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ESR Study of the Mercury-photosensitized H_2+O_2 Reaction

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The ESR technique has been applied to a study of the mercury-photosensitized reaction of H_2+O_2 mixtures in the $P_{O_2}=10$—200 μHg and $P_{H_2}=0.2$—4 mmHg regions. For the determination of this reaction, the concentration (ESR signal amplitude) of H atoms was followed with time throughout the reaction. The concentration of H atoms varied with time; its maximum was determined. The time (T_m) at which the H atom concentration reached a maximum depended on oxygen and hydrogen pressures. From the variations in T_m and some kinetic considerations, it was concluded that oxygen played an important role in this reaction in increasing the stationary concentrations of H atoms in the system. In this experiment, $I_0=2.4\times10^{15}$ molecules/sec, the rate of the production of H atoms in Reaction (1), was determined from the variations in T_m with the initial oxygen pressure:

$$H_2 + Hg^*(^3P_1) \xrightarrow{I_0} 2H + Hg(^1S_0) \qquad (1)$$

The pressure of oxygen at the maximum concentration of H atoms was found to be little dependent on the P_{H_2} used in this experiment; 5 μHg was found to be this pressure.

There have been many photochemical studies of the reaction between hydrogen and oxygen.[1] It is well known that the reaction can proceed with a chain mechanism under proper conditions. It was first established by Dickinson[2] that hydrogen and oxygen can react in the presence of mercury atoms in the electronically-excited state ($^3P_1$)

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[1] D. H. Volman, "Advances in Photochemistry," Vol. 1, Interscience Publishers, New York (1964), p. 43.

[2] R. G. Dickinson, *Proc. Natl. Acad. Sci. U. S.*, **10**, 409 (1924).

at room temperature. $Hg^*(^3P_1)$ can react with hydrogen as follows:

$$Hg^*(^3P_1) + H_2 \rightarrow HgH + H \rightarrow Hg(^1S_0) + 2H \quad (1)$$

The deactivation of the excited mercury atom by energy transfer to oxygen would be of importance at relatively high oxygen concentrations, because the quenching cross section of oxygen is approximately three times that of hydrogen for $Hg^*(^3P_1)$. The reaction, therefore, depends on the hydrogen and oxygen pressures. On this point, the following conclusions have been established1): a) in the higher-pressure regions and with relatively high concentrations of oxygen, the product is almost entirely hydrogen peroxide, formed by a nonchain mechansim for which the quantum yield is less than unity, while b) at low concentrations of oxygen and low total pressure, water is formed by a chain mechanism. In the latter case, discussed in this paper, H, OH, and HO_2 radicals are formed as the intermediates of this chain reaction. For the determination of this reaction, it is of an interest to follow the concentrations of these intermediates during the reaction, since it is unlikely that the reaction mechanism can be determined by a method dependent on the analysis of the final products. From this point of view, we tried to measure the relative concentrations of the radicals by means of the electron spin resonance technique, we thus obtained a fairly intense ESR signal of atomic hydrogen, formed by a mercury-photosensitized reaction between hydrogen and oxygen, at relatively low partial pressures of oxygen and at low total pressures. The main purpose of this paper is to determine the reaction mechanism, especially the role of oxygen in the reaction.

Atomic hydrogen was formed by Reaction (1) without oxygen, but, as will be discussed later, the stationary concentrations of H atoms were too low to be detected by ESR. Moreover, at relatively high partial pressures of oxygen, the atomic hydrogen could not be detected by ESR. From the changes in the concentration of H atoms as measured by the intensity of the ESR absorption under various hydrogen and oxygen pressures, the conditions under which the stationary concentrations of H atoms reached a maximum in this reaction were determined, and kinetic considerations were made.

This experiment was also concerned with the ESR absorption of unstable paramagnetic species in the gas phase. There have been several reports on these, such as on the atomic species of H,3) O,4) N,5) and halogens,6) and diatomic free radicals of OH,7) SH,8) and SO8); few of these species, however, were photo-initiated.

The hydrogen and oxygen mixture was circulated by a mercury diffusion pump in an 8-mm i. d. vycor tube through the microwave cavity of a JES 3110 X spectrometer, where the microwave absorption of the paramagnetic species and its intensities at a 3-cm wavelength were measured. The hydrogen and oxygen mixture with mercury vapor was irradiated by the mercury resonance line at 2537 Å at the point of the gas inlet into the ESR cavity.

The arrangement of the gas-handling system, the low-pressure mercury lamp, the absorption cell, and the spectrometer system is shown in Fig. 1. The cavity is a circular cylindrical reflection cavity; its dimensions are chosen to make it resonate in the TE_{012} mode.

When the mercury-photosensitized reaction was applied to the hydrogen and oxygen mixture at a low pressure, strong doublet absorption lines were observed at a relatively low partial pressure of oxygen. These doublet lines, with equal intensities and with about a 500-Oe separation between lines, have been identified with those of atomic hydrogen produced by the microwave discharge of hydrogen or water vapor. No other radicals, such as atomic oxygen and hydroxyl radicals, were however, observed.

For relative atom concentration measurements, the microwave power feed has been kept as low as possible in order to avoid power saturation in this experiment. Under the conditions used here, the power saturation has not been observed, even in the lowest detectable concentration of H atoms produced by the microwave discharge of pure hydrogen at $P_{H_2}=0.1$—4 mmHg. It has been established that a trace of O_2 in the system is efficient in reducing the spin-lattice relaxation time. In this experiment, O_2 was initially present in the system, and there were no remarkable changes in the linewidth of the spectrum during the reaction. The differential intensity of the spectrum, therefore, was proportional to the H atom concentration in the system. Recently, Westenberg

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3) R. Beringer and E. B. Rawson, *Phys. Rev.*, **87**, 228 (1952); **95**, 1474 (1954); T. M. Shaw, *J. Chem. Phys.*, **31**, 1142 (1959); T. M. Shaw and C. Milazzo, *Gen. Elec. Microwave Lab. Rept.* TIS-R 60, ELM-178 (1960).

4) E. B. Rawson and R. Beringer, *Phys. Rev.*, **88**, 677 (1952); V. W. Hughes and J. S. Geiger, *ibid.*, **99**, 842 (1955); H. E. Radford and V. W. Hughes, *ibid.*, **114**, 1274 (1959).

5) M. A. Heald and R. Beringer, *ibid.*, **96**, 645 (1954).

6) Chlorine: V. Beltran-Lopez and H. G. Robinson, *ibid.*, **123**, 161 (1961); Fluorine: H. E. Radford, V. W. Hughes and V. Beltran-Lopez, *ibid.*, **123**, 153 (1961).; Bromine: N. Vanderkooi and J. S. Mackenzie, *Advan. Chem. Ser.*, **36**, 98 (1962); Iodine; K. D. Bowers, R. A. Kamper and G. D. Lustig, *Proc. Phys. Soc. (London)*, **B 70**, 1176 (1957).

7) H. E. Radford, *Phys. Rev.*, **122**, 114 (1961).

8) C. C. McDonald, *J. Chem. Phys.*, **39**, 2587 (1963).

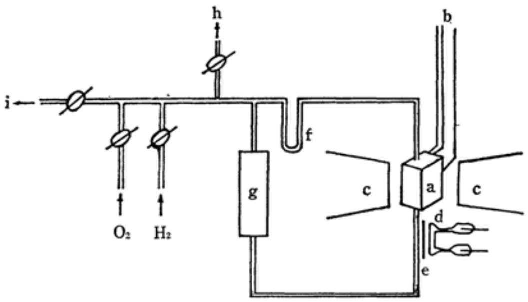
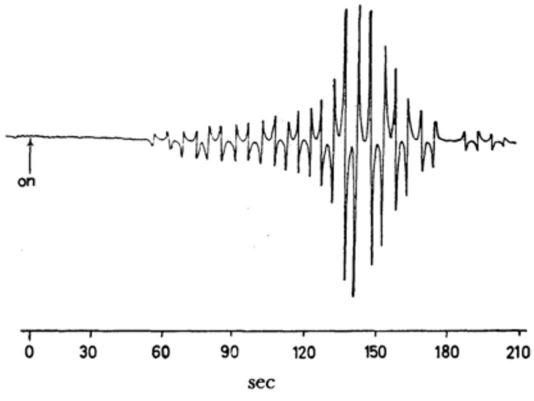


Fig. 1. Schematic experimental arrangement.

a : ESR cavity
b : To ESR spectrometer
c : Electromagnet
d : Low pressure mercury lamp
e : Shutter
f : Trap
g : Mercury diffusion pump for circulation of gases
h : To pressure gauge
i : To high vacuum

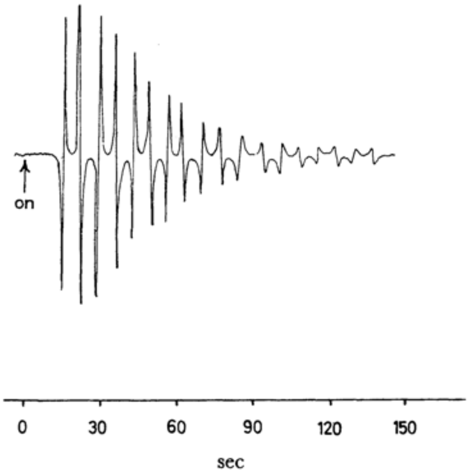
and de Hass[9] have proposed a new method to measure N, O, and H atom concentrations in the gas phase by means of the ESR technique. H atom concentrations were not absolutely measured in this experiment, however, because only relative signal amplitudes were necessary to the later discussion. It was estimated, from a comparison of the signal amplitudes with DPPH, that the maximum H atom concentration was about 10^{14} atoms/cc.

The H atom line increased in intensity with time until it reached a maximum, and then it gradually disappeared within ten minutes or so. Figure 2 shows this change in the high-field spectrum. The time, T_m, which gave the maximum intensity varied with the initial hydrogen and oxygen pressures.



$P_{H_2}=1.14$ mmHg $P_{O_2}=150\ \mu$Hg

(a)



$P_{H_2}=3.76$ mmHg $P_{O_2}=50\ \mu$Hg

(b)

Fig. 2. The time dependence of the ESR absorption of H atoms at 9.4 kMc/sec with scanning back and forth around the resonance field.

It is important to investigate the relation between H atom concentrations in the irradiation region and in the cavity, because in this experiment the distance between the irradiation region and the cavity was 2 cm. When even this distance was made 2 cm longer, no remarkable change occurred in the H atom signal amplitude when strong signals of H atoms could be observed, and it did not cause any change in T_m. Wise *et al.*[10] have also reported only a slight decrease in the H atom concentration along a quartz tube in their experiment on the self-diffusion of H atoms produced by the microwave discharge of H_2 containing a small amount of H_2O.

Results and Discussion

General Consideration of the Reaction Mechanism. When the mercury photosensitization was applied to H_2+O_2 mixtures in the $P_{O_2}=10-200\ \mu$Hg and $P_{H_2}=0.2-4$ mmHg regions, the ESR absorption of atomic hydrogen was observed. Figure 3 shows the changes in H atom signal intensities at $P_{O_2}=50$ and 150 μHg and at various P_{H_2} values with the reaction time. It is considered, as has been mentioned before, that the signal amplitudes could be proportional to the H atom concentrations, because the spectrometer was operated without changing the conditions throughout the reaction. When the P_{O_2} value was larger than 50 μHg and the P_{H_2} value was less than 2 mmHg, initially no signal of H atoms was observed, but it gradually

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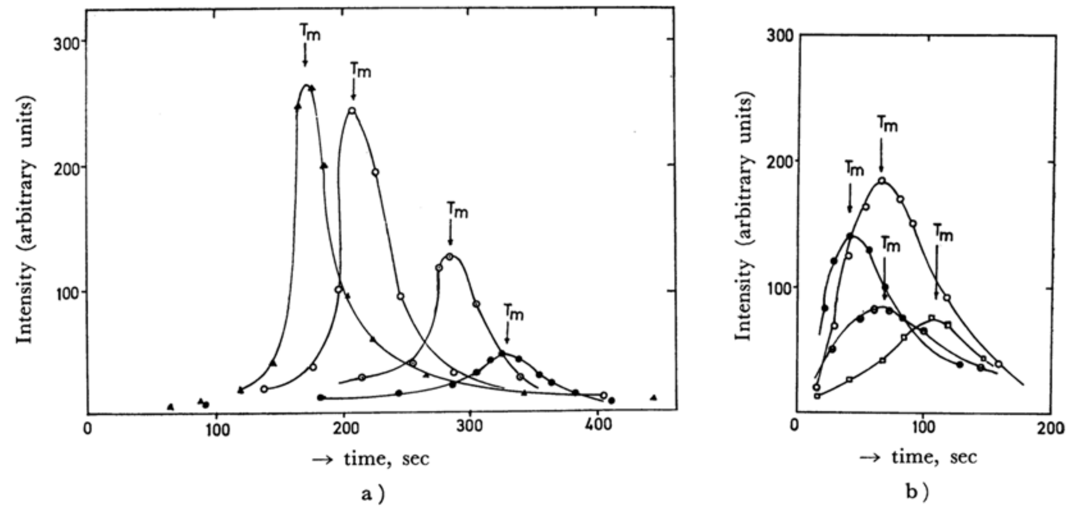
[9] A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **40**, 3087 (1964).

[10] H. Wise, C. M. Ablow and K. M. Sancier, *ibid.*, **41**, 3569 (1964).



a) b)

Fig. 3. Variations of the ESR absorption intensities of H atoms with time.
a) $P_{O_2}=150\ \mu$Hg and various P_{H_2}. b) $P_{O_2}=50\ \mu$Hg and various P_{H_2}.

$P_{O_2}=150\ \mu$Hg

	P_{H_2} (mmHg)
—●—	0.90
—⊙—	1.14
—○—	1.86
—▲—	2.67

$P_{O_2}=50\mu$Hg

	P_{H_2} (mmHg)
—●—	3.8
—○—	2.3
—⊖—	1.5
—□—	0.3

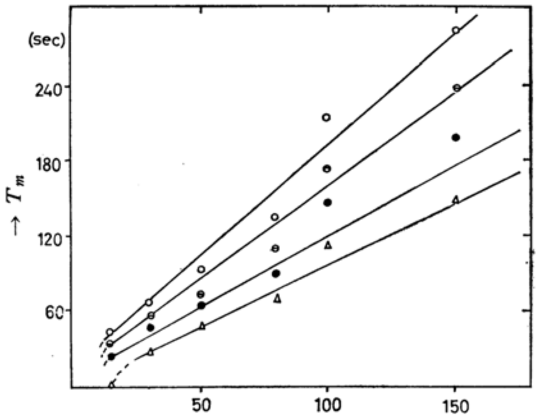


Fig. 4. Variations of T_m as a function of P_{O_2} at various P_{H_2}.

P_{H_2}: —○— 1.0 mmHg —⊖— 1.5 mmHg
—●— 2.0 mmHg —△— 3.0 mmHg

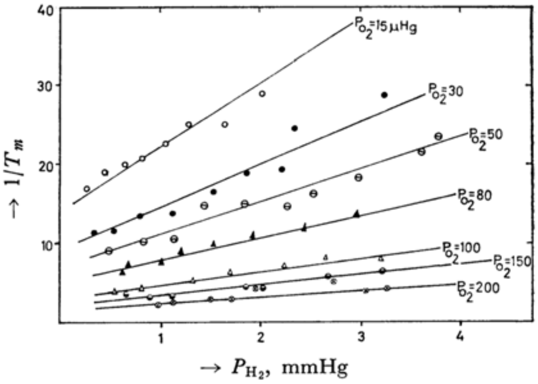


Fig. 5. Variations of $1/T_m$ as a function of P_{H_2} at various P_{O_2}.

appeared. It was also observed, as is shown in Fig. 3, that each curve has a maximum point, and that the time (T_m) which gives this point varies with the P_{H_2} and P_{O_2} from 0 to about 400 sec. The variation in T_m as a function of P_{O_2} at various P_{H_2} values, and also the reciprocal of T_m as a function of P_{H_2} at various P_{O_2} are shown in Figs. 4 and 5.

It seems possible to follow the concentration of oxygen throughout the reaction, since it is well known that molecular oxygen is paramagnetic in its ground state, and that it can be observed by ESR spectroscopy at low pressures.[11,12] Though the conditions under which the spectra of both hydrogen atoms and oxygen could be observed are limited within a very narrow range, the spectra were obtained with little pressure broadening.

The following effects must be considered in accounting for these results: (a) the spin relaxation of H atoms by oxygen; (b) the inhibition of a heterogeneous recombination of H atoms on the wall by water or hydrogen peroxide initially

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[11] R. Beringer and J. C. Castle, Jr., *Phys. Rev.*, **75**, 1963 (1949).

[12] M. Tinkham and M. W. P. Strandberg, *ibid.*, **97**, 951 (1955).

produced by the reaction, and (c) changes in the stationary concentration of H atoms due to the chain reaction expected in this system, together with some wall effect. As has been mentioned before, (a) would not be expected in this experiment, and it does not offer any reasonable explanation for the initial lack of a H atom signal when a larger quantity of oxygen is present. As for (b), this effect has been of interest to many workers, and it has been assumed, in general, that the increased lifetime of hydrogen atoms in the presence of water vapor is due to a poisoning of the wall for atom recombination. However, recently it has been indicated that water vapor does not affect the surface catalytic efficiency of Pyrex glass for the recombination of hydrogen atoms.[13,14] In this experiment, no change in H atom concentrations was observed with or without a liq. N_2 trap. It may be concluded, therefore, that the main effect is that of (c).

It has been known, by the experiment of the explosion limit, that at an elevated temperature, the reaction proceeds explosively, with the following chain-branching step:

$$H + O_2 \rightarrow OH + O \qquad -16.7\,\text{kcal} \tag{2}$$

However, this endothermic process could not occur under our conditions. The following mechanism was proposed by Callear and Robb[15] to explain their results:

$$H_2 + Hg^*(^3P_1) \overset{I_0}{\rightarrow} 2H + Hg(^1S_0) \tag{1}$$

$$H + O_2 + M \overset{k_3}{\rightarrow} HO_2 + M \tag{3}$$

$$H + HO_2 \overset{k_4}{\rightarrow} 2OH \tag{4}$$

$$OH + H_2 \overset{k_5}{\rightarrow} H_2O + H \tag{5}$$

$$HO_2 + HO_2 \overset{k_6}{\rightarrow} H_2O_2 + O_2 \tag{6}$$

$$H\ (\text{wall}) \overset{k_7}{\rightarrow} 1/2\ H_2 \tag{7}$$

The $H+O_2 \rightarrow HO_2^*$, $HO_2^* \rightarrow H+O_2$, and $HO_2^*+M \rightarrow HO_2+M$ reactions could be replaced by Reaction (3). In the higher pressure region and at relatively high concentrations of oxygen, it was proposed by Volman[16] that hydrogen peroxide was formed by Reactions (1) and (3) and that it vanished upon Reaction (6), with a non-chain mechanism. For the chain mechanism,[15,17] Reaction (1) is the initiation step and Reactions (3), (4) and (5) are the chain-propagating steps. Another propagating step (8) may also be considered:

$$HO_2 + H_2 \overset{k_8}{\rightarrow} H_2O + OH \tag{8}$$

This reaction is exothermic to the extent of 54 kcal and was proposed by Smith and Napravnik[18] to explain the formation of water with a high quantum yield. However, since Reaction (8) requires a fairly large activation energy (24 kcal),[19] it would be very slow at low oxygen concentrations, and thus at low HO_2 concentrations as well.

Another mechanism for the formation of OH radicals from the photolysis of hydrogen peroxide has been proposed,[17,20] but in the case of a system at low total pressures and low oxygen concentrations, this mechanism can be neglected.

The termination reaction must be of great importance in this experiment. There are two main terminating processes. One is the recombination of hydroperoxy radicals [Reaction (6)]. The other is the recombination of hydrogen atoms through the termolecular collisions in the gas phase [Reaction (9)];

$$H + H + M \overset{k_9}{\rightarrow} H_2 + M \tag{9}$$

or through the adsorption of hydrogen atoms on the wall. If there is no oxygen in the system, the hydrogen atoms reaching the wall remain intact and eventually react with H atoms to give hydrogen, and at these low pressures the termolecular recombination reaction (9) in the gas phase can be neglected. However, if some oxygen is present in the system, H atoms adsorbed on the wall may form hydroperoxy radicals by reaction with oxygen. If so, the following reactions may be substituted for Reaction (7):

$$H + W \xrightarrow{k'_{10}} WH, \tag{10}$$

the adsorption of H atoms on the wall;

$$WH + O_2 \xrightarrow{k_{11}} HO_2 + W \tag{11}$$

the reaction between WH and O_2; and

$$WH + H \xrightarrow{k_{12}} H_2 + W \tag{12}$$

the formation of H_2 on the wall.

Variations in the Stationary Concentration of H Atoms. The present results show that the concentration of H atoms in the system varies with the reaction time. As will be discussed below, the rate of oxygen consumption before T_m was estimated to be nearly equal to 10^{15} molecules/sec, which corresponded to the number of input photons. By taking the flow rate (10 cm/sec) into consideration, the amount of oxygen

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[13] F. D. Coffin, *J. Chem. Phys.*, **30**, 593 (1959).

[14] H. Wise and W. A. Rosser, Symp. Combust. 9th, Cornell Univ., Ithaca, N. Y. 738 (1963).

[15] A. B. Callear and J. C. Robb, *Trans. Faraday Soc.*, **51**, 649 (1955).

[16] D. H. Volman, *J. Chem. Phys.*, **14**, 707 (1946).

[17] J. S. Watson, Symp. Combust. 7th, Butterworths, London, p. 17 (1959).

[18] H. A. Smith and N. Napravnik, *J. Am. Chem. Soc.*, **62**, 358 (1940).

[19] V. V. Voevodsky, Ref. 17, p. 34.

[20] D. H. Volman, *J. Chem. Phys.*, **23**, 2458 (1955); **25**, 288 (1956).

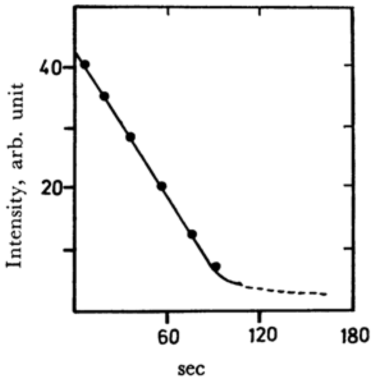

Fig. 6. Decay of the ESR absorption intensities of O_2.

$P_{O_2}=80\ \mu$Hg $P_{H_2}=1.26$ mmHg

consumed in the reaction zone (2 cm. long) was estimated to be less than 10% in the pressure range between 15 and 200 μHg. As is shown in Fig. 6, on the other hand, since there was a turning point near T_m in the rate of oxygen consumption, and since after that point, the rate decreased more than nine-tenths, the loss of oxygen in the reaction zone was also less than 10%, even at pressures of oxygen lower than 10 μHg, which is to be expected after T_m during the reaction. Therefore, it may be possible to treat the reaction by the use of the stationary state method. A stationary state treatment of Eqs. (1) to (12), using (6) and (12) as the terminating steps and neglecting Reactions (8), (9) and (2), then gives the following equations. The rate of the adsorption of H atoms is simply written as $k'_{10}[H]/[M]$, where [M] is the concentration of the third body in the gas phase:

$$[H] = \frac{2I_0+k_5[OH][H_2]}{k_3[O_2][M]+k_{10}+k_4[HO_2]+k_{12}[WH]} \tag{13}$$

$$I_0 = k_{12}[WH][H] + k_6[HO_2]^2 \tag{14}$$

where $k_{10}=k'_{10}/[M]$. At the initial step of the reaction in the experiments at relatively high oxygen pressures, H atoms adsorbed on the wall have more chance to react with oxygen [Reaction (11)] than with H atoms [Reaction (12)], but the gas phase reaction (3), though it may be slow[21] because of its termolecular processes, will, more or less, obstruct Reaction (4), and subsequently, the reproduction of H atoms through Reaction (5). In this case, Eq. (13) may take the following form:

$$[H] = \frac{2I_0}{k_3[O_2][M]+k_{10}} \tag{15}$$

This equation indicates that the stationary concentration of H atoms increase with a decrease in oxygen at relatively high oxygen pressures.

When the system contains only a small amount of oxygen (this is the case which also occurs with the process of the reaction, bacause oxygen is consumed to form water and hydrogen peroxide), the termination reaction by the recombination of hydroxyl radicals [Reaction (6)] could be less important because of the low concentrations of hydroperoxy radicals. Here the diffusion of H atoms to the wall becomes easier, and the addition of H atoms to O_2 is negligibly small in the gas phase, so that Reaction (12) may become the main terminating step. However, since the hydroperoxy radicals formed by Reaction (11) can reproduce H atoms by Reactions (4) and (5), it is likely that the stationary concentrations of H atoms in the system is still higher; in other words, oxygen molecules consequently controle the wall recombination of H atoms by Reaction (11), followed by Reactions (4) and (5). Therefore, the following equation could be obtained as the stationary concentration of H atoms, neglecting Reaction (6):

$$[H] = (I_0/k_{10})\{1/2+\sqrt{1/4+k_{11}k_{10}[O_2]/I_0k_{12}}\} \tag{16}$$

This equation would give a possible explanation for the mechanism of the obstruction of H atom recombination on the wall. The $k_{11}[O_2]/k_{12}\cdot(I_0/k_{10})$ term in Eq. (16) would also give the ratio of the probabilities of reproduction by Reactions (11), (4) and (5), and of recombination by Reaction (12). Therefore, the probability of Reaction (12) would be more or less, reduced by oxygen, and the stationary concentration of H atoms would increase with the increase in oxygen.

When there is no oxygen in the system, the H atoms produced by Reaction (1) would eventually recombine to form H_2 by Reactions (10) and (12). In this case the stationary concentration of H atoms becomes lower than when the system contains a small amount of oxygen. Equation (16) then becomes:

$$[H] = I_0/k_{10} \tag{17}$$

From these considerations, it may be concluded that, when the system initially contains a considerable amount of oxygen, the stationary concentration of H atoms increases with a decrease in the amount of oxygen, corresponding to Eq. (15); that it reaches a maximum as a result of the reproduction of H atoms by Reactions (11), (4) and (5), and that it then decreases with a further decrease in oxygen, corresponding to Eq. (16).

Variations in T_m. Figure 4 shows the variations in T_m as a function of P_{O_2} at varuous P_{H_2} values. In addition, the variations in T_m^{-1} as a function of P_{H_2} at various P_{O_2} values are shown

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[21] M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc.*, **A275**, 559 (1963).

in Fig. 5. Using the same treatment as Eq. (14), the following equation for the rate of the consumption of oxygen can be obtained:

$$-\frac{d[O_2]}{dt} = \frac{1}{2}k_5[OH][H_2] + k_6[HO_2] \qquad (18)$$

Before T_m, and when the system contains much oxygen, Reaction (12) may be neglected compared with Reaction (6). Then,

$$-\frac{d[O_2]}{dt} = I_0 + \frac{1}{2}k_5[OH][H_2] \qquad (19)$$

can be obtained from Eq. (14). The linear relations in Fig. 4 and Fig. 5, together with Fig. 6, suggest that the second term in Eq. (19) dose not depend on the oxygen concentration in the region before T_m. The concentration of OH radicals produced by Reaction (4) is a function of the concentrations of H and HO_2, and before T_m the concentration of H atoms is inversel relative to the concentration of O_2, while on the other hand, the concentration of HO_2 is relative to that of O_2. Then, on the assumption that $1/2\ k_5[OH][H_2]$ does not depend on the concentration of O_2 in this region, we may integrate Equation (19) from $t=0$ to $t=T_m$ and obtain the following equations:

$$T_m = \frac{[O_2]_0}{(I_0+k_5'[H_2])} - \frac{[O_2]_m}{(I_0+k_5'[H_2])} \qquad (20)$$

$$\frac{1}{T_m} = \frac{I_0}{[O_2]_0-[O_2]_m} + \frac{k_5'[H_2]}{[O_2]_0-[O_2]_m} \qquad (21)$$

where $[O_2]_m$ is the concentration of O_2 at T_m; $[O_2]_0$, the initial concentration of O_2 (these concentrations can also be expressed in terms of the respective partial pressures), and $k'_5=1/2\ k_5[OH]$. These equations would give a reasonable explanation of the linear relations in Figs. 4 and 5 respectively. The slope of each plot in Fig. 5 is a function of $[O_2]_0$ (*i. e.*, P_{O_2}). Therefore, the following relation between S^{-1} and P_{O_2} can be obtained:

$$\frac{1}{S} = \frac{P_{O_2}}{k_5'} - \frac{(P_{O2})_m}{k_5'} \qquad (22)$$

where S is the slope of the curves in Fig. 5 and where $(P_{O_2})_m$ is the partial pressure of oxygen at T_m. This equation was confirmed by the linear relation between S^{-1} and P_{O_2} shown in Fig. 7. From the intercept and the slope of this figure, $(P_{O_2})_m$ and k_5' can be obtained as follows:

$$(P_{O_2})_m = 5\ \mu\text{Hg}$$

$$k_5' = 1/2\ k_5[OH] = 1.7\times 10^{-4}\ \text{sec}^{-1}$$

The extraporation of each plot in Fig. 5 also gives the following equation:

$$1/E = P_{O_2}/I_0 - (P_{O_2})_m/I_0 \qquad (23)$$

where E is the intercept of each plot in Fig. 5.

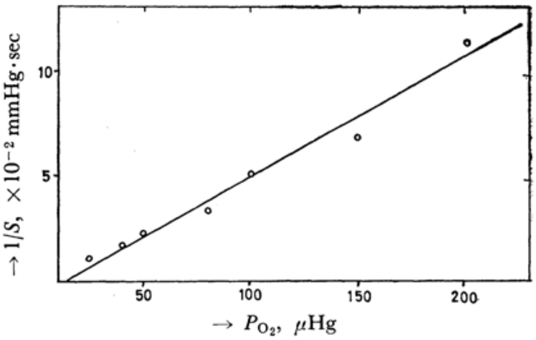

Fig. 7. Dependence of $1/S$ on P_{O_2}.

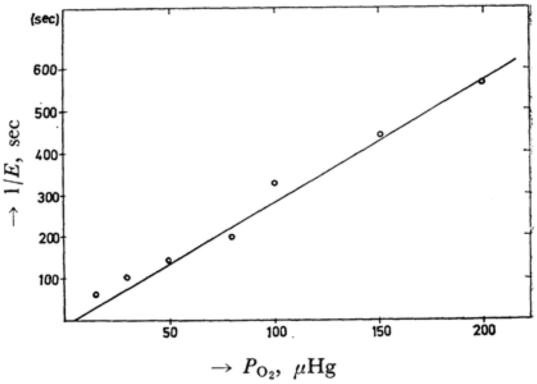

Fig. 8. Dependence of $1/E$ on P_{O_2}.

Figure 8 shows the linear relation between E^{-1} and P_{O_2} which corresponds to Eq. (23). From the intercept and the slope of Fig. 8, the following values were obtained for $(P_{O_2})_m$ and I_0:

$$(P_{O_2})_m = 5\ \mu\text{Hg}$$

$$I_0 = 1.2\times 10^{13}\ \text{molecules/cc sec}$$

The oxygen to be consumed by the reaction with H atoms is distributed in total volume of 200 cc, while the H atoms produced by Reaction (1) are concentrated in the irradiation region (about lcc); therefore, I_0 can be expressed as:

$$I_0 = 2.4\times 10^{15}\ \text{molecules/sec}$$

The value of k_5 has been reported by several authors.[10,22] The stationary concentration of OH in this region could be calculated to be 2.4×10^{10} molecules/cc (or 4.8×10^{12} molecules when it is concentrated in the reaction region) using the value of k_5 reported by Kaufman[22] ($k_5=4.3\pm 1.0\times 10^6$ l/mol sec). Therefore, in order to observe OH radicals formed as an intermediate during this reaction, it is necessary to use a spectrometer which is more sensitive than the present one by the factor of 10^2—10^3.

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[22] F. Kaufman and F. P. Del Greco, Symp. Combust. 9th, Cornell Univ. Ithaca, N. Y. 659 (1963).