[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES, UNIVERSITY OF CHICAGO]

The Photochemical Decomposition of Hydrogen Peroxide. Quantum Yields, Tracer and Fractionation Effects

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The quantum yield of the photochemical decomposition of hydrogen peroxide at relatively high light intensity is independent of the concentration of hydrogen peroxide, of acidity and of the presence in the solution of Br^-, Cl^-, NH_4^+ or Mn^{++}. At 25°, the limiting quantun yield at λ 2537 Å. is 0.98 ± 0.05 and at 0° it is 0.76 ± 0.05. The primary efficiencies are taken as $^1/_2$ of the limiting quantum yields. Tracer experiments show that the oxygen formed in the photodecomposition originates entirely in the hydrogen peroxide. The exchange between O_2 and H_2O_2 during the photodecomposition is at most very slight. The fractionation effects associated with the non-chain process for decomposition have been determined. They do not appear to be compatible with hydroxyl radicals as the sole net products of the primary act.

The original purpose of the work described in this paper was to measure the isotope fractionation effects in the reaction

$$HO + H_2O_2 \longrightarrow H_2O + HO_2$$
$$HO_2 + H_2O_2 \longrightarrow HO + H_2O + O_2$$

using light acting on hydrogen peroxide to generate the radicals. The fractionation factors for these reactions are of interest in comparison with the factors which have been measured for a number of catalysts acting on hydrogen peroxide.[1] In order to determine the fractionation factors in a simple way from measurement on the photodecomposition, it is necessary to choose conditions so that the total decomposition produced by the chain process be large compared to that by the separate path consisting of the chain-initiating and -terminating steps, *i.e.*, the chains must be long. The work of others has demonstrated,[2-4] and our experience has confirmed, the great difficulty that arises in purifying the solvent and the reagents and otherwise conducting the experiments so that the chain decomposition is restricted to some intrinsic path for the system such as is represented above. The original goal has been set aside at least for the present and, in the work reported here, we have limited our studies to conditions under which the chain decomposition is eliminated. This is achieved by using light of sufficiently high intensity[5] and results in a system which is much less sensitive to impurities.

Our results on the kinetics of the photodecomposition in general confirm those obtained by Lea,[5] and considerably amplify his. In addition to experiments on the quantum yield of the reaction, results obtained in tracer experiments and in the study of fractionation effects are presented and discussed with reference to mechanisms for the primary act and subsequent processes.

Experimental

The light source was a G.E. 4-watt germicidal lamp operating from a Sola constant voltage transformer. The light emitted in the wave length region affecting the uranyl oxalate actinometer is almost entirely 2537 Å. Shorter wave lengths are efficiently removed by the glass walls of the lamp. When a Pyrex glass filter was interposed, the effect on the uranyl oxalate actinometer was observed to be only 3% of the effect when it was omitted, thus showing that mercury lines of longer wave lengths contribute little to the light energy. The lamp was placed in a fused quartz tube closed at one end, and this end was lowered into the neck of the reaction flask. Provision was made for sealing the quartz tube to the mouth of the flask. The flask was fitted with an entry tube for adding solutions, and an exit tube, which could be used to collect evolved gases.

In most of the experiments, the light was used without collimation, the lamp being held several centimeters above the surface of the solution. The light flux for each particular geometry was determined by replacing the hydrogen peroxide solution with an equal volume of actinometer solution.[6] The geometry described required correction of the results for incomplete absorption of light when the hydrogen peroxide was at low concentration. In the worst case this correction was estimated to be 22%. Since the correction cannot be made accurately, a series of quantum yield determinations were made using a collimated light beam which was confined to the central portion of the solution. For this geometry the maximum correction amounted to only 6% and the results agreed with those obtained using full illumination. The solutions were stirred by rocking the reaction cell assembly, or by inserting a glass stirring blade. No difference in results was noted for the two methods.

Except where the influence of tap distilled water was studied, redistilled water was used. The hydrogen peroxide was Merck and Co., Inc., 30%, inhibitor free. The results at high light intensity were found to be independent of lot number of the hydrogen peroxide, of the perchloric acid and of the redistilled water, and as the results will show are remarkably independent of the concentration of certain "catalysts."

Analyses for hydrogen peroxide were made by titration with standardized ceric sulfate solution. This was added in excess and the excess determined by titration with standardized ferrous sulfate solution using the iron orthophenanthroline indicator.

Results

Table I contains a summary of the experiments devoted to a study of the kinetics of the photoreaction.

No special effort was made to vary the intensity of the light. However, during the course of the work on changing the geometry, it varied *ca.* 2-fold, but no effect on ϕ was observed. The observation that the quantum yield is substantially independent of (H_2O_2) further supports the conclusion that it is also independent of the rate of absorption of light since the number of quanta absorbed per unit volume changes. The rate of absorption of light was $< 5 \times 10^{17}$ quanta l.$^{-1}$ sec.$^{-1}$ for all the experiments.

In some experiments, the effect of passing gases through the hydrogen peroxide solution was tested. When CO_2, A or O_2 was swept through, the rate of decomposition was unaffected. The tests were made with H_2O_2 at 8×10^{-3} *M*, with acid at 10^{-4} *M* and at 1 *M* at 0°. Under the same conditions, H_2 does affect the rate, enhancing it when the gas is passed at a high rate. The gases were scrubbed by a solution of potassium iodide after leaving the reaction vessel. Only with O_2 was a noticeable amount of oxidizing agent carried

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(4) L. J. Heidt, THIS JOURNAL, **54**, 2840 (1932).

(5) D. E. Lea, *Trans. Faraday Soc.*, **45**, 81 (1949).

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TABLE I

THE QUANTUM YIELD OF THE PHOTODECOMPOSITION OF HYDROGEN PEROXIDE AT HIGH LIGHT INTENSITY

Concentrations in moles/liter; time of insolation, 4 to 6 hr.

No.	T, °C.	($HClO_4$)	Other subs.	(H_2O_2)	ϕ
1	25 ± 1	1.0	....	0.017	0.99
2	25 ± 1	1.0	....	.048	1.06
3	25 ± 1	1.0	....	.186	1.29
4	25 ± 1	1.0	....	.186	1.30
5	0	1.0	....	.020	0.77
6	0	1.0	....	.020	.76
7	0	1.0	....	.047	.84
8[a]	0	1.0	....	.047	.92
9	0	1.0	0.02 M NaCl	.047	.86
10	0	1.0	2×10^{-3} M NH_4Cl	.047	.86
11	0	1.0	2×10^{-3} M NaBr	.047	.89
12	0	1.0	0.05 M $Mn(ClO_4)_2$	.047	.85
13	0	1.0	0.01 M $Fe(ClO_4)_3$	.048	.49
14	0	10^{-1}	....	.021	.80
15[b]	0	1.0	....	.0078	.77
16[b]	0	1.0	....	.020	.79
17[b]	0	1.0	....	.054	.85
18[b]	0	10^{-4}	....	.022	.84

[a] Tap distilled, rather than redistilled water was used. [b] Collimated light beam.

over. The amount, which represented only a small fraction of the hydrogen peroxide decomposed was very nearly the same even when hydrogen peroxide is omitted from the system, and is attributed to the formation of O_3 in the oxygen.

The effect of $Ce(ClO_4)_3$ was also studied, as part of the series in Table II. The presence of Ce^{+++} at 0.011 M caused a decrease in ϕ of *ca.* 10%.

A tracer experiment showed that in the photodecomposition under the conditions we have employed, the oxygen comes solely from the hydrogen peroxide. Therefore, the intermediates which yield O_2 cannot undergo appreciable exchange with the solvent, nor can the hydrogen peroxide undergo appreciable exchange with water during the reaction. The experiment was conducted by dissolving hydrogen peroxide of normal isotopic composition in water 8-fold enriched in O^{16}, without added acid. The mole fraction of O^{18} in the initial hydrogen peroxide (N_p^0) was 2.123×10^{-3}, in the oxygen liberated after decomposition of 0.4 of the hydrogen peroxide, (N_g) 2.117×10^{-3}, and in the residual hydrogen peroxide (N_p) was 2.148×10^{-3}. The deviations of N_g and N_p from N_p^0 are real. Within experimental error they are the same as those observed when the environment has the same isotopic composition as the peroxide, and are attributed to isotope fractionation.

The second type of tracer experiment was performed in which O_2 of normal isotopic composition was passed through a solution of hydrogen peroxide *ca.* 8-fold enriched in O^{18} in water of normal isotopic composition. After a considerable fraction of the hydrogen peroxide had decomposed photochemically, its isotopic composition was determined. In an experiment with the concentration of H_2O_2 initially at 0.037 M and no acid added to solution, analysis of the oxygen released from the residual hydrogen peroxide (17%) on oxidation with Ce(IV) showed it to be enriched in O^{18} by 1.8%. This increase is about what would be expected of normal isotope fractionation in the photodecomposition (*vide infra*) and is opposite in direction from changes expected for exchange. We conclude that exchange between oxygen and H_2O_2, direct and catalyzed by the photoprocesses is very slight, at any rate not great enough to invalidate the measurements of fractionation factors which are reported. A slight exchange effect (1% change in N_p produced by the photolysis) would however have escaped notice.

The method of determining fractionation factors for the isotope effects in the decomposition of hydrogen peroxide, and the significance of data of this type, were outlined in an earlier paper.[1] Three fractionation factors are defined[7]

$$f_o = \frac{dO_g^{18}}{dO_g^{16}} \frac{(O_p^{16})}{(O_p^{18})}$$

$$f_r = \frac{dO_w^{18}}{dO_w^{16}} \frac{(O_p^{16})}{(O_p^{18})}$$

$$f_t = \frac{dO_g^{18} + dO_w^{18}}{dO_g^{16} + dO_w^{16}} \frac{(O_p^{16})}{(O_p^{18})}$$

The subscripts g, p and w refer to oxygen, hydrogen peroxide and water, respectively. f_o and f_r describe the fractionation for the production of oxygen and water, respectively, and f_t, the fractionation on formation of products, irrespective of their identity. With sufficient accuracy for our purposes

$$f_t = \frac{f_o + f_r}{2}$$

f_t is obtained by comparing the isotopic composition of the residual hydrogen peroxide after a measured fractional decomposition (x) with that of the hydrogen peroxide initially

$$f_t = \log \frac{N_p}{N_p^\circ} (1 - x) \Big/ \log \frac{(1 - N_p)}{(1 - N_p^\circ)} (1 - x)$$

The ratio f_o/f_r is given by

$$\frac{N_g}{1 - N_g}\left[\frac{x}{2N_p^\circ - xN_g - 2N_p(1 - x)} - 1\right]$$

The sum and ratio of f_o and f_r being known, each factor can be calculated. The highest precision in measuring f_o can be obtained by comparing N_g after very small fractional decomposition with N_p°. In the limit as $x \rightarrow 0, f_o = N_g/N_p^\circ$. This procedure was adopted in a number of the experiments, the value being corrected for the slight change in N_p during decomposition.

The results obtained in a study of the fractionation effects are presented in Table II. Measurements of the quantum yield were made for some of the experiments, more as a check on the process being studied than as quantum yield determinations. It is of interest to note that at 25° without added acid, substituting tap distilled water for the redistilled water introduces a chain decomposition. At 0° with added acid, the corresponding substitution caused only a slight increase in ϕ (*cf.* experiments 7 and 8, Table I).

Discussion

Lea[5] has shown that at sufficiently high light intensity (> 2.4×10^{17} quanta $1.^{-1}$ $sec.^{-1}$ when (H_2O_2) is *ca.* 0.01 M) the quantum yield for the decomposition of hydrogen peroxide approaches a limit which is independent of acidity and of the concentration of hydrogen peroxide. Our observations made in the range of high light intensity confirm these conclusions. However, the limiting value of ϕ (0.98 ± 0.05) at 25° we have measured is lower than that obtained by Lea, 1.39 ± 0.11. We are unable to account for the difference.

The observation that ϕ decreases as markedly as it does when the temperature falls proves that the limiting value of $\phi \sim 1.0$ at 25° cannot be attributed to a primary efficiency of unity. Two mechanisms which are consistent with the requirement on the primary efficiency, with the kinetics of the change and which otherwise appear reasonable are

I

$$H_2O_2 + h\nu \longrightarrow 2HO \qquad (1)$$

$$HO + H_2O_2 = HO_2 + H_2O \qquad (3)$$

$$2HO_2 = H_2O_2 + O_2 \qquad (4)$$

II

$$H_2O_2 + h\nu \longrightarrow H_2O + O \qquad (1')$$

$$O + H_2O_2 = HO + HO_2 \qquad (2)$$

(1′) and (2) followed by (3) and (4) as above.

A reaction scheme in which the products of the primary act are H and HO_2 has been considered but rejected because changing the concentration

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(7) The definition of the fractionation factors differs from that in reference 1. Although the present form is more correct, the values yielded are identical at low enrichment levels.

TABLE II

ISOTOPE FRACTIONATION EFFECTS IN THE PHOTODECOMPOSITON OF H_2O_2 AT = 2537 Å.

Concentrations in moles/liter

$(H_2O_2)_0$	$(HClO_4)$ added	Temp., °C.	x	f_o	f_r	f_t	Remarks	ϕ
0.1	None	25 ± 1	0.378	0.990	0.976	0.983	....	..
.1	None	25 ± 1	.097	.991	...	...	....	0.99
.1	None	25 ± 1	.204	.990	...	...	....	1.00
.1	None	0.5 ± 0.5	.162	.991	...	...	....	..
.1	None	25 ± 1	.05	.989	...	...	....	..
.05	None	25 ± 1	.985	.989	.978	.984	....	1.19
.025	None	25 ± 1	.436	...	...	.988	....	..
.1	None	25 ± 1	.815	.988	.950	.969	Tap distilled H_2O	3.8
.05	1.00	25 ± 1	.679	.989	.995	.992	....	1.00
.05	1.00	25 ± 1	.697	.989	.995	.992	....	0.99
.05	1.00	25 ± 1	.740	...	...	.993	....	.96
.05	1.00	25 ± 1	.67	...	...	.986	6×10^{-5} M Fe^{+++}	.91
.05	1.00	25 ± 1	.687	.981	.951	.966	10^{-3} M Fe^{+++}	.88

of oxygen over a wide range has no effect on the rate. Oxygen competes effectively against H_2O_2 for hydrogen atoms,[8] and would therefore cause a decrease in ϕ if hydrogen atoms were present.

Both mechanisms I and II are consistent with the tracer experiments. By each mechanism a limiting value of ϕ is reached which is twice the primary efficiency. The primary process can be considered in terms of the scheme

$$H_2O_2 + h\nu \longrightarrow H_2O_2^*$$
$$H_2O_2^* \longrightarrow H_2O_2,\ k_d$$
$$H_2O_2^* \longrightarrow \text{dissociation},\ k_r$$

$H_2O_2^*$ represents the activated entity, whether an electronically excited species or radicals trapped in a solvent cage. Using the limits of ϕ as establishing the primary efficiencies as 0.49 and 0.38 at 25 and 0°, respectively, k_r/k_d at the two temperatures is 0.96 and 0.61. If the temperature coefficient of k_d is assumed to be unity, the activation energy corresponding to dissociation to effective products is 2.9 kcal. This value seems reasonable in comparison with *ca.* 7 kcal. for the corresponding process for bromine and the value for chlorine (wave length dependent) of *ca.* 3 kcal.[9] In all cases, the values represent lower limits for the activation energies of the dissociation steps.

Even if hydroxyl radicals are assumed to be formed as primary products of the absorption of light (mechanism I), it is not unreasonable to suppose that they can undergo reaction in the solvent cage to form the products $H_2O + O$ (mechanism II). "Escape from the solvent cage" on this interpretation means formation of these products in competition with reunion and deactivation. Good evidence that the reaction of hydroxyls to form $H_2O + O$ takes place has been presented by Hardwick.[10]

The fact that substances such as Br^- and Cl^- which are known to react with HO[11] do not affect the quantum yield does not prove that HO is absent. The effect of the reaction

$$HO + Br^- \longrightarrow OH^- + Br$$

for example, may merely be to replace reaction 3 by

$$Br + H_2O_2 \longrightarrow H^+ + Br^- + HO_2$$

Similarly with Mn^{++}, the formation of Mn^{+++} would be followed by

$$Mn^{+++} + H_2O_2 \longrightarrow Mn^{++} + HO_2 + H^+$$

without necessarily producing a change in quantum yield. Evidence that Fe^{+++} does participate, although affecting ϕ only slightly at low concentration is that f_o and f_r change when Fe^{+++} is added. The changes in the fractionation factors prove that new substances are reacting with H_2O_2 when Fe^{+++} is present. When tap distilled water replaces redistilled water, a chain decomposition of hydrogen peroxide is initiated. The values of f are different from those observed when the limiting quantum yield is observed, and show that new intermediates are involved. It is very doubtful that these are HO and HO_2, and they are presumably formed from some impurity, dissolved or solid, in the tap distilled water. The experiments with Fe^{+++} added are difficult to evaluate quantitatively. At $10^{-2}M$ Fe^{+++} only 3% of the light is absorbed by H_2O_2; however, the quantum yield is decreased by only 40%. A question of interest which will require more data to be settled is whether light absorbed by Fe^{+++} is also photochemically effective. If Fe^{+++} acts as an efficient internal filter, it must act also to increase the chain length since it produces a relatively slight change in ϕ when present in sufficient amount to absorb nearly all the light. The decrease in ϕ produced by Ce^{+++} may be due to an internal filter action.

It is of interest to consider the measured values of f_o and f_r in relation to mechanism I and II. For mechanism I, $f_o = f_3 f_4$ and $f_r = f_1$. f_1 describes the discrimination between isotopic forms of H_2O_2 in reaction (1), f_3 in reaction (3) and f_4 describes the isotope discrimination when HO_2 forms O_2. On the basis of mechanism I, the fractionation of isotopes in forming water takes place only in the primary act (HO once formed yields water with no further isotope discrimination). The observations on f_r are inconsistent with this mechanism since it provides no way of explaining the change of f_r with acidity. Further, the magnitude of the fractionation effect in low acid ($f_r = 0.977$) seems too great to be attri-

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[8] H. Fricke, *J. Chem. Phys.*, **2**, 349 (1934).

[9] A. C. Rutenberg and H. Taube, THIS JOURNAL, **73**, 4426 (1951).

[10] T. J. Hardwick, *Can. J. Chem.*, **30**, 23 (1952).

[11] H. Taube and W. C. Bray, THIS JOURNAL, **62**, 3357 (1940).

buted to a primary act of efficiency nearly 0.5. Mechanism II as written similarly gives $f_r = f_1'$ and meets the same difficulty. However, if it is supposed that at low acid, reaction 2 takes place as

$$O^* + OOH^- = O^*O + OH^-$$

the necessary degree of freedom to account for the change in f_r is introduced. An analogous change in mechanism does not appear as reasonable with HO as the reactant. The fractionation data tend to disqualify mechanism I, and favor II as a means of explaining all the observations.

The transition from the limiting decomposition to the chain decomposition has been discussed by Lea.[5] The slight trend in ϕ with concentration of hydrogen peroxide (Table I, experiments 1–4 and 5–7) is presumably due to a residual chain decomposition, which diminishes as the peroxide concentration decreases. It is by no means certain that the chain decomposition which sets in is carried by HO and HO_2. The difficulty that has been experienced in obtaining reproducible data when the chain lengths are long makes it questionable to assume that the chain carriers are these radicals in any particular case. The fractionation factors f_0 and f_r should be useful in characterizing the intermediates in future work. They have the advantage over rate measurements that they are independent of chain length, and are affected only by changing the identity of the intermediates. Thus an accidental inhibitor that acts only by breaking chains will affect the quantum yield but not the values of f_0 and f_r. It is assumed in these remarks that the chains are long enough so that the principal path for decomposition of H_2O_2 is by the chain mechanism.

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Kinetics of the Gas Phase Reaction of Olefins with Ozone

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A rapid gas phase reaction occurs between ozone and various olefins. The over-all reactions are quite complicated, more olefin disappears than ozone on a mole basis, and the stoichiometry varies with reactant pressures. By extrapolating rates back to initial conditions, a relatively simple second-order rate law was observed. The initial rate was mostly homogeneous and independent of foreign gas pressure. Within experimental error the rates are also independent of temperature. Certain aspects of a mechanism are discussed.

The reaction of ozone and olefins has been studied in the liquid phase, especially with respect to reaction products.[1]

The present paper reports a study of the kinetics of the gas phase reaction of olefins with ozone. Another group in this Laboratory has been investigating the products of the gas phase reaction between olefins and ozone,[2] and this study will be reported separately. This work was part of a broad program to investigate reactions which may occur in contaminated atmospheres, and thus particular emphasis has been placed on low concentrations.

Experimental

The olefins investigated were 1-hexene, ethylene, cyclohexene and (very briefly) 1-decene, 1-octene, 1-heptene, 1-pentene and propylene. They were obtained from commercial sources. The liquid hydrocarbons were purified by distillation. The ethylene was condensed in a trap cooled with liquid nitrogen. Gaseous ethylene was produced as needed by allowing the trap to warm slightly. Ozone was prepared from cylinder oxygen by a corona discharge ozonizer.

Two techniques were used to follow the course of the reactions. One involved mixing the reactants in the air of a galvanized iron chamber of 10 m.^{3} volume. Samples of the air in the chamber were withdrawn periodically and analyzed chemically for oxidant using a modification of the method of Crabtree and Kemp.[3] This method had the advantage that very low concentrations of reactants could be employed.

The other technique employed the cell of a recording infrared spectrometer as the reaction vessel. This cell was 10 cm. long and 3 cm. in inside diameter. The chemical reaction was followed by measuring absorption at a fixed wave length. The gas handling system was similar to that used by Mills and Johnston for reactions at intermediate pressures.[4]

The reaction cell, mixing cell and double stopcock were immersed in a thermostated oil-bath. Each of the lines leading to the gas-handling system included a coil immersed in the oil-bath which aided in bringing the gases to bath temperature. A run was started by evacuating the reaction cell, closing the stopcock between cell and pump, and admitting reactants through the double stopcock. This technique required higher concentrations of reactants than the chamber technique, but temperature and total pressure were more easily controlled.

The rates of decomposition of ozone in the two types of equipment were investigated. The rate of disappearance of ozone in the chamber was about 15% per hour. No observable decomposition of ozone occurred in the cell of the spectrometer during two minutes which was longer than most of the runs.

Results

1-Hexene.—The gas phase reaction of 1-hexene with ozone was studied entirely with the chamber technique. Two sets of runs were made to determine the order and stoichiometry of the reaction.

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