# The Effect of Crown Ethers on the Reactivity of Alkoxides. Part 2.[1] The Reaction of Potassium Isopropoxide and 2,4-Dinitrohalogenobenzenes in Propan-2-ol–Benzene [2]

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The reaction between potassium isopropoxide and 1-chloro- (3) or 1-iodo- (4) 2,4-dinitrobenzene has been studied in propan-2-ol–benzene (1 : 1) with and without added crown ethers dicyclohexano-18-crown-6 (1), and 18-crown-6 (2). Substantial amounts of 2,4-dinitrophenol are formed upon addition of the crown ethers together with the expected 1-isopropoxy-2,4-dinitrobenzene derived from normal nucleophilic substitution. The kinetic order in base in the presence of the potassium complexing agents is less than unity. The radical anion of 1-chloro-2,4-dinitrobenzene has been identified in the system containing (1). These results are explained in terms of the intervention of a nucleophilic-radical reaction pathway of the $S_{RN}1$ type leading to the phenol.

WE discussed in a previous paper [1] the changes in the reactivity of potassium methoxide toward 1-chloro-2,4-dinitrobenzene in methanol–benzene mixtures upon addition of the crown ethers eicosahydrodibenzo-[b,k][1,4,7,10,13,16]hexaoxacyclo-octadecin [dicyclohexano-18-crown-6, (1)] and 1,4,7,10,13,16-hexaoxacyclo-octadecane [18-crown-6 (2)]. There is practically no
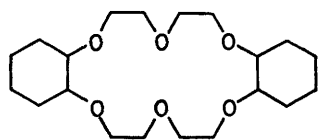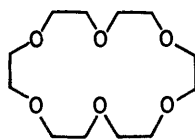

(1)   **(2)**

change in reactivity in solvents containing <50% benzene, whereas an increase in rates of reaction is observed in solvents containing a higher percentage of benzene, which depends on the [crown] : [alkoxide] ratio (the maximum increase is observed for a ratio slightly larger than unity) and on the amount of benzene in the solvent mixture (a *ca.* 300-fold increase in rate coefficients was observed in 99% benzene).[1] We have extended this work to the propan-2-ol–benzene system, and have found quite different results which we report and discuss now.

RESULTS

We have selected as solvent for this study a 1 : 1 mixture (v/v) of propan-2-ol and benzene. As in the previous study [1] the complexing agents for potassium were the crown ethers (1) [3] and (2).[4] Since both crown ethers act as a very strong complexing agent for potassium in pure alcohols,[5] we expect even larger complexation constants ($K > 10^6$) in the propan-2-ol–benzene mixed solvent used in this study.

Reaction of Potassium Isopropoxide with 1-Halogeno-2,4-dinitrobenzenes.—This reaction was studied at 25 °C using the chloro- (3) and iodo- (4) derivatives. The reaction yields quantitatively the expected 1-isopropoxy-2,4-dinitrobenzene (5), as shown by u.v. spectroscopy after completion of the reaction. The kinetics were evaluated by following the changes in the u.v. spectra or by titrating the I⁻ formed. The values derived in this way for the rate constants are

collected in Table 1. For both substrates the kinetic law is second order, first order in both the halogenobenzene and the base concentration.
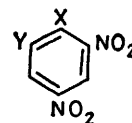
(3) X = Cl, Y = H	(7) X = Cl, Y = NO₂
(4) X = I, Y = H	(8) X = MeO, Y = H
(5) X = OPrⁱ, Y = H	(9) X = MeO, Y = NO₂
(6) X = OH, Y = H	

Effect of Crown Ethers.—The addition of either (1) or (2) to solutions of 1-halogeno-2,4-dinitrobenzenes causes a dramatic change in their reaction with potassium isopropoxide in propan-2-ol–benzene (1 : 1). The formation of the ether (5) is accompanied by comparatively large amounts of 2,4-dinitrophenoxide ion, which is the major product in the reaction of the iodo-derivative. Moreover, the kinetic order in the base concentration appears to be less than unity. The kinetic data, obtained from u.v. measurements, are collected in Table 2 for (3) and in Table 3 for (4). The reaction of (3) was followed by monitoring the absorption at 300 nm, the wavelength corresponding to the absorption maximum for the product (5). Similar results were obtained by following the reaction at 412 nm, the wavelength of the absorption maximum for potassium 2,4-dinitrophenoxide in propan-2-ol–benzene in the presence of crown ethers. The reactions of (4) were followed at 412 nm. The relative amounts of (5) and (6) formed were obtained

TABLE 1

Reactions of 1-chloro- (3) and 1-iodo- (4) 2,4-dinitrobenzenes with potassium isopropoxide [a]

10⁴[ArX]/M	10²[PrⁱOK]/M	10³$k_{obs.}$/s⁻¹	10²k_2/ l mol⁻¹ s⁻¹
Compound (3) [b]			
0.99	0.50	0.457	9.07
0.99	1.00	0.893	8.93
0.99	1.51	1.31	8.72
Compound (4) [c]			
10.6	2.04	1.79	8.80
21.4	2.94	2.55	8.60
20.8	3.05	2.68	8.70

[a] In PrⁱOH–C₆H₆ (1 : 1), at 25 °C. [b] Monitored by u.v. spectroscopy. [c] Monitored by titration of the I⁻ formed.

TABLE 2

Reaction of 1-chloro-2,4-dinitrobenzene (3) (0.5—1 × 10^{-4}M) with potassium isopropoxide in the presence of the crown ethers (1) and (2) [a]

$10^3[Pr^iOK]/$ M	$10^3[crown]/$ M		$10^3 k_{obs.}/$ s^{-1}	% ArOR [b]	% ArO⁻ [c]
4.10	(1)	8.51	3.73	52.6	47.4
11.6	(1)	22.8	9.51	56.5	43.5
17.4	(1)	39.2	12.2	61.4	38.6
5.3 [d]	(1)	10.4 [d]	0.82 [d]	57.6 [d]	42.4 [d]
0.9	(2)	1.29	1.25	39.7	60.3
1.8	(2)	2.04	1.29	46.7	53.3
1.86	(2)	7.44	2.20	41.5	58.5
2.7	(2)	3.61	2.43	49.7	50.3
2.7	(2)	3.44	2.81	53.4	46.6
5.4	(2)	6.14	3.71	51.7	48.3
8.1	(2)	11.3	5.37	57.0	43.0
10.9	(2)	12.8	8.44	65.5	34.5

[a] In $Pr^iOH-C_6H_6$ (1 : 1) at 25 °C. [b] % of 2,4-dinitrophenyl isopropyl ether formed, as evaluated by u.v. spectroscopy. [c] % of 2,4-dinitrophenoxide ion formed, as evaluated by u.v. spectroscopy. [d] The solvent contains 0.96M of water.

TABLE 3

Reaction of 1-iodo-2,4-dinitrobenzene (4) (4.73—5 × 10^{-5}M) with potassium isopropoxide in the presence of 18-crown-6 (2) [a]

$10^3[Pr^iOK]/$ M	$10^3[crown]/$ M	$10^3 k_{obs.}/$ s^{-1}	% ArOR [b]	% ArO⁻ [c]
1.51	6.86	0.998	17.8	82.2
2.44	5.22	1.41	19.1	80.8
3.02	9.34	2.03	37.4	62.6
3.66	8.56	2.30	27.8	72.1
7.30	10.3	5.08	39.2	60.8
11.7	25.5	5.76	35.9	64.1
14.6	32.0	7.68	43.6	56.6

[a] In $Pr^iOH-C_6H_6$ at 25 °C. [b] % of 2,4-dinitrophenyl isopropyl ether formed, as evaluated by u.v. spectroscopy. [c] % of 2,4-dinitrophenoxide ion formed, as evaluated from the u.v. spectroscopy.

from the absorbances at 300 and 412 nm after the disappearance of the halogenobenzene. However, (5) may react to give (6) and although in our system this reaction is slower than that leading directly to (6) (see later), it does lead to difficulty in determining the final absorbance needed to evaluate the rate constants and the relative amounts of (5) and (6). This is reflected in some scatter of the data in Tables 2 and 3.

There are two obvious routes which could explain the formation of (6) : (i) base-induced elimination of 2,4-dinitrophenol from (5); or (ii) reaction of the halogenobenzenes with adventitious water in the solvent. Both hypotheses can be checked experimentally. The reaction between (5) (0.5 × 10^{-4}M) and potassium isopropoxide (6.9 × 10^{-3}M) to give (6) was studied in propan-2-ol–benzene (1 : 1) in the presence of the crown ether (1) (1.6 × 10^{-2}M). The second-order rate coefficient obtained ($k_2 = 6.9 \times 10^{-3}$ l mol⁻¹ s⁻¹) shows that this reaction is about 100-times slower than that leading from the halogenobenzenes to (5) and (6) (cf. Tables 2 and 3). It is also possible to monitor the transformation (5) ⟶ (6) directly in the solutions in which (5) and (6) are formed from the halogenobenzenes. When this was done, e.g. as in 2nd entry in Table 2, the same value of 6.9 × 10⁻³ l mol⁻¹ s⁻¹ was obtained for the second-order rate constant for the elimination reaction. In the 4th entry in Table 2, we deliberately added water (0.96M) to the reaction solution. Although the overall pseudo-first-order rate coefficient is decreased, there is practically no

change in the amount of 2,4-dinitrophenol formed. In the light of these results, the foregoing routes (i) and (ii) to explain the formation of (6) must be dismissed.

We have also searched for other evidence that (5) and (6) are both primary reaction products. The reaction of 1-chloro-2,4-dinitrobenzene (3) and potassium isopropoxide in the presence of the crown ether (2) (Table 2, 7th entry) was monitored at 300 and 412 nm. From the known absorbance coefficients of (3), (5), and (6) and from the experimental rate coefficient, we calculated (see Experimental section) the concentration of the ether and of the phenol during the reaction. The data obtained are shown in Figure 1. The fact that the concentration ratio [(5)] : [(6)] remains practically constant during the reaction is further proof that the two products derive from independent reaction pathways
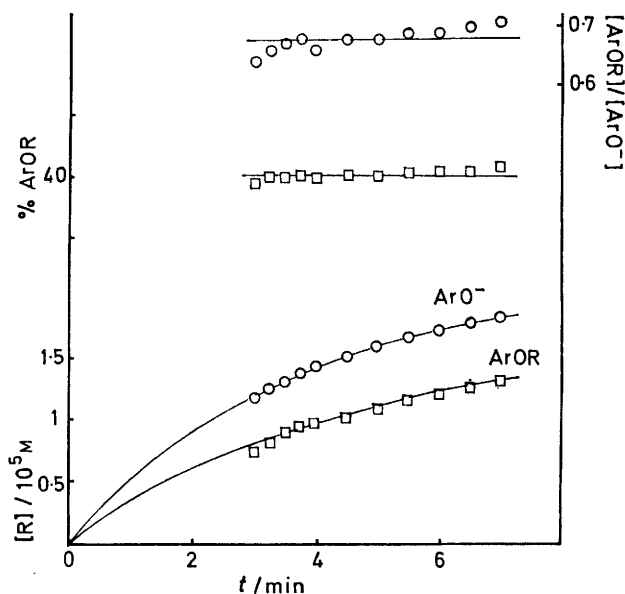

FIGURE 1 1-Isopropoxy-2,4-dinitrobenzene (ArOR, □) and 2,4-dinitrophenol (ArO⁻, ○) formation during the reaction of 1-chloro-2,4-dinitrobenzene (3) (4.78 × 10^{-5}M) and Pr^iOK (1.86 × 10^{-3}M) in the presence of 18-crown-6 (2) (7.44 × 10^{-3}M) in $Pr^iOH-C_6H_6$ (1 : 1)

The overall pseudo-first-order rate constants ($k_{obs.}$) were dissected into that for formation of 1-isopropoxy-2,4-dinitrobenzene ($k_{DNIP} = k_{obs.} \times ArOR\%$) and that for formation of 2,4-dinitrophenoxide ($k_{DNP} = k_{obs.} \times ArO^-\%$). Plots of log k_{DNIP} and log k_{DNP} vs. log $[Pr^iOK]$ are shown in Figures 2 and 3 for the reaction in the presence of the crown ether (2) for the chloro-(3) and iodo-(4) derivatives, respectively. The slopes of these plots are: (3), k_{DNIP} 0.94, k_{DNP} 0.56; (4), k_{DNIP} 1.25, k_{DNP} 0.76. Although the complexity of the evaluation of the rate coefficients does not allow very precise results to be determined, the reaction leading to the ether seems to have an approximately first-order dependence on the base concentration, whereas a fractional order in base is found for the reaction leading to the phenoxide. The second-order rate coefficients for the formation of 1-isopropoxy-2,4-dinitrobenzene (5) in the presence of the crown ether (2) are ca. 0.43 and ca. 0.17 l mol⁻¹ s⁻¹ for the 1-chloro- and 1-iodo-2,4-dinitrobenzene, (3) and (4), respectively. The rates of formation of 2,4-dinitrophenoxide from the two halogenobenzenes are
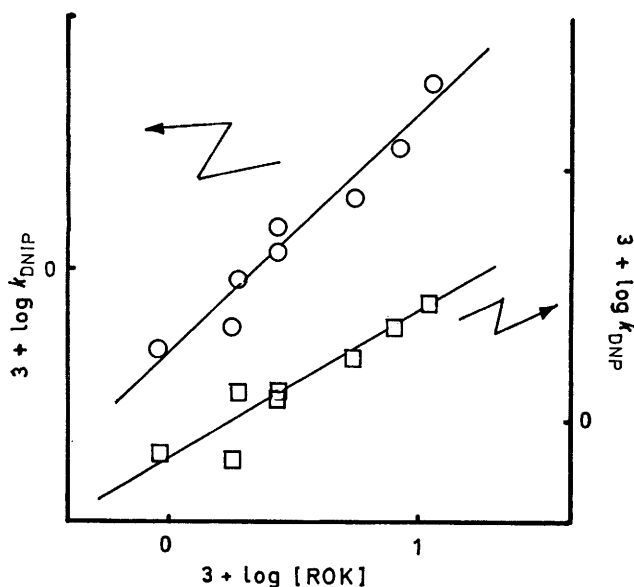
Figure 2 Dependence on Pr^{i}OK concentration of the pseudo-first-order rate coefficients for the formation of 1-isopropoxy-2,4-dinitrobenzene (k_{DNIP}) and 2,4-dinitrophenol (k_{DNP}) from 1-chloro-2,4-dinitrobenzene in Pr^{i}OH–C$_6$H$_6$ (1:1) in the presence of 18-crown-6 (2)

practically the same: rate coefficients 6.03 × 10^{-4} and 2.69 × 10^{-3} s^{-1} for the chloro and 6.03 × 10^{-4} and 2.63 × 10^{-3} s^{-1} for the iodo-derivative with [Pr^{i}OK] = 1 × 10^{-3} and 1 × 10^{-2}M, respectively.

The fractional kinetic order in base concentration suggests the intervention of chain mechanisms for the reaction leading to the phenoxide. Further information on this point was obtained from the following e.s.r. experiments. A solution of 1-chloro-2,4-dinitrobenzene (3) (4 × 10^{-2}M) and potassium isopropoxide (3.5 × 10^{-2}M) gave no e.s.r.
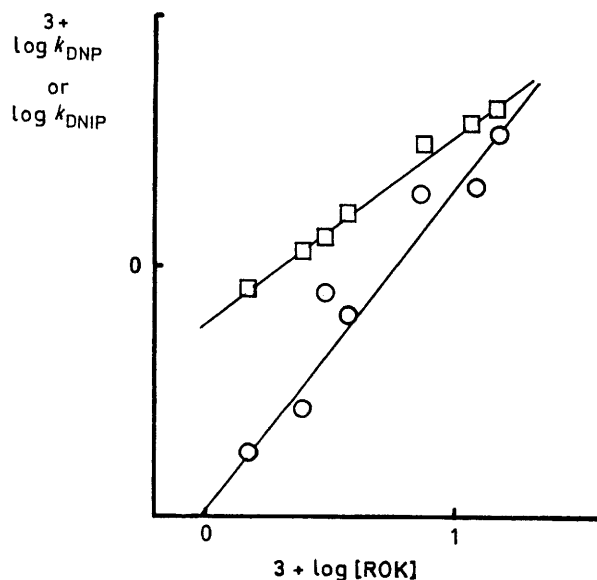
Figure 3 Dependence on Pr^{i}OK concentration of the pseudo-first-order rate coefficients for the formation of 1-isopropoxy-2,4-dinitrobenzene (k_{DNIP}) and 2,4-dinitrophenol (k_{DNP}) from 1-iodo-2,4-dinitrobenzene (4) in Pr^{i}OH–C$_6$H$_6$ (1:1) in the presence of 18-crown-6 (2)

signal at 25 and 3 °C. However, addition of the crown ether (1) (4 × 10^{-2}M) causes the appearance of a signal at 25 °C which is well defined at 3 °C. It consists of a main triplet, attributed to hyperfine interaction with a nitrogen nucleus (a_H 10.1 G). Each line is further split into triplets of doublets by two approximately equivalent protons (a_H 3.6 G) and a third proton (a_H 1.19 G). A small splitting of about 0.4 G, attributed to the nitrogen of the second nitro-group is not clearly resolved. The spectrum is consistent with the presence of a radical anion derived from the 1-chloro-2,4-dinitrobenzene.[6] The signal at 3 °C reaches a maximum intensity ca. 10 min after mixing and disappears in ca. 30 min. Under the same conditions the 1-iodo-2,4-dinitrobenzene gives an e.s.r. signal which, however, is not well resolved.

Addition of di-t-butyl nitroxide (DTBNO), which may act as a radical scavenger,[7] has a small effect on rates even when its concentration is about double that of the aromatic component. For instance, the reaction between 1-iodo-2,4-dinitrobenzene (4) (9.46 × 10^{-5}M) and potassium isopropoxide (3.09 × 10^{-3}M) in the presence of 18-crown-6 (2) gives, with DTBNO (3.39 × 10^{-4}M), k_{DNIP} = 5.4 × 10^{-4} s^{-1} and k_{DNP} = 8.8 × 10^{-4} s^{-1} (the values extrapolated from Figure 3 for the reactions without DTBNO are 5.3 × 10^{-4} and 1.4 × 10^{-3} s^{-1}, respectively).

Finally, the electrochemical behaviour of 1-chloro-2,4-dinitrobenzene (3), 1-chloro-2,4,6-trinitrobenzene (7), 1-methoxy-2,4-dinitrobenzene (8), and 1-methoxy-2,4,6-tri-
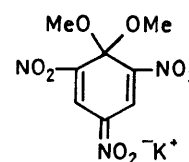
(10)   (11)

nitrobenzene (9), and of the derived Meisenheimer complexes (10) and (11), has been briefly examined using potassium perchlorate in dimethyl sulphoxide as electrolyte. The results are in Table 4.

Table 4

Electrochemical behaviour of nitroaromatic compounds [a]

Compound	Oxidation potentials (E_{pa}) [b]	Reduction potentials (E_{pc}) [b]
(3)	c	—1.09,[d] —1.43,[e] —1.80
(7)	c	—0.84, —1.48
(8)	c	—1.28,[d] —1.55,[e] —1.83
(9)	c	—0.94, —1.42
(10) [f]	+0.57, +0.17, —0.18	—1.58,[g] —1.85
(11)	+0.95	—1.44,[g] —1.59

[a] At 25 °C in DMSO with KClO$_4$ (0.2M) and a platinum electrode. [b] The anodic (E_{pa}) and cathodic (E_{pc}) peak potentials were determined (in volts) vs. an Ag–AgNO$_3$ (0.1M in DMSO) electrode at a sweep rate of 0.4 V s^{-1}. [c] No oxidation peaks detectable before decomposition of the electrolyte (ca. +0.95 V). [d] Reversible formation of the radical anion. [e] Reversible formation of the dianion. [f] This compound decomposes slowly in the DMSO solution with a half-life of ca. 2 h. A new voltammetric peak is then found at —1.27 V, probably due to the reversible reduction of (8). [g] Reversible formation of the radical dianion. In the case of (11) the radical dianion is persistent enough to be detected by e.s.r. spectroscopy when it is produced by in situ electroreduction in the cavity of an e.s.r. spectrometer at room temperature.

The commercial platinum electrode used had far from an ideal planar geometry, since we also found a relatively large peak separation of 80—100 mV in the case of reversible electrode processes. Nevertheless, we believe that the-measurements reported in Table 4 may provide an indication of the ease of reduction or oxidation of the compounds studied.

DISCUSSION

The reaction of potassium isopropoxide and 1-halogeno-2,4-dinitrobenzenes gives, in propan-2-ol–benzene (1 : 1 v/v), 1-isopropoxy-2,4-dinitrobenzene (5), the expected product for a nucleophilic aromatic substitution. The addition of crown ethers, however, induces the formation, together with (5), of substantial amounts of 2,4-dinitrophenol. The phenol is not derived from (5) via a base-catalysed elimination, since this reaction is more than 100 times slower than the direct formation of phenol from 1-halogeno-2,4-dinitro-benzenes, nor is it formed by adventitous water, since the deliberate addition of water (0.96M) does not change the relative amounts of ether and phenol formed (see Table 2). The overall rates for the reactions of 1-chloro- and 1-iodo-2,4-dinitrobenzene have been dissected, after evaluation of the relative ether and phenol concentrations, into the specific rates for the two processes: k_{DNIP} for the reaction leading to 1-isopropoxy-2,4-dinitrobenzene and k_{DNP} for the reaction leading to the 2,4-dinitrophenol. For both halogenobenzenes studied, an approximate first-order dependence on the base concentration was found for the k_{DNIP} rate coefficient, whereas the k_{DNP} rate coefficient appears to have a fractional dependence on the concentration of potassium isopropoxide. Moreover, the formation of the phenol is accompanied by the appearance of an e.s.r. signal which, in the case of 1-chloro-2,4-dinitrobenzene, has been clearly identified as that of the radical anion derived from the halogenonitrobenzene. We therefore believe that the usual nucleophilic aromatic substitution (S_NAr), leading to the ether, is accompanied in this case by an electron-transfer process leading to the phenol. For the sake of simplicity we discuss separately the nucleophilic aromatic substitution and the electron transfer induced reaction.

Nucleophilic Aromatic Substitution.—Inspection of Table 1 shows that the second-order rate coefficients for the reaction of 1-chloro-(3) and 1-iodo-2,4-dinitro-benzene (4) with potassium isopropoxide in propan-2-ol–benzene (1 : 1) are almost equal [8.91×10^{-2} and 8.70×10^{-2} mol^{-1} s^{-1} for (3) and (4), respectively]. The values reported [8] for the reactions with sodium methoxide in methanol at 25 °C are 2.96×10^{-2} and 5.76×10^{-3} l mol^{-1} s^{-1} for (3) and (4), respectively. Reactivity in nucleophilic aromatic substitution is a complex function of the substrate, nucleophile, and solvent.[9] On the basis of the qualitative Hughes–Ingold solvent theory,[10] we expect, as found, an increase in rates going from a more polar (MeOH) to a less polar (Pr^{i}OH–C$_6$H$_6$) solvent, since the transition state for an S_NAr reaction is less

polar than the reactants. We note that, in changing from methanol to propan-2-ol–benzene, we are also changing to a more nucleophilic, and hence more reactive [11] and less selective,[10] lyate ion. The decrease in the $k_{\text{Cl}}/k_{\text{I}}$ ratio may be due to the greater polarizability of the isopropoxide ion [9] and/or to different solvent effects on the aryl halides and on the transition states. This latter point could in principle be checked by measuring the activity coefficients for the transfer from methanol to propan-2-ol–benzene of the aryl halides (3) and (4), and of the Meisenheimer complexes (10) and (11), which may be taken as models for the transition states.[12] In practice, however, these data, the collection of which would require solubility measurements of saturated solutions, cannot be obtained owing to the large solubility of (3) and (4) in alcohol–benzene mixtures, and to the easy decomposition of the Meisenheimer complexes in non-basic solutions. We are not able therefore to assess the relative importance of the above factors in changing the $k_{\text{Cl}}/k_{\text{I}}$ ratio.

The addition of crown ethers causes an increase in the rates of formation of the isopropyl ether (5) (k_{DNIP}) from both halogenobenzenes. This increase is, however, larger in the case of the 1-chloro-compound (3) than in the case of the 1-iodo-compound (4) [k''_{DNIP} for (3) = 0.43; for (4) = 0.17 l mol^{-1} s^{-1}, for the reactions in the presence of 18-crown-6 (2)]. The *ca.* 5-fold increase in rates observed for compound (3) is of the expected order of magnitude on the basis of the data reported for the reactions of the same substrate with potassium methoxide in several methanol–benzene mixtures in the presence of crown ethers.[1] [If we assume that there is a linear relationship between dielectric constants and molar fraction, we estimate that the dielectric constants for the solvent mixtures Pr^{i}OH–C$_6$H$_6$ (1 : 1) and MeOH–C$_6$H$_6$ (17.5 : 82.5) are similar. For the reaction of (3) with MeOK in the latter solvent, interpolation of the published data leads to the prediction that the addition of di-cyclohexano-18-crown-6 (1) will cause a 4.6-fold increase in the rate coefficient.] The different effect observed upon addition of crown ether on the rates of reaction of (3) and (4) shows that factors other than the RO$^-$K$^+$ ion pair separation are also responsible for the rate increase. Given the very large complexation constant of the crown ethers for the potassium ion, the most important effect of their addition will result from the substitution of the K$^+$ cation with the larger crown–K$^+$ complex. Therefore, the kinetic effect may be treated as a type of salt effect and we may write to Brönsted–Bjerrum rate equation for the reaction between an alkoxide (RO$^-$) and a 2,4-dinitrohalogenobenzene (Ar) as in equation (1),

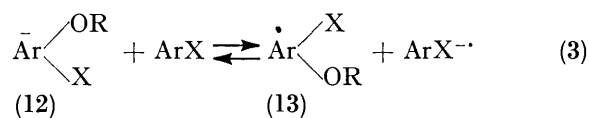$$k_{\text{s}} = k_0 f_{\text{Ar}} f_{\text{RO}^-}/f_{\ddagger} \tag{1}$$
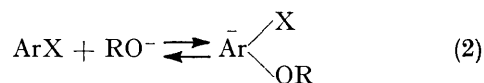
where k_{s} and k_0 are the rate constants for the reaction with and without crown, respectively, and the f's are the activity coefficients (*i.e.* the overall energy of transfer from the solvent containing the potassium salt to that containing the crown complex) for the indicated reactant and transition state ($\ddagger$). It is unfortunately impossible

to evaluate the f parameters of equation (1) (see above), and therefore discussion of the effect of the crown ethers must be qualitative. Although most of the rate increase should result from an increase in the alkoxide ion activity coefficient,[1] the different effects on the reaction rates of the iodo- and chloro-derivatives indicate that the activity coefficients of the substrate and transition state are also affected by the addition of crown ether. This is in agreement with Crampton's results [13] on the interactions of crown ethers with Meisenheimer complexes and with the salt effect reported by Bunton and Robinson [14] on the activity coefficients of 1-chloro-2,4-dinitrobenzene in aqueous solutions. We conclude this section by recalling the recommendation of Bunton and Robinson [14] that great care must be exercised in trying to interpret kinetic salt effects since they result from the complex, and as yet not completely understood, influence of anions and cations on the activity of the neutral and charged species involved in the reaction.

Electron Transfer Processes.—Electron transfers from anions to nitrobenzenes are well known.[15] Russell and Janzen [16] have reported the formation of radical anions in t-butyl alcohol and dimethyl sulphoxide solutions for several nitro-substituted benzenes in the presence of potassium t-butoxide. More recently Relles *et al.*[17] have obtained [13]C n.m.r., [1]H n.m.r., and e.s.r. evidence that electron transfer processes occur in the reaction between 4-methylphenoxide and di-isobutyl 3-nitrophthalate in NN-dimethylformamide. Moreover, the reduction of nitrobenzenes by alkoxides in alcohols, a reaction which must involve electron transfer processes, is well documented.[18] It is therefore not surprising that in the system potassium isopropoxide–propan-2-ol–benzene such electron transfers processes may also occur, as shown by our e.s.r. experiments. In our reaction we have two anions which in principle may act as electron donor: the alkoxide and the Meisenheimer complex which is formed as an intermediate in the nucleophilic aromatic substitution.[9a,12] The lack of measurements on the oxidation potential of the two anions does not allow a clear-cut choice between them. We have, however, carried out electrochemical experiments in dimethyl sulphoxide (DMSO), a solvent in which nitroaromatic radical anions have been observed and studied.[16] In this solvent, no oxidation peaks for potassium methoxide or butoxide appear at potentials more negative than that for decomposition of the electrolyte (*ca.* +0.95 V). However an irreversible oxidation peak is found at +0.57 V for (10) and at +0.95 V for (11), the two Meisenheimer complexes choosen as model compounds. The difference between the oxidation potentials of the Meisenheimer complexes (10) and (11) and the reduction potentials of the parent methoxy-compounds (8) or (9), or their chloro analogues (3) or (7), is quite large (>1.5 V, see Table 4), but the significance of this value is low, since the oxidation potentials refer to irreversible heterogeneous charge transfers and allow no calculation of equilibrium constants for the homogeneous charge transfers between the Meisenheimer
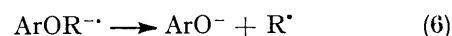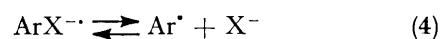
complexes (10) or (11) and compounds (3) and (7)—(9). However, the fact that the Meisenheimer complex is indeed oxidized at lower potentials than the alkoxides makes it a likely choice as the electron source in our reaction, as well as in the other cases in which radical anions have been observed in basic solutions of nitrobenzenes.

We may therefore write the first steps of our reaction as in equations (2) and (3). The Meisenheimer complex

$$ArX + RO^- \rightleftharpoons \bar{Ar}{\diagup}^{X}_{\diagdown OR} \qquad (2)$$

$$\bar{Ar}{\diagup}^{OR}_{\diagdown X} + ArX \rightleftharpoons \dot{Ar}{\diagup}^{X}_{\diagdown OR} + ArX^{-\cdot} \qquad (3)$$
$$\quad (12) \qquad\qquad\qquad (13)$$

(12) may also evolve to give the normal product for a nucleophilic aromatic substitution. In fact, this happens in the absence of crown ethers. However, the addition of a complexing agent for the potassium makes it possible to separate the ion pairs formed between the Meisenheimer complex and the cation.[13] The unshielded negative charge of the complex makes it more reactive and more prone to lose one electron.

Once the radical anion of the halogenobenzene is formed, its fate may be described following a variant of the general scheme proposed by Bunnett *et al.*[19] and labelled $S_{RN}1$ [equations (4)—(6)]. Steps (4) and (5) are

$$ArX^{-\cdot} \rightleftharpoons Ar^{\cdot} + X^- \qquad (4)$$

$$Ar^{\cdot} + RO^- \rightleftharpoons ArOR^{-\cdot} \qquad (5)$$

$$ArOR^{-\cdot} \longrightarrow ArO^- + R^{\cdot} \qquad (6)$$

now well documented.[20] It is also known that radical anions of aryl ethers, as formed for instance by reaction of the aryl ether with alkali metals, may fragment to give the phenoxide ion and an alkyl radical.[21] The alkyl radical may establish a chain process by reacting with ArX and RO$^-$ to form ArX$^{-\cdot}$, propene, and propan-2-ol. Alternatively, R$^{\cdot}$ may regenerate the Meisenheimer complex through electron exchange with (13). Disproportionation of the alkyl radical would, on the other hand, yield propene and propane as end products for the alkyl unit. In our hands, the only aliphatic product isolated is, in fact, propene.

In conclusion, we have shown that electron transfer processes may compete with the S_NAr reaction pathway under conditions for nucleophilic aromatic substitutions. We must add, however, a word of caution that, as shown, this competition will be important, and possible to investigate, only under unusual experimental conditions.

EXPERIMENTAL

Solvents and Materials.—Propan-2-ol, methanol, benzene, and dimethyl sulphoxide were reagent-grade commercial products and were purified by using standard procedures.[22] The 1 : 1 solvent mixture was prepared by mixing equal volumes of thermostatted (25 °C) propan-2-ol and benzene.

1-Chloro-2,4-dinitrobenzene (3), m.p. 51—52 °C (lit.,[23] m.p. 52 °C), and 2,4-dinitrophenol (6), m.p. 114—115 °C (lit.,[23] 114 °C) were recrystallized from ethanol; 1-methoxy-2,4-dinitrobenzene (8) and 1-isopropoxy-2,4-dinitrobenzene (5) were obtained by the reaction of (3) with the appropriate sodium alkoxide in the parent alcohol, and recrystallized from the alcohol: (8) m.p. 86—87 °C (lit.,[24] 87—88 °C); (5) m.p. 53—54 °C (lit.,[25] 53.4—53.6 °C); 1-iodo-2,4-dinitrobenzene (4) was synthesized from (3) following a reported procedure,[26] m.p. 89—90 °C, [from ligroin–benzene (3 : 1)]; 1-methoxy-2,4,6-trinitrobenzene (9) was synthesized following the procedure described by Damschroder and Shiner,[27] m.p. 50—51 °C (from MeOH). The two Meisenheimer complexes (10) and (11) were synthesized following the procedures described respectively by Crampton and Gold[28] and Byrne et al.[29] Eicosahydrodibenzo[b,k][1,4,7,10,13,16]-hexaoxacyclo-octadecin (1) was synthesized according to the procedure reported by Pedersen.[3] The mixture of isomers with m.p. 50—52 °C was used throughout.[1] 1,4,7,10,13,16-Hexaoxacyclo-octadecane (2) was synthesized and purified according to the procedure reported by Gokel et al.[4] Di-t-butyl nitroxide (DTNO) was obtained following the procedure described by Hoffmann et al.[7]

Product Identification.—1-Iodo-2,4-dinitrobenzene (4) (2.9 g) in propan-2-ol–benzene (20 ml; 1 : 1 v/v) was added to a stirred solution of 18-crown-6 (2) (3.1 g) and potassium isopropoxide in the same solvent mixture (100 ml; 1.35M in base). The resulting solution was stirred under nitrogen for 10 min, the purge gas being bubbled through a solution of bromine (0.7 g) in carbon tetrachloride (100 ml). The reaction solution was neutralized with dilute sulphuric acid, solvent distilled off under reduced pressure, and the residue chromatographed (silica gel; light petroleum–diethyl ether, 1 : 1 and then methanol). Elution with light petroleum–ether led to the recovery of unchanged (4) (1 g) and 1-isopropoxy-2,4-dinitrobenzene (5) (1 g), as identified by comparison (m.p. and mixed m.p.) with authentic samples. Elution with methanol led to the recovery of a mixture of compounds (2) and (6) (1 g; ca. 1 : 1 as shown by g.l.c. on a TENAX column). On the basis of the amount of (4) which had reacted the amounts of (5) and (6) recovered corresponded to yields of 68 and 34%, respectively. Extrapolation of the results in Figure 3 for potassium isopropoxide solution 0.112M leads to relative yields of (5) and (6) of 65 and 35%, in good agreement with the results of the preparative scale experiment.

The solution of bromine in carbon tetrachloride through which the purge gas had been bubbled was washed with sodium thiosulphate (10% in water) and water, and then dried ($CaCl_2$). Most of the solvent was then distilled off, bromobenzene was added as internal standard, and the solution analysed by g.l.c. (FFAP; 120 °C). The 1,2-dibromopropane formed corresponds to a yield of propene of 0.9%, based on the amount of which had reacted. G.l.c. analysis of the propan-2-ol–benzene solution, prior to the neutralization with sulphuric acid, showed no formation of low-boiling products in significant yields.

Kinetics.—All kinetic experiments were carried out under nitrogen at 25 °C. The spectrophotometric experiments were conducted following the same procedure as described in our previous paper.[1] The crown ethers and the DTNO were added to the halogenobenzenes prior to the addition of base, and the reactions were monitored at 300 nm (appearance of the ether) and 412 nm (appearance of the phenol). After complete consumption of the halogenobenzene, as judged from a constant reading at the two wavelengths, the absorbance values at 300 and 412 nm were used to compute the concentration of the ether (5) and the phenol (6) (see later). The pseudo-first-order rate constants were obtained from plots of log $(A_\infty - A)$ vs. t, where A_∞ is the absorbance value at 300 or 412 nm determined as just described at the end of the reaction. A few reactions of the 1-iodo-compound (4) were followed by titrating the I^- ion formed. A solution of potassium isopropoxide in propan-2-ol–benzene (made by diluting a solution of potassium in propan-2-ol with an equal amount of benzene) were added to a solution of (4) (100 ml) in propan-2-ol–benzene (1 : 1), at 25 °C. Aliquot portions (10 ml) were withdrawn at intervals, quenched in acidic (HNO_3) water, and the iodide ion was titrated by Volhard's method.[30] The experiments were run using an excess of base, and the pseudo-first-order rate coefficients ($k_{obs.}$) computed by applying standard formulae.[31]

Evaluation of the Relative Amounts of 1-Isopropoxy-2,4-dinitrobenzene (5) and 2,4-Dinitrophenol (6) formed.—In experiment no. 7 in Table 2 we have evaluated the concentration of (5) and (6) at various times during the reaction. A solution in propan-2-ol–benzene (1 : 1) of 1-chloro-2,4-dinitrobenzene (3) (4.78 × 10^{-5}M) and potassium isopropoxide (1.86 × 10^{-3}M) in the presence of 18-crown-6 (2) (7.44 × 10^{-3}M) was monitored, by using a Gilford 2400 instrument, at 300 and 412 nm. The molar extinction coefficient (ε) of the three compounds at 300 nm are: (3) 1 740; (5), 10,060; (6) + crown, 1 930. Only the complex crown + (6) has a significant absorbance at 412 nm (ε 14,480). From the reading at 412 nm it is therefore possible to derive directly the concentration of the phenol. A plot of log $(A_\infty - A)$ at 300 (and at 412) nm vs. t allowed the evaluation of the pseudo-first-order rate coefficient as 2.2 × 10^{-3} s^{-1}. From this the residual concentration of (3) can be evaluated at each time. By subtracting from the experimental absorbance at 300 nm the contribution for the residual (3) and for (6) which had been formed we may obtain the absorbance, and hence the concentration, of the ether (5) formed. The data are reported in Figure 1. For the other reactions, where only the final concentrations of (5) and (6) are needed, the procedure is somewhat simplified in that the final reading at 300 nm has to be corrected only for the amount of phenol formed (evaluated from the absorbance at 412 nm).

Voltammetric Measurements.—Electrochemical measurements were made on an assembly consisting of a Wenking ST 72 potentiostat, a VSG 72 voltage scan generator, and a PPT 70 potentiometer (all from Bank-Elektronik, Göttingen), together with an RE-551 XY-recorder. (Metrawatt, Nürnberg). The undivided voltammetric cell (EA 880; Metrohm) contained the platinum electrode (EA 222) used as stationary working electrode and a platinum foil counter-electrode. A silver wire dipping in a solution of silver nitrate (0.1M) in dimethyl sulphoxide (DMSO) served as reference electrode and was connected to the electrolyte (0.2M $KClO_4$ in DMSO) by a salt bridge consisting of the same electrolyte. (The peak potential of the reversible oxidation of ferrocene in DMSO–$KClO_4$ under our conditions was +0.19 V vs. Ag–$AgNO_3$, the peak separation being 110 mV). The electrolyte was prepared by adding potassium perchlorate (dried over P_2O_5 in vacuo at room temperature) to DMSO to make a 0.2M solution. The electrolyte was stored under nitrogen and pure nitrogen was bubbled through the electrolyte solution immediately before the measurements.

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