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HETEROLYTIC ISOMERIZATION OF SOME ACYL-SULPHONYL PEROXIDES

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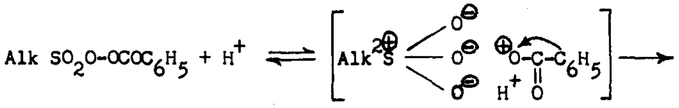
In the study of the thermal decomposition of new peroxides such as $AlkSO_2O\text{-}OCOC_6H_5$, heterolytic isomerization to the mixed anhydride of the alkane sulphonic acid and phenoxyformic acid was observed. Such a decomposition process for acyl-sulphonyl peroxides has not been noted until recently. The data obtained showed that the isomerization is catalysed by the alkanesulphonic acid formed by the homolytic decomposition of the peroxide, and does not depend on the solvent polarity. The phenomenon differs from the known heterolytic isomerization of 4-methoxy-4'-nitro-benzoyl peroxide which preceeds only in polar solvents.[1]

Decomposition of peroxide where Alk=CH_3-(I) and C_2H_5-(II) yielded 83%[*] of the mixed anhydride in benzene, 80% in isopropyl alcohol, and 45% in carbon tetrachloride.

The following scheme is suggested for formation of the mixed anhydride (V):



III

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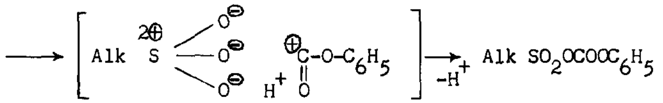
[*] Per mole of decomposed peroxide.

[1] J.E. Leffler, J.Amer.Chem.Soc. 72, 67 (1950).



IV V (1)

Initial proton addition results in a heterolytic degradation to give the sulphonic acid anion and the benzoyloxy-cation (III). The latter rearranges into the carbonium cation (IV) (rearrangement being facilitated by the availability of the electron-donating phenyl group). Mixed anhydride formation (V) then takes place by proton loss.

To verify this suggestion, the peroxide was decomposed in isopropyl alcohol in the presence of dry finely divided potash. In the solvent distillate 75% of acetone was found, in comparison to 17% in the absence of potash. Alternatively, when sulphonic acid is introduced into the peroxide solution in carbon tetrachloride, the reaction can be substantially affected. Thus, up to 65% of mixed anhydride was found as compared to 45% in the absence of the sulphonic acid. At the same time it was shown that aprotonic acids ($AlCl_3$, $SnCl_4$ and $SbCl_5$) in the amount of 5% M also favour heterolytic isomerization of the peroxides. Up to 85% of the mixed anhydride was isolated. The explanation of the activating effect of aprotonic acids lies in the ability of the latter to complete their valency shells by co-ordination with the sulphonic acid anion. In this case the benzoyloxy-cation is also formed.

In the presence of potash, sulphonic acids, and aprotonic acids a considerable acceleration of peroxide decomposition was observed.

The mixed anhydride of methane-sulphonic acid and phenoxyformic acid was separated by vacuum distillation of the reaction mixture resulting from the decomposition of peroxide (I) in benzene.

The α-naphthyl urethane, m.p. 133-133.5°, was obtained by reaction of the anhydride with α-naphthyl amine. A mixture with a sample of the urethane derived from α-naphthylisocyanate and phenol melted without depression. A similar anhydride was obtained from the silver salt of methane-sulphonic acid and phenylchloroformate. B.p. 144/4 mm Hg.

n_D^{20} - 1.5106; d_4^{20} - 1.3400. Calc. MR - 48.45; Found MR - 48.25.

For $C_8H_8O_5S$: Calc. % C-44.50, H - 3.70, S-14.80, M - 216. Found % C - 44.38, H - 3.79, S - 14.37, M - 214.5 - cryoscopically in benzene.

The mixed anhydrides proved to be active acylating agents of substances having labile hydrogen atoms.