

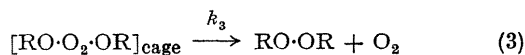
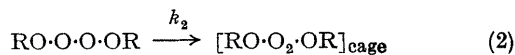
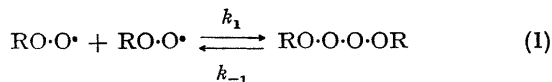
Di-t-alkyl Tetroxides

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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.

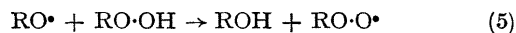
THE self-reaction of t-alkylperoxy-radicals in the liquid phase can be represented by the following reaction sequence,¹⁻⁵



Bartlett and Guaraldi⁶ 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



At 30° , $2k_t$ is *ca.* $1 \times 10^3 \text{M}^{-1}\text{sec}^{-1}$ for $\text{R} = \text{Bu}^t$, *ca.* $7 \times 10^3 \text{M}^{-1}\text{sec}^{-1}$ for $\text{R} = \text{PhCMe}_2$, and $\sim 6 \times 10^4 \text{M}^{-1}\text{sec}^{-1}$ for $\text{R} = \text{Ph}_2\text{MeC}$.^{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

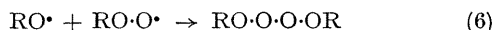
Activation parameters for di-t-alkyl tetroxides (RO₄R)

R	ΔH_1^a	K_1	ΔS_1^b	E_{esr}^a	k_{esr}	$\log_{10} A_{\text{esr}}^c$	E_2^a	k_2	$\log_{10} A_2^c$	$\log_{10} 2k_4^c$ (at 30°) ^{d,9}
Bu ^t ^d	8.8 ± 0.4	34 ± 1	34 ± 1	8.7 ± 0.3		9.7	17.5		16.6	3.1
Bu ^t ^e	8.0 ± 0.2	31 ± 1	31 ± 1	5.1 ± 0.2		5.5				
Bu ^t ^f	8.4 ± 0.4	30								
Me ₂ PhC ^d	9.2 ± 0.4	32 ± 1		7.3 ± 0.3		10.7	16.5		17.1	3.8
Me ₂ PhC ^e	10.6 ± 0.8	— ^g								
1-Methylcyclohexyl ^e	7.0 ± 0.4	35		6.1 ± 0.5		7.7				3.0
Me ₂ Pr ¹ C ^f	8.6 ± 0.4	33 ± 1								3.0
Me ₂ (Me ₃ C·CH ₂)·C	7.8 ± 0.5	31		4.0 ± 0.2		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 Log₁₀ (M⁻¹sec.⁻¹). ^d From RN-NR in CF₂Cl₂. ^e From RO·OH in CF₂Cl₂. ^f From RO·OH in isopentane. ^g ΔS₁ 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 ΔH₁ and ΔS₁ for 1,1-diphenylethyl and cyclohexyl tetroxides although evidence for tetroxide formation was obtained in both cases.

photolysis of 10⁻²M azoalkanes in oxygen-saturated CF₂Cl₂ (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 ΔH₁ and ΔS₁ 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 ΔS₁ 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· radicals formed in reaction 4 have no effect on the RO·O· radical concentration. In the experiments using hydroperoxides as the radical sources the RO· radicals will be scavenged by RO·OH

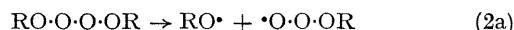


(reaction 5) and RO·O· (reaction 6).[‡] If all the RO· are scavenged by reaction (5) then $k_{\text{esr}} = 2(k_2/K_1)[k_3/(k_3 + k_4)]$ and if all are scavenged by reaction (6) then $k_{\text{esr}} = (2k_2/K_1)[1 + k_4/(k_3 + k_4)]$. The poor reproducibility of k_{esr} in the hydroperoxide experiments presumably reflects variations in the relative contributions of reactions 5 and 6 to RO· 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· 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 $k_{\text{esr}} = 4k_2/K_1$.

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 ΔH₁ and ΔS₁ for the formation of di-t-alkyl tetroxides imply that differences in the behaviour of t-alkylperoxy-radicals in the termination of oxidation chains ($2k_4$) 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,



The A factors for simple 1-bond fission are expected¹² to be in the range 10¹⁵–10¹⁷ sec.⁻¹, lower values obtaining if two O–O bonds are cleaved at the same time. Our own values of 10^{16.6} and 10^{17.1} sec.⁻¹ and Bennett *et al.*'s¹¹ value of 10^{17.5} imply that reaction (2a) is rate determining. Further support for one-bond scission comes from Fessenden's¹³ identification of the radical CF₃O·O·O·.

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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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