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ELECTROPHILIC AROMATIC SUBSTITUTION OF SOME ALKYL PHENYL ETHERS AND SULPHIDES BY BROMINE IN 95% AQUEOUS ACETIC ACID

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Relative reactivities of aromatic compounds towards bromine in solvents, such as acetic acid, are more usually based on times for percentage reactions than on rate constants.[1] Such an incomplete kinetic analysis is open to criticism, particularly as the rate equations for these brominations are not necessarily of the same form for all the reactants being compared.[2] We now wish to report reactivities of some alkyl phenyl ethers and sulphides based on the second order rate constants for bromination in 95% aqueous acetic acid containing sodium bromide (TABLE). Rate constants for bromination of phenyl ethers in glacial acetic acid, in which the overall order is third, have been recently reported by Ganesan and Seshadri.[3] Our reactions were conveniently studied spectrophotometrically at 15°C by following the decrease in the tribromide ion absorption. Pseudo first order conditions were adopted and good first order plots for at least three half lives were obtained.

The ethers and sulphides were treated successively with bromine and potassium hydroxide before distillation using a 1 m column packed with glass helices. VPC [using a column (2 mm x 3 mm) packed with D.G.S. 10% on chromosorb W] indicated each compound was pure. (n_D^{20} = 1.5161, 1.5069, 1.4990 and 1.5885 for PhOMe, PhOEt, PhOPr^i and PhSMe, respectively.)

The reactivity of the ethers decreased in the order Pr^i (4.4) > Et (2.3) > Me (1); Ganesan and Seshadri[3] obtained the sequence from their third order rate constants at 30° - Pr^i (5.1) > Et (2.5) > Me (1). Thus the change in the temperature and the solvent system with the attendant change in the reaction order scarcely affected the relative reactivities. Analyses by VPC of the products of bromination showed that the <u>para</u> isomer was the major product in all cases, with the <u>meta</u> isomer undetectable; at 25°C, 98.8, 99.4, 99.9 and 99.3% <u>para</u> bromo derivatives of PhOMe, PhOEt, PhOPr^i and PhSMe were obtained.

TABLE

Second order rate constants for the bromination of alkyl phenyl ethers and methyl phenyl sulphide in 95% aqueous acetic acid at 15 ± 0.05°.

$$[ArH] = 4 \times 10^{-3} \text{ to } 5 \times 10^{-2} \text{ M.} \qquad [Br_2] \simeq 10^{-4} \text{ M.}$$

Rate constants are the average of at least two values; reproducibility ± 3%.

[NaBr]	[NaClO$_4$]	PhOMe	PhOEt	PhOPr^i	PhSMe
M	M	10^2 k ℓ mole^{-1}			
0.10	-	3.61	8.75	18.1	20.0
0.15	-	3.02	7.38	13.9	13.4
0.20	-	2.69	6.26	10.8	10.7
0.15	0.05	4.03	9.10	18.1	19.2
0.10	0.10	6.52	14.7	29.8	32.0
0.05	0.15	13.9	31.1	57.5	97.7

Various comparisons of reactivities of phenyl ethers and sulphides towards electrophiles have been made.[4a-c] From our kinetic data, PhSMe was more reactive than PhOMe but not by a constant factor; the reactivity ratio of PhSMe to PhOMe varied regularly (from 4 to 7) with decreasing [Br$^-$]. Previously ethers have always been shown to be more reactive than the corresponding sulphides but not however by large factors, <u>e.g.</u>, from 10% reaction times, a reactivity ratio of 80 for PhOMe to PhSMe was calculated for bromination in glacial acetic acid. (A slightly smaller ratio was obtained with our samples in glacial acetic acid containing 0.02 M [Br$^-$].) The differences in the relative reactivities in aqueous and glacial acetic acid are striking and must be due to the effect of the water in the aqueous solvent on equilibria involving the complex,[5] PhSMe:Br$_2$, in particular on the ionisation of this complex. Although the bromination of PhSR in aqueous methanol, a nucleophilic and basic solvent, produces predominantly sulphoxides,[6] there was no (VPC) evidence for sulphoxide products arising from bromination in aqueous acetic acid.

The dependence of the rates on the concentration of added salts is seen from the Table. Increasing [ClO_4^-] caused a rate enhancement while increasing [Br^-] produced a rate retardation. A reduced rate was anticipated on increasing [Br^-] as the free [Br_2] was being decreased (by a factor $\{1 + K\ [Br^-]\}^{-1}$ where K is the tribromide ion formation constant[7]). However, the rate retardation found for all the substrates studied was greater than suggested by this factor alone. However k^{-1} varied regularly if not linearly with [Br^-] at a constant salt concentration. Whether this non-linear dependence was a result of a regular change in the ionic strength of the medium despite the constant salt concentration or another inverse dependence of the rate[8] on [Br^-], or other reasons, has not been resolved. The rate of bromination of methyl 4-D-phenyl ether (90% isotopic purity) is only slightly less than that of PhOMe ($^{k_H}/_{k_D}$ = 1.25 at [Br^-] = 0.10 M), and this seems to exclude the S_E2 mechanism.[8]

REFERENCES

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2. The general rate equation for bromination, according to Ref. 1 is $[ArH]\{k_1[Br_2] + k_2[Br_2]^2 + k_3[Br_3]^3\}$. One or possibly two of these terms in [Br_2] usually dominates for a given substrate in a particular solvent.

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4. a. S. Clementi and P. Linda, Tetrahedron, 26, 2869 (1970).
   b. S. Oae, O. Ohno and W. Tagaki, Bull. Chem. Soc. Japan, 35, 681 (1962).
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5. Such complexes are well established, see A. R. Forrester and J. L. Wardell, Rodd's Chemistry of Carbon Compounds, ed. S. Coffey, Vol. IIIa, Chapter 5, p.431 (1971), (2nd Edition).

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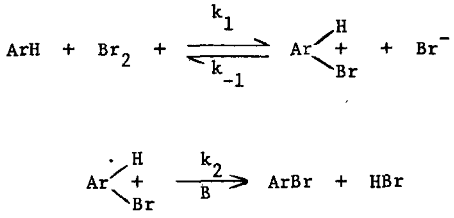
7. K = 265 ± 10 ℓ $mole^{-1}$ in 95% aqueous acetic acid at 15°C.

8. This could arise from the following mechanism (S_E2)



$$ArH + Br_2 + \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Ar\overset{+}{<}{}^{H}_{Br} + Br^-$$

$$Ar\overset{+}{<}{}^{H}_{Br} \xrightarrow[B]{k_2} ArBr + HBr$$

and the rate, including the $[Br_3^-]$ correction factor,

$$= \frac{k_1 k_2 [ArH][Br_2]}{(k_{-1}[Br^-] + k_2)(1 + K[Br^-])}$$