the discrepancies.

Our k_{13} value determined in the present study is smaller than the value by Brabbs et al.,[7] but larger than the extrapolated values by Thielen and Roth[1] as well as Baulch et al.;[3] examinations of the present results through any appropriate criterions are thus required. We adopted Gardiner's view points for the examination. His view point concerned with the emission spectroscopy could be excluded in the present case. Gardiner's second view point is based on the vibrational relaxation of CO, which depends on the compositions of test gas mixtures; it could be ignored in the present case, since the present experimental conditions, including the composition of the test gas mixtures, are almost the same as those adopted by Gardiner et al.[2]

The first view point of the Gardiner et al.[2] concerns impurities of the test gas mixtures used; we examined our experiments in terms of this view point. The purities of H_2, O_2 and Ar used for the experiments were above 99.999%; we discarded them for the present from considerations of the impurities. Although the purity of CO was given as 99.6%, we mainly focused our attention on the impurity problem origining from the CO gas used.

A trial experiment for CO/Ar mixtures both with and without O_2 was carried out under the same experimental conditions as the present by using the ARAS. It was observed that only a small absorption, starting at the shock front and continuing with a constant value, appeared. Since no growing absorption was observed during the reaction period, the influence of the impurities, if any, on the progress of reaction is considered to be negligible within the present temperature range.

With regard to the influence of impurities,[3] a question always arises whether or not a trace amount of H_2O derived from the CO container might accelerate the reaction to be measured. We, therefore, studied the reactivity of H_2O both by computer modeling and experiment. Computer modeling was carried out according to the reaction mechanism given in Table 1 for a test gas mixture of $H_2/O_2/CO/H_2O=1/1/1/0.01$ in Ar. No acceleration of the reaction (estimated from the growth rates of O-atoms and H-atoms) with the presence of H_2O was observed to occur in the modeling. Furthermore, the experimental verifications were done for test gas mixtures of H_2O/Ar and $H_2O/O_2/Ar$. No absorption under the present experimental conditions was observed for the growth of O- and H-atoms, which could be produced directly or indirectly by the decomposition of H_2O. It has been confirmed that H_2O is very stable within the present temperature range. The influence of H_2O on the reaction progress is thus also negligible. Detailed reports on the reaction of H_2O measured using the present technique may appear elsewhere.

In conclusion, we could establish a reliable k_{13} in the lower temperature region, though we could not elucidate the discrepancies between the present k_{13} value and extrapolations of the reported k_{13} values[1,3,4] to the lower temperature region.

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