

## Nucleophilic Reactivity

### Part 8. Reactivity of Alkoxide Ions, Alcohols, and Water towards Picryl Fluoride

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The alkaline alcoholysis reactions of picryl fluoride in aqueous-alcoholic solvents of low alcohol content have been studied by the product ratio method described in Part 2.<sup>2</sup> The rate constants are of the order of  $10^4$  l mole<sup>-1</sup> s<sup>-1</sup>, and satisfy the relationship  $\log k_a^\circ = 0.209 \text{ p}K_a + 0.79$  (at 25°), where the  $\text{p}K_a$  refers to the conjugate acid of the incoming group. The slope of this plot is about the same as for the reactions of 2,4-dinitrofluorobenzene.<sup>2</sup> The alkoxide/hydroxide reactivity ratios are about 15, and the true activation energies of the reactions of alkoxide and hydroxide ions are nearly equal. The reactions of picryl fluoride with alcohols and water in their mixtures were also studied at 25°. A product ratio quantity  $N_{wa}'$  that refers to the neutral reactions was defined; for picryl fluoride it varied with the solvent similarly as the quantity  $B_{ha}'$  for the alkaline reactions of 2,4-dinitrofluorobenzene. It was found also that 2,2,2-trifluoroethanol markedly retards the reaction of picryl fluoride with water, whereas less acidic alcohols accelerate this reaction considerably. Water, methanol, and ethanol react with fluoronitrobenzenes at comparable rates. No visible Meisenheimer complexation was observed in the alkaline or neutral reactions of picryl fluoride at the low initial concentrations employed.

In Parts 1–3<sup>1-3</sup> and 10<sup>4</sup> of this series the hydrolysis and alcoholysis reactions of 2,4-dinitrofluorobenzene (DNFB) were studied. Part 2 dealt specially with the alkaline alcoholysis of DNFB in aqueous solvents of low alcohol content.

In the present paper the alkaline and neutral alcoholysis and hydrolysis of picryl fluoride are discussed. The following paper<sup>6</sup> deals with the reactions of other picryl compounds and the mechanisms of the reactions.

Picryl fluoride has been known only for a few years,<sup>7,8</sup> and because of this and the very great rapidity of its reactions, the alkaline hydrolysis and alcoholysis of this compound have not been studied previously. Parker and Read<sup>8</sup> have studied its reaction with aniline at low temperatures.

## EXPERIMENTAL

*Chemicals.* Picryl fluoride was synthesized according to Shaw and Seaton<sup>7</sup> and isolated and purified according to Parker and Read.<sup>8</sup> Immediately after preparation it melted at 123° (labile form<sup>7</sup>); after two months, the melting point had risen to 131° (stable form<sup>7</sup>).

The alcohols were the same samples as were used previously.<sup>2</sup> They were redistilled immediately before use. The water was purified as described in the following paper.<sup>6</sup> Dioxan was freed from peroxides by passing it through aluminium oxide "Woelm basisch, akt. Stufe I" immediately before use.

*Reactions with alkali.* The neutral water hydrolysis of picryl fluoride is so rapid (half-life about 8 min at 25°) that aqueous or alcoholic stock solutions of this compound cannot be prepared. The following procedure was therefore adopted: picryl fluoride was dissolved in dioxan, and 10  $\mu$ l of this solution was injected with a Hamilton syringe equipped with a Chaney adapter into 10 ml of water (that contained a small amount of the alcohol in question) in one compartment of the reaction vessel.<sup>9</sup> The reproducibility of the injected amounts was found to be better than 0.5 %. The initial concentration of picryl fluoride was evaluated by injecting picryl fluoride solution into dilute aqueous alkali and measuring the absorbance of the solution.

The other compartment of the vessel contained 5 ml of about 0.005 N aqueous-alcoholic sodium hydroxide solution, and the contents of the two compartments were mixed within 2–3 seconds after the injection of the picryl fluoride solution to keep the error due to water hydrolysis of picryl fluoride as low as possible. The reaction went to completion almost instantaneously, after which the ether formed in the alkoxy reaction began to hydrolyse through the action of hydroxide ion. This reaction is 10<sup>4</sup> times slower than the formation of the ether. To stop this undesirable reaction, 5 ml of 0.02 N hydrochloric acid was added. The picrate anion was then determined spectrophotometrically at 380  $m\mu$  (cf. the preceding paper<sup>6</sup>). Picric acid is so strong an acid ( $pK_a$  0.33) that it is almost completely in the anionic form in this dilute hydrochloric acid solution.

Several determinations were made, the hydrochloric acid solution being added after varying periods of time (4–30 s) after the solutions had been mixed, and the absorbance reading was extrapolated to zero reaction time to correct for the hydrolysis of the ether.

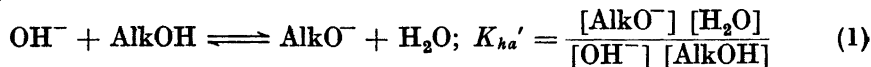
The strong colour formed in the solutions of diols and polyols disappears on adding hydrochloric acid, leaving only the colour of the picrate anion which could thus be measured. The solutions of pentaerythritol were somewhat turbid, the turbidity increasing with time, and the absorbance readings of these solutions were taken using as a blank a solution that had been prepared at the same time as the sample solution but contained no picryl fluoride.

When working with the halogenoethanols, the base solution did not contain alcohol.

*Neutral reactions.* Weighed amounts of the alcohol and water were pipetted into a 40-mm cell of the Unicam SP. 600 spectrophotometer to give a total volume of about 10 ml. The temperature of the cell housing was kept constant by pumping water from a thermostat through a jacket that surrounded the cells on three sides. After about half an hour, when the temperature no longer changed, picryl fluoride in 10  $\mu$ l of dioxan was injected with the Hamilton syringe. The solution was mixed thoroughly and absorbance readings were taken at appropriate intervals. A drop of 0.02 N hydrochloric acid had also been added to the solution to minimize the possible influence of basic impurities. The infinity absorbance was taken after ten half-lives. To evaluate also the product ratios, dilute aqueous sodium hydroxide instead of water was pipetted into the cell, the picryl fluoride solution injected, and after a few seconds, after the picryl fluoride had been completely hydrolysed to picrate, the alcoholic component of the solvent was added and the absorbance reading taken. From this and the infinity reading for the non-alkaline solution, the product ratio could be computed. The rate constants were computed from eqns. (7) and (8). The rate constants did not drift with time.

RESULTS AND DISCUSSION

*Reactions with alkali.* These reactions are complicated by the pre-equilibrium <sup>10,2</sup>



where the subscript *h* refers to hydroxide ion and the subscript *a* to the alkoxide ion. Thus only apparent rate constants are obtained from the measurements unless assumptions are made concerning this equilibrium.<sup>1,2</sup> If the alcohol content of the solvent is low, the equilibrium constant  $K_{ha}'$  can be computed <sup>2</sup> from the  $pK_a$  value of the alcohol in water.

Reactions with different alkoxides can be compared in terms of the quantities <sup>10,2</sup>  $B_{ha}'$  that are related to the product ratios:

$$B_{ha}' = \frac{x}{y} \frac{[\text{H}_2\text{O}]}{[\text{AlkOH}]} = \frac{k_a^\circ}{k_h^\circ} K_{ha}' \quad (2)$$

where *x* and *y* are the concentrations of the products of the reactions with alkoxide and hydroxide ion, respectively, and  $k_a^\circ$  and  $k_h^\circ$  are the corresponding

*Table 1.* Reactions of picryl fluoride with alkoxide and hydroxide ions in aqueous-alcoholic solvents of low alcohol content. The subscript *a* refers to the alkoxide reaction, the subscript *h* to the hydroxide reaction, and *x/y* is the product ratio. Initial concentrations:  $[\text{NaOH}] = 1.6 - 1.7 \times 10^{-3}$  M,  $[\text{PF}] \approx 2 \times 10^{-5}$  M. For references concerning the  $pK_a$  values, see the previous papers.<sup>2,5</sup>

No	Compound RH	$pK_a$ of RH at 25°	Wt. % org. comp.	<i>x/y</i>				$E_h - E_a$	$\log \frac{A_h}{A_a}$	$B_{ha}'$ 25.00°
				0.00°	15.00°	25.00°	40.00°			
1	2-Propanol	17.1	20.2			0.096				1.3
	»	17.1	20.2			0.095				1.3
2	Ethanol	15.93	12.1	1.05	0.76	0.62	0.47	3.44	2.73	11.5
	»	15.93	12.1			0.62				11.5
3	Water	15.74	0	(1)	(1)	(1)	(1)	(0)	(0)	(1)
4	Methanol	15.09	1.04			0.39				66
	»	15.09	1.60	1.16	0.79	0.63	0.45	4.03	3.16	69
5	1,2-Ethanediol	14.77	3.29			1.05				106
6	2-Chloroethanol	14.31	3.00	2.9	1.90	1.45	1.04	4.44	3.09	210
7	Pentaerythritol	14.10	2.00			1.08				400
8	2,2,2-Trifluoroethanol	12.39	0.231 <sup>a</sup>			3.2 <sup>a</sup>				7900
	»	12.39	0.415			5.1				7000
9	2,2,2-Trichloroethanol	12.25	0.167 <sup>b</sup>	4.2	2.6	1.72 <sup>b</sup>	1.07	5.88	4.07	9000
10	Phenol	9.97	0.00169 <sup>c</sup>			1.36				$6.9 \times 10^4$
	»	9.97	0.00674 <sup>c</sup>			6.3				$5.5 \times 10^4$

<sup>a</sup> Initial concentrations in this solution at 25°, as computed with the aid of  $pK_a$ :  $[\text{AlkOH}] = 0.02231$  M;  $[\text{AlkO}^-] = 0.000789$  M;  $[\text{OH}^-] = 0.000891$  M. <sup>b</sup> Initial concentrations at 25°, as computed with the aid of  $pK_a$ :  $[\text{AlkOH}] = 0.01057$  M;  $[\text{AlkO}^-] = 0.000600$  M;  $[\text{OH}^-] = 0.001008$  M. <sup>c</sup> The amount of phenol added was so small that only a part of the hydroxide was converted into phenoxide.

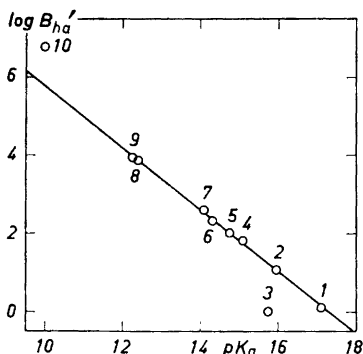


Fig. 1. Plot of  $\log B'_{ha}$  against the  $pK_a$  of the alcohol at 25°. The numbering of the alcohols refers to Table 1.

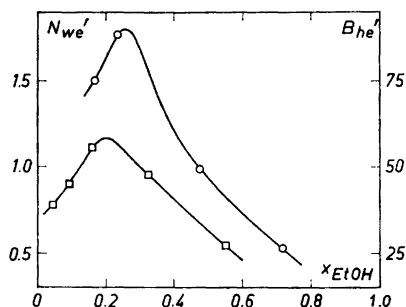


Fig. 2. Quantities related to the product ratio in ethanol-water mixtures at 25°:  $\square$ ,  $B'_{he}$  for the alkaline reactions of DNFB,<sup>1</sup> and  $\circ$ ,  $N_{we'}$  for the neutral reactions of picryl fluoride.

“true” rate constants (*i.e.*, rate constants already corrected for the influence of equilibrium (1)).

Table 1 summarizes the experimental results. As the reactions are very fast, only the product ratios could be determined directly. From these, the values of  $B'_{ha}$  were computed with the aid of eqn. (2). The product ratios also give the differences between the apparent activation energies of the hydroxide and alkoxide reactions,  $E_h - E_a$ , and the differences between the apparent logarithmic frequency factors of these reactions,  $\log A_h - \log A_a$  (*cf.* eqn. (2) in Ref. 2).

The differences  $E_h - E_a$  are somewhat smaller than those found for DNFB.<sup>2</sup> Indeed, they are of about the same absolute magnitude as the quantities  $\Delta H_{ha}$ , the heats of the proton transfer reactions (1), estimated previously.<sup>10,2</sup> As<sup>10</sup>  $E_h - E_a = E_h^\circ - E_a^\circ - \Delta H_{ha}$ , where  $E_h^\circ$  and  $E_a^\circ$  are the true energies of activation, this result indicates that  $E_h^\circ \approx E_a^\circ$  in the alkaline reactions of picryl fluoride in water.

In Fig. 1  $\log B'_{ha}$  has been plotted against the  $pK_a$  of the alcohol. The point for water lies below the straight line that represents “normal” reactivity; the situation is similar also for the reactions of DNFB.<sup>2</sup> Phenol gives a positive deviation, but it is highly probable that the correlation between reactivity and  $pK_a$  in the series of phenoxides is different from that found for alkoxides.<sup>5,6,11,12</sup>

If water and phenol are neglected, the remaining eight points give by the method of least squares the relationship (at 25°):

$$\log B'_{ha} = 13.685 - 0.791 pK_a \quad (3)$$

from which we obtain,<sup>2</sup> taking  $k_h^\circ = 7 \times 10^2 \text{ l mole}^{-1} \text{ s}^{-1}$  (*cf.* the following paper<sup>6</sup>),

$$\log k_a^\circ = 0.209 pK_a - 0.79. \quad (4)$$

An uncertainty in the value of  $k_h^\circ$  does not affect the slope of the plot of  $\log k_a^\circ$  vs.  $pK_a$ . This slope is about the same as was found for DNFB (for

which the value 0.215 was reported<sup>2</sup>). For further discussion of the Brønsted plots, see the following paper.<sup>6</sup>

The values of  $\log k_a^\circ$  were computed also for each alkoxide separately from the  $B_{ha}'$  values and are plotted in Fig. 1 in the following paper.<sup>6</sup>

This plot shows that the reactivity ratio methoxide/hydroxide and ethoxide/hydroxide is about 15. In the reactions of DNFB<sup>2</sup> and 1,2-dinitrobenzene,<sup>10</sup> in both of which the removal of the substituent is influenced by only one *ortho* nitro group, it is about 40, and in the reactions of 1,4-dinitrobenzene<sup>10</sup> it is about 200. Thus the *ortho* nitro groups seem to suppress the reactivity of the alkoxide ions. Another possibility is that the nitro groups increase the reactivity of the hydroxide ion by stabilizing the transition state by forming a hydrogen-bonded cyclic structure.

It might be expected that Meisenheimer complexation occurs in the reactions studied (see also the following paper<sup>6</sup>). It was thus somewhat surprising to note that no colour developed in the reactions of picryl fluoride with hydroxide ion and alkoxides of the monohydroxylic alcohols or in the reactions<sup>6</sup> of the picryl ethers of monohydroxylic alcohols with hydroxide ion in water at the low alkali concentrations used. In the case of diols and polyols a very strong brown colour was always instantaneously formed, but this is most probably due to a subsequent reaction, an internal cyclic complexation of the ether formed in the reaction.<sup>13,14</sup> The formation of these ethers from picryl fluoride seems to be a normal reaction, as the points for ethanediol and pentaerythritol in Fig. 1 (and in Fig. 1 in Ref. 6) are close to the straight line of normal reactivity.

*Neutral reactions.* In many studies of neutral solvolysis reactions in aqueous alcohols the occurrence of two concurrent reactions, alcoholysis and hydrolysis, has not been taken into consideration. This can be easily done in the case of picryl fluoride, as the progress of the reaction is followed by determining the concentration of one of the products, the coloured picrate anion, and the reactions are so fast that also the product ratios can be determined conveniently.

The rate equations are

$$dx/dt = k_a (a-x-y) \quad (5)$$

$$dy/dt = k_w (a-x-y) \quad (6)$$

where  $x$  and  $y$  are the concentrations of picryl ether and picrate anion formed, respectively,  $a$  is the initial concentration of picryl fluoride, and the subscripts  $a$  and  $w$  refer to the reactions with alcohol and water, respectively. From these equations we obtain, on taking  $x = y = 0$  at  $t = 0$ ,

$$k_a/k_w = x/y \quad (7)$$

$$k_a + k_w = \frac{1}{t} \ln \frac{a}{a-x-y} = \frac{1}{t} \ln \frac{y_\infty}{y_\infty-y} \quad (8)$$

Thus  $k_a$  and  $k_w$  can be evaluated by following the formation of the picrate anion and determining the product ratio.

To allow comparisons between different alcohols, and between the alkaline and neutral reactions, we define, analogously to eqn. (2), a quantity  $N_{wa}'$  that

Table 2. Reactions of picryl fluoride with alcohols and water in alcohol-water mixtures at 24.8°. [PF] =  $1.33 \times 10^{-5}$  M, and [HCl]  $\approx 10^{-4}$  M.

Alcohol	Wt. % alcohol	$\frac{x}{y}$	$10^5 k_a$ (s <sup>-1</sup> )	$10^5 k_w$ (s <sup>-1</sup> )	$N_{wa}'$
2-Propanol	43.6 <sup>b</sup>	0.084	84	1000	0.36
Ethanol	33.9	0.300	145	485	1.50
»	43.8 <sup>b</sup>	0.541	332	614	1.77
»	69.6	0.887	701	789	0.99
»	86.6	1.34	892	663	0.53
Water <sup>a</sup>	—	(1)	(144)	144	(1)
Methanol	44.0 <sup>b</sup>	1.41	320	227	3.20
2,2,2-Trifluoroethanol	58.0 <sup>b</sup>	0.059	2.2	36.8	0.24

<sup>a</sup> See the following paper. <sup>b</sup> 50 vol. %.

refers to the neutral solvolyses; it can be computed from the known product ratio and solvent composition:

$$N_{wa}' = \frac{x}{y} \frac{[\text{H}_2\text{O}]}{[\text{AlkOH}]} = \frac{k_a}{k_w} \frac{[\text{H}_2\text{O}]}{[\text{AlkOH}]} = \frac{k_a'}{k_w'} \quad (9)$$

In the derivation of this equation use was made of eqn. (7).  $k_a' = k_a/[\text{AlkOH}]$  and  $k_w' = k_w/[\text{H}_2\text{O}]$  are second-order rate constants (which are also apparent quantities,<sup>3</sup> as the interaction of the solvent molecules is great).

$N_{wa}'$  thus varies as the ratio  $k_a'/k_w'$ . Similarly, if  $K_{ha}'$  is taken to remain constant when the solvent composition is varied,  $B_{ha}'$  reflects changes in the corresponding reactivity ratio  $k_a^0/k_h^0$  in the alkaline reactions.

The experimental results are given in Table 2 and Figs. 2 and 3. In Fig. 2 values of  $B_{he}'$  for DNFB in ethanol-water mixtures<sup>1</sup> are also plotted. The two curves, that of  $N_{we}'$  for picryl fluoride and that of  $B_{he}'$  for DNFB (the subscript *e* refers to ethanol or ethoxide ion), are very similar in form. This similarity shows that the solvent dependence of the alcoholysis/hydrolysis reactivity ratio is much the same for the neutral and alkaline reactions.

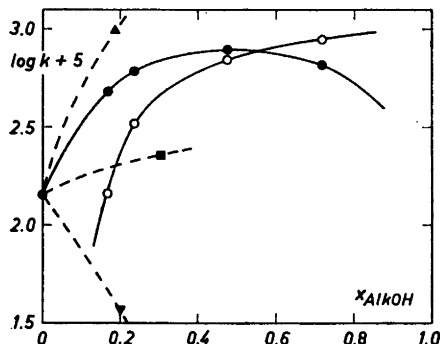


Fig. 3. Plots of  $\log k$  (first-order rate constant) for the reactions of picryl fluoride with alcohols and water in the aqueous alcohols. ▲ Hydrolysis in aq. 2-propanol, ● hydrolysis in aq. ethanol, ○ ethanolysis in aq. ethanol, ■ hydrolysis in aq. methanol, ▼ hydrolysis in aq. 2,2,2-trifluoroethanol.

Comparison of Fig. 3 with the figures in Ref. 1 shows that addition of an alcohol to water changes the rate constant of the neutral hydrolysis similarly as it influences  $k_h^\circ$  in the alkaline reaction. In the case of the less acidic alcohols,  $k_w$  increases although the concentration of water decreases, and the increase is the more marked the higher the  $pK_a$  of the alcohol.  $k_w$  (and, of course, also  $k_w'$ ) correlates roughly with the  $pK_a$  of the alcoholic component of the solvent; for example, at  $x_{\text{ALCOH}} = 0.2$  the slope of a  $\log k_w - pK_a$  plot (not shown) would be ca. 0.3. This behaviour is most probably connected with changes in the extent of hydrogen bonding of water. In aqueous 2,2,2-trifluoroethanol the water and alcohol molecules seem to be so tightly bound that their mobility and ability to react are much diminished, whereas in aqueous 2-propanol the water molecules are more free to react than in water. Apparently the mobility of the hydroxide ion varies with the solvent similarly as that of water, which explains the similar solvent dependence of  $B_{hc}'$  and  $N_{we}'$ .

The thermodynamics of aqueous mixtures of polyfluoroalcohols will be studied later.

The quantities  $N_{wa}'$  in Table 2 are not correlated with the  $pK_a$  values of the alcohols; they do not refer to the same solvent, and the very marked increase of the water reactivity causes the values of  $N_{wa}'$  to change in an unexpected direction when going from aqueous methanol to aqueous 2-propanol.

As mentioned above,  $N_{wa}'$  is a measure of the alcohol/water reactivity ratio. The product ratios  $x/y = 4.1$  in 76.7 wt. % methanol-water mixture and 0.84 in 55.3 wt. % ethanol-water mixture have been reported<sup>2</sup> for DNFb at 40°. These ratios give  $N_{wm}' = 2.2$  for the methanol-water mixture, and  $N_{we}' = 1.7$  for the ethanol-water mixture. Although the temperature and substrate were different from those in the present study, it can be said that the alcohol/water reactivity ratio obviously varies relatively little with the activation due to nitro groups and is almost independent of the *ortho* effect (see also the following paper<sup>6</sup>) and that the neutral hydrolysis, methanolysis, and ethanolsis reactions of a fluoronitrobenzene proceed at comparable rates.

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