

Kinetics of the Reactions of 2,4-Dinitrofluorobenzene with Hydroxide and Alkoxide Ions in Alkanol-Water Mixtures

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The kinetics of the reactions of 2,4-dinitrofluorobenzene with hydroxide and alkoxide ions in methanol-water, ethanol-water, and 2-propanol-water mixtures have been studied. The solvents varied from pure water to the anhydrous alcohols, and apparent rate constants were determined separately for the concurrent alkaline hydrolysis and alcoholysis reactions, usually at four temperatures. The parameters of the Arrhenius equation were evaluated. By taking into consideration the equilibria between hydroxide and alkoxide ions, "true" rate constants and Arrhenius parameters were calculated and plotted graphically. Equilibrium constants were obtained at three temperatures for the hydroxide-2-propoxide ion equilibrium in 2-propanol-water mixtures. Other solvent effects and the mechanisms of the reactions are discussed.

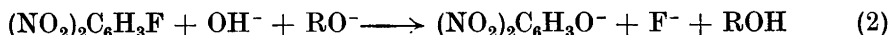
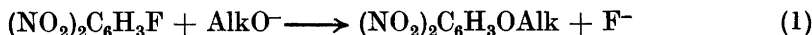
In previous studies rate constants have been determined for the reactions of methyl iodide¹ and dinitrobenzenes² with hydroxide and alkoxide ions in alcohol-water mixtures, chiefly in order to obtain information about the influence of the hydroxide-alkoxide equilibria on these reactions.

The dinitrobenzenes react with alkoxide ions 40–200 times faster than with the hydroxide ion;¹ similarly, halogenonitrobenzenes react much faster with alkoxide ions than with the hydroxide ion.³ Thus the apparent rate constants of the alkoxide reactions increase very rapidly with increasing proportion of the alcohol at low alcohol contents in the solvent. Unfortunately, however, these nitro compounds are very sparingly soluble in water. In addition, the dinitrobenzenes react relatively slowly and coloured by-products are formed at elevated temperatures. Thus no measurements could be carried out with these compounds in solvents of high water content.

The reactions of 2,4-dinitrohalogenobenzenes are much faster than those of dinitrobenzenes, and by allowing the reactions to proceed to completion the product ratios and apparent rate constants for both concurrent reactions can be determined spectrophotometrically in 10^{-4} – 10^{-3} M solutions of the nitro compound. The reactions of 2,4-dinitrofluorobenzene (DNFB) were examined in this study because these reactions are considerably faster than

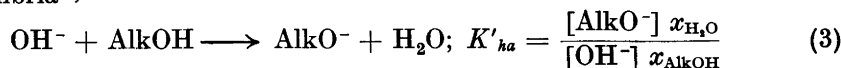
those of the other 2,4-dinitrohalogenobenzenes and thus are much less complicated by the hydrolysis of the ether formed in the reactions. Relatively few rate data have been reported previously because of the rapidity of the reactions.⁴⁻⁸

The reactions are



In (2) RO^- is a hydroxide or alkoxide ion, required to remove the proton from the 2,4-dinitrophenol.

The relative amounts of hydroxide and alkoxide ions are determined by the equilibria^{1,2}



The subscript h refers to the hydroxide ion and the subscript a to the alkoxide ion.

The rate equations are^{1,2}

$$\frac{dx}{dt} = k_a^\circ(a-x-y)(b-x-2y)s_a = k_a(a-x-y)(b-x-2y) \quad (4)$$

$$\frac{dy}{dt} = k_h^\circ(a-x-y)(b-x-2y)s_h = k_h(a-x-y)(b-x-2y) \quad (5)$$

where a and b are the initial concentrations of the substrate and base (sodium hydroxide + alkoxide), respectively, and x and y are the concentrations of the dinitroether and dinitrophenol formed.

The base fractions¹ $s_a = [\text{AlkO}^-]/([\text{OH}^-] + [\text{AlkO}^-])$ and $s_h = [\text{OH}^-]/([\text{OH}^-] + [\text{AlkO}^-])$ cannot be computed unless the equilibrium constant K'_{ha} is known, and thus only the apparent rate constants $k_h = k_h^\circ s_h$ and $k_a = k_a^\circ s_a$ can be evaluated without knowing the equilibrium constant.

Eqns. (4) and (5) have been integrated previously² for the case where $a = b$; if $a \neq b$, one obtains in a similar way the equations

$$k_a = \frac{1}{t [(b-a) + (b-2a)\frac{x}{y}]} \ln \frac{a(b-x-2y)}{b(a-x-y)} \quad (6)$$

$$k_h = k_a \frac{x}{y} \quad (7)$$

In the absence of secondary disturbing reactions the ratio x/y is constant from the beginning to the end of the reaction.

For an example of the calculations, see Table 1.

Table 1. Reactions of DNFB with hydroxide and ethoxide ions in 9.57 wt. % ethanol-water at 40.00°. Eqn. (6), where $a = 3.203 \times 10^{-4}$ M, $b = 0.00980$ M, and $x/y = 1.204$. Absorbances A were measured at 440μ (30 ml of the reaction mixture was diluted with 20 ml of buffer solution). p is the percentage of DNFB that has reacted.

Time seconds	A	$10^4 y$	$10^4 x$	p %	k_e l mole ⁻¹ s ⁻¹
7.0	0.068	0.127	0.153	8.7	0.729
10.0	0.096	0.179	0.216	12.3	0.735
20.0	0.181	0.338	0.407	23.3	0.742
30.0	0.255	0.476	0.573	32.8	0.743
50.0	0.371	0.693	0.834	47.7	0.731
70.0	0.461	0.861	1.037	59.3	0.727
90.0	0.538	1.005	1.210	69.2	0.743
120.0	0.621	1.160	1.397	79.9	0.762
150.0	0.671	1.254	1.510	86.3	0.759
180.0	0.700	1.308	1.575	90.1	0.735
∞	0.778 ^a	1.453	1.749	100.0	
					Mean 0.7406

^aMean of three values, from which 0.8 % has been subtracted as a correction for the hydrolysis of the product ether (time 600 seconds).

When corrected for solvent expansion, $k_e = 0.7458$ l mole⁻¹ s⁻¹. $k_h = 0.7458/1.204 = 0.6194$ l mole⁻¹ s⁻¹.

EXPERIMENTAL

2,4-Dinitrofluorobenzene (*purissimum p.a.*, Fluka AG) was distilled in a vacuum, after which it contained 0.01 % dinitrophenol (as determined spectrophotometrically) and melted at 26.4–26.8°. "Baker Analyzed" methanol was purified by the method of Lund and Bjerrum.⁹ Spectroscopic grade ethanol (grade AaS from the State Alcohol Monopoly, Helsinki) contained 0.83 % water (as determined from density) and was used as received. For the reactions in "100 % ethanol" it was dried by the method of Lund and Bjerrum.⁹ "Baker Analyzed" 2-propanol was dried with anhydrous calcium sulphate and distilled, after which it contained 0.20 % water (as determined by Karl Fischer titration). The base solutions in the absolute alcohols were prepared by dissolving sodium in the alcohol in question; in the other solvents, pure sodium hydroxide solution ("Titrisol", E. Merck AG) was used.

The distilled water was boiled before use. The thermostats were the same as previously. For -21° a salt-ice-water bath and for -15° an ammonium chloride-ice-water bath was used.

Reactions in solvent mixtures of low alcohol content. The initial concentration of the total base was always about 0.01 M. DNFB was dissolved in the alcoholic component of the solvent, except for the measurements in water and mixtures of very low methanol content. In these cases DNFB was dissolved in acetone (0.1 % in the solvent mixture). Ten ml of the DNFB solution and 5 ml of an about 0.03 M base solution in the same solvent mixture were pipetted into two-compartment reaction vessels.¹⁰ The reaction was arrested with an approximately neutral McIlvaine's citric acid-disodium phosphate buffer solution, and the absorbance of the solution that had been heated or cooled to 19.0° was measured with an Unicam SP. 1400 Prism Absorptiometer at 440μ (test tube cuvettes 1" in diameter). The molar extinction coefficient of dinitrophenol varies considerably with the solvent composition,¹¹ and the absorbance of a 5×10^{-5} M solution was thus determined for each solvent mixture separately. To determine the final dinitrophenol concentrations at different temperatures, the reaction mixtures were allowed to stand in thermostats for periods of about ten times the half-lives of the reactions (nearly first-order conditions!) A small correction (always less than 3 %) was applied

to these final values because of the ether hydrolysis; the rate constants for these hydrolysis reactions have been determined previously.¹² By heating the reaction mixture at 100° in a sealed ampoule for 1–2 h, also the ether hydrolysed completely and the initial concentration of DNFB could then be determined. The ratios x/y were evaluated from these data and the rate constants were computed from eqns. (6) and (7). For an example, see Table 1. Usually, however, only 5 to 7 values were recorded.

Reactions in solvent mixtures of high alcohol content. The initial concentrations of DNFB and base were both 0.01 M. The reaction was now arrested by adding hydrochloric acid. The excess acid was titrated with barium hydroxide solution, employing cresol red as indicator, after the solution had been cooled by adding ice. The final dinitrophenol concentrations were measured after the reaction mixtures had stood in the thermostats for periods of several hundred times the first half-life. The solvolysis of DNFB produces

Table 2. The reaction of DNFB with methoxide ion in methanol at 25.00°.

Time seconds	Ml of 0.01825 N Ba(OH) ₂	<i>p</i> %	<i>k_m</i> l mole ⁻¹ s ⁻¹
0	0.00	0	
4.5	6.72	40.9	15.4
5.0	7.15	43.5	15.4
7.0	8.58	52.2	15.6
8.0	9.00	54.7	15.1
10.5	10.10	61.4	15.2
15.0	11.43	69.5	15.2
20.0	12.40	75.4	15.4
30.0	13.42	81.6	14.8
∞	16.44	100	Mean 15.26

When corrected for solvent expansion, $k_m = 15.35$ l mole⁻¹ s⁻¹.

a much higher ratio of dinitrophenol in alcohol-water mixtures than does the alkaline reaction,¹³ and the solutions become progressively more yellowish. The absorbance of the DNFB solution was therefore measured several times during the working day and appropriate corrections were applied to the actual measurements. In some cases the solutions, if they had stood overnight, on mixing immediately turned brownish. For these reasons the spectrophotometric determinations were performed as soon as possible after the preparation of the solutions. It was impossible to obtain good rate constants for reactions in aqueous 2-propanol of low water content because of the rapid development of a brown colour.

The amount of dinitrophenol formed in methanol-water mixtures of high methanol content is small. If we put $y = 0$ in eqn. (6), this reduces to the usual second-order rate equation from which k_a can be computed.

The data for the reactions in solvent mixtures of high alcohol content are somewhat less accurate than the data for the reactions in mixtures of low alcohol content because of the rapidity of the reactions, the somewhat indistinct end-points in the titrations, and the development of brown colour.

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 error in all cases. The rate constants were corrected for the thermal expansion of the solvent.

RESULTS AND DISCUSSION

Influence of the hydroxide-alkoxide equilibrium. The results of the kinetic experiments are summarized in the accompanying tables. The data are plotted in the figures together with the calculated values of the "true" quantities k_a° , k_h° , E_a° , E_h° , $\log A_a^\circ$, and $\log A_h^\circ$. These were computed as described previously¹ using the values^{1,14} $K'_{hm} = 4.5$ (methanol-water mixtures) and $K'_{he} = 0.65$ (ethanol-water mixtures) for the equilibrium constants at 25°, and the values¹ $\Delta H_{hm} = \Delta H_{he} = -3.5$ kcal mole⁻¹ for the heats of the equilib-

Table 3. Apparent rate constants (1 mole⁻¹ s⁻¹), activation energies (kcal mole⁻¹), and logarithms of frequency factors for the reactions of 2,4-DNFB with hydroxide ion (subscript *h*) and with methoxide ion (subscript *m*) in methanol-water mixtures. Initial concentration of the total base (sodium hydroxide + alkoxide) was 0.01 M.

Wt. % MeOH	x_{MeOH}	10 ⁴ [DNFB]	t°	x/y	k_h	k_m	E_h	E_m	$\log A_h$	$\log A_m$	$E_h - E_m$	B'_{hm}	
0	0	3.750	0.00	0	0.00939	0	16.94	(ca. 12.5)	11.53	(-∞)			
			15.00	»	0.0469	»							
			25.00	»	0.129	»							
			40.00	»	0.504	»							
0.783	0.00442	3.320	0.00	1.72	0.00925	0.0159	16.99	12.60	11.55	8.28	4.39	387	
			15.00	1.12	0.0458	0.0515							
			25.00	0.850	0.126	0.107							
			40.00	0.616	0.502	0.309							
1.59	0.00899	3.320	0.00	3.68	0.00927	0.0341	17.03	12.31	11.58	8.37	4.72	406	
			15.00	2.32	0.0455	0.106							
			25.00	1.76	0.127	0.222							
			40.00	1.25	0.492	0.616							
2.38	0.0135	3.236	25.00	2.78	0.123	0.341	17.16	12.54	11.66	8.96	4.62	203	
			3.98	0.0228	3.276	0.00							9.72
			15.00	6.35	0.0443	0.281							
			25.00	4.81	0.121	0.581							
			40.00	3.28	0.488	1.60							
			8.03	0.0468	4.911	0.00							
15.00	13.9	0.0406	0.566										
25.00	10.4	0.117	1.21										
40.00	7.26	0.478	3.48										
16.3	0.0985	7.87	0.00	57.0	0.00559	0.319	18.62	13.61	12.65	10.40	5.01	522	
			15.00	36.1	0.0348	1.26							
			25.00	26.1	0.102	2.67							
			40.00	17.7	0.447	7.91							
55.9	0.416	100.0	0.00	471	0.00293	1.38	19.49	13.62	13.06	11.04	5.87	661	
			15.00	274	0.0190	5.20							
			25.00	197	0.0582	11.4							
			40.00	118	0.289	34.1							
76.7	0.649	100.0	0.00	1120	0.00165	1.85	19.91	13.75	13.14	11.27	6.16	606	
			15.00	644	0.0110	7.05							
			25.00	438	0.0355	15.6							
			40.00	264	0.179	47.1							
100	1	100.0	0.00	∞	0	1.89	(ca. 21.0)	13.52	(-∞)	11.10			
			15.00	»	»	7.05							
			25.00	»	»	15.4							
			40.00	»	»	45.6							

rium reactions (3). For 2-propanol-water mixtures, the values $K'_{hp} = 0.043$ and $\Delta H_{hp} = -3.3$ kcal mole⁻¹ were used. These plots give a crude picture of the solvent effects in the reactions.

The quantities $^1 E_h - E_a = E_h^\circ - E_a^\circ - \Delta H_{ha}$ and

$$B'_{ha} = \frac{x}{y} \cdot \frac{x_{H_2O}}{x_{AlkOH}} = \frac{k_a^\circ}{k_h^\circ} K'_{ha} \quad (8)$$

($B'_{ha} = 1/B'_{ah}$ in the previous notation ¹) are also given in the tables. If $E_h^\circ - E_a^\circ$ and ΔH_{ha} are constant when the solvent component ratio varies, also $E_h - E_a$ should be constant, and similarly, if k_a°/k_h° and K'_{ha} are constant, B'_{ha} should be constant. A constancy of B'_{ha} or of k_a°/k_h° does not mean, however, that

Table 4. Apparent rate constants (l mole⁻¹ s⁻¹), activation energies (kcal mole⁻¹), and logarithms of frequency factors for the reactions of 2,4-DNFB with hydroxide ion (subscript *h*) and with ethoxide ion (subscript *e*) in ethanol-water mixtures. Initial concentration of the total base was 0.01 M.

Wt. % EtOH	x_{EtOH}	10 ⁴ [DNFB]	t°	x/y	k_h	k_e	E_h	E_e	log A_h	log A_e	$E_h - E_e$	B'_{he}	
0	0	3.750	0.00	0	0.00939	0	16.94	(ca. 13.3)	11.53	(-∞)			
			15.00	»	0.0469	»							
			25.00	»	0.129	»							
			40.00	»	0.504	»							
3.94	0.0158	2.381	0.00	1.17	0.00988	0.0115	16.95	13.25	11.55	8.66	3.70	72.9	
			15.00	0.820	0.0502	0.0412							51.1
			25.00	0.658	0.136	0.0896							41.0
			40.00	0.490	0.532	0.261							30.5
9.57	0.0397	3.203	0.00	3.00	0.0115	0.0346	16.94	13.05	11.61	8.97	3.89	72.6	
			15.00	2.03	0.0576	0.117							49.1
			25.00	1.61	0.157	0.252							38.9
			40.00	1.20	0.619	0.746							29.0
20.2	0.0902	4.868	0.00	8.36	0.0170	0.142	17.01	12.82	11.83	9.40	4.19	84.3	
			15.00	5.61	0.0828	0.465							56.6
			25.00	4.45	0.227	1.01							44.9
			40.00	3.11	0.932	2.90							31.4
33.1	0.162	6.533	0.00	24.5	0.0281	0.689	16.49	11.08	11.65	8.71	5.41	127	
			15.00	14.9	0.139	2.06							77.1
			25.00	10.7	0.369	3.95							55.4
			40.00	6.87	1.36	9.31							35.5
55.3	0.326	100.0	0.00	56.7	0.0404	2.29	16.01	10.27	11.42	8.57	5.74	117	
			15.00	32.2	0.192	6.18							66.6
			25.00	23.1	0.484	11.2							47.8
			40.00	14.7	1.75	25.7							30.4
76.0	0.553	100.0	-21.12	172	0.00374	0.643	17.48	12.16	12.74	10.36	5.32	139	
			0.00	76.8	0.0590	4.53							62.1
			15.00	44.2	0.311	13.7							35.7
			25.00	33.8	0.815	27.6							27.3
100	1	100.0	40.00	21.2	(3.48)	(75.2)						17.1	
			-21.12	∞	0	1.28		12.66	(-∞)	11.07			
			0.00	»	»	8.48							
			15.00	»	»	29.8							
25.00	»	»	63										
40.00	»	»	(173)										

Table 5. Apparent rate constants ($l \text{ mole}^{-1} \text{ s}^{-1}$), activation energies (kcal mole^{-1}); and logarithms of frequency factors for the reactions of 2,4-DNFB with hydroxide ion (subscript h) and with 2-propoxide ion (subscript p) in 2-propanol-water mixtures. The initial concentration of the total base was 0.01 M.

Wt. % PrOH	x_{PrOH}	10^4 [DNFB]	t°	x/y	k_h	k_p	E_h	E_p	$\log A_h$	$\log A_p$	$E_h - E_p$	B'_{hp}
0	0	3.750	0.00	0	0.00939	0	16.94		11.73	($-\infty$)		
			25.00	»	0.129	»						
			40.00	»	0.504	»						
19.4	0.0674	2.091	0.00	0.478	0.0274	0.0131	16.53	13.7	11.66	9.1	2.9	6.61
			25.00	0.325	0.363	0.118						4.50
			40.00	0.240	1.33	0.319						3.32
51.9	0.245	3.276	0.00	3.13	0.122	0.381	13.50	8.61	9.88	6.47	4.89	9.65
			25.00	1.49	0.953	1.42						4.59
			40.00	0.987	2.94	2.90						3.04
76.3	0.491	6.184	0.00	3.27	0.384	1.26	13.35	9.19	10.26	7.45	4.16	3.39
			15.00	2.25	1.35	3.02						2.33
			25.00	1.76	3.02	5.30						1.82
			40.00	1.23	8.84	10.9						1.28
92.5 ^a	0.786	10.8	-21.12	6.4	0.10	0.64	14.6	11.5	11.7	9.8	3.1	1.7
			0.00	3.8	0.98	3.7						1.0
			15.00	2.9	3.9	11						0.79
			25.00	2.4	(9.1)	(22)						0.65
99.80	0.9934	100.0	-21.12			2.93		12.00		10.89		
			-15.18			5.43						
			0.00			19.7						
			15.00			60.1						
			25.00			(123)						

^a The measurements were carried out within some minutes after preparation of the solutions. The rate constants given in parentheses were computed from the Arrhenius parameters.

Table 6. Values of K'_{ha} .

x_{AlkOH}	K'_{he} in ethanol-water			K'_{hp} in 2-propanol-water		
	0°	25°	40°	0°	25°	40°
0.2	0.54	0.38	0.33	0.043	0.025	0.021
0.3	0.72	0.45	0.42	0.065	0.038	0.028
0.4	0.86	0.51	0.50	0.069	0.043	0.030
0.5	0.92	0.58	0.57	0.070	0.043	0.032
0.6	0.96	0.65	0.64	0.074	0.044	0.036
0.7	0.94	0.71	0.69	0.072	0.048	0.043
0.8	0.98	0.77	0.73	0.079	0.055	0.057

k_a° and k_h° are independent of solvent composition. This fact has been overlooked in a recent kinetic determination¹⁵ of K'_{he} in ethanol-water mixtures; the value reported for the constant at 60° is probably in error by a factor of ten.

The higher the alcohol homologue in question, the more marked is the variation of B'_{ha} with solvent composition. This reflects the increasing non-ideality of the solvent system.

It is interesting to compare the plots for the reactions of DNFB with those for the corresponding reactions of methyl iodide,¹ a simple aliphatic compound, and with those for aromatic dinitro compounds.^{1,2,12} The following general features are observed in all cases:

1. When water is added to an alcohol, the apparent (measured) rate constant of the alkoxide reaction initially increases (or remains approximately constant) in methanol-water and decreases in ethanol-water mixtures. The true rate constants increase in both cases.

2. When alcohol is added to water, the apparent rate of the hydroxide reaction decreases in methanol-water and increases in ethanol-water mixtures. Again, the true rates increase in both cases. The curves plotting $\log k_h$ are s-shaped at low alcohol contents.

3. The curves plotting $\log k_m^\circ$, $\log k_e^\circ$, and $\log k_p^\circ$ have flat maxima. At low alcohol contents they run parallel to the $\log k_h^\circ$ curves and thus k_a°/k_h° is approximately constant. Plots of $\log k_e^\circ$ are also s-shaped at low alcohol contents.

4. The measured rate constants k_m of the reactions in methanol-water mixtures of high methanol content are close to the true ones, k_m° , since the hydroxide-methoxide equilibrium lies in the favour of the latter ion. The measured constants k_h of the reactions in 2-propanol-water mixtures approximate the true ones up to high alcohol contents since the equilibrium is in favour of the hydroxide ion.

5. The curves plotting apparent and true activation energies and logarithmic frequency factors for DNFB are similar to those obtained for methyl iodide.

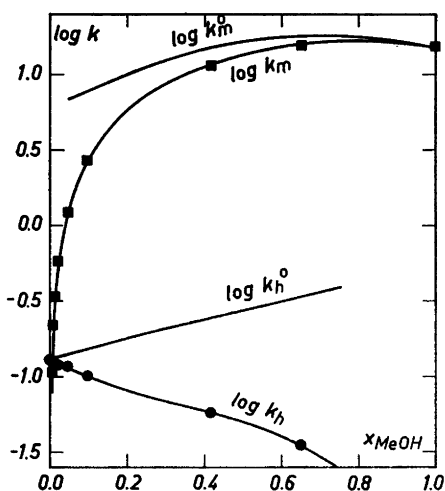


Fig. 1. Rate constants of the anionic solvolyses of DNFB in methanol-water mixtures at 25°. $K'_{hm} = 4.5$.

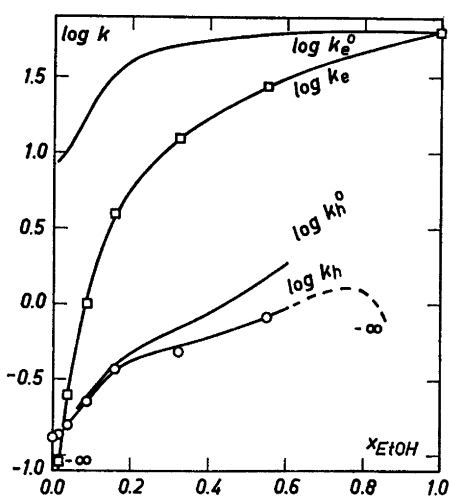


Fig. 2. Rate constants of the anionic solvolyses of DNFB in ethanol-water mixtures at 25°. $K'_{he} = 0.65$.

6. The nucleophilic reactivity of the alkoxide ions is much greater than that of the hydroxide ion¹ (see also the following paper¹³). From Figs. 1 and 2 we can see that $k_a^\circ/k_h^\circ \approx 50$ for DNFB in methanol-water and ethanol-water mixtures. Thus the amount of dinitroether formed is considerable at very low alcohol contents. This effect is most marked in methanol-water mixtures, as the hydroxide-methoxide equilibrium lies in favour of the latter ion.

7. All the compounds studied react much more rapidly in alcohols than in water. This is in part due to the higher reactivity of alkoxide ions as compared with

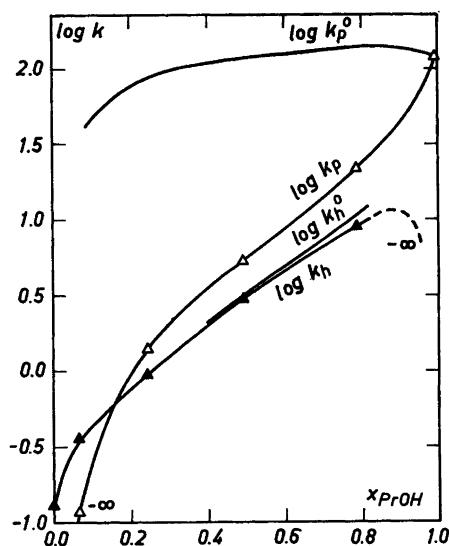


Fig. 3. Rate constants of the anionic solvolyses of DNFB in 2-propanol-water mixtures at 25°. $K'_{hp} = 0.043$.

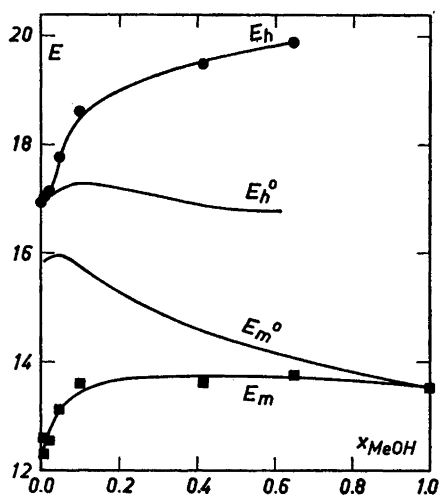


Fig. 4. Energies of activation in methanol-water mixtures.

hydroxide ion, and in part to the increase in the true rate constants on going from water to alcohols (see the figures). Thus DNFB reacts at 0° 2000 times faster in 2-propanol and 200 times faster in methanol than in water.

Evaluation of hydroxide-alkoxide equilibrium constants. The true rate of the hydroxide reaction increases with the alcohol content of the solvent in all solvent mixtures studied, and also the apparent rate constants increase rapidly in the ethanol-water and 2-propanol-water mixtures. These rate constants cannot hence be used to compute the equilibrium constants. The values of k_a° seem to be less dependent on solvent composition at high alcohol contents, and at least an estimate is obtained for K'_{hp} in 2-propanol-water mixtures, as the equilibrium favours the hydroxide ion in these solvent mixtures and the addition of water to 2-propanol results in a rapid decrease in the concentration of the propoxide ion and consequently also in the apparent rate constant. The equilibrium constants in Table 6 were computed from

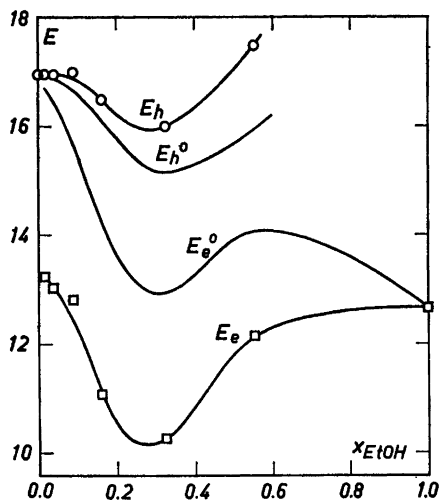


Fig. 5. Energies of activation in ethanol-water mixtures.

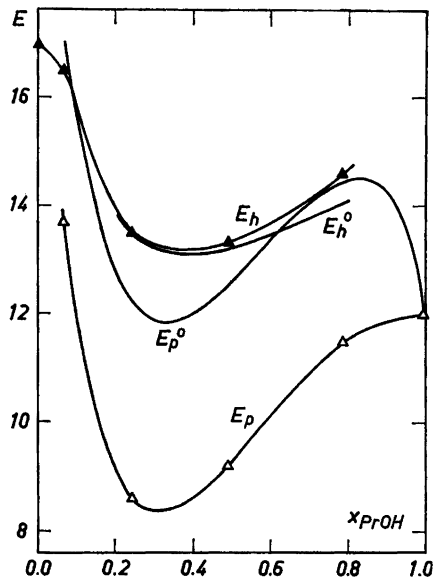


Fig. 6. Energies of activation in 2-propanol-water mixtures.

the equation¹ $K'_{ha} = x_{H_2O} k_a / [x_{AlkOH} (k_a^\circ - k_a)]$, taking for k_a° the value obtained for the corresponding absolute alcohol.

Of these values, those at about $x_{AlkOH} = 0.5$ may be considered to be the most reliable ones. The value 0.043 for 2-propanol-water mixtures at 25° is somewhat smaller than the value 0.063 for absolute 2-propanol at 27° computed from the data of Hine and Hine.^{16,1} The plot of $\log K'_{hp}$ vs. $1/T$ is almost linear and yields $\Delta H_{hp} = -3.3$ kcal mole⁻¹; this is very close to the values obtained previously for methanol-water and ethanol-water mixtures. The equilibrium constant in ethanol-water at 25°, $K'_{he} = 0.58$, is of the same order of magnitude as the estimates obtained previously.¹ The values of K'_{he} at 40° are somewhat in error in relation to the values obtained for other temperatures.

Other solvent effects. The true rate constants of the alkoxide reactions of DNFB vary only slightly with solvent composition in solvents of high alcohol content. Burns and England^{7,8} obtained $k_m^\circ = 1.85$ l mole⁻¹ s⁻¹ in methanol and $k_e^\circ = 8.97$ l mole⁻¹ s⁻¹ in ethanol at 0°. The rate increase in methanol-water mixtures with increasing water content of the solvent observed by them was somewhat more marked than that found in the present study. The rate constants for the reaction of 2,4-dinitrochlorobenzene with methoxide ion vary very little with solvent composition in methanol-benzene mixtures¹⁷ but increase somewhat on adding dioxan¹⁸ or methyl acetate¹⁹ to methanol. Addition of water to methanol enhances the rate of the methoxide reaction of this compound²⁰ more than that of DNFB.

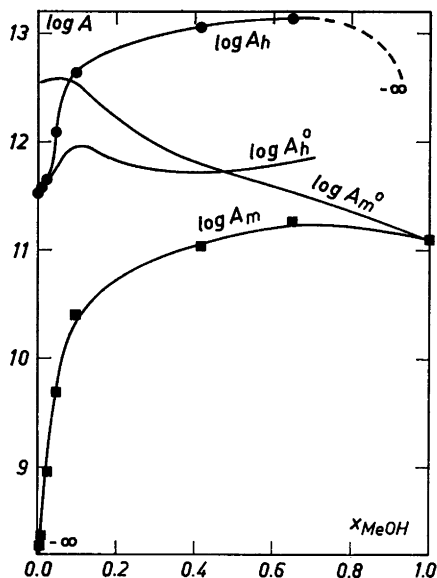


Fig. 7. Frequency factors in methanol-water mixtures.

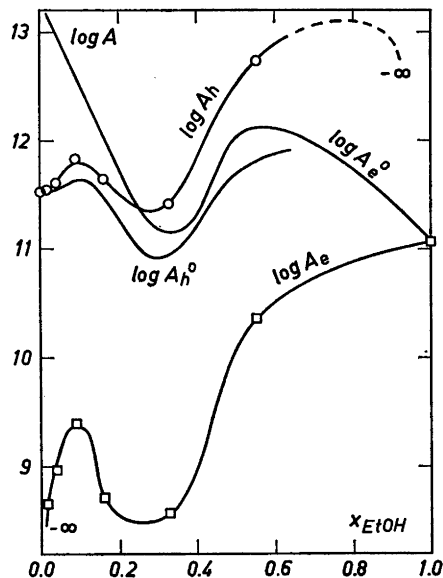


Fig. 8. Frequency factors in ethanol-water mixtures.

The increase of k_a° with increasing water content of the solvent does not agree with predictions based on the Hughes-Ingold²¹ theory of solvent action. According to the data of Riklis²² the rate of the reaction of methoxide ion with *o*-chloronitrobenzene at 80° should decrease on adding water; however, Burns and England⁷ have found that these results are in error and that the rate actually increases at 60°.

This increase is observed also in the corresponding reactions of methyl iodide.^{23,1} However, the rate constants of the reactions between methyl iodide and iodide ion or between methyl iodide and thiosulphate ion decrease on adding water to methanol,⁷ in accordance with Hughes and Ingold's predictions.

If the solvation of the transition state decreases relative to that of the initial state on adding water to an alcohol, the activation energy and entropy of activation, and also the frequency factor, will increase, as is actually observed for the reactions discussed in this paper. The effects of changes in E_a° and $\log A_a^\circ$ compensate each other so that only a negligible increase in rate is observed.

The effects of solvation and dielectric constant are of minor significance in the reactions of DNFB with alkoxide ions. However, phenomena such as the decreasing solubility of DNFB with increasing water content of the solvent, specific solvation effects,^{24,17} ion-pair equilibria,¹ and changes in the internal structure of the solvent may be of some importance under certain circumstances

The rate changes are in the expected direction in mixtures of high water content, and, as stated above, the reactions of aromatics are similar to the reactions of methyl iodide. There is some similarity also between the hydroxide reaction of DNFB in alcohol-water mixtures and the hydroxide reaction of ethyl bromide in acetone-water mixtures:²⁵ E_h° has a maximum value in methanol-water, $\log A_h^\circ$ in methanol-water and ethanol-water mixtures, and both E and $\log A$ have a maximum value in acetone-water mixtures when the percentage of the organic component of the solvent is about 20. For the hydroxide reactions of methyl iodide such maxima occur in the 10 % ethanol-water mixture.¹ In many reactions, such as the alkaline hydrolysis of ethyl acetate, minima are observed in about 20 % alcohol-water mixtures.^{26,24,1} In the reactions of aromatic nitro compounds such minima occur at higher alcohol contents. There are no maxima in the plots for the hydrolyses of 2,4-dinitroanisole and 2,4-dinitrophenetole.¹²

k_h° for DNFB is about 10^2 times greater in 2-propanol than in water. Dioxan also accelerates the hydroxide reaction considerably; Bunnett and Randall⁶ obtained the value $0.114 \text{ l mole}^{-1} \text{ s}^{-1}$ for the reaction in 60 vol. % dioxan-water at 0° . This value is twelve times the value obtained in the present study for the reaction in water. This increase is of the same order of magnitude as that observed by Tommila and Murto² for *p*-dinitrobenzene in dioxan-water mixtures.

As the solvent contained 0.1 % of acetone in some runs, its influence on the rate of DNFB was also studied. It was found that $k_h^\circ = 0.162 \text{ l mole}^{-1} \text{ s}^{-1}$ at 25° in 4.91 wt. % acetone-water. This is 25 % higher than the value obtained for the reactions in water. Thus the influence of 0.1 % of acetone on the rate constant is of the order of 1 % or less.

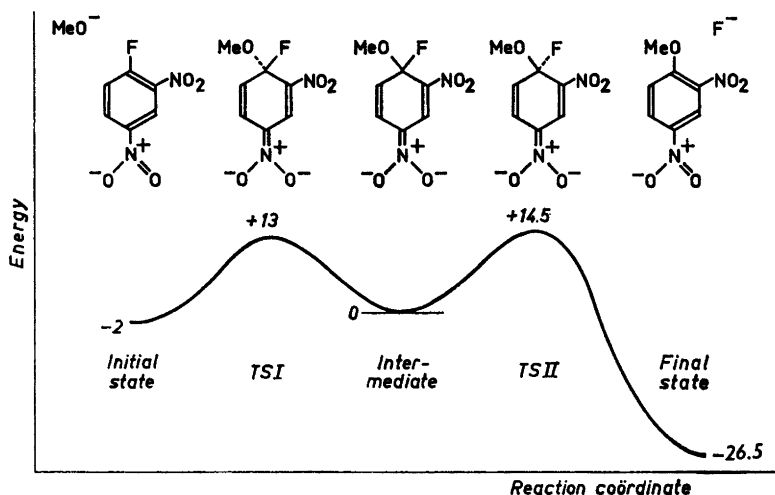


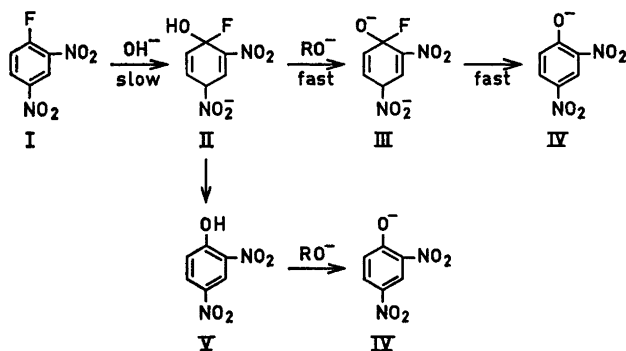
Fig. 9. Energy profile for the reaction of DNFB with methoxide ion in methanol (according to Miller's model²⁹).

Some data in dimethyl sulphoxide-water mixtures will be published later.²⁷

Mechanism of the reaction. It has been generally assumed^{28,29} that nitro-activated aromatic nucleophilic substitution reactions involve the formation of a cyclohexadienide intermediate, in which the carbon at the reaction center uses four tetrahedral sp^3 hybrid orbitals and thus resembles an aliphatic saturated carbon. The transition states I and II (Fig. 9) for the formation and decomposition of the intermediate closely resemble this intermediate.

Miller²⁹ has performed quantitative calculations assuming this model for the reaction path. These calculations, although they are rough and involve several only approximately known energy quantities, give for many reactions activation energies that agree well with experimental values.²⁹ The energy profile for DNFb + MeO⁻ in methanol in Fig. 9 has been obtained by Miller's method, using the same values of the energies as he employed for the corresponding reactions. This calculation gives an activation energy of 16.5 kcal mole⁻¹; the experimental value obtained in the present paper is 13.5 kcal mole⁻¹.

The mechanism of the reaction with hydroxide ion deserves further consideration. Now a second equivalent of base is required to remove the proton from the hydroxyl attached to the carbon at the reaction center; such proton transfer reactions are known to be very fast. There are at least two possible routes from I to IV:



The route I→II→V is analogous to the alkoxide reaction. However, Bunnett and Davis³ point out that the reaction may actually involve the formation of a doubly charged anion III as the negative charge on the oxygen greatly facilitates the expulsion of the halogen; thus the process II→III→IV is more rapid than the process II→V→IV. Whatever the route from II to IV may be, the method of computing the apparent and true rate constants is always the same as that given in the present paper.

Acknowledgement. The author gratefully acknowledges a Government Fellowship for Young Scientists.

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Received March 6, 1964.

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

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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 $\log k_a^\circ = a pK_a + \beta$, 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 Scott¹ 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