Tetrahedron Letters No. 5, pp 331 - 332, 1976. Pergamon Press. Printed in Great Britain.

SUPEROXIDE CHEMISTRY. A NEW, CONVENIENT SYNTHESIS OF DIACYL PEROXIDES

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(Received in USA 25 November 1975; received in UK for publication 18 December 1975)

The superoxide radical anion, $O_2^{\cdot-}$, reacts as a nucleophile with alkyl halides or sulfonate esters, giving dialkyl peroxides [1-3] and/or the alcohol[1,3-5] in synthetically useful quantities. The superoxide required for this reaction may be generated electrochemically[1,2] or may be made available in an organic reaction medium by solubilization of potassium superoxide (KO_2) with a crown ether.[3-7]

This report describes a new use for KO_2 in which diacyl peroxides are conveniently produced in the reaction of KO_2 with acyl chlorides according to equation 1. In contrast to the conditions

$$2\ R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Cl + 2\ KO_2 \longrightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + 2\ KCl + O_2 \qquad \text{(equation 1)}$$

used for dialkyl peroxide synthesis,[3] the present reaction proceeds readily without the use of a crown ether, even when benzene is used as the reaction medium. The following procedure is used for this synthesis.

Potassium superoxide (0.00535 mole) is weighed directly into a dry flask containing a magnetic stirring bar and is covered immediately with dry benzene (10-25 ml). The acyl chloride (0.0050 mole) is added. The pieces of KO_2 are carefully crushed and the resulting mixture is stirred vigorously. Bubbles of gas can be seen rising from the surfaces of the solid KO_2 and are presumed to be oxygen. The reaction usually is complete within 1 to 3 hours. The presence of peroxide can be detected by tlc as previously described.[3] The reaction is worked up by pouring into aqueous NaCl solution (30 ml) and then extraction with CH_2Cl_2 (3 x 20-30 ml). The combined extracts are dried ($MgSO_4$) and, following filtration, the solvent is removed under reduced pressure.[8] The residue may be recrystallized from methanol or CCl_4-methanol. In this way the results listed in Table I were obtained. Yields reported are based on the quantity of recrystallized product obtained.

It is advantageous to work up the reactions soon after it has been determined that the acyl chloride has been consumed. A reaction of benzoyl chloride with excess KO_2 was left standing overnight with the result that a greatly reduced yield of dibenzoyl peroxide (15%) was obtained. Instead, benzoic acid was isolated as the main reaction product (80%). Small amounts of carboxylic acids (see Table I) are isolated from all these reactions by acidification of the aqueous layer following extraction.

Table I. Synthesis of Diacyl Peroxides from the Reaction of Acyl Chlorides with KO_2.

R-C(=O)-Cl, R =	R-C(=O)-O-O-C(=O)-R, Yield (%)	M.P. (°)	Lit. M.P. (°)[a]	R-COOH, Yield (%)
C_6H_5	61	105-107	106-107	6
p-$CH_3OC_6H_4$-	62	125-127 dec.	126-128	b
p-ClC_6H_4-	69	139-142 dec.	140	8
o-ClC_6H_4-	57	100-103 dec.	95	5
o-$CH_3C_6H_4$-	53	52-53	52-54	5
$CH_3(CH_2)_{12}$-	74	63-64	63.9-64.4	b
$CH_3(CH_2)_{14}$-	50	68-71	70-72	b

[a]Literature melting points are from reference 10. [b]Not determined.

This new reaction provides an alternative method for the preparation of diacyl peroxides under anhydrous conditions. A previous anhydrous method gives excellent yields of diacyl peroxides but does require the use of anhydrous ether solutions of hydrogen peroxide.[9] A number of efficient syntheses of diacyl peroxides that require aqueous conditions also are available.[10]

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8. The reader is reminded of the potentially hazardous nature of lower molecular weight diacyl peroxides, such as diacetyl peroxide, and it is suggested that isolation of such compounds be approached with extreme caution.
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