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Nucleophilic Reactivity

Part 7. Kinetics of the Reactions of Hydroxide Ion with 1-Substituted 2,4-Dinitrobenzenes in Water

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The kinetics of the reactions of hydroxide ion with nine 2,4-dinitrophenyl alkyl ethers, five 2,4-dinitrophenyl aryl ethers, 2,4-dinitrochlorobenzene, and 1,2,4-trinitrobenzene in water have been studied, in most cases at three or four temperatures. The results are discussed in terms of log k–pK_a plots, where the pK_a refers to the conjugate acid of the leaving group. The rate constants for the alkyl ethers satisfy the relationship log $k = -0.218$ pK_a -0.20, and those for the aryl ethers the relationship log $k = -0.215$ pK_a -1.56 (at 25°); the slopes of these plots have the same absolute values but are opposite in sign to the slope of the plot for the defluoroalkoxylation reactions of 2,4-dinitrofluorobenzene studied in Part 2.[2] Also the transetherification reactions of the ethers in methanol are discussed.

The great mobility of substituents in aromatic nitro compounds at positions *ortho* or *para* relative to the nitro groups is well known. If the reagent is hydroxide ion or water, the progress of the reaction is easily followed by determining spectrophotometrically the coloured nitrophenoxide ion formed. The alkoxylation and hydroxylation reactions occur concurrently in aqueous alcohols, and the rate constants for both reactions can be determined under favourable conditions.[1]

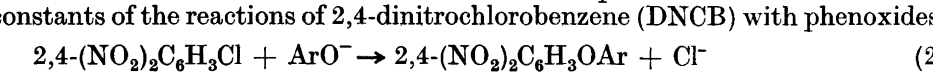
Hydrolysis and alcoholysis reactions of 1-substituted 2,4-dinitrobenzenes have been studied previously by one of us.[1–6] Parts 1–3 [1–3] and 10 [6] in the present series deal with the reactions of 2,4-dinitrofluorobenzene (DNFB). In Part 2 it was found [2] that the Brønsted relationship, log $k_a^\circ = 0.215\,\mathrm{p}K_a - 2.56$, applies to the alkaline defluoroalkoxylation reactions of DNFB,

$$2,4\text{-}(NO_2)_2C_6H_3F + AlkO^- \rightarrow 2,4\text{-}(NO_2)_2C_6H_3OAlk + F^- \quad (1)$$

in water of low alcohol content at 25°. Here k_a° is the true rate constant of the reaction, and pK_a refers to the alcohol AlkOH.

Unfortunately, the water hydrolysis of DNFB is so rapid that the reactions of this compound with nitrophenoxides could not be studied. However,

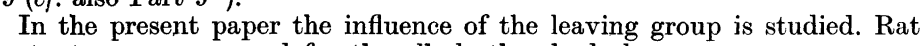
Miller *et al.*[7] and Knowles *et al.*[8] found that it is possible to measure the rate constants of the reactions of 2,4-dinitrochlorobenzene (DNCB) with phenoxides:



$$2,4\text{-}(NO_2)_2C_6H_3Cl + ArO^- \rightarrow 2,4\text{-}(NO_2)_2C_6H_3OAr + Cl^- \quad (2)$$

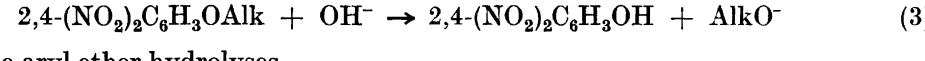
These reactions also satisfy a Brønsted relationship, the slope being about 0.9 (*cf.* also Part 9 [9]).

In the present paper the influence of the leaving group is studied. Rate constants were measured for the alkyl ether hydrolyses



$$2,4\text{-}(NO_2)_2C_6H_3OAlk + OH^- \rightarrow 2,4\text{-}(NO_2)_2C_6H_3OH + AlkO^- \quad (3)$$

the aryl ether hydrolyses



$$2,4\text{-}(NO_2)_2C_6H_3OAr + OH^- \rightarrow 2,4\text{-}(NO_2)_2C_6H_3OH + ArO^- \quad (4)$$

and also for the reactions of DNCB and 1,2,4-trinitrobenzene with hydroxide ion.

The reactions of 2,4-dinitroanisole, 2,4-dinitrophenetole, and 2,4-dinitrophenyl propyl ether with hydroxide ion [4] in water and alcohol-water mixtures and with alkoxide ions [5] in alcohols and their binary mixtures have been studied previously. Rochester [10] has studied the hydrolysis of 2,4-dinitroanisole in concentrated aqueous sodium hydroxide solutions.

In Parts 8 [11] and 9 [9] and forthcoming papers the reactions of picryl compounds are discussed. Also the neutral hydrolyses and alcoholyses of these compounds are easily studied, and the results obtained for these reactions can then be compared with those obtained for the alkaline reactions.

The reactions (3) and (4) and the corresponding reactions of the picryl compounds were studied in water, irrespective of the fact that the solubility of the ethers, especially the diaryl ethers and 2,4-dinitrophenyl benzyl ether, is low in this solvent. Alcohols cannot be used as solvents because of difficulties in the measurement of the rate constants of transetherification reactions.[5] No transetherification occurs in aqueous dioxan or dimethyl sulphoxide, but we still prefer to use pure water as solvent as the pK_a values and the Brønsted plot for reactions (1) refer to water, as this solvent does not contain foreign solvent components that might affect the rate constants, and also as the colour-forming side reactions (which are very prominent in acetone) are in most cases negligible in water.

The use of water as solvent makes a comparison of the leaving abilities of alkoxy and aryloxy groups easy. Also the alkoxylation and aryloxylation reactions can then be compared with the dealkoxylation and dearyloxylation reactions in terms of Brønsted $\log k - pK_a$ plots.

EXPERIMENTAL

Chemicals. Many of the ethers were synthesized in dimethyl sulphoxide as described previously.[12] 2,4-Dinitrophenyl isopropyl ether, m.p. 53°, 2,4-dinitrophenyl allyl ether,[13] m.p. 45°, 2,4,2′,4′-tetranitrodiphenyl ether,[14] m.p. 197°, and 1,2,4-trinitrobenzene,[15] m.p. 60°, were prepared by known methods.

The following compounds are not described in the literature:

2,4-Dinitrophenyl propargyl ether was prepared similarly as the allyl ether [13] (from dinitrochlorobenzene and propargyl alcohol). It was crystallized twice from methanol

after which it melted at 100.5°. Complete hydrolysis in 25 % dioxan-water and spectrophotometric determination of the 2,4-dinitrophenol formed gave 225 as the molecular weight (calc. 222).

2,4-Dinitrophenyl 2,2,2-trifluoroethyl ether. To a mixture of 10 ml of dimethyl sulphoxide and 2 ml of 2,2,2-trifluoroethanol was added 2.0 g of 2,4-dinitrochlorobenzene. The solution was cooled below room temperature, and 5 ml of 2 N aqueous sodium hydroxide was added. After several minutes, the reaction mixture was poured into water. The precipitate was crystallized twice from methanol. The ether melted at 78°, and complete hydrolysis gave 271 as the molecular weight (calc. 266).

Kinetic measurements. The absorbance of the 2,4-dinitrophenoxide ion formed in the reactions was measured at 380 or 440 mμ with a Unicam SP. 600 spectrophotometer (temperature 22.0°). As the solubility of the ethers in water is low, cells of 40 mm path length were used.

The initial concentration of sodium hydroxide was in most cases 0.05 N, and that of the substrate, with some exceptions, $10^{-5}-10^{-4}$ M. Thus the reactions were run under pseudo first order conditions. The nitro compound was dissolved in dioxan, and 1 ml of this solution was mixed with 500 ml of water. 10 ml of the ether solution was pipetted into one compartment of a two-compartment reaction vessel,[16] and 5 ml of the sodium hydroxide solution into the other compartment. In most cases the reaction was arrested with an approximately neutral McIlvaine's citric acid-Na_2HPO_4 buffer solution. As the reactions were relatively slow, no buffer was added when studying the reactions of the most sparingly soluble ethers (the absorbances of the solutions were low).

The second-order rate constants were computed from equation

$$k = \frac{2.303}{b\,t} \log \frac{A_\infty}{A_\infty - A_t} \tag{5}$$

where b is the concentration of sodium hydroxide, A_t the absorbance at time t, and A_∞ the infinity absorbance (measured after the reaction mixture had been kept at 100° for 2 h).

The rate constants were corrected for the thermal expansion of the solvent. The activation energies and logarithms of frequency factors were computed by the method of least squares. The Arrhenius equation was obeyed within the limits of experimental accuracy in all cases.

RESULTS AND DISCUSSION

The experimental results are shown in Table 1. In Fig. 1 values of log k are plotted against the pK_a of the conjugated acid of the leaving group. The evaluation of the pK_a values of the alcohols has been discussed previously.[2]

Inspection of Table 1 reveals that the values of log A and thus the entropies of activation are remarkably constant.

The Brønsted plot for the alkyl ether hydrolyses (3) was drawn through the point of the 1-fluoro compound (*cf.* also Part 9 [9]). The point of the 1-nitro compound lies somewhat below this straight line; this may be due to steric reasons, as the activation energies of the 1-fluoro and 1-nitro compounds are the same and the lower rate of hydrolysis of the latter compound is due to a smaller value of log A (see, however, also Parts 5 [17] and 9 [9]).

DNFB reacts 700 times faster than DNCB at 25°. Hydrochloric acid is a much stronger acid than hydrofluoric acid, and thus the rate constant of DNCB does not satisfy the Brønsted relationship of reactions (3), *i.e.*, in this case the factors that govern acidity do not determine the leaving ability of the halide ions.

If a straight line is drawn through the points for the phenoxy and 4′-nitrophenoxy ethers (compounds where there is no steric interaction due to an

Table 1. The reactions $2,4\text{-}(NO_2)_2C_6H_3\text{-}R + OH^- \rightarrow 2,4\text{-}(NO_2)_2C_6H_3OH + R^-$ in water. Initial concentrations: [NaOH] = 0.05 M (unless otherwise stated); [substrate] = $3 \times 10^{-6} - 1 \times 10^{-3}$ M.

No	R	pK_a of RH at 25°	Wt.% di-oxan	$10^5\ k$ (l mole^{-1} s^{-1}) 0.00°	15.00°	25.00°	40.00°	50.00°	60.00°	E kcal/mole	log A
1	$OCHCH_3$ | CH_3	17.1				8.84	44.7	123	323	20.28	10.81
2	$OCH_2CH_2CH_3$	16.1				20.1	104	293		20.48	11.32
3	OCH_2CH_3[a]	15.93				20.9[b]	105	283		19.95	10.95
4	$OCH_2CH{=}CH_2$	15.52				28.4	141	385	954	19.86	11.01
5	$OCH_2C_6H_5$	15.4				27					
6	OCH_3	15.09				33.8	175	490		20.47	11.53
6	OCH_3[a]	15.09				34.5[c]	182	499		20.48	11.55
7	OCH_2OH	14.77				30.3					
8	$OCH_2C{\equiv}CH$	13.55			14.1	44.9	223	623	1580	20.04	11.34
9	OCH_2CF_3	12.39			47.1	147	670			19.02	11.10
10	OC_6H_5	9.97[20]				20.2	109	318		21.11	11.78
11	$OC_6H_4NO_2$ (3′)	8.42[21]				59.1					
12	$OC_6H_4NO_2$ (2′)	7.23[22]				44.3					
13	$OC_6H_4NO_2$ (4′)	7.15[23]				80.9	406	1080	2720	19.82	11.44
14	$OC_6H_3(NO_2)_2$ (2′,4′)	4.02[24]	0			320					
	»		15.2			500					
	»		34.6			1100					
	»		48.3			2040					
15	$OC_6H_2(NO_2)_3$ (2′,4′,6′)[d]	0.33[25]				3.38 $\times 10^5$					
16	NO_2[f]	3.40[26]		629	3200	8 520	33 700			16.91	11.32
17	F[e,f,g]	3.17[27]		939	4690	12 900	50 400			16.94	11.53
18	Cl	−7[27,28]			6.12	18.5	92.0	251		19.67	10.69

[a] From Ref. 4; [NaOH] = 0.016 N. [b] 45.7 at 32.00°. [c] 76.6 at 32.00°. [d] Reaction in the picryl ring; see Part 9.[9] [e] From Ref. 1. [f] [NaOH] = 0.01 N. [g] For the influence of pressure on this reaction, see Ref. 6.

o′-nitro group), it runs parallel to that for the alkyl ethers, but much lower (*cf.* also Part 9 [9]). The experimental point for 2,4,2′,4′-tetranitrodiphenyl ether also lies on this straight line, but as there are two equally reactive centres in this compound, the value plotted in Fig. 1 was obtained by dividing the experimental value by a statistical factor of two. The reactivity of this compound and that of 2,4,2′-trinitrodiphenyl ether (which has a similar *o′*-nitro group) is thus one half of the "normal" reactivity.

The rate constants for the hydrolysis of the 2,4-dinitrophenyl alkyl ethers (reaction (3)) and DNFB satisfy the relationship $\log k = -0.218\ pK_a - 0.20$, and those for the hydrolysis of the 2,4-dinitrophenyl aryl ethers (reaction (4)) the relationship $\log k = -0.215\ pK_a - 1.56$ (at 25°). Thus the slopes are of the same absolute value but opposite in sign to the slope [2] for reaction (1), where the incoming group was varied (*cf.* also Part 9 [9]).

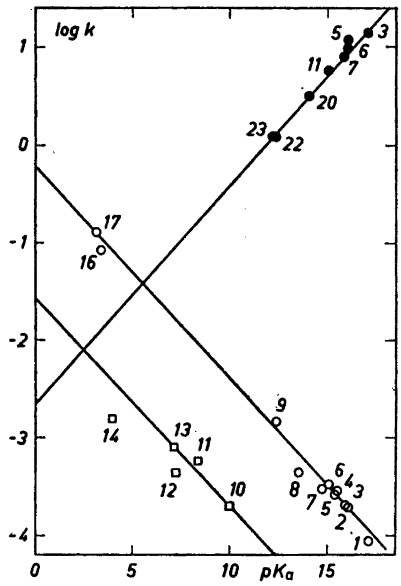


Fig. 1. Brønsted plots for the reactions in water at 25°. Filled circles: defluoroalkoxylation reactions (1) of DNFB; open circles: dealkoxyhydroxylation reactions (3); open squares: dearyloxyhydroxylation reactions (4). The numbering of the compounds denoted by open symbols refers to Table 1 in the present paper and that corresponding to the alkoxylations of DNFB (filled circles) to Table 2 in Part 2.[2]

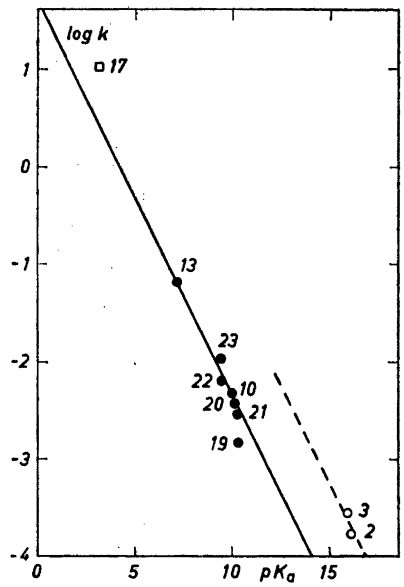


Fig. 2. Brønsted plots for methanolic methoxylation reactions at 20° (the pK_a values refer to water at 25°). Black circles: reactions of diaryl ethers.[19] The numbering of the compounds refers to Table 1 in the present paper, with the additions 19 = 2-methoxyphenol, 20 = 3-methoxyphenol, 21 = 4-methoxyphenol, 22 = α-naphthol, and 23 = 4-chlorophenol (the values of the pK_a's of the latter compounds are from Ref. 29). Open circles: transetherification reactions of dinitrophenyl alkyl ethers.[5]

The value of the slope for the aryloxylation reactions (2) of DNCB in methanol,[7] 0.941 (at 25°), differs much from the absolute values of the slopes of the plots for the reactions (1), (3), and (4) in water, and this difference cannot be explained to be due solely to the different substrate and solvent. However, this discrepancy disappears (*cf.* Part 4 [18]) when log k is plotted, not as a function of pK_a, but against the π-electron density (as computed [18] by the simple LCAO—MO method) of the phenolic oxygen of the reagent or of the 1-carbon in the substrate. Also the 1-chloro compound then behaves normally.

This shows the dangers associated with the relatively common practice of drawing conclusions concerning the extent of bond formation between reagent and substrate in the rate-determining transition state from the value of the slope of the Brønsted plot (see also Part 9 [9]).

The electron density seems to be a much better correlation parameter than pK_a, which refers to a proton-transfer equilibrium. However, as the pK_a values are known with a much higher accuracy and reliability than any

electron density values can be computed at present by simple methods (especially in the case of alkyl alkoxides), the discussions in this and the following papers will be mainly in terms of the Brønsted plots. A third, in many respects equivalent, presentation would be in terms of the Hammett type relationships.

Ogata and Okano [19] have studied the alkaline methoxylation of several diaryl ethers in methanol at 20°. Their rate constants are plotted in Fig. 2, which also contains the points of the alkaline methoxylation of DNFB,[1] 2,4-dinitrophenetole, and 2,4-dinitrophenyl propyl ether.[5] The straight line was drawn through the points of the phenoxy and 4′-nitrophenoxy ethers. Also in this case the points for alkoxy replacement lie above the straight line of aryloxy replacement. The slope of the latter straight line is about −0.40.

The mechanism of aromatic nucleophilic substitution reactions is discussed in Part 9 [9] and the relative reactivities at the carbon atoms 1 and 1′ in diaryl ethers in Part 4.[18]

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