Nucleophilic Reactivity of Alkoxide Ions toward 2,4-Dinitrofluorobenzene and the Acidity of Alcohols

JUHANI MURTO

Department of Chemistry, University of Helsinki, Helsinki, Finland

The kinetics of the reactions of 2,4-dinitrofluorobenzene with hydroxide ion, twenty alkoxide ions, and phenoxide ion in water have been studied. The rates of the concurrent reactions with hydroxide and alkoxide ions have been measured at 25° and the product ratios determined at three temperatures. If log B'_{ha} (a quantity related to the product ratio) is plotted *vs.* pK_a, a straight line results, and with the aid of this plot the pK_a values of 2-methyl-2-propanol and 2-butanol in water at 25° were estimated at 19.2 and 17.6, respectively. The existence of a linearity of this kind implies the existence of a Brønsted linearity of the form log $k_a° = a\, pK_a + \beta$, where $k_a°$ is the true rate constant of the alkoxide reaction. The slope a was found to be 0.22 at 25° for the reactions studied, and it can be evaluated without having to know the values of any rate constants. The values of pK_a of 2,2,2-trifluoroethanol and 2,2,2-trichloroethanol in water were also determined kinetically, the former at three temperatures, the latter at 25°. The solvolysis reactions of 2,4-dinitrofluorobenzene were found to be very slow in the absence of alkali, and in aqueous alcohols these reactions produce much more dinitrophenol than the corresponding reactions with alkali.
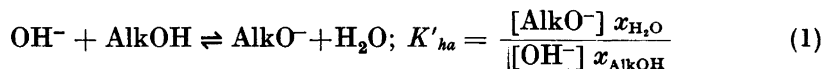
Much work has been done in recent years to correlate the reactivities of nucleophiles with properties such as basicity and polarizability.[1-9] Swain and Scott [1] found that the equation log $k/k_{H_2O} = sn$ correlates the rates of reaction of many substrates with a series of nucleophiles. Here k_{H_2O} is the rate constant of the reaction with water and k that of the reaction with the nucleophile, s is a constant characteristic of the substrate and is defined as 1.00 for methyl bromide in water at 25°, and n is characteristic of the nucleophilic reagent and defined as 0.00 for water. This equation implies that a common nucleophilic reactivity order should hold for all reactions, irrespective of the nature of the substrate and solvent. This is now known not to be the case, and the equation of Swain and Scott has limited validity.[7]

Edwards [2,3] proposed a four-parameter equation that relates the nucleophilic reactivity of a reagent to its basicity and polarizability. Similar correlation equations have been derived theoretically by Hudson.[4] Edwards and

Pearson,[3] Hudson,[4] and Bunnett [7] have recently thoroughly discussed the factors that affect nucleophilic reactivity.

The so-called Brønsted relation of the form $\log k = \alpha p K_a + \beta$ has been found to apply to many base-catalysed and some nucleophilic displacement reactions.[4-9] Here $p K_a$ refers to the conjugate acid of the nucleophile and α and β are constants, the former smaller than unity.

For correlation equations such as those mentioned above to hold, the rate constants should refer to a common solvent. However, difficulties are encountered when working with alkoxide ions because of the solvolysis of the alkoxides in hydroxylic solvents. In aqueous-alcoholic solvents the rate measurements are influenced by the pre-equilibria [10-13]

$$\text{OH}^- + \text{AlkOH} \rightleftharpoons \text{AlkO}^- + \text{H}_2\text{O}; \quad K'_{ha} = \frac{[\text{AlkO}^-] \, x_{\text{H}_2\text{O}}}{[\text{OH}^-] \, x_{\text{AlkOH}}} \tag{1}$$

and thus only apparent rate constants are obtained from the measurements unless assumptions are made concerning these equilibria.[11-13]

To collect experimental data for reactions of an aryl halide with alkoxide ions in water, the reactions of 2,4-dinitrofluorobenzene (DNFB) with a variety of alkoxide ions in water were studied in a similar way as in the preceding study.[18]

EXPERIMENTAL

The *alcohols* were the purest obtainable commercial products, mostly from Fluka AG or E. Merck AG. *2-Phenoxyethanol, 1,3-propanediol,* and *2,2,2-trichloroethanol* were of practical grade only (from Fluka AG). All liquid alcohols were distilled through an efficient column at ordinary or reduced pressure, and a small middle fraction was used for the kinetic experiments. *Pentaerythritol* was crystallised from water. The other chemicals were the same as in the previous work.[13]

Rate measurements were carried out spectrophotometrically as previously described,[13] and also the method for the computation of the rate constants was the same. To ensure maximum accuracy in the determination of product ratios, the alcohol content of the solvent was relatively high with butanols and propanols and low with the acidic alcohols. DNFB was dissolved in the alcoholic component of the solvent. When working with solid alcohols, DNFB was dissolved in dioxan (0.1 % in the solvent), as in some cases the presence of acetone (which was used in the preceding work) caused the development of a brownish colour. The measurements were carried out within a few hours after the preparation of the solutions.

The 2,4-dinitrophenyl alkyl ether formed in the reaction hydrolyses slowly to dinitrophenol in the presence of hydroxide ion, and this side reaction may lead to some inaccuracy in the determination of product ratios. The rate constants for most of these hydrolysis reactions are not known, and the complication caused by these reactions was avoided by plotting infinity absorbances against time (time between 10 and 40 half-lives) and extrapolating to zero reaction time. This correction was most marked with trifluoroethanol, as the corresponding ether hydrolyses rapidly and the relative amount of dinitrophenol formed in the actual reaction is small. For an example, see Table 1.

The molar extinction coefficient of 2,4-dinitrophenol varies with the solvent, and appropriate corrections were determined and applied to the absorbance readings. The ethers formed from benzyl alcohol, 2-phenoxyethanol, 2,2,2-trichloroethanol, and phenol are extremely sparingly soluble in water, and to dissolve these ethers, acetone was now added to the buffer solution used to arrest the reaction. The solutions containing pentaerythritol became slowly turbid on standing, and thus the differences in absorbance of neutral and highly acidic solutions were determined when working with pentaerythritol.

Table 1. Reactions of DNFB with hydroxide and 2,2,2-trifluoroethoxide ions in 0.363 wt.% 2,2,2-trifluoroethanol-water at 25.00°. Rate constants were computed by eqns. (6) and (7) of the preceding paper;[13] $a = 3.308 \times 10^{-4}$ M, $b = 0.00990$ M, and $x/y = 11.67$. The absorbances A were measured at 440 mμ. The reaction was arrested by adding an equal volume of buffer solution. p is the percentage of DNFB that has reacted.

Time seconds	A	$10^4\ y$	$10^4\ x$	p %	k_a l mole^{-1} s^{-1}
20.0	0.017	0.036	0.420	13.8	0.692
40.0	0.030	0.064	0.747	24.5	0.657
60.0	0.045	0.096	1.120	36.8	0.716
90.0	0.060	0.128	1.494	49.0	0.704
120.0	0.071	0.152	1.774	58.2	0.685
180.0	0.089	0.191	2.229	73.2	0.691
240.0	0.101	0.216	2.521	82.8	0.694
1200	0.133				
2400	0.143				
3600	0.156				
4800	0.164				
∞^a	0.122^a	0.261	3.047	100	
					Mean 0.6913

^{a} Corrected value (see text).

When corrected for solvent expansion, $k_a = 0.6920$ l mole^{-1} s^{-1}. $k_h = 0.6920/11.67 = 0.05930$ l mole^{-1} s^{-1}.

2-Chloro- and 2,2,2-trichloroethanol react with anion bases, the former so rapidly that rate determinations with DNFB were not possible. The product ratios for 2-chloroethanol were estimated by adding concentrated aqueous solution of sodium hydroxide drop by drop until the absorbance of the solution did not change markedly. When working with halogenoethanols, the alcohol was in the DNFB solution and the base solution contained no alcohol.

The ether resulting from the reaction of DNFB with diols and polyols is also an alcohol and forms an alkoxide ion. However, this ion is probably present in a very low concentration and does not complicate the kinetic picture. If the ether-alcohol is so acidic that it is converted to the alkoxide form to a considerable extent, its rate of reaction will be low (*cf.* Fig. 3). The same is true for the 2,4-dinitrophenoxide ion; the absorbance of an aqueous solution, about 5×10^{-4} M in DNFB and sodium 2,4-dinitrophenoxide, underwent no appreciable change in two days at 40°. The reaction was probably approximately counterbalanced by the neutral solvolysis of DNFB.

K'_{ka} for phenol is 594 000 at 25°, and thus, if undissociated phenol is present in the solution, the hydroxide ion concentration is negligibly low as is consequently also the amount of dinitrophenol formed in the reaction. To avoid this, the amount of phenol added to the base solution was so small that only a part of the hydroxide was converted into phenoxide. As practically no free phenol is present, equilibrium (1) cannot maintain a constant ratio [AlkO$^-$]/[OH$^-$] as the reaction proceeds. However, as the concentration of DNFB is low compared with the base concentrations, the error introduced does not invalidate the results.

As the concentration of phenoxide cannot vary much with temperature, the plot of log x/y *vs.* $1/T$ gives directly the value of the difference $E_h° - E_a°$ for phenol.

With 2-ethoxyethanol and prop-2-yn-1-ol the apparent rate constant k_h of the hydroxide reaction was 50—100 % higher than the rate constant in pure water, and reproducible results were not obtained in different runs. The cause of this phenomenon remained unknown, and data will not be given for these alcohols.

RESULTS

Table 2 summarizes the results of the measurements. The apparent rate constants k_h and k_a for the hydroxide and alkoxide reactions at 25° have been calculated by eqns. (6) and (7) of the preceding paper.[13] The product ratios x/y (where x is the concentration of dinitrophenyl alkyl ether and y that of dinitrophenol) are given at three temperatures.

If the Arrhenius equation $\log k_h = \log A_h - E_h/2.303\ RT$ for the hydroxide reaction is subtracted from that for the alkoxide reaction, $\log k_a = \log A_a - E_a/2.303\ RT$, and if x/y is substituted [13] for k_a/k_h, one obtains

$$(2) \qquad \log \frac{x}{y} = \frac{E_h - E_a}{2.303\ RT} - \log \frac{A_h}{A_a}.$$

Thus, if $\log x/y$ is plotted against $1/T$, the slope gives $E_h - E_a$ and the intercept is $\log A_h/A_a$. These quantities, as computed by the method of least squares, are also given in Table 2.

As [11] $E_h - E_a = E_h^° - E_a^° - \Delta H_{ha}$, where $E_h^°$ and $E_a^°$ are the true energies of activation and ΔH_{ha} is the heat of the proton transfer reaction (1), the differences $E_h^° - E_a^°$ can be evaluated if ΔH_{ha} is known.[11] $E_a^°$ can also be estimated if $E_h^°$ is assumed to have the value 16.94 kcal mole^{-1} found for the reaction in water. Values of $E_a^°$, $\log A_a^°$ (the latter as computed by eqn. (47) of Ref.[11]), and $\Delta S_a^{*°}$ are given for some alcohols in Table 3.

To arrive at the true rate constants $k_h^°$ and $k_a^°$ of the hydroxide and alkoxide reactions, the equilibrium constants K'_{ha} of (1) must be known. Some of these have been estimated previously by the author,[11-13] and some can be calculated from known pK_a values [14-16] of these alcohols in water. If one writes

$$\text{AlkOH} + H_2O \rightleftharpoons \text{AlkO}^- + H_3O^+; K_a = \frac{[\text{AlkO}^-]\,[H_3O^+]}{[\text{AlkOH}]} \qquad (3)$$
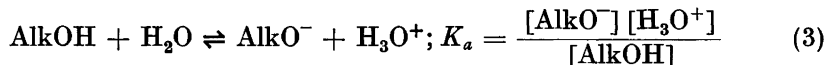
then

$$K_a = \frac{K'_{ha}K_w}{[H_2O]} \qquad (4)$$

where K_w is the ionic product of water. Also, if the van't Hoff equation is applied to (4), then

$$\Delta H_a = \Delta H_{ha} + \Delta H_w \qquad (5)$$

where ΔH_a is the heat of ionization of the alcohol and ΔH_w that of water. As ΔH_w varies somewhat with temperature, also ΔH_{ha} is temperature-dependent.

The values of pK_a for the rest of the alcohols in Table 2 were obtained as follows. Hine and Hine [17] have determined the acidities of many alcohols in 2-propanol, and pK_a values for some of these alcohols in water are known from the work of Ballinger and Long.[14] A graph was thus constructed (Fig. 1) by plotting pK_a in water against values of $\log K_e$ reported by Hine and Hine (in 2-propanol). It can be seen that there is a good correlation between the acidities in these two solvents, and pK_a values were read from this curve for alcohols whose K_e values in 2-propanol are known.

Table 2. Reactions of 2,4-DNFB with hydroxide and alkoxide ions in aqueous-alcoholic solvents of low alcohol content. The subscript h refers to the hydroxide reaction, the subscript a to the alkoxide reaction. Rate constants are in l mole^{-1} s^{-1}, energies of activation in kcal mole^{-1}. The initial concentration of DNFB was $3.0 \times 10^{-4} - 3.4 \times 10^{-4}$ M ($2.0 \times 10^{-4} - 2.1 \times 10^{-4}$ M for butanols and 2-phenoxyethanol), and the initial concentration of total base (sodium hydroxide + alkoxide) $98 \times 10^{-4} - 99 \times 10^{-4}$ M, unless otherwise stated.

No.	Compound	pK_a 25.00°	Wt.% org. comp.	x/y 0.00°	x/y 25.00°	x/y 40.00°	k_h 25.00°	k_a 25.00°	E_h-E_a	$\log(A_h/A_a)$	B'_{ha} 25.00°
1	2-Methyl-2-propanol	19.2	18.6	0.005	0.006	0.003	0.316	0.002			0.1_0
2	2-Butanol	17.6	9.77	0.079	0.049	0.043	0.217	0.011	2.7		1.9
3	2-Propanol^a	17.1^c	19.4	0.478	0.325	0.240	0.363	0.118	2.9	2.6	4.5
4	2-Methyl-1-propanol	16.1^b	4.84	0.587	0.345	0.269	0.164	0.0567	3.33	2.90	27.9
5	1-Propanol	16.1^b	8.13	1.70	0.978	0.722	0.171	0.167	3.63	2.67	39.8
6	1-Butanol	16.1^b	4.87	0.784	0.470	0.366	0.158	0.0744	3.25	2.70	37.7
7	Ethanol^a	15.93^c	3.94	1.17	0.658	0.490	0.136	0.0896	3.70	2.89	41.0
8	Water^a	15.74	0	(1)	(1)	(1)	0.129	(0.129)	(0)	(0)	(1)
9	Allyl alcohol	15.52^{14}	2.28	3.00	1.50	1.04	0.126	0.189	4.51	3.13	208
10	Benzyl alcohol	15.4^b	1.23	2.33	1.08	0.753	0.140	0.151	4.83	3.50	520
11	Methanol^a	15.09^c	3.98	9.72	4.81	3.28	0.121	0.581	4.62	2.70	206
12	2-Phenoxyethanol	15.1^b	1.73	2.54	1.34	0.934	0.143	0.192	4.24	2.99	585
13	1,3-Propanediol	15.1^b	2.71	2.75	1.26	0.817	0.127	0.160	5.15	3.68	191
14	1,4-Butanediol	15.1^b	3.92	2.56	1.18	0.808	0.159	0.188	4.91	3.52	145
15	1,2-Propanediol	14.9^b	4.11	3.82	1.69	1.14	0.126	0.213	5.15	3.54	167
16	2-Methoxyethanol	14.82^{14}	3.85	3.77	1.66	1.13	0.133	0.222	5.15	3.55	176
17	1,2-Ethanediol	14.77^{14}	2.21	4.63	2.04	1.38	0.128	0.261	5.16	3.46	312
18	1,2,3-Propanetriol	14.40^{14}	2.34	4.54	2.07	1.45	0.137	0.282	4.87	3.24	441
19	2-Chloroethanol	14.31^{14}	4.70	12	5.5	3.9		0.71^d	5.0	2.9	500
20	Pentaerythritol	14.10^{14}	2.39	7.48	3.46	2.47	0.121	0.418	4.75	2.93	1070
21	D-Mannitol	13.29^e	1.99	3.25	2.00	1.59^f	0.144	0.288	3.05	1.93	996
22	2,2,2-Trifluoroethanol ^{g,h}	12.39	0.363	37	11.7	6.50	0.0593	0.692	7.36	4.32	20900
„	2,2,2-Trifluoroethanol^i	„	0.552	59	18.5	9.95	0.0416	0.768	7.55	4.27	20500
23	2,2,2-Trichloroethanol^j	12.25	0.408	37	11.7	6.49	0.0578	0.674	7.41	4.36	29500
24	Phenol^k	9.97^{16}	0.0267	1.80	1.65	1.50	0.0985	0.162	9.11^l		2.5 × 10^6
„	Phenol^m	„	0.0471	4.19	3.82	3.50	0.0709	0.271	9.09^l		2.2 × 10^6

^{a} See preceding paper.[13] ^{b} Estimated from Fig. 1. ^{c} From own kinetic estimate [11,12] of K'_{ha}. ^{d} On the assumption that $k_h = 0.13$. ^{e} From data of Thamsen.[15] ^{f} 50.00°: 1.34; 70.0°: 1.00. ^{g} 0.00°: $k_h = 0.00269$, $k_a = 0.0986$; 40.00°: $k_h = 0.289$, $k_a = 1.88$. ^{h} Initial concentrations at 25.00°: [AlkOH] = 0.0309 M, [AlkO$^-$] = 0.00535 M, [OH$^-$] = 0.00455 M. ^{i} Initial concentrations at 25.00°: [AlkOH] = 0.0499 M, [AlkO$^-$] = 0.00533 M, [OH$^-$] = 0.00254 M. ^{j} Initial concentrations at 25.00°: [AlkOH] = 0.0219 M, [AlkO$^-$] = 0.00545 M, [OH$^-$] = 0.00443 M. ^{k} Initial concentrations at 25.00°: [AlkOH] = 3.66×10^{-5} M, [AlkO$^-$] = 0.00280 M, [OH$^-$] = 0.00714 M. ^{l} See text. ^{m} Initial concentrations at 25.00°: [AlkOH] = 9.57×10^{-5} M, [AlkO$^-$] = 0.00490 M, [OH$^-$] = 0.00503 M.
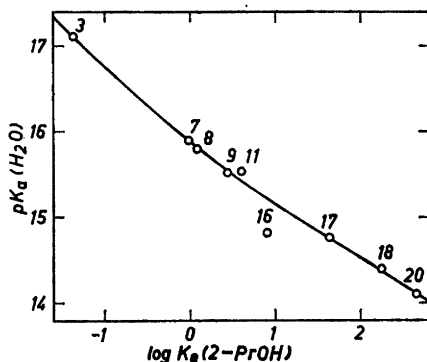
Fig. 1. pK_a of alcohols in water [14] at 25° vs. log K_e of Hine and Hine in 2-propanol at 27°. The numbers refer to Table 2.
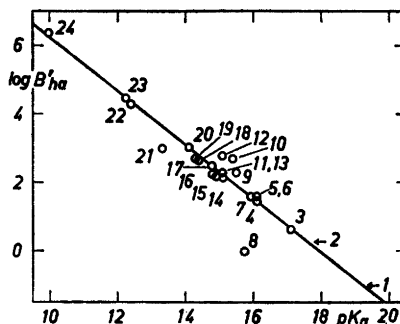
Fig. 2. Plot of log B'_{ha} for various alkoxides at 25°. The numbers refer to Table 2.

Table 2 also contains the values of B'_{ha} at 25°:

$$B'_{ha} = \frac{x}{y} \cdot \frac{x_{H_2O}}{x_{AlkOH}} = \frac{k_a^{\circ}}{k_h^{\circ}} K'_{ha} \qquad (6)$$

This quantity is relatively insensitive to small changes in solvent composition, and the B'_{ha} values of different alcohols may be compared in spite of the fact that the data do not refer to pure water as solvent. In Fig. 2 log B'_{ha} has been plotted vs. the pK_a of the conjugate alcohol of the alkoxide ion in question. A relatively good linearity results, extending from phenol (pK_a ca. 10) to 2-propanol (pK_a ca. 17). Water and mannitol give negative deviations, 2-phenoxyethanol, benzyl, and allyl alcohols positive deviations from this straight line, which may be defined to represent a "normal" reactivity of DNFB. The scatter of the points may be due to some extent to the fact that the pK_a values of many alcohols are known only very approximately.

Excluding the exceptional points mentioned, the remaining 17 points give by the method of least squares the relationship

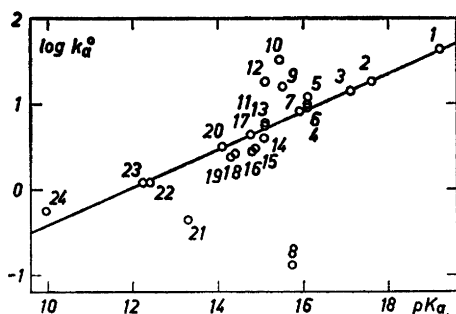$$\log B'_{ha} = 14.066 - 0.7847 \ p K_a \qquad (7)$$

Fig. 3. Plot of log k_a° for various alkoxides at 25°. The numbers refer to Table 2.

With the aid of the eqns. (4) and (6), one obtains the Brønsted linearity (*cf.* also Fig. 3):

$$\log k_a{}^\circ = 0.2153\ \mathrm{p}K_a - 2.564 \qquad (8)$$

This refers to water as solvent, as the value $k_h{}^\circ = 0.129\ \mathrm{l\ mole^{-1}\ s^{-1}}$ in water at 25° was used when the expression was derived. This procedure is justified as the ratio $k_a{}^\circ/k_h{}^\circ$ seems not to change much on adding small amounts of methanol, ethanol, or 2-propanol to water,[13] although the absolute magnitudes of the rate constants may change considerably.[13]

Table 3. True quantities (quantities not affected by the hydroxide-alkoxide equilibrium) for the reactions of 2,4-DNFB with some alkoxide ions at 25°. The data presented refer to the alcohol-water mixtures given in Table 2, with the exception that $k_a{}^\circ$ refers to pure water as solvent (see text). Rate constants are in $\mathrm{l\ mole^{-1}\ s^{-1}}$, energies in $\mathrm{kcal\ mole^{-1}}$, and entropies of activation[11] in cal degree^{-1}.

Compound	$\mathrm{p}K_a$	K'_{ha}	ΔH_{ha}	$k_a{}^\circ$	$E_a{}^\circ$	$\log A_a{}^\circ$	$\Delta S_a{}^{*\circ}$
2-Methyl-2-propanol	19.2[a]	3.10⁻⁴		43			
2-Butanol	17.6[a]	0.014		18			
2-Propanol	17.1	0.043[13]	−3.3[13]	14	17.0	14.0	+3
1-Propanol	16.1[b]	0.4		12			
1-Butanol	16.1[b]	0.5		10			
Ethanol	15.93	0.65[11]	−3.5[11]	8.1	16.7	13.2	0
Water	15.74	1	0	(0.129)	16.94	11.53	−8
Methanol	15.09	4.5[11]	−3.5[11]	5.9	15.9	12.6	−3
D-Mannitol	13.29[15]	282	−2.17[c]	0.46			
2,2,2-Trifluoroethanol	12.39[a]	2200[d]	−5.49	1.22[d]	15.0[d]	11.1[d]	−10[d]
2,2,2-Trichloroethanol	12.25[a]	3120		1.22	15.0[e]	11.1[e]	−10
Phenol	9.97[16]	594000	−8.35[f]	0.51	16.2[d]	11.7[d]	−7[d]

[a] Estimated in the present paper. [b] Estimated from Fig. 1. [c] From the $\mathrm{p}K_a$ data of Thamsen,[15] temperature interval 0−18°. [d] Mean of two values. [e] On the assumption that $\Delta H_{ha} = -5.49$ kcal mole⁻¹. [f] From the $\mathrm{p}K_a$ data of Binns,[16] computed for the temperature interval 0−40°.

The relationship (7) was deduced from the product ratio data without any knowledge about reaction rates. If a linearity such as (7) exists, this implies that also a Brønsted linearity exists, and an expression for it is thus obtainable if $k_h{}^\circ$ in water is known. The slope a of the Brønsted plot, which is the quantity of interest, can be evaluated without having to know even the rate constant $k_h{}^\circ$. This method for evaluating a may be useful when the reactions studied are too fast to allow the determination of rate constants.

Butanols. The $\mathrm{p}K_a$ values for 2-butanol and 2-methyl-2-propanol in water are not known as these compounds are very weak as acids. McEwen[18] estimated the $\mathrm{p}K_a$ of the latter compound to be 19 ± 1, but this value does not refer to water as solvent.

It emerges on inspection of Figs. 2 and 3 that the points for all unsubstituted alkanols lie on the straight line representing "normal" reactivity. As the

B'_{ha} values are known for 2-butanol as well as for 2-methyl-2-propanol, eqn. (7) gives for 2-butanol $pK_a = 17.6$, $K'_{ha} = 0.014$, and for 2-methyl-2-propanol $pK_a = 19.2$, $K'_{ha} = 3 \times 10^{-4}$ at 25°. Thus only low butoxide concentrations can exist in the aqueous mixtures of these butanols, and although the reactivities of butoxide ions are high, the amount of ether formed in the reaction with DNFB is still very small.

Diols and polyols. The values for these, with the exception of mannitol, fall close to the straight lines representing normal reactivity in Figs. 2 and 3. The absolute value of ΔH_{ha} for mannitol is also smaller than expected (*cf.* Table 3 and Fig. 4). The plot of log x/y *vs.* $1/T$ for mannitol is linear from 0° to 70°. The situation with polyols is complicated by the existence of several alkoxide equilibria.

2,2,2-Trifluoro- and 2,2,2-trichloroethanol. These alcohols are relatively acidic,[14] and addition of small amounts of them to water results in a rapid decrease in hydroxide ion concentration and consequently also a decrease in the apparent rate constant k_h of the hydroxide reaction occurs. Assuming that the true rate constant of the hydroxide reaction, $k_h°$, is the same as in water, K_{ha}' was evaluated by the equation [11]

$$K'_{ha} = \frac{x_{H_2O}(k_h° - k_h)}{x_{AlkOH}\, k_h} \qquad (9)$$

and eqn. (1). As the conversion into the alkoxide form diminishes the concentration of free alcohol, this latter concentration was evaluated by equating the two expressions (1) and (9) for K'_{ha}. The rates in trifluoroethanol-water were measured at three temperatures; at 0°, however, the absorbances were small, and consequently also the rate constants are less accurate at the lower temperatures (*cf.* also Table 1).

The following acidity values were derived. 2,2,2-Trifluoroethanol: $pK_a = 13.01$, $K'_{ha} = 4700$ at 0°; $pK_a = 12.39$, $K'_{ha} = 2200$ at 25°; $pK_a = 12.17$, $K'_{ha} = 1280$ at 40°; 2,2,2-trichloroethanol: $pK_a = 12.25$, $K'_{ha} = 3120$ at 25°. The plot of pK_a *vs.* $1/T$ for 2,2,2-trifluoroethanol gives $\Delta H_{ha} = -5.49$ kcal mole^{-1}. The pK_a values of the present study compare favourably with those obtained conductometrically by Ballinger and Long [14] at 25°, namely, 12.37 for trifluoroethanol and 12.24 for trichloroethanol.

The 2,4-dinitrophenyl ether of 2,2,2-trifluoroethanol formed in the reaction of DNFB with 2,2,2-trifluoroethoxide hydrolyses relatively rapidly under the action of hydroxide ion. With the aid of the data given in Table 1 the rate constant for this hydrolysis reaction is estimated at 14×10^{-4} l mole^{-1} s^{-1} at 25°. The rate constants of hydrolysis of 2,4-dinitrophenyl methyl and ethyl ethers are [19] 3.45×10^{-4} and 2.09×10^{-4} l mole^{-1} s^{-1}, respectively, in water at 25°. Thus the rate is higher the less basic the leaving alkoxide ion. The hydrolysis of 2,4-dinitrophenyl alkyl ethers will be studied in more detail later.

Solvolyses without added alkali. The solvolysis reactions of halogenonitrobenzenes are very slow in the absence of alkali at low temperatures, also when there are several activating nitro groups present, and thus quantitative measurements seem not to have been carried out previously. Some measure-

ments were done with DNFB without added alkali in connection with the present work.

The first-order rate constant of the hydrolysis of DNFB in water at 40.00° is 20×10^{-8} s^{-1}. In a 0.01 M aqueous potassium fluoride solution the rate constant is 22×10^{-8} s^{-1} and in 0.01 M hydrogen chloride solution 20×10^{-8} s^{-1}, also at 40.00°. These data were obtained spectrophotometrically with about 5×10^{-4} M solutions of DNFB.

The alkalimetric titration does not give reliable results in the presence of hydrofluoric acid, and thus only the following data will be given for aqueous-alcoholic solvents. The reactions produced dinitrophenol and dinitroether in constant ratio as the reaction proceeded. The product ratio was $x/y = 4.1$ in 76.7 wt. % methanol-water and 0.84 in 55.3 wt. % ethanol-water at 40.00°. The product ratios for the corresponding alkaline reactions [13] are 264 in the methanol-water and 14.7 in the ethanol-water mixture. Thus the neutral solvolysis produces much more dinitrophenol than the anionic solvolysis. The product ratios given above imply also that alcoholysis proceeds only 2—3 times faster than the hydrolysis in the absence of alkali.

If the rate constant in water is divided by the molar concentration of water, we obtain for the second-order constant the value 36×10^{-10} l mole^{-1} s^{-1} at 40°. The alkaline hydrolysis is 1.4×10^8 times faster than this.

DISCUSSION

Nucleophilic reactivity of hydroxide ion. The low reactivity of hydroxide ion in aromatic nucleophilic substitution reactions was discovered by Bunnett and Davis.[20] Inspection of Fig. 3 reveals that the reactivity of hydroxide ion with DNFB in water at 25° is only 1/50 of the "normal" reactivity. Also in alcohol-water mixtures alkoxide ions react with DNFB 50 times faster than the hydroxide ion.[13] In the reactions of p-dinitrobenzene in aqueous-alcoholic mixtures alkoxide ions react 200 times faster.[10,11] The low reactivity of hydroxide ion may be in part due to its high solvation.[4]

It is evident from the experimental data in this and the preceding paper [13] that the rate of reaction of DNFB with hydroxide ion increases as the alkanol or dioxan content of the solvent increases, and this effect is the more marked the higher the alcohol homologue. At low alcohol contents of the solvent the true rate constants of the alkoxide and hydroxide reactions change similarly, the ratio $k_a°/k_h°$ being approximately constant. At high alcohol contents the rate increase seems to be specific to hydroxide ion, the rates of alkoxide reactions being relatively insensitive to changes in solvent composition.

Dipolar aprotic solvents, such as dimethyl sulphoxide, greatly accelerate the rates of nucleophilic substitution reactions of anions [21,22] and also inversions in the relative reactivities of anions may occur. This acceleration has been explained by attributing it to an increase in the activity of the hydroxide ion due to its decreased solvation,[21-23] as the bulky solvent molecules cannot fit closely around small anions.[21] Thus, dimethyl sulphoxide greatly accelerates the rate of reaction of methyl iodide with hydroxide, methoxide, and ethoxide ions, and hydroxide ion is the most reactive ion in pure dimethyl sulphoxide.[22]

The explanation for the observed behaviour of the hydroxide reaction of DNFB in aqueous-alcoholic mixtures of high alcohol content may be somewhat similar to that given for aprotic solvents, although the magnitude of the effect is much smaller.

The Brønsted relationship. The validity of Brønsted catalysis law for many reactions is a testimony of a close correlation between nucleophilic reactivity toward hydrogen, carbon, sulphur, *etc.*, and basicity.[24],[7] The lesser the extent of bond formation in the transition state, the less sensitive should the reaction rate be to the electron density on the incoming anion, and thus a small value of a as found for the reactions of DNFB (0.22) implies a loose bond formation in the transition state.[4],[7]

Jencks and Gilchrist [6] studied the reactions of an ester, *p*-nitrophenyl acetate, with alkoxide ions. They plotted log k_a° *vs.* pK_a of the conjugate alcohol of the alkoxide and drew a straight line of slope 0.76 through the point for the phenoxide ion, as the reactivity of less basic anions follows such a relationsnip.[8] The points for strongly basic alkoxide ions deviated greatly from this line and
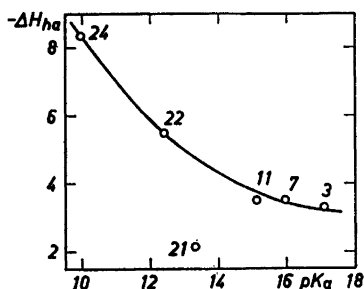

Fig. 4. Heats of proton transfer reaction (1) for various alcohols. The numbers refer to Table 2.
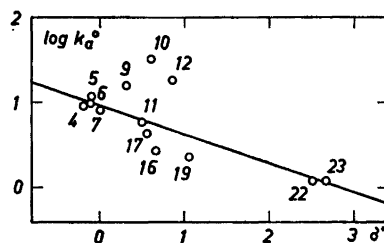
Fig. 5. A Taft-Ingold plot. The numbers refer to Table 2.

show that the reactivity of the alkoxide ions is relatively insensitive to basicity. However, if phenoxide ion is ignored, a line of slope of about 0.2—0.3 can be drawn through the points for the alkoxide ions. The scatter of the points does not allow of accurate determination of the slope.

The Taft-Ingold relationship. Many of the alcohols discussed in the present paper can be considered to be monosubstituted methanols. To examine the influence of polar inductive effects on the reactivity of alkoxide ions in reactions with DNFB, a Taft-Ingold plot was constructed (Fig. 5; statistical factors were neglected). Taft [25] has shown that when steric and resonance effects are negligible, the rates of many reactions are correlated with substituent parameters as indicated by equation log $k = \varrho^{*}\sigma^{*} +$ constant, where σ^{*} is the polar substituent parameter for a substituent group,[25],[14] k the corresponding rate constant, and the constant ϱ^{*} a measure of the susceptibility of the particular reaction to polar substituents. Fig. 5 closely resembles Fig. 3, and the slope of the line is $\varrho^{*} = -0.34$, a relatively small value. This also illustrates the small sensitivity of the reaction to the basicity of the alkoxide ion.

REFERENCES

1. Swain, C. G. and Scott, C. B. *J. Am. Chem. Soc.* **75** (1953) 141.
2. Edwards, J. O. *J. Am. Chem. Soc.* **76** (1954) 1540; **78** (1956) 1819.
3. Edwards, J. O. and Pearson, R. G. *J. Am. Chem. Soc.* **84** (1962) 16.
4. Hudson, R. F. *Chimia (Switz.)* **16** (1962) 173; Hudson, R. F. and Klopman, G. *J. Chem. Soc.* **1964** 5.
5. Miller, B. *J. Am. Chem. Soc.* **84** (1962) 403.
6. Jencks, W. P. and Gilchrist, M. *J. Am. Chem. Soc.* **84** (1962) 2910.
7. Bunnett, J. F. in *Ann. Rev. Phys. Chem.* **14** (1963) 271.
8. Bruice, T. C., Fife, T. H., Bruno, J. J. and Brandon, N. E. *Biochemistry* **1** (1962) 7.
9. Bruice, T. C., Bruno, J. J. and Chou, W.-S. *J. Am. Chem. Soc.* **85** (1963) 1659.
10. Tommila, E. and Murto, J. *Acta Chem. Scand* **16** (1962) 53.
11. Murto, J. *Ann. Acad. Sci. Fennicæ A II* (1962) No. 117.
12. Murto, J. *Suomen Kemistilehti* **B 35** (1962) 157.
13. Murto, J. *Acta Chem. Scand.* **18** (1964) 1029.
14. Ballinger, P. and Long, F. A. *J. Am. Chem. Soc.* **82** (1960) 795; **81** (1959) 1050; Long, F. A. and Ballinger, P. in Pesce, B. *Proc. Intern. Electrolytes Symposium, Trieste, June 1959*, Pergamon Press, London 1962, p. 152.
15. Thamsen, J. *Acta Chem. Scand.* **6** (1952) 270.
16. Binns, E. H. *Trans. Faraday Soc.* **55** (1959) 1900.
17. Hine, J. and Hine, M. *J. Am. Chem. Soc.* **74** (1952) 5266.
18. McEwen, W. K. *J. Am. Chem. Soc.* **58** (1936) 1124.
19. Murto, J. and Tommila, E. *Acta Chem. Scand.* **16** (1962) 63.
20. Bunnett, J. F. and Davis, G. T. *J. Am. Chem. Soc.* **76** (1954) 3011.
21. Miller, J. and Parker, A. J. *J. Am. Chem. Soc.* **83** (1961) 117; Parker, A. J. *J. Chem. Soc.* **1961** 1328, 4398; **1963** 4061; *Quart. Rev.* **16** (1962) 163.
22. Murto, J. *Suomen Kemistilehti* **B 34** (1961) 92.
23. Tommila, E. and Murto, M.-L. *Acta Chem. Scand.* **17** (1963) 1947.
24. Bell, R. P. *The Proton in Chemistry*. Cornell University Press, Ithaca, N. Y. 1959, p. 155.
25. Taft, R. W., Jr. in Newman, M. S. *Steric Effects in Organic Chemistry*, John Wiley & Sons, 1956, p. 556.