# PHOTOCHEMICAL REACTIONS OF OZONE IN SOLUTION

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When ozone dissolved in water absorbs light of wavelength corresponding to the strong absorption band in the ultra-violet, the reaction  $O_3 + H_2O \rightarrow 2O_2 + H_2O_2$  takes place with almost exact stoichiometry. To demonstrate this reaction, substances such as dilute HCl or HOAc which inhibit the (chain) reaction of  $O_3$  and  $H_2O_2$ , must be present in solution. Tracer experiments have shown that the  $H_2O_2$  formed derives approximately one-half its oxygen from the solvent, the other from the  $O_3$ . When the solutes  $SO_4^{2-}$  or HOAc are present in high concentration, the addition of oxygen atoms to form  $HSO_5^-$  and HOOAc is observed; with  $CIO_4^-$  as solute at high concentration,  $CIO_3^-$  is formed. The quantum yields for the disappearance of  $O_3$  at  $\lambda = 254 \text{ m}\mu$ , 310 m $\mu$  and  $\sim 600 \text{ m}\mu$  are 0.62, 0.23 and 0.002-0.005 respectively. When light in the long wavelength region is absorbed,  $H_2O_2$  formation is not observed.

The effects at short wavelength are attributed to the formation of electronically excited atomic oxygen. On this interpretation,  $O^{1}D$  but not  $O^{3}P$  can react efficiently with H<sub>2</sub>O to knit an O—O bond.

The work to be described was undertaken in the hope of learning something about the reactions of atomic oxygen in solution. A consideration of the spectrum and properties of  $O_3$  suggested the action of light on this substance as a possible means of generating atomic oxygen. Ozone absorbs light strongly at wavelengths convenient to work with, which are not absorbed strongly by water and some other solvents of interest. Furthermore, the primary co-product which can be expected is oxygen, and this substance does not complicate the chemistry of at least some of the systems which can be studied. A disadvantage of ozone as a source of atomic oxygen is its own reactivity, which is great enough to restrict severely the choice of solvent or of added solute. A more fundamental difficulty is the lack of definite knowledge of the nature of the primary act. The absorption spectrum in the u.-v., as well as the weaker one in the visible consists of diffuse The lack of rotational structure is consistent with, but does not prove bands. the interpretation<sup>2</sup> that predissociation follows light absorption. However, every author recently <sup>3</sup> in dealing with this problem has assumed that atomic oxygen is produced as an intermediate in the photo-induced decomposition of ozone. It is to be expected that when ozone is brought under the perturbing

Table 1.—Limiting wavelengths  $(m\mu \times 10^2)$  for the production of  $O_2$  + O from  $O_3$ 

	$O_2 {}^3\varSigma$	$O_2  {}^1\Delta$	$\mathrm{O}_2{}^1\varSigma$
O 3 <i>P</i>	11.4	5.9	4.6
O 1 D	4.1	3.1	2.6

influence of the solvent moleules especially when they are highly polar, predissociation is more likely, and it seems safe to assume that when the energy of the quantum absorbed is great enough, the formation of atomic oxygen ensues.

This assumption provides a simple and natural explanation of observations which have been made in the course of the present work.

In table 1 are shown the wavelengths of light corresponding to the minimum

# EXPERIMENTAL

MATERIALS.—Tank oxygen, dried, was used for the production of O<sub>3</sub>. The ozonized gas was found to be free from reactive oxides of nitrogen. The test applied was to pass a large volume of the ozonized gas through water, and to look for the formation of acid. The ozonizer used yielded about 2-3 mole % ozone at a flow rate of ca. 1 l./min. Chlorine dioxide was prepared by the method described by Bray,<sup>4</sup> passing the gas generated through a solution of Na<sub>2</sub>CO<sub>3</sub> to remove chlorine. The water used as solvent was redistilled from alkaline permanganate. Other reagents were of A.R. quality, used without further purification.

APPARATUS.—A mercury resonance lamp (Detectolite) having the quartz envelope in the shape of a flat spiral was used as the source of light at 254 m $\mu$ . Solutions were exposed in a cylindrical quartz cell with plane windows. The cell was 2 cm thick and 7 cm diam. It was placed *ca*. 5 cm from the lamp, with the distance exactly fixed for each series of experiments. With a lamp of this type, a filter is unnecessary to limit the photochemical activity in O<sub>3</sub> (*aq*) to substantially 254 m $\mu$ , although filters are still necessary to determine the light intensity. The current for the lamp was drawn through a constant voltage transformer. For light of longer wave lengths, a "point-source" high-pressure mercury are was used (Mazdalux), fed by current drawn from a voltage regulator. Using a Pyrex cell and a filter solution containing K<sub>2</sub>CrO<sub>4</sub>, the light acting on O<sub>3</sub> can be limited largely to 313 m $\mu$ , because the absorption of light at the longer wavelengths which may be transmitted as well as the quantum efficiency is small.

Two exposures are necessary in doing the actinometry (uranyl oxalate),<sup>5</sup> one using the light as described, and another, interposing glass to reduce the intensity of 313 m $\mu$  relative to that of the longer wavelengths. By using Pyrex glass lenses, the light acting on O<sub>3</sub> is limited to that in the long wavelength absorption region.

PROCEDURE.—Many series of experiments were performed by passing  $O_3$  through a solution while it was being illuminated, removing  $O_3$  at the end of the period of illumination by a stream of air and looking for evidence of chemical change in the solution. For each series, the light intensity was constant, but because it changed from series to series an experiment using dilute HOAc as the reaction medium was always included to make intercomparisons possible. Experiments of this kind did not serve to establish stoichiometry because the consumption of  $O_3$  was not measured. For the experiments requiring accurate assay of the ozone concentration, a large volume of solution saturated with ozonized oxygen was prepared, and from this, solution was dispensed into two calibrated bulbs and the reaction vessel, these being filled in rapid succession. One of the bulbs served to fix the initial concentration of ozone, and the second to measure the spontaneous decomposition. This decomposition is small when inhibitor is present in solution, and did not exceed 2 % in any of the experiments. The analysis of ozone was made as described elsewhere.<sup>6</sup> The analysis of the solutions left after ozone was removed (with a stream of air) is described later.

The determination of the extinction coefficients of the ozone solution at short wavelengths was made in 1 cm quartz cuvettes. Because the size of the cuvettes, and the ratio of opening to volume was so different from that of the bulb used for determining the concentration of ozone, comparison could not be relied on to give the concentration of O<sub>3</sub> in the cuvettes. A direct determination was made, emptying the O<sub>3</sub> solution (which is acid) into acidic Mn<sup>2+</sup> (*aq*)—whereupon Mn<sup>2+</sup> (*aq*) is oxidized quantitatively—then adding I<sup>-</sup> and determining the I<sub>2</sub> formed spectrophotometrically. The values of [O<sub>3</sub>] determined directly agreed with those calculated from the blanks to within 5 %. A 10-cm cell was used in the determination of the extinction coefficient of O<sub>3</sub> at longer wavelength.

Where comparisons within a series of experiments are made of the rates of reaction, as in tables 3, 4 and 5, the rates are corrected to correspond to complete absorption of light. At 254 m $\mu$ , in water, 90 % or more of the light was absorbed by the O<sub>3</sub> solution but using HClO<sub>4</sub> (*aq*) or H<sub>2</sub>SO<sub>4</sub> (*aq*), ozone is salted out, and the absorption fell to as low as 75 %.

# RESULTS

The values obtained for the extinction coefficients of  $O_3$  in water solution are shown in table 2. To compare with them, some values for the gas phase interpolated from the

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data quoted by Läuchle <sup>7</sup> and corrected to the units used here:  $\alpha$  (in cm<sup>2</sup> molecule<sup>-1</sup>) =  $\frac{1}{cd} \log \frac{I_0}{I}$ , are also given. A detailed comparison of the values for gas and solution in the long wavelength absorption region is difficult because whereas in solution the values develop along a smooth curve, in the gas phase the absorption is resolved into bands.<sup>8</sup>

#### TABLE 2.—THE EXTINCTION COEFFICIENTS OF O3 IN GAS AND AQUEOUS SOLUTION

λ <sub>1</sub> , mμ	$\alpha_1 \times 10$	$\alpha_1 \times 10^{-2}$		α×10−2	
	soln.	gas	$\lambda_1, m\mu$	soln.	
245	25		480	0.007	
250	30	32.8	500	·017	
254	33	33.6	520	·023	
258	36 (max)		540	·033	
265	35	27.8	546	·036	
270	32		560	·043	
280	20	10-3	580	·048	
290	9.3		590	·051 (max)	
300	3.0	-9	600	·046	
305	1.60		625	·033	
310	·86		650	·025	
313	·60	·21	675	·016	
320	·25				
330	·08				
340	·02				

The maximum value of  $\alpha$  for gaseous ozone at long wavelengths is 1.5 at 601 m $\mu$ . The values of  $\alpha$  quoted for the region of stronger absorption were considered to be within 5% of the true values. However, they do not agree within this accuracy with the values recently published by Kilpatrick, Herrick and Kilpatrick.<sup>9</sup> These authors report for  $\alpha_{max}$ . the value  $2.9 \times 10^3$  as compared with  $3.6 \times 10^3$  reported in this paper. The positions of the maxima, however, agree reasonably well. The values of  $\alpha$  in the region of weak absorption are considered to be within 15 to 20% of the true values. Measurements in this wavelength region were not reported by Kilpatrick *et al.*<sup>9</sup> It should be noted that the measurements are made difficult by the decomposition, apparently initiated by the light and aggravated by the large surface-to-volume ratio of the cells, in the visible by the small optical density of the solutions. In spite of their inaccuracy, the values are useful for comparison with the gas phase, and for interpreting the data on the quantum yields. Since a large fraction of the light is adsorbed when using 254 m $\mu$ , the values of the quantum yield at this wavelength are not very sensitive to the values of  $\alpha$ . However, at 313 m $\mu$  and at longer wavelengths, error in  $\alpha$  is directly reflected in the values of quantum yield.

Other subsidiary data necessary for the analysis of the results are the solubilities of  $O_3$  in the various solvents used. The relative solubilities, as determined by saturating the solutions in succession by a stream of  $O_3$  are :

medium	72 % H by	ClO <sub>4</sub> /H <sub>2</sub> O volume	water	HC by	Ac/H <sub>2</sub> O volume		
	8	1.23		1.00	<b>4</b> ·00	ø	
relative solubility	0.32	0.69	1.00	1.6	3.2	7.8	

These values are not accurate, because slight variations in the  $O_3$  content of the gas occur, but are correct to within 10 %, a level of accuracy which suffices for the present use of the data.

Table 3 shows the results obtained in a series of experiments in each of which  $O_3$  was passed continuously through the solutions, and an iodimetric determination was made of the oxidizing agent left after  $O_3$  was removed. This oxidizing agent reacts slowly with I<sup>-</sup>, and the reaction is subject to catalysis by Mo(VI). The substance is oxidized by  $MnO_4^-$  in acid, forming oxygen, and requires as many equivalents of  $MnO_4^-$ , as it yields of I<sub>2</sub>. From these observations, and the composition of the system it can

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be concluded that the oxidizing agent formed is  $H_2O_2$ . It is also to be noted that using solutions of the compositions described in table 3, appreciable quantities of Cl<sub>2</sub>, AcOOH, or other substances capable of reacting rapidly with I<sup>-</sup> are not formed.

TABLE 3.—FORMATION OF H<sub>2</sub>O<sub>2</sub> ON ILLUMINATION OF O<sub>3</sub> SOLUTION  $(\lambda = 254 \text{ m}\mu; \text{ temp., } 16^{\circ} \pm 2)$ 

composition of solution	time min	[H <sub>2</sub> O <sub>2</sub> ] × 104M	average rate × 105 mole 11min-1
0.15 M HOAc	30	0.00(a)	
H <sub>2</sub> O	15	0.00	
$5 \times 10^{-3} \text{ M Cl}^{-1}$	12	0.49	
$5 \times 10^{-3}$ M Cl <sup>-</sup> and 0.01 M HClO <sub>4</sub>	12	3.19	<b>2.</b> 66
	43	10.2	2.36
	70	14.5	2.07
$1 \times 10^{-3}$ M Cl <sup>-</sup> and 0.01 M HClO <sub>4</sub>	12	3.18	2.65
$3.3 \times 10^{-3}$ M HOAc	12	3.44	2.87
0.15 M HOAc	12	3.39	2.83
	30	8.65	2.88
	47	13.5	2.87
	200	56.6	2.83
	12	3.46	2.88
~	(and 12 in dark)		

(a) no illumination.

Experiments on stoichiometry and quantum yield are reported in table 4.

TABLE 4.—QUANTUM YIELDS OF  $O_3$  CONSUMPTION AND  $H_2O_2$  FORMATION (Reaction medium, 0.06 M HOAc, 0.05 M HClO<sub>4</sub>)

$(O_3)_0  imes 10^4$	$-\Delta(O_3)$ × 10 <sup>4</sup>	$\begin{array}{c} \Delta H_2 O_2 \\  imes 10^4 \end{array}$	time min	λ, mμ	temp.	$\phi O_3$
2.18	1.00	-99	4	254	14	0.61 (a)
2.12	1.02	1.00	4	254	14	.62(a)
3.24	1.03	1.02	4	254	4	.58(a)
3.32	1.32	1.30	31	313	4	·23 (a)
2.63	·27 (b)	·02	60	> 313 (c)	4	·002-·005
2.77	·25 (b)	·01	65	> 313 (c)	4	·002-·005

(a) corr. for contribution by longer wavelengths.

(b) corr. for spontaneous decomposition. It was shown that  $H_2O_2$  present in traces as found did not induce significant decomposition of  $O_3$ , and that the  $H_2O_2$  was largely preserved.

(c) The principal wavelengths absorbed are 546 and 578 m $\mu$ . The estimate of the quantum yield is based on a determination of the intensity of light at 436 m $\mu$ , and estimates of the relative line intensities for lamps of this type.

Ozone persists for a long time when it is dissolved in acetic acid, and it is possible therefore to do photochemical experiments with it using acetic acid + water mixtures over the whole range of composition. The oxidizing agent formed when glacial acetic acid is used as solvent reacts rapidly with I<sup>-</sup>, but is not attacked rapidly by MnO<sub>4</sub><sup>-</sup>, and is almost certainly peracetic acid. When mixtures of H<sub>2</sub>O and HOAc are used, part of the oxidizing agent is peracetic acid, and part is hydrogen peroxide. In table 5 are reported the results of experiments on the production of the two oxidizing agents as a function of time and of solvent composition. In analysing for the two components, advantage was taken of the differing rates at which they react with I<sup>-</sup>. A correction has been applied to the values of the rates which are recorded, to allow for the absorption of light by HOAc, the assumption being made that this light has no photochemical consequences. In appraising the results shown in table 5, it should be noted that equilibrium between HOAc, H<sub>2</sub>O<sub>2</sub> and HOOAc is established too slowly for the spontaneous reaction to affect appreciably the distribution of the peroxides in the time of the experiment.

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When  $O_3$  is photochemically decomposed in a medium containing  $H_2SO_4$  and  $H_2O_2$ , in addition to  $H_2O_2$  there is again formed an oxidizing agent which reacts rapidly with I-. This reactive oxidizing agent is presumably permonosulphuric acid. The results using  $H_2SO_4 + H_2O$  mixture are reported in table 6.

TABLE 5.—The formation of peroxides by the action of light on  $O_3$  in  $HOAc + H_2O_2$  mixtures

(using  $\lambda = 254 \text{ m}\mu$ ; at  $18^\circ \pm 2$ )

mole ratio HOAc/H <sub>2</sub> O	time min	rate prod. of peroxides M <sup>-1</sup> min <sup>-1</sup> × 10 <sup>5</sup>	HOOAc HOOH	$\frac{\text{HOOAc}}{\text{HOOH}} / \frac{\text{HOAc}}{\text{HOH}}$
0.003	20	4.5	0.00	
·169	20	4·2	·27	1.6
·315	20	4·2	·54	1.7
1.26	20	<b>4</b> ·0	1.75	1.4
2.84	20	3.8	3.90	1.4
gl. acetic	15	3.6	$\sim$ 20	-
,	30	3.5		
**	60	3.4		

### TABLE 6.—The formation of peroxides by the action of light on $O_3$ in $H_2SO_4 + H_2O$ mixtures

(using  $\lambda = 254 \text{ m}\mu$ , at  $16^{\circ} \pm 2$ ; composition of reaction medium HOAc: H<sub>2</sub>SO<sub>4</sub>:  $H_2O::0.003:141:85$ , except in first experiment, in which  $H_2SO_4$  is omitted)

time min	rate prod. peroxides M min <sup>-1</sup> × 10 <sup>5</sup>	rate prod. H <sub>2</sub> SO <sub>5</sub> M min <sup>-1</sup> × 10 <sup>5</sup>
10	2·78 (a)	
7.5	2.91	0.28
7.5	2.86	<u> </u>
10	2.43	•56
30	1.48	•59
30	1.49	•58

# (a) 0.05 M HOAc.

Using  $HClO_4 + H_2O$  mixtures, an oxidizing agent besides  $H_2O_2$  is again formed, but in contrast to that produced from HOAc or  $H_2SO_4$ , it does not react rapidly with  $I^-$ , and in fact, reacts at a rate useful for analysis only when [H+] is ca. 6 M or higher, and [I-] is ca. 0.5 M. Under the conditions ordinarily used for the H<sub>2</sub>O<sub>2</sub> analysis, it does not react appreciably with I<sup>-</sup>. The substance is reduced by  $Fe^{2+}$  to form Cl<sup>-</sup>. From the characteristics of the reaction with I-, the behaviour with Fe2+, and the known behaviour of chlorine in its various oxidation states, it can be concluded that the oxidizing agent formed is ClO3<sup>-</sup>. (The species Cl<sub>2</sub>, HClO, HClO<sub>2</sub> and ClO<sub>2</sub> are immediately removed from consideration, because no substance is present which reacts rapidly with  $I^-$  in dilute acid.) The mixtures were analysed, titrating an aliquot with  $MnO_4^-$  to measure H<sub>2</sub>O<sub>2</sub>, and treating another with solid KI to measure the total oxidizing agent. The results of two series of experiments with solutions of  $O_3$  in  $H_2O + HClO_4$  mixtures are shown in table 7.

A tracer experiment was done to learn the source of the oxygen which is formed when  $O_3$  is converted to  $H_2O_2$  in water. Ozonized oxygen of normal isotopic composition was passed through a dilute aqueous solution of acetic acid (made up using water enriched in O<sup>18</sup>) while the solution was being illuminated with light of  $\lambda = 254 \text{ m}\mu$ . The illumination was continued until the concentration of  $H_2O_2$  built up to  $7 \times 10^{-3}$  M. The oxygen was liberated from the peroxide using an excess of Ce (IV). Isotopic analysis of the oxygen showed 55 % to be derived from the ozonized oxygen and 45 % from the water. Two items of evidence showed that under the prolonged irradiation, there was some attack of acetic acid: the amount of Ce (IV) consumed was considerably in excess of

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that corresponding to the amount of gas evolved and the gas liberated contained also CO<sub>2</sub>. It should be noted that a slight primary attack of the acetic acid could lead to considerable net change, for the reaction of HOAc with  $O_2 + O_3$  by a chain mechanism is not at all unlikely under the conditions of the experiment.

TABLE 7.—THE FORMATION OF H<sub>2</sub>O<sub>2</sub> AND ClO<sub>3</sub><sup>-</sup> BY THE ACTION OF LIGHT ON O<sub>3</sub> IN HClO<sub>4</sub> + H<sub>2</sub>O MIXTURES (using  $\lambda = 254 \text{ m}\mu$ ; at 20 ± 2°; reaction medium A contains

 $HOAc: HClO_4: H_2O:: 0.001: 146: 853)$ 

	reaction	other	time	av. rate prod., I	$M \min^{-1} \times 1$
no.	medium	solutes	ume	of ClO3-	of H <sub>2</sub> O <sub>2</sub>
1	H <sub>2</sub> O	0.003 M HOAc	10		3.65
2	Ā		10	1.87	1.89
3	Α		20	1.58	1.70
4	A	_	40	1.23	1.41
5 (a)	A		10	1.68	1.65
6	A	$[H_2O_2]_0 = 6.0 \times 10^{-4}$	20	1·19 (b)	1·36 (b)
7	А	$[ClO_3^{-}]_0 = 4.2 \times 10^{-4}$	20	1·40 (b)	1·66 (b)
8	A	$[H_2O_2]_0 = 6.0 \times 10^{-4}$	20	·65 (b)	1·21 (b)
		$[ClO_3^-]_0 = 4.2 \times 10^{-4}$			
9	72 % HClO4	0.003 M HOAc	20	1.87	·11
10 (c)	A		5.5	1.92	2.12
11 (c)	A		10	1.52	1.96

(a) temp.  $\sim 8^{\circ}$ .

(b) calculated by subtracting that added initially, from  $H_2O_2$  and  $ClO_3^-$  found.

(c) Expt. 2-9 constitute a single series, 10-11 another, with new solutions but at the same light intensity.

Evidence was sought for the photochemical formation of peroxides from other solutes besides  $O_3$  in water. A solution 0.15 M in NaClO<sub>3</sub> was illuminated for 3 h, using light of  $\lambda = 254 \text{ m}\mu$ , and of intensity similar to that for the experiments of table 6. After this time, only a trace of oxidizing agent responding to dilute HI developed, and this oxidizing agent responded rapidly. A solution of H<sub>2</sub>O<sub>2</sub> in glacial HOAc was illuminated at  $\lambda = 254 \text{ m}\mu$  until 10 % of the H<sub>2</sub>O<sub>2</sub> was decomposed. The amount of peracetic acid formed corresponds at most to 5 % of the H<sub>2</sub>O<sub>2</sub> decomposed. The photochemistry of ClO<sub>2</sub> in water was also explored to some extent. Because rather complete results have been reported <sup>10</sup> for wavelengths 313 m $\mu$  and longer, most attention was directed to experiments using the line at 254 m $\mu$ . Chlorine, hypochlorite and chlorite are not formed in appreciable amounts, and the important products are Cl<sup>-</sup>, ClO<sub>3</sub><sup>-</sup> and O<sub>2</sub>. In some experiments, the net change approached that expressed by the equation

$$\frac{3}{2}$$
 H<sub>2</sub>O + 3ClO<sub>2</sub> = 2 ClO<sub>3</sub><sup>-</sup> + Cl<sup>-</sup> +  $\frac{3}{4}$  O<sub>2</sub>,

in others, the disproportionation of ClO<sub>2</sub> to ClO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> without the formation of O<sub>2</sub>. The quantum yield for the decompositions, however, remained constant. Formation of H<sub>2</sub>O<sub>2</sub> was not demonstrated. Direct evidence for its formation by observing it as a product cannot be expected. The observation that part of the O<sub>2</sub> formed originates from H<sub>2</sub>O is perhaps an indication that it is an intermediate. A tracer experiment showed the oxygen liberated in the photodecomposition of ClO<sub>2</sub> originated largely in the ClO<sub>2</sub>; at 254 mµ, about 15 % originated in the ClO<sub>2</sub>; at 313 and longer, only 5 %.

The photochemical oxidation by O<sub>3</sub> is not confined to reactions in condensed phases. Thus when a mixture at atmospheric pressure containing approximately equal amounts of O<sub>2</sub> and N<sub>2</sub>O, and 1 % of O<sub>3</sub>, is streamed through a quartz tube illuminated by light of  $\lambda = 254 \text{ m}\mu$ , and then bubbled through water, white fumes immediately appear above the surface of the water, and acid develops in it. A more efficient means of absorbing the acidic oxides is to pass the gas through CCl<sub>4</sub> saturated with H<sub>2</sub>O. Assuming that two moles of acid are produced for each N<sub>2</sub>O oxidized (nitrogen is presumably oxidized to the pentavalent state once the N—N bond is ruptured), the quantum yield is estimated to be as high as 0·1. In the various blank experiments : N<sub>2</sub>O alone under illumination, O<sub>3</sub> alone under illumination, the mixture N<sub>2</sub>O + O<sub>3</sub> without illumination, no acid is developed.

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In another experiment, a stream of ozonized oxygen was passed through a quartz tube, this section being illuminated, and the effluent gas was carried by a delivery tube of small volume through water containing a small amount of HOAc. No  $H_2O_2$  could be detected in solution even after 1 h. Taking account of the rate of gas flow, the volume of the delivery tube, and the upper limit on the concentration of  $H_2O_2$  built up, the lifetime in the ozonized gas of the chemically active species produced by the light is  $<10^{-3}$  sec.

#### DISCUSSION

The data of table 4 show that when small concentrations of HCl or HOAC are present in solution, light in the short-wavelength region of absorption acting on  $O_3$  causes the net change :

$$H_2O + O_3 = H_2O_2 + O_2.$$
 (1)

The added materials act as preservatives for the  $H_2O_2$  formed, and do not appear to be involved in the process of forming this substance. The observations supporting this conclusion are (i) the initial rate of formation of  $H_2O_2$  is independent of the concentration of the preservative over a wide range of concentration, and is the same for the two preservatives; (ii) there is no net oxidation of Cl<sup>-</sup> accompanying the formation of  $H_2O_2$ , and a noticeable oxidation of HOAc only in a prolonged experiment (this oxidation almost certainly is a side-reaction); (iii) the general features of the observations recorded in table 3 relating to the formation of  $H_2O_2$  can be understood completely by assuming that  $H_2O_2$  is formed at a rate which does not depend on the concentration or nature of the preservatives, and recorded observations on the inhibition by HOAc and HCl of the reaction of  $H_2O_2$  with  $O_3$ .<sup>11</sup>

The observations on the nature of the products in various media, on the distribution of the products between  $H_2O_2$  and other forms, and the almost constant value of quantum yield in the various media, suggest the conclusion that the reactive entity formed from  $O_3$  by light of short wavelength, combines efficiently with whatever oxygen is immediately presented to it, and does not survive to seek out more readily oxidizable substances present only in trace amounts. This kind of behaviour is reasonable for atomic oxygen in the <sup>1</sup>D state. In contrast to  $O {}^{3}P$  (ground state), which has all orbitals occupied and will tend to act as a radical,  $O {}^{1}D$ , corresponds to an electronic structure in which a p orbital is vacant, so that it is expected to be a strongly "acidic" reagent.

From the point of view suggested,  $H_2O_2$  is formed directly by the addition of  $O^1D$  to  $H_2O$ . This conclusion is supported by the almost strict adherence of the system activated by light of wavelength 254 m $\mu$  to the stoichiometry of eqn. (1), and by the results of the tracer experiment. (The deviation in the tracer experiments from the 1 : 1 ratio in the source of oxygen can be ascribed to a side reaction, by which organic peroxides are formed by radicals reacting with  $O_2$ .) For a mechanism with OH as an intermediate in the formation of  $H_2O_2$  a linear build-up of  $H_2O_2$  would not be expected, nor would the stoichiometry of eqn. (1) be followed. HOOAc and  $HSO_5^-$  presumably result from the direct addition of  $O^1D$  to HOAc and to  $HSO_4^-$ . The reaction with  $ClO_4^-$  can be understood as following a similar course, but with the difference that the peroxy product formed is unstable :

$$\begin{array}{c} 0\\ 0\text{ClOO}^- \rightarrow \text{ClO}_3^- + \text{O}_2.\\ 0\end{array}$$

Although the most striking feature in a comparison of rates for various media is their great similarity, the differences are interesting and significant. The quantum yield in glacial HOAc is *ca.* 20 % lower than in water, while in the  $HClO_4 + H_2O$  mixture, it is *ca.* 15 % greater than in water. The competition

involved in fixing the quantum yield is presumably the reaction of  $O^1D$  with the substrates on the one hand, and with the  $O_2$  formed in the same primary act on the other. The total quantum yields for all the systems cannot be understood simply by attributing differing reactivities to the various substrate species, but the reactivities do depend on the medium. The relative reactivities when calculated from the product data for mixtures with water are (expressed per mole of available O):

$H_2O$	HOAc	HSO <sub>4</sub> -	ClO <sub>4</sub> -
1	0.8	$\sim 0.4$	1.5

Although both  $H_2SO_4 + H_2O$  and  $HClO_4 + H_2O$  mixtures show quantum yields greater than in water, the reactivity of oxygen in  $SO_4^{2-}$  is less than in water. It is to be expected that an important factor determining the product ratio will be the availability of the oxide which is to react. The results suggest that  $SO_4^{2-} +$  $H_2O$  interaction is so strong, that sulphate oxygen is not readily available to  $O^{1}D$ , although the net effect is to win a greater fraction of the intermediate from recombination with  $O_2$ , by forming  $H_2O_2$ . For  $HOAc + H_2O$  mixtures, composed as they are of more nearly alike molecules, the contributions are more nearly additive.

The interpretation of the chemical changes following absorption of light by  $O_3$  as reactions of atomic oxygen finds support in the observations made with light of longer wavelength. In contrast to the behaviour at short wavelength, reaction (1) is much less important than the decomposition of  $O_3$ ,

$$2O_3 = 3O_2.$$
 (2)

At wavelength above 410 m $\mu$ , atomic oxygen can be formed only in the  ${}^{3}P$  ground state. The reaction of this species to add to water is expected to compete much less favourably against the recombination with O<sub>2</sub> than is the case for O  ${}^{1}D$ , if for no reason other than this, that a spin change would be required to give the product H<sub>2</sub>O<sub>2</sub> in the ground state, but is not required to form O<sub>3</sub> in the ground state. The lower quantum yield at long wavelengths is a consequence partly of the higher rate of recombination of O  ${}^{3}P$  with O<sub>2</sub> ${}^{3}\Sigma$  and of the requirement that O must survive to attack another molecule of O<sub>3</sub> for net decomposition to occur. The quantum yield at long wavelength may be sensitive to the ratio O<sub>3</sub>/O<sub>2</sub>, but this feature has not been tested.

The present observations correlate well with those dealing with the effect of water vapour on the photochemical decomposition of  $O_3$  in the gas phase. When light of short wavelength is used, water vapour greatly increases the rate of decomposition <sup>12</sup>, <sup>13</sup> but when red light is used, there is no effect of water vapour.<sup>14</sup> Applying the results of the present work, H<sub>2</sub>O<sub>2</sub> is expected to be formed only when light of short wavelength is used; H<sub>2</sub>O<sub>2</sub> can be taken as a catalyst for the decomposition of O<sub>3</sub> in the gas phase, as it is in solution. The observations that H<sub>2</sub>O<sub>2</sub> is not formed when light of long wavelength is used, correlates with the work of Harteck and Kopsch,<sup>15</sup> who observed no effect on water of atomic oxygen which was produced by a discharge (according to their conclusions almost certainly in the <sup>3</sup>P state).

The suggestion that O  ${}^{1}D$  is formed when light of short wavelength acts on O<sub>3</sub> was first made by Schumacher,<sup>16</sup> but only on the basis of the properties of the absorption spectrum, without adducing any direct evidence for the formation of this species. However, there are described in the literature several well-defined examples of a difference in the reactivity of atomic oxygen, presumably  ${}^{1}D$ , and of atomic oxygen formed in the ground state. Thus Popov  ${}^{17}$  showed fairly conclusively that atomic oxygen was formed under the conditions of his experiments, viz., O<sub>2</sub> and CO at low pressure, light of  $\lambda = \sim 175 \text{ m}\mu$ , and that this atomic oxygen reacts with almost zero activation energy with CO absorbed on the surface.

Atomic oxygen formed in the electric discharge produces no noticeable change in CO. The atomic oxygen produced <sup>18</sup> by light of short wavelength on O<sub>2</sub> reacts efficiently with H<sub>2</sub>, in a gas-phase reaction, requiring essentially no activation energy. However, with atomic oxygen obtained from an electric discharge, only 1 collision in 107 leads to reaction.19

However, not all the conclusions in the area are internally consistent, or are as consistent with the present work as those cited. On the basis of the present work we would conclude that  $O^{1}D$  reacts efficiently with N<sub>2</sub>O. Henriques, Duncan and Noyes,<sup>20</sup> however, concluded that the activation energy for the reaction of either O  $^{1}D$  or O  $^{3}P$  with N<sub>2</sub>O is at least 14 kcal, it being assumed that these species are formed when NO<sub>2</sub> absorbed light of  $\lambda = 220 \text{ m}\mu$  and  $> 300 \text{ m}\mu$ These wavelengths correspond to separate predissociation regions, respectively. with an energy difference between the beginning of the regions corresponding approximately to that for O<sup>1</sup>D, O<sup>3</sup>P. Zelikoff and Aschenbrand <sup>21</sup> who studied the photochemical decomposition of N<sub>2</sub>O at  $\lambda = 147.0$  and at 184.9 m $\mu$ , found evidence for the reaction  $O + N_2O = 2NO$  at *both* wavelengths, with essentially equal reactivity of the atomic oxygen. On the basis of the close correspondence of the long wavelength limits 155.5 m $\mu$  and 210.0 m $\mu$  of the continuous absorption regions in which the wavelengths 147 and 185 m $\mu$  lie, with the energies for the processes

$$N_2O = N_2 \,{}^{3}\Sigma + O \,{}^{3}P,$$
  
 $N_2O = N_2 \,{}^{1}\Sigma + O \,{}^{1}S,$ 

the authors concluded that at the shorter wavelength,  $O^{3}P$  is formed, but at the longer O  $^{1}S$  is formed. From the intercomparison of the three systems, the suspicion arises that the assignments of primary process is incorrect at least in some of the cases, and further that activated molecules rather than atoms may be reactants in some of them, including the system under present study.

Returning to the results on the formation of peroxides, some features of the build-up to the steady state may be noted. While the initial rates of product formation are quite reproducible, depending as they apparently do only on the composition of the system with respect to major constituents, the rate of absorption of light, and possibly to a slight extent on the temperature, the later rates and the steady states are much less reproducible. The steady-state levels of products are fixed by the further reactions of the substances rather than by their photochemical decomposition. Reaction with  $O_3$  limits the indefinite accumulation Observations made in the study of this reaction explain the qualitative of  $H_2O_2$ . features of many of the observations recorded in table 3. HOAc and Cl- were proved <sup>11</sup> to be inhibitors for the reaction, the efficiency of Cl<sup>-</sup> increasing when  $H^+$  is increased. Furthermore, HCl is not as effective as HOAc because the radical derived from it, though less effective than the intrinsic radicals, is a more effective catalyst for the reaction of H2O2 with O3, than is the radical derived from HOAc. Rates with Cl<sup>-</sup> as inhibitor are not as readily reproducible, because the intermediate formed from it is still reactive and the system remains sensitive to impurities. With HOAc as inhibitor, the initial rates are preserved to quite high levels of  $H_2O_2$  concentration, although even here the rates after 1 h illumination were not always reproducible. Little definite can be said in the way of interpreting the steady state effects for solutions containing large concentrations of HOAc,  $HSO_4^-$  or  $ClO_4^-$ , and the discussion is confined to pointing out some features of the observations. The products HOOAc and  $H_2SO_5$  appear to be fairly resistant to further attack by O3; H2O2 approaches a steady-state level much earlier than H<sub>2</sub>SO<sub>5</sub> when both are formed in the same system. The steady state phenomena for the  $HClO_4 + H_2O$  mixture are very complex. A noteworthy feature is that reaction of O<sub>3</sub> with ClO<sub>3</sub><sup>-</sup> is indicated. The direct reaction is slow, but it may be catalyzed by intermediates which are formed during the

illumination. Furthermore,  $ClO_3^-$  and  $H_2O_2$  appear to be mutually limiting. The reactions destroying these products are apparently chain reactions, for the results even for short periods of illumination are difficult to reproduce (cf. 7·01-·08, and 7·10, 7·11). Lowering the temperature does not increase the yield of  $ClO_3^-$ . It is therefore possible that the yield of  $ClO_3^-$  is limited not only by its being consumed but also by its formation being prevented, as could be the case for example, by the reaction

0

The change in stoichiometry in the photo-decomposition of  $ClO_2$  from experiment to experiment was not observed by Bowen and Cheung, who observed a rather close adherence of the stoichiometry to that described by the equation

$$H_2O + 2ClO_2 = Cl^- + ClO_3^- + O_2 + 2H^+.$$

It should be mentioned explicitly that the reaction of  $O \ D$  (from ClO<sub>2</sub>) with H<sub>2</sub>O to form H<sub>2</sub>O<sub>2</sub> as intermediate would lead to a good fraction of the O<sub>2</sub> formed, coming from the water. If the appearance of solvent oxygen in the oxygen evolved is interpreted as arising from  $O + H_2O = H_2O_2$ , the tracer experiments imply that 30 % of any atomic oxygen formed at  $\lambda = 254 \ m\mu$  reacts this way, but only 10 % at the longer wavelengths. The system is so complex that this suggestion cannot be offered as a conclusion, and further work is necessary.

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