

The Hydrogen-Sensitized Decomposition of Hydrogen Peroxide

R. R. Baldwin, D. Brattan,* B. Tunnicliffe,† R. W. Walker, and S. J. Webster‡

Department of Chemistry, The University, Hull, England

Although the homogeneous decomposition of H_2O_2 vapor is a nonchain process, a chain reaction occurs in the presence of H_2 , as a result of the reaction $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$ (1), followed by $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{OH}$ (14). At low concentrations chain termination results from the reaction $\text{OH} + \text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{HO}_2$ (15), while at high H_2 concentrations the chain length is limited by the reaction $\text{H} + \text{H}_2\text{O}_2 = \text{H}_2 + \text{HO}_2$ (14a). The chain reaction is inhibited by O_2 , as a result of the reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ (4). The ratios $k_{15}/k_1 = 5.0 \pm 1.0$ and $k_{14a}/k_{14} = 0.125 \pm 0.015$ show no significant variation over the temperature range 440–500°C, while the ratio $k_4/k_{14} = 3.8 \times 10^{-4}$, 2.7×10^{-4} , and 1.8×10^{-4} ($\text{mm Hg})^{-1}$ at 440°, 480°, and 500°C, respectively. From the known values of k_3/k_4 and of the velocity constant k_3 of the reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (2), the corresponding values of k_{14} are 6.9×10^8 , 8.5×10^8 , and 12.0×10^8 liter mole $^{-1}$ sec $^{-1}$, respectively.

Introduction

Relatively few studies have been made using H_2O_2 as a thermal source of OH radicals because of the difficulty of eliminating a substantial and variable contribution from the heterogeneous decomposition at temperatures where the study of the homogeneous reaction is feasible. To interpret the reproducible kinetics obtained with $\text{H}_2 + \text{O}_2 + \text{N}_2$ mixtures at 500°C in vessels coated with boric acid and aged by repeated use, Baldwin and Mayor [1] were forced to assume that the ageing process reduced the surface destruction of HO_2 and H_2O_2 to negligible proportions. This assumption was confirmed by a study [2] of the

homogeneous decomposition of H_2O_2 in an aged vessel, using a flow system over the temperature range 440–560°C. Baldwin and Brattan [2] found a substantial contribution from surface decomposition of H_2O_2 with HF-washed pyrex vessels at their temperatures, but Hoare, Prothero, and Walsh [3] have successfully used these vessels in the higher temperature range 569–659°C, their results forming a common $\log k$ versus $1/T$ plot with those for aged boric-acid-coated vessels at lower temperatures.

To explain the behavior of the second limit in boric-acid-coated vessels, Baldwin, Doran, and Mayor [4] concluded that H atoms reacted predominantly with H_2O_2 via reaction 14* and

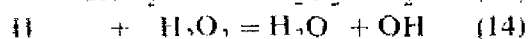
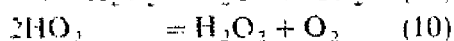
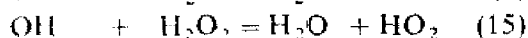
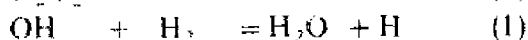
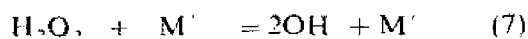
* Now at the Department of Chemistry, Harris College, Preston.

† Now at the Cleveland College of Technology, Redcar.

‡ Now at the Atomic Energy Authority Laboratories, Culcheth, Warrington.

* A nonconsecutive system of numbering has been adopted so as to maintain consistency with previous papers in which these reactions are involved.

that k_{14a}/k_{14} was not greater than 0.1–0.2. The decomposition of H_2O_2 in an inert atmosphere is a nonchain process through the reaction sequence 7, 15, and 10, and the rate is given by $-d[\text{H}_2\text{O}_2]/dt = 2k_7[\text{H}_2\text{O}_2][\text{M}']$. If reaction 14a is the sole reaction of H atoms with H_2O_2 , the rate expression remains unaffected and the only effect of H_2 arises from the increase in the value of M' . If reaction 14 occurs, however, the sequence 1 and 14 gives a chain decomposition of H_2O_2 .



A study of the decomposition of H_2O_2 in the presence of H_2 thus offers the possibility of evaluating the ratios k_{15}/k_1 and k_{14a}/k_{14} .

Experimental Apparatus and Procedure

A flow system was used at atmospheric pressure. The carrier gas, normally N_2 , was saturated at 20°C by passage through two bubblers in series containing 99% H_2O_2 . Further streams of N_2 and H_2 could be added after the saturators, and passage through a large bulb was found essential to ensure complete mixing. The gas was then split into two almost equal streams by two capillary tubes in parallel. One stream passed immediately through two traps in series at -80°C, which condensed the peroxide vapor. The second stream passed through the reaction vessel, and then through two cooled traps of 20-mm bore, with internal tubing of 6-mm bore. Tests showed that the percentage of H_2O_2 condensed in the second trap never exceeded 2% of that in the first trap provided side-arm entry was used; with central entry, the percentage in the second trap rose to over 10% at the highest flow rates used. The by-pass ratio was checked regularly, both by measuring

the peroxide condensed in the two traps in the absence of decomposition and by measuring the flow rate through each section, and was found to be constant to within 0.5% over a wide range of conditions.

Reaction vessels 20 cm long and 6 or 12 mm in internal diameter were used, with inlet and exit tubes of 6-mm bore. The vessel surface was coated with boric acid, as described earlier [1]. The surface of the vessel could be aged [1] by carrying out repeated slow reactions between $\text{H}_2 + \text{O}_2$ mixtures, but a more convenient way was to pass a stream of N_2 saturated with H_2O_2 over the vessel at 500°C for about 24 hr until the decomposition had reached a minimum. The surface produced in this way appeared to have the same inertness to H_2O_2 destruction as that produced by $\text{H}_2 + \text{O}_2$ reactions.

The furnace, about 45 cm long, was wound so that the temperature was constant to $\pm 1^\circ\text{C}$ over the main reaction vessel and fell rather sharply in the entry and exit tubes. However, preliminary calculations indicated that significant decomposition could be expected in the entry and exit tubes. These variations in temperature were allowed for by calculating the "effective volume" V_e of the whole volume within the furnace as the volume which, maintained at the maximum temperature T_m along the vessel, would give the same decomposition as that occurring in the actual vessel and the entry and exit tubes. V_e is given* by

$$V_e = \sum k_T T_m \Delta V / k_{T_m} T$$

where ΔV is a volume element at temperature T , and k_T , k_{T_m} are the velocity constants at temperatures T , T_m , respectively. The evaluation of V_e thus required the temperature distribution in the gas for each temperature and flow rate studied, together with the activation

* This equation is strictly valid only if k is the apparent first-order velocity constant. However, the variation of M' with temperature is negligible compared to the variation of k_7 .

energy of the reaction, which determines the ratio k_T/k_{T_m} . The effective volume differed for the homogeneous and heterogeneous reactions because of the differing activation energies. The temperature distribution was measured at centimeter intervals, so that ΔV is the volume per centimeter.

The surface reaction was examined in the temperature range 260–400°C, where the homogeneous reaction either was negligible or could be allowed for with sufficient accuracy, and an activation energy of 5 ± 0.5 kcal mole⁻¹ was obtained. The surface decomposition was checked frequently at 360°C, and the surface velocity constant k_s extrapolated to the experimental temperature using this activation energy. As the surface contribution was only a few per cent in the main studies, any error in the activation energy was not significant.

If both heterogeneous and homogeneous reactions are first order, as in the absence of H₂, the integrated rate equation can be written:

$$\ln a/(a-x) = k_s t_s + k_h t_h$$

The effective contact times t_s , t_h , for the heterogeneous and homogeneous reactions, respectively, were obtained by dividing the corresponding effective volumes V_s , V_h by the volume flow rate at the maximum furnace temperature. A plot of $\ln a/(a-x) - k_s t_s$ against t_h made it possible to determine k_h . In the presence of H₂, however, the order of the homogeneous reaction was not unity, and changed during the reaction as the $[H_2O_2]/[H_2]$ ratio changed, so that use of initial rates was essential. It was assumed that the surface decomposition x_s could be represented by the equation $\ln A/(A-x_s) = k_s t_s$, where A is the mean of the inlet and outlet H₂O₂ concentrations, and that the homogeneous portion of the decomposition $x_h = x - x_s$. Hypothetical calculations with homogeneous orders of 0, 1, and 2, where integration was possible, confirmed that this procedure gave accurate values of x_h for the small values of k_s involved. Calculations using

the formula developed by McLane [5] have shown that the effects of radial and longitudinal diffusion are negligible with the vessel diameters, flow rates, and decomposition rates used.

Under many conditions, the percentage decomposition was quite high, even with the shortest contact times, and direct determination of initial tangents to the x_h-t_h curve would have been unreliable. Suitable values of n in the equation $dx/dt = k(a-x)^n$ were chosen, and initial gradients drawn to the almost linear function plots:

$$(n-1)kt = 1/(a-x)^{n-1} - 1/a^{n-1}$$

If a and x are in percentages ($a = 100$), the initial gradient g is related to the apparent velocity constant k by the equation $k = g(c_0/100)^{1-n}$, where c_0 is the initial H₂O₂ concentration. The initial rate is then given by kc_0^n or $gc_0(100)^{n-1}$. Values of n used varied from 0.7 at low H₂ concentrations to 1.5 at high concentrations of H₂ in the presence of O₂. Values of n could be estimated in two ways: (a) by measuring the half-life time with respect to H₂O₂ at two different initial concentrations of H₂O₂, and (b) by choosing the value that gave the best straight-line plot, using the appropriate function.

Results

Tests with Cylinder Hydrogen

Figure 1 shows the x_h-t_h plots for H₂ + N₂ mixtures containing 0.097 mole fraction of H₂, and partial pressures of H₂O₂ from 0.17 to 1.02 mm Hg. The variation in half-life times indicates an order in H₂O₂ of about 0.6. Figure 2 shows the variation of initial rate with H₂ for two H₂O₂ pressures, 0.68 and 0.34 mm Hg. The marked increase in rate indicates the occurrence of a chain reaction through reactions 14 and 1, and confirms the conclusion from H₂ + O₂ studies [4] that reaction 14 rather than 14a is the predominant reaction

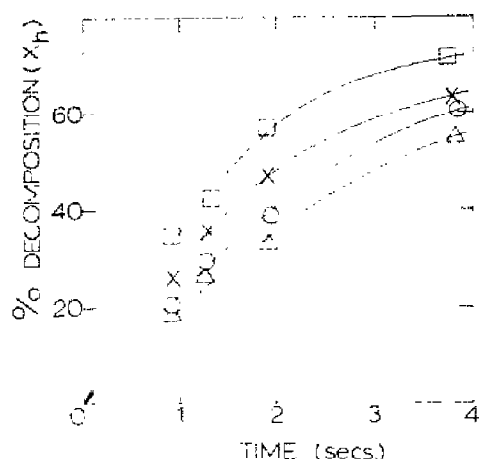


Figure 1. Reaction-time curves for decomposition of H_2O_2 in the presence of H_2 , 12-mm-i.d. vessel at 440°C . Total pressure, 760 mm Hg. Mole fraction of $\text{H}_2 \approx 0.097$. H_2O_2 , mm Hg: Δ , 1.02; \circ , 0.68; \times , 0.34; \square , 0.17.

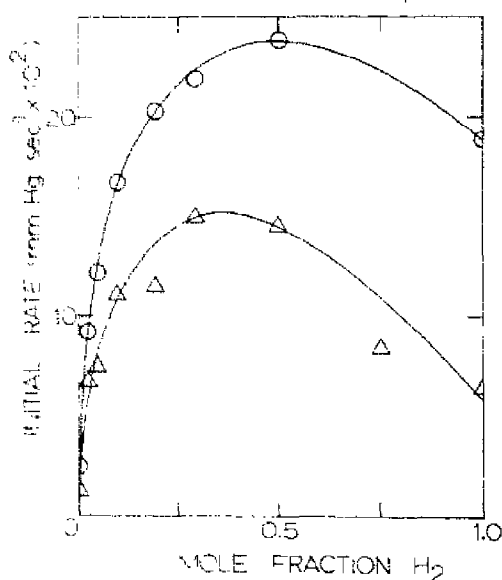


Figure 2. Variation of initial rate with mole fraction of H_2 , 12-mm-i.d. vessel at 440°C . Total pressure, 760 mm Hg. H_2O_2 , mm Hg: \circ , 0.68; Δ , 0.34.

between H atoms and H_2O_2 . The almost linear increase in rate for small additions of H_2 is consistent with a mechanism involving reactions 7, 1, 10, 14, and 15, which gives the rate expression:

$$R_H = \frac{-d[\text{H}_2\text{O}_2]}{dt} = 2k_7[\text{H}_2\text{O}_2][M'] \left[1 + \frac{k_1[\text{H}_2]}{k_{15}[\text{H}_2\text{O}_2]} \right] \quad (\text{i})$$

The initial gradient in Fig. 2 gives an approximate value of $k_{15}/k_1 = 5$ in good agreement with the values of 4.7–6.0 obtained from studies [6] of the $\text{H}_2 + \text{O}_2$ reaction in aged boric-acid-coated vessels over the range 460 – 500°C . Expression i, however, predicts a chain length of 250 with pure H_2 and 0.65 mm Hg of H_2O_2 , as compared to the eightfold increase found experimentally. Moreover, the results in Fig. 2 show an order in H_2O_2 above unity at high concentrations of H_2 , whereas expression i predicts an order tending to zero.

As the rate at high H_2 is below that predicted from expression i, an additional termination reaction is required, and the obvious reaction is 14a. Addition of this reaction gives the rate expression:

$$R_H = \frac{-d[\text{H}_2\text{O}_2]}{dt} = 2k_7[\text{H}_2\text{O}_2][M'_H] \left[\frac{k_1[\text{H}_2] + k_{15}[\text{H}_2\text{O}_2]}{\beta k_1[\text{H}_2] + k_{15}[\text{H}_2\text{O}_2]} \right] \quad (\text{ii})$$

where $\beta = k_{14a}/(k_{14} + k_{14a})$. Expression ii shows that at low H_2 concentrations the chain length is largely determined by the competition between reactions 1 and 15, whereas at high concentrations the chain length is determined by competition between reactions 14 and 14a, which gives a limiting chain length $(1 + k_{14}/k_{14a})$ independent of H_2 concentration.

In testing expression ii, allowance is made for the increase in M' with increasing H_2 concentration by assuming that the relative efficiency of N_2 to H_2 is the same (0.43) in reaction 7 as in reaction 4. This assumption is justified, first by the agreement found [2, 3, 7] for the relative efficiencies of O_2 , N_2 , He, and Ar in reactions 4 and 7, and second by the fact that the plot of R_H/M'_H , using $m_{\text{N}_2} = 0.43$, approaches a limiting value, as shown in Fig. 3, curve B, when purified H_2 is used. Since the relative efficiency of H_2O_2 to N_2 is 6.4, M'_H (relative to H_2) is given by:

$$M'_H = [\text{H}_2] + 0.43 [\text{N}_2] + 2.7 [\text{H}_2\text{O}_2]$$

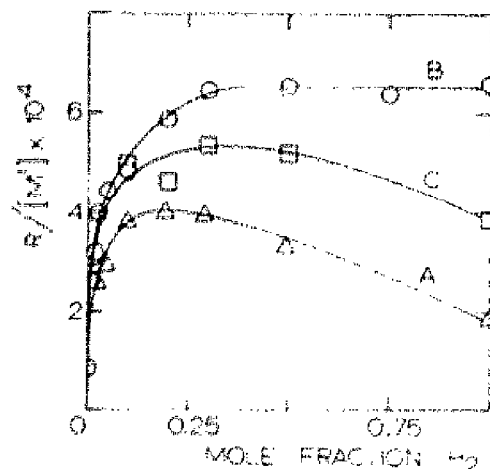


Figure 3. Plot of rate/[M'] against mole fraction of H₂. 12-mm-i.d. vessel at 440°C. Total pressure, 760 mm Hg. H₂O₂ = 0.65 mm Hg. ○, pure H₂; □, H₂ + 0.05% O₂; △, cylinder H₂.

With cylinder H₂, however, Fig. 3, curve A, shows that the plot of R_H/M'_H against H₂ concentration goes through a maximum at about 0.2 mole fraction of H₂. Moreover, the order in H₂O₂ rises above unity to nearly 1.5 with pure H₂, in contrast to the predicted limiting order of unity from expression ii. The decrease in R_H/M'_H requires an additional chain termination reaction, and the only possibility appears to be reaction 4, which occurs as a result of traces of O₂ (about 0.07% according to later tests) in the H₂ gas:



Tests with Purified Hydrogen

This explanation was confirmed by repeating the observations with H₂ freed from O₂ by passage over platinized asbestos at 300°C, the water formed being removed by a liquid air trap. This gave the results shown in Fig. 3, curve B.

To interpret quantitatively the results with purified H₂, it is convenient to use the rate of decomposition R_N in pure N₂, where $M' = M'_N$ so that:

$$R_N = 2k_7[H_2O_2][M'_N] \quad (iii)$$

Combining expressions ii and iii gives the relation:

$$\frac{R_N[M'_H]}{R_H[M'_N]} \left[1 + \frac{k_{15}[H_2O_2]}{k_1[H_2]} \right] = \beta + \frac{k_{15}[H_2O_2]}{k_1[H_2]}$$

which can be written

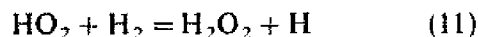
$$B' = \beta + \frac{k_{15}[H_2O_2]}{k_1[H_2]} (1 - B') \quad (iv)$$

where $B' = R_N[M'_H]/R_H[M'_N]$

Equation iv is tested by plotting B' against $(1 - B')[H_2O_2]/[H_2]$. The gradient gives $k_{15}/k_1 = 4.0$ and $\beta = 0.127$ at 440°C.

With pure N₂ at 440°C, it was difficult to obtain the Arrhenius parameters $A = 3.19 \pm$ percentage decomposition was only about 15% even with the longest contact times possible (4 sec) in the 12-mm vessel. A more accurate evaluation of R_N at 440°C was obtained by using the observations of Baldwin and Brattan [2] for reaction vessels of 6-, 12-, and 23-mm diameter over the range 440–560°C. Their velocity constants were fitted statistically to obtain the Arrhenius parameters $A = 3.19 \pm 1.2 \times 10^{14}$ liter mole⁻¹ sec⁻¹ ($M = N_2$) and $E = 47.0 \pm 0.7$ kcal mole⁻¹. These values were then used to obtain $k_7 = 6.54 \times 10^{-5}$ (mm Hg)⁻¹ sec⁻¹ ($M' = H_2$), and hence to obtain R_N at 440°C. Tests (see later) confirmed that at higher temperatures the values of k_7 obtained experimentally agreed with those of Baldwin and Brattan. A significant rise in the experimentally determined k_7 at 440°C above the quoted value indicated deterioration of the surface with consequent substantial heterogeneous decomposition, in which case the vessel was recoated and aged.

The Effect of Reaction 11



Studies of the H₂ + O₂ reaction in aged boric-acid-coated vessels [6] have shown that reac-

tion 11 plays a reasonably important part under conditions where the stationary concentration of H_2O_2 is comparable to the present values.

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = 2k_7[\text{H}_2\text{O}_2][\text{M}'_{\text{H}}](1 + \alpha) \left[\frac{1 + k_{15}[\text{H}_2\text{O}_2]/k_1[\text{H}_2]}{\beta + k_{15}[\text{H}_2\text{O}_2]/k_1[\text{H}_2]} \right] \quad (\text{v})$$

where

$$\alpha = \frac{k_{11}[\text{H}_2](1 - \beta)}{2k_{10}^{1/2}(k_7[\text{H}_2\text{O}_2][\text{M}'_{\text{H}}])^{1/2}}$$

It is surprising that, although reaction 11 produces H_2O_2 , its occurrence increases the rate of decomposition of H_2O_2 . This arises because the H atoms produced in reaction 11 decompose another H_2O_2 molecule, so that the sequence 11 and 14 removes HO_2 without forming any H_2O_2 , whereas in the absence of reaction 11 two HO_2 radicals give one H_2O_2 by reaction 10. Studies [6] of the slow reaction between $\text{H}_2 + \text{O}_2$ at 500°C give $k_{11}/k_{10}^{1/2} = 1.19 \pm 0.05 \times 10^{-3} (\text{mm Hg})^{-1/2} \text{min}^{-1/2}$; and, using an estimate of $(E_{11} - \frac{1}{2}E_{10}) = 22 \text{ kcal mole}^{-1}$, this gives $k_{11}/k_{10}^{1/2} = 4.7 \times 10^{-5} (\text{mm Hg})^{-1/2} \text{sec}^{-1/2}$ at 440°C . With this value, α varies from 0.01 at 0.1 mole fraction of H_2 to 0.09 with pure H_2 . Equation iv is modified to:

$$\frac{R_{\text{N}}[\text{M}'_{\text{H}}]}{R_{\text{H}}[\text{M}'_{\text{N}}]}(1 + \alpha) = B = \beta + \frac{k_{15}[\text{H}_2\text{O}_2]}{k_1[\text{H}_2]}(1 - \beta) \quad (\text{vi})$$

From the intercept and gradient of the appropriate plot (Fig. 4), $k_{15}/k_1 = 3.95$, $\beta = 0.133$, showing that reaction 11 has a very minor effect.

In addition to the graphical interpretation, the values of β and k_{15}/k_1 giving the best fit with the experimental results were obtained using a computer program. Two criteria of the best fit were adopted:

(a) The rms percentage deviation between observed and calculated rates was minimized, giving $k_{15}/k_1 = 3.8$, $\beta = 0.138$, with an rms deviation of 5.3% .

(b) As the results at low H_2 concentrations are least accurate, procedure (a) tended to overweight these results, and as an alternative, which overweighted the results at high H_2 , the

Addition of this reaction to the previous mechanism involving reactions 7, 1, 14, 14a, and 15 gives the rate expression:

sum of the numerical values of the absolute deviations was minimized, giving $k_{15}/k_1 = 3.7$, $\beta = 0.137$. The various values are summarized below:

	β	k_{15}/k_1
Reaction 11 omitted, graphical	0.127	4.0
Reaction 11 included, graphical	0.133	3.95
Minimization of rms deviation	0.138	3.8
Minimization of absolute deviation	0.137	3.7

The variations in k_{15}/k_1 and β , resulting from the different treatments, are within experimental error, since 5% errors in the estimation of R_{N} and R_{H} can cause 15% error in k_{15}/k_1 and 10% error in β . The mean values at 440°C can thus be taken as $k_{15}/k_1 = 3.9 \pm 0.6$, $\beta = 0.135 \pm 0.015$.

Studies at 460°C

Measurements were also made (B.T.) in a 12-mm-diameter vessel at 460°C . Although the

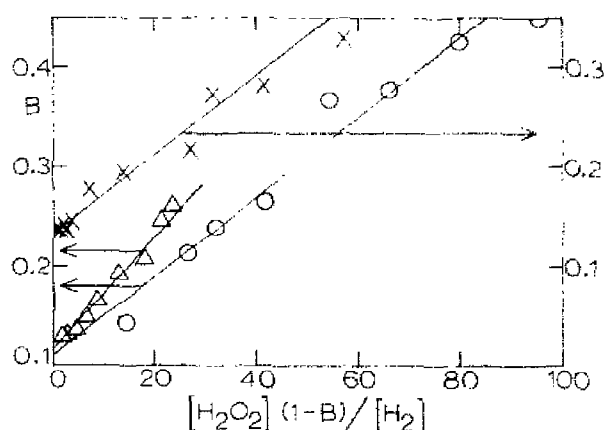


Figure 4. Plot of $B = R_{\text{N}}[\text{M}'_{\text{H}}](1 + \alpha)/R_{\text{H}}[\text{M}'_{\text{N}}]$ against $[\text{H}_2\text{O}_2](1 - B)/[\text{H}_2]$. X, 440° ; Δ , 460° ; O, 480°C .

value of R_N was higher, the value of k_7 for this vessel was more than twice that for the vessel used at 440°C, so that the corrections for heterogeneous decomposition at the two temperatures were comparable. The value of R_N (0.0444 mm Hg sec⁻¹) used in equation vi was obtained from Baldwin and Brattan's expression and agreed with the mean experimental value of 0.044 ± 0.002 . The plot of $R/[M']$ is shown in Fig. 5, and the appropriate plot for Eq. vi is shown in Fig. 4, which gives $k_{15}/k_1 = 5.7 \pm 0.7$, $\beta = 0.115 \pm 0.015$; computer treatment gives $k_{15}/k_1 = 6.0$, $\beta = 0.112$.

Results at 480°C and 500°C

Because of the increased decomposition rate at these temperatures, a 6-mm-diameter vessel was used to reduce the contact time, but even then the highest H₂ concentration that could be used was restricted to 0.05 mole fraction at 480°C and 0.01 at 500°C. The values of R_N in Eq. vi were again obtained from the expression for k_7 satisfying Baldwin and Brattan's results (0.155 mm Hg sec⁻¹ and 0.341 mm Hg sec⁻¹ at 480°C and 500°C, respectively, with [H₂O₂] = 0.65 mm Hg), these being in good agreement with the mean measured values of 0.150 and 0.339, respectively, in the present work.

Figure 5 shows the variation of initial rate with H₂ concentration at 480° and 500°C. Figure 4 shows the appropriate plot from ex-

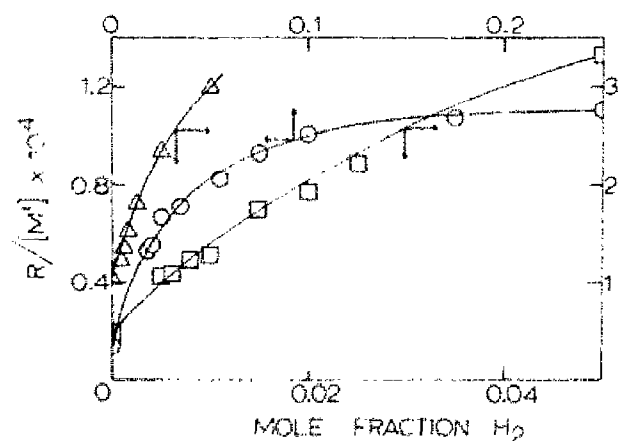


Figure 5. Plot of rate $[M']$ against mole fraction of H₂ at 460°, 480°, and 500°C. ○, 460°; □, 480°; △, 500°C.

pression vi; at 480°C, α has a maximum value of 0.005 at the highest H₂ concentration used, and it is even smaller at 500°C. The gradient and intercept give $\beta = 0.11 \pm 0.02$, $k_{15}/k_1 = 4.1 \pm 0.6$ at 480°C. Since β becomes rate controlling only at the higher H₂ concentrations, β can be evaluated only with limited accuracy at 480°C, and with very poor accuracy at 500°C. Computer treatment shows that, as β is varied from 0.11 to 0.15, the optimum value of k_{15}/k_1 varies from 4.1 to 3.5 at 480°C and from 3.9 to 3.5 at 500°C. Accurate evaluation of β is limited by the difficulty of estimating the low decomposition rate in pure N₂ at 440°C, and of measuring the high decomposition rate in pure H₂ at the higher temperatures.

Since the expected variation of β with temperature is small compared to experimental errors, the mean of the values at 440°C and 460°C will be taken, giving $\beta = 0.125 \pm 0.015$ as the best available value over the range 440–500°C. k_{15}/k_1 should also vary only slightly with temperature, and a mean value of 5.0 ± 1.0 is the best available over the range 440–500°C. Values of k_{15}/k_1 between 4.7 and 6.0 have been obtained over the range 460–500°C from studies of the slow reaction between H₂ and O₂ in aged boric-acid-coated vessels [6]. Somewhat higher values would be expected from these studies, since they include a contribution from the reaction $O + H_2O_2$, which is kinetically similar to reaction 15. The absolute value of k_{15} can be obtained from the recommended [8] value of $k_1 = 2.19 \times 10^{10} \exp(-5150/RT)$ liter mole⁻¹ sec⁻¹, cal units.

The Inhibiting Effect of Oxygen

To confirm the explanation of the anomalous results obtained at high H₂ concentrations with unpurified cylinder H₂, and to obtain further values for certain velocity constants, the effect of O₂ on the H₂-sensitized decomposition of H₂O₂ was examined at 440°C. Tests were first made by adding O₂ equivalent to 0.05% of the H₂ flow. Considerable care was necessary in

metering the small amounts of O_2 involved at low H_2 concentrations, and all stagnant volumes had to be flushed out before starting systematic observations. Initial rates were obtained as described previously. With high H_2 concentrations, values of n as high as 1.5 were necessary. Curve C, Fig. 3, shows the marked inhibiting effect of O_2 , and comparison of the rate (in the absence of N_2) with the rates in Fig. 6, given later, suggests that the unpurified H_2 contained about 0.08% of O_2 .

Because of the difficulty in metering the very low flows of O_2 , quantitative interpretation was made on results obtained at a fixed mole fraction of H_2 with varying additions of O_2 . Two H_2 concentrations (pure H_2 and 0.25 mole fraction) and two partial pressures (ca. 0.6 and 0.3 mm Hg) of H_2O_2 were used. The results are shown in Fig. 6. The rates with O_2 absent make it possible to obtain values of β by using equation v; the figures of 0.136, 0.138, and 0.121 for the three mixtures are consistent with the mean value of 0.125 ± 0.015 quoted earlier.

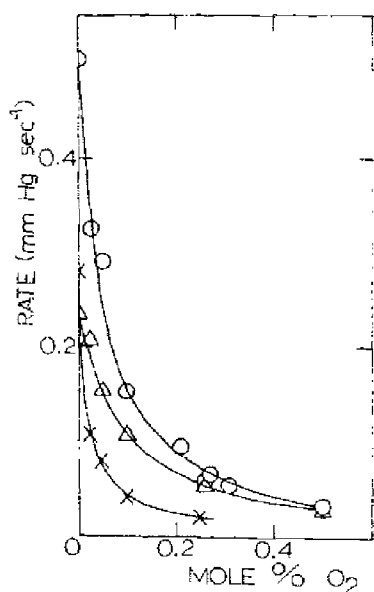


Figure 6. Inhibiting effect of O_2 on the H_2 -sensitized decomposition of H_2O_2 . 12-mm-i.d. vessel at $440^\circ C$. Total pressure, ca. 760 mm Hg. \odot , $H_2O_2 = 0.65$ mm Hg, pure H_2 ; \times , $H_2O_2 = 0.31$ mm Hg, pure H_2 ; Δ , $H_2O_2 = 0.60$ mm Hg, mole fraction $H_2 = 0.25$.

If reaction 11, which is of minor importance, and reaction 15, which is a minor termination reaction at high H_2 concentrations, are omitted, the mechanism involving reactions 7, 1, 10, 14, 14a, and 4 gives a rate expression:

$$R_0 = 2k_7[H_2O_2][M'_0] \left[\frac{k_{14} + k_{14a}}{k_{14a} + k_4[O_2][M]/[H_2O_2]} \right] \quad (vii)$$

where R_0 , M'_0 are the values in the presence of O_2 . Combining expression ii, with $k_{15} = 0$, and expression vii gives the relation:

$$\frac{R_H[M'_0]}{R_0[M_H]} = 1 + \frac{k_4[O_2][M]}{k_{14a}[H_2O_2]} \quad (viii)$$

From the plot of $R_H[M'_0]/R_0[M_H]$ against $[O_2][M]/[H_2O_2]$, a value of $k_4/k_{14a} = 2.7 \times 10^{-3} (\text{mm Hg})^{-1}$ is obtained ($M = H_2$) at $440^\circ C$.

If reaction 11 is introduced, Eq. viii is modified to:

$$\frac{R_H[M'_0](1 + \alpha_2)}{R_0[M_H](1 + \alpha_1)} = 1 + \frac{k_4[O_2][M]}{k_{14a}[H_2O_2]} \quad (ix)$$

where

$$\alpha_1 = \frac{k_{11}[H_2](1 - \beta)}{2k_{10}^{1/2}(k_7[H_2O_2][M_H])^{1/2}}, \quad \alpha_2 = \frac{k_{11}[H_2](1 - \beta - \gamma)}{2k_{10}^{1/2}(k_7[H_2O_2][M'_0])^{1/2}} \quad (x)$$

and

$$\gamma = \beta k_4[O_2][M]/k_{14a}[H_2O_2]$$

Equation ix is tested graphically by plotting $R_H[M'_0](1 + \alpha_2)/R_0[M_H](1 + \alpha_1)$ against $[O_2][M]/[H_2O_2]$. The results at $440^\circ C$ (Fig. 7) for two different H_2O_2 concentrations and two different H_2 concentrations fit a common line, the gradient of which gives $k_4/k_{14a} = 2.45 \times 10^{-3} (\text{mm Hg})^{-1}$. In evaluating α_1 , α_2 , and γ , the mean value of $\beta = 0.125$, obtained from studies in the absence of O_2 , is used; the value obtained for k_4/k_{14a} is not sensitive to the

value of β used. With this value of β , k_4/k_{14} is then obtained as 3.5×10^{-4} (mm Hg)⁻¹. As with the O₂-free system, the results were treated by a computer method, in which k_4/k_{14} is varied until the rms deviation is a minimum. When applied to all the results in Fig. 7, this method gave $k_4/k_{14} = 3.8 \times 10^{-4}$ (mm Hg)⁻¹, the rms deviation being 10.1%.

At 480° and 500°C, the rate R_H was too fast to measure directly for pure H₂, and R_H was obtained from the rate with pure N₂, using Eq. vi. The plots are shown in Fig. 8. The value obtained for k_4/k_{14} is thus dependent on the value taken for β . As the studies at these temperatures with O₂ absent did not permit the accurate evaluation of β , k_4/k_{14} could not be determined accurately, but the value obtained for k_4/k_{14} proved to be insensitive to β over the probable range of values. Thus, with $\beta = 0.110$ and 0.140, the values for k_4/k_{14} were 2.90×10^{-4} and 2.88×10^{-4} (mm Hg)⁻¹, respectively, for M = H₂ at 480°C, and 1.78×10^{-4} and 1.74×10^{-4} , respectively, at 500°C. These values were confirmed by computer treatment as at 440°C, the minimum rms deviation being obtained with $k_4/k_{14} = 2.7 \times 10^{-4}$ and 1.8×10^{-4} at 480°C and 500°C, respectively, independent of β over the range 0.110–0.140

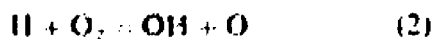


Table 1 gives the values of k_{14}/k_2 obtained by combining the values of k_4/k_{14} with k_2/k_4 from second-limit studies [4, 9]. The values of k_{14}/k_2 obtained from studies [6] of the slow reaction of H₂ + O₂ mixtures are also given at

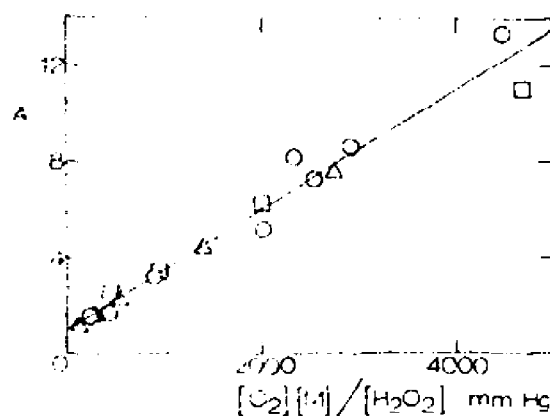


Figure 7. Plot of $A = R_H[M_O](1 + z_2)/R_O[M_H](1 + z_1)$ against $[O_2][M]/[H_2O_2]$ at 440°C. \odot , H₂O₂ = 0.65 mm Hg, pure H₂; \square , H₂O₂ = 0.31 mm Hg, pure H₂; Δ , H₂O₂ = 0.60 mm Hg, mole fraction H₂ = 0.25.

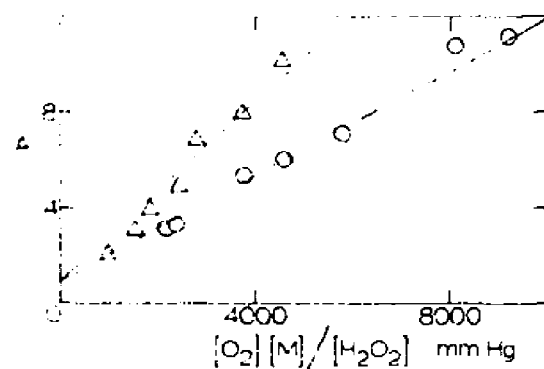


Figure 8. Plot of $A = R_H[M_O](1 + z_2)/R_O[M_H](1 + z_1)$ against $[O_2][M]/[H_2O_2]$ at 480° and 500°C, 6-mm-i.d. vessel. Total pressure, ca. 760 mm Hg. Δ , 480°C; \odot , 500°C.

480° and 500°C: no independent estimate of k_{14}/k_2 is available at 440°C. Absolute values of k_{14} , obtained using the recommended value [10] of k_2 , are also included in the table.

Table 1

Temp., C	k_2/k_4 , mm Hg (M = H ₂)	k_4/k_{14} , mm Hg (M = H ₂)	Present work		H ₂ + O ₂ studies [6]
			k_{14}/k_2	k_{14} , liter mole ⁻¹ sec ⁻¹	k_{14}/k_2
440	6.1	3.8×10^{-4}	430 ± 30	6.9×10^8	...
480	11.0	2.7×10^{-4}	285 ± 20	8.5×10^8	280
500	18.5	1.8×10^{-4}	300 ± 20	12.0×10^8	270

In addition to establishing the values of k_4/k_{14} , the agreement of these independent estimates provides general confirmation of the mechanism adopted for the $\text{H}_2 + \text{O}_2$ reaction, and for the H_2 -sensitized decomposition of H_2O_2 .

Thanks are due to Laporte Chemicals, Limited, for the generous provision of samples of hydrogen peroxide, and to the Hull Education Department for a grant to D.B. The work by S.J.W. and B.T. was supported by the United States Air Force under Grants AF EOAR 63-31, EOAR 65-58, and EOAR 67-01, with the European Office of Aerospace Research. Miss Janet Smith's assistance with the computation is gratefully acknowledged.

References

1. BALDWIN, R. R., and MAYOR, L., *Trans. Faraday Soc.*, **56**, 80 (1960).
2. BALDWIN, R. R., and BRATTAN, D., *Eighth Symposium (International) on Combustion*, p. 110. Williams and Wilkins; Baltimore (1962).
3. HOARE, D. E., PROTHERO, J. B., and WALSH, A. D., *Trans. Faraday Soc.*, **55**, 548 (1959).
4. BALDWIN, R. R., DORAN, P., and MAYOR, L., *Trans. Faraday Soc.*, **56**, 93 (1960).
5. McLANE, C. K., *J. Chem. Phys.*, **17**, 379 (1949).
6. BALDWIN, R. R., JACKSON, D., WALKER, R. W., and WEBSTER, S. J., *Trans. Faraday Soc.*, **63**, 1665, 1676 (1967).
7. FORST, W., *Can. J. Chem.*, **36**, 1308 (1958).
8. BAULCH, D. L., DRYSDALE, D. D., and LLOYD, A. C., O.S.T.I. Project 2, Leeds University, Leeds (1968).
9. EGERTON, A., and WARREN, D. R., *Proc. Roy. Soc. (London)*, *Ser. A*, **204**, 465 (1951).
10. BAULCH, D. L., DRYSDALE, D. D., and LLOYD, A. C., O.S.T.I. Project 3, Leeds University, Leeds (1969).

(Received May 1970; revised July 1970)