

ABSOLUTE MEASUREMENTS OF RATE COEFFICIENTS FOR THE REACTIONS OF H AND O ATOMS WITH H₂O₂ AND H₂O

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The reactions of O and H atoms with hydrogen peroxide and water were investigated at temperatures between 300° and 1045°K, using several discharge-flow reactors, coupled either to a combination of ESR and conventional mass spectrometer, or to a TOF mass spectrometer with nozzle-beam sampling.

It was found that, in the H + H₂O₂ system, a chain reaction involving OH and HO₂ radicals takes place. The first step of this reaction could be determined separately by replacing H atoms with D atoms and adding O atoms:

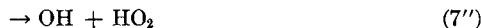


giving a rate constant

$$k_{1\text{D}} = 7 \times 10^{12} \exp(-4200 \pm 400 \text{ cal}/RT) \text{ cm}^3/\text{mole sec}$$

for the temperature range 294°–464°K.

The rate of the reaction



measured between $T = 370^\circ$ – 800°K , can be represented by

$$k_7 = 2.8 \times 10^{13} \exp(-6400 \pm 600 \text{ cal}/RT) \text{ cm}^3/\text{mole sec}.$$

The subsequent reactions which give as end products O₂, H₂O, and H atoms, are discussed.

Rate constants for the reaction of O atoms in the presence of water are given over a wide temperature range. For the direct attack of O atoms on water,



rate coefficients are measured which can be expressed as

$$k_{10} = 4 \times 10^{13} \exp(-17300 \pm 500 \text{ cal}/RT) \text{ cm}^3/\text{mole sec}$$

for temperatures of $753 < T < 1045^\circ\text{K}$.

Introduction

Accurate knowledge of the rate constants of elementary reactions of the hydrogen-oxygen system is necessary in order to understand the combustion and explosion processes of all hydro-

gen fuels. In recent years, some of the important reaction steps in that system have been investigated very accurately and over a rather large temperature range. One example is the reaction $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$. Its absolute rate constants could be obtained directly and accurately with

isothermal discharge flow systems and ESR atom detection.¹⁻⁴ Good agreement exists now, even between different authors. In addition, data up to about 2500°K fit well with those at temperatures between 300° and 1000°K.

The present paper describes experiments performed in discharge-flow systems, in order to obtain more accurate information on reactions in a specific part of the H-O system, namely the reactions of H and O atoms with hydrogen peroxide. The situation here appeared to be more complicated than in the example mentioned above.

To derive the rate constants for the primary reaction steps $\text{H} + \text{H}_2\text{O}_2$ and $\text{O} + \text{H}_2\text{O}_2$, the mechanism of the subsequent reactions had to be investigated. In the $\text{H} + \text{H}_2\text{O}_2$ system which is discussed first, chain reactions are important even at low concentrations. These chains could be suppressed, however, by adding O atoms. In the second part of the paper, the reaction of O atoms with H_2O_2 is treated.

One of the main products of the above reactions is H_2O , which is known to be a very effective third body for the recombination of H and O atoms. Moreover, in the presence of O atoms, water is consumed even at low temperatures. Thus, it was also necessary to investigate the reactions of O atoms with water up to rather high temperatures. The results are given in the third part of this paper.

In order to obtain detailed information for the reactions mentioned, the isothermal flow system was coupled either to a combination of ESR and normal mass spectrometer (Atlas CH4), which allowed accurate measurements of the concentrations of atoms and stable molecules, or to a time-of-flight mass spectrometer (TOF) with molecular-beam inlet system.

Experimental

The experimental equipment (flow systems, sampling arrangements) and procedure were basically the same as those described at the previous symposium for the $\text{NH}_3 + \text{O}$ work.⁵ The main change to the apparatus used in the present work was the incorporation of a solid-silver tube (36 mm i.d., 50 mm o.d., 300 mm length) in the electrically heated furnace. With the silver tube, it was possible to attain an essentially flat temperature profile at the wall of the flow reactor (quartz, 36 mm o.d.) and a precise automatic temperature control in the whole temperature range (300°–1100°K).

Gases of the highest purity commercially available were used: He (99.9995%); Ar, H_2 , O_2 (99.99%); D_2 , N_2O (99%).

H_2O_2 was prepared from "85%" H_2O_2 (Elektrochemische Werke, München) by pumping off one-half of a sample giving 97 mole % H_2O_2 in aqueous solution. This sample was passed to a saturator (Pyrex, Pyrex-Teflon valves, cleaned with 5% solution of HF and deionized H_2O , temperatures of $40^\circ\text{--}80^\circ \pm 0.1^\circ\text{C}$). H_2O_2 was introduced into the flow reactor by passing He through the saturator. The H_2O_2 content of the He could be determined most reliably by passing the gases for a fixed time through a liquid- N_2 trap, then warming them up and titrating with KMnO_4 . These determinations agreed well with the values calculated from the vapor-pressure data. H_2O was introduced by passing He through a three-stage saturator containing bidistilled water.

Experimental Results and Discussion

Reaction of H Atoms with H_2O_2

The reaction between H atoms and H_2O_2 could be observed easily from 800°K down to room temperature. Water was found to be the major

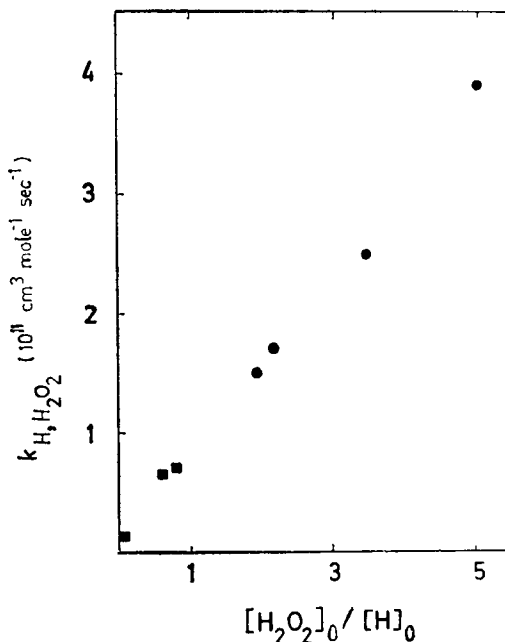
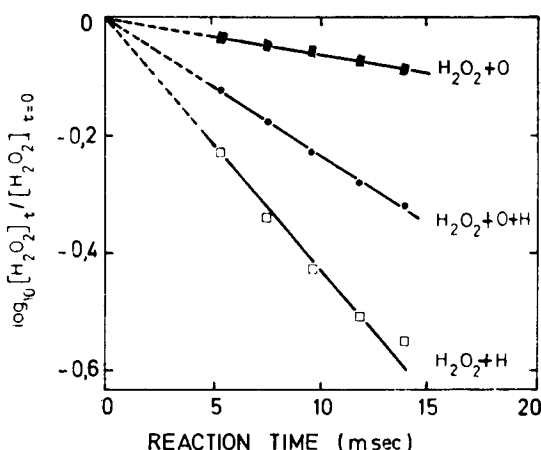
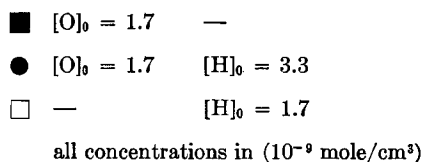


FIG. 1. Dependence of measured rate constants of the $\text{H} + \text{H}_2\text{O}_2$ reaction on the initial $\text{H}_2\text{O}_2/\text{H}$ ratio.

■ $k_{\text{H}_2\text{O}_2}$; $p = 8.1$ torr, $T = 320^\circ\text{K}$.

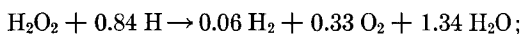
● k_{H} ; $p = 2.5$ torr, $T = 307^\circ\text{K}$.

FIG. 2. Effect of O atoms on the first-order decay of H₂O₂ in the H + H₂O₂ reaction. $p = 9.85$ torr, $T = 375^\circ\text{K}$, $[\text{H}_2\text{O}_2]_0 = 1.6$.

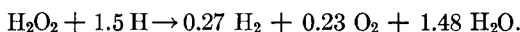


reaction product. The over-all stoichiometry, measured between 300° and 800°K , changed slightly with temperature:

At 300°K , with an initial $[\text{H}_2\text{O}_2]/[\text{H}]$ ratio of 2.5:



and at 800°K , with $[\text{H}_2\text{O}_2]_0/[\text{H}]_0 = 1.4$:



With H₂O₂ added in excess, the H atom decays measured with ESR were first-order with respect to H. Under H-atom-rich conditions, a first-order decay of H₂O₂ was observed with the nozzle-beam inlet system. However, rate constants at one temperature calculated by the usual pseudo-first-order relations

$$k_{\text{H}} = \frac{\Delta \ln [\text{H}]/[\text{H}]_0}{\Delta t [\text{H}_2\text{O}_2]}$$

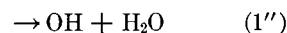
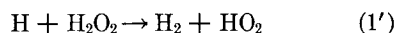
and

$$k_{\text{H}_2\text{O}_2} = \frac{\Delta \ln [\text{H}_2\text{O}_2]/[\text{H}_2\text{O}_2]_0}{\Delta t [\text{H}]}$$

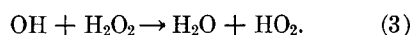
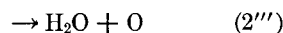
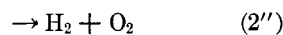
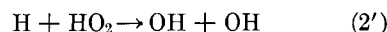
were not independent of the initial H₂O₂/H ratio. As shown in Fig. 1, the measured rate constants increase by a factor of 30 if $[\text{H}_2\text{O}_2]_0/[\text{H}]_0$ was varied between 0.05 and 5. Therefore, the reaction was investigated with the TOF mass spectrometer, where, in addition to H atoms and the stable products H₂, O₂, H₂O, the concentrations of the intermediate OH and HO₂ radicals could be measured. The OH concentration (relative to H₂O₂) decreased with increasing $[\text{H}_2\text{O}_2]_0/[\text{H}]_0$, while HO₂ showed contrary behavior.

The results mentioned above indicate that the

first step



is followed by the rapid reactions^{6,7}

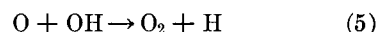
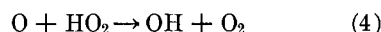


Evidently, direct information about the initial step (1) can be obtained only if the attack of the OH radicals on H₂O₂ is suppressed.

This was done by adding atomic oxygen. Figure 2 shows that the consumption of H₂O₂ by H atoms is significantly decelerated in the presence of O atoms. (The reaction $\text{O} + \text{H}_2\text{O}_2$ is discussed later in detail.)

Using the conditions of Fig. 2 with an initial $[\text{H}_2\text{O}_2]:[\text{O}]:[\text{H}]$ ratio of 1:1:0.3, no variation of the H-atom concentration with reaction time (15 msec) could be detected with ESR, whereas 80% of the H atoms were consumed when oxygen atoms were absent.

These observations can be explained by assuming that, at equal concentrations of O atoms and H₂O₂, the reaction of the OH and HO₂ radicals with O



is much faster than with H₂O₂ ($k_5/k_3 > 20$).^{7,8} Thus, for every H atom removed by Reaction (1), one H atom is produced by (5) or by (4) and (5).

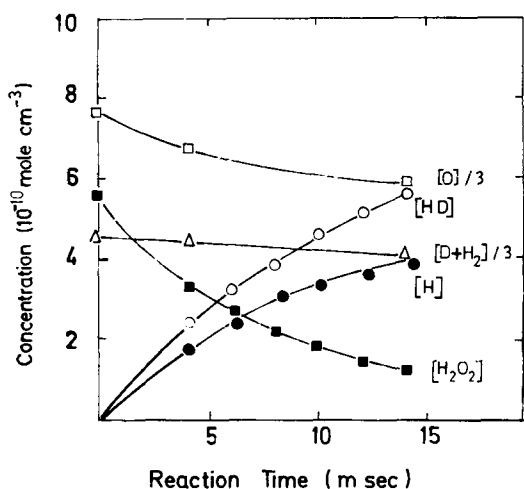


FIG. 3. Product distribution as a function of reaction time in the $O + D + H_2O_2$ system. $p = 8.15$ torr, $T = 421^\circ K$.

Reaction of D Atoms with H_2O_2 in the Presence of O Atoms

To obtain direct evidence as to the relative importance of Reactions (1') and (1''), the H atoms were replaced by D atoms. The kinetic behavior of this system is shown in Fig. 3. HD and H atoms are the major reaction products. HDO is formed at much lower concentrations. Unfortunately, the HDO production could not be measured as accurately as HD and H, since approximately the same amount of HDO was already formed in the absence of H_2O_2 . However, the yield of HDO was around 10% of the HD produced. Thus, one comes to the conclusion that Reaction (1D') is the main reaction mechanism under the conditions used ($k_{1D'}/k_{1D''} \approx 10$,

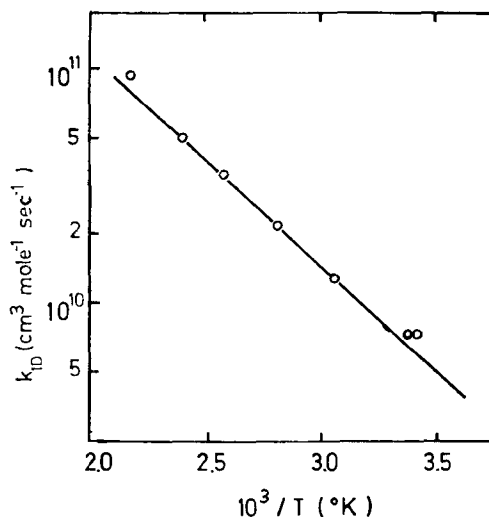
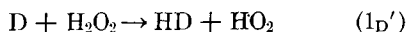


FIG. 4. Arrhenius plot of measured k_{1D} for $D + H_2O_2$.

$T = 421^\circ K$):



A direct determination of k_{1D} could now be carried out by measuring the decay of $[D]$ under conditions such that (i) enough O atoms were present for the reaction to attain a nonchain character, and (ii) H_2O_2 consumption by reaction with H atoms formed by (7), (4), (5), and with O atoms was not significant. ESR is well suited for very accurate determinations of small D-atom decays (Table I), since there is no interference due to H_2 formation (Fig. 3). Simultaneous measurements with the mass spectrometer showed that most of the D atoms consumed were

TABLE I
Measured rate constants for $D + H_2O_2$ in the presence of O atoms

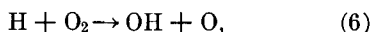
T (°K)	p (torr)	H_2O_2	D	O	D_2	O_2	$(\ln [D]/[D]_0)/t$ (sec ⁻¹)	$k_{1D} \times 10^{-9}$ (cm ³ /mole sec)
mole fraction (%)								
294	7.51	0.42	0.11	0.8	0.01	0.8	12.4	7.3
297	5.89	0.46	0.50	0.8	0.09	0.8	11.0	7.4
299	6.84	0.44	0.33	0.7	0.04	0.8	11.1	6.8
328	5.98	0.35	0.70	0.75	0.10	0.8	13.1	13.0
358	6.00	0.36	0.4	0.80	0.05	0.8	20.7	22.0
389	6.05	0.31	0.30	0.60	0.03	0.6	26.7	35.0
422	5.88	0.26	0.4	0.60	0.05	0.6	28.6	50.0
464	5.21	0.26	0.4	0.60	0.05	0.6	42.3	92.0

found as HD. The measured values are summarized in Table I and plotted in Arrhenius form in Fig. 4. As the conditions noted above cannot be maintained at high temperatures, the temperature range was limited to 294°–464°K, where

$$k_{1D} = 7 \times 10^{12}$$

$$\exp(-4200 \pm 400 \text{ cal}/RT) \text{ cm}^3/\text{mole sec.}$$

Only a few investigations, which can be compared with the present results, are reported in the literature. At higher temperatures, Baldwin *et al.*⁹ were able to measure k_1 relative to



and k_1'/k_1'' (0.16 ± 0.02 at 713°K; 0.13 ± 0.03 at 773°K) by studying the influence of H₂ on the homogeneous decomposition of H₂O₂. Using $k_6 = 2.5 \times 10^{14} \exp(-16.8/RT) \text{ cm}^3/\text{mole sec}$, their absolute k_1' is a factor of 2 below the extrapolated k_{1D}' . However, due to the zero-point energy difference between the activated complexes, a ratio of $k_1'/k_{1D}' < 1$ is expected at this temperature. An evaluation of k_1' from the decay of H₂O₂ shown in Fig. 2 gives

$$k_1'/k_{1D}' = 0.43 \text{ at } 375^\circ\text{K.}$$

Nevertheless, the observed difference of the k_1'/k_1'' ratios seems to indicate that the relative rates of Reactions (1') and (1'') change drastically with the temperature. At low temperatures, Reaction (1') dominates. This is demonstrated by the formation of HD (Fig. 3) and H₂ (Fig. 6), produced by reaction of D or H atoms with H₂O₂ in the presence of O atoms. This conclusion is also supported by results of the vacuum-ultraviolet photolysis of H₂O₂ at room temperature.¹⁰

With increasing temperature, k_1'/k_1'' decreases, as will be seen by comparing the data obtained at 421°, 719°, and 773°K.

The apparent rate constant of

$$k_H = 6 \times 10^{10} \text{ (cm}^3/\text{mole sec)} \text{ at } 300^\circ\text{K}$$

reported by Foner and Hudson¹¹ can be attributed to the chain process (Fig. 1).

Reaction of O Atoms with H₂O₂

When sufficient excess of H₂O₂ was added to O atoms, the O decays, measured with ESR, were first-order with respect to [O], and increased in proportion to [H₂O₂]₀, as long as the decays were limited to 10%–20%. At temperatures between

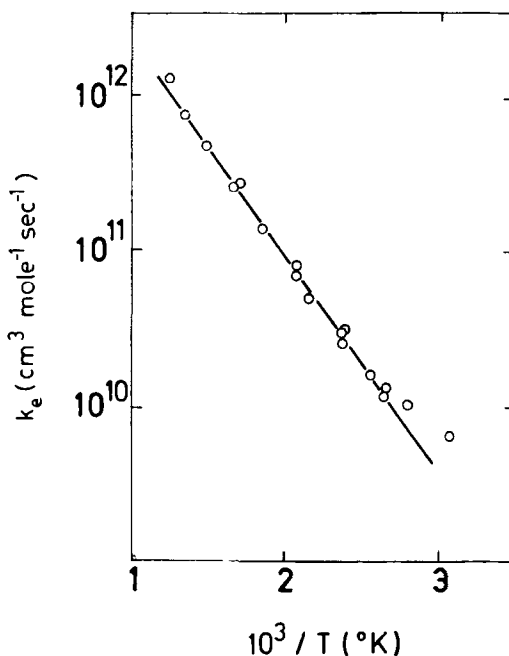


FIG. 5. Arrhenius plot of experimental rate coefficient k_e for $\text{O} + \text{H}_2\text{O}_2$.

370° and 800°K, the experimental rate constants (k_e) can be represented by the Arrhenius expression (Fig. 5), as follows:

$$k_e = 7 \times 10^{13}$$

$$\times \exp(-6400 \pm 600 \text{ cal}/RT) \text{ cm}^3/\text{mole sec.}$$

As monitored with the mass spectrometer, no decomposition of H₂O₂ occurs in the flow system under the conditions for which k_e was determined ($p = 2\text{--}5$ torr; $[\text{H}_2\text{O}_2]_0 = 10^{-10}$ to 10^{-9} mole/cm³, $[\text{O}]_0 = 10^{-11}$ to 10^{-10} mole/cm³, $v = 5\text{--}40$ m/sec). No differences could be detected in the measured values of k_e , whether the O atoms were produced from O₂ or from the N + NO titration. Large amounts of H atoms were observed during the reaction, causing an increase of k_e at high O-atom consumption. ESR measurements showed that, at 805°K, $\Delta[\text{H}]/\Delta[\text{O}] = 0.37$ ($t = 18.6$ msec), and at 300°K, $\Delta[\text{H}]/[\text{O}] = 0.41$ ($t = 9$ msec).

Between 500° and 800°K, an average value of

$$n = \Delta[\text{O}]/\Delta[\text{H}_2\text{O}_2] = 2.5 \pm 0.3$$

was obtained with ESR for conditions where the consumption of H₂O₂ by Reaction (1) was negligible. From 300° to 500°K, n could be evaluated from the variation of the product

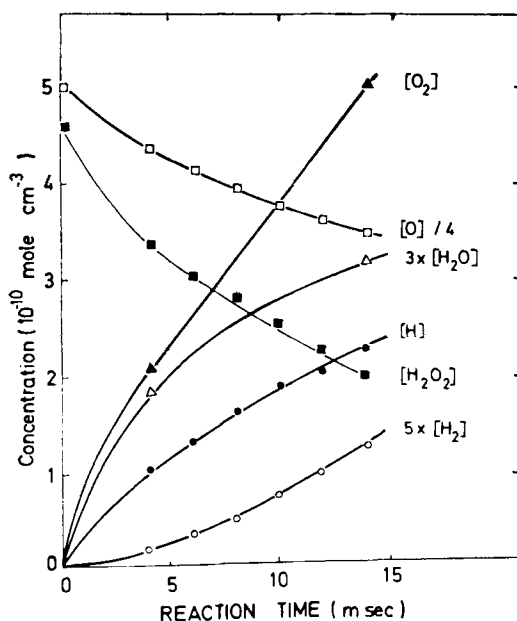
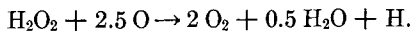


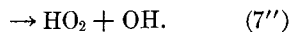
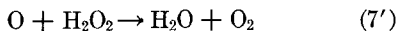
FIG. 6. Product distribution as a function of reaction time for $O + H_2O_2$. $p = 9.1$ torr, $T = 454^\circ K$.

distribution with reaction time (Fig. 6) measured with the molecular beam inlet system. All observations are in agreement with a stoichiometry of



Additional evidence in support of $n = 2.5$ comes from a comparison of k_e with rate constants derived from simultaneous measurements with the second mass spectrometer of H_2O_2 and O-atom decay. With $[H_2O_2]_0/[O]_0 \approx 1$ at equal temperatures, the latter were lower than k_e by a factor of 2.3 ± 0.2 .

In view of the above, a reasonable preliminary explanation of the experimental observations is to assume about equal probability for (7') and (7'')



Reaction (7'') is followed by (4) and (5). Thus, for $n = 2.5$,

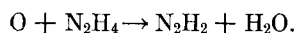
$$k_7 = 2.8 \times 10^{13}$$

$$\times \exp(-6400 \pm 600 \text{ cal}/RT) \text{ cm}^3/\text{mole sec}.$$

The occurrence of an energy chain involving

vibrationally excited H_2O ($\Delta H_{298}^\circ(7') = -85$ kcal/mole) could be ruled out by replacing the He or Ar carrier gas by an effective third body (N_2O). No variation of product distribution was found.

It seems worthwhile to mention that the reaction of O atoms with N_2H_4 , which is isoelectronic to H_2O_2 , proceeds predominantly via^{12,13}



This reaction step corresponds to Reaction (7').

Reaction of O Atoms with H_2O

Since water is present or produced in the $H-H_2O_2$ and $O-H_2O_2$ systems, the reactions of H and O atoms with water must be considered in detail.

It is known¹⁴ that water acts very effectively (being about a factor of 20 more effective than Ar) as a third body in the recombination reaction



to give $k_8 = 9 \times 10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$ at room

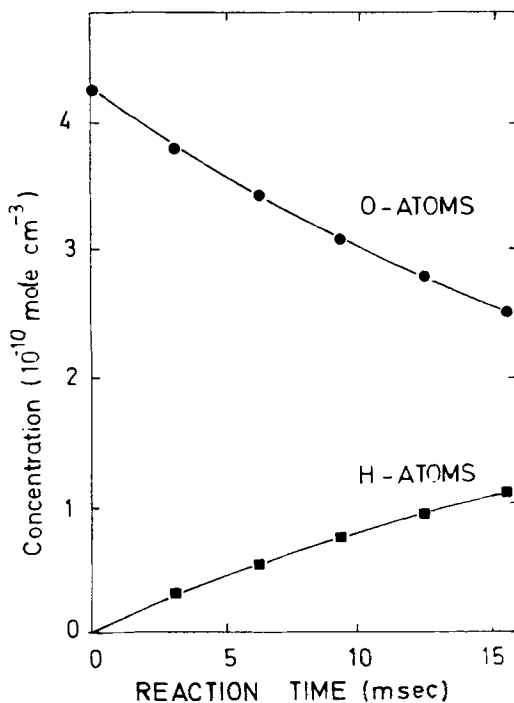


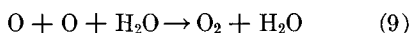
FIG. 7. Decrease of O-atom and increase of H-atom concentration with reaction time for $O + H_2O$. $p = 5.5$ torr, $T = 849^\circ K$.

$$[H_2O]_0 = 7.7 \times 10^{-9} \text{ mole/cm}^3.$$

TABLE II
Measured rate constants for O + H₂O

<i>T</i> (°K)	<i>p</i> (torr)	<i>V</i> (cm/sec)	[H ₂ O] × 10 ⁸ (mole/cm ³)	<i>k</i> ₁₀ × 10 ⁻⁸ (cm ³ /mole sec)
753	9.50	660	2.28	3.44
773	8.70	780	2.39	5.94
814	9.80	527	1.02	7.75
814	10.9	516	1.37	6.88
814	10.6	578	1.60	7.28
849	5.55	677	0.77	15.75
859	5.96	761	1.23	13.1
935	6.32	640	0.303	31.1
1045	6.80	675	0.213	94.5

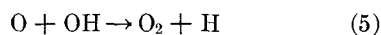
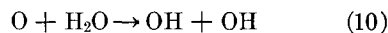
temperature. The recombination of O atoms in the presence of water



is more complicated. In addition to the high rate coefficient $k_6 = 6 \times 10^{16}$ cm⁶/mole² sec, large amounts of H atoms are produced even at room temperature. The ratio $\Delta[\text{H}]/\Delta[\text{O}] \approx 0.1$ is remarkably high.¹⁴ At higher temperatures, the direct attack of O atoms on the water predominates over the recombination reaction. To study the O + H₂O reaction, water was mixed

with a stream of O atoms in He at temperatures from 753°–1045°K. The excess of [H₂O]₀, relative to [O]₀, was in the range of 18 to 35. Measurements at different H₂O concentrations showed that the decay in $\Delta \ln [\text{O}]/[\text{O}]_0/\Delta t$ was proportional to the given H₂O concentration. The decrease of the O-atom concentration was accompanied by a production of H atoms with the reaction time as measured by ESR, and shown in Fig. 7. The decay in [O] was less than 50%. Thus, the reaction of H atoms with water played only a minor role.

Careful determination of the stoichiometry $\Delta[\text{H}]/\Delta[\text{O}]$ gave 0.62 ± 0.06 . Therefore, the reaction sequence



leading to $\Delta[\text{H}]/\Delta[\text{O}] = 0.67$, is the most favorable one.

The direct determination of the reaction rate of (10) for

$$k_{10} = (1/n) (\Delta \ln [\text{O}]/[\text{O}]_0 / \Delta t [\text{H}_2\text{O}]), \quad n = 3,$$

was carried out at different temperatures and is summarized in Table II and Fig. 8. In the Arrhenius form,

$$k_{10} = 4 \times 10^{13} \times \exp(-17300 \pm 500 \text{ cal}/RT) \text{ cm}^3/\text{mole sec}$$

Corrections of less than 5%, due to back diffusion¹⁵ are included.

On the basis of JANAF tables,¹⁶ the rate for the reaction k_{-10} has a value of 2.6×10^{12} cm³/mole sec at 1000°K.

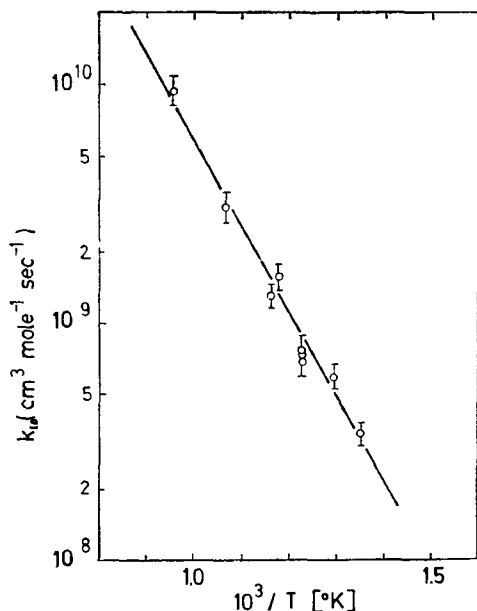


FIG. 8. Arrhenius plot of k_{10} for the reaction
 $\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{OH}$.

Thus, Reactions (8)–(10) at 300°–1045°K could not influence the reactions of H and O atoms with H₂O₂ under the conditions applied.

Acknowledgments

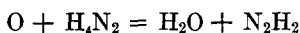
The continuous interest of Professor W. Jost, and the financial support by the Stiftung Volkswagenwerk and the Deutsche Forschungsgemeinschaft are gratefully acknowledged.

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COMMENTS

Z. A. Szabo, University of Budapest. What evidence have you to support the proposition that the reaction

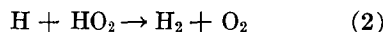


proceeds in *one* step? It would involve a five-membered transition state, which is highly improbable. The reaction can occur in two elementary steps if the second step is very fast.

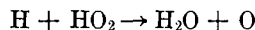
Authors' Reply. A detailed discussion of this reaction is given in the paper of M. Gehring, K. Hoyerman, H. Gg. Wagner, and J. Wolfrum: Ber. Bunsenges. Physik. Chem. **73**, 956 (1969).

rate constants between the first and second alternatives for these reactions. Possibly this argument may help in selecting the more probable process.

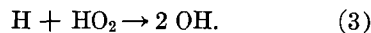
D. R. Blackmore, Shell Research Limited. Can you obtain any information on the rates of



and



compared with the rate of your reaction



Authors' Reply. The results on the reaction $\text{H} + \text{H}_2\text{O}_2$ give an upper limit of

$$k_2/k_3 \leq 1 \text{ at } 300^\circ\text{K}.$$

S. H. Bauer, Cornell University. With reference to the second alternative in the reactions between $\text{H} + \text{H}_2\text{O}_2$ and $\text{O} + \text{H}_2\text{O}_2$, i.e., the direct production of OH and O₂, respectively, one would expect a long-lived intermediate (or complex). There should be significant differences in the pre-exponential factors and, hence, in the