

Kinetic Parameters of the Deuterium+Oxygen Reaction

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Studies have been made at 500°C of the second limit, and of the induction period and maximum rate of the slow reaction, of $D_2 + O_2 + N_2$ mixtures in aged boric-acid-coated vessels. The results enable the velocity constant ratios $k_{11D}/k_{10D}^{1/2}$, $k_{8D}/k_{2D}k_{10D}^{1/2}$, k_{14D}/k_{2D} and k_{15D}/k_{1D} , to be evaluated. From a comparison of the rates and peroxide concentrations in the hydrogen and deuterium systems, a value of k_{7D} can be obtained.



Relatively few studies have been made of the $D_2 + O_2$ reaction. Early studies by Hinshelwood and Williamson¹ were made in silica vessels where the mechanism of the reaction is not established, so that quantitative interpretation is not possible, while the second limit results reported by Frost and Alyea² were made in small diameter KCl-coated vessels under conditions when surface termination is important. Boudart and Kurzius³ have obtained values for the velocity constants of reactions (2) and 2(D) by measuring the first limit of $H_2 + O_2$ and of $D_2 + O_2$ mixtures over a wide range of temperature. Linnett and Selley⁴ have determined the relative efficiencies of a number of molecules in reaction (4D) from studies of the second limit in KCl-coated vessels, while the efficiencies of both H_2O and D_2O in both reactions (4) and (4D) have been obtained⁵ in a similar manner using both KCl-coated and aged boric-acid-coated vessels.

With most types of vessel surface, uncertainty as to surface processes makes precise kinetic interpretation difficult. With boric-acid-coated vessels aged by repeated use, measurements are extremely reproducible because of the absence of surface effects, and determinations of second limits, and of the induction periods and maximum rates in the slow reaction, have enabled the kinetic parameters of the $H_2 + O_2$ reaction to be evaluated.^{6, 7} Similar studies of the $D_2 + O_2$ reaction have been made, both to examine isotope effects in the reactions involved, and to enable

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the $D_2 + O_2$ reaction to be used in an investigation of the reactions involved in hydrocarbon oxidation. The use of the $H_2 + O_2$ reaction in this way has been described,^{8, 9} and the scope can be considerably extended by the use of $D_2 + O_2$ mixtures. As an example, when CH_4 is added to slowly reacting $H_2 + O_2$ mixtures, the results¹⁰ indicate that over 80 % of the CH_3 radicals regenerate CH_4 by reaction with H_2 . With $H_2 + O_2$, the existence of this reaction can only be inferred indirectly, but with $D_2 + O_2$ mixtures, the presence of CH_3D can be shown directly by mass-spectrometric analysis. Evaluation of the kinetic parameters of the $D_2 + O_2$ reaction is a necessary preliminary to such studies.

EXPERIMENTAL

The procedure for the determination of second limits, and of the induction periods and maximum rates of the slow reaction, has been described,^{6, 7} and the same range of mixture compositions has been used. The maximum concentrations of D_2O_2 in the slow reaction were determined as described previously.¹¹ All studies were made in a 52 mm diam. vessel which had been coated with boric acid, and aged until the standard rate¹² for a given $H_2 + O_2 + N_2$ mixture had been reached.

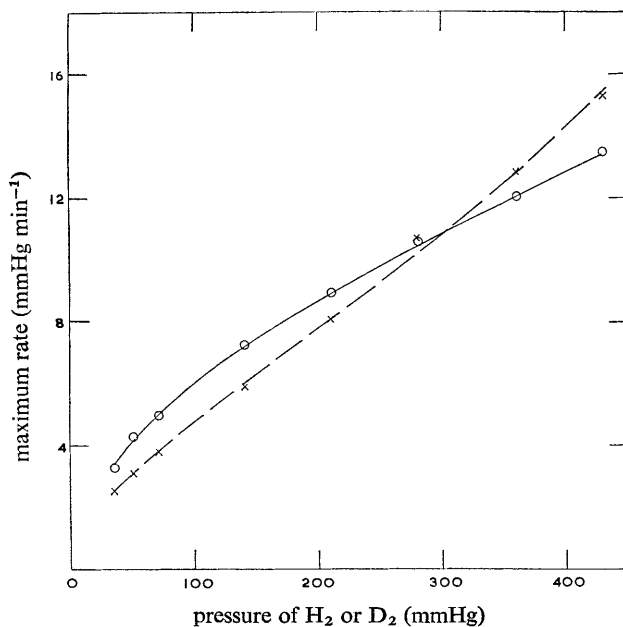
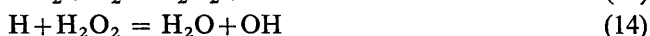


FIG. 1.—Variation of maximum rate with pressure of H_2 or D_2 . Aged boric-acid-coated vessel at $500^\circ C$; $[O_2] = 70$ mmHg. O, varying $[D_2]$; x, varying $[H_2]$.

Fig. 1 shows the variation of maximum rate with mol fraction of H_2 and D_2 . In this figure, the observed maximum rates have been corrected to allow for consumption of reactants (see later). The fact that the curves cross illustrates the misleading conclusions that can be reached from studies over a narrow range of mixture composition. Table 3, given later, shows the experimental second limits over a wide range of composition, and table 4 gives the induction periods and maximum rates for the mixtures studied.

RESULTS

The mechanism of the $H_2 + O_2$ reaction in aged boric-acid-coated vessels involves the following reactions* :



The computer programmes ^{6, 7} which calculate the second limit, the maximum rate, and the induction period, with this mechanism, require the numerical values of seven parameters, viz., k_7 , k_2/k_4 , k_{14}/k_2 , k_{14a}/k_2 , k_{15}/k_1 , k_{11}/k_{10}^\ddagger , and $k_8/k_2k_{10}^\ddagger$. The induction period also requires a primary initiation rate θ , but this does not have to be critically defined.⁶

Previous calculations ⁷ have shown that the second limit is determined predominantly by the parameters k_7 , k_2/k_4 and $k_8/k_2k_{10}^\ddagger$, the induction period by k_7 , k_2/k_4 and k_{11}/k_{10}^\ddagger , and the slow reaction by k_7 , k_2/k_4 , k_{11}/k_{10}^\ddagger , k_{14}/k_2 , and k_{15}/k_1 . It is not realistic to evaluate all seven parameters from second limit, induction period and maximum rate measurements, and for the $H_2 + O_2$ reaction, three of these parameters can be obtained independently. k_7 is obtained from studies ¹³ of the homogeneous decomposition of H_2O_2 , while k_{14a}/k_{14} can be obtained from a study ¹⁴ of the H_2 -sensitised decomposition of H_2O_2 . k_2/k_4 is most conveniently obtained from the second limit in KCl-coated and other salt-coated vessels, allowance being made if necessary for the occurrence both of reaction (11) and of surface termination of H atoms. In addition, since M and M' are given by the equations,

$$M = [H_2] + a[O_2] + b[N_2] + c[H_2O] + d[H_2O_2], \quad (i)$$

$$M' = [H_2] + a'[O_2] + b'[N_2] + c'[H_2O] + d'[H_2O_2], \quad (ii)$$

the coefficients for O_2 , N_2 , H_2O and H_2O_2 , relative to $H_2 = 1$, are required for reactions (4) and (7). The values of c and c' are required since significant amounts of H_2O are formed in the induction period before maximum rate is reached; the values of d and d' are less critical, as only small amounts of H_2O_2 are formed. The coefficients a , b , c can be obtained from second limit measurements in KCl-coated vessels,^{4, 5} and the value obtained for c is in good agreement with that obtained from studies in boric-acid-coated vessels ¹⁵; d cannot be determined experimentally, and it is assumed that $d = c$. The values of a' , b' , c' and d' have been obtained from studies ^{13, 16, 17} of the homogeneous decomposition of H_2O_2 . It is found that $a = a'$, $b = b'$, and the values are consistent with the relative collision frequencies of H_2 , O_2 and N_2 .

Before using the experimental measurements to evaluate the parameters $k_{8D}/k_{2D}k_{10D}^\ddagger$, k_{11D}/k_{10D}^\ddagger , k_{14D}/k_{2D} and k_{15D}/k_{1D} , it is necessary, therefore, to obtain

* The subscript D is used to denote the corresponding reactions with D_2 .

values for the parameters k_{7D} , k_{2D}/k_{4D} , and k_{14aD}/k_{2D} , as well as for the coefficients for the molecules involved in reactions (4) and (7).

COEFFICIENTS $a_D - d_D$

The coefficients a_D and b_D have been determined⁵ by examining the variation of the second limit over a wide range of $D_2 + O_2 + N_2$ mixtures in KCl-coated vessels at 540°C. The temperature of 540°C was chosen so as to minimize the effect of surface destruction of D atoms, and there is no evidence for any variation of the coefficients between 540°C and the temperature of 500°C used in the present studies.

When different molecules are involved as M in reactions (4) and (4D), it is convenient to refer all coefficients to a common collision frequency, which has been chosen to be that for $HO_2 + H_2$; the values of k_4 and k_{4D} obtained in this way are denoted by $k_4(M = H_2)$ and $k_{4D}(M = H_2)$. The experimental coefficient obtained for a molecule such as O_2 in the D_2 system gives the ratio $m_{O_2} = k_{4D}(DO_2 + O_2)/k_{4D}(DO_2 + D_2)$. To convert this coefficient m_{O_2} to the value a_D , expressed on a common collision frequency basis, it is multiplied by the collision frequency ratio $Z(DO_2 + D_2)/Z(DO_2 + H_2)$ and by the ratio $Z(DO_2 + H_2)/Z(HO_2 + H_2)$, which have values of 0.727 and 0.999, respectively. This conversion assumes that the efficiency per collision of D_2 in reaction (4D) is the same as that for H_2 in reaction (4). However, no error is introduced into the subsequent calculations if this assumption is not valid, since the errors introduced in this way into the coefficients $a_D - d_D$, and into the coefficient for D_2 , are exactly compensated by the error introduced into the parameter $k_{2D}/k_{4D}(M = H_2)$. A similar procedure has been adopted for the relative coefficients in reactions (7) and (7D).

The values obtained for the coefficients m_{O_2} and m_{N_2} for O_2 and N_2 relative to $D_2 = 1$ were 0.54 and 0.77, respectively.⁵ Using the collision frequencies given above, $a_D = 0.39$, $b_D = 0.56$. Studies⁵ of the effect of D_2O on the second limit of $D_2 + O_2 + N_2$ mixtures gave $c_D = 6.4$. Since the value of d_D is not critical, it is assumed that $d_D = c_D$.

PARAMETER k_{2D}/k_{4D}

The value of k_{2D}/k_{4D} could have been obtained from second limit measurements at 500°C in KCl-coated vessels, since a mechanism involving reactions (1D)–(4D) gives a limit $M_{2D} = 2k_{2D}/k_{4D}$, if it is assumed that all DO_2 radicals are destroyed at the surface. However, there would undoubtedly be some modification of this simple expression due to surface destruction of D atoms, and with KCl-coated vessels, a detailed study of the first limit is necessary if allowance is to be made for such surface termination.¹⁸ It seemed more accurate, therefore, to calculate the value of k_{2D}/k_{4D} at 500°C from the value of $k_2/k_4 = 18.5$ mmHg ($M = H_2$) at 500°C, the experimental value of the ratio $(k_2/k_4)/(k_{2D}/k_{4D})$ at 540°C, and the experimentally determined³ activation energy difference $(E_2 - E_{2D}) = 1\,300$ cal mol⁻¹. Second limit studies⁵ give the mean value of M_{2D} for the $D_2 + O_2 + N_2$ system as 102.8 mmHg at 540°C with $M = D_2$. Using the collision frequency ratio of 0.726 given earlier, $M_{2D} = 74.7$ ($M = H_2$). The corresponding value M_2 for the $H_2 + O_2 + N_2$ system is 74.4 mmHg ($M = H_2$). Although, for reasons given elsewhere,⁵ the value of M_2 is likely to be a few per cent higher than the value of $2k_2/k_4$ given by the simple mechanism involving reactions (1)–(4), the ratio $(k_2/k_4)/(k_{2D}/k_{4D})$ will be accurately the ratio M_2/M_{2D} of 0.995. The activation energy difference of 1 300 cal mol⁻¹ will decrease the ratio k_2/k_{2D} by a factor of 1.04 in going from 540°C to 500°C, and as it is reasonable to suppose that k_4/k_{4D} will be independent of temperature, the ratio $(k_2/k_4)/(k_{2D}/k_{4D}) = 0.955$ at 500°C, giving $k_{2D}/k_{4D} = 19.4$ ($M = H_2$).

PARAMETER k_{7D} AND THE COEFFICIENTS $a'_D - d'_D$

Because of the difficulty of obtaining pure D_2O_2 , it was not considered feasible to determine k_{7D} by direct studies of the homogeneous decomposition of D_2O_2 , and the following alternative approach was adopted. By making approximations which have been shown to be reasonably justified, the rate expression is obtained¹⁹ as

$$R = d[H_2O]/dt = 2k_7[H_2O_2][M']G \quad (\text{iii})$$

where

$$G = (1 + (1 + \delta)k_2/k_4[M]) / (1 - (1 + \delta)k_2/k_4[M]) \quad (\text{iv})$$

$$\delta = [k_1k_{14}[H_2](1 + \alpha)] / [k_1k_{14}[H_2] + k_4k_{15}[O_2][M](1 - \beta)]$$

$$\alpha = k_4[M]\beta/k_2$$

$$\beta = [k_{11}[H_2]\{1 + k_2(1 + \delta)/k_4[M]\}^\dagger \{1 + k_2(1 - \delta)/k_4[M]\}^\ddagger / (2k_{10}R)]^\ddagger$$

As $k_2/k_4[M] \approx 0.05$, and $\delta \approx 1$, the value of G is close to unity and is almost insensitive to the parameters k_{14}/k_2 , k_{15}/k_1 and k_{11}/k_2^\ddagger that determine δ . If eqn (iii) is written with subscripts H and D for the $H_2 + O_2 + N_2$ and $D_2 + O_2 + N_2$ reactions respectively, then

$$R_H/R_D = (k_{7H}[H_2O_2][M'_H][G_H]) / (k_{7D}[D_2O_2][M'_D][G_D]) \quad (\text{v})$$

The ratio k_7/k_{7D} can be evaluated if the maximum rates R_H and R_D , and the peroxide concentrations at maximum rate are measured. Although previous studies¹¹ have indicated that there is some loss of peroxide (about 10 %) during sampling, such errors will be almost completely eliminated when the ratio $[H_2O_2]/[D_2O_2]$ is involved. G_D can be evaluated to within 0.5 % from approximate values of the deuterium parameters. In evaluating $[M'_D]$, it has been assumed, as found for H_2O_2 , that the coefficients a'_D , b'_D of O_2 and N_2 have the collision frequency values of 0.35, 0.43 relative to $H_2 = 1$, and that the coefficient for D_2 , relative to $H_2 = 1$, is also the

TABLE 1.—EVALUATION OF k_{7D}

mixture composition mmHg			$\frac{d[H_2O]/dt}{d[D_2O]/dt} = \frac{2k_{7H}[H_2O_2][M'_H]G_H}{2k_{7D}[D_2O_2][M'_D]G_D}$				
H_2	O_2	N_2	$\frac{d[H_2O]}{d[D_2O]}$	$\frac{[D_2O_2]}{[H_2O_2]}$	$\frac{M'_D}{M'_H}$	$\frac{G_D}{G_H}$	$\frac{k_{7H}}{k_{7D}}$
430	70	0	1.16	0.99	0.76	1.00	0.87
140	70	290	0.85	1.14	0.88	0.97	0.83
35	70	395	0.85	1.08	0.96	0.94	0.84
140	360	0	0.90	1.03	0.90	0.98	0.82
140	35	325	0.86	1.10	0.88	0.98	0.81
220	280	0	0.96	1.07	0.85	0.99	0.87
35	280	185	0.96	0.92	0.96	0.97	0.82
mean							0.835 ± 0.03

collision frequency value of 0.727. For D_2O , it has been assumed that the ratio of the efficiencies of D_2O in reactions (4D) and (7D) is the ratio of the efficiencies of H_2O in reactions (4) and (7), i.e., $c/c_D = c'/c'_D$. Using the established values of $c = 6.4$, $c_D = 6.4$, $c' = 2.0$, gives $c'_D = 2.0$. The value of d'_D was similarly estimated as 2.6 from $c'/d' = c'_D/d'_D$. In calculating M' (and M'_D), it is necessary to know the amount of H_2O (or D_2O) formed at maximum rate and this quantity also enters, though to a very much smaller extent, into the calculation of G and G_D .

The above treatment is based on a mechanism in which reactions (8) and (14a) are

omitted. As a final refinement once the parameters had been located close to their correct values, the computer programme (III), described later, was used to calculate the rate, and also the concentration of H_2O_2 ; as this programme does not allow for consumption of reactants, this was allowed for by estimating the amount of water formation at maximum rate from the $(\Delta P, \text{time})$ curves. Knowing the value of k_7 and $[M']$, eqn (iii) then enables G to be calculated. Depending on mixture composition, the ratios $G_{\text{H}}/G_{\text{D}}$ obtained in this way are 0.5-4 % greater than the values calculated from the approximate equation (iv). These values of G were then used in eqn (v) to obtain $k_7/k_{7\text{D}}$.

Table 1 shows that the results for a wide range of mixture composition give remarkably constant values of the ratio $k_7/k_{7\text{D}}$, with an r.m.s. deviation of 2.9 %. This constancy provides confirmation of the values used for the relative coefficients of H_2 , O_2 , N_2 and D_2O in reaction (7); in particular, the agreement of mixtures 1, 4 and 6 which contain no N_2 , with mixtures 3 and 5 which contain the highest N_2 content, indicates that the value of $b_{\text{D}}' = b' = 0.43$ is correct. If b_{D}' is taken as 0.56, the value obtained for b_{D} , and $a_{\text{D}}' = a_{\text{D}} = 0.39$, the agreement is much less satisfactory, the r.m.s. deviation being 7.2 %; moreover, the value from mixtures 1, 4 and 6 is now nearly 15 % higher than the value from mixtures 3 and 5. From the value $k_7 = 0.0481 \text{ (mmHg min)}^{-1}$, $k_{7\text{D}} = 0.0574 \text{ (mmHg min)}^{-1}$, or $46.2 \text{ l mol}^{-1} \text{ s}^{-1}$ at 500°C .* In view of the consistency of the results, and the estimated accuracy of $G_{\text{H}}/G_{\text{D}}$ (within 0.5 %), this value is considered accurate within $\pm 5 \%$.

PARAMETER $k_{14\text{aD}}/k_{14\text{D}}$

Since studies of the $\text{H}_2 + \text{H}_2\text{O}_2$ system¹⁴ show that $k_{14\text{a}}/k_{14} = 0.159$ at 500°C , reaction (14aD) only plays a relatively minor part, and accurate evaluation of $k_{14\text{aD}}/k_{14}$ is not critical. The basis of this evaluation is discussed later.

OPTIMIZATION OF SECOND LIMITS, INDUCTION PERIODS AND REACTION RATES

With the parameters $k_{7\text{D}}$, $k_{2\text{D}}/k_{4\text{D}}$ and $k_{14\text{aD}}/k_{14\text{D}}$ established, the procedure adopted^{6, 7} for the $\text{H}_2 + \text{O}_2 + \text{N}_2$ system can be used, in which second limits give $k_{8\text{D}}/k_{2\text{D}}k_{10\text{D}}^{\frac{1}{2}}$, induction periods give $k_{11\text{D}}/k_{10\text{D}}^{\frac{1}{2}}$, and rate measurements give $k_{14\text{D}}/k_{2\text{D}}$ and $k_{15\text{D}}/k_{1\text{D}}$.

The second limit computer programme (V)† predicts the second limit for each mixture examined, and calculates the r.m.s. deviation between observed and calculated values. By coupling this programme to an optimization programme, the value of $k_{8\text{D}}/k_{2\text{D}}k_{10\text{D}}^{\frac{1}{2}}$ giving minimum r.m.s. deviation can be obtained.

The induction period programme (II)‡, though accurate to within 0.2 %, cannot be used with an optimization programme, as the calculated induction periods are not a uniformly continuous function of the kinetic parameters because of the procedure adopted. A series of values of $k_{11\text{D}}/k_{10\text{D}}^{\frac{1}{2}}$ is therefore taken, and the optimum value giving minimum r.m.s. deviation is determined by inspection. For the induction period programme, it is necessary to specify the value of the primary initiation rate θ . Studies with the $\text{H}_2 + \text{O}_2 + \text{N}_2$ system have shown first that $\theta_{\text{H}} \approx 0.0001 \text{ mmHg min}^{-1}$

* Both these values are for $M' = \text{H}_2$, and the value for $k_{7\text{D}}$ is dependent on the assumption that the efficiency of D_2 relative to H_2 in reaction (7D) is the collision frequency ratio of 0.727. The value $k_{7\text{D}} = 0.0417 \text{ (mmHg min)}^{-1}$ or $33.6 \text{ l mol}^{-1} \text{ s}^{-1}$ with $M' = \text{D}_2$ is the directly determined experimental quantity which is not subject to this assumption.

† Programmes referred to are described in ref. (6) and (7).

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at 500°C and 500 mmHg, and secondly that, in this range of temperature and pressure, the precise value of θ_H is not critical. Similar studies with D_2 , involving examination of the very early stages of reaction, showed that $\theta_D \approx 0.0001$.

The maximum rate programme (IV), which allows for reactant consumption and product formation, is also not suitable for optimization procedures. With two unknown parameters k_{14D}/k_{2D} and k_{15D}/k_{1D} to evaluate, however, an optimization procedure is desirable and the method used for the $H_2 + O_2 + N_2$ system was adopted. A second programme (III) calculated the maximum rate on the assumption that the equilibrium peroxide concentration was reached without loss of reactants or formation of water. The difference between the rates for a particular mixture given by programmes (III) and (IV) gives a percentage correction, which can then be applied to the experimental rates so as to give the rates that would have been obtained in the absence of reactant consumption. These "corrected" rates were then used in programme (III), coupled to an optimization programme, to obtain the values of k_{14D}/k_{2D} , k_{15D}/k_{1D} , giving minimum r.m.s. deviation between the observed "corrected" rates, and the calculated rates.

Since all four parameters $k_{8D}/k_{2D}k_{10D}^\ddagger$, k_{11D}/k_{10D}^\ddagger , k_{14D}/k_{2D} , k_{15D}/k_{1D} , are initially unknown, a re-iterative sequence using all four programmes is necessary. However, since the second limits and induction periods are not very dependent on k_{14D}/k_{2D} , and k_{15D}/k_{1D} , convergence of values is quickly reached.

TABLE 2.—COMPARISON OF VELOCITY CONSTANT RATIOS FOR H_2 AND D_2 REACTIONS AT 500°C

velocity constant ratio	$H_2 + O_2$	$D_2 + O_2$
k_2/k_4 mmHg	18.5 (M = H_2)	26.5 (M = D_2)
k_7 mmHg $^{-1}$ min $^{-1}$	0.0481 (M = H_2)	0.0417 (M = D_2)
k_{14}/k_2	265	167
k_{15}/k_1	4.7	5.4
k_{11}/k_{10}^\ddagger (mmHg min) $^{-\ddagger}$	0.00119	0.00051
$k_8/k_2k_{10}^\ddagger$ (mmHg min) ‡	10.4	13.2

TABLE 3.—OBSERVED AND CALCULATED SECOND LIMITS FOR $D_2 + O_2 + N_2$ MIXTURES

Aged boric-acid-coated vessel, 51 mm diam., 500°C

D_2	mol fraction		limit mmHg	
	O_2	N_2	obs.	calc.
0.28	0.72	0.00	98.0	97.7
0.28	0.56	0.16	97.0	97.0
0.28	0.28	0.44	99.5	100.8
0.28	0.14	0.58	108.5	109.8
0.28	0.10	0.62	114.5	115.7
0.28	0.07	0.65	124.5	123.1
0.28	0.035	0.685	142.5	141.2
0.28	0.0175	0.7025	167.5	165.6
r.m.s. deviation			1.2 %	

The best values for the parameters $k_{8D}/k_{2D}k_{10D}^\ddagger$, k_{11D}/k_{10D}^\ddagger , k_{14D}/k_{2D} and k_{15D}/k_{1D} , are shown in table 2, which also compares all the parameters for the hydrogen and deuterium reactions. Table 3 shows the agreement between the limits calculated with these parameters, and the experimental value, the r.m.s deviation being only 1.2 % for a very wide range of mol fractions. Table 4 shows the agreement of the

observed and calculated maximum rates,* the r.m.s. deviations being 5.5 and 7.4 % respectively. These three r.m.s. deviations are very similar to the values of 1.6, 4.0 and 4.8 % obtained with the $\text{H}_2 + \text{O}_2 + \text{N}_2$ system. The slightly high r.m.s. deviation for the rates arises largely from four mixtures, where because of the high rate, some self-heating of the reaction mixture may be occurring. Some support comes from the fact that for these mixtures (no. 1, 2, 3 and 8 in table 4), the observed rates are significantly higher than the calculated value. Omission of these four mixtures reduces the r.m.s. deviation to 4.0 %, the optimum values of $k_{14\text{D}}/k_{2\text{D}}$ and $k_{15\text{D}}/k_{1\text{D}}$ being 169 and 5.7 respectively. The small change from the values $k_{14\text{D}}/k_{2\text{D}} = 167$, $k_{15\text{D}}/k_{1\text{D}} = 5.4$ for all eighteen mixtures indicates the reliability of the values obtained for $k_{14\text{D}}/k_{2\text{D}}$ and $k_{15\text{D}}/k_{1\text{D}}$.

TABLE 4.—OBSERVED AND CALCULATED INDUCTION PERIODS AND MAXIMUM RATES FOR $\text{D}_2 + \text{O}_2 + \text{N}_2$ MIXTURES

Aged boric-acid-coated vessel, 51 mm diam., 500°C; total pressure 500 mmHg

mol fraction			induction period (s)		max. rate † (mmHg min ⁻¹)	
D ₂	O ₂	N ₂	obs.	calc.	obs. †	calc.
140	360	0	104.5	95.8	15.39	13.28
140	280	80	101.8	95.6	13.73	12.33
140	210	150	100.0	94.5	12.57	11.20
140	140	220	95.5	91.5	10.28	9.45
140	70	290	82.5	82.9	6.51	6.46
140	50	310	73.8	77.8	5.14	5.19
140	35	325	63.6	71.9	3.89	4.05
220	280	0	87.8	79.5	21.23	17.83
70	280	150	116.8	119.8	7.27	7.08
50	280	170	130.7	130.6	5.03	5.37
35	280	185	141.5	140.8	3.66	3.97
430	70	0	41.9	42.2	12.84	13.51
360	70	70	48.8	47.7	11.39	11.81
280	70	150	56.5	56.2	9.93	9.89
210	70	220	64.6	66.8	8.24	8.22
70	70	360	108.5	111.5	4.27	4.36
50	70	380	120.5	124.7	3.48	3.57
35	70	395	126.0	137.4	2.62	2.84
r.m.s. deviation			5.6		7.4	

† expt. value, corrected only for dead volume.

The cross-over of the curves in fig. 1 can be attributed to the fact that at high mol fractions of H_2 (or D_2), the dominant factors are the higher coefficient of H_2 in reaction (7) compared to that for D_2 in (7D), and the higher value of k_{11} compared with $k_{11\text{D}}$. At low mol fractions of H_2 (or D_2), the important factors are the higher value of $k_{7\text{D}}$ compared to k_7 (since M' is now largely determined by the $\text{O}_2 + \text{N}_2$ content), and the lower value of $k_{14\text{D}}/k_{2\text{D}}$ compared to k_{14}/k_2 , which results in a higher stationary concentration of peroxide in the $\text{D}_2 + \text{O}_2$ reaction.

* The table gives the experimentally measured rates, corrected only for dead volume. The calculated rates have been obtained using programme (IV) which allows for consumption of reactants. These rates cannot, therefore, be compared with the rates given for the $\text{H}_2 + \text{O}_2$ system in ref. (7), which have been corrected for reactant consumption as described earlier.

DISCUSSION

To discuss isotope effects, it is necessary to know the zero-point energies, and hence the vibrational frequencies of HO_2 , H_2O_2 , DO_2 and D_2O_2 . Various values have been quoted²⁰⁻²⁴ for H_2O_2 and D_2O_2 , and the most recent²⁴ are given below (in cm^{-1}). The values obtained from the fundamental bands corresponding to ω_1 and ω_5 have been corrected on the assumption that the value for the anharmonicity factor for these vibrations is the same as the relatively high value found for the O—H vibration in water.^{25, 26} No corrections for anharmonicity have been applied to the other vibrations.

	ω_1	ω_2	ω_3	ω_4	ω_5
H_2O_2	3774	1380	880	3788	1266
D_2O_2	2750	1040	880	2765	947

The torsional vibration ω_4 is less well established. Earlier estimates²² of *ca.* 575 cm^{-1} for H_2O_2 are now considered to result from overtones, and values of 230²⁷ and 314²⁸ cm^{-1} have been given. A mean value of 280 cm^{-1} is taken, with a corresponding estimate of 200 cm^{-1} for D_2O_2 .

The only experimental determination of the HO_2 vibrational frequencies is for HO_2 radicals in an argon matrix²⁹ at 4 K. In view of uncertainties both in interpretation and in the anharmonicity correction, it is probably at least as accurate to use estimates for the O—H stretching frequency and for the bending frequency, based on the corresponding frequencies for H_2O_2 and D_2O_2 , of 3780 and 1330 for HO_2 , and 2760 and 990 for DO_2 . The value for the O—O stretching frequency is not critical in this discussion, and the value of 1230 cm^{-1} , estimated by Walsh³⁰ as the mean of the O—O frequencies in O_2 and in H_2O_2 will be used.

VELOCITY CONSTANT k_7

The results obtained by sampling the reaction mixture for H_2O_2 or D_2O_2 suggest that $k_{7D}/k_7 = 1.19 \pm 0.04$. There are three possible explanations for this result. (a) The zero-point energy is greater for the activated state than for the reactants, so that the consequent increase in activation energy due to zero-point energy is greater for H_2O_2 than for D_2O_2 . Walsh³¹ gives reasons for believing that the O—H bond is stronger in the OH radical than in H_2O_2 , and this view appeared to be supported by the original value of *ca.* 3550 and 2630 cm^{-1} given²² for the O—H and O—D vibrational frequencies in H_2O_2 and D_2O_2 respectively, as compared to the values of 3735 and 2721 cm^{-1} , respectively, given for the OH and OD radicals. These values would give a difference of 520 $cal\ mol^{-1}$ between the zero-point energy of the two O—H vibrations in H_2O_2 and in two OH radicals, compared to the corresponding value of 270 $cal\ mol^{-1}$ for the deuterium compounds, but it is unlikely that the whole of this difference would apply in going from reactant to transition state. An activation energy difference of 270 $cal\ mol^{-1}$ is required to account for the above ratio of k_{7D}/k_7 . However, Redington, Olson and Cross²⁴ give reasons, based on arguments by Bent,³² for supposing that the O—H bond is stronger in H_2O_2 than in the OH radical, and this is supported by the higher value of the corrected vibration frequency in H_2O_2 compared to the OH radical. It is difficult to see why the zero-point energy of the other vibrations of H_2O_2 should increase in the transition state.

(b) The pre-exponential factor could be greater for reaction (7D) than for (7). The ratio $A_{7D}/A_7 = (P_D^*/P_D)/(P_H^*/P_H)$, where P^* , P are the partition functions for activated state and reactant respectively. The two moments of inertia I_B and I_C

are very similar for H_2O_2 (19.29, 20.11 a.m.u. \AA^2 , respectively) and D_2O_2 (21.28, 22.80 respectively), so that the effect of any changes in these values in the transition state would be expected to cancel. The third moment of inertia I_A changes from 1.67 for H_2O_2 to 3.11 for D_2O_2 . However, there seems no reason to expect any difference in the dimensions of the transition state in the two cases, so that the changes should cancel even in this case. All the vibrational partition functions are close to unity, and thus cancel, except for the vibration associated with ω_4 . As the partition function due to this vibration will be significantly different from unity, it is possible that the ratio of the partition functions in the transition state and in the reactant is higher for D_2O_2 than for H_2O_2 .

(c) The conversion of the experimentally determined value $k_{7\text{D}} = 0.0417 \text{ (mmHg min)}^{-1}$ ($M = \text{D}_2$) to the value $k_{7\text{D}} = 0.0574$ ($M = \text{H}_2$), given earlier, is based on the assumption that the efficiency per collision of H_2 in reaction (7) is the same as that for D_2 in reaction (7D). There seems no reason to doubt this assumption since the relative efficiencies of H_2 , O_2 and N_2 in reaction (7) are the ratio of the collision frequencies, and the same is true for D_2 , O_2 and N_2 in reaction (7D); it may, however, not be valid.

In view of the absence of a clear explanation for the value obtained for the ratio $k_{7\text{D}}/k_7$, a direct study of the decomposition of D_2O_2 is clearly desirable so as to confirm the present value.

RATIO k_2/k_4

The ratio $(k_2/k_4)/(k_{2\text{D}}/k_{4\text{D}}) = 0.955$ is obtained from second limit studies⁶ on the assumption that the relative efficiency of D_2 and H_2 in reaction (4D) is the collision frequency ratio of 0.727. From studies of the first limit over the temperature range 800–1000 K, Boudart and Kurzius³ obtain the expressions $k_2 = 1.7 \times 10^{11} \exp(-16,200/RT)$, $k_{2\text{D}} = 8.85 \times 10^{10} \exp(-14,900/RT)$, in $\text{l mol}^{-1} \text{s}^{-1}$ and cal mol^{-1} . This gives the ratio $k_2/k_{2\text{D}} = 0.82$ at 500°C , so that $k_4/k_{4\text{D}} = 0.86$. This value is consistent with the ratios of 0.7 ± 0.2 , 0.9 ± 0.2 and 0.9 ± 0.2 for $M = \text{Ar}$ at 293, 244 and 225 K respectively, and of 0.6 ± 0.2 for $M = \text{He}$ at 293 K obtained by Clyne and Thrush.³³

RATIO $k_{11}/k_{11\text{D}}$

Induction period studies give the parameters $k_{11}/k_{10}^\ddagger = 0.00119$, and $k_{11\text{D}}/k_{10\text{D}}^\ddagger = 0.00051$ in $(\text{mmHg min})^{-\frac{1}{2}}$ units at 500°C . The value of $1.8 \times 10^9 \text{ l mol}^{-1} \text{s}^{-1}$ suggested³⁴ for k_{10} at 25°C indicates little or no activation energy; moreover, even if reaction (10) has a small activation energy, it is unlikely that there will be much change in the OH vibrational frequency (which makes the main contribution to the zero-point energy) between the HO_2 radicals and the transition state. It will, therefore, be assumed that $k_{10} = k_{10\text{D}}$, so that $k_{11}/k_{11\text{D}} = 2.33$. On the assumption that the pre-exponential factors are in the ratio of the collision frequencies, 1.38, the activation energy difference $(E_{11\text{D}} - E_{11}) = 800 \text{ cal mol}^{-1}$.

The difference in zero-point energy between H_2 and D_2 is $1800 \text{ cal mol}^{-1}$, while the difference in zero-point energy of the HO_2 and DO_2 radicals due to the difference in OH and OD frequencies given earlier is $1460 \text{ cal mol}^{-1}$, and the difference of the bending frequencies (1330 and 990 cm^{-1}) adds another 475 cal mol^{-1} . The difference in the total zero-point energy of the reactants is thus $3735 \text{ cal mol}^{-1}$, so that the difference of zero-point energies in the transition state must be $2935 \text{ cal mol}^{-1}$. This difference will arise mainly from the effect of isotopic change on the "permanent" O—H vibration and on the transitional H...H and H...O vibrations, though there

may be small contributions from other vibrations in the transition state, and possibly also from tunnelling. This reaction thus provides yet another example where the main primary isotope effect due to the breaking of the H—H bond has been significantly reduced by the considerable zero-point energy of the transition state. A similar reduction is found in the reaction of C_2H_5 radicals with H_2 and D_2 , and other examples are quoted in ref. (35).

RATIO k_{14}/k_{14D}

From the values $k_{14}/k_2 = 265$, $k_{14D}/k_{2D} = 167$, and $k_2/k_{2D} = 0.82$, $k_{14}/k_{14D} = 1.30$. Although the difference between this ratio and the value of $A_{14}/A_{14D} = 1.40$, given by collision theory, is probably within experimental error, the results do indicate either that $E_{14D} = E_{14}$, or that E_{14D} is slightly less than E_{14} , the latter situation implying that the effect of isotopic substitution on zero-point energy is greater for the transition state than for the reactants. This is to be expected, since the discussion of reaction (7) has suggested that the difference in zero-point energy between reactants and transition state is likely to be the same for H_2O_2 and for D_2O_2 , while the newly-formed O...H link of the transition state will have greater zero-point energy than the O...D link.

RATIO k_{14aD}/k_{2D}

As no studies have been made of the $D_2O_2 + D_2$ system, it is necessary to assume a value for k_{14aD}/k_{2D} , although this value is not critical. The ratio $(k_{14aD}/k_{14D})/(k_{14a}/k_{14}) = (A_{14}A_{14aD})/(A_{14D}A_{14a}) \exp([E_{14D} - E_{14}] + [E_{14a} - E_{14aD}])/RT$. It is reasonable to suppose that $A_{14}A_{14aD}/A_{14D}A_{14a}$ is close to unity, and $(E_{14a} - E_{14})$ has been shown above to be close to zero. The difference of the zero-point energy of reactants in reactions (14a) and (14aD) is the difference of the zero-point energies between H_2O_2 and D_2O_2 . From the frequencies $\omega_1 - \omega_6$ given earlier, this difference is obtained as $4040 \text{ cal mol}^{-1}$. Since the difference in zero-point energy of the transition state has been shown to be $2935 \text{ cal mol}^{-1}$, $(E_{14a} - E_{14aD}) = -1105 \text{ cal mol}^{-1}$. Thus, $(k_{14aD}/k_{14D})/(k_{14a}/k_{14}) = \exp(-1105/RT) = 0.49$. Since $k_{14a}/k_{14} = 0.16$, $k_{14aD}/k_{14D} = 0.08$. As $k_{14D}/k_{2D} = 167$, $k_{14aD}/k_{2D} = 13$.

RATIO k_8/k_{8D}

From the values $k_8/k_2k_{10}^{\frac{1}{2}} = 10.4$, $k_{8D}/k_{2D}k_{10D}^{\frac{1}{2}} = 13.2$, $k_2/k_{2D} = 0.82$, and assuming $k_{10} = k_{10D}$, $k_8/k_{8D} = 0.65$. If it is assumed that the pre-exponential factors are in the collision frequency ratio of 1.395, then $(E_8 - E_{8D}) = 1170 \text{ cal mol}^{-1}$. The difference in zero-point energy of the reactants is the difference of $1945 \text{ cal mol}^{-1}$ between HO_2 and DO_2 . If the transition state had the structure of H_2O_2 , the maximum difference in zero-point energy on changing to the deuterium reaction would be $4040 \text{ cal mol}^{-1}$, so that the maximum difference in activation energy is $2100 \text{ cal mol}^{-1}$. The observed value of $1170 \text{ cal mol}^{-1}$ is consistent with a transition state that has moved only partially towards the peroxide molecule.

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