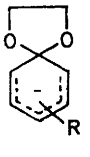
The Stabilities of Meisenheimer Complexes. Part VIII.[1] Equilibrium and Kinetic Data for Spiro-complex Formation in Water

By **Michael R. Crampton** * and **Michael J. Willison**, Chemistry Department, The University, Durham

Equilibrium and rate constants for the formation in water of spiro-complexes from four ring-activated aromatic glycol ethers are reported. Values of the rate constants k_{-1} for opening of the dioxolan ring of these complexes are much higher than those for the expulsion of base from non-cyclic analogues. This may indicate ring strain in the spiro-complexes.

In moderately concentrated (>0·1M) sodium hydroxide solutions complexes are formed by addition of hydroxide ions at unsubstituted ring positions in the spiro-complexes. Addition of hydroxide ions at two ring positions to the spiro-complex from the glycol ether of 2,4,6-trinitrobenzene gives an adduct (XIII) which may be regarded as a 1 : 3 σ-complex.

SPIRO Meisenheimer complexes are of considerable current interest and have been used as models for the intermediates in nucleophilic aromatic substitution reactions. We have previously reported equilibrium and kinetic data for the formation in methanol of complexes of general structure (I),[2] while Bernasconi and his co-workers have reported data for (II)[3] and (III)[4] in water. We report here results obtained in water for four differently activated complexes (IV)—(VII). This allows comparison between complexes of types (I)—(III) in a common solvent and also solvent effects between water and methanol on complexes of structure (I). Perhaps the most significant point deriving from the present study is the very fast rate of spontaneous ring opening of spiro-complexes compared to the analogous decomposition process for similarly activated 1,1-dimethoxy-complexes.



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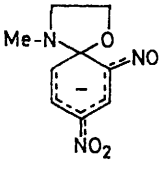

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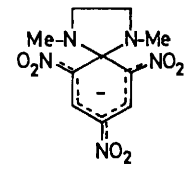

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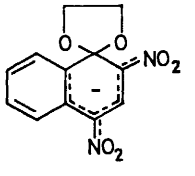

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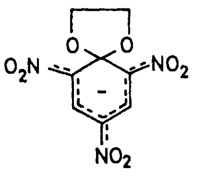

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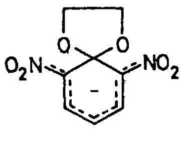

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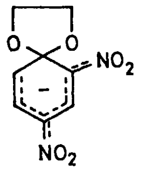


(VII)

Measurements in moderately concentrated aqueous sodium hydroxide indicate interaction of the spiro-complexes (IV)—(VII) with base to yield interesting covalently-bound addition complexes.

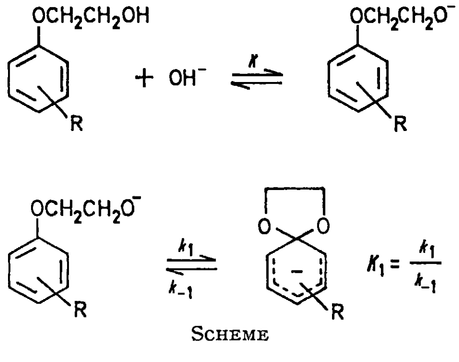
EXPERIMENTAL

1-(2-Hydroxyethoxy)-2,4,6-trinitrobenzene was prepared[5] by reaction of picryl chloride with one equiv. of base in ethylene glycol. Recrystallisation from water yielded a yellow solid, m.p. 62° (lit.,[5] 61°). Other glycol ethers were prepared as before.[2] Boiled-out, distilled water was used for all measurements. Solutions of suitable concentration were prepared immediately before use from freshly made stock solutions of reagents. U.v.–visible spectral measurements were made with a Unicam SP 8000 recording instrument or SP 500 spectrophotometer. Kinetic measurements were made using a 'Canterbury' stopped-flow apparatus described previously.[2] ^{1}H N.m.r. measurements were made with a Varian HA 56/60 spectrometer. The spectrum of the glycol ether of 2,4,6-trinitrobenzene gave δ 9·1 (s, equivalent ring protons), 4·6 (s, OH), and 3·7 and 4·2 (2 m, CH_2). The spectrum in water in the presence of one equiv. of base showed δ 8·55 (s, ring H) and 4·3 (s, CH_2) attributed to the spiro-complex (V). Measurements were attempted in concentrated base solutions but were unsuccessful due to insolubility of the substrate.

RESULTS

The results refer to four substrates to which the following general considerations apply.

Spiro-complex Formation.—The probable mechanism for spiro-complex formation in alkaline media is that suggested previously[2,3] and shown in the Scheme. The parent glycol ether is in fast equilibrium with glycolate anion whose internal cyclisation is the slow step. Equilibrium and kinetic measurements were made in the visible region at the absorption maxima of the spiro-complexes.



SCHEME

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

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[1] Part VII, M. R. Crampton, M. A. El Ghariani, and M. J. Willison, *J.C.S. Perkin II*, 1974, 441.

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

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

[4] C. F. Bernasconi and C. L. Gehriger, *J. Amer. Chem. Soc.*, 1974, **96**, 1092.

[5] J. J. Blanksma and P. G. Fohr, *Rec. Trav. chim.*, 1946, **65**, 711.

coefficients at these wavelengths similar to those of the parent ethers. A measured stoicheiometric equilibrium constant is then defined by equation (1) from which can be deduced equation (2).

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

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

Kinetic measurements were made either in solutions where the base concentration was in large excess of the substrate concentration or in buffer solutions whose pH did not vary during the course of any one kinetic run. Under these conditions the observed first-order rate constant corresponding to attainment of equilibrium between the spiro-complex and its precursors is given by equation (3).

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

Formation of Hydroxide Adducts from Spiro-complexes.—In alkaline media containing $>0{\cdot}1$M-sodium hydroxide the fast formation of intensely coloured spiro-complex was followed by a slower reaction giving a decrease in absorption in the visible region and an increase in the u.v. region of the spectrum. These changes were reversible and did not result in destruction of the substrate. The assumption of an interaction of spiro-complex with one hydroxide ion to form an adduct (A) gives equation (4).

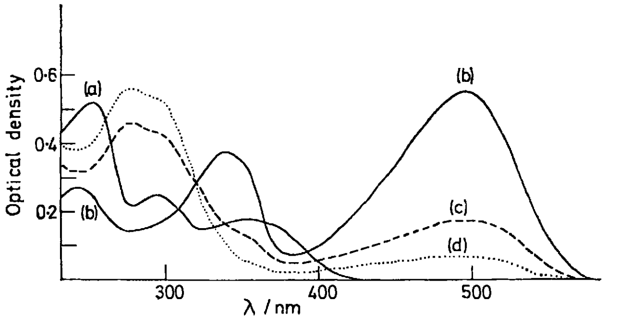

FIGURE 1 Spectra of $3{\cdot}0 \times 10^{-5}$M-1-(2-hydroxyethoxy)-2,4-dinitronaphthalene in water containing (a), 0; (b), 0·01; (c), 1·0; and (d), 2·0M-sodium hydroxide

$$\text{Spiro} + \text{OH}^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\text{A}) \quad K_2 = \frac{k_2}{k_{-2}} \qquad (4)$$

Measurement of the relaxation times by stopped-flow spectrophotometry showed that the second relaxation time associated with the decrease in colour was in all cases at least an order of magnitude slower than that for spiro-complex formation. A kinetic treatment by standard methods [6] gives equation (5) for the observed first-order rate constant k_{obs}' for the slower process.

$$k_{\text{obs}}' = k_{-2} + \frac{k_2KK_1[\text{OH}^-]^2}{1 + K[\text{OH}^-] + K_1K[\text{OH}^-]} \qquad (5)$$

Also present were very much slower irreversible reactions resulting in destruction of the parent with the formation of the respective substituted phenols.

The results for the four compounds studied are sufficiently distinct to warrant their individual treatment.

1-(2-*Hydroxyethoxy*)-2,4-*dinitronaphthalene.*—Two reversible equilibria are present as shown in Figure 1. The first interaction dominant in dilute base solutions gives rise to spiro-complex (IV), $\lambda_{\text{max.}}$ 495 (ε $1{\cdot}8 \times 10^4$) and 342 nm ($1{\cdot}3 \times 10^4$). In more concentrated base the spectra indicate conversion into a second species with $\lambda_{\text{max.}}$ 275 (ε $2{\cdot}0 \times 10^4$) and 300 nm ($1{\cdot}8 \times 10^4$). Eventually a very slow reaction gives a species whose visible spectrum with $\lambda_{\text{max.}}$ 390 and 430 nm is identical with that of 2,4-dinitronaphthol.

Equilibrium and kinetic data for formation of the spiro-complex from the parent glycol ether are in Table 1. Conversion into spiro-complex is virtually complete in 1×10^{-2}M-sodium hydroxide so that measurements of optical density in aqueous buffers allowed the direct determination of K_C. The values obtained are independent of base concentration showing that there is no apparent variation in the denominator of equation (2); hence $KK_1 = (3 \pm 0{\cdot}3) \times 10^4$ l mol^{-1} and $K[\text{OH}^-] \ll 1$. The value of the rate constant k_{obs} for spiro-complex formation decreases with decreasing pH to a minimum of $2{\cdot}3 \pm 0{\cdot}1$ s^{-1}. This corresponds to the value of k_{-1} [equation (3)]. A plot of k_{obs} *versus* $[\text{OH}^-]$ is linear with slope ($=k_1K$) $(9 \pm 1) \times 10^4$ l mol^{-1} s^{-1}. The results show that variation of buffer concentration at constant pH does not affect the value of the rate constant within experimental error indicating the absence of catalysis by buffer.

TABLE 1

Equilibrium and kinetic data for formation of complex (IV) from 1-(2-hydroxyethoxy)-2,4-dinitronaphthalene in aqueous buffers at 25°

pH	Conditions	O.D.$_{495}$ [h]	$10^{-4}K_C$/ l mol^{-1}	k_{obs}/s^{-1}
7·1	*a*			2·2 ± 0·1
7·4	*b*			2·4
7·6	*b*			2·3
8·0	*c*	0·003		2·5
8·97	*c*	0·123	3·2	3·2
9·0	*d*			3·2
9·23	*c*	0·180	3·0	
9·36	*c*	0·239	3·5	4·4
9·65	*c*	0·301	2·9	6·3
9·77	*c*	0·347	3·1	
9·9	*e*			9·1
10·0	*f*			10·1
10·04	*c*	0·393	2·5	
10·14	*c*	0·431	3·0	
10·32	*c*			22
10·5	*c*	0·480	2·8	32
10·72	*c*			51
10·86	*c*			65
12	*g*	0·535		

[a] Phosphate buffer, $2{\cdot}5 \times 10^{-2}$M. [b] Phosphate buffer, 5×10^{-2}M. [c] Borax buffer, $1{\cdot}25 \times 10^{-2}$M. [d] Borax buffer, 5×10^{-2}M. [e] Phenol–sodium phenoxide, $2{\cdot}5 \times 10^{-2}$M. [f] Phenol–sodium phenoxide, 0·25M. [g] Sodium hydroxide, 1×10^{-2}M. [h] Measured with Unicam SP 500 for 3×10^{-5}M-substrate.

Observations by stopped-flow spectrophotometry at 495 nm in solutions containing $>0{\cdot}1$M-sodium hydroxide show a very fast build up of colour due to spiro-complex followed by a slower fading reaction. Measurements of optical density after attainment of the second equilibrium are in Table 2. Values of K_2, the equilibrium constant for higher complex formation, were calculated using $K_2 = (0{\cdot}535 - \text{O.D.}_{495})/\text{O.D.}_{495} \times [\text{NaOH}]$. The values so obtained increase with base concentration reflecting no doubt that the basicity of the medium should be represented

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[6] M. Eigen and L. De Maeyer in 'Technique of Organic Chemistry,' ed. A. Weissberger, Wiley-Interscience, New York, 1963, vol. VII, part 2, p. 895.

by an acidity function.[7] In fact these results could be used to define a J_{2-} function. Rate constants for the fading reaction at two base concentrations are in Table 2. In this case equation (5) reduces to (6). Combination of

$$k_{obs}' = k_{-2} + k_2[OH^-] \qquad (6)$$

k_{obs}' with the known values of K_2 allowed the calculation of values for k_2 and k_{-2}.

1-(2-*Hydroxyethoxy*)-2,4,6-*trinitrobenzene*.—In aqueous solutions the parent glycol ether is in equilibrium with the spiro-complex, $\lambda_{max.}$ 417 (ε 2·5 × 10^4) and 470 nm (1·8 × 10^4). Even in neutral media some complex is present indicating a high value for K_1K. We accept Murto's value [8] of 1·8 × 10^7 l mol^{-1}.

TABLE 2

Equilibrium and kinetic data for hydroxide addition to spiro-complex (IV) (3 × 10^5M) in water at 25°

[NaOH]/M	O.D.$_{495}$	K_2/l mol^{-1}	k_{obs}'/s^{-1}
0·01	0·535		
0·10	0·490	1·0	0·04 ± 0·01
0·15	0·46	1·1	
0·20	0·43	1·2	
0·31	0·38	1·3	
0·51	0·29	1·6	0·05 ± 0·01
0·71	0·22	2·0	
1·0	0·16	2·3	

Rates of colour formation were measured at 420 nm by mixing solutions of the parent in 10^{-4}M-hydrochloric acid with alkaline buffers. In all cases the approach to equilibrium was accurately first order. Values of the rate constant are in Table 3 and are, within experimental error, independent of buffer concentration. From a plot of k_{obs} *versus* [OH^-] which was linear a value for k_1K of (1·6 ± 0·3) × 10^6 l mol^{-1} s^{-1} was obtained. The intercept is too small to allow direct determination of k_{-1}. However calculation of values point by point using equation (3) for solutions where $6 \leqslant pH \leqslant 7$ gave $k_{-1} = 0{\cdot}095 \pm 0{\cdot}01$ s^{-1}. In more acidic solutions the rate increases from the minimum value due to an acid catalysed pathway between complex and parent.[9] However these effects are unimportant above pH 6.

TABLE 3

Kinetic data for formation of complex (V) from 1-(2-hydroxyethoxy)-2,4,6-trinitrobenzene in water at 25°

pH	Conditions [a]	k_{obs}/s^{-1}
5·8	*b*	0·11 ± 0·01
6·0	*b*	0·11
6·0	*c*	0·11
6·0	*d*	0·11
6·2	*b*	0·12
6·6	*b*	0·15
7·0	*b*	0·25
7·5	*b*	0·56
8·0	*b*	1·4
8·5	*e*	5·3
8·7	*e*	8·4
9·0	*e*	15·6
9·0	*f*	14 ± 1
9·25	*e*	30

[a] Substrate concentration is in the range 5 × 10^{-6}—1 × 10^{-4}M. Phosphate buffer, 5 × 10^{-2}M. [c] Phosphate buffer, 2·5 × 10^{-2}M. [d] Phosphate buffer, 0·1M. [e] Borax buffer, 1·25 × 10^{-2}M. [f] Borax buffer, 0·125M.

In solutions containing >0·1M-sodium hydroxide further reversible reactions occur. Spectra are in Figure 2. In the range 0·1—1·0M-base the absorption at 417 nm decreases in intensity and that at 480 nm increases. As the base concentration is further increased a band in the u.v., $\lambda_{max.}$ 290 nm, grows in intensity at the expense of the visible absorption. These changes are interpretable in terms of two equilibria giving adducts of the spiro-complex with one (A) and two (B) hydroxide ions respectively. Using the changes in absorption with base concentration we have calculated approximate values for the equilibrium constants K_2 and K_3 (defined as [B]/[A][OH^-]). It was necessary to make the assumption that, as with other dianionic species,[10] complex (A) will show only a single absorption maximum in the visible region. The value of K_2 is *ca.* 0·1 l mol^{-1} at 1M-base and increases to *ca.* 0·2 at 2M- and 0·5 l mol^{-1} at 3M-base. The value of K_3 is *ca.* 0·5 l mol^{-1} at 2M-base and increases with base concentration.

Kinetic measurements of the formation of adduct (A) from spiro-complex were made at 420 nm in solutions containing 0·3—0·5M-base. The value obtained for the first-order rate constant k_{obs}' is 0·9 ± 0·2 s^{-1}. In this case equation (6) is applicable but since $k_{-2} \gg k_2[OH^-]$ the observed value will be close to that of k_{-2}.

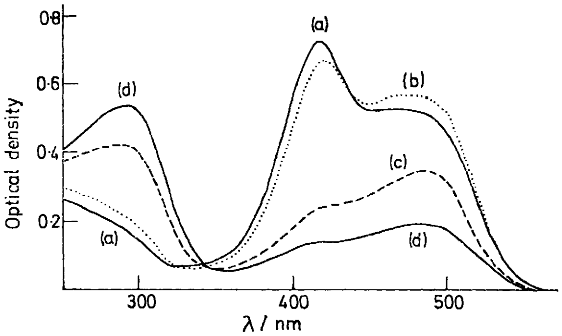

FIGURE 2 Spectra of 3·0 × 10^{-5}M-1-(2-hydroxyethoxy)-2,4,6-trinitrobenzene in water containing (a), 0·1; (b), 1·0; (c), 3·0; and (d), 4·0M-sodium hydroxide

1-(2-*Hydroxyethoxy*)-2,6-*dinitrobenzene*.—The visible spectrum of (VI) shows a maximum at 575 nm. Measurements of optical density are in Table 4. In dilute (<0·1M) sodium hydroxide solutions visible spectra show a maximum at 575 nm due to complex (VI). In more concentrated solutions there is also present a second interaction giving rise to species (A) with $\lambda_{max.}$ 297 nm (ε 2·2 × 10^4). In this case it was not possible to achieve complete conversion to spiro-complex in water and hence measure the extinction coefficient directly. However extrapolation, as before,[2] of data obtained in dimethyl sulphoxide–water mixtures where conversion to complex was complete gave ε (1·85 ± 0·2) × 10^4. Any inaccuracy in this value will affect the values of K_O in Table 4. The measured values of K_O are constant in dilute base solutions but appear to decrease in solutions containing >0·1M-base. One explanation for this decrease would be in terms of the denominator of equation (2). However examination of the system by stopped-flow spectrophotometry indicates that the true explanation is formation of a higher adduct (A) which has smaller absorption than the spiro-complex at 575 nm. Thus in these solutions the rapid formation

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[7] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970, 234.

[8] J. Murto, *Suomen Kem.*, 1965, **B38**, 255.

[9] M. R. Crampton and M. J. Willison, following paper.

[10] M. R. Crampton, *Adv. Phys. Org. Chem.*, 1969, 211; M. J. Strauss, *Chem. Rev.*, 1970, 667.

of spiro-complex is followed by a slower fading reaction which results in a decrease in visible absorption. The optical density measured with a conventional spectrophotometer corresponds to the value after attainment of the second equilibrium. The apparent decrease in values of K_C results mainly from the loss of absorption at 575 nm due to this second reaction. In this circumstance the value of K_2 is given by equation (7), where K_C' is the measured

$$K_2 = \left(\frac{1}{K_C'} - \right)\frac{1}{K_C}\frac{1}{[HO^-]^2} \qquad (7)$$

value and K_C is the value (in this case 1·30) in the absence of higher complex formation. Treatment of the data in Table 4 using equation (7) gives a value for K_2 of 0·6 ± 0·2 l mol^{-1}.

TABLE 4

Equilibrium and kinetic data for complex formation from 1-(2-hydroxyethoxy)-2,6-dinitrobenzene in water at 25°

10^5[Parent]$_{stoich}$/M	[NaOH]/M	Equilibrium [a] O.D.(575 nm)	K_C [b]/l mol^{-1}	k_{obs} [c]/s^{-1}	k_{obs}' [d]/s^{-1}
27	0·010	0·064	1·29	138 ± 3	
24	0·020	0·113	1·30		
21	0·030	0·147	1·31		
15	0·051	0·172	1·31	155 ± 8	
15	0·051 [e]	0·167	1·25	143 ± 4	
7·5	0·051	0·085	1·30		
9·0	0·071	0·141	1·31		
6·0	0·103	0·131	1·30	152 ± 5	
6·0	0·206	0·230	1·28	180 ± 8	0·105
6·0	0·31	0·30	1·21		
3·0	0·35			185 ± 8	0·110
6·0	0·41	0·36	1·16		
6·0	0·51	0·40	1·09	218 ± 8	0·115

[a] Measured with a Unicam SP 500. [b] Calculated using K_C = O.D.(575)/{[Parent]$_{stoich}$ × 1·85 × 10^4 − O.D.(575)}[HO$^-$]. [c] Rate of colour formation at 575 nm. [d] Rate of colour fading at 575 nm. [e] Made up to ionic strength 0·2M with NaCl.

An alternative approach to the calculation of K_2 is afforded by measurements by stopped-flow spectrophotometry. The two relaxation times corresponding to formation and fading of colour are sufficiently well separated to allow the determination of % transmittance (%T) both before and after attainment of the second equilibrium. For example in a solution containing 0·2M-base and 4·7 × 10^{-5}M-parent %T was 92·6 after attainment of the first equilibrium and increased by 0·24 ± 0·04% after attainment of the second equilibrium. This allowed the change in spiro-complex concentration Δ[Spiro] between the first and second equilibria to be calculated. The equilibrium concentration of diadduct could then be calculated using equation (8). A value of K_2 could then be calculated.

$$[\text{Diadduct}] = \Delta[\text{Spiro}](1 + 1/K_C[HO^-]) \qquad (8)$$

Measurements using a series of different base and substrate concentrations gave K_2 = 0·6 ± 0·2 l mol^{-1}, in good agreement with the value determined independently.

A plot, not shown, of the first-order rate constant for spiro-complex formation k_{obs} *versus* base concentration showed no obvious curvature [*cf.* equation (3)]. The intercept gives a value for k_{-1} of 137 ± 5 s^{-1}. The slope gives the value for $k_1K/(1 + K[HO^-])$. The absence of curvature indicates that $K < 1$ and that k_1K = 160 ± 20 l mol^{-1} s^{-1}.

The dependence of the rate constant for the fading reaction k_{obs}' on base concentration is given by equation (5). Using the known values for K_1K and K_2 values were calculated for k_2 (=6 × 10^{-2} l mol^{-1} s^{-1}) and k_{-2} (=0·1 s^{-1}).

There is also a much slower reaction producing 2,6-dinitrophenol, $\lambda_{max.}$ 430 nm.*

1-(2-*Hydroxyethoxy*)-2,4-*dinitrobenzene*.—The results in this case are qualitatively similar to those of the 2,6-dinitrobenzene isomer. The spiro-complex shows absorption in the visible region with $\lambda_{max.}$ 487 nm [ε (1·5 ± 0·3) × 10^4]. Measurements of optical densities in dilute solutions of base (<0·1M) gave a value for K_C of 0·050 l mol^{-1} which was independent of base concentration. Examination at 487 nm by stopped-flow spectrophotometry in solutions containing higher base concentrations showed that the very rapid formation of colour was followed by a slower fading reaction in which the absorption decreased to a slightly lower level and then remained constant for some time. This is interpreted as indicating the formation of a second adduct (A) having smaller visible absorption than the spiro-complex. For example in solutions containing 2·5 × 10^{-3}M-substrate and 0·56M-sodium hydroxide %T was 71 after establishment of the first equilibrium and increased by 0·32 ± 0·05% during attainment of the second equilibrium. These data allowed the determination of the equilibrium concentration of higher adduct *via* equation (8). A value of K_2 = 0·8 ± 0·2 l mol^{-1} was then calculated.

The rate of colour formation at 487 nm was very fast. Measurement by the stopped-flow technique at 0·5M and 0·8M-base gave a minimum value for k_{obs} of 620 s^{-1}. Hence $k_{-1} > 620$ s^{-1}. The rate constant for the fading reaction k_{obs}' had a value of 0·7 s^{-1} at 0·5M-sodium hydroxide giving an approximate value for k_{-2}.

A much slower irreversible reaction gave 2,4-dinitrophenol, $\lambda_{max.}$ 360 and 400 nm (shoulder).

DISCUSSION

The spectroscopic evidence for the formation in methanolic sodium methoxide of spiro-complexes rather than, for example, alkoxide adducts has been summarised previously.[2] Visible spectra in water containing dilute base correspond closely to those in methanol and the general similarities of the interactions indicate that in this solvent too we are observing spiro-complex formation. In addition ^{1}H n.m.r. spectra in water indicate formation of (V) from the parent glycol ether.

The values of equilibrium and rate constants for the formation in water of spiro-complexes from the parent

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* For a detailed study of this compound in water–dimethyl sulphoxide see C. F. Bernasconi and H. S. Cross, *J. Org. Chem.*, **1974**, **39**, 1054.

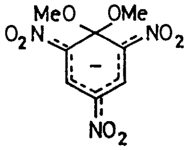
glycol ethers are collected in Table 5. The increase in values of KK_1 with increase in activation in the aromatic system results both from increases in values of Kk_1 and decreases in k_{-1}. Our measurements do not allow determination of the values of K, the equilibrium constant governing proton loss from the glycol side-chain. However for comparison the corresponding values for reaction of hydroxide ions with 2-methoxyethanol and 2-chloroethanol are 0·16 and 0·5 l mol^{-1} respectively.[11] It seems probable in view of the isolation of the hydroxy-proton from the aromatic system that the values of K for the four glycol ethers studied will not vary greatly so that the measured equilibrium constants will largely reflect differences in values of K_1.

TABLE 5

Equilibrium and kinetic data for spiro-complex formation in water at 25°

Complex	KK_1/l mol^{-1}	Kk_1/l mol^{-1} s^{-1}	k_{-1}/s^{-1}
(IV)	3×10^4	9×10^4	2·3
(V)	$1{\cdot}8 \times 10^7$	$1{\cdot}6 \times 10^6$	0·095
(VI)	1·3	$1{\cdot}6 \times 10^2$	137
(VII)	0·05	>30	>620

Perhaps the most significant fact deriving from these results is the high value of k_{-1} compared to the value for the corresponding process for 1,1-dimethoxy-Meisenheimer complexes. For example the value for k_{-1} of 0·095 s^{-1} for complex (V) can be compared with values of $5{\cdot}5 \times 10^{-4}$ and 6×10^{-4} s^{-1} reported[12,13] for the cleavage of methoxide ion from complex (VIII) in water.

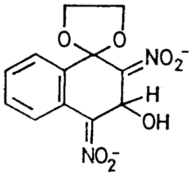


(VIII)

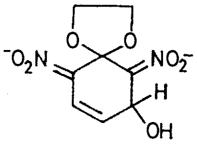
Similarly the value for k_{-1} for complex (IV) is three orders of magnitude larger than that ($1{\cdot}8 \times 10^{-3}$ s^{-1})[14] for methoxide loss from 1,1-dimethoxy-2,4-dinitronaphthalene in water. These results confirm our conclusion[2] reached previously from more limited data that the rate constants for ring opening of spiro-complexes are much higher than for base expulsion from non-cyclic analogues. This has particular significance in view of the use of spiro-complexes as models for the intermediates in nucleophilic aromatic substitution reactions.[3,4] A possible explanation for this difference is the release of ring strain on opening of the dioxolan ring of the spiro-complexes. A further effect indicating ease of ring opening of spiro-complexes is the observation[9] of general acid catalysis in their catalysed decomposition.

The values of KK_1 in water for complexes (IV), (VI), and (VII) are between five and ten times larger than the corresponding values in methanol,[2] this increase resulting from larger values of Kk_1 and smaller values of k_{-1}. Some of this increase may result from the larger values of K expected in water than in methanol.[15] It is also of interest to compare data for complex (VII) with those for the similarly activated complex (II). The equilibrium constant for formation of (II) is 5×10^{-3} l mol^{-1}, a factor of ten smaller than the value for (VII) while the value of k_{-1} (930 s^{-1}) for (II) is similar to that for (VII). These figures suggest that in general there may not be very large differences between complexes of these two types.

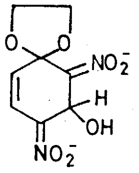
Formation of Higher Complexes.—There is evidence in more concentrated (>0·1M) sodium hydroxide solutions for further reversible interactions. In view of the many known examples[10] of the formation of hydroxide and alkoxide adducts from activated aromatic compounds it seems likely that the observed interactions are of this type. In the case of spiro-complexes (IV), (VI), and (VII) the results indicated only one further interaction with hydroxide ions so that the most probable structures for hydroxide adducts are respectively (IX), (X), and (XI). Two interactions are observed from complex (V) and likely structures for the interaction with one and two hydroxide ions are (XII) and (XIII) respectively. Unfortunately ^{1}H n.m.r. measurements which would unambiguously prove these structures were not successful due to solubility problems. However as would be expected for structures having no delocalised negative charge, (IX)—(XI) and (XIII) show absorption in the u.v. region of the spectrum, at about 300 nm, and not in the visible region. The absence of visible absorption in the spectra of these complexes rules out the possibility that they might arise from hydroxide addition to the parent glycol ethers rather than to the spiro-complexes. Complex (XIII) is, to our knowledge, the first example of an adduct formed by addition of three basic groups to a



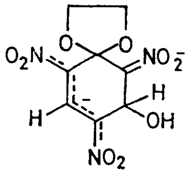
(IX)



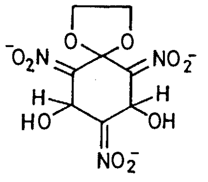
(X)



(XI)



(XII)



(XIII)

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benzenoid ring, although multi-charged adducts have previously been postulated.[16]

During measurements of spiro-complex formation in dilute methanolic sodium methoxide the formation of higher complexes was not observed.[2] However similar interactions would presumably also be observed in methanol at sufficiently high sodium methoxide concentration. Nevertheless it is noteworthy that there appears to be a special propensity for the formation of diadducts in water.[17] For example *NN*-dimethylpicramide gives an adduct by addition of two hydroxide ions in water containing dilute sodium hydroxide [18] and several examples have been reported of the formation of diadducts with sodium sulphite in water.[18,19] The ready formation of these complexes in water may result from the ability of this polar solvent to stabilise multi-charged species. In addition complexes (IX)—(XIII) contain negative charges localised on nitro-groups. It has previously been suggested [17] that these will be well solvated by water.

The equilibrium and rate constants associated with formation of the hydroxide adducts are summarised in Table 6. These values were obtained in solutions containing 0·1—1·0M-sodium hydroxide and are not therefore thermodynamic values. They should be regarded as giving the orders of magnitude of the parameters quoted rather than precise values. However, it is notable that the value of the equilibrium constant K_2 for formation of the hydroxide adduct (XII) from the trinitro-substituted compound is smaller than the values for K_2 for hydroxide addition to the dinitro-substituted compounds. This may be associated with the very high stability of the spiro-complex (V).

TABLE 6

Collected data for formation of hydroxide adducts from spiro-complexes

Adduct	$\lambda_{max.}$/nm	K_2 [a]/l mol^{-1}	k_2/l mol^{-1} s^{-1}	k_{-2}/s^{-1}
(IX)	275, 300	1·0	0·04	0·04
(X)	297	0·6	0·06	0·1
(XI)		0·8	0·5	0·7
(XII)	*ca.* 500	0·1	0·09	0·9
(XIII)	290			

[a] Equilibrium constant defined as [Hydroxide adduct]/[Spiro][OH$^-$].

In the case of all four compounds studied the ultimate reaction product resulted from substitution of glycol by hydroxide to give the respective substituted phenol or naphthol.[8] Reaction presumably occurs by straightforward S_NAr substitution in the parent glycol. There was no evidence for the build-up of a reaction intermediate.

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[4/997 *Received*, 21*st May*, 1974]

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