Synthesis of a Novel Cyclic Peroxalate, its Thermolysis and Photolysis†

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Summary The thermolysis and photolysis of the novel cyclic peroxalate (**1**) affords acetone and 3,3,6,6-tetramethyl-1,2-dioxan (**2**), and on the basis of kinetic and thermochemical studies it is shown that multiple bond fragmentation in (**1**) is inhibited due to conformational effects.

THE low thermal stability of acyclic peroxalates[1] encouraged us to investigate cyclic analogues as potential low temperature sources of oxygen diradicals.[2] We now report the preparation of 7,7,10,10-tetramethyl-1,2,5,6-tetroxecan-3,4-dione (**1**), the first cyclic peroxalate, and its chemical transformations during thermolysis and photolysis.

Treatment of a THF solution of 2,5-dihydroperoxy-2,5-dimethylhexane with oxalyl chloride in the presence of pyridine catalyst below 0 °C afforded a solid residue,‡ which on trituration with cold pentane and repeated recrystallization from hexane gave colourless needles. Osmometry in chloroform gave a molecular weight of 233 ± 2. Like the acyclic analogues,[1] the purity of (**1**) could not be assessed by iodometric titration due to ionic decomposition during the analysis. The i.r. spectrum in CCl_4 shows a split carbonyl band at 1812 and 1775 cm^{-1}, suggesting a transoid oxalate configuration, while the n.m.r. spectrum (100 MHz) in CCl_4 exhibits singlet methyl protons at 1·20 and 1·51 p.p.m., and doublet methylene protons at 1·58 and 2·02 p.p.m. (J 12·5 Hz), with relative intensities 3 : 3 : 1 : 1, respectively, suggesting a staggered conformation of the carbon skeleton.

The products of the thermolysis at 120 °C for 3 h and the photolysis at 350 nm for 20 h of a 0·20M solution of (**1**) in benzene were carbon dioxide, ethylene (trapped as 1,2-dibromoethane), acetone, and 3,3,6,6-tetramethyl-1,2-dioxan (**2**) (by i.r. and g.l.c.). Not even traces of 2,2-dimethyloxetan could be detected, although control experiments indicated that this oxetane is stable towards the photolysis and thermolysis conditions of (**1**). The product composition (quantitative g.l.c.) is summarized in Table 1. Furthermore, control experiments revealed that the 1,2-dioxan is completely stable under the conditions of photolysis and thermolysis of (**1**). However, on prolonged heating at 200 °C and prolonged irradiation at 310 nm the 1,2-dioxan is quantitatively converted into acetone and ethylene.

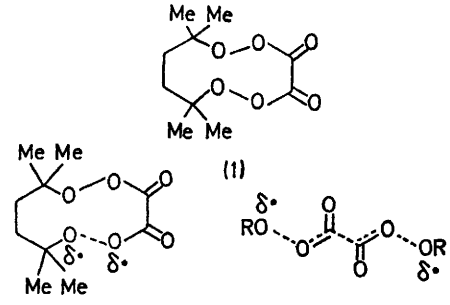
TABLE 1

Absolute yields of volatile products[a] *in the thermolysis and photolysis of* (**1**)

(**1**)	C_6H_6	(**2**)	+	Me_2CO
	Δ (120°)	18·6%		60·4%
	hν (350 nm)	18·4%		65·4%

[a] Approximately 10—13% by weight of non-volatile residue is formed in each case.

Since multiple bond cleavage has been demonstrated for di-t-butyl peroxalate (**3**),[1] see transition state (**3a**), and



(1a) (3a)

since on conformational grounds (**1**) is expected to suffer single bond cleavage, see transition state (**1a**), it was of interest to compare the thermal stability of (**1**) and (**3**) by measuring the heats of reaction and the activation parameters of their thermal decomposition.

The heats of reaction of (**1**) and (**3**) were determined by differential scanning calorimetry, employing a Perkin-Elmer DSC-1B apparatus.[3]§ The heats of decomposition were found to be $\Delta H = -99 \pm 2$ kcal mol^{-1} for (**1**) and $\Delta H = -57 \pm 4$ kcal mol^{-1} for (**3**). The non-isothermal activation parameters calculated from the thermograms is summarized in Table 2. As a check on the non-isothermal kinetic results, the activation parameters were determined by ordinary isothermal kinetics. For this purpose samples of 1·0—1·5M solutions of (**1**) in CCl_4 were heated under isothermal conditions and the disappearance of the 1812 cm^{-1} peroxalate carbonyl band was followed by i.r. The results are given in Table 2.

The kinetic data clearly demonstrate that the cyclic peroxalate is considerably more stable than the acyclic one. In fact, at 300 K we calculate that the half-life of (**1**) is about 3000 times larger than for (**3**). However, in view of the larger exothermicity (2-fold) of the cyclic peroxalate compared to the acyclic analogue, we would have expected that (**1**) should be thermally less stable than (**3**). Thus, conformational inhibition of multiple bond cleavage, *i.e.* transition state (**1a**) for the cyclic peroxalate, is an effective tool in stabilizing peroxides.

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‡ Utmost care in handling this residue is advocated! When 1 g of the triturated residue, dispersed on a fluted filter paper, was accidently allowed to dry, a violent explosion occurred shattering the funnel.

§ As a check on the procedure, the thermal decomposition of aspartic acid was studied and $\Delta H = 158 \pm 6$ cal g^{-1} was obtained, which is in good agreement with the published value of 158 cal g^{-1}.

TABLE 2

Activation parameters of the peroxalates

Method		Peroxalate (3)	Peroxalate (1)
Non-isothermal	$\Delta H^{\ddagger}$ (kcal mol^{-1})	22·6 ± 0·4	29·8 ± 0·6
	$\Delta S^{\ddagger}$ (Gibbs mol^{-1})	1·2 ± 1·0	8·9 ± 1·3
Isothermal	$\Delta H^{\ddagger}$ (kcal mol^{-1})	25·5[a]	31·2 ± 0·1
	$\Delta S^{\ddagger}$ (Gibbs mol^{-1})	5·1[a]	7·9 ± 9·1

[a] Taken from ref. 3.

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