445. *The Kinetics of the Autoxidation of* n-*Decanal. Part II.** *The Velocity Constants.*

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

The retardation of the autoxidation of *n*-decanal by small amounts of quinol has been studied. The overall-reaction kinetics of the system show that the retarder operates by reacting with the peroxidic radicals. A method is described whereby the rate of chain initiation, R_i, can be calculated from the rates of oxygen absorption at constant pressure.

Application of the method of intermittent illumination to the unretarded reaction enables the chain life, τ, to be measured. From R_i and τ, along with the thermal-, photo-, and retarded-reaction rates, it is possible to obtain absolute values of the velocity constants for all the processes involving peroxidic radicals and also for the thermal-initiation step. Owing to experimental difficulties, the corresponding energies of activation were obtained by carrying out similar measurements in *n*-decane solution. When coupled with the velocity coefficients determined in the pure liquid, these give rise to frequency and steric factors which compare favourably with published values for related systems.

In the preceding paper, kinetic evidence has been presented which enabled a free-radical mechanism to be established for the formation of peracid by the autoxidation of *n*-decanal. The equation deduced to represent the overall rate of oxygen absorption was of the form :

$$-\frac{d[O_2]}{dt} = \frac{k_3}{\sqrt{k_6}}[\text{R·CHO}]R_i^{\frac{1}{2}} \quad \ldots \ldots \ldots \quad (1)$$

and it can be seen that, if some method of determining the rate of initiation, R_i, is available then the ratio of the velocity constants for propagation and termination, $k_3/k_6^{\frac{1}{2}}$, can be found.

Under the experimental conditions for which equation (1) holds, *i.e.*, at high oxygen pressures, the addition of oxygen to the aldehydic radicals is considered to occur so much more rapidly than the abstraction of hydrogen atoms by the peroxidic radicals that it takes up a negligible part of the time of one chain cycle. The lifetime of the kinetic chain may therefore be represented by $\tau = \nu\bar{\tau}$, where ν is the chain length and $\bar{\tau}$ is the mean time required for a peroxidic radical to dehydrogenate an aldehyde molecule. The fate of the peroxidic radicals is the sole factor determining the chain lifetime which can be expressed in the form :

$$\tau = \frac{\text{Concentration of peroxidic radicals}}{\text{Rate of removal of peroxidic radicals}} = \frac{1}{k_6[R_2]} \quad \ldots \ldots \quad (2)$$

where $[R_2]$ represents the concentration of the peroxidic radicals. From the reaction mechanism quoted in the preceding paper it follows that, under stationary-state conditions, $R_i - k_6[R_2]^2 = 0$. Substituting for $[R_2]$ in (2), we have

$$\tau = 1/\sqrt{k_6R_i} \quad \ldots \ldots \ldots \quad (3)$$

It follows from (1) and (3) that :

$$k_3 = R_L/(\tau[\text{R·CHO}]R_i) \quad \ldots \ldots \ldots \quad (4)$$

$$k_6 = 1/\tau^2R_i \quad \ldots \ldots \ldots \quad (5)$$

and hence, if R_i and τ are known, then absolute values of k_3 and k_6 can be found.

The Rate of Initiation.—It has been shown by Burnett and Melville (*Proc. Roy. Soc.*, 1947, *A*, **189**, 456) that the rate of initiation in the photopolymerisation of vinyl acetate may be measured by following the course of the reaction inhibited by benzoquinone. In this case, polymerisation was stopped completely by the inhibitor for lengths of time which were dependent on the inhibitor concentration, and so, by measuring these induction periods it was possible to estimate the rate of removal of benzoquinone and hence to obtain the rate of chain initiation.

With autoxidising systems, however, only high inhibitor concentrations will stop the reaction completely. Furthermore, the length of the induction period is not easy to assess,

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* Part I, preceding paper.

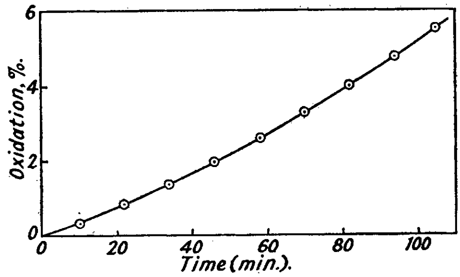
because there is no sudden onset of reaction; instead, a gradual increase in the rate of oxygen absorption occurs as the concentration of antioxidant diminishes.

Fortunately, it has proved possible to find the rate of initiation by following the course of autoxidation in the presence of low concentrations of a retarder. The material used was quinol, recrystallised three times from water under an atmosphere of nitrogen. Complications caused by internal filter effects cannot occur with this substance for, as shown by Klingstedt (*Compt. rend.*, 1922, **175**, 366), the molecular extinction coefficient of quinol falls to zero at 3180 A. and remains at this value over the whole region transmitted by the Corning 597 R.P. Ultra glass filter.

The Course of the Retarded Reaction.—By using quinol concentrations of the order of 10^{-5} mole per litre, oxygen absorption was found to follow the course shown in Fig. 1, a gradual increase in reaction rate being observed. As in other experiments (preceding paper), the separation of the products from solution prevented the process from being followed beyond 6% oxidation at 5°.

FIG. 1.

The course of photo-oxidation retarded by quinol at 5°.



Dependence of the Rate on Quinol Concentration.—In order to establish the dependence of the reaction rate on quinol concentration it is necessary to have some means of extrapolating back to the time when measurements of the oxygen absorption were commenced. The method of extrapolation employed has been to plot the reciprocal of the rate against time and to find the intercept at zero time.

TABLE I.

Dependence of the retarded rate on quinol concentration.

Temp., 5°. Oxygen pressure, 650 mm.

Initial quinol concn., $[H_2Q]_0$ (mol./l. × 10^5).	$\frac{1}{10^4[H_2Q]_0}$.	Initial retarded rate, R_{R_0} (mol./l.sec., × 10^5).	$R_{\mathrm{R}_0} \times [H_2Q]_0 \times 10^9$.
3·16	3·17	7·40	2·34
5·43	1·84	4·95	2·69
6·10	1·64	3·95	2·41
7·40	1·35	3·50	2·59
42·80	0·23	0·82	3·51

The corresponding uninhibited rate was 4·40 × 10^{-4} mol./l./sec.

TABLE II.

Dependence of retarded rate on the light intensity.

Temp., 5°. Oxygen pressure, 650 mm.

$[H_2Q]_0$ (mol./l. × 10^5).	Mean rate at full intensity (mol./l.sec., × 10^5).	Rate at reduced intensity (mol./l.sec., × 10^5).	Transmission of screen (%).	Intensity exponent.
3·16	9·56	4·26	41·6	0·93
6·10	6·25	2·73	41·6	1·02
7·40	4·05	1·62	41·6	1·05
42·80	1·34	0·55	41·6	0·95
				Mean 0·99

Estimates of the initial rates of oxygen absorption obtained in this way are shown in Table I and the results indicate that the retarded rate is inversely proportional to the retarder concentration.

Dependence of the Rate on Light Intensity.—The method used was identical with that employed to establish the dependence of the uninhibited process on the light intensity. The results quoted in Table II indicate that a first-power relationship holds in this case.

Dependence of Rate on Aldehyde Concentration and Oxygen Pressure.—No experiments were carried out in the present instance to establish the relationship between the rate of the retarded reaction and the aldehyde concentration or oxygen pressure, but Bowen and Tietz (*J.*, 1930, 234) showed that for acetaldehyde oxidation retarded by alcohol:

$$\text{Retarded rate} \propto [\text{R·CHO}]^1[\text{O}_2]^0$$

Mechanism of the Retarded Reaction.—The above results lead to an empirical expression for the retarded reaction rate of the form:

$$R_R = k[\text{R·CHO}]^1[\text{O}_2]^0[\text{H}_2\text{Q}]^{-1}I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

It is now well established that the mode of action of a retarder in stopping autoxidation chains at high oxygen pressures is by removing peroxidic radicals from the system. This conclusion was reached by Bäckström (*Z. physikal. Chem.*, 1934, *B*, **25**, 99) from his work with aldehydes, and recently even more convincing evidence in support of this mechanism has been presented by Bolland and ten Have (*Trans. Faraday Soc.*, 1947, **43**, 201) in the case of the olefins. They suggest that chain termination by quinol leads to formation of a comparatively stable semiquinone radical, two of which may interact at some later stage:

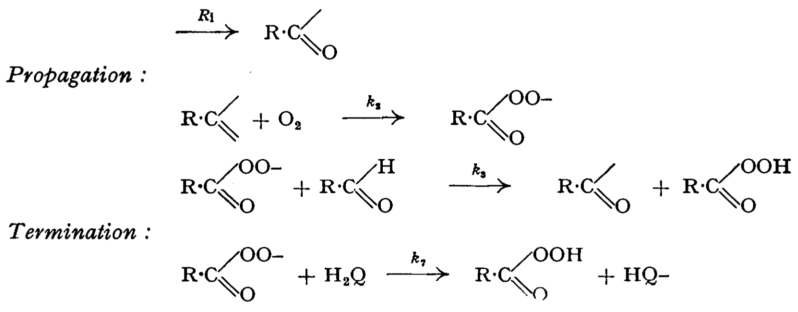
$$\text{RO}_2\text{–} + \text{H}_2\text{Q} \longrightarrow \text{RO·OH} + \text{HQ–}$$
$$\text{HQ–} + \text{HQ–} \longrightarrow \text{H}_2\text{Q} + \text{Q}$$

On this basis, each quinol molecule can terminate two reaction chains. That a similar state of affairs holds true in the autoxidation of *n*-decanal is supported by the appearance of a slight yellow colour in the reaction mixture after a sample containing quinol has been exposed to oxygen under ultra-violet radiation.

It was observed that, even with such low quinol concentrations, thermal autoxidation was reduced to such small proportions as not to be measurable under the experimental conditions. A given amount of retarder would be expected to have more effect on the thermal than on the photochemical process because the chain length is much longer in the former case. Hence, the thermal reaction can be neglected in calculations concerning the retarded rates of oxidation. Moreover, it is the total rate of initiation under illumination that these experiments are designed to measure.

The gradual increase in reaction rate in presence of quinol cannot be attributed to the action of autoxidation products derived from the aldehyde, for autocatalysis is not encountered with the uninhibited material. The products derived from the retarder, quinonoid in type, would not be expected to catalyse the process and, in fact, have been shown (Bolland and ten Have, *loc. cit.*) to be very weak retarders themselves. Hence the acceleration of the oxygen absorption may be attributed solely to the consumption of quinol in stopping chains. The non-interference of the products has been assumed in the evaluation of the rate of initiation.

The mechanism of the retarded oxidation would therefore be simply:



Assuming that, over short intervals, the concentration of the radicals remains sensibly constant, we have from this scheme :

$$-\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = R_\mathrm{i}\left(1 + \frac{k_3[\mathrm{R{\cdot}CHO}]}{k_7[\mathrm{H_2Q}]}\right)$$

Now, at low inhibitor concentrations the chain length is still quite large and so the rate of initiation will be small in comparison with the overall rate of oxygen absorption. Taking into account the relative magnitudes of R_i and $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t$, we may write for the retarded rate :

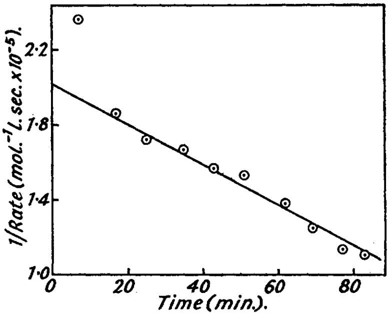
$$R_\mathrm{R} = R_\mathrm{i}k_3[\mathrm{R{\cdot}CHO}]/k_7[\mathrm{H_2Q}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

which obviously has the same form as the empirical equation (6).

Determination of the Rate of Initiation.—If we still assume that the radical concentration remains sensibly constant and that one quinol molecule can stop two reaction chains, it follows that the rate of removal of quinol is given by $-\mathrm{d}[\mathrm{H_2Q}]/\mathrm{d}t = R_\mathrm{i}/2$. On integration, with the limiting condition that at $t = 0$, $[\mathrm{H_2Q}] = [\mathrm{H_2Q}]_0$, this gives $[\mathrm{H_2Q}] = [\mathrm{H_2Q}]_0 - \frac{1}{2}R_\mathrm{i}t$. On substitution in (7) for $[\mathrm{H_2Q}]$, we have,

Fig. 2.

The retarded reaction at 5°. Plot of reciprocal rate against time : $[\mathrm{H_2Q}]_0 = 5{\cdot}43 \times 10^{-5}$ *mol./l.*



$$R_\mathrm{R} = \frac{k_3[\mathrm{R{\cdot}CHO}]R_\mathrm{i}}{k_7([\mathrm{H_2Q}]_0 - \frac{1}{2}R_\mathrm{i}t)}$$

hence

$$\frac{1}{R_\mathrm{R}} = \frac{k_7[\mathrm{H_2Q}]_0}{k_3[\mathrm{R{\cdot}CHO}]R_\mathrm{i}} - \frac{k_7t}{2k_3[\mathrm{R{\cdot}CHO}]}$$

Therefore it would be expected that a plot of $1/R_\mathrm{R}$ against t would be a straight line. Further, we have

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{R_\mathrm{i}}{2[\mathrm{H_2Q}]_0}$$

and since $[\mathrm{H_2Q}]_0$ is known, R_i, the rate of initiation, may be calculated.

Fig. 2 illustrates an example of the type of $1/R_\mathrm{R}$–t plot obtained. It was always observed that in the very early stages of reaction the value of $1/R_\mathrm{R}$ was too large. The experimental difficulties in accurately measuring rates of oxygen absorption are very great, but the displacement is too large to be accounted for by experimental error. This discrepancy has been neglected in extrapolating back to zero time.

Table III shows the results of determinations of the rate of initiation which have been made in this way for a number of different initial quinol concentrations. The mean value of $1{\cdot}1 \times 10^{-7}$ mol./l.sec. is a weighted mean based on the number of determinations made at each concentration of quinol. To show that the reaction chains are still quite long under the experimental conditions, values of the initial chain lengths are also included, calculated from $\nu_0 = R_{\mathrm{R}_0}/R_\mathrm{i}$. $R_\mathrm{i} = 1{\cdot}1 \times 10^{-7}$ mol./l.sec. will be a mean value for the thermally and photochemically initiated processes since the rate of initiation determined is a composite one: $R_\mathrm{i} = k_1[\mathrm{R{\cdot}CHO}][\mathrm{O_2}] + I$.

The Chain Lifetime.—A method of determining this quantity by irradiating the system with an intermittent illumination is mentioned by Noyes and Leighton (" Photochemistry of

TABLE III.

The rate of initiation.

Temp., 5°. Oxygen pressure, 650 mm.

$[H_2Q]_0$ (mol./l. × 10^5).	Initial rate, R_{R_0} (mol./l.sec., × 10^5).	$\frac{\text{Slope}}{\text{Intercept}} = \frac{R_i}{2[H_2Q]_0}$.	R_i (mol./l.sec., × 10^8).	ν_0.
3·16	7·40	14·80	9·4	675
5·43	4·95	9·74	10·6	450
7·40	3·50	7·86	11·6	360
42·80	0·82	1·71	14·6	75
		Mean	11·0	

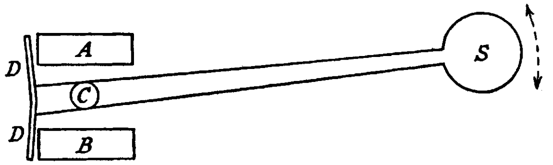
Gases," p. 202, Reinhold, 1941) and has been successfully applied to the polymerisation of vinyl compounds by Burnett and Melville (*loc. cit.*) and others and more recently to the autoxidation of olefins by Bateman and Gee (*Proc. Roy. Soc.*, 1948, *A*, **195**, 376). Measurements of reaction rates at a number of different flashing speeds, with the application of an appropriate theoretical treatment, enable τ to be calculated. In the present instance, due allowance must be made for the background thermal reaction, and this has already been shown to be possible by Bateman and Gee.

EXPERIMENTAL.

Apparatus.—In order to interrupt the light at regular intervals, an automatic shutter mechanism was constructed which gave a very rapid movement of an opaque screen across the light beam. By using a Megatron photocell coupled with a Cossor Oscillograph it was found that the time required for the movement of the arm was less than 20 millisecs. The method of operation of this shutter is illustrated in Fig. 3, where it can be seen that, by energising coil *A* all the time and the larger coil *B* intermittently, the light metal plates *D* are attracted in turn and the duralumin shutter arm *S* oscillates pivoting on shaft *C*. Regularity of the movement was achieved by passing the current to coil *B* through commutators rotated at a constant speed by a gramophone motor. The range of the instrument (flash times of 0·25—25 secs.) was increased by variation of the number of segments on the commutators and also by suitable reduction gearing.

FIG. 3.

The automatic shutter.



Determination of the Lifetime.—The theory of intermittent illumination requires that the reaction system should satisfy certain conditions: (*a*) The reaction must be a chain process, capable of being initiated photochemically. (*b*) The mechanism of the thermal and photo-reactions must be the same apart from the initiation step. (*c*) The photo-rate must not be dependent on the first power of the light intensity. (*d*) The absorption of the light must take place uniformly throughout the reaction medium. (*e*) The interruption of the light beam must be instantaneous so that scanning of the reaction vessel does not occur.

Conditions (*a*), (*b*), and (*c*) have been shown to be satisfied in the autoxidation of *n*-decanal. The glass filter ensured that the wave-lengths initiating the photo-reaction were only weakly absorbed, and the shutter device was designed to move quickly enough to satisfy condition (*e*) over the range of flash times investigated.

Mathematical treatment of the system along the lines suggested by Bateman and Gee (*loc. cit.*) and Matheson (*J. Amer. Chem. Soc.*, 1949, **71**, 497 gives:

$$\gamma = \frac{1+\omega}{2} + \frac{1}{2K}\ln\frac{(1+x)(1+y/\omega)}{(1+y)(1+x/\omega)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where

$$\gamma = \frac{\text{light rate under intermittent illumination}}{\text{light rate at full intensity}}$$

$$\omega = \frac{\text{thermal reaction rate}}{\text{light rate at full intensity}}$$

$K = k_6[R_2]\,\theta$, $x = [R_2]_1/R_2]_s$, $y = [R_2]_2/[R_2]_s$, θ = flash time (in sec.)

$[R_2]_s$, $[R_2]_1$, and $[R_2]_2$ are the concentrations of peroxidic radicals in the system respectively under steady illumination, at the beginning of the light period, and at the end of the light period; x and y in the above equation can be expressed in terms of K by the solution of :

$$ay^2 + by - c = 0 \quad \ldots \quad (9)$$

$$ax^2 - bx - c = 0 \quad \ldots \quad (10)$$

where

$$a = \tanh \omega K + \omega \tanh K$$

$$b = (\omega^2 - 1)\tanh K \tanh \omega K$$

$$c = \omega\,(\tanh K + \omega \tanh \omega K)$$

Substitution of the expressions obtained for x and y from (9) and (10) in (8) enables γ to be written in terms of a single variable quantity, K, but it is not possible to rearrange the resulting equation so that K can be calculated from the readily measured ratios γ and ω. However, if a series of values are given to K, then the corresponding values of γ can be calculated. The limiting values can be obtained from :

$$\gamma_{\theta \to \infty} = \frac{1 + \omega}{2} \qquad \gamma_{\theta \to 0} = \left\{\frac{1 + \omega^2}{2}\right\}^{\frac{1}{2}}$$

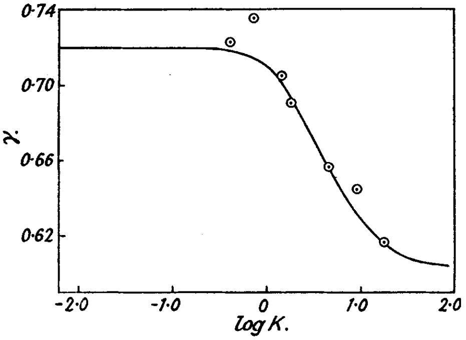
A curve relating γ and $\log K$ may then be plotted, the general form of which is shown in Fig. 4. If the experimental values of γ obtained at different flash times are plotted on the same scale, then since

$$\log \theta - \log K = \log \frac{1}{k_6[R_2]_s} = \log \frac{1}{\sqrt{k_6 R_i}} = \log \tau$$

the lifetime, τ, may be calculated by measuring the distances of the experimental points from the theoretical curve along lines of constant γ.

Fig. 4.

Determination of chain lifetime at 5° : $\omega = 0{\cdot}20$.



Results.—The procedure adopted in measuring γ was to compare the light rate under intermittent illumination with the mean value of the full light rates determined immediately before and after the latter. For pure *n*-decanal at 5° the value of ω is 0·2, based on the mean value of the thermal rates before and after the light rate measurements. The theoretical curve for $\omega = 0{\cdot}2$ and the experimental points from Table IV are both plotted in Fig. 4.

Table IV.

Variation of light rate with flash time.

θ (sec.).	$\log \theta$.	γ.	$\log K$.	$\log \theta - \log K = \log \tau$.	τ (sec.).
0·42	−0·38	0·723	—	—	—
0·74	−0·13	0·736	—	—	—
1·45	0·16	0·705	0·100	0·06	1·15
1·84	0·265	0·691	0·280	−0·015	0·97
4·58	0·66	0·657	0·652	0·008	1·02
9·10	0·96	0·645	0·790	0·17	1·48
17·60	1·25	0·617	1·250	0·00	1·00
					Mean 1·10

The points in Fig. 4 from which the lifetime of 1·1 sec. has been determined are, as usual, mean values of several observations at each flashing speed; $\log K$ was read off the theoretical curve corresponding to the measured values of γ. The mean value of the light rate was $4{\cdot}40 \times 10^{-4}$ mol./l./sec.

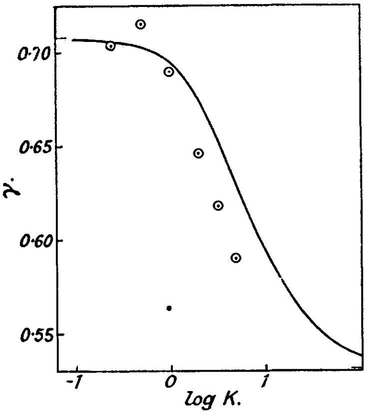
The Reaction in Solution.—In order to obtain the energies of activation of the individual radical processes it is necessary to measure reaction rates, lifetimes, etc., at a minimum of two different temperatures. Unfortunately, in the present case, a temperature increase of more than 5° led to rates of oxygen absorption which were dependent on rates of solution in the aldehyde, and a temperature decrease of more than 5° led to similar difficulties owing to the rapid separation of reaction products. Variation of the temperature within the experimental limitations encountered in the autoxidation of pure *n*-decanal, therefore, cannot lead to values of the activation energies which are sufficiently reliable to have any significance.

In Part I (preceding paper), the results of some experiments in *n*-decane solution were presented in connection with the dependence of the reaction rate on the aldehyde concentration and the oxygen pressure. These experiments indicated that the solvent did not seriously interfere with the propagation of the reaction chains, and, since reliable rates of oxygen uptake could be obtained over a much wider temperature range in solution, measurements of rates of initiation and chain lifetimes were carried out at 10° and 26° with 30% solutions of *n*-decanal in *n*-decane. At both temperatures, the intensity exponent remained at 0·5 for the unretarded reaction, showing that the observed rates were independent of the rate of solution of oxygen throughout.

Rates of Initiation.—In the presence of quinol the oxygen absorption of 30% solutions in decane showed similar behaviour to that observed with pure aldehyde, the reaction rate steadily increasing as the retarder was consumed. Calculation of the rates of initiation, therefore, could again be made by the method already described. The initial quinol concentration was $3{\cdot}18 \times 10^{-4}$ mol./l. Extrapolation of the linear plots of reciprocal rate against time gave, for Slope/Intercept $= R_i/2[H_2Q]_0$: at 10° $1{\cdot}3 \times 10^{-4}$ sec.$^{-1}$; at 26°, $1{\cdot}4 \times 10^{-4}$ sec.$^{-1}$. Hence $R_i = 8{\cdot}3 \times 10^{-8}$ and $9{\cdot}1 \times 10^{-8}$ mol./l.sec. at 10° and 26°, respectively.

FIG. 5.

Determination of chain lifetime at 10° *in* 30% n-*decane solution :* $\omega = 0{\cdot}062$.



Chain Lifetimes.—The procedure adopted in determining the chain lifetimes was identical with that in the case of the pure aldehyde. The results given in Table V and plotted in Fig. 5 show that τ has a value of 0·6 sec. at 10°. In this case $\omega = 0{\cdot}062$ and the mean full light rate was $2{\cdot}3 \times 10^{-4}$ mol./l.sec.

Similar experiments at 26°, when $\omega = 0{\cdot}14$ and the mean full light rate was $3{\cdot}4 \times 10^{-4}$ mol./l.sec., gave a mean chain lifetime of 0·66 sec., but this value is considered to be within experimental error the same as that at 10°.

TABLE V.

Variation of the light rate with flash time.

θ (sec.).	log θ.	γ.	log K.	log τ.	τ (sec.).	θ (sec.).	log θ.	γ.	log K.	log τ.	τ (sec.).
0·244	−0·61	0·704				1·96	0·30	0·646	0·54	−0·24	0·58
0·485	−0·31	0·715				3·26	0·50	0·618	0·78	−0·28	0·52
1·000	0	0·690	0·11	−0·11	0·78	4·63	0·69	0·590	1·04	−0·35	0·45
											Mean 0·6

TABLE VI.

Energies of activation.

Process.	Rates of oxidation (mol./l.sec., $\times 10^6$) : at 10°.	at 26°.	Energy of activation (kcals.).
Thermal.			
Pure aldehyde	11·7	39·1	$E_T = 12{\cdot}8$ Mean 11·5
In solution	1·37	3·59	$E_T = 10{\cdot}2$
Photochemical.			
In solution	22·8	33·7	$E_P = 3{\cdot}7$
Inhibited.			
In solution	0·91	1·41	$E_R = 4{\cdot}8$
Initiation.			
In solution	0·0083	0·0091	$E_i = 1{\cdot}0$

Energies of Activation.—In Table VI are presented the results of measurements of the various autoxidation rates at corresponding extents of reaction in solution at 10° and 26°. The energies of activation are calculated on the assumption that the Arrhenius law is obeyed.

From the appropriate rate expressions :

$$E_T = \tfrac{1}{2}E_1 + E_3 - \tfrac{1}{2}E_6$$
$$E_P = E_3 - \tfrac{1}{2}E_6$$
$$E_R = E_3 + E_i - E_7$$

since the activation energy for photo-initiation can be taken as zero, we have

$$E_T - E_P = \tfrac{1}{2}E_1 = 7{\cdot}8 \text{ kcals.}; \text{ whence } E_1 = 15{\cdot}6 \text{ kcals.}$$

The determinations of the rates of initiation and chain lifetimes are not sufficiently accurate to enable precise values of E_3, E_6, and E_7 to be calculated, but it is clear that neither R_{i} nor τ is temperature dependent to more than a slight degree. The rates of initiation are consistent with a value of approx. 1 kcal. for E_{i}, which probably arises from the thermal contribution to R_{i}, and the same figure can be taken as an upper limit for E_6.

Hence, E_3 cannot be greater than 4·2 kcals. and E_7 is approximately zero, as would indeed be expected because the reaction of quinol with the peroxidic radicals must be an extremely facile process in order to replace the normal radical–radical termination of the uninhibited reaction.

Collected Kinetic Data.—From equations (4) and (5), since at 5° :

	Pure aldehyde.	30% Solution in decane.
R_{L}, mol./l.sec.	$(4{\cdot}54 \pm 0{\cdot}17) \times 10^{-4}$	$(2{\cdot}04 \pm 0{\cdot}08) \times 10^{-4}$
R_{i}, mol./l.sec.	$(1{\cdot}1 \pm 0{\cdot}1) \times 10^{-7}$	$(8{\cdot}1 \pm 0{\cdot}7) \times 10^{-8}$
[R·CHO], mol./l.	5·25	1·58
τ, sec.	$1{\cdot}1 \pm 0{\cdot}15$	$0{\cdot}6 \pm 0{\cdot}1$
therefore		
k_3, mol.$^{-1}$/l.sec.	$(7{\cdot}2 \pm 1{\cdot}2) \times 10^{2}$	$(2{\cdot}7 \pm 0{\cdot}5) \times 10^{3}$
k_6, mol.$^{-1}$/l.sec.	$(7{\cdot}5 \pm 1{\cdot}2) \times 10^{6}$	$(3{\cdot}4 \pm 0{\cdot}8) \times 10^{7}$

These values of k_3 and k_6, although not affected in order of magnitude, do indicate that the *n*-decane has a slight influence on the reaction; hence in the following calculations the energies of activation are the only quantities which have been derived from the experiments conducted in solution.

It follows from equation (7) that, since at $[H_2Q] = 10^{-4}$ mol./l., $R_{\text{R}} = (2{\cdot}6 \pm 0{\cdot}1) \times 10^{-5}$ mol./l.sec., then

$$k_7 = \frac{k_3[\text{R·CHO}]R_{\text{i}}}{R_{\text{R}}[H_2Q]} = (1{\cdot}6 \pm 0{\cdot}3) \times 10^{5} \text{ mol./l.sec.}$$

Further, from the previous paper :

$$R_{\text{T}} = (k_1^{1/2}k_3/k_6^{1/2})[\text{R·CHO}]^{3/2}[O_2]^{1/2}$$

The oxygen term in this expression represents the concentration of oxygen in the liquid phase, and this may be estimated from the oxygen pressure if the absorption coefficient is taken to be 0·1 (Taylor and Hildebrand, *J. Amer. Chem. Soc.*, 1923, **45**, 682. Hence, since at 5° and 650 mm. of oxygen, $[O_2] = 3{\cdot}8 \times 10^{-3}$ mol./l. and $R_{\text{T}} = (1{\cdot}0 \pm 0{\cdot}2) \times 10^{-4}$ mol./l.sec., therefore $k_1 = (2{\cdot}6 \pm 0{\cdot}7) \times 10^{-7}$ mol./l.sec.

Evaluation of the velocity constants k_2 and k_4, which characterise the reactions of the aldehydic radicals, cannot be made under the present conditions because the oxygen pressure cannot be lowered sufficiently without encountering the complication of inadequate supply of oxygen.

Since velocity constants may be separated into temperature-independent and temperature-dependent terms in the manner :

$$k = A\text{e}^{-E/RT} = PZ\text{e}^{-E/RT}$$

values of the frequency factors, A, can now be obtained. The steric factors, P, are calculated on the assumption that the number of bimolecular collisions occurring per second in a normal liquid is 10^{11}. Hence :

$k_1 = (2{\cdot}6 \pm 0{\cdot}7) \times 10^{-7}$ mol./l.sec.;	$E_1 = 15{\cdot}6 \pm 1{\cdot}0$ kcals.;	$A_1 = 4 \times 10^{5}$;	$P_1 = 10^{-6}$
$k_3 = (7{\cdot}2 \pm 1{\cdot}2) \times 10^{2}$,,	$E_3 = 4{\cdot}2 \pm 0{\cdot}6$,,	$A_3 = 2 \times 10^{6}$;	$P_3 = 10^{-5}$
$k_6 = (7{\cdot}5 \pm 1{\cdot}2) \times 10^{6}$,,	$E_6 \sim 1$,,	$A_6 \sim 10^{8}$;	$P_6 \sim 10^{-3}$
$k_7 = (1{\cdot}6 \pm 0{\cdot}3) \times 10^{5}$,,	$E_7 \sim 0$,,	$A_7 \sim 2 \times 10^{5}$;	$P_7 \sim 10^{-6}$

The knowledge of the four velocity constants enables further information concerning the thermal process to be derived. This is summarised in Table VII, along with the corresponding data for the photo-oxidation, all results referring to a temperature of 5°.

TABLE VII.

	Thermal process.	Photo-process.
Rate of initiation, mol./l.sec.	$4{\cdot}2 \times 10^{-9}$	$1{\cdot}1 \times 10^{-7}$
Chain length	24,000	4,000
Chain lifetime, secs.	5·6	1·1
Stationary radical concn., mol./l.	$2{\cdot}4 \times 10^{-8}$	$1{\cdot}2 \times 10^{-7}$

DISCUSSION.

It is interesting to compare the present results with those of other workers in the field of autoxidation reactions. Table VIII contains all the detailed kinetic data available concerning such systems. The tetralin measurements have been made by Bamford and Dewar (*Proc. Roy. Soc.*, 1949, *A*, **198**, 252) and those of the other unsaturated hydrocarbons by Bateman and Gee (*loc. cit.*). The velocity coefficients quoted in the table have been adjusted by means of the corresponding activation energies to correspond to 15° where necessary.

TABLE VIII.

Kinetic data for autoxidation processes.

	Propagation reaction.			Termination reaction.		
Material.	k_3 (mol./l.sec.).	E_3 (kcals.).	A_3.	k_6 (mol./l.sec.).	E_6 (kcals.).	A_6.
*cyclo*Hexene	0·65	9·5	10^7	$0{\cdot}95 \times 10^6$	<2	10^6—10^9
Methyl*cyclo*hexene ...	1·10	8·5	—	$0{\cdot}5 \times 10^6$	<2	10^6—10^9
Dihydromyrcene ...	0·40	9·0	10^7	$0{\cdot}65 \times 10^6$	<2	10^6—10^9
Ethyl linoleate	6·8	7·0	10^6	$0{\cdot}5 \times 10^6$	<2	10^6—10^9
Tetralin	10·2	4·5	10^4	$2{\cdot}0 \times 10^7$	1	10^8
n-Decanal	$1{\cdot}1 \times 10^3$	4·2	10^6	$7{\cdot}5 \times 10^6$	<1	10^8

Certain points emerge from an examination of this information. Consider, first, the termination process involving the interaction of two peroxidic radicals. The activation energy in every case is very low, as would be expected for such a reaction. From the constancy of their k_6 values, Bateman and Gee concluded that the reactivity of peroxidic radicals is independent of the structure of the molecules from which they are derived. Although the results for tetralin and *n*-decanal are somewhat larger, the variations in k_6 are not very large and the corresponding frequency factors lie within much narrower limits than have been found for the radical–radical termination steps of polymerisation reactions, for which values as low as 10^4 have been encountered (Burnett, *Quart. Rev.*, 1950, IV, 292).

As would be expected from the readiness with which the autoxidation of *n*-decanal occurs even at low temperatures, the velocity constant for the rate-controlling propagation step has a much higher value than is observed with the other materials studied. Apart from the result for tetralin, which seems to be rather low, the frequency factors, A_3, correlate well with those of transfer reactions in polymerisation calculated by Gregg and Mayo (*Faraday Soc. Disc.*, 1947, **2**, 328) and those found by Steacie, Darwent, and Trost (*ibid.*, p. 79), for hydrogen-exchange reactions with paraffin hydrocarbons. Each of these processes involves the abstraction of a hydrogen atom from a molecule either by a free radical or by an atom.

From the data published by Bateman and Gee and by Bolland and ten Have for the autoxidation of ethyl linoleate, it is possible to calculate a velocity coefficient for the interaction of the peroxidic radical with quinol at 5° :

For ethyl linoleate, $k_7 = 7 \times 10^6$ mol./l.sec.

For *n*-decanaldehyde, $k_7 = 1{\cdot}6 \times 10^5$ mol./l.sec.

Comparison of these results would indicate that the reactivity of peroxidic radicals may not be entirely independent of the nature of the molecules from which they are derived, although the structural influence is not very great.

The value of k_1 is of particular interest, if the proposed mechanism of reaction is indeed correct, for it represents the first known determination of the velocity coefficient for chain initiation by the direct attack of molecular oxygen. The corresponding frequency factor brings the process into line with radical–molecule reactions, a reasonable result in view of the nature of the oxygen molecule. It is the high energy of activation which accounts for the relative inefficiency of the thermal chain initiation.

As can be seen from Table VIII, the number of autoxidation reactions which have been subjected to detailed kinetic analysis is still very small, and further investigations are needed before it is possible to assess more accurately the factors which control the radical reactivities.

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