The Photochemical Autoxidation of iso*Propylbenzene.*

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[Reprint Order No. 4673.]

The hydroperoxidation of liquid *iso*propylbenzene is a chain reaction which can be initiated by the free radicals produced from azonitriles by thermal decomposition or by irradiation with light in the near ultra-violet.

The course of the reaction has been followed by measurement of the oxygen absorbed, by means of an automatically controlled manostat.

The kinetics of the reaction show that the chains are propagated by the cycle

$$R\cdot + O_2 \longrightarrow RO_2\cdot$$

$$RO_2\cdot + RH \longrightarrow RO_2H + R$$

where R is a free radical $C_6H_5\cdot CMe_2\cdot$. With oxygen pressures above 200 mm. the first of these reactions is fast and the rate is controlled by the second of them. Termination is by removal of peroxy-radicals by a second-order reaction.

The rate of production of free radicals during the autoxidation has been obtained from the rate at which the sensitiser evolves nitrogen when under irradiation. The life-time of the reaction chains has been determined by the use of intermittent light. These data enable the rate coefficients for the rate-controlling propagation and termination steps to be obtained.

IT has previously been observed that when *iso*propylbenzene is shaken at 85° with dry oxygen under irradiation from a mercury-vapour lamp oxygen is slowly taken up and a hydroperoxide is formed (Hock and Lang, *Ber.*, 1944, **77**, 257). The reaction occurring was sown to be $C_6H_5\cdot CHMe_2 + O_2 \longrightarrow C_6H_5\cdot CMe_2\cdot O\cdot OH$, and the yield of peroxide, based on the oxygen absorbed, was almost quantitative.

Other workers (Armstrong, Hall, and Quin, *J.*, 1950, 130, 666) have shown that a similar reaction occurs when oxygen is passed through an aqueous emulsion of *iso*propylbenzene at 85°. Preliminary investigation of the kinetics of the reaction occurring under these conditions indicated that it was similar to other autoxidations, such as those of olefins, aldehydes, and tetralin, which were known to proceed by free-radical chain mechanisms.

It has been found for several other substances that the mechanism of thermal and photochemical autoxidation differs only in the method by which chains are initiated. It therefore seemed likely that photochemical autoxidation of *iso*propylbenzene would proceed by the mechanism common to the other substances studied, and that the methods used to determine their rate coefficients would be applicable also to *iso*propylbenzene.

The direct photo-oxidation is, however, not suitable for this type of study, as the absorption spectrum of *iso*propylbenzene shows that intense light absorption would occur and the distribution of free radicals in a reaction vessel would probably not be uniform. For this reason azonitriles were used as photosensitisers. These have the additional advantages that they absorb in spectral regions which are readily accessible and do not seem to undergo a decomposition by free-radical attack, which would complicate the kinetics.

EXPERIMENTAL

The apparatus used was, in most respects, similar to that used by Melville and Cooper (*J.*, 1951, 1984) for studying the autoxidation of decanal. A mercury diffusion pump, backed by an oil-pump, was used to evacuate the system, which was provided with liquid-air traps, manometers, oil-trap, safety-valve, and storage bulbs for oxygen and nitrogen. The manostat was the same as in Melville and Cooper's Fig. 2, but without the refilling devices. The dibutyl phthalate was replaced by silicone oil. The thermionic relay was that described by Bolland (*Proc. Roy. Soc.*, 1946, *A*, **186**, 218) but the Sunvic hot-wire switch was replaced by a magnetic switch. The manostat was immersed as completely as possible in a water thermostat maintained at 25° ± 0·1° by means of an A.C. thyratron relay operated by a mercury–toluene regulator.

In the present work the oxidation was carried out at temperatures up to 80°; for this reason a reaction vessel of Pyrex glass was used which incorporated a condenser through which tap water could be circulated.

The connection from the reaction vessel to the manostat was through a standard B10 Quickfit joint and a glass spiral of 2-mm. tubing. The spiral consisted of about 6 coils, each about 2 inches in diameter. This is flexible enough to permit vigorous shaking, which was effected by connecting an elliptical wheel through a metal rod and flexible connection to a screw clip on the socket at the end of the spiral. The axle carrying the elliptical wheel was connected by gears to a small electric stirring motor. The motor was generally run at high speeds and geared down to provide about 300—400 shaking cycles per min. The required range of shaking speeds (100—600 cycles per min.) could be obtained by altering the motor speed.

The reaction vessel was in a separate thermostat (a 4-l. Pyrex beaker) maintained within ±0·05° of the required temperature by means of a mercury–xylene regulator and a Sunvic hot-wire vacuum switch.

It is necessary to evacuate the system before filling it with oxygen. As *iso*propylbenzene is fairly volatile, it was necessary to freeze it in liquid air during the evacuation. For this reason it was arranged that the 4-l. beaker could be lowered clear of the reaction vessel.

The ultra-violet-lamp housing was placed in front of the reaction vessel and the shaking mechanism behind it. All three were thus in the same straight line and the reaction vessel was shaken along this line. This method of shaking along the light beam reduces fluctuations in the light intensity during the shaking cycle.

The ultra-violet lamp used was a G.E.C. Osira high-pressure mercury arc, and it was used with the recommended choke and condenser and run at constant voltage.

Intermittent light was obtained by rotating a sheet-metal sector in front of the lamp, giving equal light and dark periods. The rate of evolution of nitrogen was measured by observing the pressure build up in the manostat. To enable the sensitivity to pressure increases to be measured, the manostat was slightly modified. Cooper and Melville's arrangement (their Fig. 2) was modified by sealing a vertical tube to the horizontal tube connecting C_2 to A_2. This vertical tube led through a capillary tap to a small bulb. Small quantities of gas could then be added to the manostat from the bulb. For the present purpose the electrolytic cell was isolated from the manostat by a tap.

The main supply of *iso*propylbenzene was kept sealed in glass. Small quantities were removed for use and stored under nitrogen in a pipette similar to that used by Cooper and Melville. Apiezon grease M was used as a general lubricant for taps and ground-glass joints, except for those in close proximity to the hydrocarbon where silicone grease was used.

Materials.—iso*Propylbenzene.* This was obtained pure for kinetic purposes. Its ultra-violet absorption spectrum was examined with a Hilger " Uvispec " Spectrophotometer. Over the range 2550—2750 Å the spectrum was identical with that of the N.B.S. standard (99·95±0·02 mole per cent. of *iso*propylbenzene). The absorption of wave-lengths transmitted by Pyrex glass, *i.e.*, greater than about 3000 Å, was negligible.

A sample of the peroxide-free *iso*propylbenzene was exposed to air for several weeks in order to allow it to accumulate peroxide. The spectrum was then measured and showed greatly increased absorption above 3000 Å. The peroxide was estimated iodometrically and so it was found that the molar decadic extinction coefficient at 3400 Å, which is near the absorption peak for azo-sensitiser, is about 0·7. It could then be calculated that the screening effect of the hydroperoxide on the sensitisers was not serious even at the maximum extent of oxidation which was obtained.

*α-Azo*iso*butyronitrile.* This was prepared according to Thiele and Heuser (*Annalen*, 1896, **290**, 1) and, recrystallised from ethanol, had m. p. 102—103° (Overberger, *J. Amer. Chem. Soc.*, 1949, **71**, 2661, gives 103—104°) with decomp. Its ultra-violet spectrum is almost identical with that reported by Overberger.

1-*Azo*-1-*cyano*cyclo*hexane.* This was obtained commercially and, recrystallised from ethanol, had m. p. 114° (Overberger gives m. p. 114°). The absorption spectrum (Fig. 1) was determined in solution (10 g./l.) in ethanol. The absorption is more intense than that of azo*iso*butyronitrile, in contrast to Overberger's finding—his values are about 60—70% of those obtained here, though the shape and the position of this spectrogram are the same as we found.

Chlorobenzene. The B.D.H. product was twice fractionated through a 1-ft. Dufton column.

Oxygen. Gas was obtained from commercial cylinders and passed through a liquid-air trap.

Nitrogen. This was of oxygen-free grade.

*Results with Azo*iso*butyronitrile.*—This sensitiser was found to give appreciable thermal rates if used at temperature above 50°. At 30° the thermal rate could be reduced to 10% of the total rate under irradiation, which is sufficiently low to permit investigation of the photo-reaction.

The primary product of the reaction was hydroperoxide; the yield based on the oxygen absorbed was nearly 100%. The rate dependence on light intensity was slightly less than ½ power, and the rate was independent of oxygen pressure over the range 250—700 mm. It was subsequently found that with the amounts of catalyst used in these experiments there was an appreciable amount of nitrogen evolved in the initiation step. The true peroxide yield was therefore less than that calculated on the basis of the gas absorbed. The deviation from ½ power dependence on the light intensity was also due to this phenomenon.

The reaction vessel was cleaned out between runs in two ways. In both cases silicone grease was removed from the cone by wiping it with cotton wool soaked in benzene. The vessel was then washed out 3 times with ethanol. It was then either pumped out to a high vacuum for 20 min., or washed 3 times with distilled water and heated in the oven, air being periodically blown through it. Both methods gave the same rates, so the first method was adopted as standard.

FIG. 1. *Ultra-violet absorption of* 1-*azo*-1-*cyano*cyclo*hexane* (ε = *molar decadic extinction coefficient*).

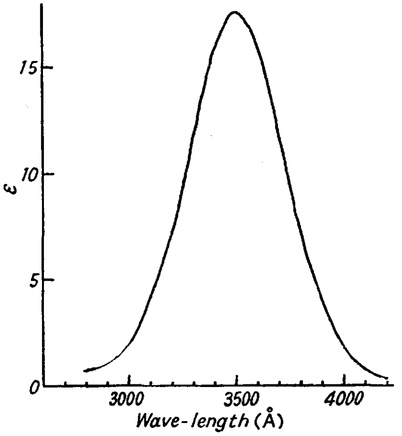
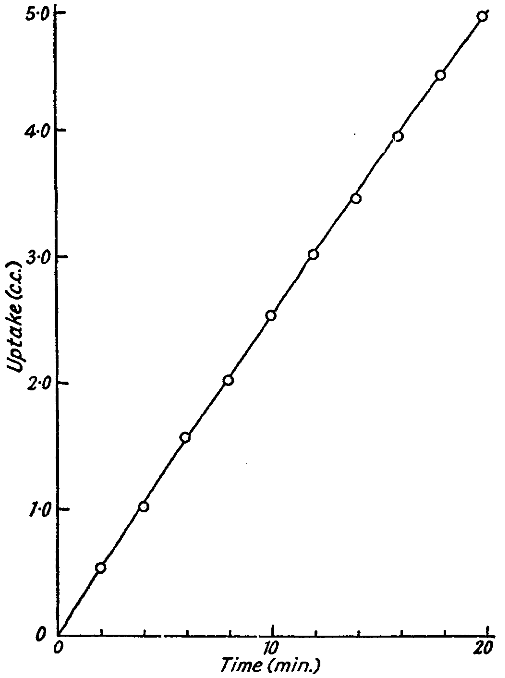


FIG. 2. *Course of reaction at* 50°.



In order to increase the kinetic chain length of the oxidation it is necessary to work at higher temperatures. For this reason the present sensitiser is unsuitable and attention was turned to a more thermally stable azo-sensitiser.

The Reaction sensitised with 1-*Azo*-1-*cyano*cyclo*hexane.*—An 0·01M-solution of the sensitiser in *iso*propylbenzene gave suitable rates of oxidation at 50°, with oxygen pressures of 175 mm. (The rate falls off with time, owing to exhaustion of the catalyst.) The course of the reaction is shown in Fig. 2, the oxidation being carried out under the standard conditions outlined later.

In all the experiments described below it was necessary on account of the short chain lengths to correct rates of oxygen absorption for the nitrogen evolved by the sensitiser when under irradiation.

Peroxide Yields.—Samples (2·2 ml.) of *iso*propylbenzene solution were oxidised at varying temperatures, and the total oxygen absorptions (in ml. at 25°/175 mm.) were measured. The hydroperoxide was estimated by an iodometric method. Iodine was liberated from potassium iodide solution in the presence of glacial acetic acid and determined by titration against 0·01N-thiosulphate. "AnalaR" reagents were used throughout and the thiosulphate was standardised against potassium iodate solutions.

Rate of Oxygen Solution.—When oxygen is being removed by reaction, the concentration of gas in solution is lowered from its saturation value. Provided that dissolution is made easy, the change in concentration is sufficiently small to be neglected.

TABLE 1. *Peroxide yield, with* 1-*azo*-1-*cyano*cyclo*hexane.*

Temp.	O_2 absorption (ml. at 25°/175 mm.)	Peroxide yield (%)	Temp.	O_2 absorption (ml. at 25°/175 mm.)	Peroxide yield (%)
30°	4·7(4)	88	58°	9·72	93
40	7·5(0)	95	65	9·86	95
50	9·24	83		Average	91

A simple way of verifying this is to observe whether there is any variation of oxidation rate with the speed of shaking of the reaction vessel. The reaction rate was measured at a high speed, at a lower shaking speed, and then again at the high speed. A typical experiment is illustrated in Fig. 3. The second rate was found to be, within experimental error, the same as the mean of the other two for rates of shaking in the range 120—300 cycles per min.; 300 cycles per min. was adopted as the standard rate of shaking. The size of sample was also kept standard at 2·2 ml. containing 5 mg. of sensitiser.

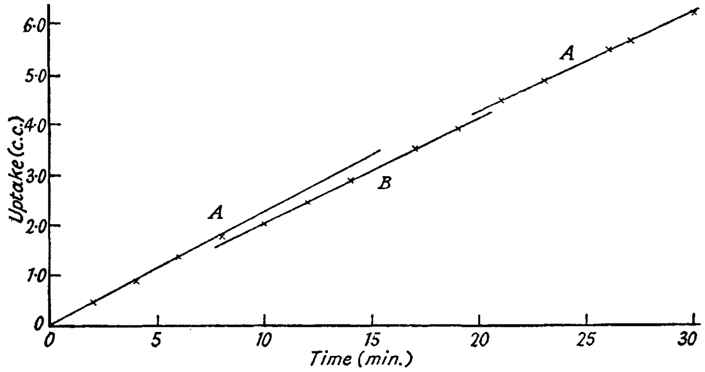


FIG. 3. *Variation of rate with speed of shaking.*
A, 300 cycles/min.
B, 130 cycles/min.

Calculation of Photo-rate.—It has been assumed that the photochemical and the thermal reaction are similar except for the initiating reaction. In these circumstances the rates of initiation are additive and the rate of oxidation due to photo-initiation (R_P) is given by

$$(R_P)^{\frac{1}{n}} = (R_L)^{\frac{1}{n}} - (R_T)^{\frac{1}{n}}$$

where R_T = thermal rate, R_L = total rate under irradiation, and n = intensity exponent later shown to be $\frac{1}{2}$. This method of obtaining the photo-rate was suggested by Noyes and Leighton ("Photochemistry of Gases," Reinhold, New York, 1941, p. 202).

Dependence of the Photo-rate on Light Intensity.—The rate was measured under a reduced light intensity and compared with the mean of the rates at full intensity measured immediately before and after the experiment. The light intensity was reduced by placing a fine calibrated wire gauze between the lamp and the thermostat. The results (Table 2) show that the exponent is $\frac{1}{2}$.

Rate Dependence on Sensitiser Concentrations.—For a photochemical reaction in which the rate is proportional to the square root of the rate of initiation, the rate will also be proportional to the square root of the sensitiser concentration providing that the light absorption is relatively

TABLE 2. *Rate dependence on light intensity.*

Temp.	Transmission of gauze	Ratio of rates R_{RP}/R_P	Intensity exponent	Rate of oxidation (10^{-5} mole $l.^{-1}$ $sec.^{-1}$)
65°	0·28	0·54	0·48	2·9
65	0·28	0·51	0·51	
50	0·28	0·51	0·53	1·75
50	0·47	0·68	0·51	
50	0·47	0·68	0·51	
50	0·47	0·69	0·49	
50	0·45	0·64	0·56	
50	0·45	0·68	0·49	
			Average 0·51	

low. The rate of oxygen absorption was measured at 50° for 2·2-ml. of *iso*propylbenzene containing varying quantities of sensitiser. The results are shown in Fig. 4.

Rate Dependence on Hydrocarbon Concentration.—Mixtures of *iso*propyl- and chloro-benzene, made up volumetrically, were oxidised under standard conditions at 50° with 5 mg. of sensitiser per 2·2-ml. sample. Fig. 5 shows a first-order dependence on hydrocarbon concentration.

Rate Dependence on Oxygen Pressure.—The variation of the rate with oxygen pressure was studied at 65° with standard samples. Fig. 6 shows that the rate is independent of oxygen pressure above about 200 mm. but below this it starts to fall off.

Overall Energy of Activation for the Photo-reaction.—A series of rate measurements at 175 mm. pressure was made over the temperature range 30—65° with a standard 2·2-ml. sample. From the plot of log rate against the reciprocal of the absolute temperature (Fig. 7) the overall energy of activation was found to be 6·53 kcal.

FIG. 4. *Rate dependence on sensitiser concentration (at 50°).*

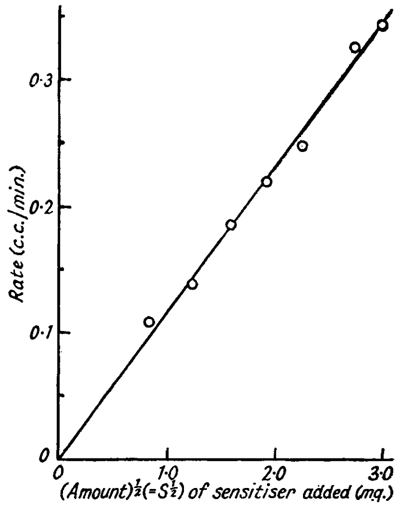
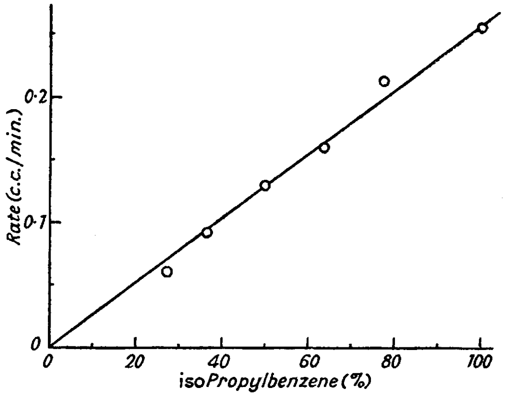


FIG. 5. *Rate dependence on hydrocarbon concentration (at 50°).*



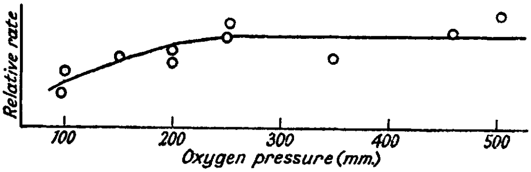


FIG. 6. *Rate dependence on oxygen pressure (at 65°).*

A second series of experiments involving many determinations at each of three temperatures was also made. The results, shown in Table 3, yield a value of 6·83 kcal.

TABLE 3.

Temp.	30°	50°	65°
Rate (10^{-5} mole l.$^{-1}$ sec.$^{-1}$)	0·881	0·175	2·88

The overall energy of activation has therefore been taken to be 6·7 kcal.

It is now possible to express the experimental results in the form of an empirical equation, giving the rate of oxidation as

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = kI^{\frac{1}{2}}C^{\frac{1}{2}}[\mathrm{RH}][\mathrm{O}_2]^0$$

where I = light intensity, C = sensitiser concentration, and [RH] = hydrocarbon concentration. The rate of chain starting may be assumed to be proportional to the light intensity, and to the sensitiser concentration where the light is not heavily absorbed. The rate equation therefore shows a square-root dependence on the rate of initiation.

This empirical rate equation is formally analogous to those generally obtained in other photochemical autoxidations, such as those of aldehydes and olefins, suggesting a close similarity in mechanism. With the usual nomenclature, that which has been established is

$$\begin{array}{ll} \text{Initiation:} & \mathrm{R\cdot \ or \ RO_2\cdot} \\ \text{Propagation:} & \mathrm{R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot} \\ & \mathrm{RO_2\cdot + R{-}H \xrightarrow{k_3} RO_2\,H + R\cdot} \\ \text{Termination:} & \mathrm{RO_2\cdot + RO_2 \xrightarrow{k_6}} \end{array}$$

Application of the stationary-state method for calculation of the rate of oxidation gives

$$-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_3[\mathrm{RH}]\mathrm{R_i}^{0\cdot5}/k_6^{0\cdot5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R_i is the rate of initiation.

In deriving this expression it is assumed that the reactions of the R• radical are not rate-determining. If this were not so, the rate would become dependent on the oxygen pressure.

The exact mechanism by which azo-catalysts initiate chains in oxidation systems is not known. However, it is well established that in their thermal decomposition, nitrogen is evolved and free radicals are formed by the reaction $\mathrm{(CN{\cdot}CMe_2{\cdot}N\dot{:})_2 \longrightarrow N_2 + 2CN{\cdot}CMe_2\cdot}$. A similar reaction must occur under irradiation by ultra-violet light. These radicals may then undergo one of two reactions: either they abstract the tertiary hydrogen atom of the *iso*propylbenzene, or they combine with an oxygen molecule, followed by hydrogen abstraction. It has been found that many radicals react rapidly with oxygen whereas hydrogen abstraction would be expected to be slower.

It has been assumed in the present work that photolysis of the sensitiser produces two free radicals and a molecule of nitrogen. R_i, the rate of initiation, then becomes equal to twice the rate of nitrogen evolution, providing that each radical from the sensitiser starts a reaction chain. As the reaction can be initiated photochemically and the rate is proportional to the square root of the light intensity it is possible to apply the sector technique to evaluate the lifetime of the kinetic chain.

In the " high-pressure " region where the concentration of $\mathrm{RO_2}$ radicals is much greater than the concentration of R radicals, the life-time (τ) obtained is that of the former.

Now,

$$\tau = \frac{\text{Free radical concentration}}{\text{Rate of removal of free radicals}} = \frac{1}{k_6[\mathrm{RO_2}]_s} \quad . \quad . \quad . \quad . \quad (2)$$

where τ and $[\mathrm{RO_2}]_s$ refer to the values in the stationary state.

Also, in the steady state,

$$I - k_6[\mathrm{RO_2}]^2 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

from (2) and (3)

$$k_6 = (\tau^2 R_i)^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and from (1) and (4)

$$k_3 = R_L/\tau[\mathrm{RH}]R_i \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The values of τ and R_i may thus be used in (4) and (5) to obtain the absolute velocity constants.

It is important for the present purpose that the concentration of radicals should be nearly uniformly distributed through the oxidising liquid. As the ultra-violet light was filtered through Pyrex glass, absorption by the hydrocarbon or its peroxide may be neglected.

The peak value of the molar decadic extinction coefficient for the *cyclo*hexane–azo-compound is about 17·5. The light beam traverses about 0·4 cm. of a 10^{-2}M-solution. Hence it may be shown that only about 15% of the light at the absorption peak is absorbed; further, the shaking of the reaction vessel will help to distribute the radicals uniformly.

The square-root dependence on the sensitiser concentration also indicates the absence of a " skin effect."

Determination of the Rate of Initiation.—A standard sample was introduced into the reaction vessel, frozen in liquid air, and degassed. The system was then filled with nitrogen. When thermal equilibrium had been reached the nitrogen pressure was adjusted to a suitable value, and the taps in the manostat were closed. The pressure build-up under irradiation could be measured by following the upward rise of the silicone fluid B_2.

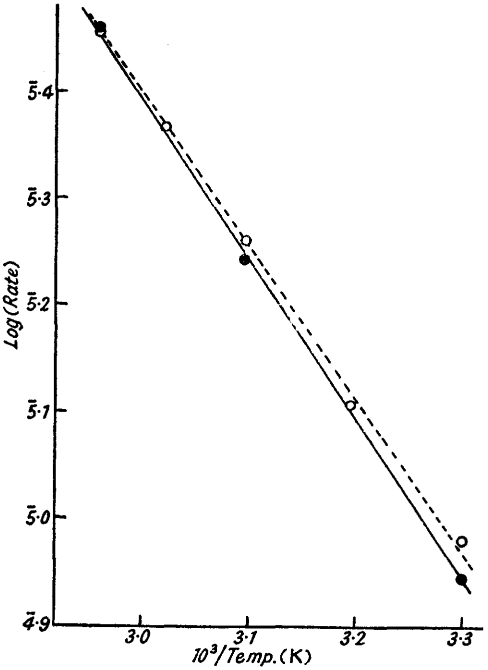
At lower temperatures it was possible to take readings during the time of irradiation, plot the results graphically, and draw a smooth curve. At higher temperatures the mean position of the level before and after irradiation was measured. The rate of nitrogen evolution in the latter case is therefore less accurately known, but should be within ±10%.

The manostat was filled with pure nitrogen to a suitable high pressure (P), and the capillary tap turned to isolate the bulb. The apparatus was then adjusted to pressure (p), as previously described, for measurement of the nitrogen evolution. The silicone level was noted. Finally, the capillary tap was opened and the resulting movement of the silicone was noted. The volume of gas (V_i) isolated at the higher pressure is equal to the volume of the bulb and of the capillary through the tap key. The latter was estimated, by filling with mercury and weighing, to be 0·49 ml.

If the nitrogen in the bulb was at a pressure P and if the final pressure in the manostat was p', then the amount of gas added to the manostat is V_i ml. at $(P - p')$ mm. and room temperature.

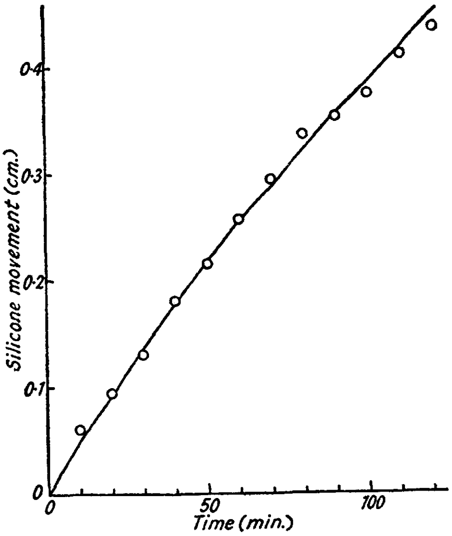
As the volume V_i is small, the error in assuming $p' = p$ should be small. By connecting the manostat to a manometer it was verified that this was so.

FIG. 7. *Energy of activation of photo-oxidation.*



Full points refer to values on p. 948.

FIG. 8. *Nitrogen evolution at* 350 *mm.*



A second method used to check the sensitivity of the manostat was to alter the temperature of the bulb of the reaction vessel. If its volume is V, then it can be shown that for an apparatus of the dimensions used, $\Delta T/T = \Delta V/V$, where T is the original temperature, ΔT = the change in temperature, and ΔV = the gas evolved which produces the same response by the manometer.

There was no measurable delay between irradiation and gas evolution, and the evolution ceased when the lamp was switched off.

A typical experimental run is shown in Fig. 8. The rate fell off considerably during measurement (120 min.) owing to exhaustion of the sensitiser. The results during the first 10 min. are shown in Table 4. For 1-cm. movement of the silicone oil, $P - p$ = 909 mm., and therefore movement of 1 cm. = 0·49 ml. of gas at 20°/909 mm. = $2{\cdot}47 \times 10^{-5}$ mole, and therefore the rate of nitrogen evolution = $11{\cdot}9 \times 10^{-8}$ mole per min.

The bulb of the vessel has a volume of 15·6 ml. and a temperature change from 49·95° to 43·3° alters the silicone level by 0·365 cm. Use of equation (6) shows that a 1-cm. movement of the silicone = $2{\cdot}2 \times 10^{-5}$ mole. The agreement is satisfactory as equation (6) is only approximately correct.

Further results are shown in Table 5.

TABLE 4. *Nitrogen evolution at* 50°/350 *mm.*

Expt.	Rate of movement of silicone level (10^{-3} cm./min.)	Pressure (mm.) in bulb (P)	Pressure (mm.) in manostat (p)	Silicone oil movement S	$10^3S/(P-p)$
1	4·2	—	—	—	—
2	5·3	705	351	0·382	1·08
3	5·3	705	351	0·400	1·13
4	5·4	715	350	0·395	1·08
5	5·2				Mean 1·1
6	3·8				
7	4·6				
	Mean 4·8				

TABLE 5. *Nitrogen evolution at* 50°/100 *mm.* [*pressure* (p) *in manostat* = 100 *mm.*].

Rate of movement of silicone level (10^{-2} cm./min.)	1·15	1·32	1·40
Pressure (P) in bulb (mm.)	228	227	227
Silicone movement (S) (cm.)	0·360	0·360	0·367

Hence $S/(P-p) = 2{\cdot}85 \times 10^{-3}$, and the rate of nitrogen evolution = $11{\cdot}9 \times 10^{-8}$ mole/min.

TABLE 6. *Nitrogen evolution at* 30°/100 *mm.* (*pressnre in bulb* 230 *mm.*; *pressure in manostat* 100 *mm.*)

Rate of movement of silicone level (cm./min.)	1·14	1·13	1·13	1·15	1·15	1·15	—	—
Silicone movement (cm.)............................	0·357	0·380	0·360	0·378	0·373	0·358	0·356	0·361

The rate of nitrogen evolution = $10{\cdot}8 \times 10^{-8}$ mole/min.

TABLE 7. *Nitrogen evolution at* 65°/100 *mm.*

Rate of movement (10^{-2} cm./min.) (4 expts.) : 1·44, 1·15, 1·21, 1·22 (mean 1·25).
Sensitivity : $9{\cdot}08 \times 10^{-6}$ mole per cm. movement.
Rate of nitrogen evolution = $11{\cdot}45 \times 10^{-8}$ mole/min.

TABLE 8. *Collected values for rate of nitrogen evolution.*

Temp.	Pressure (mm.)	No. of determinations	Rate (10^{-8} mole/min.)
30°	100	6	10·8
50	100	3	11·9
65	100	4	11·4
50	350	7	11·9
			Mean 11·3

A weighted mean was used; as the results at 30° were the most reproducible these were multiplied by 2.

From the rate of evolution the rate of initiation was found to be $1{\cdot}72 \times 10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$.

At 50°, the rate of oxidation = $1{\cdot}75 \times 10^{-5}$ mole l.$^{-1}$ sec.$^{-1}$; hence the kinetic chain length is 10 and $k_3k_6^{-\frac{1}{2}} = 3{\cdot}04 \times 10^{-3}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$.

At 65°, the rate of oxidation = $2{\cdot}88 \times 10^{-5}$ mole l.$^{-1}$ sec.$^{-1}$, and the chain length is 17; $k_3k_6^{-\frac{1}{2}} = 3{\cdot}04 \times 10\ {}^{3}$ mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$.

It is of interest to compare the value of the rate of initiation as determined directly with the value obtained by using the data for the thermal decomposition.

The oxidation rate at constant temperature is proportional to the square root of the rate of initiation. Hence $I_P = I_TR_P^2/R_T^2$, where I_P and I_T are the photo- and the thermal rates of initiation, the latter being equal to twice the rate of sensitiser decomposition; and R_P and R_T are the oxidation rates. Lewis and Matheson (*J. Amer. Chem. Soc.*, 1949, **71**, 747) state that, for 1-azo-1-cyano*cyclo*hexane, k for the first-order decomposition at 80° is $2{\cdot}82 \times 10^{-4}$ min.$^{-1}$, and the energy of activation is 39·9 kcal. per mole. Overberger, O'Shaughnessy, and Shalit (*ibid.*, p. 2661) report that at 80·2° $k = 0{\cdot}083$ sec.$^{-1}$ = $4{\cdot}98 \times 10^{-4}$ min.$^{-1}$. Arnett (*ibid.*, 1952, **74**, 2027) gives $k = 3{\cdot}2 \times 10^{-4}$ min.$^{-1}$ at 77°, or, using Matheson's energy of activation, $k = 5{\cdot}2 \times 10^{-4}$ min.$^{-1}$ at 80°.

The thermal rate at 80° was measured and compared with the " light " rate obtained with a filter of transmission = 0·28, with the following results :

Thermal rate	0·0570	0·0655	0·059	
" Light " rate	0·1145	0·1080	0·1190	
Rate of initiation (10^{-8} mole/min.)	12·9	7·1	13·2	(mean 11·1)

These values have been obtained by using Matheson's data. The directly determined value is about twice as great ($22{\cdot}6 \times 10^{-8}$). Using the results of Overberger or of Arnett gives a value 20×10^{-8} which is in good agreement with the determined value.

It will be noted from Table 8 that there does not appear to be any effect due to temperature on the photo-rate of sensitiser decomposition. This is as might be expected for a photolytic process not complicated by a secondary reaction.

Determination of the Life-time.—The use of intermittent illumination for the determination of free-radical life-times is well established, and, for a similar system, the general procedure has already been described (Cooper and Melville, *loc cit.*) and has been used in both polymerisation and autoxidation studies (Bateman and Gee, *Proc. Roy. Soc.*, 1948, A, **195**, 376).

FIG. 9. *Life-time at* 50°.

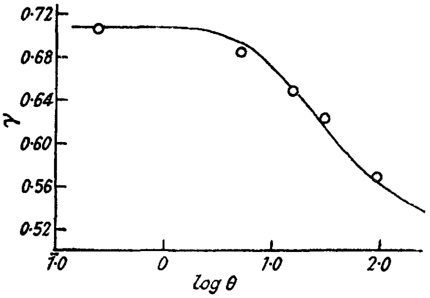
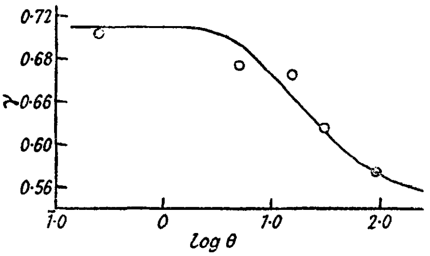


FIG. 10. *Life-time at* 65°.



The experimental procedure in the measurement of the life-time is similar to that described previously for measuring the intensity exponent. Measurements were made of the initial thermal rate during about 20 min. and of the light rate during about 8—10 min. The sector was started, and after about 1 min., during which the system becomes steady, the rate in intermittent light was measured. The sector was timed with an ordinary stop-watch and the rate measurement continued for about 10 min. The uninterrupted rate was again measured, and finally the thermal rate.

Several determinations were made at each flash time and the averaged results are shown in the following Tables, where Y = ratio of rate in intermittent light to that in uninterrupted light, and α = ratio of thermal to " light " rate.

Determination of τ *at* 50° ; $\alpha = 0{\cdot}04$.

Flash time (θ) (sec.)	0·243	5·0	15·0	30·0	90·0
Y	0·7060	0·6846	0·6496	0·6226	0·5678

Determination of τ *at* 65° ; $\alpha = 0{\cdot}10$.

Flash time (θ) (sec.)	0·248	5·0	15·0	30·0	90·0
Y	0·7038	0·6730	0·6649	0·6141	0·5729

The usual plot of γ against log θ is shown in Figs. 9 and 10 with the life-time curve in the position of best fit. This gives τ = 4·6 sec. at 50°, and 4·2 sec. at 65°. The difference, which is within expermental error, would correspond to an energy of activation for termination of about 0·25 kcal. However the precision of the data is only sufficient to establish that its value is less than 6 kcal.

Collected Kinetic Data.

	At 50°	At 65°
Rate of oxidation (mole l.$^{-1}$ sec.$^{-1}$)	$1{\cdot}75 \times 10^{-5}$	$2{\cdot}88 \times 10^{-5}$
Rate of initiation (mole l.$^{-1}$ sec.$^{-1}$)	$1{\cdot}72 \times 10^{-6}$	$1{\cdot}72 \times 10^{-6}$
Life-time of reaction chain (sec.)	4·6	4·2
k_3 (mole^{-1} l. sec.$^{-1}$)	0·31	0·56
k_6 (mole^{-1} l. sec.$^{-1}$)	$2{\cdot}8 \times 10^4$	$3{\cdot}3 \times 10^4$
$E_3 - \frac{1}{2}E_6$ (kcal./mole)	6·7	

The authors are much indebted to the Distillers Company Limited for gifts of specially purified *iso*propylbenzene. One of them (S. R.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

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[*Received, September* 24*th*, 1953.]