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PROTON MAGNETIC RESONANCE SPECTRA OF PHENOXIDE IONS

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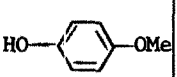
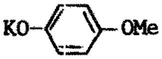
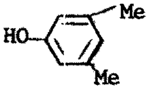
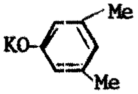
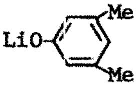
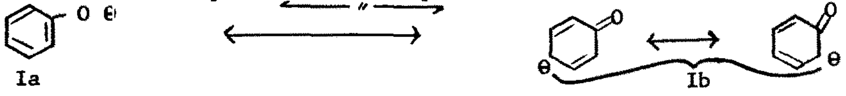
The proton magnetic resonance spectra of phenoxide ions are very markedly altered on changing the solvent from methanol to dimethyl sulfoxide (DMSO), and provide some insight into their structure in these solvents. The initial observation was made that the *ortho*- and *para*- proton signals of potassium phenoxide were shifted considerably upfield relative to the *meta*-proton signal on changing the solvent from methanol to DMSO. Owing to the complexity of the splitting pattern encountered, a series of substituted phenoxide ions was examined. Table I shows the line-positions (relative to tetramethylsilane as internal standard) of a series of alkali-metal phenoxides in methanol and DMSO, taken at a concentration of 1 molar. Solutions prepared in DMSO showed no evidence of hydroxyl protons between 5τ and -5τ (1).

The line-positions of aromatic proton resonances have been rationalised in terms of the field effects of dipoles due to ring substituents, allowance being made for a reaction field set up by the solvent and dependent on its dielectric constant (2). These effects produce a greater shift in the *ortho*-proton resonance than

TABLE I

			τ ortho	τ meta	τ para	Δ* ortho	Δ* meta	Δ* para
A		MeOH	3.14	3.14				
B		DMSO	3.12	3.12				
C		MeOH	3.25	3.25		.11	.11	
D		DMSO	3.85	3.49		.73	.37	
E		MeOH	3.47		3.47			
F		DMSO	3.50		3.50			
G		MeOH	3.56		3.71	.09		.24
H		DMSO	4.10		4.34	.60		.84
I		MeOH	3.49		3.68	.02		.21
J		DMSO	3.59		3.86	.09		.34
K		MeOH	3.16	2.91				
L		DMSO	3.19	2.91				
M		MeOH	3.30	3.07		.14	.16	
N		DMSO	3.89	3.35		.70	.44	
O		MeOH	3.08	2.74				
P		DMSO	3.06	2.66				
Q		MeOH	3.28	2.94		.20	.21	
R		DMSO	3.79	3.12		.73	.46	

* τ phenoxide - τ phenol



Ia

Ib

in that of *meta*- and *para*- protons. Inspection of the data in Table 1 for phenoxide ions in methanol relative to the phenol in the same solvent shows that, in contrast, the upfield shift is highest in the *para*-position and smaller for *ortho*- and *meta*-protons which are about equally affected. It seems probable that a contribution to the observed shift is the implantation of excess negative charge on the *ortho*- and *para*- positions by mesomeric contributions of structure Ib; a counterbalancing deshielding effect on the *ortho*-protons is provided by the presence of a positive ion and the positive end of hydrogen-bonding solvent dipoles in the region of the phenoxide oxygen atom.

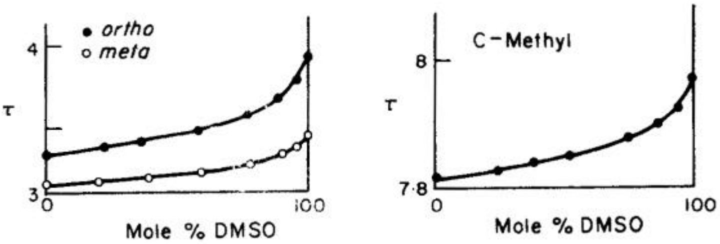


FIG I

Figure 1 shows that as the molar percentage of DMSO in methanol is increased, the *ortho*-, *meta*- and C-methyl resonance positions of potassium p-cresoxide are all shifted upfield. The effect is much more pronounced for the *ortho*-protons, particularly at high DMSO concentrations. The spectra of other phenoxides in DMSO show that the effect is highest for *para*- and *ortho*- protons, and is certainly not explicable without allowing for a considerable contribution from structures Ib. If this was the sole factor involved, charge-densities on the ring-positions might be calculated, following the procedure of earlier authors (3,4). However, field and inductive effects cannot be ignored, as evidenced by the appreciable upfield shift of *meta*-proton signals. Even allowing for these effects, a considerable portion (>10%) of the negative charge of these phenoxide ions must now be centred on the *ortho*- and *para*- carbon atoms.

Examination of the spectra of lithium 3,5-dimethylphenoxide show the same trends as the corresponding potassium salt, but shifts are less pronounced, presumably because a higher degree of ion-pairing exists in the lithium salt. Both in methanol and DMSO, the para-proton is shifted appreciably upfield on going from phenol to phenoxide, whilst the ortho-protons are very little affected. Some deshielding effect on the ortho-protons by metal-ion and aligned solvent molecules is again suggested.

In all cases the C-methyl line positions of p-methyl, p-methoxy and 3,5-dimethylphenol vary little on changing the solvent from methanol to DMSO, or on going to the corresponding phenoxide ion in methanol. However, for the phenoxide ion in DMSO, this absorption shows a considerable upfield shift which must reflect some change in the nature of the species. A strong contribution from the formally non-aromatic Ib structures, with possible lessening in the overall ring-current, could well be responsible for this effect.

Removing the possibility of hydrogen-bonding from a phenoxide ion will of course increase the free charge-density on the oxygen atoms as well as on the ring-positions. In this connection it is of interest that phenoxide ions with a tendency to alkylate on carbon in hydrogen-bonding solvents show no such tendency in dipolar aprotic solvents (5,6).

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