445. *The Kinetics of Some Fast Reactions of 4-Nitrobenzyl Cyanide in Solution at* −77°.

By E. F. Caldin and E. Harbron.

4-Nitrobenzyl cyanide (p*K* 13·4 in water) reacts with sodium ethoxide in ethanol, producing a red colour, which is discharged by weak acids such as phenols. The rates of these reactions, which are instantaneous at room temperature, have been measured for ether–ethanol solutions by means of a stopped-flow apparatus at −77°. Evidence is presented that they are proton-transfer reactions, analogous to those of 2,4,6-trinitrotoluene, but faster by five or six powers of ten. The Brönsted plot is considered. The rate constant for the reaction between ethoxonium ion and the anion of 4-nitrobenzyl cyanide appears, on certain assumptions, to be about 10^{12} l. mole^{-1} sec.$^{-1}$ at −77°.

4-Nitrobenzyl cyanide, p-$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CN$, behaves in water as an acid–base indicator of p*K* 13·4, giving a red solution at high pH.[1] Crystalline sodium and potassium derivatives can be prepared.[2,3] When treated with sodium ethoxide in ethanol, 4-nitrobenzyl cyanide gives a red solution; this is decolorised by weak acids such as phenols or acetic acid. Both reactions are instantaneous at room temperature. (The red solution slowly becomes green, but we are not concerned with this subsequent reaction.) The absorption spectrum of the red solution has been observed;[4] the molar extinction coefficient is $2{\cdot}59 \times 10^4$ at $\lambda_{\text{max.}}$ ~560 mμ.

The reactions concerned in the formation and decolorisation of the red solution may provisionally be regarded as proton-transfers, and represented as follows (BH = 4-nitrobenzyl cyanide):

$$\mathrm{BH} + \mathrm{OEt}^- \xrightleftharpoons[k_{-1}]{k_1} \mathrm{B}^- + \mathrm{EtOH} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{B}^- + \mathrm{HA} \longrightarrow \mathrm{BH} + \mathrm{A}^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

These reactions are similar to those of tri-*p*-nitrophenylmethane[5] and of 2,4,6-trinitrotoluene[6–11] whose kinetics have been investigated in this laboratory. Supporting evidence that the reactions involve proton-transfers, rather than the formation of addition products such as those of 1,3,5-trinitrobenzene[12] or 2,4,6-trinitroanisole,[13] is as follows (*a*) 4-Nitrobenzyl cyanide in presence of ethoxide is known to act as a nucleophilic reagent to benzaldehyde, producing a cyanostilbene;[4] this indicates that in such a solution the carbon atom of the methylene group can carry a partial negative charge. (*b*) Tritium-exchange experiments[14] have shown that the protons in the methylene group of the similar compound 4-nitrobenzyl chloride are labile in a solution of sodium hydroxide in methanol–water. (*c*) Our Brönsted plot (see below) confirms the proton-transfer mechanism (2) for the decolorisation and adds to the evidence in favour of mechanism 1 for the colour formation.

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[1] Stearns and Wheland, *J. Amer. Chem. Soc.*, 1945, **69**, 2025.
[2] Lifschitz and Jenner, *Ber.*, 1915, **48**, 1730.
[3] Opolsky, Zowolski, and Pilewski, *Ber.*, 1916, **49**, 2276.
[4] Bruylants, Braye, and Schonne, *Helv. Chim. Acta*, 1952, **35**, 1127.
[5] Caldin and Trickett, *Trans. Faraday Soc.*, 1953, **49**, 772.
[6] Caldin and Long, *Proc. Roy. Soc.*, 1955, *A*, **228**, 263.
[7] Ainscough and Caldin, *J.*, 1956, 2546.
[8] Caldin, *J.*, 1959, 3345.
[9] Caldin and Jackson, *J.*, 1960, 2413.
[10] Ainscough and Caldin, *J.*, 1960, 2407.
[11] Caldin and Harbron, *J.*, 1962, in the press.
[12] Ainscough and Caldin, *J.*, 1956, 2540.
[13] Ainscough and Caldin, *J.*, 1956, 2528.
[14] Wilzbach, personal communication.

Both the formation of the red colour and the decolorisation by acids appear to be instantaneous, not only at room temperature, but also at −77°, when initiated by ordinary mixing. We have, however, been able to measure rates of reaction at −77° with the help of a stopped-flow apparatus designed for work at low temperatures.[15] The solvent chosen was ether–ethanol (80 : 20 v/v), which has a low viscosity (so that it can be used in the stopped-flow apparatus), a freezing point below −130°, and appropriate solvent properties. The object of the present study was to investigate mechanisms, rather than to achieve the highest accuracy. The observed kinetics are in accord with the mechanisms suggested above.

EXPERIMENTAL

Materials.—4-Nitrobenzyl cyanide was recrystallised from ethanol to constant m. p. 117° (lit.,[16] 116—117°). Ethanol was dried by Lund and Bjerrum's method [17] and was freshly distilled as required. Diethyl ether, refluxed over sodium and fractionally distilled, had b. p. 34·6° (lit.,[18] 34·60°). Phenol, purified by distillation, had m. p. 41·0° (lit.,[18] 41·0°). 2,4-Dichlorophenol, also distilled, had b. p. 209—210° (Beilstein's " Handbuch," 209—210°). 2,4,6-Trichlorophenol, recrystallised from benzene, had m. p. 67·6° (*op. cit.*, 67—69°).

The Low-temperature Stopped-flow Apparatus and Photometer.—These have been described before.[15] The mode of operation was as in previous work, except that in each run, after six oscillograph records had been taken under identical conditions, a representative record was selected and measured, instead of all six. A temperature of −77° was maintained within ±0·2° by immersing the steel block in ethanol-solid carbon dioxide. The correction factor for the contraction of the ether–ethanol solutions on cooling was calculated as for pure diethyl ether; the value (1·15) should not be in error by more than a few per cent, since the factors for ether and ethanol differ by only 4%.

Absorption Spectrum.—The absorption spectrum of the red solution of the 4-nitrobenzyl cyanide anion in ether–ethanol was obtained with the help of an Optica double-beam recording spectrophotometer. It resembled in general the published spectrum of ethanol solutions,[4] but the broad maximum was shifted to about 500 mμ. 4-Nitrobenzyl cyanide does not absorb in this region. An Ilford 623 filter with maximum transmission at 495 mμ was used in the kinetic runs. We have confirmed Stearns and Wheland's observation [1] that the solutions obey Beer's law even though the light is not completely monochromatic. The red solutions appeared to be stable at −77°, and even at room temperature a change in colour (to purple) was noticeable only after about 2 hr. After 24 hr. the solution had become green, but this secondary reaction appears to be negligible in our work. The red solutions for the reactions with phenols were made up quickly, and immediately transferred to the low-temperature thermostat.

Analysis of Results.—We use the same symbols as in earlier papers.[5,6,12] For reaction 1, when ethoxide is in large excess, the variation of optical density (D) with time should give a linear first-order plot of log ($D_\infty - D$) against time. The slope (s) of this line is, if the concentration of ethoxide ion is b, given by the following equation, in which $k^\circ_{-1} = k_{-1}(\text{EtOH})$:

$$-2{\cdot}303s = bk_1 + k_{-1}^\circ \qquad (3)$$

Hence a plot of s against b gives k_1 (from the slope) and k_{-1}° (from the intercept).

For reaction 2, with acid in large excess, the plot of $\log_{10} D$ against time should be linear. The reverse reaction need not be considered since 4-nitrobenzyl cyanide is much weaker than any of the acids HA. The slope s'' is given by

$$-2{\cdot}303s'' = k_{-1}^\circ + k_2(\text{HA}) + k_3(\text{EtOH}_2^+). \qquad (4)$$

Here k_{-1}° is the rate constant for the reaction with the solvent (the reverse of reaction 1), and may be determined as above; k_2 and k_3 are the rate constants for reaction with undissociated

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[15] Allen, Brook, and Caldin, *Trans. Faraday Soc.*, 1960, **56**, 788; *J.*, 1961, 2171.

[16] *Org. Synth.*, Coll. Vol. II, John Wiley and Sons, Inc., New York, 1946, p. 397.

[17] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[18] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

acid and with hydrogen ions respectively. If the dissociation constant of the acid in the solvent is K_a, and the buffer ratio $(HA)/(A^-)$ is denoted by r, then $(EtOH_2^+) = K_a r$, and equation 4 becomes

$$-2{\cdot}303s'' = k_{-1}^{\circ} + k_2(HA) + k_3K_ar. \qquad (5)$$

If the reaction mixture is made up so that the formal initial ethoxide concentration is b, and the formal initial acid concentration is c, then $(HA) = (c - b)$, and $r = (c - b)/b$. Equation 5 becomes

$$-2{\cdot}303s'' = k_{-1}^{\circ} + k_2(c - b) + k_3K_ar. \qquad (6)$$

In a series of runs at constant buffer ratio, therefore, a plot of s'' against $(c - b)$ should be a straight line, whose slope gives k_2 and intercept $(k_{-1}^{\circ} + k_3K_ar)$. If the reaction with hydrogen ion can be neglected, the equation becomes

$$-2{\cdot}303s'' = k_{-1}^{\circ} + k_2(c - b). \qquad (7)$$

The first-order plots were obtained by Guggenheim's method; they were satisfactorily linear. Straight lines were fitted to the plots of s against b, and of s'' against $(c - b)$, by the method of least squares.

Concentration Ranges.—The minimum concentration of 4-nitrobenzyl cyanide was fixed by the need of a change of optical density of about 0·5 in the 2·5-mm. observation tube; it was about 6×10^{-5}M. This in turn affected the minimum concentration of ethoxide or phenol, which had to be in large excess, so that the kinetics might be of the first-order. For the runs with ethoxide, the excess was 75-fold or more; for those with phenol and 2,4-dichlorophenol, 100-fold or more. For 2,4,6-trichlorophenol, to reduce the rate the excess had to be reduced in one run to 24-fold; but there was no detectable deviation from a linear first-order plot, and the mean concentration of trichlorophenol would be altered by only 2%.

The maximum concentration of ethoxide or phenol was fixed by the maximum rate that could conveniently be measured. Reactions with half-times down to about 2 msec. have been observed, but for the runs reported here the shortest half-time is about 20 msec.

The effect of solvent composition on the rate of the reaction with ethoxide does not appear to be significant; an independent set of runs in which the ethanol concentration was 12·5% by volume instead of 20% showed no difference in the value of k_1, within the experimental error.

Preliminary work had been done in this laboratory by Dr. R. A. Jackson and Dr. A. J. W. Brook, to whom we are indebted.

RESULTS

The Reaction of 4-*Nitrobenzyl Cyanide with Sodium Ethoxide at* −77° *in Ethanol–Ether.*—The results of the kinetic runs are given in Table 1, where the observed values of s are given in the third column. The plot of s against b is linear. The slope and intercept of this plot, obtained by the method of least squares, are given in the last two columns of Table 1; values of s calculated from them are given in the fourth column, for comparison with the observed values. The corresponding values of k_{-1}° and k_1, with their standard deviations are:

TABLE 1.

Kinetic results for the reaction of 4-nitrobenzyl cyanide with sodium ethoxide at −77·0° ± 0·2°.

b = Initial ethoxide concn.; d = initial cyanide concn.; s = slope of first-order plot (decadic logs).

10^3b (mole/l.)	10^5d (mole/l.)	s (obs.) (sec.$^{-1}$)	s (calc.) (sec.$^{-1}$)	Slope (l. mole^{-1} sec.$^{-1}$)	Intercept (sec.$^{-1}$)
4·53	6·11	1·88	1·96	$10^2(2{\cdot}41 \pm 0{\cdot}32)$	0·87 ± 0·26
9·07	6·11	3·21	3·05		
13·32	6·11	3·99	4·07		

$$k_{-1}^{\circ} = 2{\cdot}0 \pm 0{\cdot}6 \text{ sec.}^{-1};\ k_1 = 10^2(5{\cdot}5_4 \pm 0{\cdot}7) \text{ l. mole}^{-1} \text{ sec.}^{-1}$$

A somewhat more reliable figure for k_{-1}° (see below) is $1{\cdot}5_2$ sec.$^{-1}$ with standard deviation ±0·4. Hence $k_1/k_{-1}^{\circ} = K^{\circ} = (B^-)/(BH)(OEt^-) = 365 \pm 100$ l. mole^{-1}.

The value of log $[K°(\mathrm{EtOH})]$, which if we take (EtOH) in our solutions as 3·9 mole l.$^{-1}$ is 3·15, should be equal to the difference of pK_a between 4-nitrobenzyl cyanide and ethanol. In water these are 13·4 and ~15·9,[19] respectively; the difference is 2·5. This is reasonable in view of the differences of solvent and temperature.

The Reaction of the Anion of 4-Nitrobenzyl Cyanide with Various Phenols.—The results of kinetic runs in which the red solution containing the 4-nitrobenzyl cyanide anion was mixed with solutions of various phenols are shown in Table 2. The values of s'' derived from the first-order plots are given in the column headed "s'' (obs.)." Plots of s'' against $(c - b)$ are shown in Fig. 1. The slopes and intercepts of the best straight lines through the points, with their standard deviations, are given in the last two columns of Table 2, and values of s'' calculated therefrom are also given. The results must be analysed in terms of equation (6) or (7), as follows.

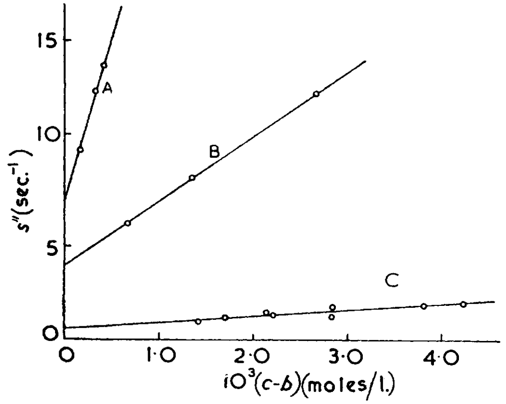

FIG. 1. Plots of first-order rate constant s'' against acid concentration $(c - b)$: A, 2,4,6-trichlorophenol; B, 2,4-dichlorophenol; C, phenol. The lines shown are the best lines calculated by the method of least squares.

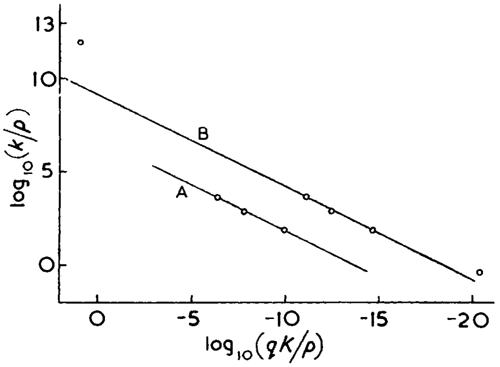

FIG. 2. Brönsted plots. A, log k_2 against log K_a for the three phenols (K_a in water). B, log (k/p) against log (qK_a/p) for the three phenols, ethanol, and ethoxonium ion (K_a in ethanol).

(*a*) *Phenol.* It appears from the following two facts that the results with phenol follow

TABLE 2.

Kinetic results for the reaction between the 4-nitrobenzyl cyanide anion and various phenols at $-77·0° \pm 0·2°$.

c = formal initial concn. of acid. $r = (c - b)/b$ = buffer ratio.

$10^2(c - b)$ (mole/l.)	10^3b (mole/l.)	10^5d (mole/l.)	r	s'' (obs.) (sec.$^{-1}$)	s'' (calc.) (sec.$^{-1}$)	Slope (l. mole^{-1} sec.$^{-1}$)	Intercept (sec.$^{-1}$)
				Phenol			
1·41	1·76	10·0	8·1	1·01	1·10	30·9 ± 6·0	0·66 ± 0·17
1·70	1·40	10·0	12·1	1·19	1·19		
2·13	2·59	10·0	8·2	1·48	1·32		
2·21	1·76	10·0	12·6	1·33	1·34		
2·83	3·51	10·0	8·1	1·28	1·54		
2·84	3·45	10·0	8·2	1·76	1·54		
3·81	1·76	10·0	21·7	1·85	1·84		
4·24	3·50	10·0	12·1	1·95	1·97		
				2,4-*Dichlorophenol*			
0·67	0·59	6·73	11·4	5·93	6·18	$10^2(3·06 \pm 0·32)$	4·13 ± 0·57
1·35	1·03	6·73	11·4	8·65	8·26		
2·66	2·41	6·73	11·1	12·15	12·27		
				2,4,6-*Trichlorophenol*			
0·157	1·40	6·46	1·13	9·10	9·12	$10^3(1·83 \pm 0·05)$	6·25 ± 0·08
0·325	2·88	6·46	1·13	12·27	12·20		
0·406	3·60	6·46	1·13	13·63	13·68		

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[19] Ballinger and Long, *J. Amer. Chem. Soc.*, 1960, **82**, 795.

equation (7) rather than (6), so that the reaction of the anion with hydrogen ion can be neglected. (*i*) While the buffer ratio varies nearly three-fold, the rate constants all fall close to the best straight line. (*ii*) The intercept, multiplied by 2·303, is $1{\cdot}5_2 \pm 0{\cdot}4$ sec.$^{-1}$, which agrees with the value of k_{-1}° derived from the reaction of 4-nitrobenzyl cyanide with ethoxide ($2{\cdot}0 \pm 0{\cdot}6$ sec.$^{-1}$). We therefore assume that equation (7) holds, and we adopt the value of $k_{-1}^{\circ} = 1{\cdot}5_2 \pm 0{\cdot}4$ sec.$^{-1}$. The value of k_2 for the reaction with undissociated phenol, derived from the slope of the best line, is 71 ± 14 l. mole^{-1} sec.$^{-1}$.

(*b*) 2,4-*Dichlorophenol and* 2,4,6-*trichlorophenol.* The kinetic runs were carried out at constant buffer ratio. The plots of s'' against $(c - b)$ are shown in Fig. 1, with the best straight lines. The slopes and intercepts with their standard deviations are given in Table 2. The slope gives k_2; the values are given in Table 3, along with that for phenol.

For each of these substituted phenols, the intercept is greater than that for phenol itself; the term k_3K_ar in equation (6), due to reaction with hydrogen ion, is thus appreciable. Taking the value of k_{-1}° from the results with phenol ($1{\cdot}5_2 \pm 0{\cdot}4$ sec.$^{-1}$), we can derive a value for k_3K_a from the intercept. The results are shown in Table 3.

Reaction with Hydrogen Ion.—To derive values of k_3, we need estimates of K_a. The acid strengths of the phenols in water are known; [20] they are given in the top line of Table 4. In ethanol they have not been determined; we therefore assume that the decrease on passing from water to ethanol is in each case the same as for dinitrophenol, which has been measured [21] ($\Delta \log K_a = 4{\cdot}71$), and so we obtain the values given in the second line of Table 4. These have been used to derive from k_3K_a the values of k_3 given in the last column of Table 3. The two estimates are in satisfactory agreement at about 2×10^{12} l. mole^{-1} sec.$^{-1}$, but in view of the assumptions they are reliable only as regards order of magnitude.

TABLE 3.

Rate constants for the reaction of the anion of 4-nitrobenzyl cyanide with various phenols at $-77°$.

Acid	k°_{-1} (sec.$^{-1}$)	k_2 (l. mole^{-1} sec.$^{-1}$)	k_3K_a (sec.$^{-1}$)	k_3 (l. mole^{-1} sec.$^{-1}$)
Phenol	$1{\cdot}5_2 \pm 0{\cdot}4$	71 ± 14	—	—
2,4-Dichlorophenol	$1{\cdot}5_2$	$10^2(7{\cdot}0_5 \pm 0{\cdot}7)$	$0{\cdot}69 \pm 0{\cdot}16$	$2{\cdot}0 \times 10^{12}$
2,4,6-Trichlorophenol	$1{\cdot}5_2$	$10^3(4{\cdot}2 \pm 0{\cdot}1)$	$11{\cdot}4 \pm 0{\cdot}5$	$1{\cdot}5 \times 10^{12}$

The Brönsted Relation.—The plot of $\log k_2$ against $\log K_a$ for the three phenols is shown in Fig. 2, line A. Here the values of K_a in water have been used; probably the relative values in the solutions at $-77°$ will not be greatly different. The slope of the best line, determined by the method of least squares, gives the Brönsted exponent (α) as 0·49.

It is of interest to construct a Brönsted plot which includes all the five acids for which rate constants are given in Table 4 (the three phenols, ethanol, and hydrogen ion). For this purpose we have used values of K_a in ethanol at 25° (Table 4). Estimates for the three phenols have been given above. A value for hydrogen ion is obtained by assuming that it is present as ethoxonium ion (the effect of any water present being neglected) and that the concentration of ethanol molecules in ethanol is 17 mole l.$^{-1}$.

For ethanol we have divided the ionic product at 25° ($7{\cdot}28 \times 10^{-20}$ mole^2 l.$^{-2}$) [22] by 17 mole l.$^{-1}$. The second-order rate constants for the phenols (k_2) and for the ethoxonium ion (k_3) are taken from Table 3; that for ethanol is obtained by dividing k°_{-1} by the concentration of ethanol in the solvent (3·92 mole l.$^{-1}$).

In order to take into account the statistical differences between the charged acid $EtOH_2^+$ and the rest which are uncharged, we have plotted $\log (k/p)$ against $\log (qK_a/p)$, where p is the number of equivalent protons detachable from the acid, and q is the number of equivalent positions at which the corresponding base can accept a proton. The data are collected in Table 4. The points for the three phenols alone give line B in Fig. 2, whose slope is naturally the same as that of line A (0·49). The point for ethanol deviates from line B by 0·65 in $\log k$

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[20] Landolt–Börnstein, " Tabellen "; Beilstein's " Handbuch der organischen Chemie."

[21] Kortüm and Buck, *Z. Elektrochem.*, 1958, **62**, 1083.

[22] Danner, *J. Amer. Chem. Soc.*, 1922, **44**, 2832.

TABLE 4.

Rate and equilibrium constants for reaction of 4-nitrobenzyl cyanide anion with various acids.

k in l. mole^{-1} sec.$^{-1}$; K_a in mole l.$^{-1}$.

	Solvent	Temp.	Ethanol	Phenol	Dichloro-phenol	Trichloro-phenol	Hydrogen ion $EtOH_2^+$
$-\log K_a$	H_2O	25°	16	9·98	7·75	6·41	—
$-\log K_a$	EtOH	25	20·4	14·7	12·5	11·1	−1·23
$-\log (qK_a/p)$	EtOH	25	20·4	14·7	12·5	11·1	−0·93
$\log k$	Et_2O–EtOH	−77	−0·41	1·85	2·85	3·6	12·2
$\log (k/p)$	,,	−77	−0·41	1·85	2·85	3·6	11·9

(see Discussion). The slope of the best line through the points for ethanol and the three phenols is 0·42. The point for ethoxonium ion deviates from line B by 2·34 in log k (see Discussion).

DISCUSSION

Mechanisms of Reactions.—The observed rate–concentration relations are those expected for the proton-transfer reactions (1) and (2). However, the same relations would obtain if an addition product were formed instead of an anion.[6,7,12,13] Evidence that the decolorisation by a phenol is a proton-transfer reaction is provided by the Brönsted relation for the three phenols, with its exponent 0·49. Further, the rate constant for ethanol lies quite close to the value predicted from this relation (Fig. 2); the deviation is probably not significant, especially when the long extrapolation and the change of acid type are borne in mind. This confirms our assumption that the rate-determining step in the reaction of the anion with ethanol is a proton-transfer. Consequently the reverse reaction, that of 4-nitrobenzyl cyanide with ethoxide, must also be a proton-transfer.

The situation is similar to that encountered with 2,4,6-trinitrotoluene[6] and tri-(*p*-nitrophenyl)methane.[5] The value (0·49) of α is not far from that (0·56) found for the corresponding reactions of the trinitrotoluene anion at −78·5°. The rate constant at a given K_a is between five and six powers of ten larger.

Reaction with Hydrogen Ion.—The estimated rate constant for the reaction between the 4-nitrobenzyl cyanide anion and ethoxonium ion is of the order of 10^{12} l. mole^{-1} sec.$^{-1}$ at −77°. This is among the highest values for proton-transfers involving a carbon acid. (Tables of fast proton-transfer reactions are given by Bell[23] and by Pearson and Dillon.[24]) The Arrhenius activation energy must be very low; even if log A is as high as 13·6, as for the corresponding reaction with trinitrotoluene,[9] E_A will be less than 2 kcal. mole^{-1}. The reaction is presumably diffusion-controlled, with a very low energy-barrier.

This rate constant for ethoxonium ion is 220 times greater than that calculated from the Brönsted relation (cf. line B in Fig. 2). This discrepancy is not, however, greater than those for other reactions where there is a long extrapolation and a change of charge-type.[25] Moreover, on a simple potential-energy interpretation of the Brönsted relation,[26] it would not be surprising if the linear relation broke down for reactions whose rate is controlled by diffusion rather than by the rate of passage over an energy barrier.

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DEPARTMENT OF PHYSICAL CHEMISTRY, THE UNIVERSITY,
LEEDS, 2.

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[23] Bell, *Quart. Rev.*, 1959, **13**, 169.
[24] Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.
[25] Bell, " Acid–Base Catalysis," Oxford, 1941, pp. 92—93.
[26] Bell, ref. 26, Chap. 8.