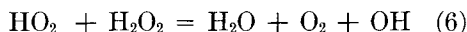
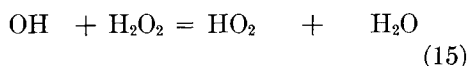


3

HOMOGENEOUS GAS-PHASE DECOMPOSITION OF HYDROGEN PEROXIDE

By R. R. BALDWIN AND D. BRATTAN

Early studies¹⁻⁴ of the decomposition of H_2O_2 vapor have emphasized the difficulty of finding a suitable vessel surface which would permit the homogeneous decomposition to be studied without serious interference from the heterogeneous reaction. The present work was initiated by the observations of Baldwin and Mayor,^{5, 6, 7} who showed that the kinetics of the slow reaction between H_2 and O_2 in aged boric-acid-coated vessels could only be explained by assuming that the aged surface was extremely inert to both HO_2 and H_2O_2 . When the present study was begun, previous work on the homogeneous gas-phase decomposition of H_2O_2 had shown considerable disagreement as to both the order of the reaction and the effect of inert gases. Satterfield and Stein,⁸ using a flow system at atmospheric pressure, found an order of $\frac{3}{2}$ which they accounted for by postulating a chain mechanism involving reactions (7), (15), (6) and (10):



In contrast, Giguère and Liu⁹ found the order to be unity with respect to peroxide. They also found the rate to be independent of total pressure. More recently, two papers^{10, 11} have been published which establish both the first-order nature of the decomposition and the dependence of rate on total pressure. The present paper confirms these conclusions which extend the range of experimental investigation, and examines the decomposition in the presence of H_2 .

Experimental Procedure

The carrier gas (normally N_2) is saturated at 20°C by passage through two bubblers in series containing 90 or 99 per cent H_2O_2 . A second stream of N_2 can be added after the saturators. A large bulb ensures complete mixing, and in experiments with H_2 a third stream containing H_2 can also be added. The gas is then split into two almost equal parts by two capillary tubes in

parallel. One stream passes directly through two traps in series which condense the peroxide vapor at -80°C . The second stream passes through the hot reaction vessel and then through cooled traps. Tests showed that condensation in the traps is complete, and that the by-pass ratio remains constant over a wide range of conditions. The system could be operated at pressures down to 25 mm Hg by use of filter pumps in conjunction with a Negretti-Zambra pressure controller.

Reaction vessels were 20 cm in length, of diameters 6, 12 and 24 mm, with inlet and exit tubes of 6 mm bore. The furnace, about 45 cm in length, was wound so that the temperature was uniform to $\pm 1\frac{1}{2}^\circ\text{C}$ over the main reaction vessel and fell rather sharply in the entry and exit tubes. Nevertheless, preliminary calculations showed that significant reaction could be expected in the entry and exit tubes, particularly in the 6-mm diameter vessel which was a straight tube. McLane¹² attempted to allow for this reaction by varying the length of the reaction vessel. This involves the subtraction of two quantities that are not very different and which are subject to significant experimental error. It seemed preferable to allow for the reaction occurring in the entry and exit tubes by calculating the total effective volume V_e of the whole volume within the furnace, that is, 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. Clearly,

$$V_e = \Sigma k_T T_m dV / k_{T_m} T,$$

where dV is a volume element at temperature T , and k_T , k_{T_m} are the velocity constants at temperatures T , T_m . A knowledge of the temperature distribution is thus required for each temperature T_m and flow rate studied, with the activation energies for the homogeneous and heterogeneous reactions, which determine the ratio $k_T:k_{T_m}$. Because of the differing activation energies for the homogeneous and heterogeneous reactions, the effective volume is different for the two cases. Successive approximation methods can easily be used to deduce the values of E_h , E_s from the experimental results.

A second problem is that of making allowance for the heterogeneous reaction. Although minimized by the use of an aged boric-acid-coated vessel, this is significant in the smaller vessels at the lowest temperatures. Preliminary experiments had indicated a transition from a low activation energy below about 440°C to a high activation energy above this temperature. The surface reaction was, therefore, investigated in the vessel with the largest surface-volume ratio at temperatures of 400°C and below. A variety of tests, some of which are shown in Fig. 1A, indicate that the percentage decomposition is constant over a ten-fold range of peroxide concentration. The velocity constant k_s for this surface reaction is not particularly reproducible. It varies ± 25 per cent over a period of days, but is more variable from coating to coating. In the 6 mm vessel, where k_s is greatest, the correction

for this surface reaction only amounts to 25 per cent of the total velocity constant, even at the lowest temperature (460°C) at which the homogeneous reaction was studied. In the larger vessels, the contribution is much smaller even at 440°C. To allow for this surface reaction, the percentage decomposition is determined under given conditions at 360°C, and the heterogeneous velocity constant at the higher temperatures is obtained by extrapolation. This extrapolation requires a knowledge of the activation energy E_s of the surface reaction, and from experiments in the temperature range 260 to 400°C (where the homogeneous reaction is either negligible or capable of being estimated with sufficient accuracy), a value of 5 ± 0.5 kcal was obtained. The maximum error in the homogeneous velocity constant k_h caused by this uncertainty in E_s is less than 2 per cent in the 6-mm diameter vessel

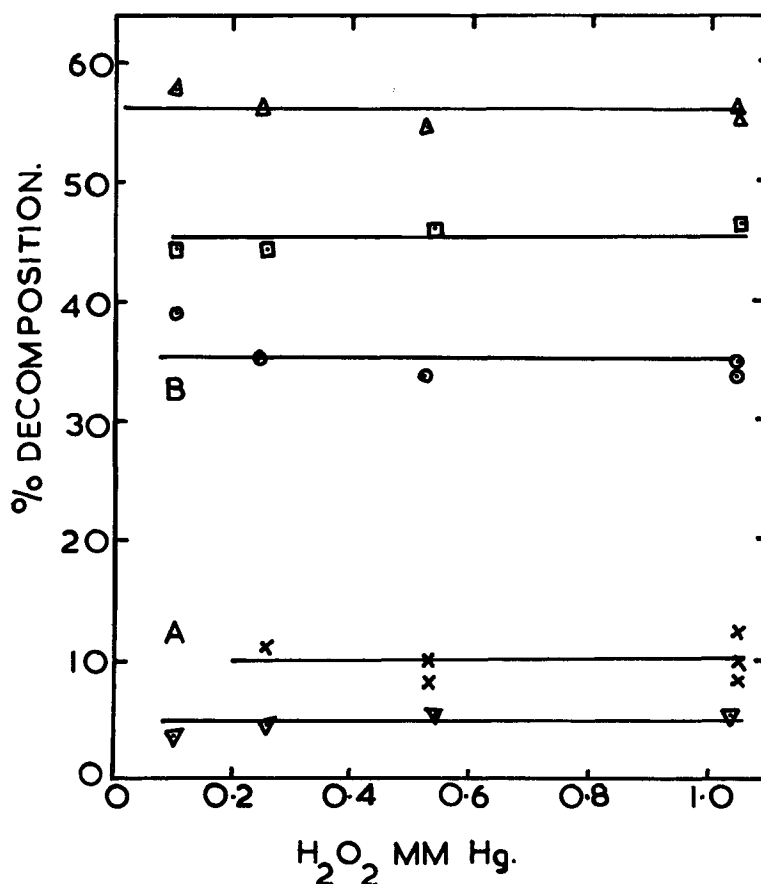


FIG. 1. Order of surface and homogeneous decomposition of H_2O_2 in aged boric-acid-coated vessel. A: Surface decomposition; \times , 6-mm diameter vessel, 360°C, $t = 6.0$ sec; ∇ , 6-mm diameter vessel, 400°C, $t = 0.4$ sec. B: Homogeneous reaction; \odot , 12-mm diameter vessel, 500°C, $t = 0.9$ sec; \triangle , 12-mm diameter vessel, 520°C, $t = 0.9$ sec; \square , 23-mm diameter vessel, 480°C, $t = 3.0$ sec.

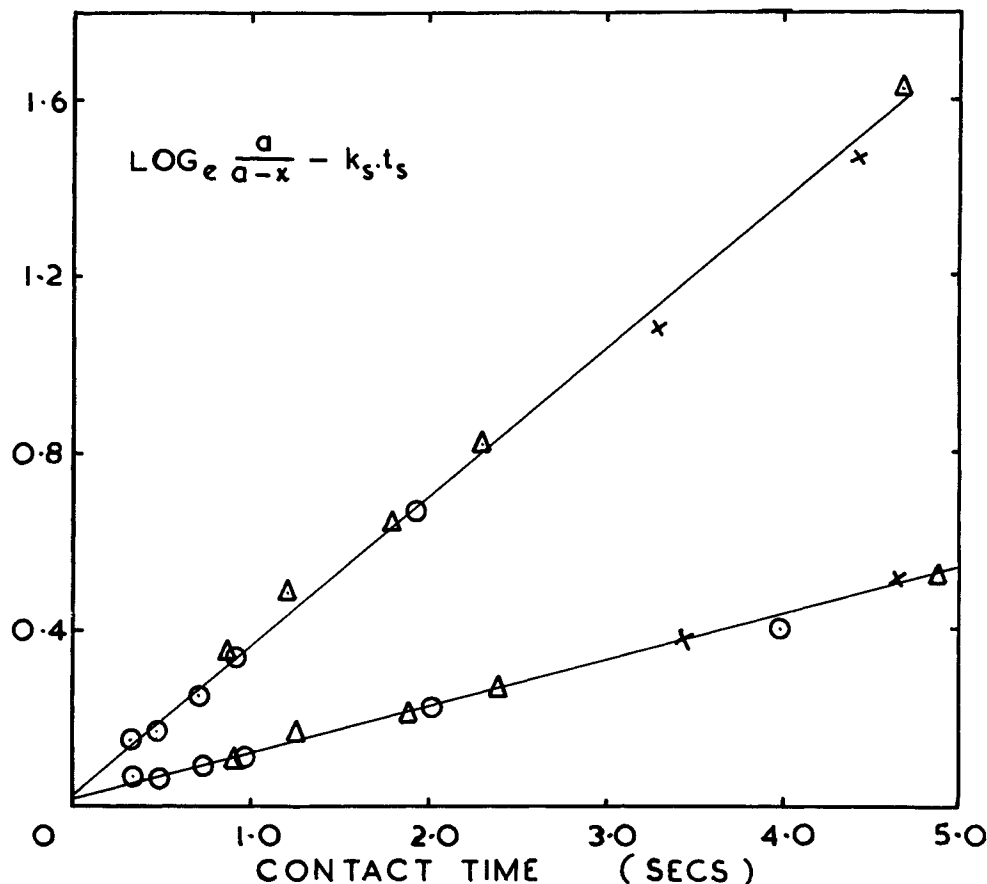


Fig. 2. First-order plot for decomposition of H_2O_2 . X, 23 mm diameter Δ, 12 mm O, 6 mm; Upper plot 489°C; lower plot 459°C.

at the lowest temperature and the error becomes much smaller as the temperature and vessel diameter are increased.

THE HOMOGENEOUS REACTION

As shown in Figure 1B, the percentage decomposition at a fixed contact time remains constant over a ten-fold range of peroxide concentration. The fact that both the surface and homogeneous reaction have the same order is particularly convenient, because the integrated rate expression can now be written:

$$\log_e a/(a-x) = k_s t_s + k_h t_h \quad (\text{i})$$

The effective contact times t_s , t_h are obtained by dividing the effective volumes V_s , V_h by the volume flow rate at the maximum temperature along the vessel length. By varying both vessel diameter and flow rate, the contact time can be varied over a range from 0.3 to 20 sec. The linear

relation between $[\log_e a/(a-x) - k_s t_s]$ and t_h confirms the first-order nature of the reaction and enables k_h to be accurately determined. The results obtained are independent of vessel diameter. This is shown in Figure 2, which gives the above plot over a wide range of contact times obtained by varying the flow rate and vessel diameter. Figure 3 shows the values^a of the velocity constant k_7 over the range 440 to 560°C for the three vessel diameters. The agreement confirms that adequate allowance has been made for the surface reaction, and that the homogeneous process is independent of diameter. From the gradient of Figure 3, $E_7 = 45.5 \pm 0.5$ kcal.

Calculations with the formula given by McLane¹² show that the effect of radial diffusion can be entirely neglected, although the effect of longitudinal diffusion only affects k_h by about 5

^a As shown later, k_h and k_7 are related by the equation: $k_h = 2k_7[M']$

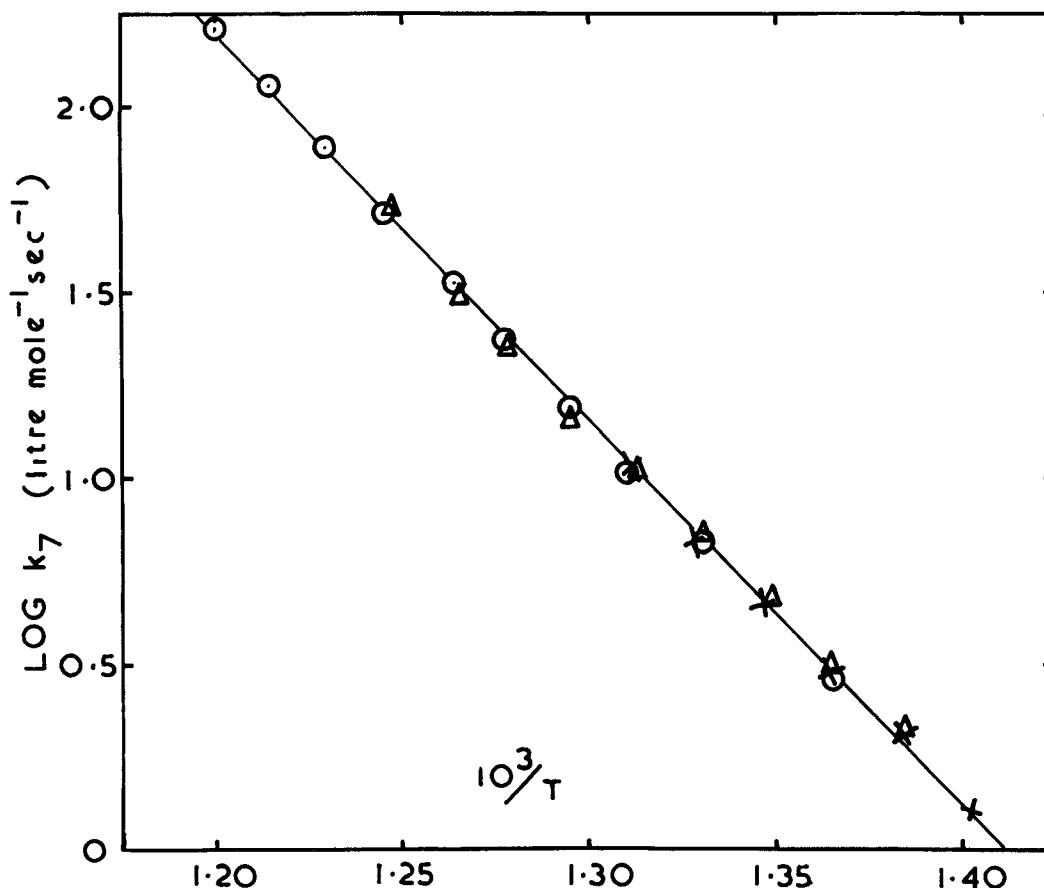


Fig. 3. Variation of velocity constant with vessel diameter and temperature. \times , 23 mm diameter Δ , 12 mm \circ , 6 mm.

per cent in the largest vessels at the highest temperatures. In the 12 mm vessel, the maximum effect of diffusion on k_h is less than 1 per cent, whereas in the 6 mm vessel it is negligible. The data given in Figures 2 and 3 have been corrected for such diffusion by methods that need not be detailed here. Allowance has been made for slight variations of pressure from the standard figure of 760 mm Hg.

Figure 4 shows the combined plot of the present results and those of other workers.^b The value for k_7 of $1.7 \times 10^{14} e^{-46,300/RT}$ mole⁻¹ liter sec⁻¹ agrees well with the value of $8.5 \times 10^{13} e^{-45,500/RT}$ obtained from Figure 3.

The above rate constant may be analyzed in terms of the low-pressure limit expression¹³ ob-

^b The authors are grateful to Doctor J. B. Prothero for providing the data from Figure 3 of reference 11.

tained from the Rice-Ramsperger¹⁴-Kassel¹⁵ theory of unimolecular reactions:

$$k_7 = \frac{Ze^{-E/RT}(E/RT)^{s-1}}{(s-1)!}$$

where s is the number of oscillators. The observed activation energy E_7 is then given by:

$$E_7 = E - (s - \frac{3}{2})RT.$$

Taking $Z = 2.8 \times 10^{11}$ mole⁻¹ liter sec⁻¹, a value of $s = 4$ satisfies most closely the expression for k of $1.7 \times 10^{14} e^{-46,300/RT}$. This gives a value for E of 50.1 ± 1.0 kcal which is consistent with the value of $\Delta H_{298}^0 = 50.3 \pm 0.7$ kcal given by Gray,¹⁶ and from which a value for the dissociation energy (ΔU_0^0) of 49.3 ± 1 kcal may be estimated.

The first-order nature of the decomposition clearly excludes a chain process involving (6),

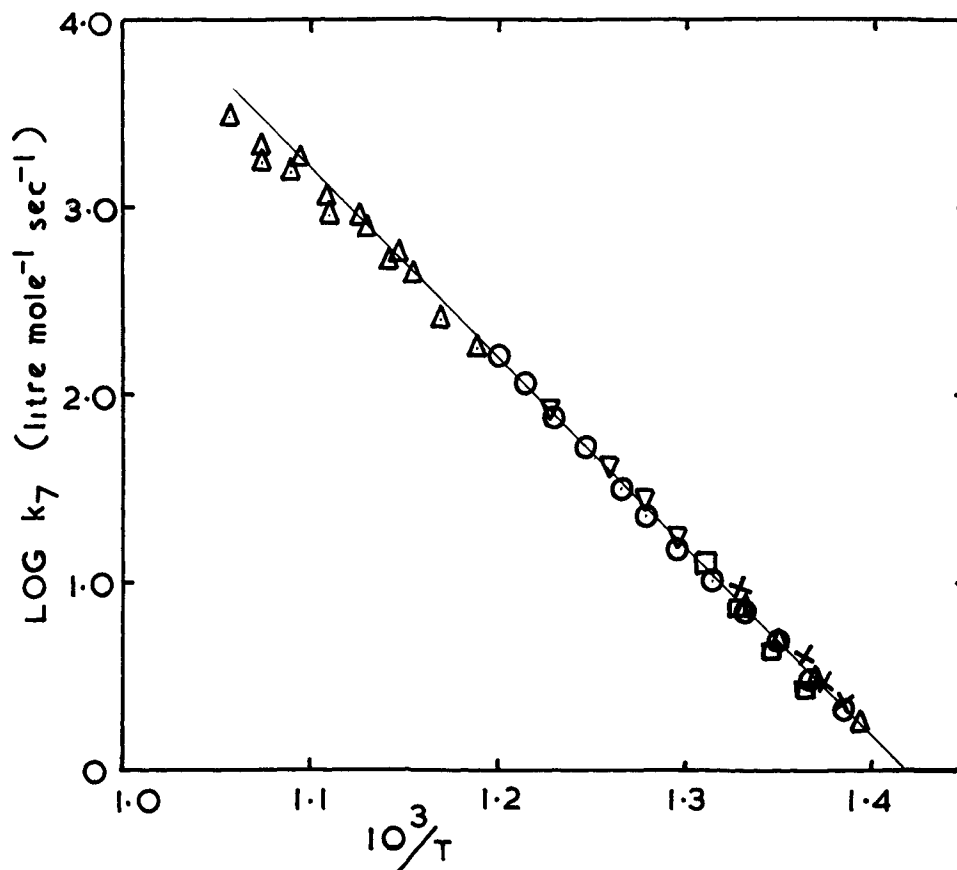


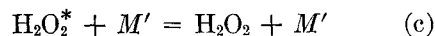
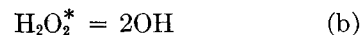
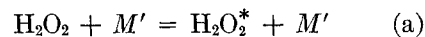
FIG. 4. Comparison of velocity constants for homogeneous decomposition of H_2O_2 . X, Giguère and Liu; Δ , Hoare, Prothero and Walsh; ∇ , McLane; \square , Satterfield and Stein; \circ , Present work.

since this would give an order $\frac{3}{2}$ or 2, depending on whether the chain-termination process was the gas-phase reaction (10), or a surface removal of HO_2 .

DECOMPOSITION AT REDUCED PRESSURE

Preliminary studies over a range of pressures from 25 to 760 mm Hg have been made in a 12-mm diameter vessel. This diameter was selected as giving the best compromise for minimizing surface effects (which increase as the diameter is reduced) and diffusion effects (which increase as the diameter is increased and the pressure reduced). The apparent homogeneous velocity constant k_h was found to be roughly proportional to the pressure. Because of this, the range of temperature and contact time that could be investigated was limited, since a percentage decomposition less than 20 per cent or greater than 80 per cent was undesirable, owing to the uncertainty which the limited accuracy of

determination (± 2 per cent) then introduced into the velocity constant. In most cases, therefore, a single contact time was used, and k_h calculated from the percentage decomposition with (i). Typical results are given in Figure 5 which shows that k_h is markedly dependent on total pressure, indicating that the dissociation is the bimolecular reaction $\text{H}_2\text{O}_2 + M' = 2\text{OH} + M'$, or more strictly, a unimolecular reaction in its second-order range. This point may be clarified by applying the Lindemann mechanism for unimolecular reactions:



which gives

$$\frac{-d[\text{H}_2\text{O}_2]}{dt} = \frac{k_a k_b [\text{H}_2\text{O}_2][M']}{k_b + k_c [M']} \quad (\text{ii})$$

In the second-order range, $k_b \gg k_c[M]$ and the rate becomes:

$$-d[\text{H}_2\text{O}_2]/dt = k_a[\text{H}_2\text{O}_2][M'].$$

Figure 5 shows, however, that the plot of k_h against total pressure does not pass through the origin, making a negative intercept on the pressure axis. This could be explained if H_2O_2 were more efficient than N_2 as the second molecule in (a), but the value of the intercept requires relative efficiencies of about 50, whereas direct tests, and data obtained by other workers,^{10, 11} suggest a value of 6. It seems doubtful whether the effect can be attributed to a contribution from $k_c[M]$

in the denominator of (ii), because the plot of $\frac{[M']}{k_h}$ against $[M']$ is markedly curved.

The method adopted by earlier workers^{10, 11} would hardly reveal the existence of this effect. Forst found an over-all first-order velocity constant that increased linearly with pressure as in Figure 5, but made no attempt to allow for the heterogeneous reaction, and assumed that the intercept of his plot measured the surface reaction, since the homogeneous velocity constant should be zero at zero pressure. Hoare, Prothero and Walsh compare the velocity constant at a temperature of about 650°C and a few mm Hg

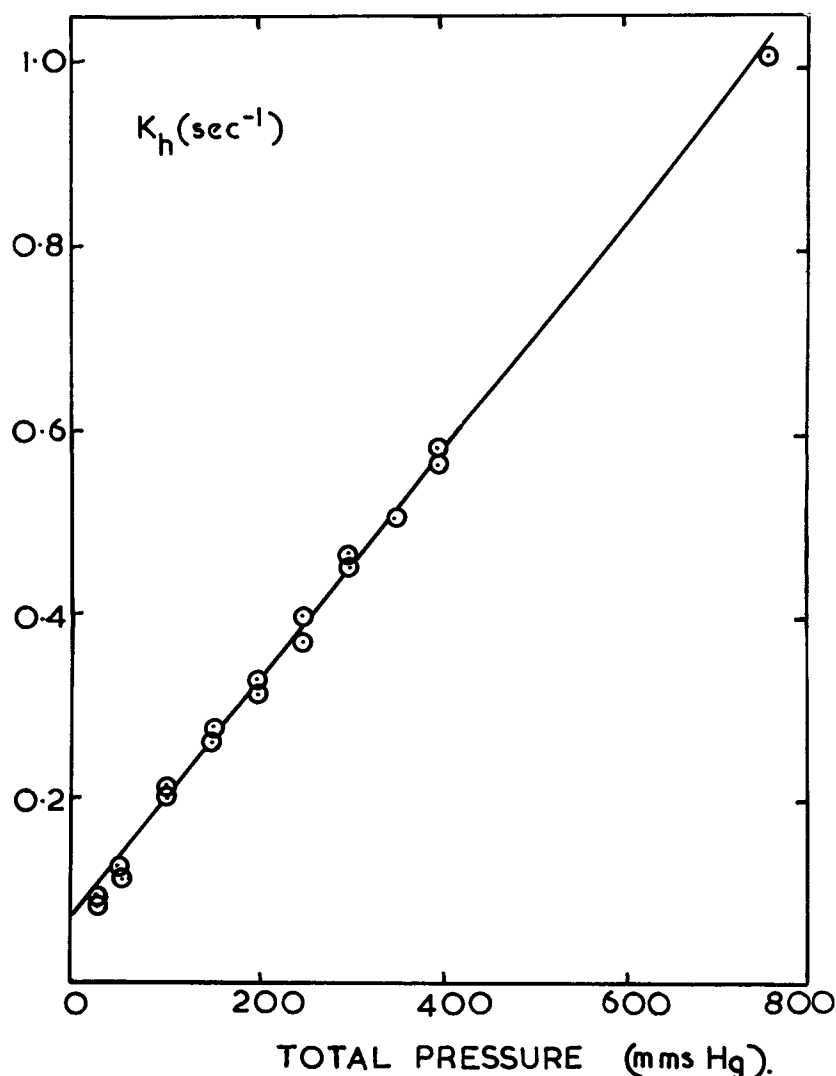


FIG. 5. Variation of k_h with pressure; 12-mm diameter vessel, 518.5°C

pressure, with that obtained at about 500°C with 760 mm Hg of nitrogen as carrier gas. The evaluation of the effect of pressure depends first on the value of the activation energy used to extrapolate k_h at 500 to 650°C, and second on the relative values used for the efficiencies of N_2 , H_2O and H_2O_2 in reaction (7). While there is little doubt from their results that k_h is markedly dependent on pressure, the sensitivity of the calculation to the factors noted makes it doubtful whether an effect similar to that shown in Figure 5 would be detected. Further tests are needed to decide whether this anomaly is real, or merely an accumulation of small experimental errors.

RELATIVE EFFICIENCIES OF DIFFERENT MOLECULES

Table 1 summarizes the results obtained by different workers for the efficiencies relative to N_2 as unity.

DECOMPOSITION IN THE PRESENCE OF HYDROGEN

The decomposition in the presence of H_2 was studied in a 12-mm diameter vessel at atmos-

pheric pressure, the mole fraction of H_2 varying from 0.02 to 1.0. Because of the marked accelerating effect of H_2 , the reaction was studied at the relatively low temperature of 440°C. Contact time was varied by alteration of the flow rate.

TABLE 1

Molecule	$H_2O_2 + M'(7)$			$H + O_2 + M(4)$
	Forst*	Hoare, Prothero and Walsh	Baldwin and Brattan	
H_2O_2	5.4	5.9	6.6	
H_2O	4.0	4.3	6.0	25-35
O_2	(0.78)	0.71	0.78	0.78
A			0.67	0.47
He	0.57	0.53		0.83
CO_2		1.24		3.4

* The results obtained by Forst were compared to O_2 , and a value for O_2 of 0.78 relative to N_2 has been used in converting his figures to the values above.

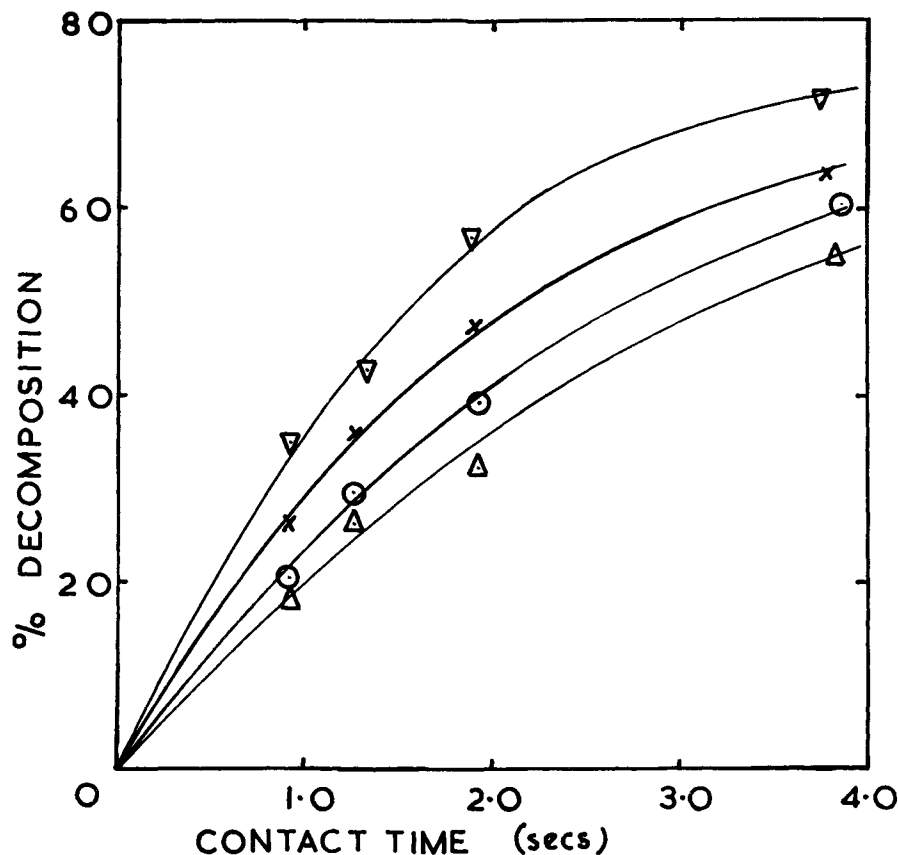


FIG. 6. Decomposition of H_2O_2 in the presence of H_2 . 12-mm vessel at 440°C; $x = 0.097$. Total pressure, 750 mm Hg; ∇ , 0.171 mm Hg H_2O_2 \times , 0.345 mm \odot , 0.683 mm Δ , 1.02 mm.

Preliminary experiments showed that at low mole fractions of H_2 , the order with respect to H_2O_2 was less than unity; typical results over a six-fold range of concentration are shown in Figure 6, the $t_{1/2} - [H_2O_2]$ relation indicating an order of about 0.7. In contrast, with pure H_2 as carrier gas, the half-life relation suggested an order of approximately 1.5.

Because the accelerating effect of H_2 depends on the $[H_2]:[H_2O_2]$ ratio, the use of the function method to study the kinetics is unsatisfactory, and initial rate measurements are indicated. To avoid limitations in accuracy consequent on drawing initial tangents to rather ill-defined curves, the following procedure was adopted. At each mole fraction of H_2 , the order with respect

to peroxide was determined by the use of the half-life time at two initial concentrations of peroxide. The appropriate function for this order was then plotted, and the mean line (or the initial tangent if slight curvature is apparent) was used to obtain an apparent velocity constant k' , from which the initial rate was calculated with the use of the relation: Initial rate = $k'[H_2O_2]^n$. The values taken for n were 0.7 for mole fractions (x) of H_2 up to 0.5; 1.0 for $x = 0.75$; and 1.5 for $x = 1.0$.

Fig. 7 shows the variation of initial rate with x for two initial concentrations of H_2O_2 . In each case, the initial rate increases linearly with x initially, then a maximum is reached, and the rate then decreases as x is further increased.

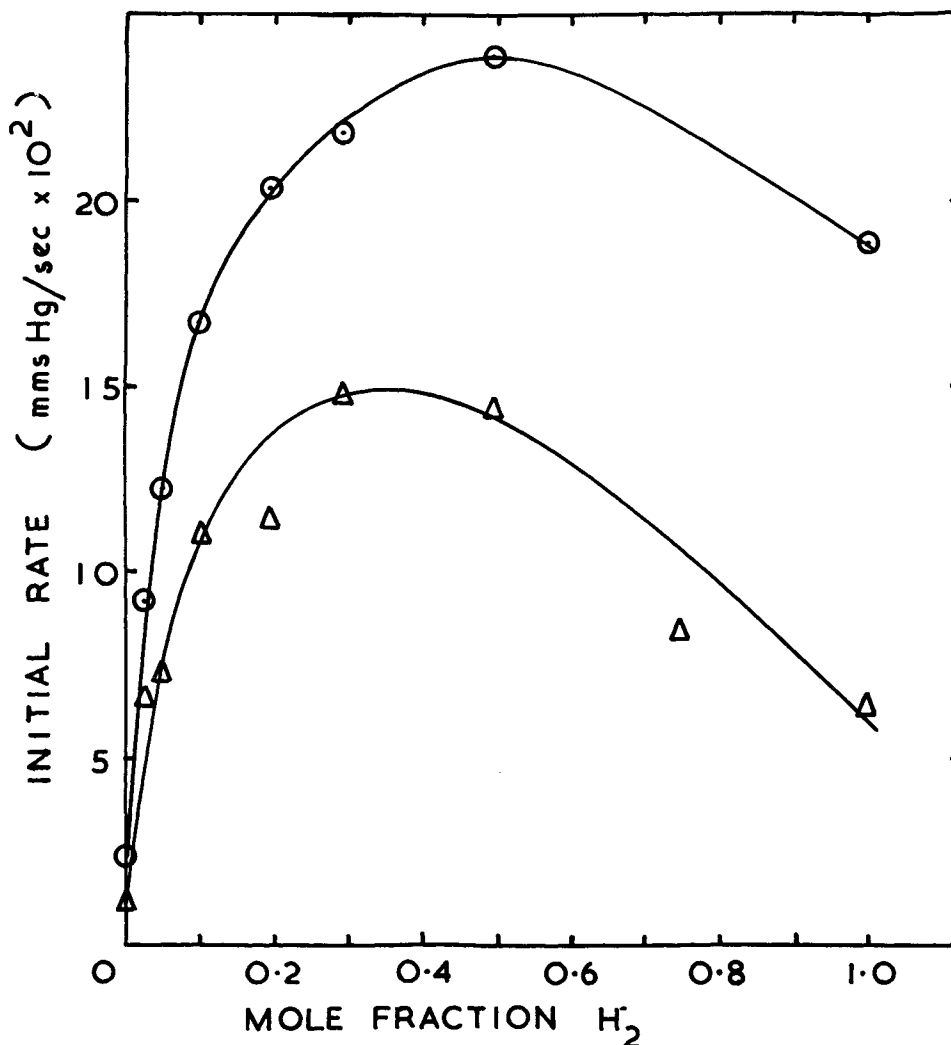
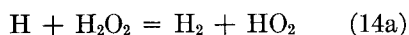
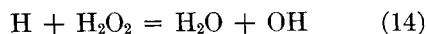
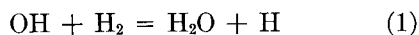


FIG. 7. Variation of initial decomposition rate with mole fraction of H_2 . 12-mm diameter vessel, $440^\circ C$; Δ , 0.34 mm Hg H_2O_2 \circ , 0.68 mm.

In the absence of H_2 , a mechanism involving reactions (7), (15) and (10) gives a net reaction rate:

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

Taking the value of 7 obtained by Baldwin and Mayor⁷ for the ratio $k_{15}:k_1$ at 500°C, the majority of OH radicals will undergo reaction (1) once the partial pressure of H_2 exceeds about 20 mm Hg. Two possible reactions, (14) and (14a), may be written for the reaction of H atoms with H_2O_2 :



If (14a) predominates, the net rate will still be given by (iii); the only increase in rate is due to the increase in $[M']$ on addition of H_2 . Assuming that the relative coefficients of H_2 and N_2 are the same in reactions (4) and (7), calculation shows this effect to be small. If, however, (14) predominates, then the decomposition becomes a chain process through reactions (7), (1), (14), chain termination occurring through (15) followed by (10). The rate expression then becomes:

$$R = -d[H_2O_2]/dt \quad (\text{iv})$$

$$= 2k_7[H_2O_2][M'](1 + k_1[H_2]/k_{15}[H_2O_2])$$

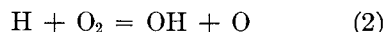
A plot of $R/[M']$ against H_2 at constant H_2O_2 should thus give a linear relation. Figure 7 shows that this occurs in the early stages, but that the rate reaches a maximum and then decreases at higher mole fractions. Since, assuming $k_{15}/k_1 \approx 7$, $k_1[H_2]/k_{15}[H_2O_2] \approx 100$ with pure H_2 as carrier gas, some other chain-termination process must operate to reduce the chain length to the value of about 3 to 5 observed with pure H_2 . Two possibilities may be suggested:

(1) If (14a) occurs to a slight extent, then the limiting chain length becomes $(k_{14} + k_{14a})/k_{14a}$. This is shown by the rate expression which becomes:

$$R = \frac{-d[H_2O_2]}{dt} \quad (\text{v})$$

$$= 2k_7[H_2O_2][M'] \left[\frac{k_1[H_2] + k_{15}[H_2O_2]}{\alpha k_1[H_2] + k_{15}[H_2O_2]} \right]$$

where $\alpha = k_{14a}/(k_{14} + k_{14a})$. This expression, however, would require $R/[M']$ to reach a limiting value as $[H_2]$ increases, and would not account for the maximum found experimentally.



(2) With the values $k_{14}/k_2 = 268$ at 500°C and $(E_2 - E_{14}) = 8.6$ kcal given by Baldwin and Mayor,⁷ a value for k_{14}/k_2 of 430 may be estimated at 440°C. Since $k_2/k_4 \approx 5$ mm Hg ($M = H_2$) at 440°C, the ratio $k_{14}/k_4[M] \approx 3$ when $M = 760$ mm Hg of H_2 . Thus with $[H_2O_2] = 0.68$ mm Hg, the ratio of reactions (14) and (4) would be 5 at a partial pressure of 0.4 mm Hg of O_2 . The oxygen may arise either from the decomposition of the H_2O_2 , in which case the reaction should show self-inhibition, or from the presence of O_2 as an impurity in the H_2 . Although use of the initial rate should overcome the difficulty of self-inhibition, this may not have been entirely achieved, because in many cases, high decomposition was obtained even at the shortest possible contact time. The presence of about 0.05 per cent of O_2 in the H_2 is an alternative possibility, and tests with O_2 -free H_2 are planned. If, at high mole fractions of H_2 , the limiting chain length is determined by competition between (14) and (4), then the rate expression becomes:

$$-d[H_2O_2]/dt = 2k_7[H_2O_2][M'] \cdot \frac{k_{14}[H_2O_2]}{k_4[O_2][M]}$$

and the order with respect to H_2O_2 should approach two, whereas (v) requires an order between 0 and 1. The order with respect to peroxide does rise to about 1.5 or higher at the highest mole fractions of H_2 , which supports this explanation. It may be concluded that the fall-off in rate at high mole fractions of H_2 can certainly be attributed to the occurrence of (4) and possibly also to (14a).

From the initial gradient of the plot of $R/[M']$ against $[H_2]$, when the effects of both (4) and (14a) may be neglected, the value of k_{15}/k_1 is obtained as approximately 6. This confirms the value obtained from a study of the slow reaction between H_2 and O_2 in aged boric-acid-coated vessels.⁷

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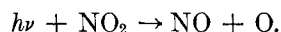
THERMAL MECHANISMS RELATED TO THE PHOTOLYSIS OF NITROGEN DIOXIDE^a

By HADLEY FORD

Introduction

The photolysis of nitrogen dioxide is pertinent to the discussion of combustion processes, especially since materials such as N₂O₄ and HNO₃ are popular oxidants in large propellant systems. When such oxidants are used, elementary reactions occur which are identical with those occurring when NO₂ is photolyzed.

When nitrogen dioxide is irradiated in the 3100 to 3700 Å region, atomic oxygen is produced in the primary photochemical step:



Depending on the particular experimental conditions, the atomic oxygen is present in a reactive matrix consisting of such varied species as O₂, O₃, NO, NO₂, NO₃, N₂O₄ and N₂O₅. Studies of the secondary reactions have led to a general quantitative mechanism which fits the facts under

widely varied conditions. The elementary reactions which constitute the mechanism are also present in a number of thermal decompositions. The photolysis of nitrogen dioxide has thus served to confirm values for rate constants measured in these thermal reactions and, in some cases, provides quantitative relationships between otherwise diverse phenomena.

At room temperature the photolysis of nitrogen dioxide has been discussed in terms of the following reactions:^b



^b See H. Ford, Seven Mechanisms in the Photolysis of Nitrogen Dioxide, Progress Report 20-393, Jet Propulsion Laboratory, California Institute of Technology, Pasadena 3, California (1960), for a detailed discussion.

^c The NO₃ and NO₃^{*} are presumed to be in the triangular and not the peroxy form in these mechanisms.

^a This report presents one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. DA-04-495-Ord 18, sponsored by the Department of the Army, Ordnance Corps.