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SULPHENATE IONS AS AMBIDENT NUCLEOPHILES

Donald R. Hogg* and Alexander Robertson
Department of Chemistry, University of Aberdeen,
Aberdeen AB9 2UE.

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Interest in the chemistry of sulphenic acids, RSOH, has been stimulated by their postulated intermediacy in reactions of penicillin derivatives[1] and by the facile rearrangement of their esters to sulphoxides.[2] Until recently only nucleophilic reactions of the sulphur atom had been reported[3] but O-silylation of the sulphenic acid generated by the thermal rearrangement of penicillin sulphoxide has now[4] been observed and prompts us to report on the ambident nucleophilicity of sulphenate anions.

The alkaline hydrolysis of bis(2-nitro-4-trifluoromethylphenyl) disulphide was used as a source[5] of sulphenate anions owing to the higher stability of the anions in this series and the convenience of using ^{19}F nmr for detection.

$$ArSSAr + 2OH^- = ArSO^- + ArS^- + H_2O$$

Reaction of sodium hydroxide (0.25M) with disulphide (0.03M) in 30% aqueous dioxan after 30 min. gave signals at 1289 and 1263 Hz downfield from trifluoroacetate ion, the internal standard, with relative intensities of 2:1 attributed[5] to thiolate ion and the labile sulphenate ion respectively. Addition of a 10-fold excess of methyl fluorosulphonate acidified the solution almost immediately and the nmr spectrum showed two main signals at 1208 and 1215 Hz in the ratio 2:1 which were assigned by comparison to the methyl sulphide and methyl sulphenate respectively. Dimethyl sulphate reacted similarly but more slowly. In contrast methyl iodide reacted very much more slowly (36 min.) and gave a mixture of methyl sulphide and methyl sulphoxide as evidenced by signals at 1208 and 1172 Hz respectively. It is noteworthy that methylation of the thiolate ion by this reagent is faster than methylation of the sulphenate anion. Addition of methyl fluorosulphonate at the beginning of the hydrolysis did not intercept the anions and demonstrated that methyl sulphenate formation does not involve methanol or methoxide ion.

$$\mathrm{ArSMe} \xleftarrow{\mathrm{MeI}} \mathrm{ArSO^-} \xrightarrow[\mathrm{Me_2SO_4}]{\mathrm{MeSO_3F}} \mathrm{ArS\text{-}OMe}$$

These results were confirmed by product isolation (0.01 mole). Methyl iodide gave only the sulphide and the sulphoxide, but methyl fluorosulphonate gave the sulphide (98%), the sulphenate (15%), and a trace of the sulphoxide ($< 1\%$). Dimethyl sulphate gave a greater relative yield of the sulphoxide. The low yield of the sulphenate was attributed to hydrolysis during workup. Sulphenate anions therefore resemble sulphinate anions[6] in reacting with soft alkylating agents predominantly at the soft sulphur atom but with harder reagents predominantly at the harder oxygen atom.

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