

Peroxyesters of Alkoxy- and Aryloxy-alkanoic Acids

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THE preparation and thermolysis constants have recently been reported¹ of t-butylperoxy-esters of α -oxy- and α -thio-substituted alkanolic acids. We have examined t-butylperoxy-esters of α -, β -, and γ -oxyalkanoic acids. These peresters are new sources of alkoxyalkyl and aryloxyalkyl radicals, and some of them are of interest as polymerisation initiators.²

α -oxy-acids decompose by a different mechanism to those in which the ether oxygen is more remote. Bartlett⁴ has shown that other peresters with low entropy and enthalpy of activation decompose by a concerted homolysis in which a CO₂ molecule is expelled in the rate-determining step. Such a mechanism is facilitated when stabilisation of the radicals formed in the homolysis can contribute to a

TABLE

Thermal decomposition of peresters R·CO·O·O·CMe₃

R	$t_{1/2}$ at 60°C (min.)	ΔH^\ddagger (kcal./mole)	ΔS^\ddagger (cal./°C mole)
Me*	5×10^5	38	17
Ph·O·[CH ₂] ₃	9×10^4	33	9
Ph·O·[CH ₂] ₂	2×10^5	34	16
Ph·O·CH ₂	80	26	3
Ph·O·CHMe	4.5	22	-4
Ph·O·CMe ₂	0.8	20	-7
Me·O·CHMe·CH ₃	1×10^5	33	9
Me·O·CH ₂	7	24	1
Bu·O·CH ₂	4	22	-4

* Values from Ref. 3.

The relationship between the molecular structure of ether peroxycarboxylates and their activation parameters (see Table) suggests³ that peresters of

lowering of the overall enthalpy of activation. Recent studies of the e.s.r. spectra of R·CH·OR' radicals indicate that such radicals do show about

30% delocalisation of the unpaired electron on to oxygen.⁵ β - and γ -Oxy-substituted alkyl radicals are less likely to show such delocalisation and the corresponding peresters decompose at rates normal for unsubstituted t-butylperoxy n-alkanoates, by one-bond homolysis.

Peroxy-esters of α -alkoxyalkanoic acids appear to be very unstable in bulk, and often decompose

spontaneously within minutes of being isolated. Their precursor acid chlorides are thermally unstable, forming alkyl chloromethyl ethers above about 50°. Our attempts to relate the bulk instability of the peresters to the presence of chloromethyl ethers or their peroxidation products have not, however, been successful.

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¹ Ch. Rüdhardt, H. Böck, and I. Rüdhardt, *Angew. Chem. Internat. Edn.*, 1966, 5, 253.

² Brit. Pat. Appl. No. 3383/65, 1422/66.

³ The rates of thermal decomposition in solution have been measured by a thermal transient method (N. H. Ray, *J. Chem. Soc.*, 1960, 4023) and in some cases iodometrically, in benzene. Since the unstable, oily, peresters could not be satisfactorily purified, the possibility of induced decomposition cannot be excluded; but the disappearance of peroxidic oxygen showed little departure from first-order kinetics. The parameters have been calculated assuming unimolecular decomposition for the compounds listed.

⁴ P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, 1958, 80, 1398; P. F. Bartlett and D. M. Simons, *ibid.*, 1960, 82, 1753.

⁵ O. H. Griffith, *J. Chem. Phys.*, 1965, 42, 2651.