The Stabilities of Meisenheimer Complexes. Part VI.[1] Spiro-complexes

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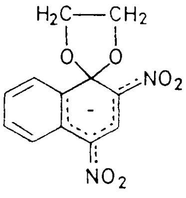
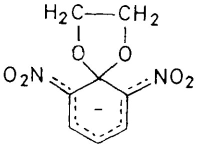
The equilibrium constants KK_1 (= [Spiro complex]/[Glycol ether][MeO$^-$]) at 25° in methanol for formation of spiro-complexes from glycol ethers and methoxide ions have the following values: 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene, $3{\cdot}5 \times 10^3$ l mol^{-1}; 1-(2-hydroxyethoxy)-2,6-dinitrobenzene, 0·22 l mol^{-1}; 1-(2-hydroxyethoxy)-2,4-dinitrobenzene, $1{\cdot}1 \times 10^{-2}$ l mol^{-1}. These values are orders of magnitude larger than those corresponding to the formation of the analogous 1,1-dimethoxy-complexes. Measurements of the rate constants for spiro-complex formation were made by stopped-flow spectrophotometry. The results when compared with those for similarly activated 1,1-dimethoxy-complexes suggest that spiro-complexes may not be good models for intermediates in aromatic nucleophilic substitutions.

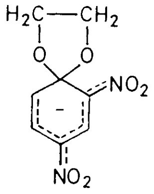
THERE is convincing structural evidence for the formation of spiro-Meisenheimer complexes from the reaction of suitably ring-activated 2-hydroxyethoxyarenes with base.[2,3] Thus solid complexes of structure (I)—(III) have been obtained respectively from 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene, 1-(2-hydroxyethoxy)-2,6-dinitrobenzene, and 1-(2-hydroxyethoxy)-2,4-dinitrobenzene. Careful analysis of the ^{1}H n.m.r. spectra of solutions of these adducts has confirmed their spiro-structure. In previous Parts[4] the equilibrium constants for formation in methanol of a series of 1,1-dimethoxy-Meisenheimer complexes, such as (IV), have been reported. These measurements are now extended to include rate and equilibrium data for some spiro-complexes. Despite several inferences[5,6] that spiro-complexes have considerably greater stabilities than their non-cyclic analogues the only measurements previously available[3] in methanol indicate rather similar stabilities for (I) and (IV). Thus Fendler *et al.* reported values of 356 and 230 l mol^{-1} respectively for formation of these adducts. The rate constants associated with the formation of the two types of adduct were also reported to be similar.[3] Our results presented here are not in accord with these findings and indicate that in the examples studied the equilibrium constants for formation of the spiro-complexes have values at least an order of magnitude greater than those for formation of the analogous 1,1-dimethoxy-adducts.



(I)



(II)



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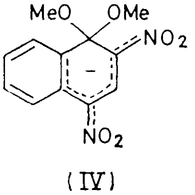

(IV)

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[1] Part V, M. R. Crampton, and H. A. Khan, *J.C.S. Perkin II*, 1973, 1103.

[2] R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron*, 1967, **23**, 227.

[3] E. J. Fendler, J. H. Fendler, W. E. Byrne, and C. E. Griffin, *J. Org. Chem.*, 1968, **33**, 4141.

[4] M. R. Crampton and H. A. Khan, *J.C.S. Perkin II*, 1972, 1173, 1178, 2286.

[5] J. Murto, *Suomen Kem.*, 1965, *B***38**, 255.

[6] M. J. Strauss, *Chem. Rev.*, 1970, **70**, 667.

In view of our previous results[1,4] indicating specific interactions between cations and Meisenheimer complexes, the effects of cations on the stabilities of the spiro-complexes have been investigated.

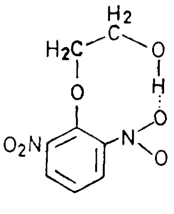
EXPERIMENTAL

Solvents and solutions of base were prepared and/or purified as before.[4]

1-(2-Hydroxyethoxy)-2,4-dinitronaphthalene was prepared by the reaction of 1-chloro-2,4-dinitronaphthalene with sodium glycolate in ethylene glycol. Light yellow crystals were obtained, m.p. 105° (lit.,[3] 95°) (Found: C, 51·8; H, 3·7; N, 10·1. Calc. for $C_{12}H_{10}N_2O_6$: C, 51·8; H, 3·6; N, 10·1%). 1-(2-Hydroxyethoxy)-2,6-dinitrobenzene was prepared by the reaction of 1-chloro-2,6-dinitrobenzene with sodium glycolate in ethylene glycol. Very light yellow crystals were obtained, m.p. 58° (lit.,[3] 54°) (Found: C, 42·1; H, 3·7; N, 12·3. Calc. for $C_8H_8N_2O_6$: C, 42·2; H, 3·5; N, 12·3%). 1-(2-Hydroxyethoxy)-2,4-dinitrobenzene was prepared by the reaction of 1-chloro-2,4-dinitrobenzene with sodium glycolate in ethylene glycol, m.p. 109° (lit.,[3] 111°). (Found: C, 42·0; H, 3·4; N, 12·0%).

Structural Studies.—^{1}H N.m.r. spectra were recorded with a Varian HA 56/60 spectrometer. All shifts are quoted on the δ scale measured relative to internal tetramethylsilane. The spectra of parent ethers and spiro-complexes are basically similar to those previously reported.[2,3] However there are several interesting features in the spectra of the parent ethers which have not previously been reported. Also, because of the lack of agreement with previous work of equilibrium and kinetic data, it is thought desirable to record our structural results. The spectrum of 0·2M-1-(2-hydroxyethoxy)-2,4-dinitrobenzene in dimethyl sulphoxide (DMSO) shows three sets of bands due to ring protons, δ 8·67 (3-H), 8·43 (5-H), and 7·57 (6-H), with $J_{3,5}$ 3 and $J_{5,6}$ 9 Hz. The methylene protons α to the ring give a triplet, δ 4·38 (J 4·8 Hz), while the methylene protons β to the ring give a multiplet, δ 3·78. The hydroxy-resonance occurs at δ 4·92 (t, J 5·1 Hz). In the presence of one equiv. of methanolic sodium methoxide the spiro-complex is formed, δ 8·50 (3-H), 6·90 (5-H), and 5·35 (6-H). The methylene protons in the dioxolan ring of the complex give a multiplet centred at δ 4·05.

The spectrum of 1-(2-hydroxyethoxy)-2,6-dinitrobenzene in DMSO is interesting because unexpectedly it indicates a non-symmetrical structure. Thus the ring protons give an ABX spectrum, δ 8·30 (3-H), 8·31 (5-H), 7·53 (4-H) ($J_{3,4}$ 7·3, $J_{4,5}$ 8·7 Hz), 4·77 (OH), 4·17 (α-CH_2), and 3·68 (β-CH_2).



(V)

The unsymmetrical nature of the molecule might presumably result from hydrogen-bonding of the hydroxy-group to a nitro-group as in (V). However the spectrum of the spiro-complex produced on the addition of one equiv. of base indicates the symmetrical structure (II), δ 7·68 (3- and 5-H), 5·10 (4-H), and 4·15 (CH_2).

The spectrum of 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene shows a sharp singlet, δ 8·78 (3-H), and multiplets centred at 8·58 and 7·90 due to the protons in the second aromatic ring. The α-CH_2 group absorbs at δ 4·32, the β-CH_2 group at 3·87, and the hydroxy-group at 4·65. The spectrum of the spiro-adduct produced on addition of base shows a sharp singlet, δ 9·03 (3-H) and multiplets at 8·73 and 7·30 due to the other aromatic ring protons. The methylene protons in the dioxolan ring give a multiplet, δ 4·35.

In all cases the n.m.r. spectra were consistent with the proposed structures and indicated negligible proportions of impurities.

Measurement of Equilibrium Constants.—Visible spectra were measured, using matched pairs of silica cells of either 1 or 4 cm pathlength, with a Unicam SP 8000 recording instrument or SP 500 spectrophotometer. The former instrument was used to determine spectral shapes and the latter for the accurate determination of optical densities. All measurements were made at 25°. Solutions of suitable concentration were prepared immediately before use from freshly made stock solutions of reagents.

In some cases solutions in methanol of low methoxide ion concentration were required. These were obtained using phenol or 4-bromophenol buffers.[7] The pK_a values in methanol of these compounds are 14·46 and 13·61 respectively[7] while the autoprotolysis constant of methanol is 16·92. Thus, for example, the residual methoxide ion concentration in a solution containing stoicheiometric concentrations of $1·25 \times 10^{-2}$M-sodium methoxide and $7·5 \times 10^{-2}$M-phenol is $6·5 \times 10^{-4}$M.

Kinetic Data.—Kinetic measurements were made using a 'Canterbury' stopped-flow apparatus (N.P. Consulting). Monochromatic light was brought by means of silica light-guides to a 2 mm pathlength silica cell and from thence to a photomultipler whose output was fed to a Tektronix storage oscilloscope (timebase calibrated to better than 2%). Test solutions, in this case methanol solutions of base and substrate, were allowed separately to attain a temperature of 25·0° in a thermostatted water tank and were then mixed by means of mechanical pressure on drive syringes. The resulting change with time of the light intensity emerging from the cell was monitored on the storage oscilloscope. In all cases the maximum change in optical density during any one kinetic run was 0·02 so that the scale readings obtained give a direct measure of the concentrations of the absorbing species.

TABLE 1

Typical data for the reaction of 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene (4×10^{-6}M) with methoxide ($1·04 \times 10^{-3}$M) in methanol

t/ms	Scale reading (arbitrary units)	k_{obs}/s^{-1}
0	2·6	
10	3·7	30·5
20	4·5	30
30	5·2	32
40	5·6	31
50	5·9	31
70	6·35	32
90	6·55	31
∞	6·8	

Measurements were made at the absorption maxima of the coloured adducts formed, at which wavelengths the reactants were transparent. Only a single relaxation time was observable on the time-scale accessible to the stopped-flow tech-

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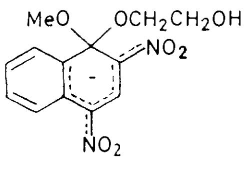
[7] C. H. Rochester and B. Rossall, *J. Chem. Soc. (B)*, 1967, 743.

nique. At the concentrations used the products were in general stable for several hours. All measurements were made with the base concentration in large excess of the parent ether concentration and first-order kinetics were obtained. Values of rate constants quoted are the means of at least five independent experiments. Typical data with calculated first-order rate constants are in Table 1.

RESULTS AND DISCUSSION

The ^{1}H n.m.r. results obtained previously [2,3] and confirmed here indicate that the spiro-complexes (I)—(III) are formed by reaction of the parent glycol ethers with base in DMSO. In addition solid complexes with spiro-structures have been isolated.[3] These facts provide strong evidence that the measurements reported here using dilute solutions in methanol also relate to spiro-complex formation. However the possibility that adducts such as (VI) are formed by methoxide addition at C-1 must be considered. The equilibrium and rate constants associated with the formation of (VI) would be expected to be quite similar to those for the formation of (IV). However the results below indicate quite different values from those for the formation of the dimethoxy-adduct. In addition measurements [8] with the glycol ethers in dilute aqueous sodium hydroxide solutions indicate that stable species similar to those formed in methanol are produced. It thus seems certain that the spiro-adducts are formed in methanol.



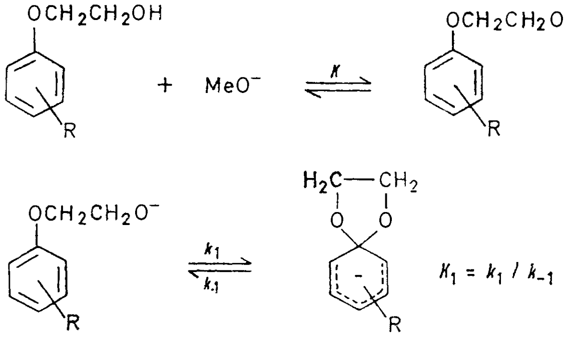
(VI)

The most likely and generally accepted [3,9] mechanism for spiro-complex formation involves two steps. The first equilibrium involving proton transfer from the glycol side chain to base will be established very rapidly and will be much too fast to measure by means of the stopped-flow technique. The second equilibrium involving internal cyclisation of the glycolate anion will be achieved less rapidly. For the general case the Scheme applies. Equilibrium and kinetic measurements were made in the visible region at the absorption maxima of the spiro-complexes. At these wavelengths the spectra of the parent glycol ethers showed zero or small absorption. The assumption is made that the glycolate anions will have low extinction coefficients at these wavelengths similar to those of the parent ethers. The measured stoicheiometric equilibrium constant is given by equation (1) from which can be deduced equation (2). The relationship of the observed first-order rate constant for complex formation to the individual rate constants is given by an expression derived by Bernasconi and de Rossi.[9] Under the conditions where base is in large excess over substrate this is of the form (3)

$$K_C = \frac{[\text{Spiro complex}]}{([\text{Glycol ether}] + [\text{Glycolate anion}])[\text{MeO}^-]} \tag{1}$$

$$K_C = KK_1/(1 + K[\text{MeO}^-]) \tag{2}$$

$$k_{\text{obs}} = k_{-1} + k_1K[\text{MeO}^-]/(1 + K[\text{MeO}^-]) \tag{3}$$



SCHEME

1-(2-*Hydroxyethoxy*)-2,4-*dinitronaphthalene*.—The visible spectrum of the parent ether in methanol shows a maximum at 350 nm. The spiro-complex produced in the presence of dilute sodium methoxide is red with maxima at 345 and 495 nm (Figure 1). There is extensive conversion into complex in the presence of 1×10^{-3}M-sodium methoxide and no increase in absorption is observed on increasing the base concentration above 2×10^{-2}M. Even at low base concentration the rate of colour formation is instantaneous as judged by eye but is amenable to study by the stopped-flow technique. Data are collected in Table 2. Measurements using dilute sodium or tetra-n-butylammonium methoxide give similar results and little effect is produced by addition of sodium chloride. Because of the low base concentrations required and the possibility of the interference of atmospheric carbon dioxide, measurements were also made using phenolic buffers.[7] There is good agreement between the data obtained with and without phenol at those methoxide concentrations where overlap occurs indicating that the only effect of the phenol is to regulate the methoxide ion concentration.

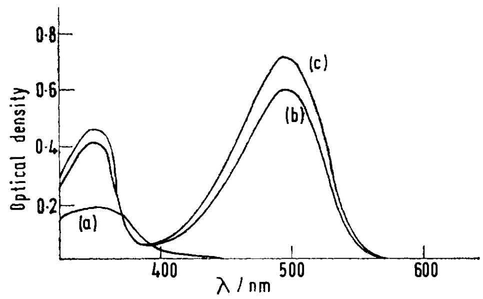


FIGURE 1 Visible spectra of $2\cdot9 \times 10^{-5}$M-1-(2-hydroxyethoxy)-2,4-dinitronapthalene in methanol containing (a) 0; (b) 1×10^{-3}M-; and (c) 2×10^{-2}M-sodium methoxide

The fact that the optical density of 495 nm is constant over a wide range of methoxide concentrations (2 ×

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[8] M. R. Crampton, unpublished observations.

[9] C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, 1973, **38**, 500.

TABLE 2

Equilibrium and kinetic data for the reaction of 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene ($2{\cdot}9 \times 10^{-5}$M) with methoxide in methanol at 25°

10^4[OMe$^-$]/M	Conditions	O.D.$_{495}$	$10^{-3}K_C$/ l mol^{-1}	k_{obs}/s^{-1}
0		0·003		
4·9	*a*	0·422	3·4	
10	*a*	0·54	3·8	32 ± 2
15	*a*	0·58	3·5	
200	*a*	0·68		
1000	*a*	0·68		
2000	*a*	0·68		
4·9	*b*	0·43	3·5	
5	*c*	0·44	3·3	
10	*c*	0·55	3·4	
15	*c*	0·59	3·3	
200	*c*	0·70		
1000	*c*	0·71		
1·15	*d*	0·193	3·4	9·5 ± 0·5
2·2	*d*	0·295	3·5	11·5 ± 0·5
1·4	*e*	0·213	3·3	
2·1	*e*	0·280	3·3	
2·9	*e*	0·338	3·4	
3·7	*e*	0·380	3·4	15·3 ± 0·3
6·5	*e*	0·47	3·4	22 ± 0·5
10·4	*e*	0·54	3·7	31 ± 2

[a] Sodium methoxide. [b] Sodium methoxide in methanol containing 0·05M-sodium chloride. [c] Tetra-n-butylammonium ethoxide. [d] Sodium methoxide and *p*-bromophenol. [e] Sodium methoxide and phenol.

10^{-2}—2×10^{-1}M) indicates that complete conversion into spiro-complex is achieved (ε $2{\cdot}3 \times 10^4$ l mol^{-1} cm^{-1}). The value of the stoicheiometric equilibrium constant K_C is $3{\cdot}5 \times 10^3$ l mol^{-1} and does not vary, within experimental error, with base concentration. In terms of equation (2) this indicates that at the base concentrations used $K[\text{MeO}^-] \ll 1$ so that $KK_1 = 3{\cdot}5 \times 10^3$ l mol^{-1}.

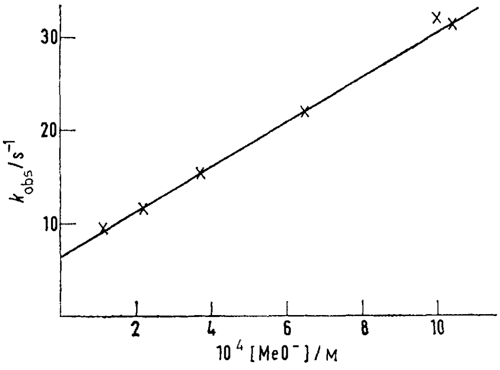

FIGURE 2 Variation of k_{obs} with methoxide concentration for reaction of 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene with base

The kinetic data confirm these results. Thus a plot (Figure 2) of k_{obs} *versus* methoxide concentration is linear showing that equation (3) reduces to $k_{obs} = k_{-1} + k_1K[\text{MeO}^-]$. From the intercept and slope values of $k_{-1} = 6{\cdot}5$ s^{-1} and $k_1K = 2{\cdot}5 \times 10^4$ l mol^{-1} s^{-1} were obtained. Combination of these values gives $KK_1 = 3{\cdot}8 \times 10^3$ l mol^{-1} in good agreement with that obtained independently.

Although our structural studies with this compound agree precisely with those of Fendler *et al.*,[3] the value of the equilibrium constant obtained here is an order of magnitude larger than their value and rate constants are several orders of magnitude higher.

1-(2-*Hydroxyethoxy*)-2,6-*dinitrobenzene*.—In the presence of methanolic sodium methoxide the violet, $\lambda_{max.}$ 575 nm, spiro-complex (II) was rapidly produced. However in this case only a small fraction of parent ether was converted into complex in dilute solutions of base. Because of this measurements were made with relatively high concentrations of parent ether. However, the results in Table 3 indicate that the measured equilibrium constants are not dependent on the parent concentration. It was not possible to achieve complete conversion into complex in methanol, and hence measure an extinction coefficient directly, since in solutions of high base concentration the initially formed complex was rapidly destroyed presumably by a nucleophilic substitution reaction. However in media rich in DMSO conversion into complex was complete and solutions were time-stable. The visible spectrum in DMSO was very similar to that observed in methanol but with absorption maximum shifted slightly to longer wavelength. Incidentally the similarity of these spectra is a strong argument that the interaction being observed in methanol does in fact produce the spiro-complex (II) and does not, for example, involve complexation of a small concentration of highly reactive impurity in the parent ether. The data in Table 4 show that as the proportion of DMSO is increased the extinction coefficient of the complex increases. This increase in extinction coefficient, and also the bathochromic shift in DMSO, is a feature common to many

TABLE 3

Equilibrium and kinetic data at 25° for the reaction of 1-(2-hydroxyethoxy)-2,6-dinitrobenzene with methanolic methoxide

10^3[Parent]$_{stoich}$/M	[NaOMe]/M	O.D.$_{575}$ [a]	K_C/l mol^{-1}	k_{obs}/s^{-1}
2·5	0	0·00		
1·0	0·01	0·059	0·22	
1·0	0·01 [b]	0·067	0·25	
2·5	0·01	0·15	0·22	360 ± 40
2·5	0·02	0·295	0·22	340 ± 40
0·5	0·04	0·120	0·22	
1·0	0·07	0·45	0·24	
0·5	0·09	0·292	0·24	370 ± 40
0·5	0·19	0·70 [c]	0·29	
0·25	0·38	0·82 [c]	0·36	
0·10	0·76	0·70 [c]	0·46	
	[Bu$^n_4$NOMe]/M			
1·0	0·010	0·072	0·26 [d]	
1·0	0·020	0·165	0·30 [d]	
0·5	0·041	0·20	0·37 [d]	
0·5	0·092	0·67	0·57 [d]	

[a] Values quoted are for 1 cm cells; in some cases measurements were made in 4 cm cells. [b] Contains 0·07M-NaCl. [c] Colour rapidly fades; values quoted are extrapolated to zero time. [d] The increase in value of K_C with base concentration is ascribed to interaction of the spiro-complex with tetrabutylammonium ions (see text). Extrapolation to zero base concentration gives a value of $K_C = 0{\cdot}22$ l mol^{-1}.

TABLE 4

Variation of the extinction coefficient of the spiro-complex (II) with solvent composition in methanol–DMSO mixtures

Vol. % DMSO	50	60	70	80	90
$10^4\varepsilon$/l mol^{-1} cm^{-1}	3·4	3·6	3·8	4·0	4·1

Meisenheimer complexes.[4] Extrapolation of the data to 0% DMSO gave an extinction coefficient in methanol of $2{\cdot}7 \times 10^4$ l mol^{-1} cm^{-1}, which value was used to calculate equilibrium constants.

The results in Table 3 indicate that K_C is independent of sodium methoxide at low base concentration but increases in more concentrated solutions. This increase is due to the fact that the activity of methoxide in this region is governed by an acidity function rather than its concentration.[10] Equation (2) predicts a decrease in K_C with increasing base concentration. The observation that no decrease within experimental error is observed in the range 0—0·1M-base, where ideal behaviour is expected, indicates that in this region $K[\text{OMe}^-] \ll 1$. Hence $K < 1$ l mol^{-1} and KK_1 has the value 0·22 l mol^{-1}.

Measurement of the rate of attainment of equilibrium showed that k_{obs} is independent of base concentration. This conforms to the situation where equation (3) reduces to $k_{\text{obs}} = k_{-1}$, giving a value of 360 ± 40 s^{-1} for k_{-1}.

1-(2-*Hydroxyethoxy*)-2,4-*dinitrobenzene*.— Measurements were made at the absorption maximum of the spiro-complex (487 nm) and data are in Table 5. With this compound, as with complex (II), it was necessary to use fairly high parent concentrations to obtain measurable optical densities in methanol. In this case the parent ether showed some absorption at 487 nm and the results were corrected for this before calculation of equilibrium constants. Complete conversion into complex was not obtained in methanolic methoxide but an extinction coefficient in methanol of $2{\cdot}1 \times 10^4$ l mol^{-1} cm^{-1} was determined by extrapolation of data obtained in methanol–DMSO mixtures where conversion into spiro-complex was complete.

TABLE 5

Equilibrium data at 25° for the reaction of 1-(2-hydroxyethoxy)-2,4-dinitrobenzene with methanolic methoxide

10^3[Parent]$_{\text{stoich}}$/M	[NaOMe]/M	O.D.$_{487}$ [a]	O.D.$_{487}$ [a] due to complex	10^2K_C/l mol^{-1}
4·5	0·00	0·050	0·00	1·1
4·5	0·02	0·128	0·08	1·1
3·36	0·04	0·16	0·12	1·1
2·26	0·06	0·145	0·12	1·1
1·13	0·08	0·098	0·082	1·1
2·8	0·095	0·29	0·26	1·2
2·8	0·095 [b]	0·29	0·26	1·2
2·8	0·19	0·60	0·57	1·3
1·13	0·19	0·24	0·225	1·3
0·56	0·38	0·295	0·29	1·6
	[Bu$^n{}_4$NOMe]/M			
4·5	0·020	0·17	0·12	1·6 [c]
3·36	0·041	0·27	0·24	2·1 [c]
2·26	0·061	0·31	0·28	2·4 [c]
1·13	0·082	0·24	0·22	2·8 [c]

[a] All measurements were made with, and are reported for, 4 cm cells. [b] Contains 0·05M-NaCl. [c] Extrapolation to zero base gives a value of $K_C = 1{\cdot}15 \times 10^{-2}$ l mol^{-1} (see text).

The results are in accord with values of $KK_1 = 1{\cdot}1 \times 10^{-2}$ l mol^{-1} and $K < 1$ l mol^{-1}.

Measurement of the rate of attainment of equilibrium in dilute sodium methoxide solutions in methanol was attempted but was too fast for the stopped-flow technique. A lower limit for the value of the rate constant k_{-1} can be estimated as 500 s^{-1}.

Effects of Cations.—In previous studies[1,4] involving 1,1-dimethoxy-Meisenheimer complexes such as (IV) the effects of ion association have been noted. It was suggested recently[1] that alkali-metal cations are held by a cage effect by the oxygen atoms at the position of addition and by the electronegative substituent at the *ortho*-position. This explanation was preferred to one involving cation association with the nitro-group *para* to the position of addition. The presence of the dioxolan ring in the spiro-complexes would be expected to reduce their ability to form ion-pairs of the type specified. In agreement with this the present work shows little association of spiro-complexes with sodium ions. Thus K_C values are independent of base concentration in dilute solutions and, more important, are not affected by the addition of sodium chloride. In fact the failure of spiro-complexes to associate with sodium ions adds weight to our previous suggestion.[1]

The increase in equilibrium constants K_C with base concentration in tetra-n-butylammonium methoxide solutions is attributed to stabilisation, by dispersion interaction, of the large polarisable spiro-anions by the tetra-butylammonium ions. Effects of similar magnitude have been observed with all Meisenheimer complexes so far studied.[4,11]

Values of K.—The results do not allow the determination of K, the equilibrium constant governing proton loss from the glycol side chain, but indicate that values are less than 1 l mol^{-1}. For comparison the values in water of the equilibrium constants for reaction of hydroxide ion with 2-methoxyethanol and 2-chloroethanol are 0·16 and 0·5 l mol^{-1} respectively.[12] For reaction of these compounds with methoxide ion in methanol somewhat smaller values would be expected.[13] It seems probable that the values of K in methanol for the three aromatic glycol ethers studied in the present work will be in the range 10^{-2}—1 l mol^{-1} and in view of the isolation of the hydroxy-proton from the aromatic system values are not likely to differ greatly between the three compounds. Hence measured equilibrium constants will largely reflect differences in values of K_1.

Comparison with 1,1-*Dimethoxy-complexes*.—It is of considerable interest to compare the equilibrium and kinetic results obtained here with similar data relating to similarly activated 1,1-dimethoxy-complexes (Table 6).

The equilibrium constants KK_1 (= [Spiro complex]/[Glycol ether][MeO$^-$]) for formation of the spiro-complexes are considerably greater than those, K_{eq} (= [Complex]/[Anisole][MeO$^-$]), for formation of the dimethoxy-complexes. In addition rate constants k_1 and k_{-1} for the spiro-complexes are much greater. In particular k_{-1} for

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TABLE 6

Comparison of rate and equilibrium data for spiro- and 1,1-dimethoxy-complexes

	Spiro-complex			1,1-Dimethoxy-complex		
	KK_1/l mol^{-1}	Kk_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}	K_{eq}/l mol^{-1}	k_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}
2,4-Dinitronaphthalene	$3{\cdot}5 \times 10^3$	$2{\cdot}5 \times 10^4$	6·5	205 [a]	0·93	$4{\cdot}6 \times 10^{-3}$
2,4-Dinitrobenzene	$1{\cdot}1 \times 10^{-2}$	$>5{\cdot}5$	>500	$4{\cdot}6 \times 10^{-5}$ [a]	$2{\cdot}1 \times 10^{-3}$	42 [b]
2,6-Dinitrobenzene	0·22	80	360	9×10^{-5} [a]		

[a] Ref. 4. [b] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1968, **90**, 4982.

the spiro-complex (I) is more than three orders of magnitude larger than for the dimethoxy-analogue (IV). Also k_{-1} for spiro-complex (III) is much greater than for its dimethoxy-analogue. This has relevance to recent work[9] by Bernasconi and de Rossi concerned with the rate of leaving-group expulsion in aromatic nucleophilic substitutions. They make the assumption that the rate constant, k_{-1}, for ring opening of spiro-complexes will be similar or slower than that for expulsion of base from a non-cyclic analogue. The present results in methanol indicate that for compounds (I) and (III) at least this is not the case.

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