# THE THERMAL DECOMPOSITION OF HYDROGEN PEROXIDE VAPOUR

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A flow system has been used to investigate the decomposition of hydrogen peroxide vapour between the temperatures of 241 and 659°C. It is shown that above 420°C a homogeneous decomposition predominates which is second-order and occurs by the reactions :

$$H_2O_2 + M \rightarrow 2OH + M,$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2,$$
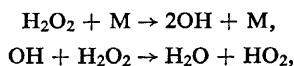
followed, under our conditions, probably by

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2.$$
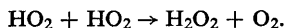
The first reaction, which is rate-determining, occurs at a velocity depending upon the efficiency of M; the experimental order of efficiencies being

$$H_2O_2 > H_2O > CO_2 > N_2 > O_2 > He.$$
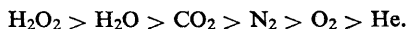
When hydrogen peroxide is taken as M the rate constant of the first reaction is calculated to be $10^{15.4} \exp(-48000/RT)$ l. mole^{-1} sec^{-1}.

It is shown that the results of other workers are all consistent with the above reaction scheme and rate constant.

Although there have been several recent investigations into the kinetics of the decomposition of hydrogen peroxide vapour,[1, 2, 3] there is no general agreement with respect to the order of the reaction or the magnitude of the activation energy. Yet this subject is of considerable importance to the developing knowledge of unimolecular reactions and also of the oxidation of many gaseous fuels that form hydrogen peroxide as an intermediate product of combustion. It was therefore considered appropriate to attempt another study of the reaction.

It was the purpose of this work to obtain definite information about the order and activation energy of the reaction; and, if possible, to correlate the apparently contradictory earlier work. The achievement of the latter aim can be illustrated by fig. 3 which successfully correlates the results of the present work with those of the three main earlier investigations.

EXPERIMENTAL

One of the chief experimental difficulties involved in this work is the elimination of heterogeneous decomposition. McLane[1] used reaction vessels coated with boric acid. Giguère and Liu[2] found that this coating was unsatisfactory and recommended the use of clean Vycor glass. On the other hand, Satterfield and Stein[3] used phosphoric acid-coated vessels, which might have different degrees of hydration according to the water content of the gaseous mixture. In the present work it was decided to use Pyrex and silica vessels which had been cleaned by rinsing with 40 % hydrofluoric acid. It has been shown that Pyrex and silica surfaces so cleaned are effective in the preservation of liquid and gaseous hydrogen peroxide.[4, 5, 6]

Flow techniques were used. The first series of experiments employed a Pyrex vessel (38 mm int. diam. and 20 cm long) and an inert gas at 1 atm pressure as carrier, the hydrogen peroxide being decomposed at 241 to 478°C. 85 % hydrogen peroxide (containing non-volatile stabilizer) was stored in 2 or 3 bubblers whose temperatures could be

adjusted to vary the vapour pressure of hydrogen peroxide. The carrier gas (taken straight from a cylinder), after saturation with hydrogen peroxide, was passed through a preheater into the reaction vessel and thence to a trap constructed to the design of Volman.[7] This trap was cooled in liquid air and was shown to be properly efficient in condensing the hydrogen peroxide. The whole apparatus was washed with hydrofluoric acid before use and the traps were so washed after each experiment. Contact times were calculated from measurements of the flow rate of the gas with a capillary flow-meter calibrated by a rotameter. On any run, the hydrogen peroxide not decomposed in the reaction vessel accumulated in the trap and was estimated by titration with acid potassium permanganate solution (0·01 N). In practice it was found that the most reproducible results were obtained if the apparatus was allowed to run for 1 h before the hydrogen peroxide was trapped for a measured period. The vapour pressure of hydrogen peroxide was accurately found by running the apparatus whilst the furnace was cold.

In order to determine whether carrier gas pressure had any effect, it was necessary to build another apparatus in which the gases were circulated continuously by a mercury diffusion pump. The design of Gowenlock, Polanyi and Warhurst [8] was followed fairly closely for this apparatus. It was then found possible to obtain reasonable rates of flow at pressures from 3·5 to 7·0 mm of carrier gas. Some restriction in flow was caused by the passage of the gases, after removal of water and hydrogen peroxide, through a heated tube containing copper. The latter removed oxygen produced by the decomposition. Because of the low pressures used, no pre-heater was required; but, for the same reason, it was necessary to use lower vapour pressures of hydrogen peroxide so that the carrier gas was in fair excess. Variations in rate of decomposition with carrier gas nature were thus more clearly demonstrated.

The slower rate of decomposition at lower pressures necessitated the use of higher temperatures; a silica vessel (24·5 mm int. diam. and 14 cm length) was employed at 569 to 659°C. It was found that after 15 min a stationary state was reached and reproducible results could be obtained. This time probably represented that necessary for conditioning the surfaces of the apparatus and saturating the very limited amounts of silicone grease which were exposed.

For the low-pressure work, the carrier gases used (except carbon dioxide) were taken from cylinders and dried by passage through a liquid-air trap. Carbon dioxide was purified by sublimation. Also for the low-pressure work, 85 % hydrogen peroxide was used without stabilizer except in a few experiments where 99·2 % (without stabilizer) was used. In some experiments, no carrier gas was employed. In these, 99·2 % hydrogen peroxide was allowed to distil through the furnace to the trap, the oxygen produced being continuously pumped away.

RESULTS

CARRIER GAS AT 1 ATM PRESSURE

In these initial experiments, a simple apparatus was used. The greatest experimental difficulty was the appreciable time taken for the gases to attain the temperature of the furnace (several seconds). This is illustrated in fig. 1. However, it was still possible to make valid deductions about the kinetics of the system.

The first problem concerned the determination of the order of the reaction with respect to hydrogen peroxide. The order had been found by Giguère and Liu [2] to be unity and by Satterfield and Stein [3] to be 1·5. The time taken for the concentration of hydrogen peroxide to be halved ($t_{\frac{1}{2}}$) should be independent of the initial concentration for a first-order reaction but should be inversely proportional to the square root of the concentration for a 1·5 order reaction. Fig. 1 shows that at 434°C, $t_{\frac{1}{2}}$ does not decrease with increase in hydrogen peroxide concentration. Therefore it is likely that the reaction is first-order. In fig. 2 it is shown in fact that a plot of log $[H_2O_2]$ against time yields a straight line plot as expected for a first-order reaction. Consistent first-order rate constants were obtained from such plots over the 6-fold range of hydrogen peroxide pressures used for the experiments recorded in fig. 1, viz., 0·049, 0·059, 0·053 sec⁻¹ for initial pressures of 3·1, 1·50, 0·49 mm respectively.

Experiments were performed over the temperature range 241 to 478°C and rate constants were deduced from the amount of decomposition occurring in a known time (due allowance being made for the small " induction period "). The results are illustrated in the inset to fig. 2. A discontinuity is observed at *ca.* 420°C. The reaction below 420°C was shown as above to have $t_{\frac{1}{2}}$ independent of the hydrogen peroxide pressure, i.e. to be

first-order; and to be increased in rate by an increase in the surface/volume ratio. Taken in conjunction with the results of others,[2, 3] it is clear, therefore, that the discontinuity at *ca.* 420°C is due to heterogeneous reaction predominating below this temperature and
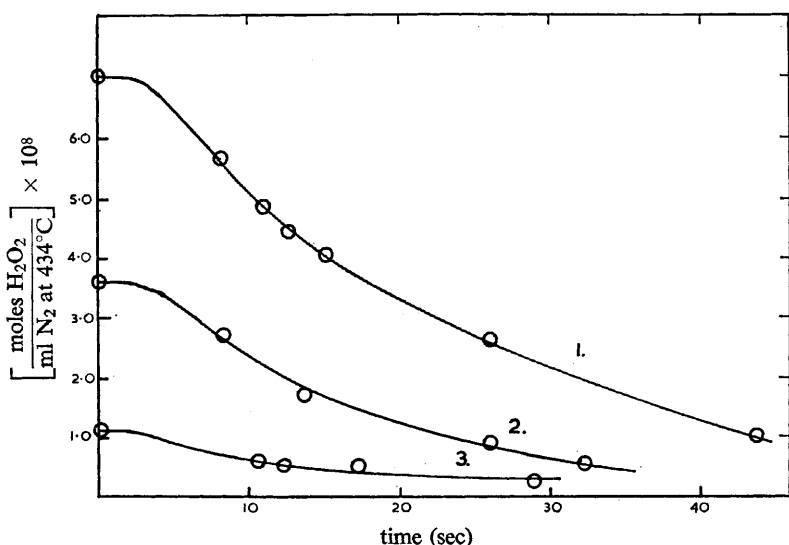

FIG. 1.—The decomposition of hydrogen peroxide in the presence of 1 atm of nitrogen in a Pyrex vessel at 434°C. Initial concentrations: (1) 7.0×10^{-8} mole/ml, (2) 3.6×10^{-8} mole/ml, (3) 1.1×10^{-8} mole/ml. These correspond to 3.1, 1.5 and 0.49 mm Hg respectively.
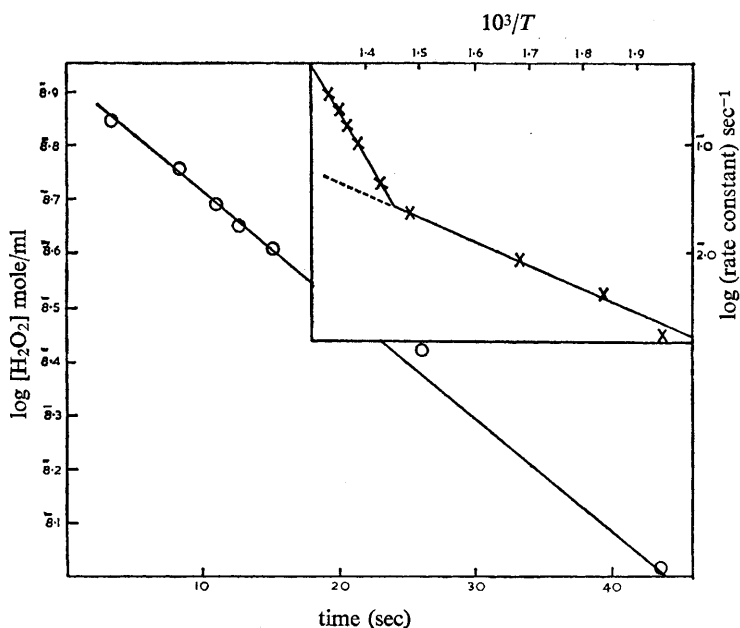

FIG. 2.—The decomposition of hydrogen peroxide in the presence of nitrogen in a Pyrex vessel at 434°C; initial concentration $= 7.0 \times 10^{-8}$ mole/ml $= 3.1$ mm Hg.
INSET.—Variation with temperature of the first-order rate constants for the decomposition of hydrogen peroxide in the presence of 1 atm of nitrogen in a Pyrex vessel.

homogeneous reaction above this temperature. Others [2, 3] have found the discontinuity temperature to vary between 390 and 420°C according to the vessel used. The heterogeneous reaction was found to have an activation energy of 10 kcal/mole (cf. ref. (2), (3)). After correction for the heterogeneous reaction, an activation energy for the homogeneous reaction of 48 ± 4 kcal/mole was obtained.

The results shown in the inset to fig. 2 imply that at 434°C a substantial fraction of the total rate of decomposition is still due to heterogeneous reaction. However, the fact that the total rate is still first-order implies that the homogeneous reaction rate, like the heterogeneous, is first-order with respect to hydrogen peroxide. Further data, obtained at 486°C (where the fraction of reaction proceeding heterogeneously is small) support this conclusion.

A few experiments were performed with 1 atm of helium, carbon dioxide or oxygen as a carrier gas instead of nitrogen. The rate of hydrogen peroxide decomposition was found to decrease in the order $CO_2 > N_2 > O_2 > He$. This suggested that the first step in the decomposition of hydrogen peroxide is

$$H_2O_2 + M \rightarrow products. \tag{1}$$

Since hydrogen peroxide and water might be expected to be particularly efficient as M (see later), this suggestion would explain why Satterfield and Stein (who used no carrier gas) obtained rates of decomposition which were about four times those which we obtained using nitrogen as a carrier gas. From such considerations, it became clear that it was important to examine the effect of changing the concentration of inert gas M, i.e. that a new apparatus designed for sub-atmospheric pressures was necessary for further progress.

CARRIER GAS AT LOW PRESSURES

In the low-pressure work, greater accuracy was obtained and there was no appreciable " induction period " necessary for the gases to reach the temperature of the furnace. The results are set out in table 1. When nitrogen was used as an inert gas, variation of the hydrogen-peroxide pressure had little effect upon the rate constant calculated by assuming the rate at constant temperature to be proportional only to the hydrogen-peroxide concentration. This, and also experiments in which the assumed first-order rate constant was shown to be hardly affected by a 40 % change in the contact time, indicate that the reaction is indeed approximately first-order with respect to hydrogen peroxide. But an increase in the carrier gas pressure did increase the rate constant. This effect was particularly clearly shown in the experiments using oxygen and carbon dioxide as carrier gases. To test it further we made a comparison with our high-pressure experimental

TABLE 1.—THE DECOMPOSITION OF HYDROGEN PEROXIDE AT 646°C

H_2O_2 (liq)	carrier gas	$P_{H_2O_2}$ (mm)	P_{H_2O} (mm)	$P_{inert\ gas}$ (mm)	P total (mm)	k (sec^{-1})
%						
85	N_2	0·27	0·53	4·0	4·8	0·40
85	N_2	0·27	0·53	4·0	4·8	0·43
85	N_2	0·113	0·20	5·0	5·3	0·47
85	N_2	0·113	0·20	5·5	5·8	0·41
85	N_2	0·113	0.20	6·6	6·9	0·45
85	N_2	0·113	0·20	6·7	7·0	0·55
85	CO_2	0·113	0·20	2·8	3·1	0·25
85	CO_2	0·113	0·20	4·0	4·3	0·38
85	CO_2	0·113	0·20	6·6	6·9	0·56
85	O_2	0·113	0·20	4·0	4·3	0·23
85	O_2	0·113	0·20	5·0	5·3	0·28
85	O_2	0·113	0·20	6·1	6·4	0·35
85	He	0·113	0·20	5·3	5·6	0·26
85	He	0·113	0·20	6·3	6·6	0·28
99·2	He	0·16	0·015	5·8	6·0	0·25
99·2	He	0·16	0·015	4·7	4·9	0·20
99·2	He	0·44	0·04	6·1	6·6	0·35
99·2	He	0·51	0·05	2·9	3·5	0·20
99·2	—	1·45	0·15	—	1·6	0·57
99·2	—	1·45	0·15	—	1·6	0·55

results. The latter, by use of the experimental value of 48 kcal/mole for the activation energy, can be extrapolated to yield a rate constant for *purely* homogeneous reaction in the presence of 1 atm of nitrogen around 60 sec⁻¹ at 646°C. This is approximately 120 times the rate constant for pressures of nitrogen around 5 mm, i.e. around 1/150 atm.* Hence one can conclude that the reaction is not only first-order with regard to hydrogen peroxide but is also first-order with respect to carrier gas over the whole of this large pressure range. This conclusion is consistent with the initial step being reaction (1). As reported above, our previous results, using high pressures, indicated that different molecules varied in their efficiencies as M. At lower pressures, the same order of efficiency
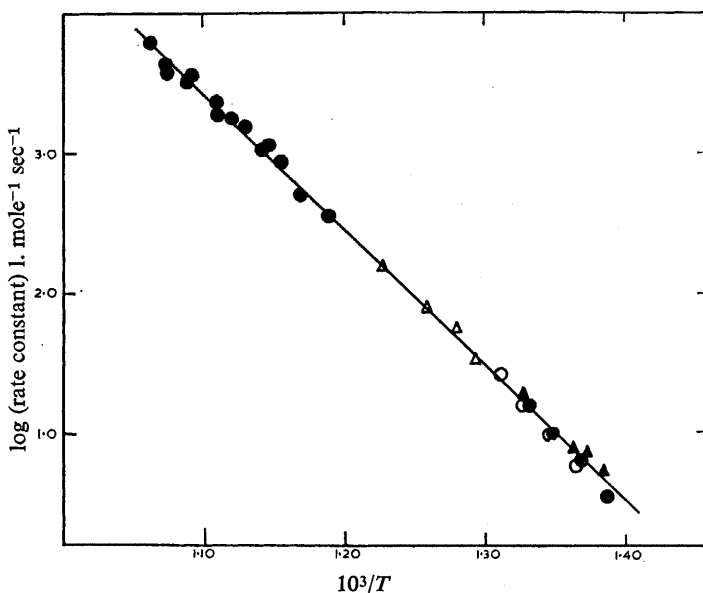

FIG. 3.—Variation with temperature of the second-order rate constants for hydrogen-peroxide decomposition (corrected so as to refer to nitrogen as inert gas). ● = present work, ○ = Satterfield and Stein,[3] ▲ = Giguère and Liu,[2] △ = McLane.[1]

—$CO_2 > N_2 > O_2 >$ He—was indicated by the magnitude of the rate constants obtained using these gases as carriers. In order to find the efficiencies of water and hydrogen peroxide as M, it was necessary to use 99·2 % hydrogen peroxide. A comparison of the rate constants with varying hydrogen peroxide and helium pressures showed that the efficiency as M of the former was eleven times that of the latter. Similarly, water was found to be eight times as efficient. Expressed as efficiencies compared with the efficiency of hydrogen peroxide as unity, the values for the other gases are He = 0·09, O_2 = 0·12, N_2 = 0·17, CO_2 = 0·21, H_2O = 0·73.

It was now possible to correct the rate constants derived using (for example) nitrogen as carrier gas, to allow for the high efficiency of the small amounts of water and hydrogen peroxide present. The true second-order rate constants for nitrogen gas as M were thus obtained over the temperature range 569 to 659°C. The results, illustrated in fig. 3, yield an activation energy of 45 ± 3 kcal/mole.

DISCUSSION

We have seen above that the decomposition of hydrogen peroxide occurs according to a second-order rate process. It was probably because of the greater efficiency of water and hydrogen peroxide as M and the small amounts of other

* The agreement is closer still if we allow for the fact that in the low-pressure work not only N_2 but also H_2O and H_2O_2 play important roles as M.

gases which they added that Giguère and Liu [2] failed to notice the effect of inert gases in their experiments.

It is important in experiments to determine the order of the reaction to keep the inert-gas pressure considerably higher than that of the hydrogen peroxide so that, e.g. as far as reaction (1) is concerned, in effect, only the inert gas plays the part of M. Otherwise the decomposition of hydrogen peroxide to water and oxygen, which have lower efficiencies as M, might cause an apparently higher order with respect to hydrogen peroxide. Under conditions of high inert-gas pressure it has been shown that the homogeneous decomposition is first-order with respect to hydrogen peroxide. This is in accord with the results of Giguère and Liu [2] and of McLane,[1] but differs from the conclusion of Satterfield and Stein [3] who obtained a 1·5 order. However, the latter used only a twofold change in pressure of hydrogen peroxide and did not have an inert-gas carrier. The results of Huang [9] which they report include only one experimental point (that at the lowest pressure) are inconsistent with a rate that is first-order with respect to hydrogen peroxide. It is likely that a first-order decomposition (with respect to hydrogen peroxide) was taking place even under the conditions used by Satterfield and Stein. Indeed, as Satterfield and Stein conclude, decomposition by a 1·5-order reaction implies a chain reaction; and Conway [10] has pointed out that such a chain reaction would mean an expected activation energy too low to be compatible with the experimental results of Satterfield and Stein.

If one recalculates the data of Satterfield and Stein assuming a first-order rate for the homogeneous reaction, one obtains an activation energy of about 39 kcal/mole. If the first-order rate constants for heterogeneous decomposition are extrapolated to higher temperatures and subtracted from the rate constants for total decomposition (cf. Giguère and Liu [2]) one obtains a corrected value of 50 kcal/mole for the activation energy of the homogeneous decomposition. This value is in reasonable agreement with the corrected value found from our own work at 428 to 478°C and with that of Giguère and Liu in the same temperature range. McLane obtained uncorrected values of 40 kcal/mole for the activation energy in a 7 cm^{-1} surface/volume ratio vessel and 50 kcal/mole in a 3-cm^{-1} ratio vessel. If one assumes that in the latter vessel there was little heterogeneous reaction but with the former a correction of the data is necessary for heterogeneous reaction, then McLane's data for both vessels are not necessarily inconsistent with an activation energy of approximately 48 kcal/mole.

The heterogeneous reaction has been shown to have an activation energy of approximately 10 kcal/mole (cf. Giguère and Liu [2]). There is some disagreement about the order of the reaction. Our own work indicates that the order is one; but at pressures below 1 mm it seems that the order is two [11, 12] and changes to one at higher pressures.[13]

In the present work, a surface reaction was predominant up to about 420°C at the higher pressures. Extrapolation of the heterogeneous and homogeneous reaction rates to higher temperatures and lower pressures would lead to the expectation that for the decomposition of 0·1 to 0·2 mm of hydrogen peroxied in the presence of 4 mm of nitrogen a heterogeneous reaction would not predominate above 580°C. However, if account is taken of the change to a second-order heterogeneous mechanism at low pressures of hydrogen peroxide, a temperature of about 530°C seems more likely for the changeover. In fact, experiments performed at 550°C showed that little heterogeneous reaction was taking place at this temperature. Hence the activation energy obtained for experiments performed between 569 and 659°C needs but little correction for heterogeneous reaction. Consistent with this is the higher uncorrected activation energy of 45 ± 3 kcal/mole found under these conditions. It is therefore clear that all the data mentioned above are consistent with an activation energy of ca. 48 kcal/mole, which is close to that expected from thermochemical data as the minimum energy necessary to break the O—O bond.[2]

In order further to demonstrate how the data obtained in the present work can be used to correlate other, apparently conflicting data, we have recalculated the rate constants for the work of Giguère and Liu,[2] Satterfield and Stein[3] and McLane,[1] assuming first-order dependence on both hydrogen peroxide and M and using the efficiencies for M derived in the present work. Corrections for heterogeneous reaction observed by the authors have been included. Then the second-order rate constants so derived have been plotted, together with our own results at both high and low pressures in fig. 3. The excellence of the agreement is ample corroboration of the validity of the present work. An activation of 45 ± 4 kcal/mole results.

If one adopts the value of 48 kcal/mole for the activation energy the largest second-order rate constant for the overall decomposition, obtained with hydrogen peroxide as M, is $10^{15 \cdot 7} \exp(-48,000/RT)$ l. mole^{-1} sec^{-1}. It will be noticed that the pre-exponential term is much higher than the normal collision rate. It was partly because of this that Satterfield and Stein postulated a chain reaction.

Giguère and Liu[2] have summarized the reasons for the initial products of the decomposition of hydrogen peroxide being two hydroxyl radicals. In view of our present results, we therefore write the initial step as reaction (1) in the more explicit form,
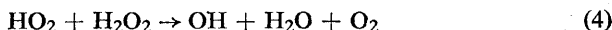
$$H_2O_2 + M \rightarrow 2OH + M. \tag{2}$$

That this step would be second-order at ordinary pressures was predicted by Hoare and Walsh.[14] The next step can be written with confidence as

$$OH + H_2O_2 \rightarrow H_2O + HO_2. \tag{3}$$

It is then impossible to write plausible straight or branched chain reactions which would give a reaction first-order with respect to hydrogen peroxide.

Thus the reaction

$$HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2 \tag{4}$$

adopted by Warren[15] and by Lewis and Von Elbe[16] would necessitate a chain-ending step involving H_2O_2 and either OH or HO_2 in order to give the required first-order kinetics. This seems unlikely. One must conclude that the homogeneous decomposition is not a chain reaction and that the high pre-exponential term is caused by some effect other than a chain.

Similarly, in the high-intensity photolysis of aqueous hydrogen peroxide, reaction (4) is not important and there are no chains.[17, 20] The intrinsic implausibility of reaction (4) is itself an argument against a chain reaction occurring in the decomposition of hydrogen peroxide. It is significant that (4) was postulated by Haber and Weiss[18] in the ferrous ion-catalyzed decomposition of aqueous hydrogen peroxide, but had later to be abandoned.[19]

Therefore only a reaction removing HO_2 radicals, that does not also remove H_2O_2, such as

$$HO_2 \rightarrow \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}O_2, \tag{5}$$

$$\text{or} \quad HO_2 \rightarrow \tfrac{1}{2}H_2O + \tfrac{3}{4}O_2, \tag{6}$$
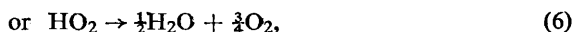
is necessary to complete the scheme of reactions. Reactions (5) and (6) would lead to decomposition rates of hydrogen peroxide of $2k_2[H_2O_2][M]$ and $3k_2[H_2O_2][M]$ respectively. Reaction (5) is to be preferred because there is evidence[4, 5] that hydrogen peroxide is formed from HO_2 radicals in hydrofluoric acid-treated vessels. It is significant that Dainton and Rowbottom[21] found that in the photolysis of aqueous hydrogen peroxide the limiting high intensity yield for the decomposition was 1·9. Indeed this scheme of reactions, i.e. (2), (3) and (5), has been shown by Hunt and Taube[20] to explain completely the kinetics observed in the high-intensity photolysis of 0·01 M hydrogen peroxide solutions. It is probable, therefore, that the rate constant k_2 is to be taken as half the

rate constant for the "overall" decomposition, i.e. to have a value of $10^{15\cdot4} \exp(-48{,}000/RT)$ when M is H_2O_2.

To explain why the pre-exponential term obtained experimentally is greater than the normal value of 10^{11} l. mole^{-1} sec^{-1} for second-order reactions, it is important first to consider the decomposition rates of the di-alkyl peroxides. The observed rates differ from the decomposition rate of hydrogen peroxide in being—as would be expected [14] for the relatively complex dialkyl compounds— first-order instead of second. In table 2 are given values of the first-order rate constant for the decomposition of some of these peroxides.

TABLE 2.—DECOMPOSITION OF DI-ALKYL PEROXIDES.
FIRST-ORDER RATE CONSTANTS $(A \exp(-E/RT))$

peroxide	A (sec^{-1})	E(kcal/mole)	ref.
di-methyl	$4\cdot1 \times 10^{15}$	36·9	28
di-ethyl	2×10^{13}	31·7	26
di-ethyl	5×10^{14}	31·5	27
di-n-propyl	2×10^{15}	36·5	25
di-t-butyl	4 to 7×10^{14}	36	22
di-t-butyl	$3\cdot2 \times 10^{16}$	39·1	23
di-t-butyl	6×10^{14} to 6×10^{16}	36 to 40	24
di-t-amyl	5×10^{15}	37	23

In several cases, there is strong evidence that the decomposition occurs by a non-chain reaction; it is likely that all the decompositions are similar in this respect. In the decomposition of alkyl nitrites, the rate constants are about identical for a range of compounds from methyl to n-butyl.[29] Not all the data quoted for per-oxides are of high reliability, but similarly the rate constants of first-order peroxide decompositions in general appear to be almost identical, having activation energies of 36 to 37 kcal/mole and pre-exponential factors of $ca.$ 10^{15} to 10^{16}.* The latter values are higher than "normal" for a first-order decomposition. Now if we suppose a unimolecular decomposition to occur by the familiar stages,

$$AB + M \rightarrow AB^* + M, \tag{A}$$

$$AB^* \rightarrow A + B. \tag{B}$$

$$AB^* + M \rightarrow AB + M, \tag{C}$$

the first-order rate constant is $k_A k_B / k_C$, while the second-order rate constant (when $k_B \gg k_C[M]$) is k_A. It follows that when the pre-exponential factor of $k_A k_B / k_C$ is greater than 10^{13} (and $k_B \ll k_C[M]$), the pre-exponential factor of k_A must be much greater than $10^{11}/[M]$ l. mole^{-1} sec^{-1} (providing k_B/k_C has an exponential term not less than $e^{-4\cdot6}$). [M] is the minimum pressure at which the reaction is first-order, e.g. for di-alkyl peroxides, considerably below 1 atm. It further follows that, if the decomposition of dialkyl peroxides could be studied at pressures sufficiently low for the decomposition to be second-order, the rate constants would have pre-exponential factors considerably greater than 10^{11} l. mole^{-1} sec^{-1} and, indeed, greater than 10^{14} l. mole^{-1} sec^{-1}. The general argument is substantiated by the decomposition of N_2O_5 which has pre-exponential factors of $10^{14\cdot7}$ sec^{-1} for first-order, high-pressure, decomposition and $10^{16\cdot1}$ l. mole^{-1} sec^{-1} for second-order decomposition.[30]

It seems then that the abnormally high pre-exponential factor obtained in the present work for the second-order rate constant of hydrogen-peroxide decomposition is in line with, and was indeed to be expected from, the abnormally high

* The rate constant for diethyl peroxide is an unexplained exception. It may be significant that if the results of Rebbert and Laidler [26] are corrected to give an activation energy of 36 kcal/mole, then the pre-exponential factor becomes 3×10^{15} sec^{-1}, in good agreement with the other pre-exponential factors.

pre-exponential factors of the first-order constants for dialkyl peroxide decompositions; and that in devising any explanation one should attempt to apply it to peroxides as a class.

A high entropy of activation can cause a high pre-exponential factor in second- as well as first-order reactions,[31] e.g. in the second-order decomposition of ozone.[32] Such an abnormally large entropy of activation is to be expected for peroxides as a class. Spectroscopic studies [33, 34] have shown that internal rotation of the hydrogen peroxide molecule is likely to be hindered by two potential barriers of different heights. In confirmation of this, Giguère et al.[35] have shown that the observed " third-law " entropy at room temperature is greater than is to be expected if no internal rotation of the molecule is present, but less than that expected for free internal rotation. In the activated forms of both hydrogen peroxide and the dialkyl peroxides free rotation may be possible. Because of their greater moments of inertia, the increase in entropy due to free rotation is likely to be greater for the dialkyl peroxides than for hydrogen peroxide. This increase in entropy could, in fact, alone explain the high pre-exponential factors found for the decomposition of the dialkyl peroxides. Because of the smaller moment of inertia for the internal rotation of hydrogen peroxide, however, it is doubtful whether the entropy of activation resulting from free rotation in the activated form, although important, is sufficient to account fully for the experimental value of the pre-exponential factor of the rate constant for hydrogen-peroxide decomposition. Presumably other factors—such as involved in the general idea, due to Hinshelwood, of activation in many degrees of freedom—play a part.

It has been shown that there is a range of efficiencies for gases playing the role M in reaction (2). Roessler [36] has shown that when iodine is in a high vibrational level and the energy quanta between levels are small, quanta are removed (one by one) by an inert gas at almost every collision. Larger quanta are less efficiently removed.[37] With more complex energy-rich entities, there is likely to be a less efficient removal of energy by inert gases, because high vibrational levels in any one mode are unlikely to be found [14] (e.g. O_2 deactivates I_2^* at almost every collision but only 1 in 140 collisions of O_2 with O_3^* is effective in deactivating the latter [32]). One therefore expects a specificity in the efficiency of M in reactions such as (C).[14] As with fluorescence, " the most efficient deactivators are those molecules which have two states differing in energy by the same or nearly the same amount as the two states in the activated molecule ".[38] It follows that H_2O_2 would be expected —as indeed we find—to be the most efficient M in bringing about reaction (2).

If reaction (A) involves an exactly parallel specificity to (C), then all inert gases when added to a reaction proceeding by a second-order rate law could give the same limiting high-pressure first-order rate. Only second-order rates would be dependent upon the nature of the inert gas. There is no good experimental evidence upon this point but it is to be noticed that most reported deactivation (i.e. combination) reactions involve a larger range of efficiencies of M than activation (i.e. decomposition) reactions. Thus the present work discloses a range of 11 in the efficiencies of M. Similarly, in no reaction quoted by Trotman-Dickenson [39] is the decomposing molecule more than 20 times as efficient as helium in the role of M. By contrast, for third-order combination reactions, e.g. $H + O_2$,[16] $CH_3 + CH_3$,[40, 41] approximately a hundredfold variation in the efficiencies of third bodies is observed. This may mean that there is indeed a greater range of efficiencies for deactivation than for activation of any one complex molecule.

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