Studies by Electron Spin Resonance of the Reactions of Alkylperoxy Radicals

Part 2.—Equilibrium between Alkylperoxy Radicals and Tetroxide Molecules
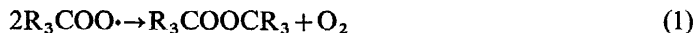
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Photolytically generated alkylperoxy radicals have been detected and their concentration measured by electron spin resonance spectroscopy. The rate of the irreversible decay of tertiary alkylperoxy radicals is negligible below $-115°C$. However, within the temperature range -160 to $-115°C$, a reduction in temperature causes the concentration of radicals to decrease to a new value which, once achieved, does not vary with time. The process is reversible. This behaviour is attributed to the existence of an equilibrium between two alkylperoxy radicals and a tetroxide molecule. Average values for the associated changes in entropy $\Delta S°$ and enthalpy $\Delta H°$ are -38 ± 4 cal deg^{-1} mol^{-1} and -8.9 ± 0.5 kcal mol^{-1} respectively. These thermodynamic constants have been combined with the rates of the irreversible decay of alkylperoxy radicals, measured at higher temperatures (-60 to $+20°C$) to provide a more complete description of the termination process.

We have described [1] the measurements of absolute rate constants for the self-termination reactions of alkylperoxy radicals ($RO_2\cdot$) by electron spin resonance (e.s.r.) spectroscopy. Studies [2-7] of systems in which t-butylperoxy and cumylperoxy radicals are formed have shown that tertiary peroxy radicals undergo both terminating and non-terminating interactions (reactions (1) and (2)). An additional termination process [8-10] is possible for primary and secondary peroxy radicals (reaction (3)). Kinetic,[11] isotopic [4] and product [8, 9] studies of autoxidation suggest that all these reactions proceed through a tetroxide intermediate (RO_4R) which may be a transition state or a molecule with an appreciable lifetime:
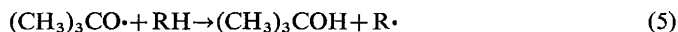
$$2R_3COO\cdot \rightarrow R_3COOCR_3 + O_2 \tag{1}$$

$$2R_3COO\cdot \rightarrow 2R_3CO\cdot + O_2 \tag{2}$$

$$2R_2CHOO\cdot \rightarrow R_2C=O + R_2CHOH + O_2 \tag{3}$$

Di-t-butyl tetroxide can be prepared [12, 13] below $-80°C$ and, in methylene chloride, it is in equilibrium [14] with t-butylperoxy radicals at temperatures in the range -110 to $-85°C$. We have reported [15] preliminary results which show that such an equilibrium is a general phenomenon for t-alkylperoxy radicals. Our results are in good agreement with those obtained by Adamic, Howard and Ingold.[16]

This work has now been extended and values for the changes in enthalpy and entropy associated with this equilibrium have been calculated from the variation of the equilibrium constant with temperature. These thermodynamic constants have been combined with the kinetic results obtained at higher temperatures [1] to provide a more complete description of the termination reactions of alkylperoxy radicals.

EXPERIMENTAL

Alkylperoxy radicals were produced by the photolysis of 5 % solutions of di-t-butyl peroxide (DTBP) in oxygen-saturated alkanes (reactions (4) to (6)).

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO\cdot \qquad (4)$$

$$(CH_3)_3CO\cdot + RH \rightarrow (CH_3)_3COH + R\cdot \qquad (5)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (6)$$

The photolysis was carried out in the cavity of the spectrometer and measurements of the dependence of the concentration of radicals on temperature were made after the cessation of photolysis. The apparatus and experimental procedures employed were identical with those described previously.[1]

RESULTS

EQUILIBRIUM BETWEEN ALKYLPEROXY RADICALS AND TETROXIDE MOLECULES

TERTIARY ALKYLPEROXY RADICALS

The rate of attack of t-butoxy radicals on an alkane [17] (reaction (5)) depends on the strength of the C—H bond broken and consequently increases in the order primary < secondary < tertiary. Thus, photolysis of a solution of DTBP in a branched alkane yielded tertiary radicals more readily than primary and secondary radicals. Also, tertiary peroxy radicals terminate at a much slower rate than the other peroxy radicals,[1] so that shortly after the end of photolysis only tertiary radicals remained.

Following photolysis at −80 to −50°C, the samples were cooled to below −115°C, at which temperature the rate of the irreversible decay of the tertiary peroxy radicals was negligible. However, a reduction in temperature within the range −160 to −115°C caused the radical concentration to decrease rapidly to a new value which, once attained, showed no variation with time. In contrast to the irreversible decay of radicals observed at higher temperatures, this process was completely reversible within this temperature range. The variations of radical concentration with temperature for tertiary peroxy radicals derived from 2-methylbutane, 2-methyl-pentane, 3-methylpentane, 2,3-dimethylbutane, 2,2,3-trimethylbutane, and cumene are shown in fig. 1. and 2. For all the compounds except 2,2,3-trimethylbutane, the concentration of radicals appropriate to each temperature was achieved in the time taken (*ca.* 2 min) for the sample to attain that temperature.

A reduction in temperature caused the alkane to contract which in the absence of any other effect would lead to a small increase in the radical concentration. The observed decrease in radical concentration with temperature was therefore slightly less than the true decrease. No correction was made for this effect as the relevant coefficients β of expansion were not available. However, values of β measured at 20°C indicate that the volume contraction over the temperature range −160 to −100°C was only *ca.* 6 %.

The reversible variation of the concentration of tertiary alkylperoxy radicals with temperature indicates that there is a temperature-dependent equilibrium between the radicals and a non-radical product or products. An equilibrium which involves the combination of t-butoxy radicals and peroxy radicals (reaction (7))

$$(CH_3)_3CO\cdot + RO_2\cdot \rightarrow (CH_3)_3CO_3R \qquad (7)$$

cannot explain the results since t-butoxy radicals produced by photolysis at −115°C are rapidly converted to peroxy radicals (reactions (4) to (6)). Also, any reaction
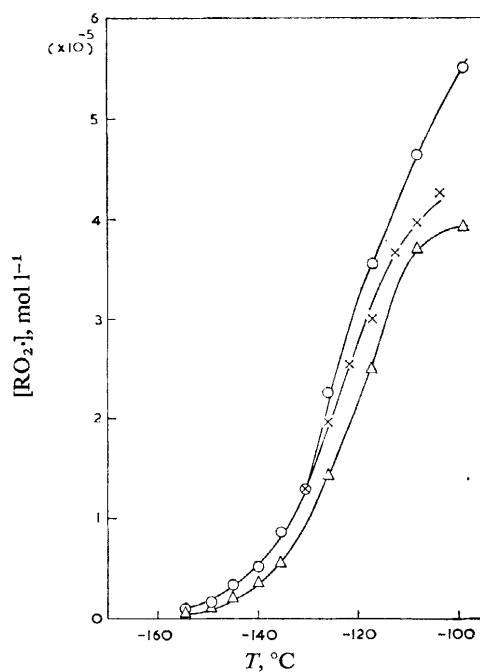
FIG. 1.—Variation of $[RO_2\cdot]$ with temperature for tertiary alkylperoxy radicals derived from: (○) 2,3-dimethylbutane; (×) 2,2,3-trimethylbutane; (△) 2-methylpentane.
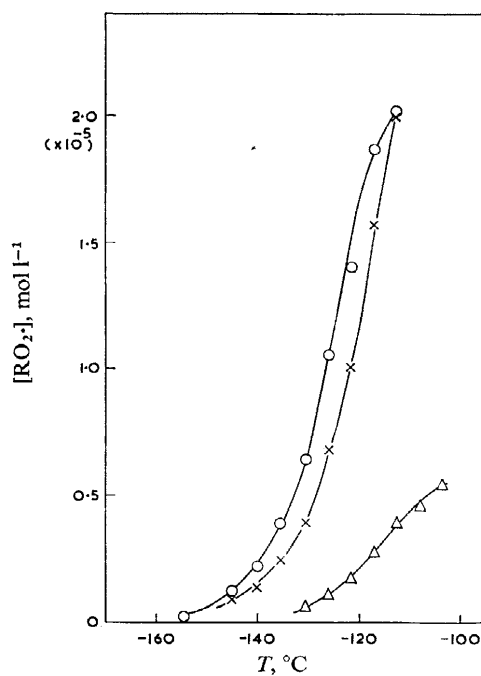

FIG. 2.—Variation of $[RO_2\cdot]$ with temperature for tertiary peroxy radicals derived from: (○) 3-methylpentane; (×) 2-methylbutane; (△) cumene.

involving the making and breaking of several bonds is considered unlikely on the grounds that it would not be rapidly reversible at $-160°C$. The results are attributed therefore to an equilibrium between two peroxy radicals and a tetroxide molecule, a process which involves the formation or scission of only one bond:

$$2RO_2 \cdot \rightleftharpoons RO_4R. \tag{8}$$

SECONDARY ALKYLPEROXY RADICALS

The corresponding variation of $[RO_2 \cdot]$ with temperature for secondary alkyl-peroxy radicals derived from n-alkanes was difficult to observe because (a) the initial concentration of radicals was small owing to the high rate of termination; (b) the n-alkanes formed opaque solids rather than transparent glasses and therefore could not be photolyzed at temperatures below their melting points; (c) the radicals decayed irreversibly at lower temperatures than did tertiary radicals. In a 5 % solution of DTBP in oxygen-saturated n-hexane the radicals produced by photolysis at $-100°C$ disappeared completely on cooling to $-160°C$. When the solution was warmed to $-120°C$ with the lamp off a small short-lived radical spectrum was detected. This suggests that tetroxides are formed with secondary peroxy radicals but that the irreversible decay rapidly reduces the radical concentration to undetectable levels.
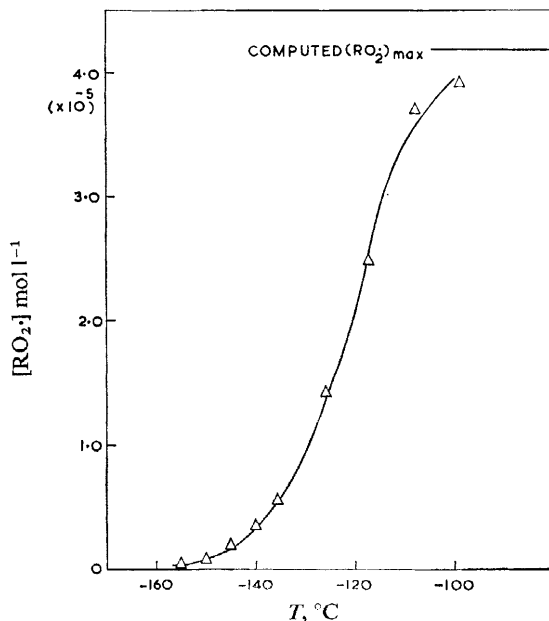

FIG. 3.—Variation of $[RO_2 \cdot]$ with temperature in 2-methylpentane: $\triangle$, experimental points; full line, computed curve.

CALCULATION OF THE ENTHALPY AND ENTROPY CHANGES ASSOCIATED WITH THE TETROXIDE EQUILIBRIUM

The variation of the equilibrium constant K with temperature T can be described by an integrated form of the van't Hoff isochore (eqn. (10)),

$$K = [RO_4R]/[RO_2 \cdot]^2, \tag{9}$$

$$\ln K = \Delta S°/R - \Delta H°/RT \tag{10}$$

where $\Delta S°$ and $\Delta H°$ are changes in the standard entropy and enthalpy.

Eqn. (9) and (10) may be combined to give

$$\ln[RO_4R] - 2\ln[RO_2\cdot] = \Delta S^\circ/R - \Delta H^\circ/RT. \qquad (11)$$

As no irreversible decay occurs at temperatures below -115°C the concentrations of tetroxide molecules and peroxy radicals are related by

$$2[RO_4R] + [RO_2\cdot] = [RO_2\cdot]_{max}, \qquad (12)$$

where $[RO_2\cdot]_{max}$ is the radical concentration at complete dissociation. Combination of eqn. (11) and (12) gives

$$\ln([RO_2\cdot]_{max} - [RO_2\cdot]) - 2\ln[RO_2\cdot] - \ln 2 = \Delta S^\circ/R - \Delta H^\circ/RT. \qquad (13)$$

The value of $[RO_2\cdot]_{max}$ could not be determined experimentally since at temperatures where dissociation of the tetroxide was nearly complete, the irreversible decay of the peroxy radicals was appreciable. Thus, the values of $[RO_2\cdot]_{max}$, ΔH° and ΔS° in eqn. (13) which gave the best fit between experimental and predicted curves for the variation of $[RO_2\cdot]$ with temperature (fig. 3) were calculated by computer. The values of the equilibrium constant K at -120°C are given in table 1 together with the corresponding values of ΔH° and ΔS°. By extrapolating the results obtained with 2-methylpentane the values of the ratio $(2[RO_4R]/[RO_2\cdot]_{max})$ at -100, 0 and 100°C were calculated to be 5.5×10^{-2}, 3.3×10^{-6} and 3.6×10^{-8} respectively.

DISCUSSION

EQUILIBRIUM BETWEEN ALKYLPEROXY RADICALS AND TETROXIDE MOLECULES

The e.s.r. spectra of different alkylperoxy radicals are almost identical, indicating that the free electron occupies an orbital which is located mainly in the O—O region and is unaffected by the alkyl group. The fact that ΔH° and ΔS° (table 1) show little dependence on the nature of the alkyl group is consistent with this observation and suggests that the bond formed in the tetroxide molecule involves only the terminal oxygen atoms.

TABLE 1.—THERMODYNAMIC CONSTANTS FOR THE EQUILIBRIUM BETWEEN TERTIARY ALKYL-PEROXY RADICALS AND TETROXIDE MOLECULES

parent alkane	alkane m.p. (°C)	K (l mol^{-1}) at -120°C	ΔH° (kcal mol^{-1})	ΔS° (cal deg.$^{-1}$ mol^{-1})
2-methylbutane	-160	6.9×10^4	-8.9 ± 1.0	-36 ± 8
2-methylpentane	-154	1.5×10^4	-8.9 ± 0.7	-39 ± 6
3-methylpentane	-118	1.8×10^4	-9.7 ± 0.5	-44 ± 4
2,3-dimethylbutane	-128	1.9×10^4	-8.2 ± 0.5	-34 ± 4
2,2,3-trimethylbutane	-25	1.3×10^4	-8.7 ± 1.0	-38 ± 7
cumene	-96	3.2×10^5	-11.2 ± 0.9	-48 ± 7

The equilibrium concentration of most alkylperoxy radicals is achieved rapidly at temperatures close to, or below, the melting point of the solvent, indicating that the radicals are either situated in pairs within a solvent cage or capable of migration through the solid matrix. An estimate of the diffusion coefficient D of the radicals can be obtained from the Stokes-Einstein equation

$$D = kT/6\pi r\eta \qquad (14)$$

where k is the Boltzmann constant, T the temperature, r the radius of the radical and η the viscosity of the solvent. The viscosities of a number of organic glasses have

been measured [18] and the variation of η with T for 2-methylpentane has been shown to obey eqn. (15)

$$\log \eta = 3.48 \times 10^3/T - 31.5 \qquad (15)$$

over the temperature range -193 to $-177°C$. When these results are extrapolated to $-155°C$, the lowest temperature used with 2-methylpentane, it is calculated that $\eta = 10^{-2}$ poise. Thus, if $r = 10^{-7}$ cm, the diffusion coefficient D of 2-methylpentyl-peroxy radicals at $-155°C$ is 8.6×10^{-7} cm^2 s^{-1}.

The concentration of peroxy radicals at $-155°C$ is 5×10^{-7} mol l^{-1} (fig. 1) and thus the average distance between adjacent radicals is 6.9×10^{-5} cm. The mean square displacement $\overline{X^2}$ of a species in a period of time t is given by eqn. (16),

$$\overline{X^2} = 2Dt, \qquad (16)$$

and when $\sqrt{\overline{X^2}} = 6.9 \times 10^{-5}$ cm and $D = 8.6 \times 10^{-7}$ cm^2 s^{-1}, then $t = 2.8 \times 10^{-3}$ s. Thus, under the conditions least favourable for diffusion, the time taken for one radical to migrate to the site of another is at least three orders of magnitude less than that required to measure the concentration of radicals. Radical diffusion is sufficiently rapid, therefore, to ensure that the equilibrium is established well before the concentration of radicals is measured in systems such as 2-methylpentane. Peroxy radicals with large alkyl groups do not form tetroxide molecules at low temperatures and this is attributed to an inability of the bulky radicals to migrate freely.

The computed values of $\Delta H°$ (table 1) are higher than that (-6 kcal mol^{-1}) measured by Bartlett and Guaraldi [14] for the t-butylperoxy equilibrium but are in good agreement with the values of Adamic, Howard and Ingold.[16] Benson [19] has estimated the heats of formation of several polyperoxides (RO$_n$R, where $n = 2$, 3 or 4) using the principle of bond additivity and calculated from these the dissociation energies, $D(\text{Bu}^t\text{O}_2 - \text{O}_2\text{Bu}^t) = 4 \pm 12$ kcal mol^{-1}, and $D(\text{Bu}^t\text{O}_2 - \text{OBu}^t) = 20.5 \pm 6$ kcal mol^{-1}, together with similar values for other tetroxides and trioxides. These calculations indicate that dialkyl trioxides should be stable below $-20°C$ whilst dialkyl tetroxides would be stable only below $-170°C$. Consequently, Benson has suggested that the compound isolated by Milas and Djokić [12] at $-75°C$ from the reaction of ozone with potassium t-perbutoxide and identified as di-t-butyl tetroxide was, in fact, the trioxide. Our results cannot be explained by the formation of a trioxide molecule and we conclude therefore that tertiary alkyl tetroxides are stable at rather higher temperatures ($-110°C$) than that estimated by Benson ($-170°C$). Furthermore, as no irreversible decay of tetroxide molecules occurs at temperatures below $-110°C$, the enthalpy change associated with reaction (17) must be considerably larger than the value
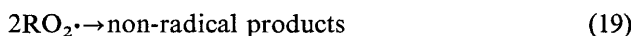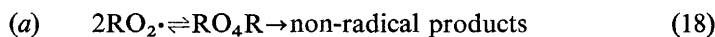
$$\text{RO}_4\text{R} \rightarrow 2\text{RO}\cdot + \text{O}_2 \qquad (17)$$

of -2 ± 10 kcal mol^{-1} estimated by Benson.[19]

Since the formation of a tetroxide molecule involves only the oxygen atoms of the alkylperoxy radicals it is expected that the associated change in enthalpy will be similar for primary, secondary and tertiary radicals.
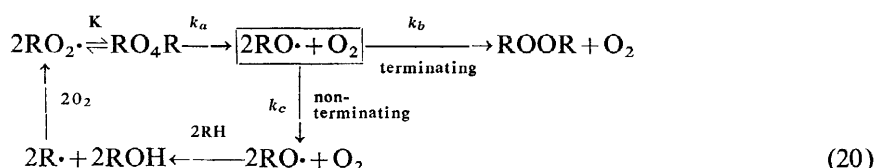
SELF-TERMINATION REACTIONS OF ALKYLPEROXY RADICALS

The preceding paper [1] was concerned with the measurement of absolute rate constants for the self-termination reactions of alkylperoxy radicals at temperatures in the range -60 to $+20°C$. The termination process may proceed either (a) via a tetroxide intermediate (reaction (18)), or (b) by a route which is independent of the tetroxide (reactions (8) and (19)).

(a) $\quad 2RO_2\cdot \rightleftharpoons RO_4R \rightarrow$ non-radical products $\qquad$ (18)

(b) $\quad 2RO_2\cdot \rightleftharpoons RO_4R$ $\qquad$ (8)

$\quad 2RO_2\cdot \rightarrow$ non-radical products $\qquad$ (19)

The present results do not allow these two mechanisms to be distinguished. However, it is reasonable to expect that the bimolecular reaction of two alkylperoxy radicals involves the formation of a tetroxide intermediate. On this basis the thermodynamic constants of the tetroxide equilibrium can be combined with the kinetic constants of the termination reaction to provide a more complete description of the termination process.

The terminating and non-terminating interactions of tertiary peroxy radicals can be represented by [20]

$$2RO_2\cdot \underset{K}{\rightleftharpoons} RO_4R \xrightarrow{k_a} \boxed{2RO\cdot + O_2} \xrightarrow[\text{terminating}]{k_b} ROOR + O_2$$

$$\begin{array}{c} \uparrow \\ 2O_2 \end{array} \qquad \begin{array}{c} k_c \end{array} \begin{array}{c} \text{non-} \\ \text{terminating} \end{array} \downarrow$$

$$2R\cdot + 2ROH \xleftarrow{\quad 2RH \quad} 2RO\cdot + O_2 \qquad (20)$$

where $\square$ denotes a solvent cage. The alkoxy radicals may also decompose unimolecularly by β-scission to yield radicals which can participate in other termination reactions. For the above mechanism the rate of termination is

$$-d[RO_2\cdot]/dt = fk_a[RO_4R], \qquad (21)$$

where $f = k_b/(k_b+k_c)$, the fraction of alkoxy radicals in the solvent cage that combine to form dialkylperoxide molecules. If the rate of the irreversible decay of tetroxide molecules is slow relative to the rate at which the equilibrium is established, then

$$-d[RO_2\cdot]/dt = f\,Kk_a[RO_2\cdot]^2. \qquad (22)$$

Thus, the measured rate constant k is equivalent to $f\,Kk_a$ and

$$\ln k = \ln f + \ln K + \ln k_a. \qquad (23)$$

Therefore

$$\ln A - \frac{E}{RT} = \ln f + \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} + \ln A_a - \frac{E_a}{RT}. \qquad (24)$$

There is some disagreement [2, 21, 22] as to whether or not the terminating and non-terminating reactions of tertiary peroxy radicals have the same activation energy. If a difference does exist, E_c is greater than E_b by only 2 to 5 kcal mol^{-1} so that the dependence of $\ln f$ on temperature is relatively small. Therefore, if the temperature-dependent and independent terms in eqn. (24) are separated and the logarithms changed to base 10,

$$E_a \simeq E - \Delta H^\circ \qquad (25)$$

and

$$\log A_a = \log A - \Delta S^\circ/2.303R - \log f, \qquad (26)$$

Then since $f \leqslant 1$ and, therefore, $\log f \leqslant 0$,

$$\log A_a \geqslant \log A - \Delta S^\circ/2.303R. \qquad (27)$$

It is difficult to estimate the magnitude of the term $\log f$, but if $f \simeq 0.2$, as measured by Thomas [2] for tertiary butylperoxy radicals, $\log f \simeq -0.7$. Values of E_a and A_a calculated from the present results [15] by eqn. (25) and (27) are given in table 2,

together with values reported by Adamic, Howard and Ingold [16] for the termination reactions of t-butylperoxy and cumylperoxy radicals. The two sets of results are in good agreement and indicate that the unimolecular decomposition of a tetroxide molecule is characterized by a high A factor (cf. peroxide decomposition [23, 24]; $A = 10^{15}$-10^{16} s^{-1}) and a significant activation energy.

TABLE 2.—ARRHENIUS PARAMETERS FOR THE IRREVERSIBLE UNIMOLECULAR DECOMPOSITION OF DI-t-ALKYL TETROXIDES

peroxy radical	change in enthalpy and entropy for the tetroxide equilibrium		measured Arrhenius parameters for the decay of $RO_2\cdot$ radicals		calculated Arrhenius parameters for RO_4R decay	
	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal deg.$^{-1}$ mol^{-1})	E (kcal mol^{-1})	A (l mol^{-1} s^{-1})	E_a (kcal mol^{-1})	A_a (s^{-1})
2-methylpentyl-2	-8.9 ± 0.7	-39 ± 6	9.3 ± 1.0	$10^{11.1\pm1.0}$	18.2 ± 1.7	$\leqslant10^{19.6\pm2.2}$
2,2,3-trimethylbutyl-3	-8.7 ± 1.0	-38 ± 7	7.5 ± 1.0	$10^{9.2\pm1.0}$	16.2 ± 2.0	$\leqslant10^{17.5\pm2.4}$
t-butyl (a)	-8.8 ± 0.4	-34 ± 1	8.7 ± 0.3	$10^{9.7}$	17.5	$10^{16.9}$
cumyl (a)	-9.2 ± 0.4	-32 ± 1	6.8 ± 0.3	$10^{10.1}$	16.0	$10^{16.8}$

(a) values from ref. (16)

Russell has proposed [8] that the termination reactions of primary and secondary peroxy radicals involve the formation of a cyclic transition state. The present evidence of tetroxide formation supports this mechanism. In addition,

$$(28)$$
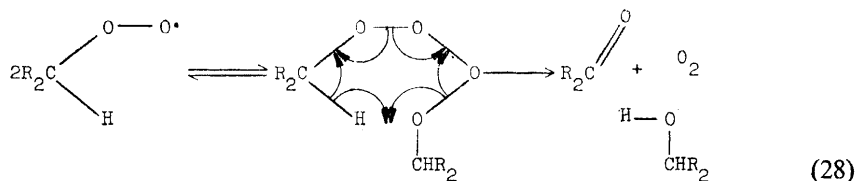
Howard and Ingold [10] have demonstrated that secondary alkylperoxy radicals decay less readily when the α-hydrogen is replaced by a deuterium. Thus, a further reaction is possible for primary and secondary radicals.

$$(29)$$
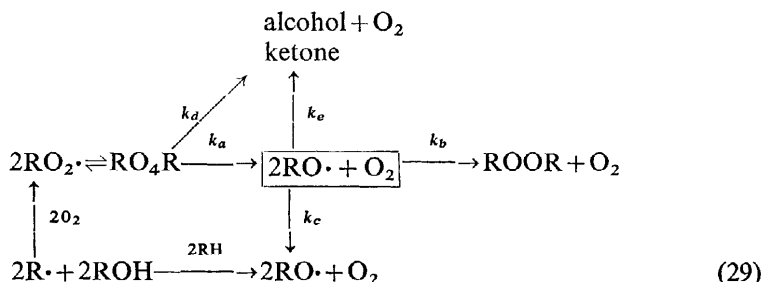
The measured rate constant for the self-termination reaction of secondary heptyl-peroxy radicals [1] is $k = 10^{7.7\pm1.0} \exp(-1.9\pm0.3)/RT$ l mol^{-1} s^{-1}. Thus, if the values of $\Delta H°$ for di-s-alkyl and di-t-alkyl tetroxides are similar it follows that the activation energy for the irreversible decomposition of the di-s-alkyl tetroxide is significantly less than those calculated for the di-t-alkyl tetroxides. The greater reactivity of the di-s-alkyl tetroxide is attributed to the predominance of reaction (29d). Eqn. (25) and (26) still apply to this mechanism but A_a an E_a are replaced by A_d and E_d, and the log f term is no longer relevant. When values for $\Delta H°$ and $\Delta S°$ obtained with tertiary alkylperoxy radicals are used, it is calculated that for secondary heptylperoxy radicals $A_d = 10^{16.2\pm2.5}$ s^{-1} and $E_d = 10.7\pm1.2$ kcal mol^{-1}.

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