Di-t-alkyl Tetroxides

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Summary Differences in the rate constants for the self-reactions of t-alkylperoxy-radicals are due to differences in the rate constants for irreversible decomposition of the initially formed tetroxides and not to differences in the equilibrium constants for tetroxide formation.

THE self-reaction of t-alkylperoxy-radicals in the liquid phase can be represented by the following reaction sequence,[1–5]

$$\mathrm{RO{\cdot}O{\cdot} + RO{\cdot}O{\cdot}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{RO{\cdot}O{\cdot}O{\cdot}OR} \qquad (1)$$

$$\mathrm{RO{\cdot}O{\cdot}O{\cdot}OR} \xrightarrow{k_2} [\mathrm{RO{\cdot}O_2{\cdot}OR}]_{\mathrm{cage}} \qquad (2)$$

$$[\mathrm{RO{\cdot}O_2{\cdot}OR}]_{\mathrm{cage}} \xrightarrow{k_3} \mathrm{RO{\cdot}OR + O_2} \qquad (3)$$

$$[\mathrm{RO{\cdot}O_2{\cdot}OR}]_{\mathrm{cage}} \xrightarrow{k_4} \mathrm{RO{\bullet} + O_2 + {\bullet}OR} \qquad (4)$$

Bartlett and Guaraldi[6] have shown that di-t-butyl tetroxide is stable at temperatures below about $-80°$ and have used e.s.r. spectroscopy to measure both the equilibrium constant K_1 $(=k_{-1}/k_1)$ and, at temperatures above $-80°$, the rate constant for irreversible tetroxide decomposition, k_2. Other t-alkyl tetroxides have also been prepared.[7,8]

In the presence of a t-alkyl hydroperoxide the measured rate constant for chain termination ($2k_t$) in the oxidation of a hydrocarbon corresponds to $2k_2k_3/K_1(k_3 + k_4)$ because the alkoxy-radicals from reaction (4) are converted to peroxy-radicals in reaction (5).[5]

$$\mathrm{RO{\bullet} + RO{\cdot}OH \rightarrow ROH + RO{\cdot}O{\bullet}} \qquad (5)$$

At 30°, $2k_t$ is *ca.* $1 \times 10^3\,\mathrm{M}^{-1}\mathrm{sec.}^{-1}$ for $\mathrm{R = Bu^t}$, *ca.* $7 \times 10^3\,\mathrm{M}^{-1}\mathrm{sec.}^{-1}$ for $\mathrm{R = PhCMe_2}$, and $\sim 6 \times 10^4\,\mathrm{M}^{-1}\mathrm{sec.}^{-1}$ for $\mathrm{R = Ph_2MeC}$.[5,9] This range is too large to be accounted for by any variation in the ratio of alkoxy-radical combination in the cage to diffusion from the cage, *i.e.* in $k_3/(k_3 + k_4)$. We report some results obtained using Bartlett and Guaraldi's general procedure which clearly indicate that our differences in chain termination rate constants for different t-alkylperoxy-radicals are due to differences in k_2 and not to differences in K_1.

Peroxy-radicals were most satisfactorily prepared by the

Activation parameters for di-t-alkyl textroxides (RO_4R)

	K_1		k_{esr}		k_2		$\log_{10}2k_t$[c]
R	ΔH_1[a]	ΔS_1[b]	E_{esr}[a]	$\log_{10} A_{esr}$[c]	E_2[a]	$\log_{10} A_2$[c]	(at 30°)[5,9]
Bu^t [d]	$8{\cdot}8 \pm 0{\cdot}4$	34 ± 1	$8{\cdot}7 \pm 0{\cdot}3$	9·7	17·5	16·6	3·1
Bu^t [e]	$8{\cdot}0 \pm 0{\cdot}2$	31 ± 1	$5{\cdot}1 \pm 0{\cdot}2$	5·5			
Bu^t [f]	$8{\cdot}4 \pm 0{\cdot}4$	30					
Me_2PhC[d]	$9{\cdot}2 \pm 0{\cdot}4$	32 ± 1	$7{\cdot}3 \pm 0{\cdot}3$	10·7	16·5	17·1	3·8
Me_2PhC[e]	$10{\cdot}6 \pm 0{\cdot}8$	—[g]					
1-Methylcyclohexyl[e]	$7{\cdot}0 \pm 0{\cdot}4$	35	$6{\cdot}1 \pm 0{\cdot}5$	7·7			3·0
Me_2Pr^iC[f]	$8{\cdot}6 \pm 0{\cdot}4$	33 ± 1					3·0
$Me_2(Me_3C{\cdot}CH_2){\cdot}C$	$7{\cdot}8 \pm 0{\cdot}5$	31	$4{\cdot}0 \pm 0{\cdot}2$	5·7			3·3

[a] Kcal./mole. The errors are standard deviations from the average value for a number of different experiments. [b] Gibbs/mole. [c] Log_{10} ($M^{-1}sec.^{-1}$). [d] From RN·NR in CF_2Cl_2. [e] From RO·OH in CF_2Cl_2. [f] From RO·OH in isopentane. [g] ΔS_1 was not measured because irreversible decay started to occur at a temperature below that at which the tetroxide was fully dissociated into peroxy-radicals. This phenomena also prevented the determination of both ΔH_1 and ΔS_1 for 1,1-diphenylethyl and cyclohexyl tetroxides although evidence for tetroxide formation was obtained in both cases.

photolysis of 10^{-2}M azoalkanes in oxygen-saturated CF_2Cl_2 (Freon 12, f.p. −155°) at liquid nitrogen temperatures.[7] Photolysis of hydroperoxides under similar conditions gave somewhat less reproducible results, particularly as regards the irreversible decomposition of tetroxide.

Our results are summarized in the Table.† The activation parameters ΔH_1 and ΔS_1 for the equilibrium constant were obtained by monitoring the peroxy-radical concentration over a range of temperatures below the temperature of irreversible decomposition. In order to evaluate ΔS_1 it was necessary that the tetroxide could be completely dissociated below this temperature. At higher temperatures the radical concentration decreases with time according to a second order rate law.[6] The measured rate constant, k_{esr},[6] is equal to $2k_2/K_1$ provided the $RO^\bullet$ radicals formed in reaction 4 have no effect on the $RO{\cdot}O^\bullet$ radical concentration. In the experiments using hydroperoxides as the radical sources the $RO{\cdot}$ radicals will be scavenged by RO·OH

$$RO^\bullet + RO{\cdot}O^\bullet \rightarrow RO{\cdot}O{\cdot}O{\cdot}OR \qquad (6)$$

(reaction 5) and $RO{\cdot}O{\cdot}$ (reaction 6).‡ If all the $RO^\bullet$ are scavenged by reaction (5) then $k_{esr} = 2(k_2/K_1)[k_3/(k_3 + k_4)]$ and if all are scavenged by reaction (6) then $k_{esr} = (2k_2/K_1)[1 + k_4/(k_3 + k_4)]$. The poor reproducibility of k_{esr} in the hydroperoxide experiments presumably reflects variations in the relative contributions of reactions 5 and 6 to $RO{\cdot}$ scavenging. The k_{esr} values in the azoalkane experiments were very reproducible and presumably correspond to $(2k_2/K_1)[1 + k_4/(k_3 + k_4)]$. For t-butylperoxy- and dimethylphenylmethylperoxy-radicals k_4/k_3 is about 6—7 at 30—60° in solvents of normal viscosity.[2,3,5,9,10] Although this ratio decreases slightly with temperature (because of the decreased rate of $RO^\bullet$ diffusion from the solvent cage) the value of $k_4/(k_3 + k_4)$ is probably reasonably close to unity in the temperature range in which k_{esr} was measured. The activation parameters for reaction (2) have therefore been calculated from the azoalkane data with the assumption the $k_{esr} = 4k_2/K_1$.

After finishing our work we learned that Bennett, Brown and Mile had also completed a similar study on the low temperature behaviour of peroxy-radicals prepared by yet another technique.[11] Our data are in excellent agreement with theirs considering the different methods employed to prepare the peroxy-radicals, the different solvent used and, in particular, the difficulties involved in the experiments.

The similarities in the values of ΔH_1 and ΔS_1 for the formation of di-t-alkyl tetroxides imply that differences in the behaviour of t-alkylperoxy-radicals in the termination of oxidation chains ($2k_t$) are due chiefly to differences in the rate constants for irreversible tetroxide decomposition (k_2). In contrast to earlier conclusions,[7] the values of the pre-exponential factors in the Arrhenius equation for reaction 2 are such as to indicate that only one bond in the tetroxide is cleaved in the rate determining step,

$$RO{\cdot}O{\cdot}O{\cdot}OR \rightarrow RO^\bullet + {}^\bullet O{\cdot}O{\cdot}OR \qquad (2a)$$

The A factors for simple 1-bond fission are expected[12] to be in the range 10^{15}—10^{17} sec.$^{-1}$, lower values obtaining if two O–O bonds are cleaved at the same time. Our own values of $10^{16{\cdot}6}$ and $10^{17{\cdot}1}$ sec.$^{-1}$ and Bennett *et al.*'s[11] value of $10^{17{\cdot}5}$ imply that reaction (2a) is rate determining. Further support for one-bond scission comes from Fessenden's[13] identification of the radical $CF_3O{\cdot}O{\cdot}O^\bullet$.

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† Peroxy-radical concentrations were determined by double integration of the first derivative e.s.r. signal at each temperature since the line width continually decreases as the temperature is lowered (*cf.* J. R. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 2064).

‡ β-Scission of the alkoxy-radicals should be relatively unimportant at the low temperatures of these experiments.

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