chiefly hexane-d_5 with small amounts of more highly deuterated hexanes. With this solvent, quantitative separation and estimation of photolysis products was not possible, but examination of the gases and vapors collected indicated clearly that about 20% of the hydrogen was HD and that somewhat less than 10% of the ethane contained deuterium. Further examination of this reaction is in progress.

Discussion

In Fig. 3, the relative iodine yields measured under the four conditions are plotted *vs.* F_β, the fraction of hydrogen atoms beta to the C–I bond. The correlation obtained with the new data is not as clear as when the older quantum yields were used.[7] However, certain qualitative regularities appear. In photolysis of the pure liquids at 3260 Å. the primary iodides (*i*-Bu, *n*-Bu, *n*-Pr, Et) follow a linear progression and it may be that the secondary iodides (*s*-Bu, *i*-Pr) would follow a similar, though distinct, progression. In photolysis of the pure liquids at 2537 Å. and in radiolysis, only an irregular trend of increase in yield with F_β can be seen. Photolysis of alkyl iodides in hexane solution at 2537 Å. appears to be quite distinct from the three former processes in that variation of yield is practically absent.

The existence of the observed qualitative connection between structure and quantum yield is in keeping with the generalized mechanism given in the introduction, although it cannot be regarded as a proof in any sense. Indeed, the proposed mechanism, which rests more on the fact of equality of alkane and alkene than on the present data, raises the additional problem of the apparent inability of the hot alkyl radical to react with hydrogens in positions other than beta. This would produce diiodide and destroy the alkane–alkene equality. Since the facts are to the contrary, one can only presume that reaction at the β-position is favored energetically by concerted loss of the iodine atom and formation of the double bond, that is, simultaneous accomplishment of reactions 1 and 2.

The observed similarity of variation of radiation yield and quantum yield indicates that the product-forming processes must be similar, in spite of the obvious differences in the primary processes. It has been shown in these laboratories[13] that the principal radical produced in radiolysis of the simple alkyl iodides is that formed by breaking the C–I bond, rather than C–C or C–H bonds. Therefore the principal reactive species is the same as in photolysis and we may easily imagine that this radical is an energetic one when formed in the highly exothermic ion neutralization process.

Previously proposed mechanisms of photolysis of alkyl iodides in solution treated the solvent as formally inert, and centered attention upon reactions of the alkyl iodide or radicals formed from it.[14] This view seems no longer even formally satisfactory. The presence of hydrogen in the products of solution photolysis, the observation of HD production in a deuterated solvent, evidence for the formation of cyclohexene and cyclohexyl iodide,[5] and the behavior of the quantum yields all point clearly to a mechanism in which the solvent contributes to the products.

NOTRE DAME, INDIANA

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[13] L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

[14] W. West and J. Fitelson, THIS JOURNAL, **62**, 3021 (1940).

[CONTRIBUTION FROM WILLIAM H. NICHOLS CHEMISTRY LABORATORIES, NEW YORK UNIVERSITY]

The Photochemical Oxidation of *n*-Heptaldehyde[1]

BY JAMES R. MCNESBY AND THOMAS W. DAVIS

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The photoöxidation of liquid *n*-heptaldehyde under conditions that ensure continuous saturation of the liquid by oxygen proceeds at a rate proportional to the pressure of oxygen (if this pressure be in excess of 400 mm.), at a rate proportional to the aldehyde concentration and at a rate proportional to the square root of the absorbed light intensity. When the oxygen pressure is between 200 and 400 mm., the oxidation rate is nearly independent of oxygen pressure. Below 200 mm. the reaction appears once again to be approximately of first order with respect to oxygen. The reaction is inhibited by the products of illumination formed either in the presence or in the absence of oxygen and is slightly inhibited by water. Acid and peracid are the main products but a little carbon dioxide is formed as well. The ten-degree temperature coefficient at constant pressure is 1.25.

The photochemical oxidation of aldehydes in the liquid phase has been studied by a number of investigators.[2] The oxidation appears to proceed chainwise with rather large quantum yields although in some instances the photal rates only slightly exceed thermal rates. The reactions are variously observed to proceed at rates proportional to the light intensity either to the one-half power or to the first power and to proceed at rates proportional to P^n where P is the oxygen pressure and n is a number between 0 and 1.

We have undertaken a study of *n*-heptaldehyde oxidation in the liquid state where the reaction is induced by ultraviolet radiation. We have examined the process as a function of (a) agitation, (b) oxygen pressure, (c) temperature, (d) rate of light absorption and (e) concentration of an inert

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[1] This paper reports work done under contract with the Chemical Corps, Washington 25, D. C

[2] H. L. J. Bäckström, THIS JOURNAL, **49**, 1460 (1927); *Medd. K. Vetenskapsakad. Nobel Inst.*, **6**, No. 15 and 16 (1927); *Z. physik. Chem.*, **B25**, 99 (1934); H. L. J. Bäckström and H. A. Beatty, *J. Phys. Chem.*, **35**, 2530 (1931); C. E. H. Bawn and J. B. Williamson, *Trans. Faraday Soc.*, **47**, 721, 735 (1951); E. J. Bowen and E. L. Tietz, *J. Chem. Soc.*, 234 (1930); R. Cantieni, *Z. wiss. Phot.*, **36**, 119 (1937); H. R. Cooper and H. W. Melville, *J. Chem. Soc.*, 1984 (1951); W. P. Jorissen and P. A. A. van der Beek, *Rec. trav. chim.*, **45**, 245 (1926); *ibid.*, **49**, 138 (1930); E. Raymond, *J. chim. phys.*, **38**, 316, 421, 480 (1941).

solvent. A major problem throughout the work was to keep the dark reaction rate low in comparison with rates of the light-induced reaction. To attain this objective very careful purification of the aldehyde was necessary as well as special cleaning of the reaction vessels. We were successful to the extent that the thermal reaction rates in normal experiments were always less than 15% of the photal rates and were considerably smaller at higher light intensities.

Experimental

Purification of *n*-Heptaldehyde.—Three hundred grams of *n*-heptaldehyde was added to a saturated aqueous solution made from 230 g. of sodium pyrosulfite. The solid addition compound of bisulfite and aldehyde was filtered after 15 minutes and was recrystallized once from a minimum amount of hot water. After being filtered and washed well with water, the compound was hydrolyzed by addition of two liters of solution containing 250 g. of anhydrous sodium carbonate. The aldehyde was thereafter twice steam distilled. The steam had to be generated from distilled water, for we found that piped steam yielded a product whose thermal oxidation rate was uncontrollably large. Following the steam distillation, the aldehyde was dried by anhydrous copper sulfate and was distilled under reduced pressure in a slow stream of pure nitrogen. The middle cut was saved. Its refractive index of 1.4130 at 25° agrees well with the value found in the literature.[3] Seven batches of aldehyde were purified at different times in the manner described.

Other Materials.—Phillips Petroleum Company research grade cyclohexane (99.95% pure) was passed through a column of silica gel which had been dried at 110°. The purified material, after the silica gel treatment, absorbed light in the 2500 Å. region less than Bureau of Standards purified cyclohexane.[4] Before the silica gel treatment, the absorption was considerably stronger than that of the Bureau of Standards preparation.

The oxygen used in this work was bought from the Matheson Company who specified it as 99.6% pure. It was passed through a trap cooled by Dry Ice and acetone and through a column of anhydrous calcium sulfate before use.

Agitation of Reaction Vessels.—Unless oxygen is absorbed as rapidly as it is consumed in a liquid undergoing oxidation, the concentration of oxygen in the liquid will fall to a steady state value and thereafter the rate of oxidation will be fixed by the rate of oxygen dissolution. To ensure rapid dissolving of oxygen and hence continuous saturation of the aldehyde, it is necessary to agitate the liquid rather violently. At first we used vessels in which the oxygen was bubbled rapidly through the reacting liquid, during illumination, but we found it easier to maintain oxygen-saturation by shaking the vessels mechanically. The vessels were made from silica tubing with polished silica end-windows attached by means of sintered silica. The vessels were about 4 cm. in diameter and 4 cm. deep. A cam turned by a variable speed motor provided a convenient way to agitate the vessels. Both speed and amplitude of displacement were easily controlled. A revolution-counter coupled to the cam axle permitted a registration of the number of shaking strokes in unit time.

Light Source.—An Hanovia SC2537 mercury vapor lamp powered by a 5,000 volt transformer provided a source of ultraviolet radiation. The manufacturer states that 95% of the radiant energy has wave length 2537 Å. Most of the remaining ultraviolet appears at 1849 Å. The lamp was fabricated as a flat spiral that illuminated the silica reaction vessels from below. A camera diaphragm interposed between the lamp and the reaction vessel allowed a variation in the rate of light absorption by reactant materials. Calibration was achieved by long exposure of uranyl oxalate solutions to the light from the lamp under the same conditions as those of the photoxidation experiments. From the amount of oxalate destroyed, the light fluxes with three separate openings of the diaphragm were found, after a "warm-up" period of about ten minutes, to be 1.4, 3.0, and 5.9×10^{14} quanta per second, respectively.

Cleaning of Reaction Vessels.—As might be expected when one works with a long-chain reaction, the rates of oxygen-uptake were not precisely reproducible. Some of the variation was attributable to trace residues in the reaction vessels. We adopted as standard practice the following regimen in cleaning the vessels. A vessel after use was allowed to soak overnight in acetone. It was then treated with hot chromic acid solution for one hour. Thirty rinsings with twice-distilled water were followed by drying in an oven at 120° for 15 minutes. The vessel was kept under vacuum until cool. With this procedure, the thermal reaction rates were in most trials satisfactorily low. Even so, the oxidation product from occasional experiments was yellow rather than colorless or the thermal oxidation rate was found on occasion to be inordinately high. More drastic cleaning of the reaction vessel usually corrected the trouble. One reaction vessel, however, after long use gave rise fairly suddenly to consistent but high dark reaction rates. All efforts to reduce the rate of the dark reactions failed and the vessel had to be discarded. A new vessel gave normal results at once.

Results

The rate of aldehyde oxidation was followed by means of oxygen disappearance at constant pressure. The photoöxidation reached a maximum speed when the reaction cell was shaken at a rate of 320 strokes a minute or at a somewhat lower rate at lower light intensities or lower oxygen pressures. No increase in reaction rate was observed on increasing the agitation from 320 to 400 cycles per minute (c.p.m.). Above 400 c.p.m., serious vibrations appeared in the whole apparatus and no rates of shaking higher than 400 c.p.m. were tried.

The ultraviolet absorption spectrum of the purified heptaldehyde was determined in the range 2460 to 3600 Å. The extinction coefficient of the aldehyde at 2537 Å. was found to be so large, namely, 35.4 cm.$^{-1}$, that practically all the incident radiation of this wave length is absorbed in the 1.6-mm. layer of aldehyde normally used in the present experiments. Even so, agitation at 320 c.p.m. destroyed the uniformity of the layer sufficiently that some of the light must have passed through the vessel unabsorbed. Evidence for this occurrence is found in the observation that the rate of oxygen absorption when the agitation was sufficient to bring the rate to a plateau value was approximately proportional to the volume of aldehyde in the vessel. Raymond[2] found exactly the same effect, and his results are probably to be explained in the same way. Since all our reported results are from experiments in which 2 ml. of fluid was used, relative quantum yields are comparable throughout but absolute quantum yields must all be too small. To check further on the adequacy of the agitation selected, however, a direct test was made in several experiments. During the illumination, the shaking rate was increased. In no case was the rate of oxygen absorption changed as a result of the more violent agitation.

Variation in the rate of radiant energy absorption caused a variation in quantum yield. The rate of oxygen consumption is a linear function of the square root of the rate of light absorption as shown in Table I. The data at 384 mm. were obtained in a single experiment, the diaphragm being reset during the course of the illumination. The data at 600 mm. were recorded in three separate trials.

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(3) M. Deffet, *Bull soc. chim. Belg.*, **40**, 385 (1931).

(4) M. E. MacLean, P. J. Jencks and S. F. Acree, *J. Research Natl. Bur. Standards*, **34**, 271 (1945).

The square root relation connecting light flux and rate is encountered frequently in photochemical work.[5]

Table I

Linearity of Photoöxidation Rate *vs.* Square Root of Light Intensity

Square root of light flux[a]	1.18	1.18	1.73	2.43
Rate[b] at P_{O_2} = 384 mm.	1.98	..	3.04	4.11
Rate[b] at P_{O_2} = 600 mm.	3.04	2.62	4.56	6.03

[a] Light fluxes were 1.40, 3.00 and 5.90 × 10^{14} quanta absorbed per sec. [b] Reaction rates in this and subsequent tables are expressed in ml. of O_2 (at S.T.P.) absorbed per 100 sec.

The effect of oxygen pressure on reaction velocity is recorded in Table II. Above 400 mm., and possibly below about 200 mm., the rate of oxidation is proportional to the pressure of oxygen. Between 200 and 400 mm., the velocity is nearly independent of the pressure. The proportionality between rate of reaction and oxygen pressure above 400 mm. was tested in another way. If the reaction is of first order with respect to oxygen, a plot for a given experiment of logarithm of oxygen pressure, at constant volume, against time should yield a straight line. Table III indicates that this is observed in the pressure range 370 to 490 mm.

Table II

Variation of Photoöxidation Rate with Oxygen Pressure

2 ml. aldehyde; temp., 28.5°; agitation rate = 350 c.p.m.

Intensity = 5.90 × 10^{14} quanta/sec.

P_{O_2} (mm.)	99	102	188	200	202	202	204	298
Rate	1.33	2.13	3.44	3.29	4.37	3.78	3.87	3.93
	384	404	504	512	595	660		
	4.11	3.81	4.12	5.33	6.03	6.45		

Intensity = 3.00 × 10^{14} quanta/sec.

P_{O_2}	198	384	599
Rate	2.66	3.04	4.56

Intensity = 1.40 × 10^{14} quanta/sec.

P_{O_2}	99	199	384	598	599
Rate	0.46	1.22	1.98	3.04	2.62

Table III

Linearity of Logarithm of Pressure of Oxygen as a Function of Time in a Constant Volume Reaction

Intensity = 5.90 × 10^{14} quanta/sec.

Time (sec.)	log P_{O_2}	Time (sec.)	log P_{O_2}
0	2.691	310	2.625
70	2.679	360	2.613
125	2.667	420	2.599
155	2.660	480	2.586
205	2.649	555	2.569
255	2.637		

The net photochemical oxidation rates reported in Tables I and II represent the rates of reaction due solely to the chains initiated by the absorption of light. These rates were computed from the total rates according to the relation given by Noyes and Leighton,[6] that is

$$R_P = (R_L^2 - R_T^2)^{1/2}$$

where R_L refers to the rate under illumination, R_T is the thermal or dark rate and R_P is the net photal rate. A nearly equivalent although approximate relationship useful for the rapid computation of net light rates is

$$R_P = R_L - \frac{1R_T}{2R_L} \times R_T$$

The form of the correction is such that a fairly large change in the dark rates makes little change in the computed net photal rates.

The effect of temperature on the rate of photoöxidation is summarized in Table IV.

Table IV

Effect of Temperature on Photochemical Oxidation of 2 Ml. of *n*-Heptaldehyde (Batch II]

Press. of oxygen = 600 ± 2 mm.; agitation = 350 c.p.m.: light absorption = 5.90 × 10^{14} quanta/sec.

Temp., °C.	Reaction rate, ml. O_2 (S.T.P.)/100 sec. In dark	In light	Net light	Quantum[a] yield
20.5	0.24	6.88	6.88	3130
21.4	.29	6.93	6.92	3150
25.5	.08	7.08	7.08	3220
25.8	.39	7.59	7.58	3450
28.0	.13	7.55	7.55	3440
29.4	.26	8.49	8.49	3860
32.0	.29	8.90	8.87	4050

[a] Molecules of O_2 per quantum.

When logarithms of the reaction velocities are plotted against the reciprocals of the absolute temperatures, the data are found to scatter rather badly. Uncertainties in individual rates seem to be of the order of 5%. The 10° temperature coefficient appears to be about 1.25 and this corresponds to an apparent activation energy of 4.0 kcal. per mole. Since the solubility of oxygen varies with temperature at constant pressure, a more significant figure for the energy of activation may be 6.9 kcal. per mole. The difference between 6.9 and 4.0, *viz.*, 2.9 kcal. per mole, is the partial molal heat of vaporization of oxygen from saturated water solutions. The temperature coefficient of the solubility of oxygen in *n*-heptaldehyde has not been reported, but it may be taken as equal roughly to the temperature coefficient in water.[7]

Table IV contains values of quantum yields, based on oxygen consumption. These are seen to be comparable with quantum yields in aldehyde oxidations estimated by other investigators. The yields listed are too low because, as mentioned above, some of the incident light escapes absorption when the reaction vessels are shaken.

To determine the influence of aldehyde concentration on the rate of photoxidation, solutions of *n*-heptaldehyde in purified cyclohexane were exposed to ultraviolet light. The concentration range of the solutions extended from 2.84 to 7.5 molar. The rate of oxygen consumption by these solutions when illuminated proved proportional to the molar concentration of aldehyde as shown in Table V. Thermal rates in every instance were very small. Melville and Cooper noticed similarly that rates of thermal oxidation of decanal in decane are negligible

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(5) (a) W. A. Noyes, Jr., and P. A. Leighton, "Photochemistry of Gases," Reinhold Publ. Corp., New York, N. Y., 1941, p. 197; (b) G. K. Rollefson and M. Burton, "Photochemistry and the Mechanism of Chemical Reactions," Prentice-Hall, Inc., New York, N. Y., 1939, p. 113.

(6) Reference 5a, p. 199.

(7) "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, p. 257.

although in the absence of the solvent, the thermal oxidation proceeds fairly rapidly.[2]

The velocity data recorded in Table I and plotted in Tables I–V represent initial steady state readings. In some but not all of the experiments, there was a short induction period (of 150 sec. at most) following the start of illumination. During this period the rate of oxidation increased to a steady state value that continued without apparent change during the rest of the experiment. The induction periods were somewhat more noticeable on the average when the preceding thermal rates were low. To see how long the steady state oxidation velocity would persist, one experiment was continued until the oxygen consumed corresponded to 25% of the aldehyde initially present, computed on a molecule for molecule basis. The rate of oxidation in this experiment began to fall when the oxygen consumption corresponded to 10% of the aldehyde and at the end of the experiment the reaction was proceeding only $^1/_5$th as fast as initially. Other experiments were carried beyond 10% consumption of the aldehyde and similar results were noted. The oxidation of the heptaldehyde seems to produce powerful oxidation inhibitors. Reiff[8] has reported the same sort of behavior during the thermal oxidation of benzaldehyde. Even though the oxidation of benzaldehyde may be easily discernible in a few minutes time initially, the reaction may be still incomplete many months later. Almquist and Branch have noted similar observations.[9]

TABLE V

DEPENDENCE OF OXIDATION RATE ON CONCENTRATION OF ALDEHYDE IN CYCLOHEXANE SOLUTION

Temp., 29.0°; P_{O_2} = 528 mm.; intensity = 1.40 × 10^{14} quanta/sec.

Molar concn. of aldehyde	2.84	3.54	4.50	4.55	5.35	5.75	6.10	7.5
Rate	0.76	1.08	1.33	1.61	1.77	1.71	2.04	2.54[a]

[a] Rate for pure aldehyde interpolated from Table II.

Pre-irradiation of the aldehyde, under an atmosphere of nitrogen, apparently produces inhibitors also. Both thermal and photal rates are greatly lowered as a result of the pre-irradiation. Water is another, although weak, oxidation inhibitor. Raymond observed the inhibiting action of water in benzaldehyde photoöxidation and suggested that this action is due to the formation of dialcohol.[2] It was observed in the present investigation that aldehyde saturated with water reacts about half as rapidly as dry aldehyde. Reiff says to the contrary that water, especially water adsorbed on the walls of the reaction vessel, is a catalyst in the thermal oxidation of benzaldehyde.[8]

A further characteristic of *n*-heptaldehyde oxidation noted in the present work is the persistence of dark reaction after the ending of irradiation. Regardless of whether the initial dark reaction proceeded at a relatively high or at a relatively low speed and regardless of whether an induction period occurred or not, the post-photal rates were always appreciable and were always higher than the pre-photal rates. The post-photal rates diminished over periods of hundreds of seconds.

In the absence of pre-irradiation, the rate of photoxidation of *n*-heptaldehyde is given by the expression

$$\text{rate of oxygen consumption} = kC_{\text{A}}P_{\text{O}_2}I^{1/2}e^{-4{,}000/RT} \quad (1)$$

where C_{A} is the concentration of aldehyde; P_{O_2} is the pressure of oxygen; I is the rate of light absorption; R is the gas constant in cal. per degree per mole; T is the absolute temperature and 4,000 is the apparent activation energy in calories per mole. This relation holds in the temperature interval 20–30°, when the pressure of oxygen exceeds 400 mm. It applies, furthermore, only when the rate of agitation is sufficient to keep the aldehyde saturated with respect to oxygen.

To secure information concerning the stoichiometry of the reaction, an examination was made of both liquid and gaseous products. The liquid from each of four runs was analyzed for content of (1) peroxide and (2) total acid. The peroxides were estimated by adding to the acidic product an ethanol solution of potassium iodide and titrating immediately, in presence of an atmosphere of nitrogen, with thiosulfate. The excess acid, not consumed in the peroxide determination, was titrated by standard potassium hydroxide in ethanol to a phenolphthalein end-point.[10] The results obtained appear in Table VI.

TABLE VI

PEROXIDE AND ACID PRODUCTION IN PHOTOÖXIDATION OF HEPTALDEHYDE

Peroxide found, mmole	Total acid found, mmoles	Vol. of O_2 consumed Calcd. ml. (S.T.P.)	Obsd. ml. (S.T.P.)
0.428	1.359	19.0	19.5
.457	2.615	34.4	34.2
.476[a]	1.455[a]	21.6[a]	18.5[a]
.379[b]	0.967[b]	19.4[b]	20.9[b]

[a] Oxidation in cyclohexane solution. [b] Thermal reaction.

The figures in Table VI indicate that acid and peracid are principal products of heptaldehyde oxidation. Fairly satisfactory agreement in three of the experiments is noticed between oxygen observed to be consumed and that expected on the basis of the products. In cyclohexane solution, the deficiency in oxygen consumption suggests that some reaction occurs that produces acid without consuming oxygen. To compete significantly with the oxidation, it too must have a chain character.[11]

Analysis of the gas remaining in the system after the photoöxidation showed the presence of a small amount of carbon dioxide but no significant amount of carbon monoxide. Roughly 2% of the oxygen consumed in the reaction appeared as carbon dioxide. Other investigators have found carbon monoxide and carbon dioxide as minor products of aldehyde oxidation, sometimes one, sometimes the other and occasionally both.[10,12]

Discussion

It seems generally to be agreed that the primary effect of 2537 Å. radiation, when absorbed by alde-

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(8) O. M. Reiff, THIS JOURNAL, **48**, 2893 (1926).

(9) H. J. Almquist and G. E. K. Branch, *ibid.*, **54**, 2293 (1932).

(10) M. J. Kagan and G. D. Lubarsky, *J. Phys. Chem.*, **39**, 837 (1935); G. D. Lubarsky and M. J. Kagan, *ibid.*, **39**, 847 (1935).

(11) F. Haber and R. Willstätter, *Ber.*, **64**, 2844 (1931).

(12) G. E. K. Branch, H. J. Almquist and E. C. Goldsworthy, THIS JOURNAL, **55**, 4052 (1933).

hyde, is to split the aldehyde molecules into equal numbers of alkyl and formyl free radicals. The free radicals can start chain-oxidation of the aldehyde. The reactions may be represented as follows (where RCHO is the original aldehyde)

$$\mathrm{RCHO} \longrightarrow \mathrm{R\cdot} + \mathrm{CHO\cdot} \qquad (2)$$

$$\mathrm{R\cdot} + \mathrm{RCHO} \longrightarrow \mathrm{RH} + \mathrm{RCO\cdot} \qquad (3)$$

$$\mathrm{RCO\cdot} + \mathrm{O_2} \rightleftarrows \mathrm{RCO_3\cdot} \qquad (4)$$

$$\mathrm{RCO_3\cdot} + \mathrm{RCHO} \longrightarrow \mathrm{RCO_3H} + \mathrm{RCO\cdot} \qquad (5)$$

$$\mathrm{RCO_3H} + \mathrm{RCHO} \longrightarrow \mathrm{2RCO_2H\cdot} \qquad (6)$$

$$\mathrm{RCO\cdot} + \mathrm{RCO\cdot} \longrightarrow \text{products} \qquad (7)$$

The dots, representing unpaired electrons, mark the free radicals in the equations above. The usual steady-state conditions together with the specification that reaction 4 be regarded as reversible lead to a rate law in keeping with experimental findings as expressed in equation 1 except for a $V^{1/2}$ term which was not tested in the present work. V is the volume of reacting liquid.

Kinetically reaction 3 would be indistinguishable from the pair of successive reactions

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{RO_2\cdot} \qquad (8)$$

$$\mathrm{RO_2\cdot} + \mathrm{RCHO} \longrightarrow \mathrm{RO_2H} + \mathrm{RCO\cdot} \qquad (9)$$

Table II indicates that at low pressures of oxygen, the oxidation rates are larger than those predicted from rates at high oxygen pressures. The effect is as if either more chains are started per quantum at low pressures or the chains are longer at low pressures. The first possibility may be interpreted simply. The HCO· radicals released in reaction 2 may either start chains by reacting with aldehyde or may be converted into peroxy radicals, *i.e.*, $\mathrm{HCO_3\cdot}$, which do not give rise to chains. The possible reactions are

$$\mathrm{HCO\cdot} + \mathrm{RCHO} \longrightarrow \mathrm{H_2CO} + \mathrm{RCO\cdot} \qquad (10)$$

$$\mathrm{HCO\cdot} + \mathrm{O_2} \longrightarrow \mathrm{HCO_3\cdot} \qquad (11)$$

$$\mathrm{2HCO_3\cdot} \longrightarrow \text{products} \qquad (12)$$

When the pressure of oxygen is high, nearly all the HCO· forms $\mathrm{HCO_3\cdot}$ and thus only one reaction chain is started per photon absorbed. When the pressure of oxygen is low nearly all the HCO· as well as the RCO· radicals may start chains, making two chains per absorbed photon. According to this picture, the rate of oxidation at low oxygen pressure may rise to a value about double the extrapolated high pressure rate and that is about what is observed.

The quantum yields measured with different batches of aldehyde differ under otherwise identical conditions. Experiments run with Batch IV, for example, at 600 mm. of oxygen and at an intensity of 5.90×10^{14} quanta per second showed about 30% lower yields than experiments run with Batch V. Despite the slower reaction observed with Batch IV, the reaction rates show proportionality to the square root of the light intensities. A parallel finding is that of Waters and Wickam-Jones in the "retarded" oxidation of benzaldehyde when benzoyl peroxide acts as the initiating agent.[13] Despite the presence of *p*-cresol, which acts as a "retarder," the oxidation velocity showed proportionality to the square root of the initiator concentration. The square root relationship is usually interpreted as due to a biradical chain-termination process. In the present study, an impurity in aldehyde of Batch IV may be responsible for the lowered quantum yields. The impurity seems not to change the nature of the chain-terminating step. It may, however, reduce the number of chains started per photon by reacting, for example, with the initiating radicals or it may interfere in one of the chain-continuing steps.

None of the reactions appearing above shows specifically the formation of carbon dioxide. It is likely that carbon dioxide is a secondary product and comes from either photochemical or thermal decomposition of a primary product, *e.g.*, peracid.[10] Carbon dioxide is too abundant to be solely a chain-termination product and it is not abundant enough to be a main product of a chain-continuation reaction.

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[13] W. A. Waters and C. Wickam-Jones, *J. Chem. Soc.*, 812 (1951).