The Kinetics of the Catalysed Photolysis of Diethyl Peroxide in Solution

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Pure diethyl peroxide was prepared and the photolysis in carbon tetrachloride, cyclohexane, and water studied. Ethyl alcohol and acetaldehyde were the sole products in all three solvents. With light of wavelength 313 nm the quantum yield for the destruction of the peroxide was much lower using cyclohexane or carbon tetrachloride then water. In water it was found that Cu^{2+} was an efficient photochemical catalyst and the kinetics of the copper ion-catalysed photolysis were then investigated using rotating sector techniques. A reaction scheme has been evaluated and rate constants for some of the suggested steps have been deduced.

PREVIOUS work [1,2] on the photolysis of diethyl peroxide has been carried out in the gas phase. At 313·0 nm and 30 °C, carbon monoxide, methane, formaldehyde, acetaldehyde, ethyl alcohol, acetone, and biacetyl were formed, while at 100 °C, the last two products were absent while ethane was present. Clearly a range of processes occur under these conditions and it was therefore decided that data on the decomposition in

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[1] A. Mortlock, Ph.D. Thesis, University of London, 1952.

[2] J. Boulton, Ph.D. Thesis, University of London, 1956.

dilute solution would be useful since then it might be possible to study the reactions of the ethoxyl radicals produced in the primary step without complications.

EXPERIMENTAL

Preparation and Purification of Materials.—Diethyl peroxide was prepared by Wiley's method[3] with some minor modifications. It was found that the explosions referred to by earlier workers could be eliminated provided friction from the stirrer was minimized and the upper part of the reaction vessel kept cool. The impure peroxide was purified by treating in turn with (*a*) KOH solution, to remove acids, (*b*) Girard Reagent P, to remove carbonyl compounds, and (*c*) distilled water, to remove reagents and traces of alcohols. After drying ($CaCl_2$), two distillations were carried out, the fraction b.p. 64—65 °C being collected. It was then stored in the dark in grease-free glass-stoppered vessels. Immediately before use the samples were further purified by injecting 0·5 ml portions into a preparative gas chromatograph. The column packing was dinonyl phthalate (5 g) suspended on Celite at 60 °C. The purity was checked by re-injecting the peroxide, until no sign of any impurities could be found. It was therefore concluded that pure peroxide, *i.e.* without the usual 4—5% of ether mentioned by previous workers, had been prepared.

May and Baker reagent-quality carbon tetrachloride was further purified by treatment with alcoholic potassium hydroxide and chlorine under u.v. radiation. After two distillations from calcium chloride the purity was checked (g.l.c. and i.r. and u.v. spectroscopy) and then vacuum distilled into the reaction cell as required. Spectroscopically pure cyclohexane was used after a single vacuum distillation. Conductivity water, prepared by distillation from very dilute alkaline permanganate solution, was distilled twice further, finally from quartz into quartz receivers.

Apparatus.—The light source was an Osram 125 W stabilized-arc mercury lamp, type MBL/D. In order to minimize flicker, rectified 3-phase a.c. was used as the power supply. The three phases were first of all fed separately into stabilizing transformers, which cut down fluctuations 15-fold, then onto 230/115 V step-down transformers and rectified. The rectified phases were then combined, a system of chokes and condensers being used to smooth out any remaining a.c. ripple detectable on a cathode ray oscilloscope.

A parallel beam of light was produced in the usual way by two quartz convex lenses of 20 cm focal length mounted on an optical bench. This light was passed into cylindrical quartz-cells which were placed in a holder inside a thermostat having a quartz window. Before reaching the quartz-cell the light passed through a stop and filters to cut out wavelengths above and below 313·0 nm. A diaphragm was mounted in front of the cell holder to cut out light which would otherwise have hit the edges of the quartz cells. All quartz cells were of 2·5 cm diameter but of 1, 2, and 5 cm lengths. A photocell was used to periodically monitor the output of the mercury lamp to check that the light intensity was effectively constant.

The rotating sector wheel (1 ft in diameter) had four sectors cut away, each representing one-sixteenth of the complete wheel and spaced evenly apart; hence the ratio of light to dark periods was 1 : 3. An infinitely-variable friction drive gear connected to an electric motor was used to supply the power, this operated through a second reduction gear-box and thence onto the sector. Meccano sprockets and chains were used to transmit the drive. With this arrangement speeds of 1—750 rev min^{-1} were obtained, and the sector could be left running for many hours with no variation in speed. High speeds were measured using a stroboscope fixed on the wheel, other speeds were measured by means of a revolution counter mounted on the gear-box.

If the rate of diffusion of radicals is relatively slow compared with the rate of flashing (as is the case in solution) then the use of non-square light pulses is permissible.[4] However to make certain that any error could only be minute, the light after passing through the stop of width 0·5 cm was brought to a focus (width *ca.* 0·3 cm) at the rotating sector. Since the sector openings were 5·2 cm long the deviation from squareness was small.

Technique.—The solvents were freed of air by vacuum distilling them into the cell or by degassing *in situ*, using a Goodman vibrator, whilst pumping on the cell at the same time. After filling with solvent to a fixed mark, the peroxide (0—0·1 ml) was then vacuum distilled into the cell and dissolved. The cell was then isolated, detached from the vacuum line, and the concentration of peroxide was found by measurements of the optical density at 245·0 nm. Early experiments using chemical analysis showed that acetaldehyde and alcohol were the sole products and that they were formed in equimolar quantities. Hence measurement of the optical density in this way was used to follow the reaction. Alcohol does not absorb in the u.v. so that one measurement is sufficient. However to increase accuracy and to check for self-consistency measurements of optical density were made at several wavelengths between 245·0 and 290·0 nm. From a plot of the ratio of extinction coefficients of acetaldehyde to peroxide against the ratio of the new optical density to the initial, the fraction of acetaldehyde formed from the peroxide was found.

All solutions used were dilute (*ca.* 1% or less) and weakly absorbing (3·5—20%), so it was assumed that light was evenly absorbed throughout the solution irradiated. Normally 10—15% of the peroxide was decomposed in a run. For the anaerobic runs in aqueous solution a few min of pre-irradiation was given in order to remove residual traces of the inhibiting oxygen. Quantum yields were estimated with potassium ferrioxalate as an actinometer.[5] Hot nitric acid was used as the sole cleaning agent for the cells and the distillation apparatus.

RESULTS

Ethyl alcohol and acetaldehyde were the sole products in all three solvents whether air was present or not. However in the absence of air, the rate in water was markedly increased over that for the other two solvents. An analysis to check whether gaseous products were formed, showed that less than 10^{-7} mol, if any, were produced from 10 ml of a 0·1M solution which had been 90% decomposed. There was no thermal reaction at either 20 or 37 °C.

The difference in anaerobic rates with solvent was impressive. It appeared that oxygen was a very efficient

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[3] R. H. Wiley, U.S.P. 2,357,298/1944.

[4] G. M. Burnett and H. W. Melville, ' Techniques of Organic Chemistry,' ed. A. Weissberger, vol. 8, ch. 3.

[5] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, 1956, *A*, **235**, 518.

inhibitor for the decomposition in water and this together with short inhibition periods due to residual oxygen and day-to-day variations in rates, which however were persistent, led to a search for a possible catalyst, presumed present as a trace impurity in the water.

The results of a series of trials are shown in Table 1. In addition to those shown in Table 1, the cations Fe^{3+}, Ag^{+}, Hg^{+}, and VO^{2+} were also tested. Quantitative data were difficult to obtain with these ions because in each case there was absorption of the u.v. radiation (which led to blackening in the case of the Ag^{+} and Hg^{+}). It was concluded that Fe^{3+} did have some catalytic activity but that the other three ions had no effect. Sulphate was chosen as the common anion for the different cations tested because sulphate has no absorption in the u.v. range covered and also does not affect the reactions. The trials showed that Cu^{2+} is an outstanding catalyst for the photochemical decomposition.

TABLE 1

Relative effects of various metallic sulphates on the rate of decomposition of diethyl peroxide

[Cation]/ 10^{-4}M	Molarity of peroxide	% Decomposition after 1 h illumination	Molarity × % Decomposition
Na^{+}	0·0525	13·0	0·6825
Zn^{2+}	0·0605	11·25	0·6805
Mn^{2+}	0·0478	15·5	0·741
Cd^{2+}	0·057	13·4	0·764
Co^{2+}	0·4017	16·0	0·667
Cu^{2+}	0·10	100	10

It was concluded from the survey that the catalytic effects found for copper(II) ion do not seem to be a general property of metallic cations, whether they have more than one valence state or not. Any slight catalytic activity the other ions tested might have, cannot be >1% of that for copper(II) ion.

Kinetics of the Copper(II) *Ion-catalysed Photolysis.—Effect of acid and alkali.* Sulphuric acid and sodium hydroxide solutions were used to check the effect of pH on the rate. No change was found provided the concentrations of these were low enough not to affect directly the acetaldehyde produced.

Temperature coefficient. Runs were carried out at 19 ± 0·25 °C and 37 ± 0·25 °C. To prevent any possible error due to distillation out of solution, the cell was immediately cooled to room temperature with running water when removed for optical density measurements. It was allowed 20 min to reach the thermostat temperature before photolysis. Blank runs confirmed that no thermal reaction had occurred. The results (Figure 1) indicated that the temperature coefficient was very low (<3% change per 10 °C) and that a wide temperature range would have been necessary to get an accurate result. This was not practicable, however, because of the low b.p.s of acetaldehyde and the peroxide. All other runs described in this paper were carried out at 20 ± 1 °C.

Variation of catalyst concentration. A stock 10^{-4}M copper sulphate solution was made up directly from quartz-distilled water and $CuSO_4$ (AnalaR), the solution being stored in a quartz flask. Portions were then pipetted into the 2 cm cell, the volumes made up with water collected immediately from the quartz still and runs carried out in the normal manner.

The results given in Figure 2 are for a fixed peroxide concentration of 0·083M, 15% being decomposed in each run.

Variation of peroxide concentration. A series of runs in 10^{-5}M-$CuSO_4$ solution with different initial concentrations of peroxide were carried out, the incident light intensity being constant. In each run 15% of the peroxide was decomposed. The results (Figure 1) show that the quantum yield is inversely proportional to the square root of the peroxide concentration.

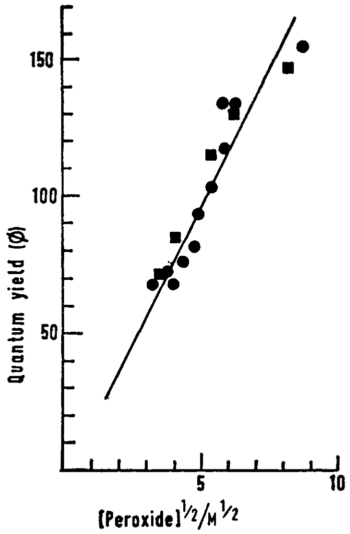

FIGURE 1 Effect of variation in peroxide concentration on the quantum yield at 19 (●) and 37 °C (■); concentration of $CuSO_4$ 10^{-5}M

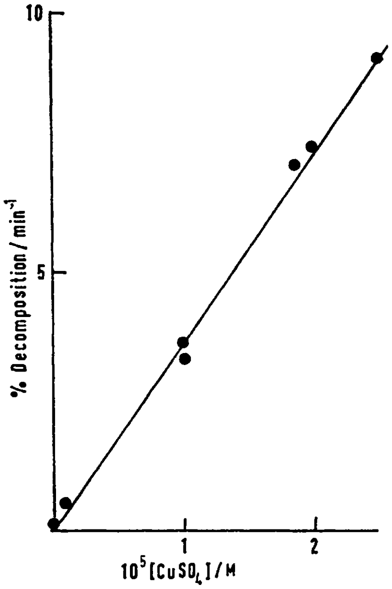

FIGURE 2 Effect of variation in copper sulphate concentration on the rate of decomposition of peroxide

Variation of light intensity. From the variations in rate which occurred when changing u.v. lamps, it was known that the rate varied accurately with the square root of the intensity. This was further confirmed without altering the optical system, by means of a wire gauze inserted close to the first of the two lenses in the optical train. The transmission (25%) was checked using uranyl oxalate as actinometer in the cell. Further confirmation was obtained in detail later, when rotating sector studies were made over the peroxide concentration range 0·016—0·075M. It was found that the rate at high flashing speeds (light period 5 ms) was always exactly twice the rate at low flashing speeds (light period 60 s).

Rotating sector studies. The theory of intermittent illumination was applied to the system in order to check the postulated reaction scheme. The mean life of the radicals was found by carrying out a series of runs at various flashing rates with (*a*) fixed initial concentration of peroxide, variable catalyst concentration and (*b*) fixed catalyst concentration, variable peroxide concentration. The initial light intensity was kept constant of course. In each run 15% of the peroxide was decomposed.

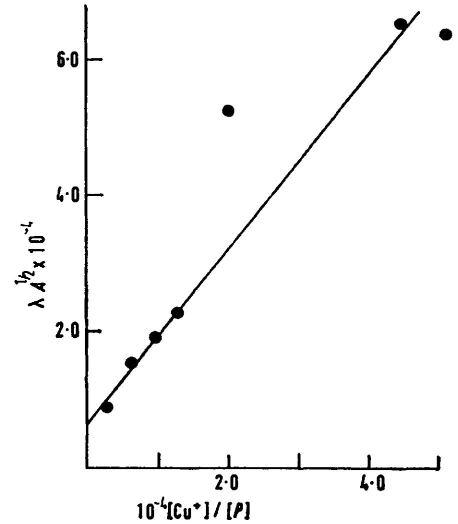

FIGURE 3 $\lambda A^{1/2}$ as a linear function of $[Cu^{2+}]/[P]$

From the plot of log $[R_r/R_s]$ against log (light period), where R_r is the rate of reaction for any given light period and R_s is the rate of reaction under steady illumination, the mean life can be obtained by comparison of the curve with a standard curve given by theory. The method used was exactly as described.[4]

Results for a typical series of runs are shown in Tables 2 and 3. No simple relationships between either the measured mean life and peroxide concentration or mean life and cupric ion concentration was apparent. However when the two sets of results were taken in conjunction and the mean life multiplied by the square root of the number of einstein l^{-1} s^{-1} absorbed was plotted against $[Cu^{2+}]/[P]$, a straight line was obtained, in agreement with the postulated reaction scheme. This plot is shown in Figure 3.

TABLE 2

Effect of peroxide concentration on the mean life of the radicals; concentration of $CuSO_4$ $0·74 \times 10^{-5}$M

[Peroxide]/M	Mean life of radicals (λ/s)
0·016	5·4
0·036	3·0
0·056	1·05
0·075	0·76

TABLE 3

Effect of $CuSO_4$ concentration on the mean life of the radicals; concentration of peroxide 0·056M.

$10^5[CuSO_4]$/M	Mean life of radicals (λ/s)
0·15	0·42
0·37	0·71
0·74	1·05
3·0	2·9

DISCUSSION

The results show that the decomposition process for the peroxide varied with environment. In carbon tetrachloride and cyclohexane the quantum yield was low and of the order of two. Because of the low rate of decomposition under these circumstances a detailed investigation was not carried out. It was found, however, that ethyl alcohol and acetaldehyde were the only products. The reaction $EtO \longrightarrow CH_3 + CH_2O$ found by Rebbert and Laidler[6] for the gas-phase decomposition in toluene at 200—245 °C evidently does not occur under these conditions.

In all the solutions the analysis for acetaldehyde was always of the order of 10% less than that for the alcohol (or decomposed peroxide). This may have been due to absorption of traces of gas in the grease of the vacuum-tight joint on the reaction cell; oxidation too, may have accounted for part of the loss. As the initial peroxide concentration was <1% and less than 15% of this decomposed, small discrepancies might be expected. Any error in the extinction coefficients of the peroxides and the acetaldehyde would also affect the determinations. It was therefore concluded that agreement was as good as could be expected.

(*A*) *Photolysis in Distilled Water.*—With the purified water as solvent the lowest quantum yield measured was five. The values varied however and it was concluded that small traces of a catalyst were still present and that without extreme precautions it would be impossible to study the non-catalysed photolysis. It appears that the solvent does not interact with any of the radicals or products. The primary process in the gas phase and in solution, *i.e.* production of ethoxyl radicals by fission of the O–O bond will be the same, *i.e.* equation (1). The subsequent steps postulated for the gas-phase reaction [equation (2)] may occur in solution also. Since EtOH and CH_3CHO are the only products, formed in equimolar quantities, then $EtO{\cdot}O{\cdot}CH{\cdot}CH_3$ must decompose either bimolecularly [equation (3)] and/or by equation (4). Reactions such as (5)—(7), although postulated for the gas phase, do not occur in the present conditions.

$$EtO{\cdot}OEt + h\nu \longrightarrow 2EtO \qquad (1)$$

$$EtO + P \longrightarrow EtOH + EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \qquad (2)$$

$$2EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \longrightarrow EtOH + 3CH_3CHO \qquad (3)$$

$$EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \longrightarrow EtO + CH_3CHO \qquad (4)$$

$$EtO \longrightarrow CH_3 + CH_2O \qquad (5)$$

$$EtO \longrightarrow H + CH_3CHO \qquad (6)$$

$$P + EtO \longrightarrow Ac + 2EtOH \qquad (7)$$

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[6] R. E. Rebbert and K. J. Laidler, *J. Chem. Phys.*, 1952, **20**, 574.

All the observations can be explained by equations (1)—(4), together with equation (8).

$$2\text{EtO} \longrightarrow \text{CH}_3\text{CHO} + \text{EtOH} \qquad (8)$$

(*B*) *Catalysed Photolysis*.—There are numerous references in the literature to the catalysed thermal decompositions of hydroperoxides and schemes for the catalysed oxidations of aldehydes have been formulated in which a hydroperoxide is catalytically decomposed by a metal ion, Co, Mn, and Fe being the metals most commonly used. Weiland[7] in 1930 discussed the metal-ion-catalysed decomposition of dialkyl peroxides. It appears that little work on the metal-catalysed decomposition of dialkyl peroxides was reported until about 1958, when the catalytic effect of copper salts on the decomposition of peroxides was noted by Kharasch and Fono[8] and also by Holder,[9] who also discussed the mechanism of the decomposition. A large number of papers on the mechanisms involved, together with review articles have been published by Kochi (*e.g.* ref. 10).

Haber and Weiss[11] suggested that Fe^{2+} reacted with hydrogen peroxide according to equation (9). The

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \qquad (9)$$

schemes proposed for the metal-catalysed decompositions of hydroperoxides contain either the step (10)

$$\text{M}^{n+} + \text{RO·OH} \longrightarrow \text{M}^{(n+1)+} + \text{OH}^- + \text{RO} \qquad (10)$$

$$\text{M}^{n+} + \text{RO·OH} \longrightarrow \text{M}^{(n-1)+} + \text{H}^+ + \text{RO}_2 \qquad (11)$$

or (11). It seems very likely that for Et_2O_2 the step occurring is (12), *i.e.* copper(I) ion should catalyse the thermal decomposition. The Cu^{2+} formed in (12) cannot

$$\text{Cu}^+ + \text{Et}_2\text{O}_2 \longrightarrow \text{Cu}^{2+} + \text{EtO}^- + \text{EtO} \qquad (12)$$

be converted into Cu^+ by (the equivalent of) (11) since this would require Cu^{2+} to be a thermal catalyst, which it is not. The products obtained if step (11) did occur would be more complex. Presumably Cu^{2+} is converted into Cu^+ according to equation (13). Hence, starting

$$\text{Cu}^{2+} + \text{EtO} \longrightarrow \text{Cu}^+ + \text{H}^+ + \text{CH}_3\text{CHO} \qquad (13)$$

from the basic steps (12) and (13) the following reaction scheme which is consistent with the kinetics was evolved [equations (14)—(18)]. Stationary state analysis gives

$$h\nu + \text{Et}_2\text{O}_2 \longrightarrow 2\text{EtO} \qquad k_0A \qquad (14)$$

$$\text{Cu}^{2+} + \text{EtO} \longrightarrow \text{Cu}^+ + \text{H}^+ + \text{CH}_3\text{CHO} \qquad k_1 \qquad (15)$$

$$\text{Cu}^+ + \text{Et}_2\text{O}_2 \longrightarrow \text{Cu}^{2+} + \text{EtO}^- + \text{EtO} \qquad k_2 \qquad (16)$$

$$\text{EtO}^- + \text{H}^+ \longrightarrow \text{EtOH} \qquad k_3 \qquad (17)$$

$$2\text{EtO} \longrightarrow \text{CH}_3\text{CHO} + \text{EtOH} \qquad k_4 \qquad (18)$$

equations (19) and (20). Now for long chains, the rate

$$[\text{EtO}] = k_0A/k_4 \qquad (19)$$

$$[\text{Cu}^+] = (k_0A/k_4)^{1/2} \,.\, k_1[\text{Cu}^{2+}]/k_2[P] \qquad (20)$$

of decomposition of the peroxide (*P*) will be given by the rate of step (16). Hence $d[P]/dt$ is given by (21).

$$d[P]/dt = k_2[\text{Cu}^+][P] = k_1[\text{Cu}^{2+}](k_0A/k_4)^{1/2} \qquad (21)$$

Thus the quantum yield (ϕ) for the peroxide is given by (22).

$$\phi = A^{-1}d[P]/dt = k_1[\text{Cu}^{2+}]k_0^{1/2}/(k_4A)^{1/2} \qquad (22)$$

Thus we obtain (23).

$$\phi \propto [\text{Cu}^{2+}]/A^{1/2} \qquad (23)$$

Now since the studies were carried out using weakly absorbing solutions we can assume a linear relationship between absorbed light energy (*A*) and peroxide concentration [*P*]. Thus we deduce (24)—(26), which were found experimentally.

$$\phi \propto [\text{Cu}^{2+}] \qquad [P] \text{ and } A \text{ constant} \qquad (24)$$

$$\phi \propto 1/[P]^{1/2} \qquad [\text{Cu}^{2+}] \text{ and } A \text{ constant} \qquad (25)$$

$$\phi \propto 1/A^{1/2} \qquad [\text{Cu}^{2+}] \text{ and } A \text{ constant} \qquad (26)$$

Intermittent Illumination.—Since two ethoxyl radicals are produced in the primary step, two chains are initiated each time step (14) occurs. Thus the mean life of a chain is given by equation (27), where *T* is the

$$\lambda = \tfrac{1}{2}\phi T \qquad (27)$$

mean duration of one propagation cycle. We can approximate (27) by replacing *T* by the sum of the mean lives of the two chain centres, *e.g.* equation (28).

$$\lambda = \tfrac{1}{2}\phi(T_{\text{Cu}^+} + T_{\text{EtO}}) \qquad (28)$$

$$T_{\text{Cu}^+} = \frac{\text{Steady-state concentration of Cu}^+}{\text{Rate of formation or removal of Cu}^+} \qquad (29)$$

$$T_{\text{Cu}^+} = [\text{Cu}^+]/k_2[\text{Cu}^+][P] = 1/k_2[P] \qquad (30)$$

$$T_{\text{EtO}} = [\text{EtO}]/k_1[\text{EtO}][\text{Cu}^{2+}] = 1/k_1[\text{Cu}^{2+}] \qquad (31)$$

$$\lambda A^{1/2} = (k_0{}^{1/2}/2k_4{}^{1/2})(1 + k_1[\text{Cu}^{2+}]/k_2[P]) \qquad (32)$$

Since T_{Cu^+} is defined by (29) we get (30). Similarly T_{EtO} is defined by (31). Substituting from (22), (30), and (31) into (28) we obtain (32) and hence from Figure 3 we deduce $k_0/k_4 = 2{\cdot}31 \times 10^{-8}$ and $k_1/k_2 = 1{\cdot}6 \times 10^4$. Now from the results for a typical run we can substitute into (22) and hence obtain (33). Substituting for k_0

$$\phi = 120{\cdot}6 = \frac{0{\cdot}74 \times 10^{-5}k_1k_0{}^{1/2}}{2{\cdot}219 \times 10^{-4}k_4{}^{1/2}} \qquad (33)$$

and k_4 we find $k_1 \simeq 2 \times 10^4$ l mol^{-1} s^{-1} and $k_2 \simeq 1{\cdot}5 \times 10^3$ l mol^{-1} s^{-1}. The validity of these values is determined in part by the small experimental errors contained in (ϕ), the correctness of Figure 3, but also by the accuracy with which the scheme postulated above represents the processes occurring during irradiation (see below). Hence rough values only are indicated for k_1 and k_2.

Insufficient data were obtained to enable calculation of k_1 and k_2 at another temperature hence the activation energies E_1 and E_2 could not be calculated. The temperature coefficient for the decomposition is low, thus the overall activation energy for the reaction is small.

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[7] H. Wieland and F. Chrometzka, *Ber.*, 1930, **63B**, 1028.

[8] M. S. Kharasch and A. Fono, *J. Org. Chem.*, 1958, **23**, 324.

[9] G. A. Holder, Ph.D. Thesis, University of London, 1958.

[10] J. K. Kochi, *Tetrahedron*, 1962, **18**, 483.

[11] F. Haber and J. Weiss, *Proc. Roy. Soc.*, 1934, *A*, **147**, 332.

It should be mentioned that the following scheme (34)—(39), which includes the radical $EtO{\cdot}O{\cdot}CH{\cdot}CH_3$

$$h\nu + Et_2O_2 \longrightarrow 2EtO \qquad k_0A \quad (34)$$
$$EtO + Et_2O_2 \longrightarrow EtOH + EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \qquad k_1 \quad (35)$$
$$Cu^{2+} + EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \longrightarrow Cu^+ + 2CH_3CHO + H^+ \qquad k_2 \quad (36)$$
$$Cu^+ + Et_2O_2 \longrightarrow Cu^{2+} + EtO^- + EtO \qquad k_3 \quad (37)$$
$$EtO^- + H^+ \longrightarrow EtOH \qquad k_4 \quad (38)$$
$$2EtO{\cdot}O{\cdot}CH{\cdot}CH_3 \longrightarrow 3CH_3CHO + EtOH \qquad k_5 \quad (39)$$

also satisfies all the results. The equation analogous to (32) is in this case equation (40). However the former mechanism is preferred because of its greater simplicity.

$$\lambda A^{1/2} = (k_0^{1/2}/2k_5^{1/2})\{1 + (k_2[Cu^{2+}]/[Et_2O_2])(1/k_1 + 1/k_3)\} \quad (40)$$

It is interesting to note the parallel between the two schemes and that proposed by Baxendale and Wilson[12] for the copper(II)-ion-catalysed photolysis of H_2O_2.

Oxygen Inhibition.—It was thought at first that the oxygen was inhibiting by directly removing Cu^+. Fenwick[13] in his study of the copper(I)–copper(II) equilibrium, attributed the low values for the equilibrium constant $K = [Cu^+]^2/[Cu^{2+}]$, found by a predecessor, to insufficient precautions in excluding air.

However, Baxendale and Wilson's work indicates that copper(I) ion exists during the photolysis of H_2O_2, when oxygen is being evolved continuously. Another possibility is removal of EtO by reaction with oxygen. The reaction (41) has been postulated.[14] The analogous

$$Et + O_2 \longrightarrow C_2H_4 + HO_2 \quad (41)$$

reaction with EtO would be that shown in (42), while with $EtO{\cdot}O{\cdot}CH{\cdot}CH_3$ a similar reaction would be (43).

$$EtO + O_2 \longrightarrow CH_3CHO + HO_2 \quad (42)$$
$$EtO{\cdot}O{\cdot}CH{\cdot}CH_3 + O_2 \longrightarrow 2CH_3CHO + HO_2 \quad (43)$$

The radical HO_2 is not very reactive, and its formation would be chain ending. Baxendale suggests as a termination step (44). Another reaction which HO_2 might undergo is (45).

$$HO_2 + Cu^+ \longrightarrow Cu^{2+} + HO_2^- \quad (44)$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \quad (45)$$

Photosensitization by Acetaldehyde.—Figure 4 shows the variation in rate as a run proceeded to completion with radiation of wavelength 313·0 nm. Clearly some factor is preventing the expected fall off with time. The extinction coefficient of acetaldehyde is double that of the peroxide at this wavelength and it was suspected that photosensitization by it was sustaining the rate. This was confirmed in two series of experiments: (*a*) small quantities of acetaldehyde were distilled into the cell at the beginning of each run when it was found that the rate was higher than normal for that concentration of peroxide, and (*b*) at 365·0 nm the ratio of the extinction coefficient of diethyl peroxide to acetaldehyde is very much greater, hence the photosensitization effect should be smaller using this wavelength. Runs with a 365·0 nm filter confirmed this, the rate–time curves all showing a fall off as the runs proceeded (see Figure 5).

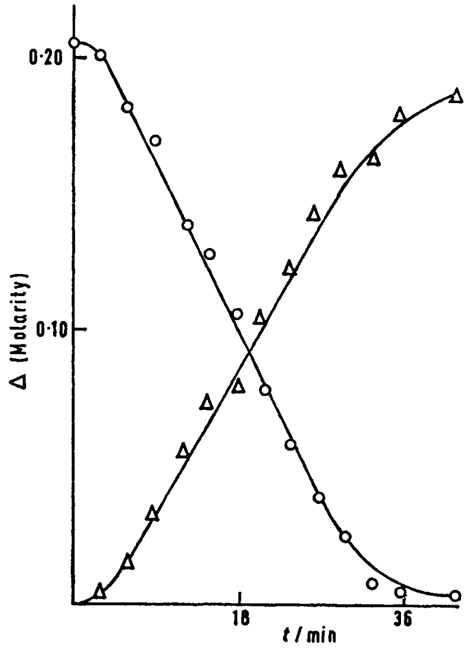

FIGURE 4 Peroxide decomposition as a function of time with radiation of wavelength 313·0 nm; ○, peroxide and △, aldehyde

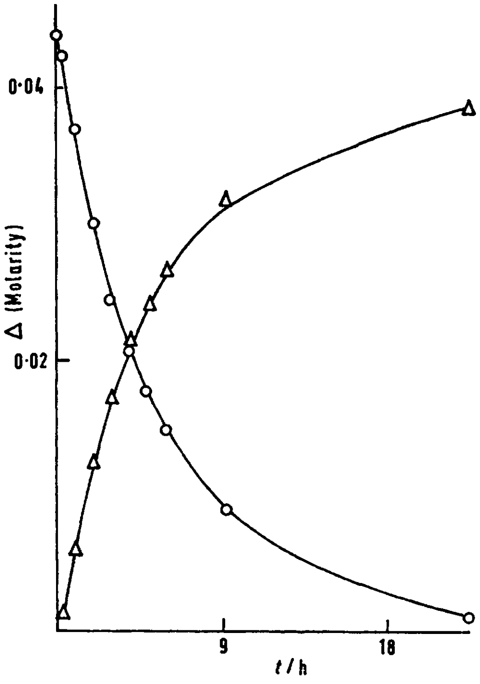

FIGURE 5 Peroxide decomposition as a function of time with radiation of wavelength 365·0 nm ○,; peroxide and △, aldehyde

[1/2158 *Received, 15th November,* 1971]

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[13] F. Fenwick, *J. Amer. Chem. Soc.*, 1926, **48**, 860.

[14] (*a*) J. A. Gray, *J. Chem. Soc.*, 1953, 741; (*b*) R. R. Baldwin, N. S. Corney, and R. F. Simmons, 5th Symposium on Combustion, Reinhold, New York, p. 503.