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OXIDATION OF ALKYL ARYL SULPHIDES
BY ONE ELECTRON TRANSFER

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The recent electrochemical oxidation[1] of phenyl sulphides in acetonitrile-water to give sulphoxides and disulphides by S-R bond fission shows the intermediacy of cation radicals which can either undergo nucleophilic attack by water or fragment to give thiophenoxy radicals. We now report a non-electrochemical oxidation of alkyl aryl sulphides to give intermediate cation radicals. In contrast to the oxidation of phenyl sulphides[1] disulphides are not major products; products are derived by nucleophilic attack. The site of such attack is determined by the nature of the cation radical but the preference for nucleophilic attack at a benzylic site[2-4] observed with cation radicals derived from alkyl aryl ethers is not observed.

Thioanisole is rapidly oxidised at 70° in acetic acid to give the acetate (1). Similarly methyl p tolyl sulphide and methyl m tolyl sulphide give the acetates (2) and (3) respectively in high yield. t-Butyl p tolyl sulphide gives the acetate (4) in 60% yield and the aldehyde (5) in 40% yield. Table 1 lists the halfwave oxidation potentials ($E_{\frac{1}{2}}$) and the initial rate of reaction of a number of alkyl aryl sulphides with manganic acetate relative to p-methoxy toluene - a compound known to react with manganic acetate by one electron transfer.[2,4]

We conclude from the correlation of $E_{\frac{1}{2}}$ and relative rates that the manganic acetate oxidation proceeds by one electron transfer to give ion radicals. In particular we note that the two t-butyl sulphides are oxidised at a similar rate to p-methoxy toluene and consider that this similarity and the gradual trend of reduction of rate in the more highly substituted sulphides indicates a common rate determining step, i.e. one electron transfer. This conclusion is significant in view of our product studies which show that t-butyl p tolylsulphide gives products by attack at a different site from that of the less substituted sulphides. Formation of the cation radical is rate determining and the fast nucleophilic attack occurs at a site determined by the nature of the cation radical. The recent electrochemical studies[1] and the formation of the acetates (1), (2) and (3) show that with sulphides there is a preference for nucleophilic attack at the thioalkyl group. Only when this attack becomes more difficult is nucleophilic attack at other sites as in the formation of (4) from t-butyl p tolyl sulphide. These results contrast with the oxidation of alkyl aryl ethers where the preferential attack on cation radicals from p-alkoxytoluenes is at a benzylic site,[2,4] and with m-alkoxytoluenes[5] attack both at a benzylic and nuclear site is observed. The different sites of attack of the respective cation radicals are probably an indication of the greater charge localisation on sulphur than on oxygen.

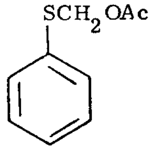
These results indicate the ease with which alkyl aryl sulphides are oxidised to give cation radicals but emphasize the limited data yet available concerning the reactivity of such intermediates.[6] Fragmentation[1] and dimerisation[7] of cation radicals are known reaction pathways but now it must be recognised that nucleophilic attack may occur at different sites. The factors that control the site of such an attack are the subject of further investigations.

TABLE 1

Compound	$E_{\frac{1}{2}}$[a]	Relative Rate[b]
p Methoxytoluene	1.18	1.00
Thioanisole	1.10	5.2
Methyl-p-tolylsulphide	0.93	37.7
Ethyl-p-tolylsulphide	0.98	40
Isopropyl-p-tolylsulphide	1.05	6.0
t-Butyl-p-tolylsulphide	1.14	0.9
Methyl-m-tolylsulphide	1.02	12.1
Ethyl-m-tolylsulphide	1.03	10.8
Isopropyl-m-tolylsulphide	1.08	5.2
t-Butyl-m-tolylsulphide	1.19	1.07

[a] Measured in acetonitrile at a platinum electrode against
Ag/0.01NAg$^+$

[b] Determined from initial rates measured spectroscopically at 510nm



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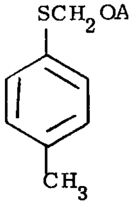

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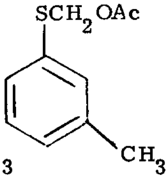

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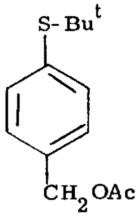

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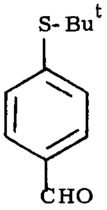

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