2480 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***62****, 2480—2484 (1989)* [Vol. 62, No. 8

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

Tohru KOIKE
Department of Chemistry, National Defense Academy, Hashirimizu, Yokosuka 239
(Received January 24, 1989)

The increases of O-atoms and of H-atoms in the reaction between H_2 and O_2 in shock waves were measured over the temperature range of 1000—1400 K by atomic resonance absorption spectroscopy. The induction times of the absorptions by these two species were evaluated and computer modeling was carried out to reproduce these values. As one of the initiations of the H_2-O_2 reaction, $H_2+O_2=H+HO_2$ was found to play an important role in the progress of the reaction. The rate constant of this reaction was evaluated as: $k=4.1\times10^{16}$ $\exp(-285\text{ kJ}/RT)$ $\text{cm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$.

The reaction of H_2-O_2 in shock waves has been studied in a wide temperature range by many researchers and is well-known to proceed through chain initiations, chain branchings, and chain terminations. Although reliable rate constants are proposed for most of the important elementary reactions of each step,[1] some of them are still controversial.

Atomic resonance absorption spectroscopy (ARAS) is very sensitive and concentrations of O-atoms and H-atoms of about 10^{-12} mol·cm^{-3} can be detected. Most of the studies by ARAS have been made to clarify the reaction of reactants highly diluted in Ar, e.g., ppm order. Two points could be given for the advantage in using the ARAS under such experimental conditions. One is that the reactions intended to measure should not be affected by secondary reactions. The other is that temperature variation by the progress of the reaction could be almost avoided. Detailed reviews of shock tube studies using this technique have recently been given by Just.[2]

ARAS has also been applied to the kinetic study of the H_2-O_2 reaction by Pamidimukkala and Skinner in the temperature range of 1919—2781 K[3] and by Frank and Just in the temperature range of 1700—2500 K.[4] They measured the test gas mixtures of $H_2/N_2O/Ar$ with or without O_2. Since the reaction mechanisms are specifically devised to explain the experimental result thus obtained, some of the elementraty reactions which are important under ordinary conditions are excluded from the reaction mechanisms.

We also applied ARAS to the H_2-O_2 reaction at lower temperatures than those of these two studies. Due to the slowness of growth rates of O- and H-atoms under such conditions at lower temperatures, these atoms are produced only in small amounts. We had to use test gas mixtures of rather higher concentrations of reactants than those previously used for ARAS. Thus, we could study the early stages of the reaction and could obtain the rate constant of $H_2+O_2=HO_2+H$.

Experimental

The test section of the rectangular shock tube used in a former study[5] on incident shock waves was reconstructed so as to be applicable to the ARAS measurements as follows.

Observation windows were located 3.3 m down-stream from the diaphragm section. Two of the 4 observation windows, made of MgF_2, had two vacuum tight flanges for the ARAS. A quartz tube was connected perpendicularly to one of the windows. A rotary pump was used to let gas mixtures of H_2 or O_2 diluted in He by 1% flow at 2 Torr (1 Torr≈133.322 Pa) through the quartz tube. A microwave generator (Raytheon, PGM10X1) was used to discharge the gas mixture and the emissions were used as the light source of the ARAS. For the other window, a vacuum-UV-monochromator (Minuteman, 302-VM, dispersion=40 nm mm^{-1}) was located to isolate the desired emission lines centered at 121.6 nm for the Lyman-α line of H-atoms and at 130.5 nm for the O-triplet line of O-atoms. The VUV monochromator having entrance and exit slits of 1 mm width was evacuated to about 5×10^{-4} Torr using a rotary pump combined with a liquid-N_2 trap. A solar blind photomultiplier (Hamamatu, R-1459) was used as a detector. The signals from the detector were fed into an operational amplifier, and then, 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. Gases for the test gas were 99.999% pure H_2, 99.999% pure O_2, and 99.999% pure Ar and were used without further purification. The compositions of the two test gases prepared are shown in the footnote of Fig. 3.

A trial run with a test gas of pure Ar was carried out and it was confirmed that no appreciable absorption was observed under the present experimental conditions. With regard to the absorptions of test gas mixtures of O_2/Ar and H_2O/Ar in the present temperature range, only small absorptions at the shock front attributable to O_2 and H_2O were observed.

Results and Discussion

Figure 1 is a sample oscillogram exhibiting the time profile of the absorption at 130.5 nm. The absorption occurs immediately after the shock arrival to the observation window; it holds a plateau value and then increases exponentially to a high value. From the oscillograms, the absorption at the shock front and the induction times, τ, defined as the time interval between the shock arrival to the observation window and the foot of the exponential absorption rise, were evaluated.

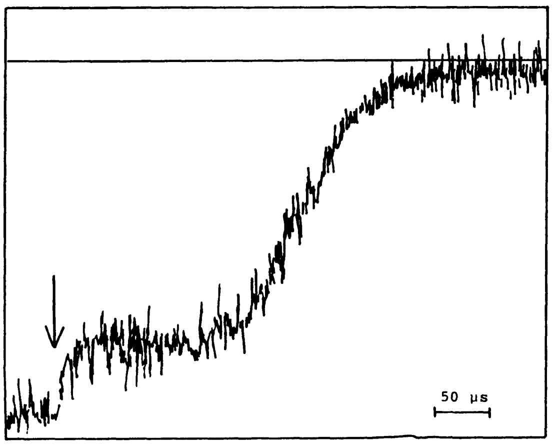

Fig. 1. A sample oscillogram of the absorption profile at 130.5 nm.
Test gas: $H_2/O_2/Ar=1.1/5.8/93.1$.
$P_1=20$ Torr, $T_2=1080$ K.
The upper line shows the zero-level of the incident light intensity. The arrow shows the shock front.

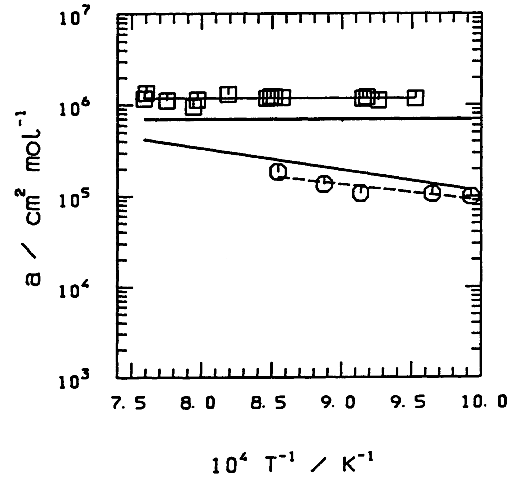

Fig. 2. Absorptivities, a, vs. $10^4/T$.
Squares; at 130.5 nm, Octagonals; at 121.6 nm.
Lines through each data point show least squares fit. Thick lines are extrapolated values:[4] Upper; at 130.5 nm, Lower; at 121.6 nm.

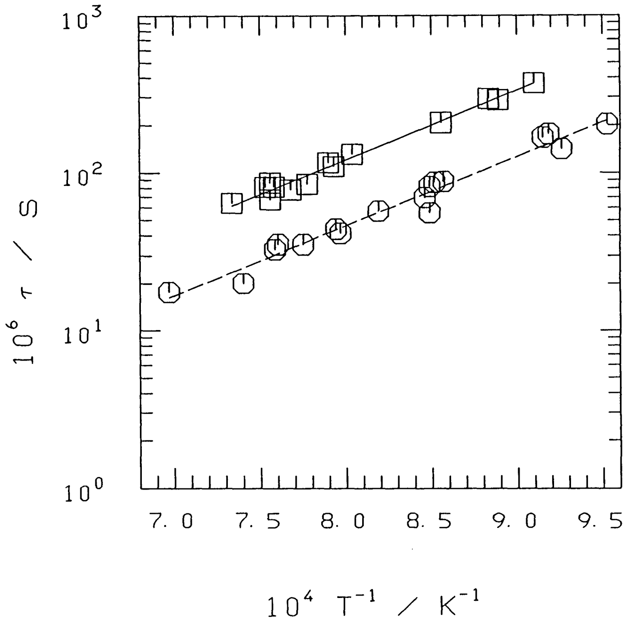

Fig. 3. Induction times, τ, obtained at 130.5 nm vs. $10^4/T$.
Squares: $H_2/O_2/Ar=4.8/1/94.2$.
Octagonals: $H_2/O_2/Ar=1.1/5.8/93.1$.
Lines through each data point show least squares fit. Computer modeling was done to reproduce these lines.

The absorption at the shock front can be attributed to the absorption by O_2, since the absorption by H_2 is reported to be negligible.[4] Figure 2 shows the absorptivity, a, evaluated from the absorption as: $a=\ln(I_0/I)/(d[O_2])$, where I_0=incident light intensity. I=transmitted light intensity at the shock front, and d=optical path length. There seems to be no temperature dependence for the a values at 130.5 nm. The a values of O_2 for the Lyman-α line at 121.6 nm are also shown in the figure. These a values are smaller than those at 130.5 nm and are seen to increase with temperature. The thick lines are extrapolated values from the reported ones[4] obtained at much higher temperatures than the present. It is seen that the present values and the extrapolated values are close to each other. Thus, the present optical system can be considered to be working well.

Figure 3 shows the temperature dependence of τ evaluated from the absorption time profile at 130.5 nm. It is seen that the temperature dependence of τ is almost the same for the two mixtures investigated. As for the absolute value of τ, it gets smaller with larger concentration of O_2. The lines are the least-squares fit for the data points.

The results shown in Fig. 3 were subjected to interpretation by computer modeling. The induction times by modeling were evaluated from the time profile of the modeled O-atom concentration, i.e., the reaction time when the concentration value reaches 1.66×10^{-12} mol·cm^{-3} for the O-atom was assumed to correspond to the induction time.[4]

The computer program used in modeling is the same one as was used in the former study.[5] In the modeling, numerical integration is carried out by taking into account both the forward and reverse rates of each elementary reaction, and the reverse rate constants are calculated from the forward rate constants combined with equilibrium constants based on appropriate thermochemical data.[6]

Warnatz et al.[1,7] has recently reviewed the reaction mechanism of H_2-O_2 and recommended the rate constants of Reactions 2—11 which are valid over the temperature range of 1000—2500 K as shown in Table

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

Reaction	A	n	E	W[a]	PS	FJ
1) $H_2+O_2=H+HO_2$	4.1 +16[b]	0	2.85+5	*		
2) $H_2+AR=H+H+Ar$	2.2 +14	0	4.0 +5	*	*	*
3) $O_2+AR=O+O+Ar$	1.2 +14	0	4.5 +5	*	*	*
4) $H+O_2=OH+O$	1.22+17	−0.91	6.91+4	*	*	*
5) $O+H_2=OH+H$	1.5 + 7	2.0	3.16+4	*	*	*
6) $OH+H_2=H_2O+H$	1. + 8	1.6	1.38+4	*	*	*
7) $H+O_2+AR=HO_2+Ar$	7. +17	−0.8	0	*	*	
8) $OH+OH=H_2O+O$	1.5 + 9	1.14	0	*	*	
9) $H+HO_2=OH+OH$	1.5 +14	0	4.2 +3	*		
10) $OH+HO_2=H_2O+O_2$	2. +13	0	0	*		
11) $O+HO_2=OH+O_2$	2. +13	0	0	*		

a) The reactions designated by * in the last three columns are those adopted by Warnatz (W), Pamidimukkala and Skinner (PS), and Frank and Just (FJ). b) The number after + exhibits an index for 10.

1. We tried to reproduce the τ values in Fig. 3 by computer modeling adopting his mechanism. As for the rate constant of Reaction 1, we adopted the value of the reverse direction, k_{-1}, recommended also by Warnatz.[1] It was found that the τ values by modeling thus carried out are larger than those measured. The present τ values could not also be reproduced using the two reaction mechanisms which are in accordance with the results by ARAS,[3,4] as described above. It can be pointed out that the two reaction mechanisms are for much higher temperatures than the present. Any of the reactions, which are important in the present lower temperature range, are expected to be ignored or treated to have a small role in their reaction mechanisms. As for the test gas mixtures measured by ARAS, N_2O was used as oxidizer with or without O_2. Since the concentration of O_2 seems to be small in the mixtures without O_2, chain termination, Reaction 7, was not taken into account in the reaction mechanism by Frank and Just.[4] With regard to the initiation reactions, $H_2+O_2=OH+OH$ was taken into account by Frank and Just.[4] In the reaction mechanism proposed by Warnatz, the reverse reaction of $H+HO_2=H_2+O_2$, Reaction 1, can also be a chain initiation. He did not, however, specify the kind of product of Reaction 1. Among the three reaction mechanisms considered, the mechanism giving the closest τ values in Fig. 3 is that of Frank and Just.[4] Since rate constants of important reactions are not so different from each other over the present temperature range, such a discrepancy between the values by experiment and those by modeling could be attributed to whether appropriate initiation reactions were taken into account in the reaction mechanism.

We accepted the rate constants by Warnatz[1] and assumed Reaction 1 to be one of the chain initiations in the H_2-O_2 reaction. The rate of the reaction having a four-center path, $H_2+O_2=OH+OH$, can be considered to be small,[8] since this reaction has much higher activation energy than Reaction 1 does. Then, we only changed the k value of Reaction 1 so as to be in accord with the least squares lines in Fig. 3 and finally we succeeded in modeling them with the following value for k_1.

$$k_1=4.1\times10^{16}\exp(-285\ \mathrm{kJ}/RT)\ \mathrm{cm^3\cdot mol^{-1}\cdot s^{-1}}$$

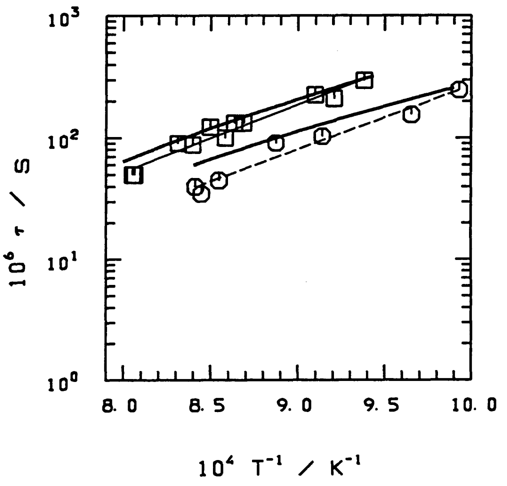

Fig. 4. τ obtained at 121.6 nm vs. $10^4/T$.
Symbols are the same as those in Fig. 3.
Lines through each data point show least squares fit. Thick lines show the values by computer modeling using the reaction mechanism in Table 1.

The reaction mechanism of the 11 elementary reactions shown in Table 1 is the conclusion of this study and the lines in Fig. 3 are the results of modeling, which agree well with the experiment.

Figure 4 shows the relation between the τ values of the absorption by H-atoms and $10^4/T$. Since the absorption by H-atoms is larger than that by O-atoms, the temperatures of the data points are seen to be shifted to a lower region than those by O-atoms shown in Fig. 3. The two thin lines are least-squares fits to the data points. The thick lines are obtained by computer modeling using the reaction mechanism in

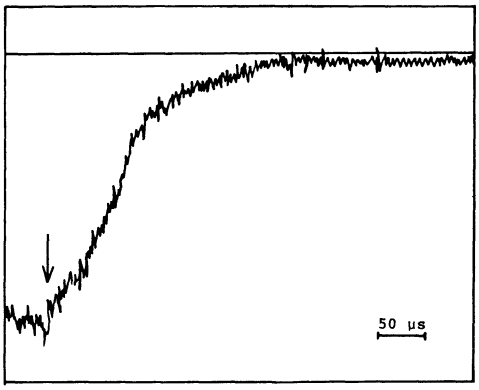

Fig. 5. A sample oscillogram showing the absorption at 121.6 nm by H-atoms.
Test gas: $H_2/O_2/Ar=4.8/1/94.2$
$P_1=20$ Torr, $T_2=1288$ K
The upper line shows the zero-level of the incident light intensity. The arrow shows the shock front.

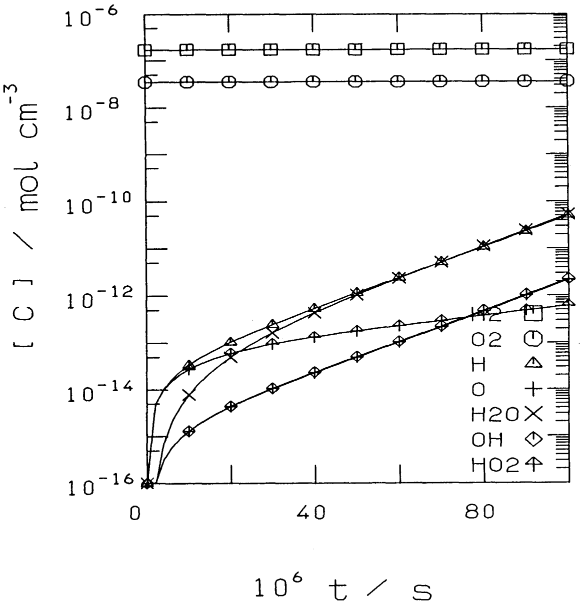

Fig. 6. Computer modeling for the absorption profile shown in Fig. 5.
It is seen that the concentration of H-atoms at 50 μs is above the threshold value of 8.3×10^{-13} mol·cm^{-3}.

Table 1. The threshold value of the H-atoms was assumed to be 8.3×10^{-13} mol·cm^{-3}.[4)] Although the relation between experiment and modeling is seen to be good for most the cases, a complete agreement between them was not established.

We could obtain an agreement of the τ values between experiment and modeling for O-atoms and H-atoms as above. Therefore, it can be concluded that the threshold values of concentrations of these two species[4)] assumed for modeling are appropriate in the present case.

Figure 5 is an oscillogram showing the absorption of the Lyman-α line obtained at much higher temperatures than that of Fig. 1. The absorption at 50 μs (lab. time) is seen to occur and can be attributed to H-atoms. We compared this with the result by computer modeling using the reaction mechanism in Table 1 under the same experimental conditions of Fig. 5. The concentration profiles of each species thus obtained are shown in Fig. 6. It is seen that the concentration of H-atoms at 50 μs is larger than the threshold value of 8.3×10^{-13} mol·cm^{-3}. If a smaller value was assigned for the k_1, the concentration at 50 μs obtained by modeling fell below the value of the detection limit. The absorption by H-atoms at 50 μs must be unobservable in this case. Therefore, it is confirmable also on the basis of such a degree of absorption that Reaction 1 plays an important role as a chain initiation in the reaction mechanism of H_2-O_2.

It should be pointed out that the present k_1 does not agree with literature values.[1,9)] Baulch et al.[9)] recommended the k_1 value. The present k_1 is larger than their value extrapolated to the temperature range of this study by almost one order. With regard to the extrapolated k_1 value derived from the k_{-1} by Warnatz,[1)] it does not accord with the value in Table 1 either. These literature values are considered to be valid below 1000 K, though not in the present temperature range.

It is also seen from Fig. 6 that the concentrations of reactants, H_2 and O_2, do virtually remain constant even if the reaction passes through the time τ. In accordance with this figure, modeling also indicates that the reaction temperature does not change at all and equals that of the shock front. Such experimental conditions of a constant temperature above 1000 K with very small concentrations of H- and O-atoms continuing a few hundred μs may give a reaction environment to study reactions between such atoms and any interesting species. Therefore, it can be inferred that this study might have introduced a new way of shock tube research using ARAS.

The author wishes to thank Prof. Kihei Morinaga, National Defense Academy, for his useful discussions and continuous encouragement throughout this work. The author wishes also to thank important comments of reviewers concerning the initiation step of the H_2-O_2 reaction.

References

1) J. Warnatz, "Combustion Chemistry," ed. by W. C. Gardiner, Jr., Springer-Verlag (1984).

2) Th. Just, "Shock Waves in Chemistry," ed. by A. Lifshitz, Marcel Dekker (1981).

3) K. M. Pamidimukkala and G. B. Skinner, *J. Chem. Phys.*, **76**, 311 (1982).

4) P. Frank and Th. Just, *Ber. Bunsenges. Phys. Chem.*, **89**, 181 (1985).

5) T. Koike and K. Morinaga, *Bull. Chem. Soc. Jpn.*, **49**, 1457 (1976).

6) D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," 2nd ed., NBS NSRDS 37 (1971).

7) S. M. Hwang, W. C. Gardiner, Jr., M. Frenklach, and Y. Hidaka, *Combust. Flame,* **67**, 65 (1987).

8) S. W. Benson, "Thermochemical Kinetics," 2nd ed., Wiley (1976).

9) D. L. Baulch, D. D. Drysdale, D. G. Horne, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions," Vol. 1, Butterworths (1973).