Calcd. for $Hg_2NBr\cdot H_2O$: Hg, 78.19; N, 2.73; Br, 15.57; H_2O, 3.51. Found: Hg, 78.56; N, 2.83; Br, 15.00; H_2O, 3.45.

Calcd. for Hg_2NI: Hg, 74.01; N, 2.58; I, 23.41. Found: Hg, 74.10; N, 2.76; I, 23.00; H_2O, < 0.1.

Calcd. for $Hg_2NOH\cdot 2H_2O$: Hg, 85.68; N, 2.99; H_2O, 7.70; OH, 3.63. Found: Hg, 85.97; N, 3.00; H_2O, 7.39; OH (by difference), 3.64.

Calcd. for $HgNH_2Cl$: Hg, 79.57; N, 5.56; H, 0.80; Cl, 14.07. Found: Hg, 79.56; N, 5.50; H, 0.83; Cl, 13.50.

Mercury content was determined by dissolving the sample in aqua regia, and precipitating as HgS. Nitrogen was determined by a modified Kjeldahl method, H by dry combustion (semimicro) with use of gold to remove free Hg, H_2O by drying for 24 hours over P_2O_5, and halogens by the usual standard methods. Loss and gain of H_2O was very sensitive to treatment of the hydroxide (Millon base), the chloride and bromide. Successive color changes on dehydration over P_2O_5 were: $Hg_2NOH\cdot 2H_2O$, white to yellow to brown; $Hg_2NCl\cdot H_2O$, white to yellow; $Hg_2NBr\cdot H_2O$, yellow to brown. The Hg_2NI dissolved in excess KI solution.

MINNEAPOLIS 14, MINN. RECEIVED OCTOBER 4, 1950

[CONTRIBUTION FROM THE GIBBS CHEMICAL LABORATORY, HARVARD UNIVERSITY]

The Photochemical Reaction between Ozone and Hydrogen Peroxide

BY DAVID H. VOLMAN[1]

The thermal and photochemical gas phase reactions of ozone and hydrogen peroxide in a flow system were studied with the object of elucidating the mechanisms of the reactions. The thermal reaction was found to be heterogeneous and to proceed rapidly in the presence of mercury vapor or mercuric oxide on the walls. For the photochemical reaction, the absence of long chains and the presence of HO radicals was shown. The proposed mechanism postulates an initiation of the reaction by interaction of O atoms formed by ozone light absorption and H_2O_2 with the formation of HO and HO_2 radicals. The kinetic equations developed from the proposed mechanism were in agreement with the experimental results.

The thermal reaction between ozone and hydrogen peroxide in acid aqueous solution has been most recently studied by Taube and Bray.[2] A chain mechanism was postulated. In a study of the photo-sensitized reaction of hydrogen and oxygen,[3] where the major product is hydrogen peroxide with some ozone formation, it was postulated that the thermal reaction between ozone and hydrogen peroxide accounted for some of the water formed in the reaction. Subsequent experiments in which ozone and hydrogen peroxide were mixed in the gas phase showed that the reaction was rapid. However, in these experiments, mercury vapor and hydrogen were present in the reaction vessel. In this paper it will be shown that the rapidity of the reaction is attributable to these components of the reaction system.

The present work had as its original object the investigation of the ozone–hydrogen peroxide gas phase thermal reaction. However, for reasons developed below this was abandoned after some preliminary experiments, and the emphasis has been placed on the photochemical reaction. It is believed that this is the first report of this light reaction.

The following equations pertinent to the discussion of the reaction mechanism are given for convenience in reference.

$$O_3 + 2537\text{ Å.} = O_3^*,\ I_a \qquad (1)$$

$$O_3^* + M = O_3 + M,\ k_1 \qquad (2)$$

$$O_3^* = O_2 + O,\ k_2 \qquad (3)$$

$$O + O_2 + M = O_3 + M,\ k_3 \qquad (4)$$

$$O + O_3 = 2O_2,\ k_4 \qquad (5)$$

$$O + H_2O_2 = HO_2 + HO,\ k_5 \qquad (6)$$

$$HO + H_2O_2 = HO_2 + H_2O,\ k_6 \qquad (7)$$

$$HO + O_3 = HO_2 + O_2,\ k_7 \qquad (8)$$

$$HO_2 + HO_2 = H_2O_2 + O_2,\ k_8 \qquad (9)$$

Of these reactions, the first five are those used in explaining the photo-decomposition of ozone, modified to the extent that the production of O atom is represented not by the initial absorption act but by the more rigorous set (1), (2), (3). The work on ozone has been reviewed extensively by Schumacher.[4,5] At low concentrations of ozone in oxygen, in addition to an O atom formation step, equations (4) and (5) must be added to explain the experimental data.

Equation (7), first proposed by Haber and Weiss,[6] was used by Taube and Bray[2] in their mechanism of the thermal solution reaction and by Volman[7] in connection with the gas phase photochemistry of hydrogen peroxide. Equation (8) is also used by Taube and Bray. Equation (9) is discussed in connection with the reaction of H atom and oxygen[3] and in connection with the photochemistry of hydrogen peroxide.[7]

The proposed mechanism is unique in its main features, since it includes all the elementary steps likely in ozone photolysis, in hydrogen peroxide photolysis and in the thermal reaction of ozone and hydrogen peroxide. It remains then, primarily, to establish that the set (1), (2), (3) is more logical than

$$O_3 + 2537\text{ Å.} = O_2 + O \qquad (10)$$

and that the reaction of O atom with hydrogen peroxide does occur and proceeds *via* (6) rather than *via*

$$O + H_2O_2 = H_2O + O_2 \qquad (11)$$

which appears to be the only other possibility, and finally that HO_2 radicals do not react under the conditions of the experiment with either ozone or hydrogen peroxide.

Experimental

Apparatus.—The apparatus is shown in Fig. 1. The gas flows were measured by calibrated flowmeters F_1, F_2, F_3,

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(1) On leave 1949–1950 from University of California, Davis, California.

(2) Taube and Bray, THIS JOURNAL, **62**, 3357 (1940).

(3) Volman, *J. Chem. Phys.*, **14**, 707 (1946).

(4) Schumacher, THIS JOURNAL, **52**, 2377 (1930).

(5) Beretta and Schumacher, *Z. physik. Chem.*, **B17**, 417 (1932).

(6) Haber and Weiss, *Proc. Roy. Soc.* (*London*), **A147**, 332 (1934).

(7) Volman, *J. Chem. Phys.*, **17**, 947 (1949).

containing dibutyl phthalate. Constant flows were maintained by allowing small amounts of gas to escape through the constant head stabilizers, S_1 and S_2. The gases were dried over magnesium perchlorate in A and B.

The ozonizer, M, was patterned after the one of Henne and Perilstein[8] with minor modifications. The vessel, D, was an ozone reservoir which allowed the ozone concentration to change only slowly since its volume was large compared to the flow rate through the ozonizer. In this manner, the effects of fluctuations in ozone output were minimized during the time of an experiment. Hydrogen peroxide was kept in the reservoir, C, maintained at a constant temperature, and the flow of peroxide was obtained by passing the proper gas through the bubbler type vessel.

The reaction vessel, R, was a quartz tube, 35 mm. i.d. and 50 cm. long. The lamps, L-L, were 15 watt G.E. germicidal lamps whose effective radiation was at 2537 Å. Although such lamps emit appreciable amounts of 1849 Å. mercury resonance radiation, this was eliminated by coating the lamps with mineral oil.

Reagents.—The gases oxygen, nitrogen, helium and carbon dioxide were tank gases and were used without purification. Some tank carbon monoxide was also used, but since it was found to contain hydrogen, which was particularly objectionable and difficult to remove, carbon monoxide was synthesized by the action of concentrated sulfuric acid on 87% aqueous formic acid solution. The hydrogen peroxide was a 90% aqueous solution kindly supplied by the Buffalo Electrochemical Company.

Analytical Procedure.—The gas mixture flowed through the trap, E, cooled to Dry Ice temperature. This trap was of the design previously used to prevent escape of hydrogen peroxide by fog formation common to condensing a small quantity of condensable gas from a large quantity of noncondensable gas in a flowing system.[3] The peroxide was then titrated in acid solution with 0.01 *N* potassium permanganate. Ozone was not retained by the trap and was removed to G in a neutral potassium iodide solution and determined iodometrically in an acid solution using 0.01 *N* sodium thiosulfate.

Although this procedure was effective, it presented some manipulation difficulties and, hence, was superseded by a somewhat different technique. The trap, E, was replaced by a bubbler tube containing neutral water. The hydrogen peroxide in the gas mixture was retained quantitatively by this trap, but the amount of ozone retained was negligible. The ozone was subsequently removed by a potassium iodide solution as before.

The flow rate was adjusted to 1000 ml. per min. for all experiments.

Results

Thermal Reaction.—In contrast to the results earlier reported,[3] the thermal reaction at 20° in mixtures of peroxide, ozone and oxygen was found to be slow. Adding mercury vapor was found to increase the rate of the reaction markedly and adding both mercury vapor and hydrogen had a still greater effect. Mercuric oxide on the walls of the vessel was also found to catalyze the reaction.

In addition to the slowness of the reaction at 20°, the results were not reproducible. At higher temperatures the results were more reproducible, and the reaction was studied up to 127°. A plot of the log bimolecular rate constant *vs.* $1/T$ yielded a fairly good straight line at the higher temperatures.

From the expression $k = Ae^{-E/RT}$, $E = 3.5$ kcal. and $A = 1.2 \times 10^7$ (moles/cc.)$^{-1}$ sec.$^{-1}$. This low activation energy and pre-exponential factor are characteristic of a heterogeneous reaction.

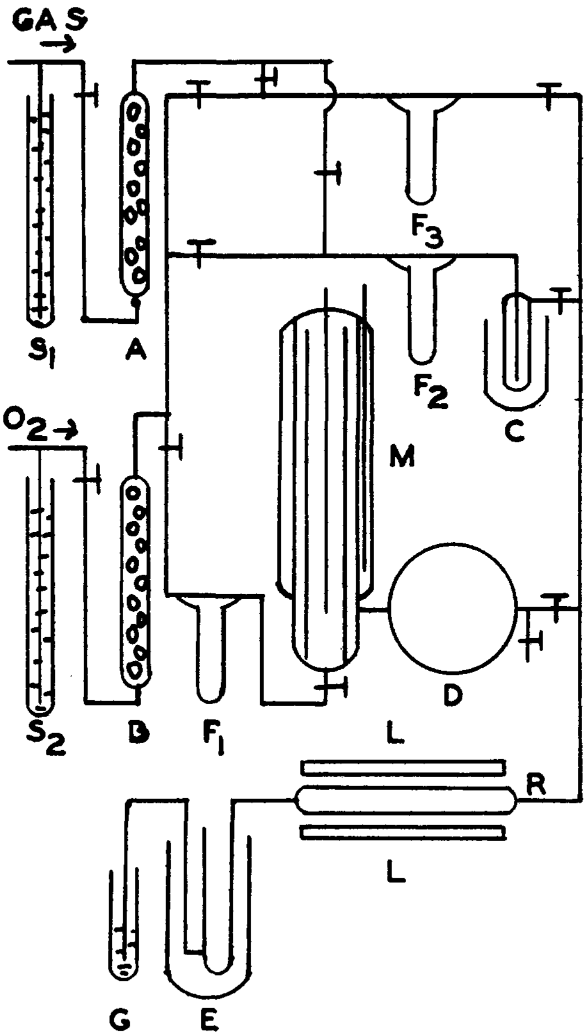

Fig. 1.—Gas flow system.

Preliminary Results of Photochemical Reaction.—The photo-decomposition of ozone in oxygen at 2537 Å. is known to have a low quantum yield, of the order of a few hundreths,[9] for a low ratio O_3/O_2. The quantum yield of hydrogen peroxide decomposition in the gas phase at 2537 Å. is known to be about 2.0.[7] However, since the absorption coefficient and concentration of hydrogen peroxide are both low, the rate of peroxide decomposition is actually small. Therefore in the present work it was expected and found that individually hydrogen peroxide or ozone decomposed when irradiated with 2537 Å. light at comparable but slow rates. However, mixtures of peroxide and ozone at partial pressures of about 1 mm. each, the remaining gas being oxygen at about 1 atm., were found to react in light at a rate which was rapid compared to the individual reactions.

Reaction in Red Light.—The absorption coefficient of hydrogen peroxide is calculated as 19.6 at 2537 Å. from the equation

$$\log_{10} I_0/I = \epsilon cl \qquad (12)$$

for c in mole per liter and l in cm., using the absorption data of Holt, McLane and Oldenberg.[10] The absorption coefficient of ozone for the same wave length and units is 3010 calculated from the

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[8] Henne and Perilstein, This Journal, **65**, 2183 (1943).

[9] Heidt, *ibid.*, **57**, 1710 (1935).

[10] Holt, McLane and Oldenberg, *J. Chem. Phys.*, **16**, 225 (1948).

absorption curves given by Bonhoeffer and Harteck.[11] Therefore it may be seen that ozone absorbs a far greater fraction of the radiant energy than does hydrogen peroxide. Even at the low concentrations used, ozone will absorb almost all of the incident 2537 Å. light in a path of a few cm. From these considerations it is apparent that the reaction is most likely initiated by light absorbed by ozone, and that the light absorbed by hydrogen peroxide need not be taken into account. In red light hydrogen peroxide is completely transparent but ozone absorbs weakly. Experimental evidence that absorption of light by hydrogen peroxide is not necessary for the reaction was obtained by carrying out the reaction in red light. Two 500 watt incandescent lamps were used as sources. Table I shows that the reaction was found to occur as predicted.

TABLE I

REACTION IN RED LIGHT

Concn., mole ml.$^{-1}$ × 10^8 H_2O_2	O_3	$\Delta c/\Delta t$, mole ml.$^{-1}$ sec.$^{-1}$ × 10^{10} H_2O_2	O_3
4.0	10.0	0.8	0.7
4.0	15.0	1.0	1.2

Quantum Yield.—The total radiant energy incident on the absorption cell was determined by following the hydrolysis of 0.5 *M* monochloroacetic acid at 2537 Å. similar to the method of Smith, Leighton and Leighton.[12] Using their value of 0.32 for the quantum yield of this actinometer, the quantum yields obtained for the reaction for a concentration of ozone = 6.0 × 10^{-8} and hydrogen peroxide = 5.0 × 10^{-8} mole ml.$^{-1}$ in oxygen at about 760 mm. are

$$\Phi_{O_3} = 0.30,\ \Phi_{H_2O_2} = 0.22$$

defined as molecules decomposed per quantum absorbed.

Reaction in Foreign Gases.—Although it was not practical to eliminate oxygen from the ozone stream, it was possible to substitute foreign gases for oxygen as the hydrogen peroxide carrier gas and to study the reaction in mixtures of oxygen, ozone, hydrogen peroxide and added gas. In the experiments shown in Table II, the partial pressure of foreign gas approximated 0.9 of the total pressure. The quantum yield of ozone decomposition in the absence of hydrogen peroxide was also determined for each mixture.

TABLE II

QUANTUM YIELD OF OZONE AND HYDROGEN PEROXIDE DISAPPEARANCE IN VARIOUS GAS MIXTURES

Concentration: O_3, 6.0 × 10^{-8}; H_2O_2, 5.0 × 10^{-8} mole ml.$^{-1}$ Pressure: oxygen, 76 mm.; foreign gas, 684 mm.

Foreign gas	Φ_{O_3} in abs. of H_2O_2	Reacn. mixt. including H_2O_2 Φ_{O_3}	$\Phi_{H_2O_2}$
Carbon dioxide	0.04	0.23	0.16
Oxygen	.05	.30	.22
Nitrogen	.07	.35	.25
Helium	.22	.71	.48

Reaction in Carbon Monoxide.—Von Elbe[13,14] has studied the photodecomposition of hydrogen peroxide in the presence of carbon monoxide to demonstrate the formation of HO radicals. Jackson and Kistiakowsky[15] have shown that oxygen atoms react much more rapidly with oxygen than with carbon monoxide, and Griffith and MacWillie[16] have obtained results on the photodecomposition of ozone in carbon monoxide which demonstrate that only trace quantities of carbon dioxide are formed. Von Elbe's work[13,14] shows that the reaction between HO and carbon monoxide produces carbon dioxide. Therefore the formation of carbon dioxide in mixtures of ozone, hydrogen peroxide, oxygen and carbon monoxide should demonstrate the presence of HO radicals. Experimentally, the irradiated gas mixture was passed through a solution of barium chloride in standard 0.01 *N* sodium hydroxide. The formation of barium carbonate was easily observed and could quantitatively be determined by titrating with hydrochloric acid to a phenolphthalein end-point. Although there was a slight dark reaction forming carbon dioxide, and the light reaction in the absence of hydrogen peroxide resulted in some carbon dioxide as well as the light reaction with peroxide in the absence of ozone, the light reaction in the mixture produced comparatively large amounts of carbon dioxide as shown in Table III.

TABLE III

CARBON DIOXIDE FORMATION IN THE PRESENCE OF CARBON MONOXIDE

Concentrations: H_2O_2, 5.0 × 10^{-8}, O_3 = 8.0 × 10^{-8} mole ml.$^{-1}$; Pressures: O_2, 76 mm.; CO, 684 mm.

Conditions	CO_2 formed mole ml.$^{-1}$ sec.$^{-1}$ × 10^{10}
Light reaction, all components present	0.5
Dark reaction, all components present	.01
Light reaction, H_2O_2 absent	.08
Light reaction, O_3 absent	.04
Dark reaction, O_3 absent	.00

The experiment in the absence of hydrogen peroxide represents the maximum to be expected from the interaction of oxygen atoms with carbon monoxide. The experiment in the absence of ozone, actually represents more than the maximum contribution of hydrogen peroxide alone since it could not absorb nearly so much light in the presence of ozone.

Temperature Effect.—A reaction of HO_2 with either ozone or peroxide would result in a chain mechanism rather than the closed set of reactions given. The low quantum yields obtained appear to preclude the possibility of a chain mechanism. However, since the reaction rate of a chain reaction often exhibits a strong temperature dependence, additional evidence for a non-chain mechanism was obtained by studying the reaction at elevated temperatures. The results given in Table IV show that the temperature coefficient is small.

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[11] Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Leipzig, 1933, p. 114.

[12] Smith, Leighton and Leighton, THIS JOURNAL, **61**, 2299 (1939).

[13] Von Elbe, *ibid.*, **54**, 821 (1932).

[14] Von Elbe, *ibid.*, **55**, 62 (1933).

[15] Jackson and Kistiakowsky, *ibid.*, **52**, 3471 (1930).

[16] Griffith and MacWillie, *J. Chem. Soc.*, **123**, 2767 (1923).

TABLE IV

RATE OF PHOTODECOMPOSITION AS A FUNCTION OF TEMPERATURE

Concentrations: H_2O_2, 5.0×10^{-8}; O_3, 6.5×10^{-8} mole ml.$^{-1}$

T., °C.	$\Delta c/\Delta t$, mole ml.$^{-1}$ sec.$^{-1}$ $\times 10^{10}$ H_2O_2	 O_3
40	2.0	2.8
70	2.4	3.2
100	2.8	3.4

For these results it is not necessary to correct explicitly for the dark reaction. If it is assumed that the dark reaction is independent of the light reaction, the concentrations of hydrogen peroxide and ozone in the flowing mixture at the exit of the reaction vessel are taken as the base concentrations. Any change in concentration is then attributable to photochemical action.

Concentration Variation.—The rate of the reaction at various concentrations of ozone and hydrogen peroxide was studied and the results are given in Tables V and VI.

TABLE V

DECOMPOSITION RATES AS A FUNCTION OF OZONE CONCENTRATION FOR A FIXED HYDROGEN PEROXIDE CONCENTRATION AT 2537 Å.

Conc. $H_2O_2 = 3.9 \times 10^{-8}$ mole ml.$^{-1}$

Ozone concn., mole ml.$^{-1}$ $\times 10^8$	$\Delta c/\Delta t$, mole ml.$^{-1}$ sec.$^{-1}$ $\times 10^{10}$ H_2O_2	 O_3
0	0.1	0
2.7	1.4	1.8
6.3	2.3	3.0
8.1	2.7	3.3
10.6	2.6	3.4
12.8	2.6	3.7
15.0	2.5	4.1

TABLE VI

DECOMPOSITION RATES AS A FUNCTION OF HYDROGEN PEROXIDE CONCENTRATION FOR A FIXED OZONE CONCENTRATION AT 2537 Å.

Concn. $O_3 = 11.0 \times 10^{-8}$ mole ml.$^{-1}$

H_2O_2 concn., mole ml.$^{-1}$ $\times 10^8$	$\Delta c/\Delta t$, mole ml.$^{-1}$ sec.$^{-1}$ $\times 10^{10}$ H_2O_2	 O_3
0	0.	0.6
1.1	0.94	2.3
2.3	1.6	3.2
3.0	2.0	3.4
5.0	2.7	3.5
7.0	3.0	3.6

Discussion

Although the actual quantum yield values given in Table II may only be approximate, the comparative values should be correct. The value of 0.05 for ozone decomposition in oxygen without hydrogen peroxide compares well with the quantum yield values given by Heidt[9] extrapolated to the low concentration used above. The order of the values in the different gases in the absence of hydrogen peroxide is in keeping with the results of other work on ozone reviewed by Schumacher.[4,5]

The parallel effect of the foreign gas on ozone decomposition and ozone plus hydrogen peroxide decomposition is best explained by assuming that both reaction rates depend on the same intermediate. Since this is an oxygen atom[4] in the case of ozone, the mechanism of the hydrogen peroxide, ozone mixture reaction is best explained by assuming a reaction between oxygen atom and hydrogen peroxide.

For this reaction two likely paths are suggested, (6) and (11). From the known structure of hydrogen peroxide, (11) would appear to have a low probability compared with (6). The results obtained in the presence of carbon monoxide confirm this view. These experiments demonstrate that HO radicals are formed in the light reaction. It might be argued that HO_2 radicals would also produce carbon dioxide on reaction with carbon monoxide. However, this does not negate the conclusion since there is no logical mechanism for the formation of HO_2 without the formation of HO also. Therefore equation (6) is to be taken as the route of oxygen atom with hydrogen peroxide.

The low quantum yield of the reaction and small temperature coefficient indicates that a mechanism involving long chains is not involved. Therefore reactions between HO_2 radicals and either ozone of hydrogen peroxide need not be considered.

Mechanism of O Atom Production.—The effects of foreign gases on ozone decomposition have been discussed by Schumacher.[4,5] For low concentrations of ozone in oxygen, the decomposition is supposed to be given by the sequence (10), (4), (5). This leads to the rate equation

$$-\frac{d[O_3]}{dt} = \frac{2k_4[O_3]I_a}{k_4[O_3] + k_3[O_2][M]}$$

or

$$\Phi = (2 - \Phi)\frac{k_4[O_3]}{k_3[O_2][M]}$$

Using this equation and the data of Table II one obtains the relative values for k_3 in the various gases

	O_2	CO_2	N_2	H
relative k_3	1	12.6	7.2	2.1

Although the comparative values for carbon dioxide, nitrogen and helium are about what would be expected from their structure, the value for oxygen is at variance with the expectation that it should be somewhere between carbon dioxide and nitrogen in its effectiveness as a third body for a recombination reaction. The data given by Schumacher lead to a similar discrepancy and therefore the above cannot be the entire mechanism.

The spectrum of ozone shows evidences of structure even at wave lengths as low as 2500 Å.[17] It is then possible to write equation (1) for the absorption act. In considering the fate of the photo-activated molecule, two possible paths are to be considered, decomposition (3) and deactivation (2). On this basis the effects of the various gases are to be attributed to their efficiencies in deactivating O_3 as well as their role as third bodies in the recombination reaction (4). Their efficiencies as deactivating bodies would be expected to follow the order CO_2, O_2, N_2, He, which is the actually found order (Table II).

Since the ozone spectrum is quite diffuse, indicating a short life in the excited state, and since hydrogen peroxide is present only in low concentra-

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[17] Wulf and Melvin, *Phys. Rev.*, **38**, 330 (1931).

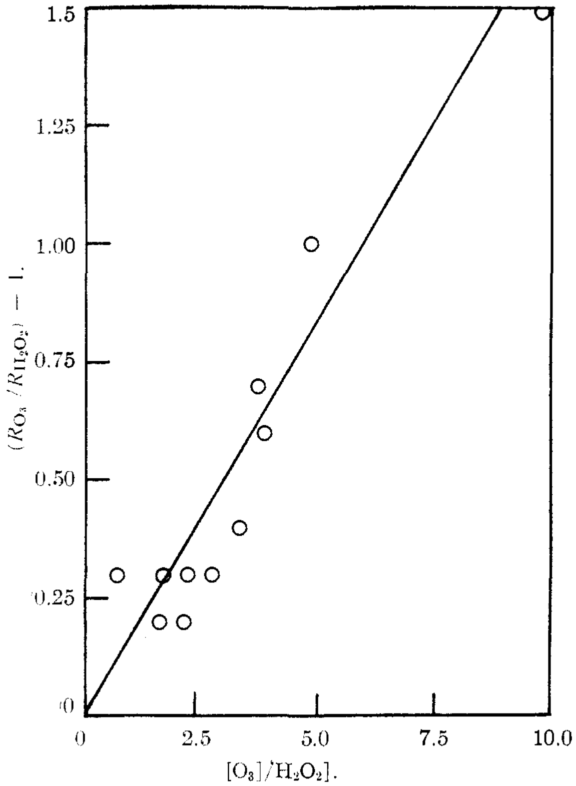

Fig. 2.—Plot of equation (16).

tion, a reaction between photo-activated ozone and peroxide need not be considered.

Kinetics of the Reaction.—From the foregoing it is then to be concluded that the set of equations (1)-(9) are a minimum for the reaction. It remains to be shown whether these equations lead to a rate equation consistent with the experimental results.

The usual steady state treatment leads to the following kinetic equation where $(k_2)/(k_1[M] + k_2)$ is just the fraction of photoactivated ozone molecules yielding O atoms or the quantum yield of the primary process designated by ϕ.

$$-\frac{d[H_2O_2]}{dt} = \frac{k_5[H_2O_2]}{k_3[O_2][M] + k_5[H_2O_2] + k_4[O_3]}\,\frac{k_6[H_2O_2]}{k_6[H_2O_2] + k_1[O_3]}\,\phi I_a$$

Since $[H_2O_2]$ and $[O_3]$ are small, comprising only about 2 mm. of the total of an atm. pressure, [M] may be taken as the concentration of oxygen in the absence of foreign gas. Also $k_4[O_3]$ must be negligible compared with $k_5[H_2O_2]$ for $[H_2O_2]$ and $[O_3]$ of the same order of magnitude. Otherwise there would not be such an increase in the quantum yields of ozone decomposition in mixtures with hydrogen peroxide. These simplifications lead to the equation

$$-\frac{d[H_2O_2]}{dt} = \frac{k_5[H_2O_2]}{k_3[O_2]^2 + k_5[H_2O_2]}\,\frac{k_6[H_2O_2]}{k_6[H_2O_2] + k_7[O_3]}\,\phi I_a \quad (14)$$

A similar treatment yields

$$-\frac{d[O_3]}{dt} = \frac{k_5[H_2O_2]}{k_3[O_2]^2 + k_5[H_2O_2]}\,\frac{k_6[H_2O_2] + 2k_7[O_3]}{k_6[H_2O_2] + k_7[O_3]}\,\phi I_a \quad (15)$$

and

$$\left(\frac{d[O_3]}{dt}\right)\Big/\left(-\frac{d[H_2O_2]}{dt}\right) = 1 + \frac{2k_7[O_3]}{k_6[H_2O_2]} \quad (16)$$

In Fig. 2 $(-d[O_3]/dt)/(-d[H_2O_2]/dt) - 1$ (for the results of Tables V and VI) has been plotted against $[O_3]/[H_2O_2]$. From equation (16) this should yield a straight line passing through the origin. Considering the experimental error, it is believed that the fit to (16) is about as good as could be expected. The slope of the line should give $2k_7/k_6$. From the slope of the line obtained, $k_6 = 12\,k_7$, indicating that HO radicals react more rapidly with hydrogen peroxide than with ozone.

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