The Stabilities of Meisenheimer Complexes. Part X.[1] Association of 1,1-Dimethoxy-complexes with Cations

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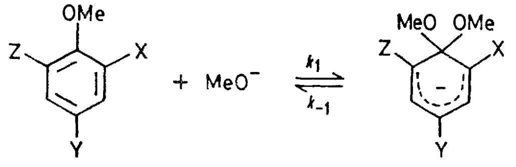
Equilibrium and kinetic measurements are reported for the formation in methanol of 1,1-dimethoxy-Meisenheimer complexes from activated aromatic anisoles and sodium methoxide in the presence of 18-crown-6-ether. Comparison of the results with those obtained without crown ether leads to the suggestion that sodium ions associate with the Meisenheimer anions through interaction with the oxygen atoms of the methoxy-groups at C(1) and the *ortho*-substituents.

EQUILIBRIUM and kinetic data for the formation [equation (1)] of 1,1-dimethoxy-Meisenheimer complexes from ring-activated anisoles in dilute methanolic sodium methoxide solutions have been reported previously.[2] The results were surprising in that the values of the stoicheiometric equilibrium constant K_c (= [complex]/[Parent] [NaOMe]) increased dramatically with base concentration even in dilute (<0·1M) solutions where ideal behaviour would be expected. These changes might be interpreted as a general medium effect.[3] However we preferred an explanation in terms of the stabilisation of the Meisenheimer complexes by association with sodium ions, then they should be very much reduced in the presence of crown ether.



(1)

(I)

RESULTS AND DISCUSSION

In the presence of methoxide ions in methanol, 2-methoxycarbonyl-4,6-dinitroanisole has been shown to give an adduct of structure (I). Equilibrium and rate data obtained in the presence of 18-crown-6-ether are in the Table. For comparison some data obtained in the absence of crown ether are given. Equilibrium data for 4-methoxycarbonyl- and 4-trifluoromethyl-2,6-dinitroanisole are represented graphically in the Figure.

The association constant for 18-crown-6-ether with sodium ions in methanol [6] is 2×10^4 l mol^{-1}. Hence the presence of a small excess of the ether will reduce the concentration of free sodium ions to a very low level. In the presence of crown ether, only small variations with base concentration in the values of K_c, k_1, and k_{-1} are observed. This confirms that the large changes found with sodium methoxide in methanol result mainly from sodium ions.[2] Evidence favouring this interpretation followed from measurements,[4,5] which showed the effects to be markedly dependent on the particular cation present. The availability of crown ethers which are known to be very effective complexing agents for cations [6] presented a means of testing this hypothesis. If the effects observed with sodium methoxide do result mainly from association of the Meisenheimer complexes interactions between the Meisenheimer anions and sodium ions. However even with crown ether present, small increases in the values of K_c with increasing base concentration are observed. These do not depend on the excess of crown ether present so are unlikely to result from incomplete complexing of the sodium ions. Their magnitude varies somewhat with the particular crown ether used being larger for dicyclohexyl-18-crown-6-ether than for 18-crown-6-ether. The most likely explanation

Equilibrium and kinetic measurements at 25° for complex formation from 2-methoxycarbonyl-4,6-dinitroanisole in methanol.

[NaOMe]/M	[Crown ether]/M	Optical density [a] (472 nm)	K_c/l mol^{-1}	10^2k_{obs}/s^{-1}	$10k_1$/l mol^{-1} s^{-1}	10^2k_{-1}/s^{-1}
0·0098	0·04	0·056	8·4	2·6	2·0	2·4
0·0195	0·10	0·109	8·9	2·9	2·2	2·5
0·0295	0·10	0·160	9·3	3·0	2·2	2·3
0·039	0·05	0·205	9·8			
0·039	0·10	0·205	9·8	3·2	2·3	2·3
0·059	0·12	0·28	10·3	3·6	2·3	2·2
0·078	0·16	0·345	11·2	4·1	2·4	2·2
0·0098	0	0·118	19·5	1·55	2·5	1·3
0·0384	0	0·45	40·5	1·97	3·1	0·74
0·077	0	0·61	61	3·6	3·8	0·63
1·0	0	0·74				

[a] For $3·84 \times 10^{-5}$M-substrate.

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[1] Part IX, M. R. Crampton and M. J. Willison, *J.C.S. Perkin II*, 1974, 1686.

[2] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1173.

[3] F. Terrier, *Ann. Chim. (France)*, 1969, **4**, 153.

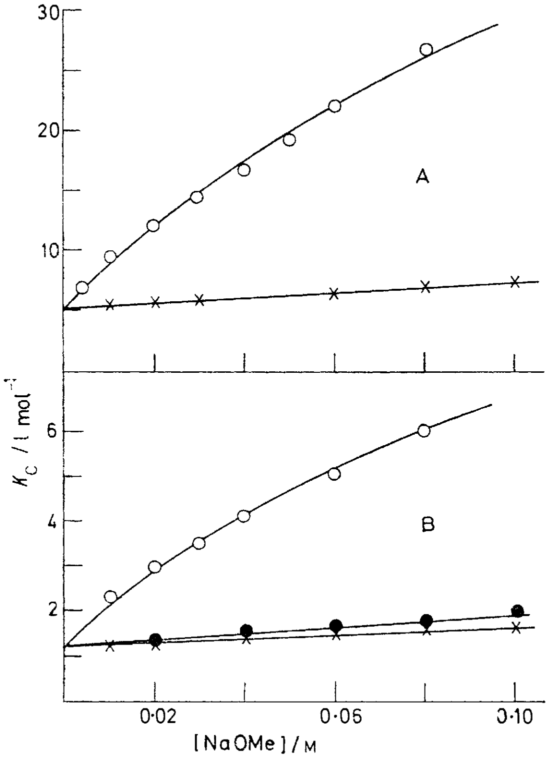
[4] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 2286; 1973, 1104.

[5] S. Ohsawa and H. Nagasue, *Nippon Kagaku Kaishi*, 1974, 79.

[6] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017; H. K. Frensdorff, *ibid.*, 1971, **93**, 600; J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351.

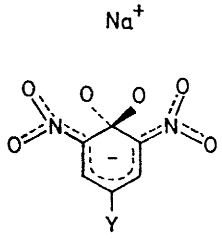
is a weak stabilising interaction, by dispersion forces, of the anionic Meisenheimer complex by the cation–crown ether adduct.

The present measurements allow the determination of accurate values for K_1, the thermodynamic equilibrium constants for methoxide addition to the parent anisoles.



Variations of K_c with sodium methoxide concentration in methanol for A, 4-methoxycarbonyl-2,6-dinitroanisole; B, 4-trifluoromethyl-2,6-dinitroanisole. ○, Sodium methoxide alone; ×, sodium methoxide with 18-crown-6-ether; ●, sodium methoxide with dicyclohexyl-18-crown-6-ether

Values are: for 2-methoxycarbonyl-4,6-dinitroanisole, 8·0 l mol^{-1}; for 4-methoxycarbonyl-2,6-dinitroanisole, 5·0 l mol^{-1}; for 4-trifluoromethyl-2,6-dinitroanisole, 1·2 l mol^{-1}. These values supersede those given previously [2] from the extrapolation of data in methanolic sodium methoxide. If it is assumed that the increases in values of K_c with sodium methoxide concentration found previously [2] result from 1 : 1 interaction of the Meisenheimer anions with sodium ions, then it can be shown that $K_c = K_1(1 + K_2[\mathrm{Na}^+])/(1 + K_3[\mathrm{Na}^+])$ where K_2 and K_3 are respectively the association constants of sodium ions with Meisenheimer anions and methoxide ions. Taking a value [2] of K_3 of *ca.* 10 l mol^{-1} and using the values of K_1 given above, the following values of K_2 are found: 2-methoxycarbonyl-4,6-dinitroanisole, 160 l mol^{-1}; 4-methoxycarbonyl-2,6-dinitroanisole, 100 l mol^{-1}; 4-trifluoromethyl-2,6-dinitroanisole, 100 l mol^{-1}. It has been found that the methoxide adduct of 1,3,5-trinitrobenzene [4] and also spiro-Meisenheimer complexes [7] show no evidence for association with cations in methanol. The interaction thus appears to be specific to 1,1-dimethoxy-complexes. The most likely structure for the associate is therefore (II) where the cation is held by the oxygen atoms of the methoxyl groups at C(1) and by the oxygen atoms of the *ortho*-substituents. In the case of the three substituted anisoles studied here there will be four such oxygen atoms available and association constants, K_2, have values of *ca.* 10^2 l mol^{-1}. These values are of the same order of magnitude as those [6] for the association of sodium ions with the tetramethyl-12-crown-4- and dicyclohexyl-14-crown-4-ethers, where again four oxygens are available for complexing.



(II)

EXPERIMENTAL

Nitro-compounds and base solutions were prepared and purified as before.[2] 18-Crown-6-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) was prepared by Mr J. Allen using known methods [8] and was purified by complexation with acetonitrile. Dicyclohexyl-18-crown-6-ether was obtained from Aldrich and was recrystallised from light petroleum.

Visible spectral measurements were made at 25° with Unicam SP 500 and 800 instruments. Solutions containing the required concentrations of reagents were prepared immediately before measurement by suitable dilution of stock solutions. Kinetic measurements were made as before.[2]

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[7] M. R. Crampton, *J.C.S. Perkin II*, 1973, 2157.

[8] G. W. Gokel, D. J. Cram, C. L. Liotta, H. P. Harris, and F. L. Cook, *J. Org. Chem.* 1974, **39**, 2445.