Studies by Electron Spin Resonance of the Reactions of Alkylperoxy Radicals

Part 1.—Absolute Rate Constants for the Termination Reactions of Alkylperoxy Radicals

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Alkylperoxy radicals, produced by the photolysis of solutions of di-t-butyl peroxide in oxygensaturated alkanes, have been detected by electron spin resonance spectroscopy. Tertiary alkylperoxy radicals terminate with second-order kinetics, and absolute termination rate constants have been measured over a range of temperatures (-60 to $+20^{\circ}$ C). The process has an unusually high activation energy (*ca.* 8 kcal mol⁻¹) for a reaction involving two radicals. Secondary alkylperoxy radicals decay more rapidly by a reaction which has a smaller activation energy (*ca.* 2 kcal mol⁻¹). The decay of primary radicals is so rapid that the radical concentration is too small to be detected. A new method is described for the measurement of cross-termination rate constants.

The oxidation of hydrocarbons by molecular oxygen in the liquid phase proceeds by a chain mechanism¹ in which peroxy radicals (RO_2 ·) are chain-propagating agents. In the absence of an antioxidant, this chain reaction is generally terminated by the bimolecular reaction of two peroxy radicals. Whilst several termination rate constants have been measured by the rotating-sector technique^{2, 3} for the peroxy radicals derived from olefinic and aromatic compounds, there have been relatively few determinations of the rates of self-reaction of alkylperoxy radicals.

Unlike the diffusion-controlled reactions of many radicals 4 ($k \simeq 10^{10}$ l. mol⁻¹ s⁻¹), the decay of tertiary alkylperoxy radicals is relatively slow 5 ($k \simeq 10^{3}$ l. mol⁻¹ s⁻¹). Thus it is possible to produce a sufficiently high concentration of these radicals (*ca.* 10^{-5} mol l.⁻¹) to observe them directly by electron spin resonance (e.s.r.) and follow their rates of decay. The decay kinetics of alkylperoxy radicals measured in this way have been reported as being of first, second and intermediate order by different authors.⁶⁻⁸

We have detected photolytically-generated alkylperoxy radicals by e.s.r. and followed the build-up and decay of radical concentration during and after photolysis at temperatures in the range -60 to $+20^{\circ}$ C. Absolute rate constants for the termination reactions of alkylperoxy radicals have been measured and the reactivities of primary, secondary and tertiary radicals compared.

EXPERIMENTAL

RADICAL GENERATION

Alkylperoxy radicals were produced in the spectrometer cavity by the photolysis of a solution of di-t-butyl peroxide (DTBP) in an oxygen-saturated alkane ⁸ contained in a 4 mm o.d. silica tube. The t-butoxy radicals produced by the photodecomposition of DTBP (reaction (1)) abstract hydrogen atoms from the alkane (reaction (2)) to form alkyl radicals which then react rapidly with oxygen (reaction (3)):

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{\sim} 2(CH_3)_3CO$$
(1)

$$(CH_3)_3CO + RH \rightarrow (CH_3)_3COH + R \cdot$$
(2)

$$\mathbf{R} \bullet + \mathbf{O}_2 \to \mathbf{R} \mathbf{O}_2 \bullet. \tag{3}$$

With this method various alkylperoxy radicals were obtained by using different alkanes. The source of ultra-violet radiation was a Thermal Syndicate, 100-W, medium-pressure, mercury lamp. A shutter mounted immediately in front of the cavity window was used to start and stop the photolysis of the sample.

E.S.R. MEASUREMENTS

A Varian V-4502 spectrometer with 100 kHz magnetic field modulation was used to detect the radicals produced by photolysis. A standard Varian variable temperature accessory V-4557 was used to regulate the sample temperature. The sample temperature was checked with an iron constantan thermocouple and, for a given setting of the controller, was reproducible to within ± 2 °C.

The g-factors of the e.s.r. spectra of peroxy radicals were determined by comparison with that of the spectrum of α, α' -diphenyl- β -picrylhydrazyl (DPPH; g = 2.0036). The concentration of radicals was determined by electronically integrating the first derivative signal which was normally obtained and measuring the area of the integral with a planimeter. This area was then compared with that obtained with a known concentration of DPPH in toluene. A correction was made for the increase in the concentration of DPPH caused by the contraction of the toluene when the sample was cooled. At temperatures below the melting point of toluene (-95° C) this solution could not be used as a standard because of a marked increase in the microwave saturation of the spectrum. In these cases, a plot of the measured area for a sample of DPPH against the reciprocal of the temperature was extrapolated to the required temperature. This method involved the reasonable assumption that the temperature-dependence of the intensity of the spectrum of alkylperoxy radicals was the same as that of the spectrum of DPPH.

Radical-decay curves were obtained by interrupting the photolysis and then following the variation of the maximum peak height of the derivative signal with time on a pen recorder. This method was satisfactory for reactions having a first half-life greater than 3 s. The ratio of the peak height of the derivative signal to the area of the integrated signal, measured from the signals obtained during photolysis, was then used to convert peak heights on the decay curve to areas and thus calculate absolute radical concentrations. At temperatures when the decay rate was slow, both derivative and integrated signals were recorded as the alkylperoxy radicals decayed and the ratio (peak height/area) was independent of the radical concentration. However, the ratio was dependent on temperature and was measured for each decay experiment.

GAS CHROMATOGRAPHIC MEASUREMENTS

For a given alkane the rate of hydrogen abstraction (reaction (2)) increases as the strength of the broken C—H bond decreases $^{9-11}$ so that the yields of peroxy radicals were in the order tertiary>secondary>primary. The relative rates of production of these radicals were determined from gas-liquid chromatographic (g.l.c.) analyses of the photolysis products.

The photolyzed samples were analyzed with a Perkin-Elmer F11 gas chromatograph with nitrogen as the carrier gas and a flame ionization detector. Photolysis products were separated before detection on a 4 m column ($\frac{1}{8}$ in. o.d.) of Carbowax 1540 (8 % w on Chromosorb W). Optimum separation was obtained by maintaining the temperature at 50°C for the first 15 min and then increasing it at a rate of 1.5° C min⁻¹ until it reached 160°C. This analysis did not, however, resolve low molecular weight alkenes from alkanes of the same structure and to separate these components a second analysis was performed on each sample using a 4 m column ($\frac{1}{8}$ in. o.d.) of silicone grease (20 % w on Chromosorb W) at 30°C. The identities of photolysis products were established by methods described previously.¹²

MATERIALS

Di-t-butyl peroxide, supplied by Koch-Light Laboratories Ltd., was washed with alkali, passed over activated silica gel and fractionated under reduced pressure at 60°C.

The hydrocarbons, obtained from Fluka AG, Koch-Light Laboratories Ltd. and Ralph N. Emanuel Ltd., were passed over activated silica gel before use and were shown by g.l.c. analysis to be generally ≥ 98 % pure.

RESULTS

E.S.R. SPECTRA OF ALKYLPEROXY RADICALS

The e.s.r. spectra of the alkylperoxy radicals at room temperature each consisted of a symmetrical single line with no detectable hyperfine structure (fig. 1(*a*)) and an isotropic g-factor of 2.015 ± 0.001 . This value is close to the isotropic g-factor calculated from the principal g-factors $(g_{\parallel} \text{ and } g_{\perp})$ of the spectra of peroxy radicals which are trapped in solid matrices and unable to rotate freely.¹³ Typical values of the calculated g-factor, $(g_{\parallel}+2g_{\perp})/3$, lie within the range 2.0120-2.0154. This good agreement confirms that the spectra observed in the photolysis experiments are due to peroxy radicals.

The spectra of the larger radicals became increasingly asymmetric as the temperature of the sample was reduced (fig. 1(b)) and the temperature range over which this occurred varied with the size of the alkyl group. Thus, the spectrum of the peroxy radicals derived from 2-methylpentane was still symmetric at -160° C whilst that of the radicals formed from 2,6,10,14-tetramethylpentadecane was asymmetric at -90° C. The peroxy radical spectra were not susceptible to saturation broadening at the microwave power level used.

GAS CHROMATOGRAPHIC ANALYSIS OF PRODUCTS

The photolyzed samples were analyzed by g.l.c. and the measured concentrations of oxidation products used to calculate the rates of formation of primary, secondary

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iOoe

1000



H

(a)

(b)

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and tertiary peroxy radicals from the parent alkane. The results obtained with 0.5 % solutions of DTBP in oxygen-saturated 2-methylpentane are summarized in table 1 and given in detail in the appendix. The selectivity of the attack on 2-methylpentane increases with decreasing temperature as expected. However, at all the temperatures examined the yield of secondary radicals is appreciable. Comparable analyses of 0.5 % solutions of DTBP in oxygen-saturated heptane showed that more than 98 % of the peroxy radicals formed are secondary (see appendix).

Table 1.—Percentage yields of peroxy radicals and relative rates of attack at different C—H bonds in 2-methylpentane

	yie	ld of peroxy radicals (relative rates of radical attack per C—H bond			
temp. °C	primary	secondary	tertiary	primary	secondary	tertiary
- 40	2.1 ± 0.4	28.6 ± 1.0	69.3 ± 1.0	0.032	1.0	9.7
-20	2.6 ± 0.4	31.3 ± 1.0	66.1 ± 1.0	0.037	1.0	8.5
0	3.4 ± 0.4	32.4 ± 1.0	64.3 ± 1.0	0.047	1.0	7.9
+20	4.2 ± 0.4	$\textbf{33.2} \pm \textbf{1.0}$	62.5 ± 1.0	0.056	1.0	7.5

RATES OF ALKYLPEROXY RADICAL TERMINATION REACTIONS

Where possible the formation of radicals during photolysis and the decay of radicals following the discontinuation of photolysis were observed directly and the termination rate constants obtained from kinetic analyses of these curves. When these processes occurred too rapidly to permit accurate measurement, the steady radical concentration produced by continuous photolysis was measured and a stationary-state analysis used to calculate the termination rate constant.

The rate-determining step in the formation of alkylperoxy radicals was the scission of the peroxide bond in DTBP to give two t-butoxy radicals ¹⁴ (reaction (1)). This process was independent of the solvent, provided that there was no significant cage effect; thus the rate of radical initiation remained effectively constant, for a given DTBP concentration, in all the systems examined. The stationary-state concentration of alkylperoxy radicals was therefore a direct measure of the rate of the radical termination reaction. This latter process was considerably slower for tertiary radicals than for primary and secondary radicals as is clear from the stationary-state radical concentrations given in table 2.

Table 2.—Stationary-state radical concentrations produced by the photolysis of 0.5 % solutions of DTBP in oxygen-saturated alkanes at $-20^\circ\mathrm{C}$

alkane	dominant radical type	[RO ₂ ·] stationary-state × 10 ⁶ (mol 1. ⁻¹)
neopentane	primary	< 0.05
n-hexane	secondary	0.79
2,2-dimethylbutane	secondary	0.90
3-methylpentane	tertiary	15.0
2,3-dimethylbutane	tertiary	20.8
2,2,3-trimethylbutane	tertiary	33.2

PRIMARY ALKYLPEROXY RADICALS

The photolysis of a 0.5 % solution of DTBP in oxygen-saturated neopentane at -20° C produced no detectable concentration of radicals, i.e., $[RO_2 \cdot] < 5 \times 10^{-8} \text{ moll.}^{-1}$. However, g.l.c. analysis showed that t-butanol and neopentanol were formed in amounts which indicated that the rate of generation of peroxy radicals in neopentane was comparable to that in other alkanes. If it is assumed that the alkylperoxy radicals decay by a second-order process and that a stationary state exists, then a minimum value for the termination rate constant k_{pp} for these primary radicals can be obtained by equating the rate of radical termination to the rate of initiation ϕI_a , where I_a is the light absorbed by the DTBP and ϕ the efficiency of the photolytic decomposition.

$$\phi I_a = k_{pp} [\mathrm{RO}_2 \cdot]^2. \tag{4}$$

From the value ((1.00±0.06)×10⁻⁶ mol 1.⁻¹ s⁻¹) of ϕI_a measured in 2-methylpentane it is calculated that $k_{pp} > 4 \times 10^8$ l. mol⁻¹ s⁻¹.

SECONDARY ALKYLPEROXY RADICALS

G.l.c. analysis indicated that the alkylperoxy radicals produced by the photolysis of a solution of 0.5 % DTBP in oxygen-saturated n-heptane were essentially all secondary. When photolysis was discontinued, these radicals decayed at a rate which was too rapid to allow accurate measurement. For this reason the rate constants were calculated from the stationary-state radical concentrations which were achieved within a few seconds of the start of photolysis. To calculate the rate constants k_{ss} for secondary heptylperoxy radicals over a range of temperatures it was assumed that ϕI_a was independent of temperature. A decrease in temperature caused the alkane to contract and increased [DTBP] and, consequently, I_a whilst ϕ decreased owing to an enhanced cage effect. However, these two effects opposed one another and the results obtained with 2-methylpentane indicate that the net effect is small. An Arrhenius plot (fig. 2) gives values for the A factor and activation energy of $10^{7.7 \pm 1.0}$ l. mol⁻¹ s⁻¹ and 1.9 ± 0.3 kcal mol⁻¹ respectively.



FIG. 2.—An Arrhenius plot of the second-order rate constants for the decay of s-heptylperoxy radicals in a 0.5 % solution of di-t-butyl peroxide in oxygen-saturated heptane.

TERTIARY ALKYLPEROXY RADICALS

DECAY KINETICS

The formation of alkylperoxy radicals by the irradiation of a 0.5 % solution of DTBP in oxygen-saturated 2-methylpentane and the radical decay following the discontinuation of photolysis are shown in fig. 3. G.l.c. analysis indicates that the

rates of formation at 20°C of primary, secondary and tertiary radicals expressed as a percentage of the total rate are 4.2, 33.2 and 62.5 respectively. Since the rates of reaction of these radicals vary considerably, the kinetics of the build-up of radical concentration are complex. With the end of photolysis, however, the primary and secondary radicals decayed rapidly to negligible concentrations and after a few seconds the decay curve represented the slower termination reaction of the tertiary radicals. This decay was second-order (eqn (5)),

$$-d[\mathrm{RO}_{2}\cdot]/dt = k_{tt}[\mathrm{RO}_{2}\cdot]^{2},$$
(5)

over the temperature range -60 to 0°C. Values for the rate constant k_{tt} were calculated from the gradients of plots of $[RO_2 \cdot]^{-1}$ against time (fig. 4).



FIG. 3.—Build-up and decay of alkylperoxy radicals in a 0.5 % solution of di-t-butyl peroxide in oxygen-saturated 2-methylpentane at $-40^{\circ}C$.



FIG. 4.—Reciprocal and log plots of the decay of alkylperoxy radicals in a 0.5 % solution of di-t-butyl peroxide in oxygen-saturated 2-methylpentane at -40°C.

The effect of the concentration of DTBP on the rate of decay of alkylperoxy radicals was examined at constant temperature and the rate of decay increased with increasing concentration of DTBP above 1 %. The faster decay rates at high [DTBP] are attributed to a non-uniform distribution of radicals caused by the strong absorption of the incident light. For this reason all the rate constants were measured in solutions containing 0.5 % DTBP which transmitted more than 88 % of the incident light. At temperatures above 0°C the rates of decay of the secondary and tertiary radicals became comparable and consequently the decay kinetics were complex, without any definite order.

The radicals derived from 2,2,3-trimethylbutane, which has no secondary C---H bonds, decayed with second-order kinetics in the temperature range -30 to $+20^{\circ}$ C. At higher temperatures the decay kinetics were also of indefinite order and this is attributed to the effect of primary radicals.

Arrhenius plots (fig. 5) of the results obtained with 2-methyl pentane and 2,2,3trimethylbutane give the following values for A and E_a :

	A, l. mol ⁻¹ s ⁻¹	E_a , kcal mol ⁻¹
2-methylpentane	$10^{11.1\pm1.0}$	9.3 ± 1.0
2,2,3-trimethylbutane	$10^{9.2 \pm 1.0}$	7.5 ± 1.0

FORMATION KINETICS

The total rate of formation of alkylperoxy radicals was determined from the initial gradient of the curve in fig. 2. In a 0.5 % solution of DTBP in oxygen-saturated 2-methylpentane, the rate of initiation (ϕI_a) was independent of temperature over the range -60 to 0°C and had a value of $(1.00\pm0.06) \times 10^{-6}$ mol l.⁻¹ s⁻¹. The same rate of initiation was measured in 2.2.3-trimethylbutane but at temperatures close to the melting point of this alkane $(-25^{\circ}C)$ the rate was reduced considerably, owing presumably to an enhanced cage effect.

Product analysis showed the rate of formation of primary peroxy radicals in 2methylpentane to be small and, since k_{pp} is high, $[RO_2^{p}]$ must be small relative to $[RO_{2}^{s},]$ and $[RO_{2}^{t},]$ and can be neglected. There are therefore three main termination reactions each having a different rate constant (reactions (6), (7) and (8)).

$$\operatorname{RO}_{2}^{s} \cdot + \operatorname{RO}_{2}^{s} \cdot \xrightarrow{\star_{ss}}_{\mu}$$

$$(6)$$

$$\begin{array}{c|c} \operatorname{RO}_2^{s} \cdot + \operatorname{RO}_2^{t} \cdot \xrightarrow{s_{\mathrm{st}}} \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$

$$\mathbf{RO}_2^t \cdot + \mathbf{RO}_2^t \cdot \rightarrow \qquad (8)$$

The variations of the concentrations of the secondary and tertiary radicals with time are described by eqn. (9) and (10):

$$d[RO_2^s \cdot]/dt = x\phi I_a - k_{ss}[RO_2^s \cdot]^2 - k_{st}[RO_2^s \cdot][RO_2^t \cdot]$$
(9)

$$d[\mathbf{RO}_2^t \bullet]/dt = y\phi I_a - k_{tt} [\mathbf{RO}_2^t \bullet]^2 - k_{st} [\mathbf{RO}_2^s \cdot] [\mathbf{RO}_2^t \bullet], \qquad (10)$$

where x and y are the fractions of the total rate of initiation which give secondary and tertiary radicals respectively (x+y=1). The measured radical concentration is given by

$$[\operatorname{RO}_{2} \bullet]_{\operatorname{measured}} = [\operatorname{RO}_{2}^{s} \bullet] + [\operatorname{RO}_{2}^{t} \bullet].$$
(11)

The values of the constants in eqn (9) and (10) which gave the best agreement between the experimental and predicted results were calculated with a computer using a standard numerical integration technique. Fig. 6 shows the computed variations with time of [RO⁵₂·] and [RO⁵₂·] in 2-methylpentane at -40° C, during and after a period of photolysis (cf. fig. 3). Preliminary results obtained by this method give values for k_{ss} , k_{st} and k_{tt} of 1.1×10^5 , 2.3×10^4 and 2.2×10^2 1 mol.⁻¹ s⁻¹ respectively. The values of k_{ss} and k_{tt} are reasonably consistent with those obtained by the methods described earlier. Cross-termination rate constants can also be obtained from rotating-sector studies ¹⁵ of the co-oxidation of two compounds. However this method, unlike that described above, requires that k_{ss} and k_{tt} be measured independently before k_{st} is determined.



FIG. 5.—Arrhenius plots of the second-order rate constants for the decay of t-alkylperoxy radicals in 0.5% solutions of di-t-butyl peroxide in oxygen-saturated 2-methylpentane and 2,2,3-trimethylbutane.



FIG. 6.—Computed concentrations of secondary and tertiary peroxy radicals in 2-methylpentane at -40° C, during and after a period of photolysis.

It was expected that 2,2,3-trimethylbutane, which has no secondary C—H bonds, would form tertiary radicals exclusively and thus give a radical build-up consistent with the simplified eqn (12). In fact g.l.c. analysis

$$d[\operatorname{RO}_{2}^{t} \bullet]/dt = \phi I_{a} - k_{tt} [\operatorname{RO}_{2}^{t} \bullet]^{2}$$
(12)

showed that the combined attack of radicals on fifteen primary C—H bonds was significant relative to the attack on the tertiary bond and the build-up resembled that in 2-methylpentane with primary radicals taking the place of secondary ones.

DISCUSSION

The decay of alkylperoxy radicals as observed by e.s.r. has been reported variously as being of first, second and intermediate order. Ingold and Morton⁶ observed

the decay of t-butylperoxy radicals to be first order; Maguire and Pink⁸ found that the decay kinetics of peroxy radicals varied between first and second order depending on the experimental conditions, and Thomas and Ingold⁷ obtained second-order decays with various radicals. In the present work, tertiary alkylperoxy radicals derived from 2-methylpentane and 2,2,3-trimethylbutane decayed with good secondorder kinetics to give non-radical products over the temperature ranges -60 to 0°C and -30 to +20°C respectively. The observed second-order decay is in accord with the occurrence of a bimolecular termination reaction.

Rate constants for the self-reactions of peroxy radicals have been measured for many olefinic and aromatic compounds^{2, 3} by the rotating-sector technique. This method is not readily applicable to alkanes, however, owing to the short chain lengths associated with the oxidation of these compounds, and except for isomeric butylperoxy radicals,¹⁶ there have been relatively few determinations of the termination rate constants of alkylperoxy radicals. Rate constants obtained by the rotating-sector technique and other methods are listed in table 3 together with values obtained by extrapolating our results. In those cases where comparisons can be made there is good agreement between the present values for the rate parameters and those obtained elsewhere.

The values obtained for the termination rate constant of tertiary peroxy radicals in the present work may be greater than the actual rate constant k_{tt} because there is a route whereby tertiary radicals may be converted to the more reactive secondary radicals. Recent studies ^{5, 20-24} have shown that in addition to the termination reaction (13), tertiary peroxy radicals also undergo the non-terminating reaction (14). The alkoxy radicals formed in reaction (14) may then abstract hydrogen atoms from alkane molecules

$$2RO_2^t \bullet \to R^tOOR^t + O_2 \tag{13}$$

$$2RO_2^t \bullet \rightarrow 2RO^t \bullet + O_2 \tag{14}$$

to give both secondary and tertiary radicals which combine rapidly with oxygen (reactions (15) and (16)). (The alternative conversion, $RO_2^t \rightarrow RO_2^{p}$, is neglected but the argument applies equally to both cases.) Since k_{st} is greater than k_{tt} , the

$$\mathrm{RO}^{\mathsf{t}} \cdot + \mathrm{RH} \rightarrow \mathrm{ROH} + \begin{cases} \mathrm{R}^{\mathsf{s}} \cdot & (15a) \\ \\ \mathrm{R}^{\mathsf{t}} \cdot & (15b) \end{cases}$$

$$\begin{array}{c}
\mathbf{R}^{\mathbf{s}} \bullet \\
\mathbf{R}^{\mathbf{t}} \bullet
\end{array} + \mathbf{O}_{2} \rightarrow
\begin{cases}
\mathbf{R} \mathbf{O}_{2}^{\mathbf{s}} \bullet \\
\mathbf{R} \mathbf{O}_{2}^{\mathbf{t}} \bullet
\end{cases}$$
(16)

rate constants obtained from plots of $[RO_2 \cdot]^{-1}$ against time (fig. 4) are greater than k_{tt} by an amount which is dependent on the extent of the conversion. The importance of this conversion depends on (a) the relative rates of reactions (13) and (14) and (b) the relative rates of reactions (15a) and (15b). Using current estimates ^{5, 7, 21, 22} of these ratios we conclude that at the temperatures used in our work the measured values of the termination rate constant are unlikely to be greater than twice the actual value of k_{tt} .

Secondary alkylperoxy radicals may terminate ²⁵ by either reaction (17) or (18):

$$2R_2CHO_2 \rightarrow R_2CHOOCHR_2 + O_2 \tag{17}$$

$$2R_2CHO_2 \rightarrow R_2C = O + R_2CHOH + O_2.$$
(18)

Since the nature of the alkyl group is not expected to have a large effect on the rate of reaction (17) the observed difference between the reactivities of the tertiary and secondary radicals is likely to be due to the predominant occurrence of reaction (18) in the latter case. Therefore the Arrhenius parameters measured for the tertiary peroxy radicals are those associated with reaction (13) while those for the secondary radicals are associated with reaction (18).

TABLE 3.—SECOND-ORDER RATE CONSTANTS FOR THE TERMINATION REACTIONS OF ALKYLPEROXY RADICALS

peroxy radical	k (1 mol ⁻¹ s ⁻¹)	temp. (°C)	solvent	E_a (kcal mol ⁻¹)	$A(l. mol^{-1} s^{-1})$	expt. method	ref.
n-butyl n-butyl neopentyl	$\begin{array}{c} 4 \times 10^{7} \\ \sim 3 \times 10^{7} \\ > 4 \times 10^{8} \end{array}$	30 7 20	α-methylstyrene methanol neopentane			RS ESR ESR	16 7 present work
s-butyl cyclohexyl cyclohexyl s-heptyl s-heptyl	$\begin{array}{c} 1.5 \times 10^{6} \\ 2.0 \times 10^{6} \\ 1.6 \times 10^{6} \\ 2.2 \times 10^{6} \\ 2.4 \times 10^{6} \end{array}$	30 30 30 25 30	tetralin tetralin cyclohexane heptane heptane	~0 1.9	107.7	RS RS PR PR ESR	16 16 17 18 present work
t-butyl t-butyl 2-methylpentyl-2 2,2,3-trimethylbutyl-3	$\begin{array}{c} 2.8 \times 10^{3} \\ 5.2 \times 10^{4} \\ 1.5 \times 10^{4} \\ 5.9 \times 10^{-3} \end{array}$	30 24 30 30	CF ₂ Cl ₂ 3-methylpentane 2-methylpentane 2,2,3-trimethylbutane	8.7 8.4 9.3 7.5	109-7 1012-1 1011-1 109-2	ESR ESR ESR ESR}	19 8 present work

ESR, [RO2-] measured by electron spin resonance; RS, rotating sector; PR, pulse radiolysis.

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- ¹ L. Bateman, Quart. Rev., 1954, 8, 147.
- ² J. A. Howard and K. U. Ingold, Can. J. Chem., 1966, 44, 1119.
- ³ J. A. Howard and K. U. Ingold, Can. J. Chem., 1967, 45, 793.
- ⁴ M. Anbar and P. Neta, Int. J. Appl. Rad. Isotopes, 1965, 16, 227.
- ⁵ J. R. Thomas, J. Amer. Chem. Soc., 1965, 87, 3935.
- ⁶ K. U. Ingold and J. R. Morton, J. Amer. Chem. Soc., 1964, 86, 3400.
- ⁷ J. R. Thomas and K. U. Ingold, Adv. Chem. Series No. 75, Oxidation of Organic Compounds-1, p. 258.
- ⁸ W. J. Maguire and R. C. Pink, Trans. Faraday Soc., 1967, 63, 1097.
- ⁹ R. Shaw and A. F. Trotman-Dickenson, J. Chem. Soc., 1960, 3210.
- ¹⁰ T. Bercés and A. F. Trotman-Dickenson, J. Chem. Soc., 1961, 348.
- ¹¹ R. Shaw and J. C. J. Thynne, Trans. Faraday Soc., 1966, 62, 104.
- ¹² D. M. Brown and A. Fish, Proc. Roy. Soc. A, 1969, 308, 547.
- ¹³ J. E. Bennett, B. Mile and A. Thomas, 11th Symp. Int. Combustion, 1967, p. 853.
- ¹⁴ J. H. Raley, F. F. Rust and W. E. Vaughan, J, Amer. Chem. Soc., 1948, 70, 1336.
- ¹⁵ J. A. Howard, W. J. Schwalm and K. U. Ingold, Adv. Chem. Series. No. 75, Oxidation of Organic Compounds-1, p.6.
- ¹⁶ J. A. Howard and K. U. Ingold, J. Amer. Chem. Soc., 1968, 90, 1058.
- ¹⁷ R. L. McCarthy and A. MacLachlan, J. Chem. Phys., 1961, 35, 1625.
- ¹⁸ B. Smaller, J. R. Remko and E. C. Avery, J. Chem. Phys., 1968, 48, 5174.
- ¹⁹ K. Adamic, J. A. Howard and K. U. Ingold, Chem. Comm., 1969, 505.
- ²⁰ H. S. Blanchard, J. Amer. Chem. Soc., 1959, 81, 4548.
- ²¹ P. D. Bartlett and T. G. Traylor, J. Amer. Chem. Soc., 1963, 85, 2407.
- ²² R. Hiatt, J. Clipsham and T. Visser, Can. J. Chem., 1964, 42, 2754.
- ²³ T. G. Traylor and C. A. Russell, J. Amer. Chem. Soc., 1965, 87, 3698.
- ²⁴ J. R. Thomas, J. Amer. Chem. Soc., 1967, 89, 4872.
- ²⁵ G. A. Russell, J. Amer. Chem. Soc., 1957, 79, 3871.

APPENDIX

DETAILS OF THE g.l.c. ANALYSIS OF PHOTOLYZED SAMPLES

Photolyzed samples were analyzed by g.l.c. and the identities and concentrations of the products of photolysis determined. All the observed products retained the carbon skeleton of the parent alkane and thus the position of the functional group indicates the position of the initial attack on the alkane. The measured concentrations of the products were therefore used to calculate the relative rates of formation of primary, secondary and tertiary peroxy radicals which are given in the results section.

2-METHYLPENTANE.—The products produced by the photolysis of oxygen-saturated 2-methylpentane containing 0.5 % DTBP are listed in table 4, together with an indication of the position of attack which led to their formation. One peak in the analysis was thought to be di-2-methylpentyl peroxide but could not be positively identified as no authentic sample of this compound was available. The build-up of products was linear provided that the total amount of alkane that had reacted remained significantly less than the available oxygen $(1.5 \times 10^{-2} \text{ mol } 1.^{-1})$.

n-HEPTANE.—Analysis of n-heptane samples showed the products listed in table 5 to be present. The relative rates of attack at the 2-, 3- and 4-positions are 1.4, 1.05 and 1.0 respectively at 20° C.

Table 4.—Products formed by the photolysis of a 0.5 % solution of DTBP in oxygen-saturated 2-methylpentane for 30 min at $20^\circ \rm C$

product	position of initial attack on alkane	[product] × 104 (mol 11)
2-methylpent-1-ene	tertiary	2.5
2-methylpent-2-ene	tertiary	0.2
2-methylpentan-3-one	secondary	1.16
2-methylpentan-4-one 2-methylpentan-1-al	secondary primary	} 1.91
2-methylpentan-5-al	primary	0.14
2-methylpentan-1-ol	primary	0.12
2-methylpentan-2-ol	tertiary	6.6
2-methylpentan-3-ol	secondary	0.37
2-methylpentan-4-ol	secondary	1.68
2-methylpentan-5-ol	primary	0.07

TABLE 5.—PRODUCTS FORMED BY THE PHOTOLYSIS OF A 0.5 % SOLUTION OF DTBP IN OXYGEN-SATURATED n-HEPTANE FOR 30 min at 20°C

product	position of initial attack on alkane	[product]×104 (mol l1)
heptanal	primary	<0.1
heptan-2-one	secondary	3.5
heptan-3-one	secondary	2.6
heptan-4-one	secondary	1.06
heptan-1-ol	primary	< 0.1
heptan-2-ol	secondary	1.7
heptan-3-ol	secondary	1.3
heptan-4-ol	secondary	0.8