Mechanism of Hydrolysis of Esters by Superoxide

Alexander R. Forrester* and Vemishetti Purushotham

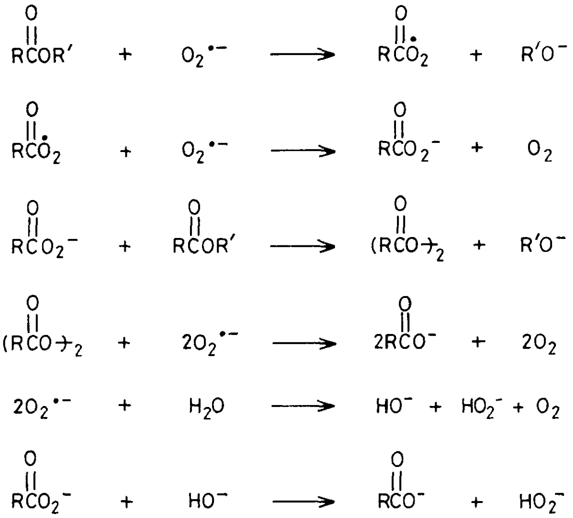
Chemistry Department, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland, U.K.

Experimental evidence is presented indicating that hydrolysis of an ester by superoxide in an aprotic solvent does not proceed *via* the corresponding acyl peroxide, although the peroxycarboxylate anion is involved.

Alkyl esters of carboxylic acids are hydrolysed by reaction with superoxide[1,2] in aprotic media–crown ethers to give, after work-up, the corresponding acid and alcohol. Reaction is thought[1—3] to proceed *via* the corresponding peroxide as indicated in equations (i)—(iv). We now present evidence to show that this sequence certainly does not occur with esters of *o*-phenylbenzoic acid and hence may not be general.

Treatment of ethyl *o*-phenylbenzoate with potassium superoxide (2.2 mol. equiv.) in benzene–18-crown-6 at room temperature for 24 h gave a good yield (88%) of *o*-phenylbenzoic acid. No acyl peroxide [*cf.* equation (iii)] was detected (t.l.c.) during the course of the reaction and when one molecular equivalent of superoxide was used about half (48%) of the ester was recovered. However, similar treatment of *o*-phenylbenzoyl peroxide (**1**) with potassium superoxide (2.2 mol. equiv.) gave a mixture of the benzocoumarin (**5**) (44%) and acid from (**3**) (52%). The former is a known[4] product of *o*-phenylbenzoyloxyl radicals (**2**). In the absence of superoxide the acyl peroxide (**1**) underwent decomposition to only a minor extent to give the benzocoumarin (**5**). The ratio (*ca.* 1 : 1) of benzocoumarin (**5**) to acid (**3**) strongly suggests that for this peroxide at least electron transfer from superoxide effects peroxy bond cleavage, (**1**) → (**2**) + (**3**). Hence cyclisation of (**2**) to give the cyclohexadienyl radical (**4**) must be fast relative to its reduction to (**3**) by electron transfer from superoxide.

Since no benzocoumarin (**5**) was formed on reaction of the ester with superoxide the peroxide cannot mediate in the hydrolysis of the ester. How then does hydrolysis of the ester proceed? Peroxy acids appear to react with superoxide to give



$$R\overset{O}{\overset{\|}{C}}OR' + O_2^{\bullet -} \longrightarrow R\overset{O}{\overset{\|\bullet}{C}}O_2 + R'O^- \quad \text{(i)}$$

$$R\overset{O}{\overset{\|\bullet}{C}}O_2 + O_2^{\bullet -} \longrightarrow R\overset{O}{\overset{\|}{C}}O_2^- + O_2 \quad \text{(ii)}$$

$$R\overset{O}{\overset{\|}{C}}O_2^- + R\overset{O}{\overset{\|}{C}}OR' \longrightarrow (R\overset{O}{\overset{\|}{C}}O\!-\!)_2 + R'O^- \quad \text{(iii)}$$

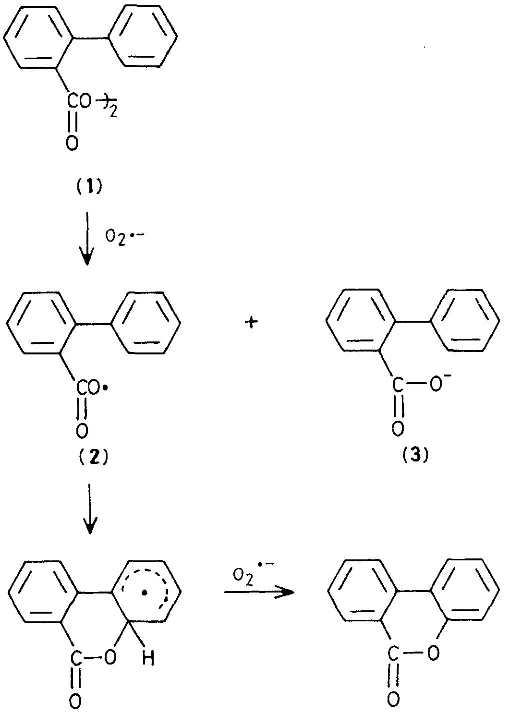
$$(R\overset{O}{\overset{\|}{C}}O\!-\!)_2 + 2O_2^{\bullet -} \longrightarrow 2R\overset{O}{\overset{\|}{C}}O^- + 2O_2 \quad \text{(iv)}$$

$$2O_2^{\bullet -} + H_2O \longrightarrow HO^- + HO_2^- + O_2 \quad \text{(v)}$$

$$R\overset{O}{\overset{\|}{C}}O_2^- + HO^- \longrightarrow R\overset{O}{\overset{\|}{C}}O^- + HO_2^- \quad \text{(vi)}$$

the parent acid. Thus *m*-chloroperoxybenzoic acid on treatment with superoxide (2.2 mol. equiv.) in benzene–18-crown-6 gives *m*-chlorobenzoic acid (95%) after aqueous work-up. However, when *m*-chloroperoxybenzoic acid is treated with an aqueous solution of superoxide the parent acid is again formed in high yield (90%). Therefore the superoxide is simply a source[1,2] of hydroxide ion [equation (v)] and the *m*-chloroperoxybenzoic acid is reduced to the acid during the aqueous work-up [equation (vi)] and not by reaction with superoxide in the aprotic solvent.[5]

Since acid chlorides are readily converted into acyl peroxides with superoxide[6] under the conditions that we employed for the ester reactions, the course of reaction of acid derivatives with superoxide depends on the rate of reaction (iii). If this is fast (as with acyl chlorides) then acyl peroxides ensue which may react further to give carboxylic acids if sufficient superoxide is present. With alkyl esters reaction (iii) is relatively slow and reductive hydrolysis to the carboxylate prevails [equation (vi)]. Interestingly, the anhydride of *o*-phenylbenzoic acid, which is more reactive than ethyl *o*-phenylbenzoate but less reactive than *o*-phenylbenzoyl chloride towards nucleophiles, reacted with superoxide (2.2 mol. equiv.) under the conditions previously described to give acid (**3**) (81%) and benzocoumarin (**5**) (16%). *o*-Phenylbenzoyl peroxide was detected (t.l.c.) as an intermediate in this reaction. The yield of (**5**) is a measure (25% corresponds to complete reaction) of the extent to which reaction proceeds *via* the peroxide.



We thank the S.E.R.C. for financial support.

Received, 20th August 1984; Com. 1191

References

1 E. Lee-Ruff, *Chem. Soc. Rev.*, 1977, **6**, 195.
2 A. A. Frimer, in 'The Chemistry of Peroxides,' ed. S. Patai, Wiley, New York, 1983, Ch. 14.
3 M. J. Gibian, D. T. Sawyer, T. Ungermann, R. Tangpoonpholvivat, and M. M. Morrison, *J. Am. Chem. Soc.*, 1979, **101**, 640; J. S. Filippo, L. J. Romano, C. Chern, and J. S. Valentine, *J. Org. Chem.*, 1976, **41**, 585.
4 F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, 1975, **25**, 1790.
5 R. Curci and J. O. Edwards, in 'Organic Peroxides,' Vol. 1, ed. D. Swern, Wiley, New York, 1970, Ch. 4.
6 R. A. Johnson, *Tetrahedron Lett.*, 1976, 331.