

# KINETICS OF THE BRANCHING STEP IN THE HYDROGEN-OXYGEN REACTION

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Lower explosion limits in hydrogen-oxygen and deuterium-oxygen mixtures have been measured in the diffusion régime. From the data, rate constants are calculated for the reactions  $H + O_2 \rightarrow OH + O$  and  $D + O_2 \rightarrow OD + O$  between 800° and 1000°K. Activation energies are found to differ by the difference in zero-point energies of OH and OD. Temperature-independent pre-exponential factors differ by a factor of two. Transition states of fixed geometry are not reconcilable with the observed kinetics; nor is the classical collision theory. With a transition state of very loose structure, the observed rate constants can be explained and successfully extrapolated down to 300°K and up to 1650°K.

## Introduction

THE rate constant  $k_H$  of the branching step  $H + O_2 \rightarrow OH + O$  has been measured many times. Recent data are collected in Table 1 together with two values for the rate constant  $k_H$  of  $OH + O \rightarrow H + O_2$ . This reverse step is

of reaction at 0°K:  $D_0(O_2) - D_0(OH) = 118.0 - 101.3 = 16.7 \text{ kcal mole}^{-1}$  (see Table 2).

Although values of  $k_H$  at 900°K are in good agreement with each other in spite of the fact that they were obtained by different methods, there remains a discrepancy between reported

TABLE 1. Values of rate constants ( $\text{cm}^3 \text{ sec}^{-1}$ )

Reaction	T (°K)	$k_H \times 10^{14}$	References
$H + O_2 \rightarrow OH + O$	900	1.8	Azatyán <i>et al.</i> <sup>1</sup>
	900	2.1	Karmilova, Nalbandyan and Semenov <sup>2</sup>
	900	4.0	Baldwin and Cowe <sup>3</sup>
	900	4.4	Fenimore and Jones <sup>4</sup>
	900	$3.3 \pm 0.7$	This work
	1650	240	Schott and Kinsey <sup>5</sup>
	1650	$190 \pm 40$	Extrapolated, this work
Reaction	T (°K)	$k_H \times 10^{11}$	References
$OH + O \rightarrow H + O_2$	310	1.8	Kaufman and Del Greco <sup>6</sup>
	293 and 265	$5 \pm 2$	Clyne <sup>7</sup>
	300	$2.8 \pm 0.6$	Extrapolated, this work

a fast reaction between free radicals and its activation energy is apparently zero or a very small quantity. Accordingly,  $E_0$ , the activation energy at 0°K of the direct process, must be either equal to or slightly larger than the heat

values of the activation energy  $E$ —which range from 15 to 18 kcal mole<sup>-1</sup>. This uncertainty is due in part to the difficulty of choosing the proper temperature dependence of the  $A$  factor in the expression  $k = A \exp(-E/RT)$ . Very accurate data or a knowledge of the structure of the transition state are required to make a correct choice. As it is necessary to know the

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TABLE 2. Spectroscopic data for species†

Quantity	Species	Value	Difference
$D_0$ , dissociation energy (kcal mole <sup>-1</sup> )	O <sub>2</sub>	117.96 ± 0.04	16.7 ± 0.3
	OH <sup>b</sup>	101.30 ± 0.3	
Zero-point energy (cal mole <sup>-1</sup> )	OH	5280	1420
	OD	3860	
$f$ , pre-exponential factor of vibrational partition function	OH	$[1 - \exp(-5140/T)]^{-1}$	
	OD	$[1 - \exp(-3790/T)]^{-1}$	
	O <sub>2</sub>	$[1 - \exp(-2240/T)]^{-1}$	
$g$ , electronic partition function	H, D	2	$5 + 3 \exp(-228/T) + \exp(-326/T)$
	O <sub>2</sub>	3	
	OH, OD	$2 + 2 \exp(-200/T)$	
	O <sup>c</sup>		

† From G. HERZBERG, *Spectra of Diatomic Molecules*, Van Nostrand: Princeton, N.J. (1950) except:<sup>a</sup> BIRK, R. P. and HERZBERG, G. J., *chem. Phys.* 21, 2240 (1953)<sup>b</sup> BARROW, R. F. *Arkiv Fysik*, 11, 281 (1956)<sup>c</sup> MOORE, C. E. 'Atomic Energy Levels', *Circ. U.S. Nat. Bui. Stand No.* 467, Vol. I, p 45. Washington, D.C. (1949)

exact temperature dependence of  $\vec{k}_H$  for extrapolations to conditions in a flame, it was decided to investigate the kinetic isotope effect in the reactions  $H + O_2$  and  $D + O_2$ . Apart from the possibility of getting in this way more information on the transition state, a study of the isotope effect in the hydrogen-oxygen system is of interest in itself. Such studies have been carried out in the past<sup>8,9</sup> but at a time when the mechanism of the hydrogen-oxygen reaction

was not sufficiently known to permit the choice of experimental conditions suitable for reaching definitive conclusions.

### Experimental

Following methods developed by other workers<sup>1,2</sup> we have observed visually the first explosion limits in mixtures of hydrogen-oxygen and deuterium-oxygen. Both hydrogen and deuterium were purified by diffusion

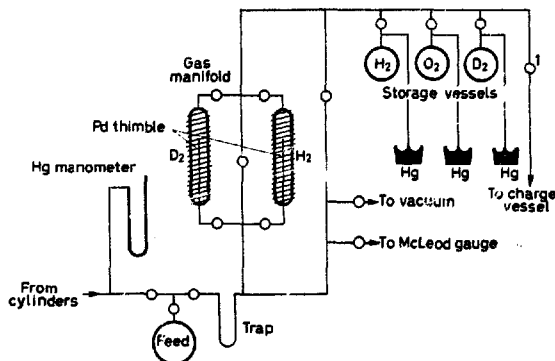


FIGURE 1. Feed purification and storage system

through palladium membranes. Purified gases were analysed by mass spectrometry. The walls of a quartz reactor of large internal diameter (10.2 cm) were coated with magnesium oxide following the method of Azatyan *et al.*<sup>1</sup> so that the destruction of hydrogen atoms was controlled by their rate of diffusion to the walls.

This point was checked by working with mixtures of different compositions containing 10 per cent as well as the stoichiometric amount of oxygen. A liquid nitrogen trap preceding the reactor protected the active surface from contaminants and ensured remarkable reproducibility. The reproducibility was assessed by

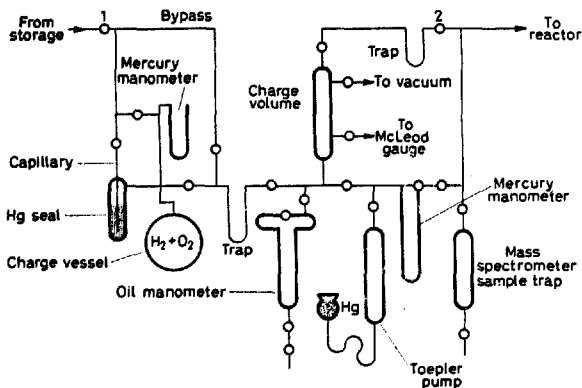


FIGURE 2. Charge preparation and delivery system

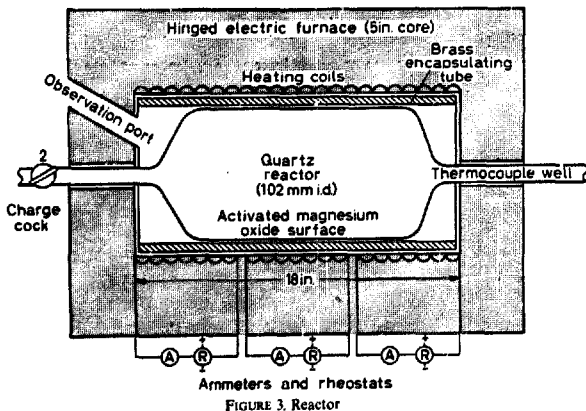


FIGURE 3. Reactor

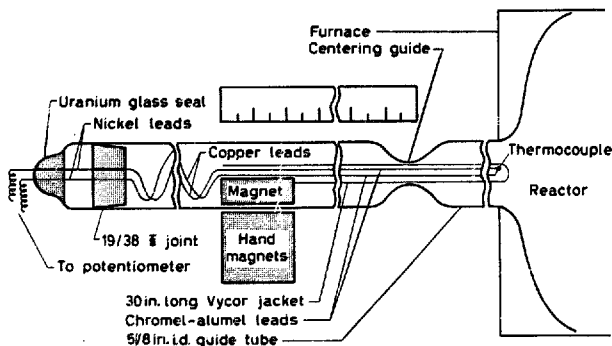


FIGURE 4. Retractable thermocouple assembly

alternating high with low temperatures and performing experiments with different concentrations in random sequences as well as by preparing a new surface on at least four different occasions, always to obtain essentially identical results. Axial temperatures in the reactor prior to explosion were measured by means of a movable thermocouple well that could be taken out of the reactor by means of a magnet. Pressure measurements were made with a manometric system which employed a mercury manometer to measure the pressure of the gases contained in a fixed volume chamber prior to their expansion into the reactor. Upon determining to within a difference less than one per cent the two pressures at which explosions just occurred and did not occur, the fixed volume chamber was charged with inert gas to the average of these two pressures and the pressure of the gas when expanded into the reactor was measured by a temperature-compensated silicone oil manometer. Details of the apparatus are shown in Figures 1, 2, 3 and 4.

### Results

Data are shown in Figure 5. At the first limit  $p_1$ , in the diffusion régime, the following expression of Semenov<sup>10</sup> relates  $p_1$  (mm Hg),  $\bar{k}_H$  ( $\text{cm}^3 \text{sec}^{-1}$ ), the diameter of the cylindrical reactor

$d$  (cm), the mole fraction of oxygen  $\gamma$ , and the diffusivity  $\mathcal{D}_0$  ( $\text{cm}^2 \text{sec}^{-1}$ ), at 1 mm Hg, of hydrogen atoms

$$p_1 d = 4.81 (\mathcal{D}_0 / 2 \bar{k}_H \gamma N_0)^{1/2} \quad [1]$$

where  $N_0 = (0.967 \times 10^{19} / T) \text{ cm}^{-3}$  (at 1 mm Hg). Limitations to equation 1 are discussed at length elsewhere<sup>11</sup> and in abbreviated form in the Appendix.

In order to calculate rate constants from the data, the diffusivities of H and D must be known. Diffusivities of H in pure hydrogen or oxygen were obtained following recent theoretical work<sup>12,13</sup>. Diffusivities of D were calculated from corresponding values for the light isotope. The method of Wilke<sup>14</sup> was then used to calculate diffusivities in the reactive mixtures. Expressions used are shown in Table 3.

Between 800° and 1000°K, the temperature dependence of diffusivities could be best represented as  $\mathcal{D} \propto T^{1.8}$ . From equation 1 it then follows that a plot of  $\log(p_1 / T^{1.4})$  versus  $1/T$  should be a straight line if  $\bar{k}_H$  obeys the Arrhenius relation. Such is the case between 800° and 1000°K. Below 800°K, the lines curve upward because of the homogeneous destruction of H atoms<sup>10</sup>:  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ . For present purposes, only data corresponding to the straight-line portions of the curves will be

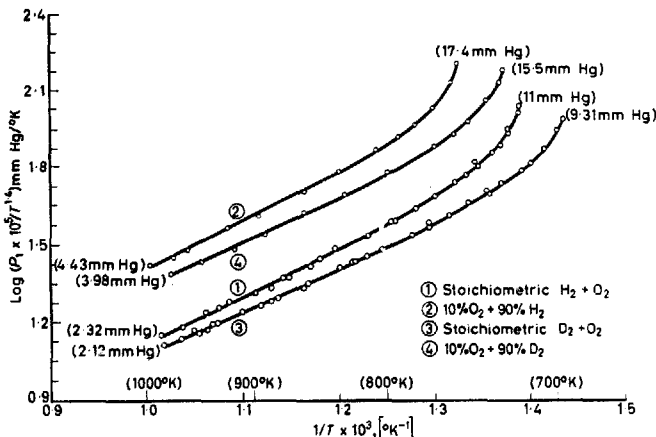


FIGURE 5. Lower explosion limits (diffusion régime)

TABLE 3. Calculated quantities

Diffusivity ( $\text{cm}^2 \text{sec}^{-1}$ ) between 800° and 1000°K, at 1 mm Hg	H in $\text{H}_2\text{-O}_2$ mixtures; $\gamma$ : mole fraction $\text{O}_2$	$\mathcal{D}_0 = \frac{0.0531 T^{1.8}}{(1-\gamma) + 1.62\gamma}$
	D in $\text{D}_2\text{-O}_2$ mixtures; $\gamma$ : mole fraction $\text{O}_2$	$\mathcal{D}_0 = \frac{0.0376 T^{1.8}}{(1-\gamma) + 1.62\gamma}$
Equilibrium constant	$\text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O}$	$K_H = 0.638 g_{\text{OH}} \Gamma_{\text{OH}} \Gamma_{\text{O}_2}^{-1} \exp(-16600/RT)$ (see Table 2)
	$\text{D} + \text{O}_2 \rightleftharpoons \text{OD} + \text{O}$	$K_D = 0.463 g_{\text{OD}} \Gamma_{\text{OD}} \Gamma_{\text{O}_2}^{-1} \exp(-15200/RT)$ (see Table 2)

considered. They are collected in Table 4 so that values of  $k_H$  and  $k_D$  may be recalculated in the future if need be.

The best values of the parameters of an Arrhenius expression were obtained from the data by the method of least squares. The expressions for  $\bar{k}_H$  and  $\bar{k}_D$  were then subjected to several corrections, all minor, due to departure from the diffusion régime, small amounts of inerts in the oxygen, and of hydrogen in the

deuterium, end effects due to the finite length of the cylindrical reactor and destruction of oxygen atoms carrying the chain. Details of these small corrections are given in the Appendix. The final expressions best fitting all data of Table 4 are given below.

$$\bar{k}_H = \frac{A_H}{1 + p_H} \frac{\Gamma_{\text{OH}}}{\Gamma_{\text{O}_2}} \exp(-16700/RT) \quad [2]$$

$$\bar{k}_D = \frac{A_D}{1 + p_D} \frac{\Gamma_{\text{OD}}}{\Gamma_{\text{O}_2}} \exp(-15300/RT) \quad [3]$$

$$A_H = 4.80 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad [4]$$

$$A_D = 2.25 \times 10^{-10} \text{ cm}^3 \text{ sec}^{-1} \quad [5]$$

$$p_H = 0.18 T^{1/2} / \theta_O \theta_{OH} \quad [6]$$

$$p_D = 0.13 T^{1/2} / \theta_O \theta_{OH} \quad [7]$$

$\Gamma_{OH}, \Gamma_{OD}, \Gamma_{O_2}, \theta_{OH}, \theta_{OD}, \theta_O$ : see Table 2.

minus the zero-point energy difference of OH and OD, 1400 cal mole<sup>-1</sup> (see Table 2). These values are obtained with pre-exponential factors  $A_H$  and  $A_D$  independent of temperature. The interpretation of the latter is not straightforward.

A *prima facie* reason to reject collision theory is the observed ratio [see equations 4

TABLE 4. First explosion limits  $p_1$  in a magnesium oxide-coated cylindrical reactor (Diameter: 10.2 cm)

2 H <sub>2</sub> -O <sub>2</sub>		2 D <sub>2</sub> -O <sub>2</sub>		9 H <sub>2</sub> -O <sub>2</sub>	
T(°K)	$p_1$ (mm Hg)	T(°K)	$p_1$ (mm Hg)	T(°K)	$p_1$ (mm Hg)
985.7	2.32	983.0	2.12	997.0	4.43
965.0	2.43	965.7	2.18	973.7	4.60
943.2	2.67	953.8	2.30	959.4	4.76
930.8	2.72	949.4	2.22	923.2	5.42
921.4	2.83	941.2	2.27	896.4	5.80
898.7	2.94	936.2	2.39	859.0	6.72
886.4	3.04	931.7	2.38	833.2	7.67
875.7	3.21	910.2	2.53	9 D <sub>2</sub> -O <sub>2</sub>	
871.4	3.29	894.2	2.60		
854.7	3.45	885.4	2.68	976.2	3.98
847.4	3.64	880.2	2.71	946.7	4.18
835.4	3.90	876.0	2.79	916.4	4.49
812.4	4.16	859.8	2.90	891.0	4.88
797.0	4.54	856.0	2.98	859.0	5.57
794.2	4.56	832.2	3.24	828.7	6.18
		823.0	3.36		
		821.4	3.36		
		813.0	3.49		
		802.7	3.62		
		783.0	3.94		
		772.2	4.16		

The reason for the appearance of the pre-exponential factors  $\Gamma_{OH}, \Gamma_{OD}, \Gamma_{O_2}, (1 + p_H)$ , and  $(1 + p_D)$ , which are very nearly unity and almost temperature independent up to 1000°K, will become clear in the discussion of these results.

### Discussion

From the experimental results, the exponential factor of  $\bar{k}_H$  gives an activation energy of 16700 cal mole<sup>-1</sup>, in perfect agreement with the heat of reaction at 0°K from spectroscopic data. Similarly the activation energy of the deuterium reaction, 15300 cal mole<sup>-1</sup>, is equal to 16700

and 5],  $(A_H/A_D) \approx 2$ , whereas collision frequencies would differ by a factor almost equal to  $\sqrt{2}$ . Clearly, it is necessary to invoke a more refined theory. However, various attempts to account for the results by means of transition state theory suggest that the transition state has a very loose structure. Indeed, linear, bent, or isosceles triangular models of the transition state failed to accommodate both  $\bar{k}_H$  and the experimental isotope effect<sup>11</sup>.

As a matter of necessity, we will therefore consider the reverse step,  $OH + O \rightarrow O_2 + H$ , calculate its rate constant  $\bar{k}_H$  and then derive  $\bar{k}_H$  by means of

$$\tilde{k}_H = \tilde{k}_H K_H \quad [8]$$

where  $K_H$  is the equilibrium constant of the reaction (see Table 3).

To calculate  $\tilde{k}_H$ , it is reasoned that  $\tilde{k}_H$  must be equal to the product of  $k_c$ , the rate constant corresponding to the rate of formation of collision complexes capable of undergoing reaction, and  $P$ , the probability that reaction occurs during the lifetime of the complex

$$\tilde{k}_H = k_c P \quad [9]$$

To evaluate  $k_c$  and  $P$  we have formulated a model of a generalized spin-allowed reaction of zero activation energy between a free radical (subscript 1) and an atom (subscript 2). The transition state is assumed to have a loose structure. It will be shown that this treatment is adequate to explain the observed kinetics of the branching step.

*Rate constant  $k_c$  for the formation of collision complexes*

It will be assumed that the complex is entirely loose with the reactants of masses  $m_1$  and  $m_2$  preserving their identity. The free radical reactant is also assumed to conserve its angular momentum in the complex. The forces exerted by one reaction partner on the other in the complex prior to their plunge into the 'chemical trap' are assumed to be adequately described by the Lennard-Jones 6-12 potential

$$V_{LJ} = 4\epsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^6 \right] \quad [10]$$

where  $\sigma$  and  $\epsilon$  are the customary Lennard-Jones collision parameters and  $R$  is the separation of the reaction partners, considered as point masses.

In a typical collision, the angular momentum of the complex as a whole gives rise to a small centrifugal potential barrier,  $V_c$ , which is at a maximum in the total potential  $V$ , the sum of  $V_{LJ}$  and of the rotational energy of the complex

$$V = \frac{J(J+1)\hbar^2}{2M_{12}R^2} + V_{LJ} \quad [11]$$

where  $\hbar = h/2\pi$ ,  $J$  is a rotational quantum

number, and  $M_{12}$  is the reduced mass  $m_1 m_2 / (m_1 + m_2)$ .

Differentiating  $V$  with respect to  $R$  and setting the result equal to zero yields for the separation,  $R_c$ , at the maximum  $V_c$  in the potential energy

$$\frac{J(J+1)\hbar^2}{2M_{12}R_c^2} = 12\epsilon \left[ \left( \frac{\sigma}{R_c} \right)^6 - 2 \left( \frac{\sigma}{R_c} \right)^{12} \right] \quad [12]$$

which yields in turn

$$V_c = 4\epsilon \left[ 2 \left( \frac{\sigma}{R_c} \right)^6 - 5 \left( \frac{\sigma}{R_c} \right)^{12} \right] \quad [13]$$

It is immediately apparent that  $V_c$  and  $J$  in equations 12 and 13 have a maximum at a particular value of  $(R_c/\sigma)$ . This corresponds physically to the fact that collisions with too high values of  $J$  do not form 'bound' collisional states, i.e. for such collisions the sum of the centrifugal and repulsive potentials is everywhere greater than the attractive potential, and no potential well exists. (This is shown schematically in Figure 6.) It is postulated here that only collisional states 'bound' in the sense just discussed can lead to reaction.

Differentiating  $V_c$ , as given by equation 13, with respect to  $R_c$  and setting the result equal to zero leads to the result that at  $J_{\max}$ ,

$$(R_c/\sigma)_{J_{\max}} = 5^{1/6} \quad [14]$$

Further, at  $J = 0$

$$(R_c/\sigma)_{J=0} = \infty \quad [15]$$

An essential theoretical difference between reactions with zero and finite activation energies is evident. In the former there is no fixed separation between the reactants in the reaction complex. If the separation were fixed,  $k_c$  would be given simply by the familiar

$$(\pi R_c^2) (8kT/\pi M_{12})^{1/2} \quad [16]$$

where  $R_c$  would then be the corresponding hard sphere collision diameter.

For the case at hand, the above must be multiplied by the ratio of what is effectively the rotational partition function for a diatomic

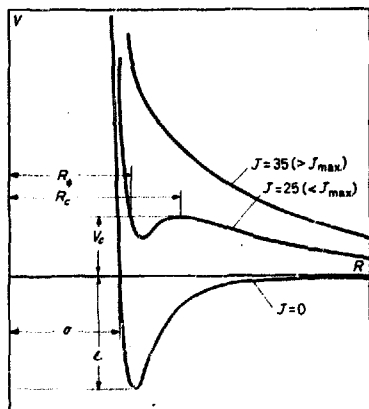


FIGURE 6. Lennard-Jones potential energy surface for O + OH collisions

rotator with variable separation to that of one with a fixed separation, viz.

$$\frac{\sum_{J=0}^{J_{\max}} (2J+1) \exp(-V_c/kT) dJ}{2kTR_c^2 M_{12} / \hbar^2} \quad [17]$$

By making use of the preceding relations involving  $J$ ,  $V_c$  and  $R_c$ , the numerator of expression 17 may readily be transformed to

$$\frac{96\pi\sigma^2 M_{12}}{\hbar^2} \int_0^{5/6} \left( \frac{5}{y^{11}} - \frac{1}{y^5} \right) \times \exp \left[ \frac{-4\epsilon}{kT} \left( \frac{2}{y^6} - \frac{5}{y^{12}} \right) \right] dy \quad [18]$$

where  $y = R_c/\sigma$ .

Normal values of  $kT/\epsilon$  at ambient and higher temperatures range upwards from three, and the integral in expression 18 is well approximated by  $(1/20) \exp(-\epsilon/3kT)$ , with the result, from 16, 17 and 18, that

$$k_c = \frac{36}{5} (\pi\sigma^2) \left( \frac{8kT}{\pi M_{12}} \right)^{1/2} \left( \frac{\epsilon}{3kT} \right) \exp \left( \frac{-\epsilon}{3kT} \right) \quad [19]$$

### Reaction probability $P$ of collision complexes

Let  $k_r^\ddagger$  refer to a rate constant for reaction and  $k_d^\ddagger$  to that for dissociation of the collision complex. Then

$$P = k_r^\ddagger / (k_r^\ddagger + k_d^\ddagger)$$

But clearly

$$k_d^\ddagger = 1/\tau_c$$

where  $\tau_c$  is the average lifetime of the collision complexes.

If we now assume—on a purely intuitive basis—that once both spins and nuclei are favourably oriented the complex falls rapidly into the 'chemical trap', then

$$k_r^\ddagger = (g^\ddagger/g_1 g_2) (1/\tau_R)$$

where  $g^\ddagger$ ,  $g_1$ , and  $g_2$  are the electronic partition functions of the complex and reaction partners 1 and 2 respectively and  $\tau_R$  is the average rotation time required for the nuclei to become oriented purely by tumbling.

Accordingly

$$P = \frac{(g^\ddagger/g_1 g_2)(\tau_c/\tau_R)}{1 + (g^\ddagger/g_1 g_2)(\tau_c/\tau_R)} = \frac{p}{1+p}$$

where

$$p = (g^\ddagger/g_1 g_2) (\tau_c/\tau_R)$$

Let us write  $G$  for the ratio  $g^\ddagger/g_1 g_2$  and  $\bar{v}_R/\bar{v}_c$  for  $\tau_c/\tau_R$ . Then

$$p = G \bar{v}_R/\bar{v}_c$$

where the  $\bar{v}$ s are averaged rotation and dissociation frequencies.

Treating the radical as a diatomic heteronuclear rotator,  $\bar{v}_R$  may be obtained<sup>15</sup> from

$$\bar{v}_R = \frac{\hbar}{2\pi r^2 M_1} \times \frac{\int_0^\infty [J'(J'+1)]^{1/2} (2J'+1) \exp[-J'(J'+1)b] dJ'}{\int_0^\infty (2J'+1) \exp[-J'(J'+1)b] dJ'}$$

where the  $J$ 's are the rotational quantum numbers (all  $J$ 's are allowed),  $r$  is the bond length,  $M_1$  is the reduced mass of the radical and

$$b = \hbar^2/(2r^2 M_1 kT)$$



The result of the integration is

$$\bar{v}_R = (1/8r)(8kT/\pi M_1)^{1/2}$$

We identify  $\bar{v}_c$  simply with the average stretching frequency of the collision complex

$$\bar{v}_c = (1/2\pi)(f_c/M_{12})^{1/2}$$

where  $f_c$  is the force constant obtained by averaging  $f_c$  over the allowable values of  $J$

$$\bar{f}_c = \frac{\int_0^{J_{\max}} (2J+1) f_c dJ}{\int_0^{J_{\max}} (2J+1) dJ}$$

in which expression:

$$f_c = \frac{d^2V}{dR^2} = \frac{3J(J+1)\hbar^2}{M_{12}R^4} + \frac{13(48)\epsilon\sigma^{12}}{R^{14}} - \frac{7(24)\epsilon\sigma^6}{R^8}$$

Details of the calculations are shown in Table 5, where calculated force constants are

The final expression for  $p$  is

$$p = G(2/27)(2\pi\sigma/8r)\left(\frac{8kT}{\pi M_1}\right)^{1/2}\left(\frac{M_{12}}{\epsilon}\right)^{1/2}$$

As  $P = p/(1+p)$ , it is evident that as  $T$  increases to infinity,  $P$  tends to unity.

Finally, according to equation 9,

$$k_{12} = k_c P$$

Combining the expressions for  $k_c$  and  $P$  leads to the result that

$$k_{12} = \frac{G}{(1+p)} \left(\frac{\epsilon}{20kT}\right)^{1/2} \left(\frac{\sigma}{r_1}\right) (\pi\sigma^2) \left(\frac{8kT}{\pi M_1}\right)^{1/2} \times \exp(-\epsilon/3kT)$$

A surprising feature of this equation is the prediction that for  $P \ll 1$ , the reaction rate is independent of the mass  $m_2$  of the atomic partner for this class of reaction.

TABLE 5. Structural parameters of collision complex

Angular momentum		Critical separation	Force constant
$J(J+1)\hbar^2$ $24\epsilon\sigma^2 M_{12}$	$J$ (for O + OH)	$\left(\frac{R_2}{\sigma}\right)^6$	$f_{c1}\left(\frac{\sigma^2}{\epsilon}\right)$
0	0	1.00	456
0.05	14	1.16	300
0.10	21	1.40	172
0.15	25	1.82	77.1
0.18	28	2.35	32.7
0.19	29	2.71	18.9
0.20	29	3.40	6.70
0.2050 (max.)	30 (max.)	5.00	0

NOTE:  $f_{c1}\left(\frac{\sigma^2}{\epsilon}\right) = (27/2)^2$ .

shown for the point of closest approach in a critically activated collision, i.e. at the point (see Figure 6) on the side of the potential well opposite the maximum where  $V = V_c(f_c, R_2)$ . We reason that the lifetime of the critically activated complex at the position of closest approach, i.e. at  $R_2$ , is rate-determining. Accordingly,

$$\bar{v}_c = (1/2\pi)[\bar{f}_c/M_{12}]^{1/2} = (27/4\pi)[\epsilon/\sigma^2 M_{12}]^{1/2}$$

#### Application to the branching reaction

The value of  $K_H$  can be calculated from spectroscopic data (see Tables 2 and 3). It can be written in the form

$$K_H = B_H g_O g_{OH} \Gamma_{OH} \Gamma_{O_2}^{-1} \exp(-E_H/RT + \epsilon/3kT)$$

where  $E_H$  is the experimental activation energy of the branching reaction ( $E_H/RT \gg \epsilon/3kT$ ),  $\Gamma_{OH}$  and  $\Gamma_{O_2}$  are vibrational partition function pre-exponential factors,  $g_O$  and  $g_{OH}$  are electronic

partition functions, and the quantity  $B_H$  is temperature independent.

It is important to note that writing  $K_H$  in this form involves certain approximations, viz. that electronic, rotational and vibrational partition functions are completely separable and that these are adequately described by the appropriate expressions for rigid rotators and harmonic oscillators. Rigorous calculations of  $K_H$  which do not invoke these assumptions can be made from the information contained in the JANAF Thermochemical Tables [ref. 16].

For the present purposes, we note that the expression

$$K_H = 0.638 g_{OH} g_{OH} \Gamma_{OH} \Gamma_{O_2}^{-1} \exp(-16530/RT)$$

closely reproduces the JANAF  $K_H$  values, at least over the temperature range from 100° to 3000°K. For example, at 100°K,  $K_H$  from the above expression is  $5.77 \times 10^{-36}$  and  $K_H$  from the JANAF tables is  $5.81 \times 10^{-36}$ ; at 3000°K, the respective values are 0.857 and 0.855. Thus the rigorous JANAF calculations, which are based upon a heat of reaction at 0°K of 16630 cal mole<sup>-1</sup> (cf.  $16700 \pm 300$  cal mole<sup>-1</sup>, Table 2) are essentially duplicated over a range of more than 35 orders of magnitude by the above simple form for  $K_H$ , although to do so it is necessary to write the energy term in the exponential factor as 100 cal mole<sup>-1</sup> less than  $\Delta H_0^\ddagger$ . For this reason, the corresponding term in Table 3 is written as 16600 rather than 16700 cal mole<sup>-1</sup>.

Equating  $\tilde{k}_H$ , as written in equation 2, to  $\tilde{k}_{H,K_H}$ , it follows then that

$$A_H = \tilde{k}_H(1 + p_H) B_H g_{OH} \exp(\epsilon/3kT)$$

Now, from the preceding formulation

$$\tilde{k}_H = \frac{g^\ddagger}{g_{OH}(1 + p_H)} \left( \frac{\epsilon}{20kT} \right)^{\frac{1}{2}} \left( \frac{\sigma}{r_{OH}} \right) \times (\pi\sigma^2) \left( \frac{8kT}{\pi M_{OH}} \right)^{\frac{1}{2}} \exp(-\epsilon/3kT)$$

To fix the ideas  $\tilde{k}_H/(\pi\sigma^2) (8kT/\pi M_{OH})^{\frac{1}{2}}$  may be regarded as a steric factor. With  $g^\ddagger = 2$ ,  $\sigma = 3.20$  Å and  $\epsilon/k = 107^\circ\text{K}$ , about one collision out of ten is effective at 300°K, one out of 23 at

900°K. The collisional efficiencies are lower for  $\tilde{k}_D$ .

Substituting the expression for  $\tilde{k}_H$  into the above expression for  $A_H$

$$A_H = g^\ddagger B_H (\sigma^3/r_{OH}) (2\pi\epsilon/5M_{OH})^{\frac{1}{2}}$$

Since  $B_H \approx \sqrt{2} B_D$  and  $[M_{OD}/M_{OH}]^{\frac{1}{2}} \approx \sqrt{2}$ , it is evident that  $A_H \approx 2A_D$ , as found experimentally. Further, the observed rate constants can be reproduced with very reasonable values of the Lennard-Jones collision parameters  $\sigma$  and  $\epsilon$ . Indeed, we assume that the spin-oriented reaction complex is a doublet, i.e.  $g^\ddagger = 2$ , and estimate that  $\epsilon/k$  for the interaction of O and OH is not substantially different from that for O and O<sub>2</sub>, i.e.  $\epsilon/k = 107^\circ\text{K}$  [ref. 17]. Using these values we get:

$$A_H = 1.43 \times 10^{-11} \sigma^3$$

$$A_D = 0.754 \times 10^{-11} \sigma^3$$

where  $A_H$  and  $A_D$  are in cm<sup>3</sup> sec<sup>-1</sup> and  $\sigma$  is in Ångströms. In order to get agreement with experimental values of  $A_H$  and  $A_D$ , a value of  $\sigma$  must now be chosen. This value should be the Lennard-Jones collision parameter for the interaction of O and OH, which can be estimated from values reported for the free radicals: 3.05 Å for O and 3.15 Å for OH [ref. 17]. With  $\sigma = 3.20$  Å, we get:

$$A_H = 4.68 \times 10^{-10} (4.80 \times 10^{-10})$$

$$A_D = 2.47 \times 10^{-10} (2.25 \times 10^{-10})$$

The values in parentheses are the experimental values obtained in this work. They are seen to be in good agreement with calculated values.

It is of interest to note that the final expression for  $\tilde{k}_H$  predicts a temperature dependence of the Arrhenius activation energy:

$T(^{\circ}\text{K})$	$E_H(\text{Arrhenius})$ (cal mole <sup>-1</sup> )
300	16700
1000	16200
1500	15400
2000	14000

This trend requires further study, but at the very least provides an answer to the enigma

<sup>†</sup> For  $K_D$ , the appropriate quantity is 50 rather than 100 cal mole<sup>-1</sup>.

presented by the fact that experimental measurements of  $E_H$ , particularly at higher temperatures, generally fall below the heat of reaction [refs. 1, 2, 5, 18].

### Conclusion

The reaction  $H + O_2 \rightleftharpoons OH + O$  seems to be reasonably well understood between room temperature and 1650°K. Indeed, with the same value  $\sigma = 3.20 \text{ \AA}$  used to fit the present data, the rate constant  $k_H$  becomes  $2.8 \times 10^{-11}$  at 900°K. The agreement with Clyne's and Kaufman and Del Greco's values is good (Table 1). Also, with  $\sigma = 3.20 \text{ \AA}$ , we calculate  $k_H = 190 \times 10^{-14}$  at 1650°K in good agreement with the observation of Schott and Kinsey (Table 1).

For safe extrapolations to still higher temperatures, it is necessary to know more about the reliability of the equation presented here for the prediction of rate constants for reactions with very loosely constructed transition states. For applications, we note that the following simplified expression can replace equation 2 to within three per cent between 300 and 2000°K:

$$k_H = (4.5 - T/1100) \times 10^{-10} \exp(-16700/RT) \text{ cm}^3 \text{ sec}^{-1}$$

likely to be small is evidenced by the good agreement between the values of  $k_H$  at 900°K reported here and the average of those reported by others (Table 1), as well as the above-cited agreements in extrapolated values.

The usefulness of deuterium in studies of the hydrogen-oxygen reaction has been demonstrated. The magnitude of the kinetic isotope effect may serve as a guide in future work, indicating whether the use of deuterium is expected to yield significant information.

## APPENDIX

### Systematic and Experimental Errors

Values of  $k_H$  and  $k_D$  were calculated from the raw data shown in Table 4 through equation 1, using the values of  $\mathcal{D}_0$  shown in Table 3. The Arrhenius form of the results of a least squares fit of the data for each composition are shown in Table 6.

These results were then subjected to several small corrections, due to departure from the diffusion régime, small amounts of impurities in the reactants, end effects, and to the heterogeneous destruction of chain-carrying oxygen atoms. The method used in applying these small

TABLE 6. Results of raw data fit: 800–1000°K;  $k = A \exp(-E/RT)$

Mixture	$A \times 10^{10}$ ( $\text{cm}^3 \text{ sec}^{-1}$ )	$E$ ( $\text{cal mole}^{-1}$ )	Standard Deviation (%)
Stoichiometric			
H <sub>2</sub>	2.34	15900	3.5
D <sub>2</sub>	1.01	14500	2.5
10 per cent oxygen			
H <sub>2</sub>	2.72	16200	3.6
D <sub>2</sub>	1.38	14900	3.7

The expression for  $k_H$  obtained here is believed to be reliable within 20 per cent (see Appendix). Half of the uncertainty lies in the assumed values of diffusivity, half in other systematic and random errors. The normalized standard deviations for the data shown in Table 4 are 3.5 per cent and 3.6 per cent for the two sets of values of  $k_H$  and 2.5 per cent and 3.7 per cent, for the two sets of values of  $k_D$ . That errors are

corrections was quite direct. Values of  $k_H$  and  $k_D$  were calculated from the simple linear fit of the raw data for two temperatures—1000°K and 850°K. Corrections were then applied to these values and the results refitted to an Arrhenius expression. They are summarized in Table 7, and discussed briefly below. A more detailed discussion is presented elsewhere<sup>11</sup>. Finally, the corrected Arrhenius expressions for the

TABLE 7. Corrected branching rate constant results (800–1000°K)

Correction	850 °K		1000 °K	
	10% O <sub>2</sub>	Stolch.	10% O <sub>2</sub>	Stolch.
Correction for departure from diffusion régime				
H <sub>2</sub>	-0.35 %	-0.60 %	-0.71 %	-1.21 %
D <sub>2</sub>	-0.43 %	-0.71 %	-0.83 %	-1.33 %
Finite cylinder correction				
H <sub>2</sub> and D <sub>2</sub>	+2.56 %	+2.56 %	+2.56 %	+2.56 %
Correction for contamination of reactants				
H <sub>2</sub>	+0.87 %	+0.87 %	+0.87 %	+0.87 %
D <sub>2</sub>	+1.13 %	+1.13 %	+0.89 %	+0.89 %
Corrected apparent net branching rate constants × 10 <sup>14</sup>				
$\bar{k}_H$ (cm <sup>3</sup> sec <sup>-1</sup> )	1.91	1.93	8.03	7.90
$\bar{k}_D$	2.10	1.90	7.85	6.86
Extrapolated branching rate constants × 10 <sup>14</sup>				
$\bar{k}_H$ (100% H <sub>2</sub> )	1.91		8.07	
$\bar{k}_D$ (100% D <sub>2</sub> )	2.16		8.12	
Experimental branching rate constants, Arrhenius form	$\bar{k}_H = 2.81 \times 10^{-10} \exp \left( -\frac{16200}{RT} \right)$			
	$\bar{k}_D = 1.47 \times 10^{-10} \exp \left( -\frac{14900}{RT} \right)$			

experimental branching rate constants, Table 7, were refitted to the theoretical expression derived above.

#### Correction for departure from the diffusion régime

For an empty, infinitely long isothermal cylindrical reactor in which, as in these experiments, convective effects are negligible<sup>11</sup> it may readily be shown<sup>10</sup> that at the lower explosion limit

$$\frac{J_1(x)}{J_0(x)} = \frac{\mathcal{E}u}{4\mathcal{D}_0} \left( \frac{\mathcal{D}_0}{2\bar{k}_\gamma N_0} \right)^{\frac{1}{2}}$$

where  $J_0(x)$ ,  $J_1(x)$  are the zero and first order Bessel functions of the first kind,

$$x = \frac{p_1 d}{2} \left( \frac{2\bar{k}_\gamma N_0}{\mathcal{D}_0} \right)^{\frac{1}{2}}$$

$\mathcal{E}$  is the first order recombination probability for H or D atoms striking the surface, and

$u$  is the mean thermal velocity of H or D atoms.

At the explosion limits the net rate of branching in the homogeneous phase is just balanced by the rate at which H or D atoms, and other chain carriers, are being destroyed. In lower explosion limit experiments this destruction of active centres is almost completely heterogeneous.

For the limiting case known as the diffusion régime, the heterogeneous destruction at the walls is limited only by the rate at which the chain carriers can diffuse out of the homogeneous phase, i.e. the surface is so active that any further increase in its activity toward recombination would not affect the limit pressure.

Thus a strict criterion for the diffusion régime would be

$$\frac{dp_1}{d\mathcal{E}} = 0 \quad \text{or} \quad \frac{d\mathcal{E}}{dx} = \infty$$

which leads to  $J_1(x)/J_0(x) = \infty$ , or  $x = 2.405$ , as Semenov<sup>10</sup> has shown.

However,  $\mathcal{E}$  cannot exceed unity, so that for

every real system there is a finite upper limit to the term  $J_1(x)/J_0(x)$ .

One can show<sup>11</sup> that for only small departures from the diffusion régime, the error involved in assuming that  $x$  is equal to 2.405 is given by

$$\text{Error in } x = +1.00\% \left( \frac{800 \mathcal{D}_0}{\mathcal{E}_{up,d}} \right)$$

This correction was applied (Table 7) to the data on the basis that  $\mathcal{E}$  was essentially unity<sup>11</sup> for the conditions of these experiments.

#### Finite cylinder correction

For the hypothetical case considered above, no axial loss of chain centres from the just-exploding section at the centre of the reactor can occur. In a real vessel, some axial loss must occur, requiring a slightly higher pressure to induce explosion in the finite cylinder than for the infinite. The net effect of this circumstance is that a correction factor greater than unity needs to be applied to  $\bar{k}$ .

This correction factor is essentially a function of the geometry of the system and is given<sup>11</sup> for an isothermal right cylinder in the diffusion régime by

Correction factor for finite cylinder

$$= 1 + \frac{1}{2}(d/L)^2$$

where  $L$  denotes reactor length = 45 cm in these experiments.

Because of heat flux through the ends of the cylinder, the temperature at the centre of a real reactor is generally somewhat higher than the reactor mean temperature. However, at the limit the explosions are just quenched at the highest temperature in the homogeneous phase. This is the temperature to which the data of Table 4 refer. In these experiments the reactor mean temperature was lower than the maximum temperature, which occurred at the centre, by only 1.2 per cent. No measurable radial thermal gradients existed within the reactor, although a thermocouple mounted adjacent to the outer reactor wall (as in the conventional techniques), and in the proximity of the heating coils of the electric furnace used, measured a temperature 16 deg.C. higher than that at the centreline of the reactor.

#### Correction for contamination of reactants

By mass spectrometric analysis, the compositions of the gases charged to the reactor were:

Deuterium  $D_2$ : 99.34% (as  $D_2$  and D in HD)  
 $H_2$ : 0.66% (as  $H_2$  and H in HD)  
 Air: Less than 10 p.p.m.

Hydrogen  $H_2$ : 100.00%  
 Air: Less than 10 p.p.m.

Oxygen  $O_2$ : 99.14%  
 $N_2$ : 0.49%  
 Ar: 0.34%

Condensables: 275 p.p.m. (by a conventional trapping technique).

A correction factor of 1/0.9914 was applied, Table 7, to both  $\bar{k}_H$  and  $\bar{k}_D$  to compensate for the contamination of the oxygen employed. No further correction to  $\bar{k}_H$  was required. (A small additional correction to  $\bar{k}_D$  was applied, Table 7, because of  $H_2$  contamination of  $D_2$  [ref. 11].)

#### Correction for the dependence of the apparent branching rate constant upon oxygen concentration

Primarily because of the removal of O atoms from the reaction chains<sup>1</sup>, the apparent value of the net branching rate constant tends to become smaller at higher oxygen concentrations than at lower, although an effect acting in an opposite direction is the greater relative rate of homogeneous destruction of H or D atoms by  $HO_2$  or  $DO_2$  radical formation at the higher limit pressures encountered with low oxygen concentrations<sup>10</sup>. The results obtained from analysis of the data of Table 4 were corrected by simple linear extrapolation against the term  $2\gamma/(1-\gamma)$  [ref. 11] to zero oxygen concentration, to obtain the final values for  $\bar{k}_H$  and  $\bar{k}_D$  shown in Table 7.

#### Estimated error in the branching rate constant

Table 8 summarizes the error estimates resulting from a detailed analysis of systematic and random error sources, presented elsewhere<sup>11</sup>. The largest source of error lies in the estimated  $\pm 10$  per cent uncertainty in the calculated values of the diffusivities of H and D atoms. (Mason *et al.*<sup>12</sup> and Yun and Mason<sup>13</sup>, upon

TABLE 8. Systematic and random error estimates

Error source	Estimated resulting error in $\bar{k}_H$ (800° to 1000°K)
Systematic:	
Diffusivity calculation	$\pm 10\%$
$\delta$ was assumed unity	$+1\%$
Extrapolation to 0% O <sub>2</sub>	Nil
High and low-temperature effects	$-4.5\%$
Initiation reaction	Nil
Impurities (after correction)	Nil
End effects (after correction)	$\pm 0.5\%$
Transient effects	Nil
Pressure measurement	$-1\%$
Temperature measurement	$\pm 2.5\%$
Detection effects	$-1\%$
Random:	
Mixture preparation	$\pm 0.5\%$
Temperature measurement	$\pm 1\%$
Pressure measurement	$\pm 2\%$

whose works the diffusivity estimates are based, believe their calculations are reliable to within  $\pm 5$  to  $\pm 10$  per cent.)

The second largest source of systematic error arises from two effects:

(1) Homogeneous removal of H or D atoms from the reaction chains to form HO<sub>2</sub> or DO<sub>2</sub> radicals, which process becomes increasingly significant at the higher limit pressures encountered at lower temperatures.

(2) The decrease of O<sub>2</sub> partial pressure by reaction during the induction period, which process becomes significant only at high temperatures because of the high activation energy of the overall reaction converting hydrogen to water during the induction period<sup>11</sup>.

For present purposes, it has been assumed that between 800° and 1000°K, because of the linear character of the data in this temperature range, the net effect of these two processes upon the apparent energy of activation of the branching step is negligible. It is quite likely, however, that the pre-exponential factors of the branching rate constants should be increased somewhat to correct for these two effects. It was estimated<sup>11</sup> that this increase in the branching rate constant would be 4.4 and 2.9 per cent, respectively, for H and D.

Another possible source of serious systematic error is that the surface recombination probability,  $\delta$ , for H and D atoms has been assumed equal to unity for a properly prepared and protected magnesium oxide surface at temperatures between 800° and 1000°K. Had  $\delta$  been substantially less than unity, the apparent branching rate constants would have appeared to be appreciably greater in stoichiometric mixtures than with ten per cent oxygen mixtures because of the poorer approach to the diffusion régime at the lower limit pressures of the stoichiometric mixtures. Such was not the case. Indeed, the opposite trend was observed (Table 7) because of a greater probability of O atom removal from the reaction chains at the higher oxygen concentrations. This is strong evidence that a value of  $\delta$  of the order of unity was actually obtained.

Other systematic and random error sources were found to be relatively small (Table 8) and the experimental error in the branching rate constants is summarized by writing the results of fitting the data to an Arrhenius expression as

$$\bar{k}_H = (2.81 \pm 0.67) \times 10^{-10} \exp - (16200 \pm 400)/RT \text{ cm}^3 \text{ sec}^{-1}$$

and

$$\bar{k}_D = (1.47 \pm 0.36) \times 10^{-10} \exp - (14900 \pm 400)/RT \text{ cm}^3 \text{ sec}^{-1}$$

with a normalized standard deviation in the values of  $\bar{k}$  of roughly 3.5 per cent, and an absolute uncertainty no greater than  $\pm 20$  per cent.

It is interesting to note that Fristrom and Westenberg<sup>19</sup> recently correlated existing data between room temperature and 1650°K. They proposed an Arrhenius expression for  $\bar{k}_H$  almost identical to our above experimental expression for the same quantity.

*This work was supported in part by the Office of Scientific Research of the United States Air Force, under Contract No. AF49(638)-32, by the M. W. Kellogg Company, and by the Higgins Fund of Princeton University. It is a pleasure to thank Professor R. H. Wilhelm and Dr D. E. Rosner for encouragement and advice. Also*

acknowledged is Dr M. A. A. Clyne's very helpful critical review of the manuscript.

(Received March 1968)

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