Hydrogen-Oxygen Reaction

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RATES OF SOME ATOMIC REACTIONS INVOLVING HYDROGEN AND OXYGEN

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Reactions of ground state oxygen and hydrogen atoms produced by an rf electric discharge were studied in a flow system at pressures of about 1 mm Hg. Hydroxyl radicals and oxygen atoms are generated in the $H + NO_2$ reaction and measurements of the rate of removal of oxygen atoms in this system led to a value for the rate constant k_3 of the rapid reaction

$$O + OH \rightarrow H + O_2 \tag{3}$$

of $3 \pm 1 \times 10^{13}$ $cm^3mole^{-1}sec^{-1}$ at 293°K and 265°K.

The reaction of H with O_2 in the presence of an argon carrier was found to have over-all third order kinetics at 293°K,

$$H + O_2 + Ar \rightarrow HO_2 + Ar \tag{7}$$

and under these conditions k_7 was found to be $1.2 \pm 0.3 \times 10^{16}$ $cm^6mole^{-2}sec^{-1}$. This rate constant is similar in magnitude to that of the analogous combination reaction,

$$H + NO + Ar \rightarrow HNO + Ar.$$

The rate of reaction of oxygen atoms (in the absence of O_2) with molecular hydrogen was measured between 409° and 733°K. Assuming the slow primary step (-4)

$$O + H_2 \rightarrow OH + H \tag{-4}$$

to be followed by the rapid reaction

$$O + OH \rightarrow O_2 + H$$
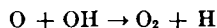
a value of $k_{-4} = 1.2 \times 10^{13}$ exp $[(-9200 \pm 600)/RT]$ $cm^3mole^{-1}sec^{-1}$ was determined in this temperature range.
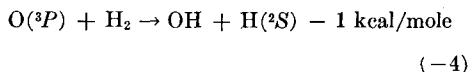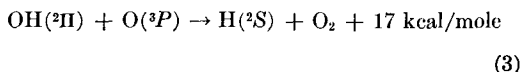
Introduction

Until recently, there have been few reliable data for the rate constants of the propagation and branching steps in the chain reaction between oxygen and hydrogen. However, the rate constant of the chain propagation reaction
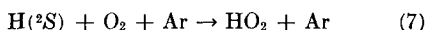
$$OH(^2\Pi) + H_2 \rightarrow H_2O + H(^2S) + 14 \text{ kcal/mole} \tag{6}$$
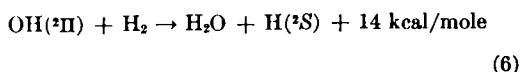
has been redetermined recently,[1] while in this

work values of the rate constants k_3 and k_{-4} are reported:

$$OH(^2\Pi) + O(^3P) \rightarrow H(^2S) + O_2 + 17 \text{ kcal/mole}$$
$$(3)$$

$$O(^3P) + H_2 \rightarrow OH + H(^2S) - 1 \text{ kcal/mole}$$
$$(-4)$$

Reaction (-4) and the reverse of reaction (3) are branching steps in the hydrogen + oxygen reaction. Direct information regarding the rate of the reaction

$$H(^2S) + O_2 + Ar \rightarrow HO_2 + Ar \qquad (7)$$

has been obtained in this work.

Experimental

Ground state hydrogen atoms and oxygen atoms (0.2–2% of total flow) were produced by an electrodeless electric discharge at 18 Mc/sec in mixtures of the molecular gas (1%) with argon (99%) or in the pure molecular gas. Partially dissociated gas from the discharge was pumped into a 28 mm internal diameter Pyrex flow tube having four backward-facing inlet jets along its length for the admission of reactants. Reactant flows were regulated by needle valves and were measured with calibrated capillary flowmeters. For experiments at temperatures up to 800°K a similar quartz flow tube enclosed in a furnace was employed. Pressures in the flow tubes were 1–4 mm Hg measured on a McLeod gauge and silicone fluid manometer. Pressure gradients at 1 mm Hg total pressure and 150 µmole/sec total flow along the 100 mm length of the reaction tube were less than 0.03 mm Hg. The total pressure p in the flow tube was controlled by a large stopcock downstream from the mixing inlets. The reaction time t could be altered by variation of the distance x along the flow tube between the reactant admission inlet and the observation point, $t = xAp/RT\sum F$, where A is the cross-section area of the tube and $\sum F$ is the total flow rate.

Two photomultiplier cells, an RCA 1P28 and an EMI 9558B, were used to measure the intensity of light emitted normally from a short section of reaction tube. The 1P28 tube fitted with a Wratten 61 filter was used for the measurement of the intensity of emission of the green-gray air afterglow spectrum $(O + NO + M \rightarrow NO_2 + M + h\nu)$ from 4900 to 5800 Å. The 9558B cell had a superior red sensitivity to that of the 1P28 and when fitted with a Wratten 88A filter had a sensitivity range from about 7350 to 8000 Å. It was therefore used for the measurement of the
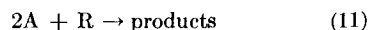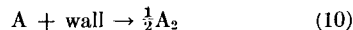
intensity of the strong (000, 000) band of HNO at 7625 Å emitted in the reaction of H with NO.[9,14] Measurements of the emission intensities from the O + NO and H + NO systems were used for the determination of the concentrations of oxygen atoms and hydrogen atoms, respectively. In systems containing O as well as H in the presence of nitric oxide, the air afterglow emission made a small contribution to the near infrared signal observed by the 9558B photomultiplier cell, and a small correction was made for this effect as described previously.[2] The photocells were operated at potentials of 800–950 V (1P28) and 850–1400 V (9558B) respectively, supplied by stabilized power sources. The isothermal-wire calorimeter described previously[4] was used in some experiments for the determination of hydrogen atom concentrations.

The Kinetic Method

Hydrogen atoms and oxygen atoms were generated in these experiments by means of an electrodeless electric discharge in a mixture of the molecular gas with 99% argon. The rates of elementary reactions involving H or O atoms can be determined directly from measurements of the rates of removal of atomic species from the flow system. In this work the rates of reaction of atoms (A) were determined by measurement of the atom concentrations remaining at a fixed point in the flow system when equal amounts of reactant (R) were introduced at each of the four inlet jets in turn. If recombination second order in [A],

$$A + A + M \rightarrow A_2 + M \qquad (9)$$
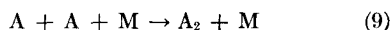
is much slower than the reactions

$$A + \text{wall} \rightarrow \tfrac{1}{2}A_2 \qquad (10)$$

$$2A + R \rightarrow \text{products} \qquad (11)$$

the rate of reaction of atoms determined in this way is equal to the rate of reaction (11) and is independent both of the first order surface decay and of the initial concentrations of atoms at the inlets. This can be demonstrated in the following manner. The rate of reaction of atoms is of the form

$$-d[A]/dt = a[A]^2 + b[A]$$

where $a = 2k_9[M]$ and $b = 2k_{11}[R] + k_{10}$.

On integration we obtain

$$\ln\left(\frac{[A]}{[A]_0}\right) - \ln\left(\frac{a[A] + b}{a[A]_0 + b}\right) = -bt$$

where $[A] = [A]_0$ when $t = 0$.

Reactant is added at time $t = t_1$, at which point $[A] = [A]_1$, and the atom concentration $[A]_3$ is then measured further downstream after a further reaction time t_2; $[A]_2$ is the concentration of atoms at the point of observation (reaction time $t_1 + t_2$) when no reactant is added. We then have the following relations:

$$\ln\left(\frac{[A]_1}{[A]_0}\right) - \ln\left(\frac{2k_9[M][A]_1 + k_{10}}{2k_9[M][A]_0 + k_{10}}\right) = -k_{10}t_1;$$

$$\ln\left(\frac{[A]_2}{[A]_0}\right) - \ln\left(\frac{2k_9[M][A]_2 + k_{10}}{2k_9[M][A]_0 + k_{10}}\right) = -k_{10}(t_1 + t_2);$$

$$\ln\left(\frac{[A]_3}{[A]_1}\right) - \ln\left(\frac{2k_9[M][A]_3 + k_{10} + 2k_{11}[R]}{2k_9[M][A]_1 + k_{10} + 2k_{11}[R]}\right) = -(k_{10} + 2k_{11}[R])t_2;$$

and therefore

$$\ln\left(\frac{[A]_3}{[A]_2}\right) - \ln\left[\left(\frac{2k_9[M][A]_3 + k_{10} + 2k_{11}[R]}{2k_9[M][A]_1 + k_{10} + 2k_{11}[R]}\right) \times \left(\frac{2k_9[M][A]_1 + k_{10}}{2k_9[M][A]_2 + k_{10}}\right)\right] = -2k_{11}[R]t_2.$$

Providing that $k_{10} + 2k_{11}[R] \gg 2k_9[A][M]$ and $k_{10} \gg k_9[M] \times ([A]_1 - [A]_2)$, this equation reduces to the simple form

$$\ln([A]_3/[A]_2) = -2k_{11}[R]t_2.$$

The condition for reaction (9) to be much slower than reactions (10) or (11) was easily fulfilled by working with low concentrations of atoms. The method was very useful for the determination of the rates of third order combination reactions, such as the H + NO + M reaction[14] and the H + O_2 + M system described here, since the measurements give the required third order rate constants without involving large corrections for concomitant atomic recombination processes.

Results

Reaction of OH *with* O. Hydroxyl radicals in the electronic ground state were generated by addition of NO_2 to a stream of atomic hydrogen and argon from the discharge.[2,3] Measurements of the red HNO and green NO_2 (air afterglow) emission intensities I_b and I_a were made at various points downstream from the NO_2 inlet. Nitric oxide was thus produced stoichiometrically in the rapid reaction (1),[2]

$$H + NO_2 \rightarrow OH + NO \tag{1}$$
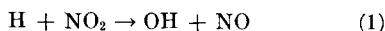
and since NO is not removed from the system,[4,5] $I_a/[NO_2]_0$ and $I_b/[NO_2]_0$ are proportional to [O] and [H], respectively.[4,5] The two emission intensities were also measured in NO + O + Ar and NO + H + Ar mixtures, respectively, with simultaneous measurement of the corresponding oxygen atom and hydrogen atom concentrations. In this way measurements of $I_a/[NO_2]_0$ and $I_b/[NO_2]_0$ gave directly the absolute atom concentrations in the H + NO_2 system. Figure 1 shows the variation of [O] and [H] with concen-

tration of added nitrogen dioxide, $[NO_2]_0$, for a constant reaction time of 0.03 sec. [H] was found to be a linear function of $[NO_2]_0$ and thus NO_2 titration to the critical extinction of the HNO emission provides a method for the estimation of H atoms in H + Ar systems.[2] Under the conditions of the author's experiments, the reaction

$$OH + OH \rightarrow H_2O + O \tag{2}$$

[followed by the rapid reaction

$$O + OH \rightarrow H + O_2 \tag{3}]$$
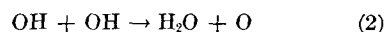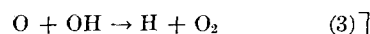
has proceeded almost to completion between the NO_2 inlet and the photomultiplier observation point. Reaction (3) regenerates hydrogen atoms and thus for each H atom initially present, critical removal of H occurs when $\frac{3}{2}NO_2$ molecules have been introduced into the system. It follows that the NO_2 titer in these circumstances is equal to $\frac{3}{2}$ of the concentration of hydrogen atoms present in the absence of NO_2.

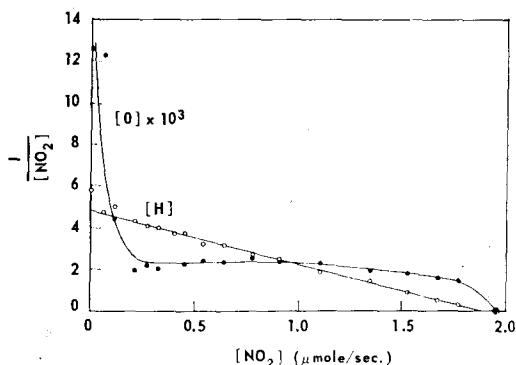The initial concentration of hydroxyl radicals

FIG. 1. The variation of [H] and [O] with concentration of added NO_2 ([OH]$_0$) at 293°K and 1.09 mm Hg total pressure. Reaction time 0.03 sec.
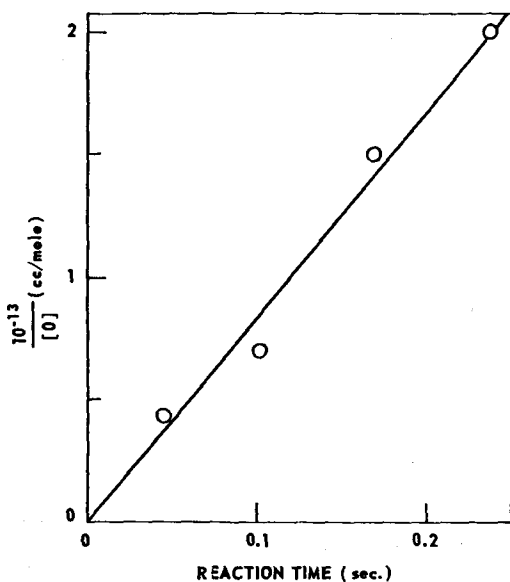
FIG. 2. Oxygen atom decay plot at 1.29 mm Hg
total pressure and 293°K.

$[OH]_0$ is equal to the concentration of NO_2 added, $[NO_2]_0$, when atomic hydrogen is in excess. Figure 1 shows that for constant reaction time, $[O]$ is independent of $[NO_2]_0 = [OH]_0$ over a wide range of $[OH]_0$. The concentrations of oxygen atoms observed are of the order of 10^{-5} to 10^{-6} mm Hg, while those of H are about 10^{-2} mm Hg. For constant reaction time, $[O]$ was found to be independent of total pressure. The decay of $[O]$ along the tube was measured at total pressures of 1.09 to 2.23 mm Hg. Plots of $1/[O]$ against reaction time t were linear, with slopes independent of total pressure and of $[OH]_0$. A typical oxygen atom decay plot is shown in Fig. 2. The slopes of these plots and the absolute values of $[O]$ were unaffected by a tenfold increase in the hydrogen atom concentration in the system. It is evident that $[O]$ decays at a rate proportional to $[O]^2$ by means of a process which does not involve H in rate-determining steps,

$$-d[O]/dt = k'[O]^2.$$
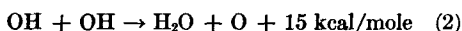
The mean value of k' at 293°K was found to be 9×10^{13} cm^{3}mole^{-1}sec^{-1} and a similar value was obtained in experiments at 265°K.

The possible reactions for the production of ground state oxygen atoms are

$$H + OH \rightarrow O + H_2 + 1 \text{ kcal/mole} \qquad (4)$$

and

$$OH + OH \rightarrow H_2O + O + 15 \text{ kcal/mole} \qquad (2)$$
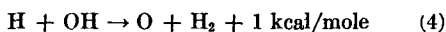
The former reaction must be excluded as a rate-determining step since $[O]$ and k' were found to be independent of $[H]$; in addition, the magnitude of the rate of this reaction calculated from the rate constant k_{-4} of the reverse reaction[6] is much less than the rate of reaction (2) in the author's experiments. Removal of O can occur by means of

$$O + NO_2 \rightarrow NO + O_2 \qquad (5)$$

and

$$O + OH \rightarrow O_2 + H \qquad (3)$$
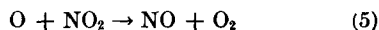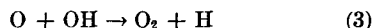
The rate of reaction (5) would be expected to be much less than that of reaction (3) under conditions where appreciable concentrations of H are present, since NO_2 is then predominantly removed by the faster reaction (1). It is therefore considered that oxygen atoms are generated by reaction (2), and removed by reaction (3); the influence of reaction (5) only becomes appreciable when $[H]$ is small, as shown by the tailing of the oxygen atom plot in Fig. 1 near the titration endpoint.

On this basis, assuming a steady state concentration of oxygen atoms,

$$[O] = k_2[OH]/k_3$$

and

$$-d[OH]/dt = 3k_2[OH]^2,$$
$$1/[OH] \quad = 1/[OH]_0 + 3k_2t.$$

It follows that $[O]$ is given by the expression

$$[O] = \frac{k_2}{k_3(1/[OH]_0 + 3k_2t)} \qquad (I)$$

For a typical reaction time of 0.05 sec and $[OH]_0 = 10^{-2}$ mm Hg, $3k_2t$ is very much greater than $1/[OH]_0$,[1] and hence (I) reduces to the simple form of Eq. (II):

$$[O] = 1/3k_3t \qquad (II)$$

consistent with the observed second order removal of $[O]$. The observed lack of dependence of $[O]$ and k' upon $[OH]_0$ and total pressure (for constant t) are in agreement with Eq. (II), which shows that $k' = 3k_3$. Values of k_3 determined at 293°K and 265°K were $3 \pm 1 \times 10^{13}$ cm^{3}mole^{-1}sec^{-1}.

Within the experimental error of the observations, the data are consistent with Eq. (II), which is based upon the assumption of a steady state concentration of oxygen atoms. The validity of this assumption can be tested by a comparison of the calculated rate of production of oxygen atoms, $k_2[OH]^2$, with the observed net rate of removal of oxygen atoms, $k'[O]^2$, which is the

difference between $k_2[OH]^2$ and $k_3[OH][O]$. For a steady state assumption to be a good approximation, this difference must be considerably smaller than the value of the individual terms $k_2[OH]^2$ and $k_3[OH][O]$. A typical observed *net* rate of removal of oxygen atoms was $\sim 1 \times 10^{-12}$ mole cm^{-3} sec^{-1}, while the value of $k_2[OH]^2$ calculated from Kaufman and Del Greco's data[1] under the same conditions was about 1×10^{-10} mole cm^{-3} sec^{-1}. It follows that the steady state assumption for $[O]$ is a good approximation in this kinetic study.

Reaction of H with O$_2$. It has been shown that the rate constant k_3 is of the order of 0.1 of the bimolecular collision frequency between OH and O at room temperature. The reverse reaction (-3) thus has an activation energy of around 17 kcal/mole,

$$H + O_2 \rightarrow HO + O - 17 \text{ kcal/mole} \quad (-3)$$
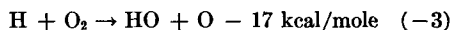
as found by Schott and Kinsey.[7] Reaction (-3) can therefore be neglected as a rate-controlling step in the flow experiments at 293°K with $H + O_2$ systems. However, the addition of O_2 to $H + Ar$ mixtures under such conditions at 1–2 mm Hg total pressure led to removal of hydrogen atoms. The nature of this reaction was investigated in the following manner. The reaction time between H and O_2 was varied by addition of the same oxygen flow $([O_2] \gg [H])$ at each of four inlets along the reaction tube, $[H]$ being measured at a downstream fixed point, the phototube housing. A small amount of nitric oxide was added to the reaction products 3 cm before the 9558P photomultiplier cell housing, and the photocurrent I_b due to the HNO emission was measured. $I_b/[NO]$ was then proportional to $[H]$.[4] The small amount of added nitric oxide was found to have a negligible effect on the rate of removal of hydrogen atoms from the system. Plots of $\log_{10}(I_b/[NO])$ against t obtained in

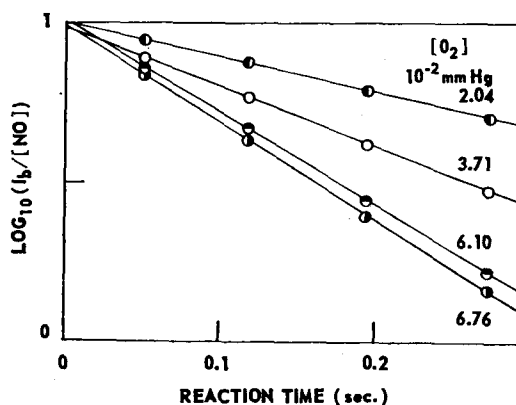FIG. 3. Kinetics of the $H + O_2 + M$ reaction at 1.64 mm Hg total pressure and at 293°K. Flow rates: Ar, 141 μmole/sec; H, 0.5 μg-atom/sec; H$_2$, 0.2 μmole/sec; O$_2$, 1.8–5.8 μmole/sec.

this way were accurately linear, with slopes proportional to $[O_2]$, as shown in Fig. 3.

The quantity

$$\frac{1}{[O_2]} \frac{d}{dt} \ln (I_b/[NO]) \quad (III)$$

was found to be proportional to total pressure $[M]$ from 1.01 to 2.42 mm Hg, as shown in Table 1. The rate of reaction of hydrogen atoms in this system is therefore given by

$$-d[H]/dt = k''[H][O_2][M]$$

and the rate-controlling reaction in the $H + O_2$ system is

$$H + O_2 + M \rightarrow HO_2 + M \quad (7)$$

It is known that the steady state concentration of HO$_2$ in such systems is very small,[8] and it is reasonable to suppose that reaction (7) is followed by one of the rapid reactions 8 a, b or c:

$$H + HO_2 \rightarrow H_2O + O \quad (8a)$$

$$H + HO_2 \rightarrow OH + OH \quad (8b)$$

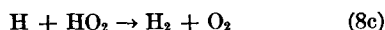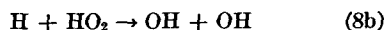$$H + HO_2 \rightarrow H_2 + O_2 \quad (8c)$$
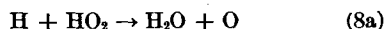
TABLE 1

The variation of (III) with total pressure at 293°K

Total pressure (mm Hg)	[M] (mole cm^{-3})	(III) (cm^{3}mole^{-1}sec^{-1})	(III)/[M] (cm^{6}mole^{-2}sec^{-1})
1.01	5.56×10^{-8}	1.43×10^9	2.6×10^{16}
1.20	6.57	1.84	2.8
1.48	8.11	2.20	2.7
1.82	10.00	2.23	2.2
2.42	13.30	2.46	1.9

On this basis,

$$-d[H]/dt = 2k_1[H][O_2][M],$$

and a value of $k_1 = 1.2 \pm 0.3 \times 10^{16}$ cm^{6}mole^{-2} sec^{-1} for M = Ar at 293°K was obtained.

Reaction of O with H_2. The rate of removal of oxygen atoms in the O + H_2 system was measured and used to determine k_{-4}. This method can only be reliably employed when O_2 is absent from the system, since reaction (7) and subsequent reactions of HO_2 must be considered to contribute to oxygen atom removal in the presence of molecular oxygen. Ground state oxygen atoms in the absence of O_2 were generated by addition of the stoichiometric quantity of nitric oxide to nitrogen atoms in a stream of active nitrogen,[6]

$$\text{N } (^4S) + \text{NO } (^2\Pi) \rightarrow \text{N}_2 (^1\Sigma) + \text{O } (^3P).$$
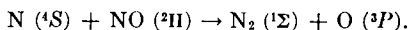
Hydrogen atoms are a product of the O + H_2 reaction and thus a method for the measurement of oxygen atom concentrations in the presence of H must be employed for following the reaction. A fixed-position 1P28 photomultiplier cell was used to measure the intensity of the air afterglow emission from the reaction products to which a known small amount of nitric oxide had been added just before the photomultiplier. When this phototube was fitted with a green transmission filter (Wratten No. 61) the HNO emission (due to the radiative combination of H with NO) made a negligible contribution to the total photocurrent (I_a), which was therefore proportional to [O][NO]. Ln[O] measured in this way was found to be proportional to reaction time t and to [H_2] when excess hydrogen was added to the stream of oxygen atoms at temperatures between 409° and 733°K. Typical data are shown in Fig. 4; $(1/[H_2])\{d(\ln[O])/dt\}$ was independent of total pressure between 1.71 and 2.77 mm Hg. The absence of any significant dependence upon total pressure is not surprising, since the only third order reaction which could be important is forbidden by the spin correlation rule:

$$\text{O } (^3P) + \text{H}_2 (^1\Sigma) + \text{M} \rightarrow \text{H}_2\text{O } (^1A) + \text{M}.$$
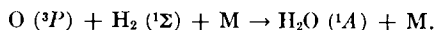
The kinetic data can be represented by the equation

$$-d[O]/dt = k'''[O][H_2].$$

The equilibrium constant of reaction (4) is around unity, but since the final concentration ratio [H]/[H_2] was typically 0.1–0.2, the reverse reaction (4) can be neglected in comparison to reaction (–4) as a rate-determining step.

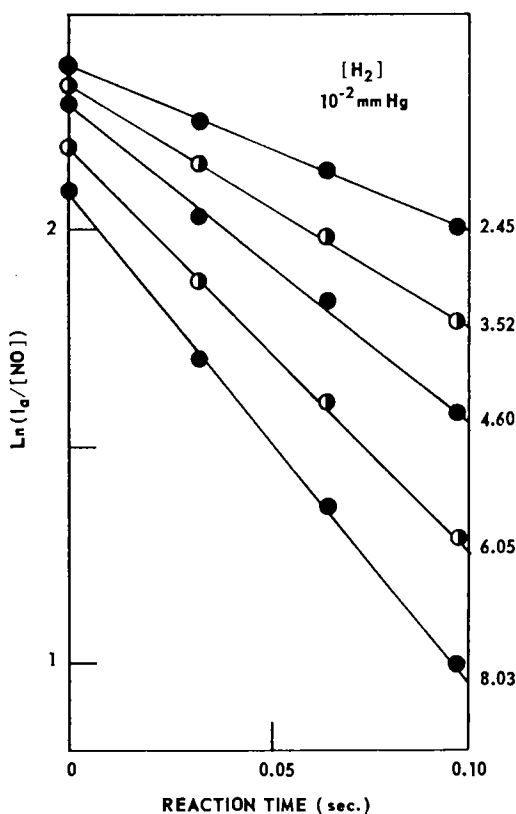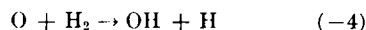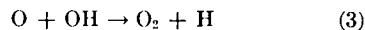FIG. 4. Kinetics of the O + H_2 reaction at 2.19 mm Hg total pressure and at 441°K. Flow rates: N_2, 197 μmole/sec; O, 0.3 μg-atom/sec; H_2, 2.2–7.3 μmole/sec.

Reaction (–4),

$$\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H} \qquad (-4)$$

can be followed by any of the three reactions (2), (3), or (6). The relative magnitudes of k_2, k_3, and k_6. [see ref (1) and this work] show that reaction (3),

$$\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H} \qquad (3)$$

is predominant for OH removal under the author's conditions. In these circumstances, k_3 is much greater than k''', and hence

$$-d[O]/dt = 2k_{-4}[O][H_2].$$

Therefore k_{-4} could be evaluated from the experimentally determined values of k''' and a value of

$$k_{-4} = 1.2 \times 10^{13}$$

$$\exp (-9200 \pm 600)/RT \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}$$
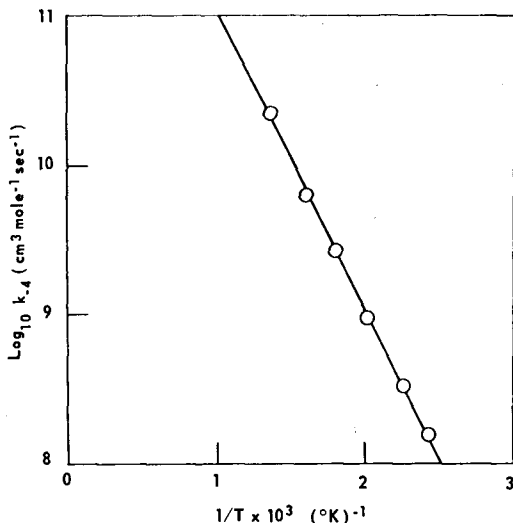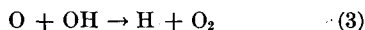
was determined in the temperature range 409 to

FIG. 5. The variation of k_{-4} (cm³mole⁻¹sec⁻¹) with temperature from 409°K to 733°K.

733°K. Figure 5 shows a plot of $\log_{10} k_{-4}$ against $1/T$.

Discussion

It has been shown that the rate constant of the reaction

$$O + OH \rightarrow H + O_2 \qquad (3)$$

is $3 \pm 1 \times 10^{13}$ cm³mole⁻¹sec⁻¹ at 293°K. The activation energy of reaction (3) is therefore near zero. This conclusion is in agreement with long extrapolations from Schott and Kinsey's[7] values of k_{-3}, and with the activation energy $E_{-3} = 17 \pm 1$ kcal/mole found by Voevodskii.[10] The present value for k_3 at 293°K is within a factor of 3 of that reported by Del Greco and Kaufman.[1] The high value obtained for k_3 (~ 0.1 of the bimolecular collision frequency) shows that O and OH cannot coexist in significant concentrations for appreciable periods of time. Products of a discharge in moist oxygen would therefore be expected to contain H as well as O but not hydroxyl. Kinetic studies (such as those of Avramenko et al.) in which a discharge in water vapor is used as a source of OH are thus open to criticism.

The activation energy of 9.2 ± 0.6 kcal/mole found for reaction (-4) is significantly different from that determined by Harteck and Kopsch[11] (6 ± 1 kcal/mole) and Azatyan et al.[12] (11.7 ± 0.7 kcal/mole) but in fair agreement with the value of 7.7 kcal/mole obtained by Fenimore and Jones.[13] However, the expressions for k_{-4} obtained by the last two groups of workers can be

extrapolated to 700°K, yielding values within a factor of 5 of those obtained in the present work. In the work of Harteck and Kopsch,[11] the amounts of water were measured which were produced when hydrogen reacted with oxygen atoms contained in oxygen from an electric discharge. It is doubtful whether the extent of water formation under these conditions is a valid measure of the extent of reaction (-4), since water may also be formed by means of reaction (7) followed by the fast step (8a). In addition, most of the OH produced in reaction (-4) would be removed by reaction (3) rather than by reaction (6) under the experimental conditions used. The difference between the values of E_{-4} reported by the author and by the Russian workers[12] could be removed by the assumption in the latter work of a slightly different temperature coefficient for the surface recombinations of atomic species.

In this work it has been shown that formation of HO_2 requires participation by a third body M,

$$H + O_2 + M \rightarrow HO_2 + M \qquad (7)$$

The observed over-all third order kinetics show that, under the author's conditions, reaction of HO_2 with H (reaction 8) is faster than dissociation of HO_2 (reaction -7). The rate constant $k_7 = 1.2 \pm 0.3 \times 10^{16}$ cm⁶mole⁻²sec⁻¹ for M = Ar at 293°K is similar to that of the reaction

$$H + NO + M \rightarrow HNO + M$$

at 293°K.[14] Several values of k_7 at room temperature (for M = H_2) have been reported previously, but since these vary from 4×10^{14} [see ref. (15)] to about 10^{18} cm⁶mole⁻²sec⁻¹, [see ref. (16)], reliance can only be placed on the determinations of k_7 at elevated temperatures, which are in fair agreement with one another. The value found in the present work for k_7 at 293°K is somewhat greater than most of those obtained from studies in the $H_2 + O_2$ system at higher temperatures. Voevodskii and Kondratiev,[17] for example, have deduced a value of $k_1 = 4.3 \times 10^{15}$ cm⁶mole⁻²sec⁻¹ for M = H_2 at about 800°K. These data, taken in conjunction with the author's results at 293°K, suggest that reaction (7) may have a small negative activation energy similar to that of -0.6 kcal/mole found for the H + NO + M reaction.[14] This possibility is now being investigated and further experiments are to include a study of the dependence of k_7 upon the nature of the third body.

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Discussion

DR. F. KAUFMAN (*Ballistic Research Laboratories, Aberdeen Proving Ground*): In another paper in this volume, Dr. Del Greco and I have measured the rate constant, k_3, for $O + OH \rightarrow O_2 + H$ in a similar, though faster flow system by following the rate of decay of OH when O and OH are mixed. Our value for k_3 near 300°K is $(1.1 \pm 0.4) \times 10^{13}$ cm^3 mole^{-1} sec^{-1}, about a factor of three smaller than Dr. Clyne's. It should be pointed out that in Dr. Clyne's steady state decay of the O atoms generated by reaction (2) [O] is extremely small, of the order of 10^{-5} mm Hg, and that both the application of the air afterglow in the measurement of such traces of O and the importance of competing processes such as $O + NO + M \rightarrow NO_2 + M$ followed by reaction (1) must be carefully considered.

DR. M. A. A. CLYNE (*University of Cambridge*): Although the concentration of atomic oxygen is small, use of the air afterglow for its measurement is a very sensitive method. Removal of atomic oxygen by $O + NO + M$ and by other third order homogeneous processes could possibly be important in the experiments at the higher pressure used in this work (2.2 mm Hg) but not at the lower pressure of 1.1 mm Hg. This is confirmed by the observation that for constant reaction time, [O] was independent of the amount of nitric oxide present in the system, as shown in Fig. 1. A small correction (-10%) to my value of k_3 should probably be made to allow for surface combination of oxygen atoms. In view of the different methods used by Kaufman and Del Greco and by us, the agreement between our respective values of k_3 seems satisfactory.

DR. R. R. BALDWIN (*University of Hull, England*): I would like to point out an important consequence of the value given by Dr. Clyne for his reaction (7), $H + O_2 + M = HO_2 + M$.

The value of k_7 at temperatures around 500°C can be obtained by combining measurements on the second limit M_2 of the H_2/O_2 reaction, which is given by $[M_2] = 2k_{-3}/k_7$, with estimates of k_{-3}.

$$H + O_2 = OH + O \qquad (-3)$$
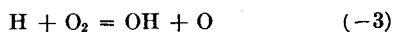
A new estimate of k_{-3} has recently been made[1] by using the inhibiting action of formaldehyde on the H_2/O_2 reaction to obtain k_{14}/k_{-3}, and combining this with independent determinations of k_{14}.

$$H + HCHO = H_2 + HCO \qquad (14)$$
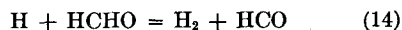
The value obtained is consistent with independent estimates by Baldwin[2] and by Semenov,[3] and the mean value of 0.6×10^7 liter mole^{-1} sec^{-1} at 540°C is considered accurate to within 50%. From second limit measurements, $2k_{-3}/k_7 = 72$ mm Hg (M = H$_2$), giving $k_7 = 0.84 \times 10^{10}$ liter^2 mole^{-2} sec^{-1} (M = H$_2$), or 0.17×10^{10} with argon as M.

Previously, the only estimates of K_7 at room temperature are those made by Hoare and Walsh[4] from the results of Robertson[5] and Patrick and Robb,[6] lower limits for k_7 being 2.9×10^{11} and 1.8×10^{11} liter^2 mole^{-2} sec^{-1}, respectively; consistent with these is the value of 6.3×10^{11} given by Burgess and Robb[7] as a result of further studies of the Hg-photosensitised H_2/O_2 reaction. As pointed out by Walsh, these estimates (M = H$_2$ in

all cases) imply a negative activation energy for reaction (7) of 3–5 kcal/mole. Support for this value comes firstly from the temperature coefficient of the photochemical reaction studies by Burgess and Robb, from which they deduce that $E_7 = -4.8$ kcal/mole; secondly, Warren[8] finds that the most accurate value for the temperature coefficient of the second limit of the H_2/O_2 reaction corresponds to $(E_{-3} - E_7) = 20$ kcal/mole. Since evidence from a variety of sources suggests $E_{-3} = 16$–17 kcal/mole, a negative value of 3–4 kcal/mole is suggested for E_7.

The new value of 1.2×10^{10} liter^2 mole^{-2} sec^{-1} (M = argon) given by Clyne provides further information on this negative activation energy, though the value $(E_7 = -(2$–$3)$ kcal/mole) is slightly less than previous estimates.

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