444. *The Kinetics of the Autoxidation of* n-*Decanal. Part I. The Mechanism of Reaction.*

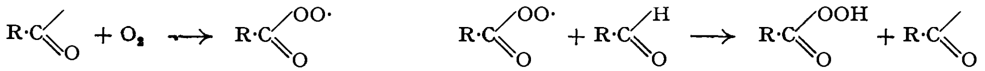
By H. R. Cooper and H. W. Melville.

The autoxidation of *n*-decanal to per-acid has been investigated kinetically by means of measurements of oxygen absorption in an automatically controlled manostat. Bäckström showed that this was a radical chain reaction which could be initiated by ultra-violet light, but the detailed mechanism remained uncertain. As usual with radical processes of long chain length, reliable results require care to ensure that the solution of oxygen in the aldehyde does not become the rate-controlling factor. To reduce the proportion of the thermal reaction, experiments were conducted at 5°. Evidence is presented which indicates that: (1) The mechanisms of the thermal and photo-processes are identical apart from the mode of initiation. (2) Chain propagation occurs by the usual cycle: $R\cdot + O_2 \longrightarrow RO_2\cdot$; $RO_2\cdot + RH \longrightarrow ROOH + R\cdot$. (3) In the pressure region $\frac{1}{2}$—1 atm., termination takes place wholly by the mutual interaction of the peroxidic radicals. (4) Thermal initiation involves direct attack by oxygen on the aldehyde molecules, and photo-initiation direct dissociation of the aldehyde into radicals.

During an investigation of "negative catalysis," reported during 1926—1934, Bäckström showed that autoxidation of aldehydes in the liquid phase proceeded by a peroxidic mechanism, the initial product being a per-acid. From the large quantum yield (of the order 10^4) observed when the process was carried out under the influence of ultra-violet radiation, and from the drastic reduction in the rate of autoxidation brought about by the addition of small quantities of substances such as α- and β-naphthol, he deduced that the per-acid formation, whether brought about thermally or photochemically, was a chain reaction; in this way the foundation of the theory of thermal chain reactions was laid. Subsequent reaction between the per-acid and further aldehyde by a non-chain mechanism gave rise to the final product of autoxidation, the carboxylic acid, and this secondary process was found to be almost insensitive to the action of ultra-violet light, *i.e.*:

(*a*) Aldehyde + Oxygen ⟶ Per-acid
(*b*) Aldehyde + Per-acid ⟶ Carboxylic acid

Bäckström concluded that the chain carriers involved in stage (*a*) were of a free-radical nature and suggested that the propagation steps were of the form :



He found experimental evidence to support the view that substances which inhibited the autoxidation acted by removing the peroxidic radicals from the system.

Bowen and Tietz's results (*J.*, 1930, 234) on the gas-phase photochemical autoxidation of acetaldehyde indicated that the reaction rate was of the form :

$$\text{Rate} \quad \propto I^{\frac{1}{2}}[\mathrm{R{\cdot}CHO}]^1[\mathrm{O_2}]^0$$

where I represents the intensity of the absorbed light, and this suggested that the chains were being terminated by mutual destruction of the radical chain-carriers.

It appeared, therefore, that the first stage in the autoxidation of aldehydes bore a formal similarity to that shown recently to hold for olefinic hydrocarbons by the investigations of the British Rubber Producers' Research Association (*Proc. Roy. Soc.*, 1946, *A*, **186**, 218 *et seq.*). This similarity has been emphasised by the results reported in the present paper. A complete kinetic examination of the thermal and photochemical autoxidation of *n*-decanal in the liquid phase has enabled a detailed mechanism to be evolved for both processes and, by the use of modern experimental techniques (see Part II), the velocity constants of some of the individual reaction steps involved have been measured. The knowledge of these quantities and of similar results from work on related systems can lead to generalisations about the reactivity of the radicals concerned.

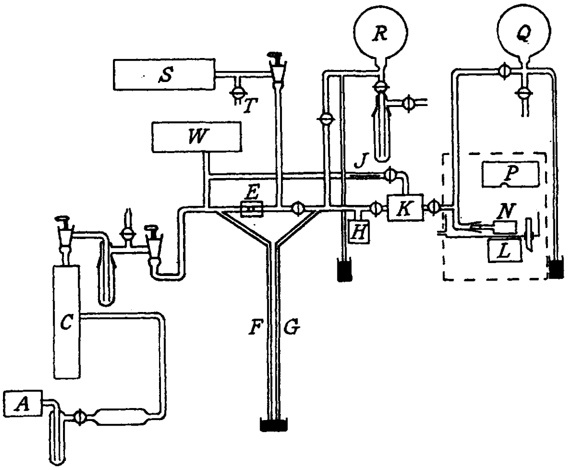
EXPERIMENTAL.

General Outline of Apparatus.—As pure oxygen was used, it was necessary to be able to evacuate the reaction system. Pressures of 10^{-4} mm. or less could be achieved by a two-stage mercury diffusion pump backed by a Speedivac rotary oil-pump.

The general lay-out of apparatus is shown in Fig. 1.

FIG. 1.

General outline of apparatus.



A, *Oil pump.* *C*, *Mercury diffusion pump.* *E*, *Vacustat.* *H*, *Mercury dropper.* *J*, *Capillary.* *K*, *Manostat.* *L*, *Electromagnetic stirrer.* *N*, *Silica reaction vessel.* *P*, *Mercury lamp.* *Q*, *Nitrogen bulb.* *R*, *Oxygen bulb.* *S*, *Distillation system.* *W*, *Aldehyde reservoir and sampling devices.* *T*, *Nitrogen inlet.*

The storage bulbs for oxygen and oxygen-free nitrogen were periodically filled from cylinders of the appropriate gases, but the oxygen was introduced through a liquid-air trap to ensure removal of condensable impurities. The actual oxygen pressure in the reaction system was measured by the difference in the mercury levels in tubes *F* and *G*.

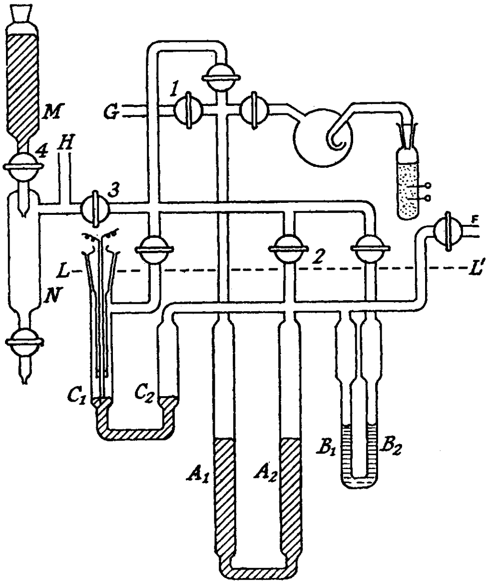
Both the manostat and the reaction vessel were immersed in water-thermostats, controlled by A.C. Thyratron relays operated in conjunction with mercury–toluene regulators of the usual type. The low temperatures required were obtained by circulating water, cooled by a refrigerating unit, through the copper tank containing the reaction vessel. The temperature in the copper tank was regulated, within ±0·01°, by running the refrigerating unit all the time and operating, in opposition, a heating lamp through the Thyratron circuit and the mercury–toluene regulator.

Except where likely to come into close contact with the aldehyde, Apiezon Grease M was used as a lubricant for taps and ground-glass joints. Otherwise, silicone grease thickened with talc was employed.

Manostat.—Fig. 2 shows the device, similar in dimensions to, but slightly modified from, that of Bolland (*Proc. Roy. Soc.*, 1946, *A*, **186**, 218), which was used to follow the oxygen uptake at constant pressure. The whole apparatus was immersed, up to a level marked in the figure, in a thermostat regulated at 25·00° ± 0·01°. The thermionic relay circuit controlling the manostat was that employed by Bolland. Current for the electrolytic cell was obtained from the D.C. mains through a potentiometer device, for it must be possible to vary the rate of production of gas in order that the manostat may function with maximum efficiency at different rates of oxygen absorption (*i.e.*, when the cell is " on " and " off " for approximately equal times). The volume of oxygen taken up was measured, within 0·02 mm., on the limb A_2 of the gas burette beside which was fixed a steel rule graduated in mm. Since the tubing was found to be of even bore, there is no appreciable loss of accuracy in using a constant factor (1·12 c.c./cm.) to convert distances along the limb into volumes of oxygen absorbed.

FIG. 2.

Manostat.



A_1A_2, Oxygen burette. B_1B_2, Dibutyl phthalate manometer. C_1C_2, Contact manometer. F, Connection to reaction vessel. G, Connection to capillary. H, Connection to oxygen supply and vacuum. LL', Water level in thermostat.

Although only the initial stage of the oxidation was examined, preliminary experiments showed that the amount of oxygen which the gas burette A_1A_2 could deliver—about 18 c.c.—was rather small. Somtimes, it was desirable to follow the reaction further. Since increasing the diameter of the limbs in the gas burette would involve less accurate measurement of the oxygen uptake, and since the depth of the thermostat tank prevented an extension of their length, there was devised instead a method of refilling A_1A_2 at an approximately constant pressure. By connecting a capillary (*J* in Fig. 1) between A_1 and the main vacuum line it was possible to reduce gradually the pressure in A_1 through tap 1. Further, with taps 2 and 3 open, mercury was allowed at the same time to flow from *M* to *N*, so reducing the volume of the oxygen in the reaction system. If the flow of mercury was carefully reguated by tap 4, the reduction of pressure and the contraction of volume could be balanced so that the oxygen pressure remained almost constant. Any deviation from the original pressure was indicated by the dibutyl phthalate manometer. The time taken for this operation was less than 3 minutes and, by noting the rate of oxygen uptake before and after refilling, the volume of oxygen absorbed by the sample in the interim could be estimated if required.

Reaction Vessel.—The silica reaction vessel used for this investigation had plane-parallel circular faces 2 cm. apart and 6 cm. in diameter. This type of vessel minimises the dispersing effects of the glass on the incident light, but its chief advantage is that it enables small samples to be distributed over a large surface area. This is particularly desirable in the present case because high rates of oxygen absorption are encountered. A uniform thickness of the aldehyde film was obtained by setting the vessel in a horizontal plane by a spirit level and inserting metal spacers between its lower surface and the bottom of the copper thermostat tank.

To assist dissolution of oxygen in the aldehyde the film was agitated by a glass-covered pin (length, 3 cm.) which was set in motion by a rotating magnetic field situated directly beneath the copper tank. This method of agitation was preferred to mechanical shaking because the latter would involve moving the reaction vessel to and fro in the light beam, thereby leading to periodic fluctuations in the intensity of the incident radiation.

FIG. 3.

Ultra-violet absorption spectrum of n-*decanal.*

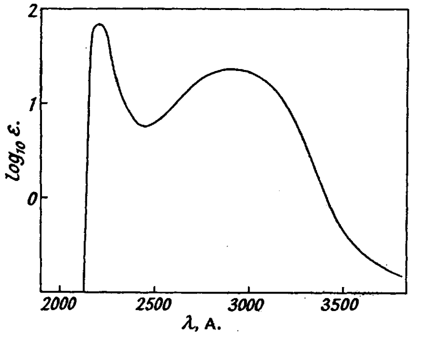


FIG. 4.

Transmission of Corning 597 *R.P. Ultra glass filter.*

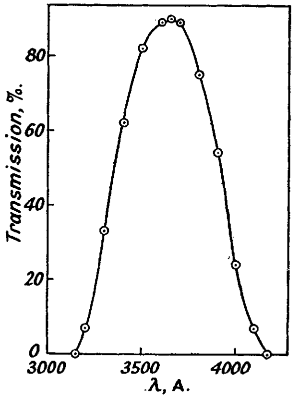
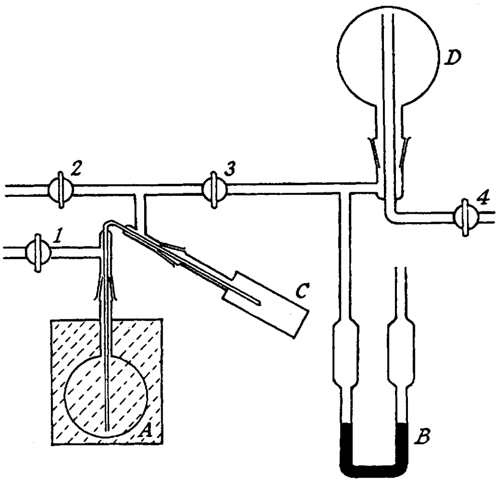


FIG. 5.

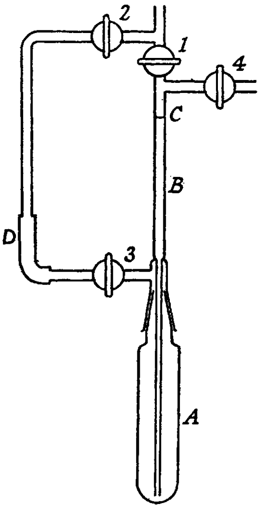
Siphon apparatus.



A, Aldehyde reservoir. B, Safety valve.
C, Reaction vessel. D, Nitrogen reservoir.

FIG. 6.

Constant-volume pipette.



Cleaning was normally carried out by repeated washing with absolute alcohol and pumping out under a high vacuum but, in the event of contamination with silicone tap grease, an alkali borate solution had to be used before the above treatment.

Optical Arrangement.—*Absorption spectrum of* n-*decanal.* There is no published information on the ultra-violet absorption of the longer-chain aliphatic aldehydes, so measurements were made on a Uvispec Spectrophotometer with solutions of *n*-decanal in *n*-decane. Beer's law was found to be obeyed and the calculated absorption curve for pure aldehyde is shown in Fig. 3.

Ultra-violet mercury lamp. The reaction vessel was illuminated from above, as shown in Fig. 1, the lamp used being of the G.E.C. " Osira " type stabilised by a constant-voltage transformer in conjunction with the choke and condenser recommended by the makers. Another precaution taken to ensure constant intensity of illumination was to allow the lamp at least 45 minutes to come to equilibrium before readings were taken.

Light filter. From the extinction-coefficient measurements mentioned above, the degree of absorption at various wave-lengths which might be expected for the pure aldehyde under the experimental conditions may be calculated. Although the thickness of the liquid film never exceeded 1 mm., light of $\lambda < 3200$ A. is very strongly absorbed. To ensure that, as nearly as possible, the light absorption is even throughout the reacting system, a Corning 597 R.P. Ultra glass filter was interposed between the lamp and the reaction vessel. The transmission of this filter is given in Fig. 4.

Methods of Charging Reaction Vessel.—In view of the readiness with which aldehydes are oxidised in air, the liquid had to be introduced into the silica vessel without contact with the atmosphere. Direct vacuum-distillation was not practicable and alternative procedures adopted were as follows.

(a) *Siphon method.* The apparatus used is illustrated in Fig. 5. In order to charge the reaction vessel *C* with a sample of aldehyde, the weighed vessel *C*, already filled with nitrogen, is connected and a current of nitrogen is blown through it for a few minutes by opening taps 1, 3, and 4. These are then closed and, by cautiously opening tap 2, a quantity of aldehyde is drawn from *A* through the delivery tube into the reaction vessel *C*. Before the latter was removed for a second weighing, a stream of nitrogen is again passed through *D*, *C*, and *A*.

(b) *Constant-volume pipette.* Since (see below) the quantities of aldehyde taken in the samples are somewhat critical, another device (Fig. 6) was designed to measure out a definite volume of liquid. The mode of operation is as follows: Taps 1 and 3 are opened and a stream of nitrogen allowed to bubble through the reservoir. By closing of tap 1 and opening of tap 2 the air in the flexible rubber connection *D* may then be displaced. With *D* attached to the side-arm of tap 3, and with taps 3 and 4 open, the flow of nitrogen through tap 2 can be regulated so that the liquid rises up the pipette tube *B* to the mark *C*. All taps are then closed and tube *D* is disconnected. The reservoir *A* is replaced by the nitrogen-filled reaction vessel and when taps 1 and 3 are opened a stream of nitrogen forces the liquid into the reaction vessel. Whilst the flow of gas is maintained, the reservoir *A* is replaced, and, after the gas has bubbled through the aldehyde for a few minutes, all taps can again be closed. Stoppers are applied to both reservoir *A* and the reaction vessel immediately after withdrawal from the nitrogen stream.

In the above methods of taking aldehyde samples the reason for the somewhat elaborate precautions to prevent access of air has been, not so much to protect the sample, but rather to protect the reservoir of purified material. As regards the sample itself, exclusion of oxygen is not so important because it is necessary in any case to allow oxygen to come into contact with it for at least 5 minutes before readings of oxygen uptake can be commenced, in order that equilibrium conditions of temperature and dissolution of oxygen may be achieved. The relatively large rate of thermal oxidation at room temperature, however, does necessitate care in handling the reservoir of pure aldehyde. Successive exposures to air while samples are being taken would have a cumulative effect and could not lead to reproducible results for, as will be seen, the reaction rate depends to some extent on the quantities of oxidised material present.

It was found, however, that, in *n*-decane solution, the rate of thermal oxidation was considerably reduced and the need for these elaborate precautions vanished. The samples in the experiments carried out in solution were simply measured directly into the reaction vessel by means of a calibrated pipette, and sufficient protection for the liquid in the reservoir was found to be afforded by sweeping out the air space over the solution with nitrogen immediately before replacing the stopper.

Choice of Materials.—*Aldehyde.* In an investigation of a gas–liquid reaction it is desirable that the liquid should have a low vapour pressure. Pumping out of the system and introduction of the reactant gas become much easier, and complications such as a screening effect by the vapour or appreciable reaction in the gas phase are avoided. These considerations indicated that the higher members of the aliphatic series would be suitable materials. Furthermore, the reaction mechanism is not likely to be affected by the length of the carbon chain and hence results obtained with the higher aldehydes should be applicable to the lower members of the series.

Solvent. Establishment of the dependence of the rate of oxidation on the aldehyde concentration requires the use of a solvent which should be chemically inert, involatile, and transparent to the wave-lengths used to initiate the reaction. The aliphatic C_{10-12}-hydrocarbons seemed to be most suitable; *n*-decane was used.

Purification of Materials.—*Aldehyde.* *n*-Decanaldehyde, supplied by L. Light and Co. Ltd., was shaken, under an atmosphere of nitrogen, twice with 5% brine and twice with distilled water, then dried (Na_2SO_4), and fractionally distilled at reduced pressure in Quickfit apparatus, in presence of nitrogen, the fraction of b. p. 91—92°/10 mm. being collected. Further purification was achieved by further distillation *in vacuo*. The low vapour pressure at room temperature makes this extremely slow, but a reasonable rate of distillation was achieved by making use of tubing of 2-cm. diameter and keeping to a minimum the distance through which the vapour had to diffuse. Batches of approx. 20 c.c. were withdrawn from the reservoir of fractionated aldehyde by means of the siphoning device, and the dissolved gases removed by alternate freezing in liquid air and melting in a vacuum. Distillation *in vacuo* could then be carried from the temperature of the room to that of liquid air at a rate of about 20 c.c. in 24 hours. It was necessary to carry out 4—5 distillations before the aldehyde was pure enough to yield consistent rates of oxidation. Impure aldehyde left a white residue containing decanoic acid and probably some aldehyde polymer. During purification the liquid was shielded as much as possible from the light to minimise polymer formation, and all reservoirs were stored in the dark.

Solvent. *n*-Decane was shaken with concentrated sulphuric acid until the acid layer no longer darkened, and then with fuming sulphuric acid and fuming nitric acid, the same criterion of purity being used. After treatment with 10% sodium hydroxide solution and distilled water (each 3 times) it was dried (Na_2SO_4) and fractionated under a reduced pressure of nitrogen. A few grams of sodium were added to the hydrocarbon before distillation to remove the last traces of water. At 15 mm., the *n*-decane boiled at 64·8—65·2°.

As a check the distillate was examined in a Grubb–Parsons Infra-red Spectrometer by Dr. G. M. Burnett : there was no trace of the absorption bands characteristic of unsaturated, carbonyl, or aromatic compounds. Some were detected, however, in the original material.

RESULTS.

Preliminary Experiments.—Preliminary experiments carried out on aldehyde which had been fractionated but not distilled *in vacuo* showed that considerable thermal reaction took place at 25°. The rate of autoxidation was found to be sensitive to diffused daylight to a small extent and so the reaction system was enclosed in a light-proof cover. However, the thermal rate remained inconveniently large.

When dealing with a process of this kind, where both thermally and photochemically initiated reaction chains are propagating side by side, it is necessary to make certain assumptions regarding the relationship of the two in order to calculate what proportion of the overall rate measured under illumination is actually due to the light itself. For example, during his work on the photo-oxidation of aldehydes, Bäckström (*J. Amer. Chem. Soc.*, 1927, **49**, 1460) assumed that the photochemical and thermal rates were additive, but when the ratio of these quantities has a value as small as 1—2 large errors may be introduced by such an assumption. In order to reduce the proportion of the thermal reaction one can either reduce the working temperature or use an inert solvent. In the present instance, by working at high oxygen pressures (650 mm.) and low temperatures (5°), a value of 10 for the ratio of the photochemical to the thermal rate was obtained. However, further purification by repeated vacuum-distillation reduced this ratio to 5, owing to the greater sensitivity of the thermal process to impurity. Hence, thermal oxidation is still very prominent even at 5° and, since further reduction of the working temperature caused the reaction products to separate out of solution at inconveniently small extents of reaction, the ratio could not be increased in this way. A slight improvement could be effected by using an inert solvent.

FIG. 7.

Dependence of the light rate on stirring speed.

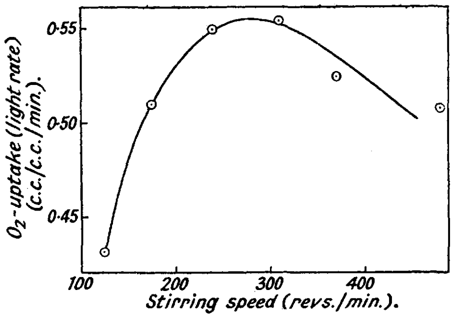
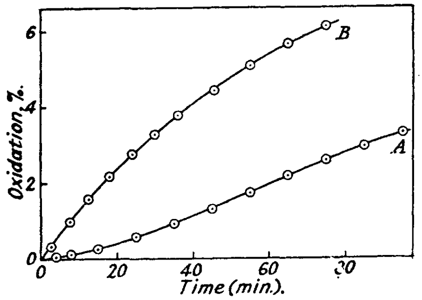


FIG. 8.

Course of thermal reaction at 5°.



Reproducibility to within ±5% was attained in the case of the photochemical and ±10% in the case of the thermal process. Further improvement was found to be impossible no matter how rigid the precautions taken, so that a number of experiments had to be carried out under identical conditions, and mean values of the rate measurements employed.

Rate of Dissolution of Oxygen.—Since the rates of oxygen uptake in this reaction are quite large it is important that the rate of dissolution of oxygen in the liquid should not be the rate-determining step. To ensure an adequate supply of dissolved oxygen an electromagnetic stirrer was employed and the sample size was kept to a minimum. Experiments were conducted to determine the effect of varying the stirring speed on the overall rate of oxygen uptake, and the results obtained are plotted in Fig. 7. It appears that, with stirring speeds above 350 revs./min., the uptake is lowered. The length of the stirring rod used was 2·5 cm. and its thickness 3 mm. so that the liquid surface was continuously being broken as the rods rotated. At the lower speeds, its action amounted to the transmission of waves across the aldehyde layer and so the whole sample was being subjected to disturbance. At the higher speeds, there was not sufficient time during a revolution for the aldehyde swept aside by the stirrer to be replaced and so the resultant effect was the formation of a circular hole in the film, the surrounding liquid being almost unaffected. As, therefore, the optimum rate of stirring appeared to be 300 revs./min., this value was selected as standard. Unfortunately, the onset of the phenomenon of hole-formation makes it impossible to tell whether, at this speed, the observed rates of oxidation are really independent of the rate of dissolution of oxygen. However, a consideration of the effect of sample size on the rate of reaction shows that this required condition is indeed satisfied.

It was found that, provided that the amount of aldehyde in the film did not exceed 2·5 c.c., the rate of oxygen uptake was independent of the quantity of material, other factors, *e.g.*, temperature, pressure, and stirring speed, being constant. Since the smallest amount of aldehyde that would maintain a uniform film was 1·5 c.c., the experimental limits in this respect are somewhat narrow. Most of the work has been performed on 1·7-c.c. samples.

The General Course of the Reaction.—Some workers (*e.g.*, Raymond, *Compt. rend.*, 1922, **194**, 258) maintained that carefully purified aldehydes would not autoxidise at all or, at most, only after an induction period which could be shortened by irradiation with ultra-violet light. Hence, it was believed that heavy-metal catalysts or peroxides must be present before reaction would proceed. Further work has shown, however, that the methods of drying used in these experiments were likely to have introduced inhibitors into the system.

A general feature of autoxidation processes, namely, autocatalysis, is now well-established in the case of hydrocarbons, but with aldehydes at low temperatures this phenomenon does not seem to occur to any marked extent. Wieland and Richter (*Annalen*, 1931, **486**, 226) and Almquist and Branch (*J. Amer. Chem. Soc.*, 1932, **54**, 2293) report that, with benzaldehyde, a gradual decrease in the thermal rate at 25° takes place from the beginning of the reaction and, as far as the photo-process is concerned, Bäckström (*loc. cit.*) and Bowen and Tietz (*loc. cit.*) agree that a similar course is followed.

As regards the present work, we shall consider first the thermal reaction. Measurements of the oxygen uptake of incompletely purified samples indicated that, at low temperatures (5°), there was initially an induction period of a few minutes. This was followed by a gradual increase in rate to a maximum value; then it fell slowly until at 6% oxidation solid products of reaction began to separate from solution. Fig. 8, curve *A*, illustrates this behaviour, the % oxidation being calculated on the basis of one molecule of oxygen per molecule of aldehyde, as required for per-acid formation. Further purification of the aldehyde revealed that the apparent induction period must have been due to impurity for there was observed instead only a gradual decrease in reaction rate right from the initial stages (Fig. 8, Curve *B*).

For the photo-reaction at 5°, there was a similar gradual decay in the rate, the diminution not, however, taking place so rapidly. Once again, beyond 6% oxidation, separation of reaction products rendered stirring of the aldehyde film impossible and no reliance could be placed on rate measurements taken under these conditions.

Fortunately these changes in the reaction rates are not so rapid that the latter cannot be regarded as being constant over short intervals of time. It is therefore possible to calculate the rates directly from the slopes of plots of the amounts of oxygen absorbed against time over 3—4-minute intervals in the case of the photo-reaction and over 8—10-minute intervals in the case of the thermal process. Further, one can assume that, in the early stages of reaction, the radical concentrations remain constant, so that stationary-state methods can be applied to a kinetic analysis of the mechanism.

In the subsequent discussion, by " photo-rate " is meant the rate of reaction due solely to chains initiated by the absorption of ultra-violet light. By " light rate " is meant the total reaction rate observed when the system is under illumination. The calculation of the photo-rates has been made according to the method suggested by Noyes and Leighton (" Photochemistry of Gases," Reinhold, 1941, p. 198) for cases in which the chain mechanisms of the thermal and the photochemical process differ only in the mode of initiation. In these circumstances, if

$$\begin{aligned} \text{Thermal rate} &= R_{\text{T}} = aT_{\text{i}}^{n} \\ \text{Photo-rate} &= R_{\text{P}} = aI^{n} \\ \text{Light rate} &= R_{\text{L}} = a(T_{\text{i}} + I)^{n} \end{aligned}$$

where T_{i} and I represent the rates of thermal and photochemical initiation, and a is a factor referring to the propagation and termination steps of the reaction, then it readily follows that :

$$(R_{\text{P}})^{1/n} = (R_{\text{L}})^{1/n} - (R_{\text{T}})^{1/n}$$

The results of previous workers suggested that the value of n was $\frac{1}{2}$ and it will be seen that further justification of this value has been obtained.

Dependence of the Photo-rate on Light Intensity.—Variation of the light intensity was achieved by interposing perforated screens between the light source and the reaction vessel. Fine copper gauze, with its surface darkened by immersion in ammonium polysulphide to cut down reflection, was found to be suitable; its transmission was measured photoelectrically. To evaluate the intensity exponent, rates of oxygen uptake were measured over 3—4-minute periods (*a*) at full, (*b*) at reduced, and (*c*) at full intensity, the mean of (*a*) and (*c*) being taken as the full light rate. Determination of the thermal rate before and after illumination enabled also a mean value of this quantity to be obtained. Results showing that the photo-rate is dependent on the square-root of the absorbed light intensity are given in Table I.

Effect of Variation of the Oxygen Pressure.—(a) *Thermal reaction.* Owing to the great sensitivity of the thermal process to traces of impurity and the impossibility of obtaining better reproducibility than ±10%, it is very difficult to establish the dependence of the reaction rate on oxygen pressures. The results shown in Table II indicate that the initial rate varies with the square-root of the oxygen pressure within the region investigated.

(b) *Photochemical reaction.* The effect on the photo-rate of altering the oxygen pressure is shown in Table III(*a*). Intensity-exponent measurements show by their tendency to fall below 0·5 that the values for the photo-rate at pressures lower than 600 mm. are not reliable and that under these conditions the rate of dissolution of oxygen is becoming the controlling factor. Hence, for pure *n*-decanal it is not possible to establish the dependence of the photo-rate on oxygen pressure.

TABLE I.

Dependence of the photo-rate on light intensity.

(Rates expressed in mol./l.sec., × 10^4.)

Mean full photo-rate.	Reduced photo-rate.	Transmission of screen (%).	Intensity exponent.
3·92	2·06	30·6	0·54
4·23	2·39	30·6	0·48
4·06	2·35	30·6	0·46
4·14	2·70	41·6	0·49
4·18	2·77	41·6	0·47
4·19	2·71	41·6	0·52
		Mean	0·49

TABLE II.

Dependence of initial thermal rate on oxygen pressure. Temp., 5°.

Pressure (p) (mm.).	$p^{\frac{1}{2}}$.	Rate (mol./l.sec., × 10^5).	$p^{\frac{1}{2}}$/Rate.
700	26·4	10·4	2·54
650	25·5	9·95	2·56
600	24·5	9·1	2·59
550	23·4	8·5	2·76
500	22·4	8·2	2·73
450	21·2	7·6	2·79
350	18·7	7·0	2·67

TABLE III.

Dependence of initial photo-rate on oxygen pressure.

Pressure (mm.).	Rate (mol./l.sec., × 10^4).	Intensity exponent.	Pressure (mm.).	Rate (mol./l.sec., × 10^4).	Intensity exponent.
(*a*) *Pure aldehyde.*	*Temp.*, 5°.		(*b*) 30% *Solution*	*of aldehyde in decane.*	*Temp.*, 10°.
700	4·44	0·51	700	2·11	0·55
650	4·32	0·49	650	2·14	0·51
600	4·35	0·48	550	2·07	0·54
550	4·01	0·46	450	1·92	0·52
450	3·66	0·42	350	1·77	0·45
350	3·32	0·40			

TABLE IV.

Dependence of initial thermal rate on aldehyde concn. Temp., 10°.

Aldehyde concn. (c) (mol./l.).	$c^{3/2}$.	Rate (mol./l.sec., × 10^5).	$c^{3/2}$/Rate.
0·53	0·38	0·45	0·8
1·58	2·00	1·34	1·5
2·63	4·27	2·68	1·6
3·67	7:08	6·42	1·1
5·25	12·30	11·4	1·1

TABLE V.

Dependence of initial photo-rate on aldehyde concn. Temp., 10°.

Aldehyde concn. (c) (mol./l.).	Rate (mol./l.sec., × 10^4).	c/Rate.
0·53	0·61	0·87
1·58	2·28	0·69
2·63	3·86	0·68
3·67	4·64	0·79

However, some experiments carried out with 30% solutions of the aldehyde in *n*-decane show that over the range 400—700 mm. variation of the oxygen pressure does not affect the photo-rate [Table III(*b*)].

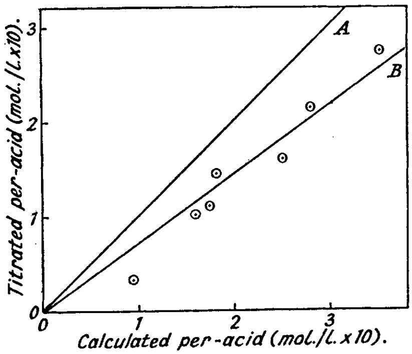
Effect of Variation of the Aldehyde Concentration.—Experiments with *n*-decane solutions to determine the dependence of the thermal reaction rate on aldehyde concentration also showed rather poor reproducibility, and mean values had again to be taken from a number of determinations under identical conditions. As can be seen from Table IV the reaction rate appears to be proportional to (aldehyde concentration)$^{3/2}$. The corresponding data for the photo-process (Table V) show that the photo-rate depends on the first power of the aldehyde concentration. The results of these experiments in solution provide no evidence that *n*-decane interferes in any way with the propagation of the autoxidation chains, *e.g.*, as shown in Table III the intensity exponent still has a value of 0·5.

Estimation of Per-acid.—During his work on benzaldehyde autoxidation, Bäckström (*Medd. K. Vet. Nobelinst.*, 1927, **6**, 15, 16) determined the concentration of perbenzoic acid in the reaction mixture by the iodine–thiosulphate method. Although the observed amounts of per-acid always fell below the value expected on the basis of the oxygen absorbed, yet the deficiency could be explained quantitatively as being caused by formation of benzoic acid by the reaction of some of the per-acid with further aldehyde.

To ensure that a similar situation exists in the present instance, the amount of perdecanoic acid present at various extents of oxidation was determined. The method adopted has been developed from those of Bäckström (*loc. cit.*) and Kolthoff (*J. Polymer Sci.*, 1947, **2**, 199). Measurements of the oxygen uptake were made on the manostat in the usual manner. The reaction was stopped at different percentages of oxidation and a mixture of 10% aqueous potassium iodide (10 c.c.) and 0·4N-acetic acid (5 c.c.) introduced immediately. Sufficient alcohol was added to give a homogeneous solution which was transferred quantitatively (by several washings with alcohol) to a flask through which a steady stream of nitrogen was flowing. The free iodine was then determined with 0·02N-sodium thiosulphate. Further addition of alcohol to maintain homogeneity was made whenever necessary. The presence of alcohol makes it impossible to use starch solution, but the disappearance of the colour of the iodine itself was sharp enough to give satisfactory results (±0·05 c.c.). All solutions and solvents used in this determination were stored under nitrogen and a stream of the gas was passed through them before they came into contact with the autoxidised sample.

Fig. 9.

Per-acid concentration at 5°.



Per-acid concentrations determined for several samples are shown in Fig. 9, curve *B*, plotted against the concentration expected from the amounts of oxygen absorbed. If the per-acid did not react further with the aldehyde line *A* would be obtained, but a comparison of the two slopes indicates that over the region examined 72% of the per-acid formed remains as such in the reaction mixture. Exact estimates of the total oxygen uptake are not easy to obtain because of the necessary time-lag which must be allowed for temperature equilibrium to be reached before taking readings on the monostat.

The reaction between per-acid and iodide may be represented by $R{\cdot}CO{\cdot}OOH + 2I^- + H^+ \longrightarrow R{\cdot}COO^- + I_2 + H_2O$, so one equivalent of per-acid corresponds to 2 equivs. of thiosulphate. The per-acid content has been calculated by use of this relationship.

It is not possible to calculate from the above results an exact value of the velocity constant for the pseudo-unimolecular secondary reaction of per-acid with aldehyde, owing to the limited region over which the measurements have been made. However, this may be estimated to be of the order 10^{-3}, which agrees with the 10—30-minute half-periods found for the corresponding reaction with benzaldehyde and acetaldehyde by Bäckström (*loc. cit.*) and Kagan and Lubarsky (*J. Phys. Chem.*, 1935, **39**, 847).

Discussion.

That the autoxidation of aldehydes proceeds by a radical chain mechanism was clearly indicated by Bäckström (*Z. physikal. Chem.*, 1934, **25**, *B*, 99). The results presented above show that, under the somewhat limited conditions in which experiment is possible, the following empirical equations may be written for the initial thermal and photo-rates of autoxidation :

$$R_T = k'[R{\cdot}CHO]^{3/2} . [O_2]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$R_P = k''[R{\cdot}CHO] . [O_2]^0 . I^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where *I* is the effective light intensity. The kinetic evidence is more reliable in the case of the photo-process because of the greater accuracy which could be achieved in the rate measurements.

It has been assumed, in calculating the photo-rates, that the mechanisms of both the thermal and the photochemical process are identical except for the initiation step. If the assumption had been made that the mechanism of the thermal and photo-processes were different, then direct subtraction of the thermal from the light rate would give the corresponding photo-rate, *i.e.*, $R_P = R_L - R_T$. If calculations of the intensity exponent are made from photo-rates derived in this way, then values consistently higher than 0·5 are obtained no matter how pure the aldehyde samples may be. For example, by this method the last result in Table I gives an intensity exponent of 0·69. Since the aldehyde used had been carefully purified, this value cannot be explained as being due to the presence of chain-breaking impurities, and so it seems that the assumptions made about the relative mechanisms of the two reactions are correct.

It is clear from the square-root dependence on the light intensity that the reaction chains are being terminated by the mutual destruction of two radical chain carriers. If this is also the case in the thermal process, then R_T must depend on $T_i^{\frac{1}{2}}$ where T_i is the rate of thermal initiation. Hence, if the reaction chains started thermally commence by some type of interaction of the aldehyde with oxygen, this process may be represented as

$$R{\cdot}CHO + O_2 \longrightarrow \text{chain carriers}$$

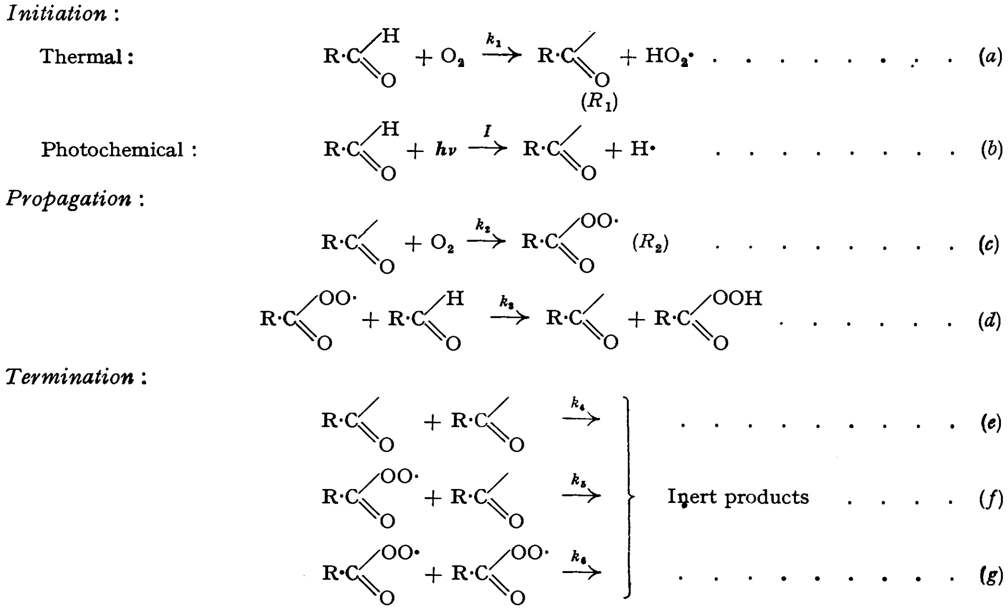
and a term $[R{\cdot}CHO]^{\frac{1}{2}}[O_2]^{-\frac{1}{2}}$would be included in the overall thermal rate expression. If (1) is rewritten as :

$$R_T = k'[R{\cdot}CHO][O_2]^{\circ}[R{\cdot}CHO]^{\frac{1}{2}}[O_2]^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad .. \quad . \quad (3)$$

it can be seen that, apart from the contribution of the initiation process, the expressions for the thermal and photo-rates become identical. Thus there is a strong likelihood that the subsequent steps are the same in the two cases.

From the general nature of the course of reaction, which shows no sign of autocatalysis in either the thermal or the photo-chemical process at low temperature provided that pure materials are used, it would seem that the products do not participate in the initiation of reaction chains in contrast to olefinic and hydroaromatic autoxidation products. Thus, initiation reactions must be postulated which do not involve the per-acid. The kinetic evidence points to a process involving the direct interaction of the aldehyde and oxygen although the exact nature of such a step must necessarily remain somewhat speculative at the moment.

The mechanism suggested to account for the above observations is :



If it is assumed that (*a*) the concentrations of the chain carriers reach stationary values, (*b*) the reaction chains are long so that the rates of the initiation and termination steps become negligible in comparison with those of propagation, and (*c*) at the relatively high oxygen pressures used the addition of oxygen to aldehyde radicals takes place much more rapidly than the abstraction of hydrogen by the peroxide radicals, and, consequently, that processes (*e*) and (*f*) may be neglected, then the above scheme gives for the overall reaction rate :

$$-\frac{d[O_2]}{dt} = \frac{k_3[\mathrm{R{\cdot}CHO}]}{\sqrt{k_6}}(I + k_1[\mathrm{R{\cdot}CHO}][O_2])^{\frac{1}{2}} \quad . \ . \ . \ . \ . \quad (4)$$

which gives :

$$R_T = \sqrt{k_1}\frac{k_3}{\sqrt{k_6}}[\mathrm{R{\cdot}CHO}]^{3/2}[O_2]^{\frac{1}{2}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$R_P = \frac{k_3}{\sqrt{k_6}}[\mathrm{R{\cdot}CHO}]I^{\frac{1}{2}} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

Expressions (5) and (6) are seen to agree with the empirical equations (1) and (2).

It makes no difference to the final result in the above scheme whether R_1 or R_2 is produced by the thermal initiation process, but R_1 would be the more likely. The exact mechanism of the photo-initiation step is not known, but evidence from studies of the photo-decomposition of aldehydes indicates that absorption of near ultra-violet radiation can bring about formation of R_1 radicals (Noyes and Leighton, *op. cit.*, p. 238).

From the great length of the reaction chains encountered here, it follows that the proportion of the products of the termination step in the resulting mixture will be very small. No attempt has been made to identify these materials.

Since the autoxidation of *n*-decanal, whether thermal or photochemical, proceeds by a chain mechanism involving termination by the mutual removal of the chain carriers, the reaction satisfies the conditions which must be fulfilled before methods similar to those of Burnett and Melville (*Proc. Roy. Soc.*, 1947, *A*, **189**, 456) can be applied in order to obtain absolute values of the velocity coefficients for the propagation and termination steps. The results of such measurements are given in the following paper.

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