Efficiency of Water as a Third Body in the Reaction $H+O_2+M$

By R. R. Baldwin and C. T. Brooks

Dept. of Chemistry, The University, Hull

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The relative efficiency of water ($m_{H_2O} = k_{4,H_2O}/k_{4,H_2}$) as a third body in the reaction $H+O_2+M = HO_2+M$ has been studied by examining the effect of water on the second limit of the H_2+O_2 reaction in KCl-coated and aged boric-acid-coated vessels. m_{H_2O} is independent of vessel surface, temperature (460-540°C) and water vapour concentration (0·4-4 %) over a wide range of mixture compositions with H_2/O_2 ratios varying from 5 : 1 to 1 : 8. The mean value of 6·4±0·7 obtained from 126 observations is substantially lower than the value quoted by Lewis and von Elbe (14·3) and by Hinshelwood and Willbourn (8-11), but is supported by several independent studies.

The reaction $H+O_2+M = HO_2+M$ is important in many gaseous oxidation reactions. It plays a particularly vital role as a chain termination process at the second limit of the H_2+O_2 reaction. In salt-coated vessels (e.g., KCl), where surface destruction of HO_2 predominates over reaction (11), the limit is determined by reactions* (1)-(5*a*):

$$OH+H_2 = H_2O+H \tag{1}$$

$$H+O_2 = OH+O \tag{2}$$

$$O+H_2 = OH+H \tag{3}$$

$$H+O_2+M = HO_2+M \tag{4}$$

$$HO_2 \overset{\text{surface}}{=} \text{destruction} \tag{5a}$$

$$HO_2+H_2 = H_2O_2+H \tag{11}$$

These reactions give the limit expression,

$$mP_2 = 2k_2/k_4, \tag{i}$$

where m is a composite third body coefficient for the mixture relative to H_2 as unity, and k_4 is the velocity constant when $M = H_2$. m is given by

$$m = x+m_1y+m_2z, \tag{ii}$$

where x, y, z, are the mole fractions of H_2, O_2 and inert gas, and m_1, m_2, are the relative coefficients for O_2 and inert gas.

For diatomic gases, the experimental values of m from second limit studies are consistent with the calculated ratio of collision frequencies. Thus, for N_2 and O_2, the experimental values[1] are 0·43, 0·35 relative to H_2 while the calculated collision-frequency ratios are 0·46, 0·42. For the monatomic gases He and A, the values[1] of m, 0·36, 0·20 are less than the calculated values of 0·60, 0·38, respectively, although the ratio is close to the calculated ratio. For the triatomic gases CO_2 and N_2O, the experimental values of m, 1·47[1] and 1·37[2] respectively, are significantly higher than the calculated value of 0·43; values of 8-11[3] and 14·3[1] have been reported for H_2O, as compared to the calculated value of 0·6-0·9. A high value for H_2O accounts for self-inhibition effects which occur at the junction of the second and third limits

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* The reaction numbers are those used in previous papers.

and for the suppression of explosion that occurs if slow withdrawal rates are used in clean and boric-acid-coated vessels.[4, 5] Recently, an accurate knowledge of m_{H_2O} has become essential in interpreting the effect of H_2O on the slow reaction and second limit of the $CO+O_2$ reaction.[6] At the same time, a re-examination was made of some measurements of the inhibiting effect of H_2O on the H_2+O_2 reaction in clean Pyrex vessels at 510°C, which had been made to assist interpretation of the effect of withdrawal rate on the second limit,[4] and which gave a value of approx. 6 for m_{H_2O}. In view of this wide range of values (6-14), a systematic investigation over a wide range of temperature and mixture composition seemed desirable.

Care is needed in selecting the vessel surface and diameter suitable for studying the inhibiting effect of water. The autocatalytic nature of the slow reaction in clean Pyrex vessels has been attributed [1] to a reduction in the surface destruction of HO_2 as water is adsorbed on the surface; if water is added, therefore, it is possible that reaction (11) may play some part even at the second limit, and thus reduce the apparent inhibiting effect. Moreover, the limit in clean Pyrex vessels normally lies between that obtained in KCl-coated vessels and that obtained in aged boric-acid-coated vessels, where a mechanism with quadratic branching operates. This uncertainty in mechanism makes interpretation of inhibition effects less certain. With salt-coated vessels, difficulty arises because the simple mechanism given above is complicated by at least two factors. At the higher temperatures reaction (11) becomes important, while at the lower temperatures, where explosion pressures are lower, surface termination of H atoms becomes important. Both these factors operate to raise the apparent value of m_{H_2O}. With aged boric-acid-coated vessels, previous studies [7, 8] have suggested that the surface plays no significant part either in the slow reaction or at the second limit. Moreover, tests [7] have shown that the surface properties are not affected by addition of water vapour. Thus, this surface is highly suitable for studying the inhibiting action of water although, as shown later, interpretation of the results becomes more complicated than when the simple mechanism operates. The rapid reaction above the limit, however, prevents accurate determination of the second limit at temperatures above about 520°C. It was decided, therefore, to examine the inhibiting effect of water in aged boric-acid-coated vessels at 460° and 500°C, and in KCl-coated vessels at 500° and 540°C. A 51-mm diam. vessel was used to minimize the effects of surface destruction of H atoms, and a wide range of mixture composition was examined.

EXPERIMENTAL

The apparatus and experimental procedure have been described earlier.[9] Cylinder O_2, H_2 and O_2-free N_2 were purified as described elsewhere.[9] Second limits were determined by the withdrawal method. One gas, normally H_2, was admitted to the evacuated reaction vessel at a pressure above the second limit and the remainder of the pre-mixed gases added from the mixing bulb; variations in this procedure did not affect the limit. After allowing 15 sec for mixing in the reaction vessel, the pressure was rapidly reduced to the vicinity of the limit, and the withdrawal then controlled through a pre-selected capillary tube. In the KCl-coated vessels, reasonably rapid withdrawal rates were used, though tests showed that the limit, both in the presence and absence of water, was independent of withdrawal rate over a wide range. In the aged boric-acid-coated vessel at 500°C, fairly rapid withdrawal rates were used to minimize any possible reaction during the withdrawal period; at 460°, fast withdrawal rates give a lower limit, and slower rates, which from experience gave correct limits,[10] were used. Ordinary distilled water was used, as well as a sample which had been passed through an ion-exchange column, its conductivity being $<10^{-5}$ mhos. The water was stored in a glass trap attached to the vacuum line, and was thoroughly degassed before use. No difference in inhibition was found between the two samples, nor as each sample was evaporated (to 25 % of its original volume). To avoid errors due to gas law deviations, the maximum H_2O measured was restricted to two-thirds of the saturation vapour pressure. The absence of errors due to such deviations, or due to adsorption of H_2O, is indicated by the consistent results obtained irrespective of whether the H_2O was introduced into the reaction vessel alone, the mixing bulb alone, or into both reaction vessel and mixing bulb. Tests gave no evidence for either instantaneous or slow adsorption of H_2O on the vessel surface, either in KCl-coated or in aged boric-acid-coated vessels. The former possibility was tested by expanding a measured pressure of H_2O into the evacuated reaction vessel, and comparing the resultant pressure with that obtained when H_2 or N_2 was used. The latter possibility was tested by admitting H_2O to the evacuated vessel and observing the pressure on a Bourdon gauge sensitive to 0·05 mm Hg.

Tests were made with a wide variety of mixture compositions. For each series, the mole fractions of $H_2(x)$ and $O_2(y)$ were kept constant, and the mole fraction of H_2O varied over the range 0·004–0·040 by interchanging with N_2.

RESULTS

Fig. 1 shows the variation of second limit with mole fraction of H_2O for some of the mixtures studied in the KCl-coated vessel at 500°C. The experimental limits were corrected for surface termination of H atoms by the procedure described elsewhere;[11] such corrections were small, the maximum value being 2·8 mm Hg at 500°C ($x = 0{\cdot}24$, $y = 0{\cdot}07$) and 2·0 mm Hg at 540°C ($x = 0{\cdot}24$, $y = 0{\cdot}07$). Eqn. (i) may be written in the form:

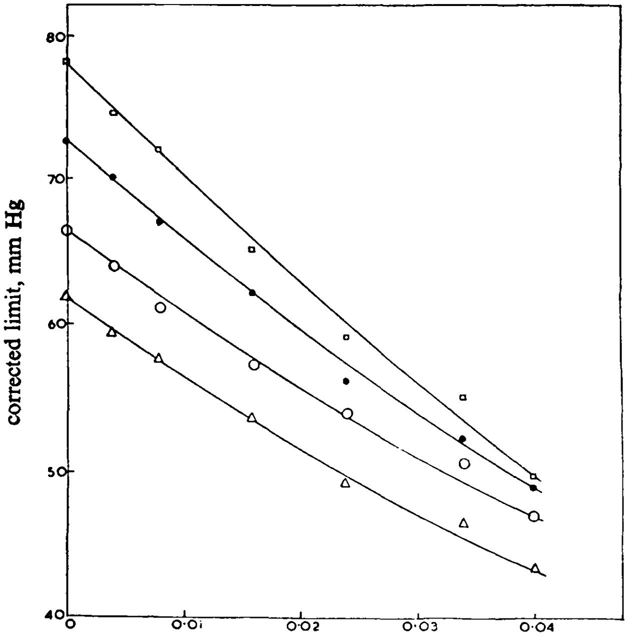

FIG. 1.—Effect of water vapour on second limit of H_2+O_2 mixtures:

□ $x = 0{\cdot}14, y = 0{\cdot}14$; ● $x = 0{\cdot}24, y = 0{\cdot}56$;
○ $x = 0{\cdot}24, y = 0{\cdot}28$; △ $x = 0{\cdot}24, y = 0{\cdot}07$.

$$m_{H_2O}P_{H_2O}+A = 2k_2/k_4, \qquad \text{(iii)}$$

where

$$A = P_{H_2}+m_1P_{O_2}+m_2P_{N_2}. \qquad \text{(iv)}$$

A plot of A against P_{H_2O} should thus give a straight line of gradient m_{H_2O}, and if m_{H_2O} is independent of mixture composition the results for different mixtures should fall on a common line. In fact, however, the value of mP_2 for the uninhibited limit varies slightly with mixture composition (from 76-80 mm Hg (M = H_2) at 540°C, from 35-38 at 500°C). This may be attributed to slight contributions from the regeneration reaction (11), or from quadratic branching, or from both. To avoid the confusion caused by lines of different intercept, it is more convenient to plot $(mP_2 - A)$ against P_{H_2O}, where mP_2 refers to the uninhibited value for each mixture composition. These plots at 540° and 500°C are shown in fig. 2. The best lines correspond to values for m_{H_2O} of 6·56 (540°C) and 6·61 (500°C), with r.m.s. deviation of 0·39 in each case. No significant variation with mixture composition is apparent.

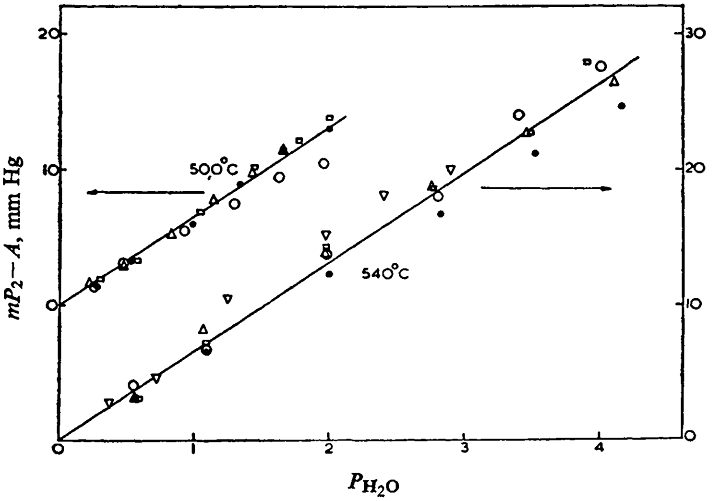

FIG. 2.—Inhibition of H_2+O_2 reaction by H_2O in KCl-coated vessel:

○ $x = 0·24, y = 0·28$; ● $x = 0·24, y = 0·56$;
△ $x = 0·24, y = 0·07$; ▽ $x = 0·68, y = 0·14$;
□ $x = 0·14, y = 0·14$; ■ $x = 0·07, y = 0·56$;
▼ $x = 0·36, y = 0·56$.

In the aged boric-acid-coated vessel, reaction (5*a*) is absent and a more complex mechanism operates,[8] involving the additional reactions:

$$2HO_2 = H_2O_2 + O_2 \tag{10}$$
$$H_2O_2 + M' = 2OH + M' \tag{7}$$
$$H + HO_2 = 2OH \tag{8}$$
$$H + H_2O_2 = H_2O + OH \tag{14}$$
$$OH + H_2O_2 = H_2O + HO_2 \tag{15}$$

The second limit is given by the relation:

$$mP_2 = K_1 + K_2 B([M][M']/[O_2])^{\frac{1}{3}}. \tag{v}$$

If $k_{15} = 0$, and if a simplified solution of a cubic equation is justified,[8] $K_1 = 2k_2/k_4$, $K_2 = 1$, and $B = (27\,k_2k_7k_8^2/4k_{10}k_{14}k_4^2)^{\frac{1}{3}}$. Since neither of these assumptions is strictly true, K_1, K_2 are modified[8] to

$$K_1 = k_2(1+\delta)/k_4, \tag{vi}$$
$$K_2 = K'\delta^{\frac{1}{3}}\{1 + k_2(1-\delta)/k_4[M]\}^{\frac{1}{3}}, \tag{vii}$$

where

$$\delta = \frac{k_{14}k_1[H_2]}{k_{14}k_1[H_2]+k_{15}(k_4[O_2][M]+k_2[O_2]+k_8[HO_2])},$$

$$[HO_2] = 2\phi/3k_8,$$

$$\phi = k_4[O_2][M]-k_2[O_2](1+\delta),$$

$$K' = \left[\frac{(1-\phi/9k_8b)^2}{(1+3ak_8/\phi^2)(1+a/3b\phi)}\right]^{\frac{1}{2}},$$

$$a = k_2k_7k_8[O_2][M]\delta/k_{10}k_{14},$$

$$b = \{k_4[O_2][M]+k_2[O_2](1-\delta)\}/k_8.$$

The term δ allows for the occurrence of reaction (15), while K' is a correction for the approximate solution of the cubic equation.[8] Over the range of mixture compositions investigated, δ lies between 0·7 and 1·0 while K' lies between 0·85 and 1·0. These two factors can be evaluated knowing the constants k_2/k_4, $k_{14}k_1/k_{15}k_4$ and B, which can be obtained from second limit and slow reaction studies. The values taken for these three constants were 18·5,[8] and 1070,[12] and 3·39,[8] respectively at 500°C, and 7·7, 700 and 2·36 respectively, at 460°C,[12] in mm Hg. The calculations are not particularly sensitive to reasonable errors in these constants. The relative values for m' in reaction (7) for O_2 and N_2 have been shown [13, 14] to be similar to those for reaction (4), and it is reasonable to assume that this applies to H_2 also; some evidence is available to support this.[15] The value of m' for H_2O has been determined relative to N_2 by a number of workers [13, 14, 16] and a value of 2·6 relative to H_2 was taken.

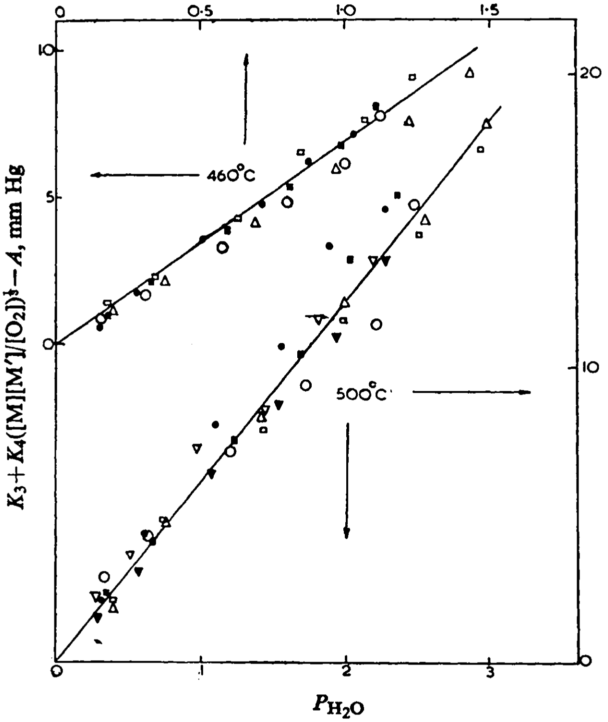

FIG. 3.—Inhibition of H_2+O_2 reaction by H_2O in aged boric-acid-coated vessels; symbols as in fig. 2.

Since δ and K_2 involve terms that are dependent on $[O_2]$, [M] and [M′], and since these vary as H_2O is added, δ and K_2 could in principle vary as H_2O is added, and any simple graphical presentation of the results would be impossible. In practice, calculations show that there is no significant change in K_1 and K_2 as H_2O replaces N_2 in a given $H_2+O_2+N_2$ mixture; the value of K_2, in fact, is effectively independent of the H_2 and O_2 mole fractions in the initial mixture, since the changes in δ and K' virtually compensate over the range investigated. Effectively, therefore, (iii) can be written,

$$mP_2 = K_3+K_4([\mathrm{M}][\mathrm{M}']/[\mathrm{O}_2])^{\frac{1}{2}}. \qquad \text{(viii)}$$

$K_4 = K_2B$ was calculated from (vii) for each H_2+O_2 mole fraction and K_3 was evaluated from the value of mP_2 for the uninhibited second limit. The values of K_3 were within 2 % of K_1 calculated from (vi), but use of the experimental uninhibited second limit ensures that all plots pass through the origin. In the presence of H_2O, (viii) becomes

$$m_{\mathrm{H_2O}}P_{\mathrm{H_2O}} = K_3+K_4([\mathrm{M}][\mathrm{M}']/[\mathrm{O}_2])^{\frac{1}{2}}-A, \qquad \text{(ix)}$$

where A is defined by (iv) and all pressures are those at the inhibited limit. Fig. 3 shows that a plot of $\{K_3+K_4([\mathrm{M}][\mathrm{M}']/[\mathrm{O}_2])^{\frac{1}{2}}-A\}$ against $P_{\mathrm{H_2O}}$ gives a common straight line for a wide range of mixture composition. The best gradients give $m_{\mathrm{H_2O}}$ as 6·11 at 500°C and 6·83 at 460°C, the r.m.s. deviation being 0·40 and 0·38 respectively. These values in fact, are not significantly different from those obtained by treating the results in the manner used for KCl-coated vessels (5·75 at 500°, 6·45 at 460°C).

Eqn. (iii) and (ix) also permit the calculation of $m_{\mathrm{H_2O}}$ from each individual experiment. The results of 126 observations are assembled in tables 1 and 2. Lines 1, 2 and lines 4, 5 of table 1 show that $m_{\mathrm{H_2O}}$ is independent of surface. Lines 3-6 show that $m_{\mathrm{H_2O}}$ is independent of temperature, while lines 7-9 show that it is independent of H_2O concentration. Table 2 shows that $m_{\mathrm{H_2O}}$ is independent of mixture composition over a range of $[H_2]/[O_2]$ ratios from 5 : 1 to 1 :8.

TABLE 1.—SUMMARY OF MEASUREMENTS OF $m_{\mathrm{H_2O}}$

surface	temp., °C	% H_2O	no. of results	r.m.s. value	standard deviation
KCl	500, 540	0·4-4·0	54	6·54	0·70
B_2O_3	460, 500	0·4-4·0	72	6·37	0·65
B_2O_3	460	0·4-4·0	30	6·59	0·72
B_2O_3	500	0·4-4·0	42	6·23	0·66
KCl	500	0·4-4·0	24	6·24	0·58
KCl	540	0·4-4·0	30	6·73	0·69
KCl or B_2O_3	460-540	0·4	21	6·12	1·09
KCl or B_2O_3	460-540	2·0	21	6·50	0·63
KCl or B_2O_3	460-540	4·0	21	6·61	0·59
KCl or B_2O_3	460-540	0·4-4·0	126	6·43	0·69

TABLE 2.—EFFECT OF MIXTURE COMPOSITION ON $m_{\mathrm{H_2O}}$

surface	temp., °C	mixture		no. of results	r.m.s. value	standard deviation
		x	y			
KCl or B_2O_3	460-540	0·24	0·07	24	6·20	0·64
KCl or B_2O_3	460-540	0·24	0·28	24	6·18	0·67
KCl or B_2O_3	460-540	0·24	0·56	24	6·34	0·69
KCl or B_2O_3	460-540	0·14	0·14	24	6·49	0·66
KCl or B_2O_3	460-540	0·68	0·14	12	6·83	0·75
B_2O_3	460, 500	0·07	0·56	12	6·46	0·43
B_2O_3	500	0·36	0·56	6	5·91	0·34

DISCUSSION

The mean value of 6·4 obtained for $m_{\mathrm{H_2O}}$ is significantly below previously reported values of 8-11 and 14·3. It is in agreement with two independent estimates of 6·0 obtained using clean Pyrex vessels.[4, 5] It is also in agreement with the value of 5·5 obtained by Nalbandyan [17] from 12 experiments over the range 439-465°C, and with the figure of 5·0 obtained by Voevodski and Talrose [18] from 9 experiments using a flow system in the temperature range 496-585°C. Tyler and Ashmore [19] have recently obtained a mean value of $6{\cdot}5 \pm 1{\cdot}6$ at 360°C, from work arising out of the NO_2-sensitized H_2+O_2 reaction. There is thus a substantial body of evidence in favour of the lower figure; the agreement of the values obtained in KCl-coated and boric-acid-coated vessels is particularly striking. It is difficult to account for the high value reported by Lewis and von Elbe.[1] The occurrence of the " regeneration " reaction (11) or of surface termination of H atoms would give a high value for m_{H_2O}, but it seems doubtful whether these factors would be sufficiently important at 530°C in the 7·4 cm vessel used by Lewis and von Elbe. Nalbandyan [17] suggests that their high value could be explained by water formation during the manipulation period. It seems unlikely, however, that such reaction could be sufficiently fast under the experimental conditions, and it would also be necessary to assume that the effect was more marked in the presence of water vapour; moreover, the experimental conditions of 530°C, 7·4 cm diam. spherical vessel, are close to our own conditions of 540°C, 5·1 cm diam. cylindrical vessel (20 cm long), where no such effects were detected.

The earliest theory to account for the high third-body coefficient of water in reaction (4) involved the formation of a complex between H atoms and H_2O, the complex then reacting with O_2:

$$H+H_2O = H_2O{-}H \tag{a}$$

$$H_2O{-}H = H_2O+H \tag{b}$$

$$H_2O{-}H+O_2 = H_2O+HO_2. \tag{c}$$

The apparent third-order velocity constant for H_2O is thus given by

$$k_{4,H_2O} = k_a k_c/(k_b+k_c[O_2]).$$

Hinshelwood and Willbourn [3] eliminate this possibility by showing experimentally that k_{4,H_2O} is independent of $[O_2]$. This observation can be accommodated, however, by assuming that $k_b \gg k_c[O_2]$, so that their argument is not decisive. Walsh [20] attributes high values of m_{H_2O} to the fact that the water molecule has fundamental vibration frequencies close to some of those possible for the HO_2 radical, and considers that this facilitates removal of energy from the excited HO_2 radical. Dickens and Linnett [21] conclude, however, that if transfer of large vibrational quanta are involved, H_2 should be exceptionally efficient in deactivating the newly formed HO_2 complex. Since this is not so they argue that the transfer of small quanta of vibrational energy must be involved, in which case the coincidence of the fundamental vibration frequencies is irrelevant.

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