Proton Transfer from Cyanocarbon Acids. IV. Kinetic Ionization Behavior of *p*-Nitrobenzyl Cyanide and Bromomalononitrile[1,2]

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Abstract: The kinetics of the ionization of bromomalononitrile (p$K°$ = 7.81) in phosphate and morpholine buffer solutions have been studied by a temperature-jump technique. The rate coefficient for the orthophosphate dianion catalyzed ionization at 25° has the value $k_1 = 8.1 \times 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ and in the reverse direction $k_{-1} = 4.3 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. These values agree well with those predicted by a normal Eigen plot for an acid with this p$K°$ from studies of other cyanocarbon acids. The rate of ionization of *p*-nitrobenzyl cyanide (p$K°$ = 13.4) has been studied in amine buffer solutions by a detritiation technique. The value of the Brønsted exponent, $\beta = 0.61$, and the magnitudes of the base catalytic coefficients demonstrate that the behavior of this cyano-substituted carbon acid is very different from those previously studied and explanations for this difference are advanced. Hydroxide ion is anomalously unreactive as a base catalyst for proton transfer from all these cyanocarbon acids, a behavior shared with many other carbon acids.

The previous papers[1] in this series have dealt with proton transfer reactions from cyano-substituted carbon acids of weak and moderate acidity. The characteristics of proton transfer resemble those shown by oxygen acids, in that the Brønsted β is unity and the reverse rate virtually diffusion controlled. This group therefore belongs to Eigen's classification of normal acids.[5] To confirm and understand this unusual finding, we have now studied the general base catalyzed ionizations of bromomalononitrile and *p*-nitrobenzyl cyanide in aqueous solution. Bromomalononitrile can provide kinetic data for a stronger acid in the "turnover" region of the Eigen plot (Figure 3, ref 6) where the ΔpK for the carbon acid and the conjugate acid of the general base catalysts are close to zero. *p*-Nitrobenzyl cyanide was chosen for another set of experiments as a carbon acid which might exhibit ionization behavior intermediate between that observed for normal cyanocarbon acids and that usually found with other classes of carbon acids.

In the proton transfers from 1,4-dicyano-2-butene[7] and *tert*-butylmalononitrile[6] conclusions were tentatively reached about the factors which control proton transfer from carbon acids generally. This paper throws additional light on this important question.

The ionization of bromomalononitrile was studied by temperature jump, observations of the relaxation process being made spectrophotometrically. The ionization of *p*-nitrobenzyl cyanide was studied by the previously used detritiation technique; all our evidence indicates that, apart from an isotope effect for the latter, both reactions involve the same slow proton transfer.

Experimental Section

Materials. Bromomalononitrile was prepared by the action of bromine on malononitrile.[8] Samples were recrystallized from chloroform immediately before use (mp 68–70°). Commercial *p*-nitrobenzyl cyanide was tritiated in a mixture of ethyl acetate and tritiated water containing sodium carbonate. It was purified by recrystallization from ethanol.

Liquid amines used in the preparation of buffer solutions were distilled under nitrogen from potassium hydroxide pellets. The solid amines were recrystallized. Potassium dihydrogen orthophosphate, disodium monohydrogen orthophosphate, and potassium chloride were AR chemicals. Dioxane was refluxed over sodium and distilled. The very dilute buffer solutions used in the temperature-jump study were made up using distilled water which had been further purified by distillation under nitrogen from alkaline permanganate. Precautions were taken to prevent contamination by atmospheric carbon dioxide.

Phosphate buffers were prepared according to Bates' method.[9] Amine buffers were prepared by mixing solutions of the amine and hydrochloric acid. In all cases the ionic strength was made up to 0.100 M by the addition of potassium chloride. The pH values of the buffers were calculated from p$K°$ values corrected to ionic strength 0.100 M using the Debye–Hückel approximation.

Measurement of Dissociation Constants. The value p$K°$ = 13.4 has been determined[10] for *p*-nitrobenzyl cyanide at 25°.

An approximate value p$K \sim 5$ for bromomalononitrile was determined by Pearson and Dillon.[11] In the present work a more accurate value was obtained using a spectrophotometric method similar to that used for *tert*-butylmalononitrile.[6] In aqueous solution the anion of bromomalononitrile shows an absorption maxium at 2350 Å (ϵ 1.37 × 10^4 cm^2 mol^{-1}),[12] whereas the undissociated acid at the same wavelength has relatively negligible absorbance (ϵ 2.59 × 10^2 cm^2 mol^{-1}). By measuring the optical density of solutions of the carbon acid of known pH the dissociation constant could therefore be determined. An aqueous solution of bromomalononitrile of known concentration was introduced from a calibrated Hamilton syringe (0.01 ml) into a phosphate buffer of known pH at 25° and an ionic strength of 0.100 M contained in a uv cell, and absorbance readings were recorded. For some solutions a slight instability in the spectrum was observable; for these the optical density reading was extrapolated back to the time of mixing. The average of 12 determinations at different pH values gave pK = 7.58 ± 0.02 (average deviation).

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[1] Part III: F. Hibbert and F. A. Long, *J. Amer. Chem. Soc.*, **93**, 2836 (1971).

[2] Work supported by a grant from the Atomic Energy Commission.

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[5] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

[6] F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **93**, 2829 (1971).

[7] E. A. Walters and F. A. Long, *ibid.*, **91**, 3733 (1969).

[8] J. P. Ferris and L. E. Orgel, *J. Org. Chem.*, 30, 2365 (1965).

[9] R. G. Bates, "Determination of pH," Wiley, New York, N. Y., 1964.

[10] (a) R. S. Stearns and G. W. Wheland, *J. Amer. Chem. Soc.*, **69**, 2025 (1947); (b) R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 5030 (1963); (c) R. Stewart, P. O'Donnell, and K. Bowden, *Can. J. Chem.*, **43**, 1225 (1965). Some doubt has been expressed (ref 10b, c) as to whether this value corresponds to a simple ionization but uncertainty on this point does not alter any of our later conclusions.

[11] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953).

[12] A value $\epsilon = 1.5 \times 10^4$ has previously been determined in methanolic potassium hydroxide.[8]

A value pK° = 7.81 ± 0.02, referring to 25° and infinite dilution, was calculated using the Debye–Hückel approximation.

Detritiation. The rates of detritiation of *p*-nitrobenzyl cyanide were measured in various aqueous solutions. Depending on their rate the reactions were initiated either by addition to the aqueous solution of solid *p*-nitrobenzyl cyanide or of a solution of the solid in dioxane. The dioxane added was always negligible compared with the volume of the aqueous solution. Samples of the thermostated reaction solution were taken at appropriate time intervals, run into 5 ml of 0.1 *M* hydrochloric acid to quench the reaction and then extracted with toluene (15 ml). The toluene layer (10 ml) was then subjected to liquid scintillation counting. Reactions were always followed under pseudo-first-order conditions by keeping the carbon acid concentration in at least tenfold deficit of the other reactant concentrations. The loss of tritium from *p*-nitrobenzyl cyanide was accurately first order and rates were calculated from the gradients of the usual plots of log ($C_t - C_\infty$) against time, where C_t and C_∞ represent the counts at time t and infinite time, respectively. The rate coefficients were usually reproducible to ±2% except for the very fast runs (±4%).

Temperature Jump. Rates of proton transfer in both directions were measured for the systems consisting of bromomalononitrile in orthophosphate monoanion–dianion and in morpholine–morpholinium buffer solutions. The pH values of the buffers were such that the carbon acid was about half dissociated. For the phosphate buffers, buffer components were always in at least tenfold excess over the carbon acid. The reaction mixture was thermostated at 17.5° in the observation chamber of the temperature-jump apparatus. The apparatus was similar to that described by Hammes and Erman.[13] After the temperature jump (7.5°), observations of the change in absorbance due to bromomalononitrile anion were taken at 2350 Å and recorded on a memory oscilloscope. Normally, about five traces were taken for each reaction mixture. In all systems studied only one relaxation was observable and the kinetic plots were accurately first order over about 2 half-lives. Relaxation times were reproducible to ±6% (average deviation).

Results

Detritiation of *p*-Nitrobenzyl Cyanide. Reaction with Solvent Water. In aqueous solutions more acidic than 0.1 *M* hydrochloric acid, the rate of detritiation was pH independent and was therefore assumed to be a base catalyzed reaction with the solvent water. The reaction at 25° is too slow to measure directly. Measurements were therefore taken at 47.0° ($k = 1.11 \times 10^{-8}\ M^{-1}\ \text{sec}^{-1}$) and 59.4° ($k = 3.84 \times 10^{-8}\ M^{-1}\ \text{sec}^{-1}$). These led to the following approximate activation parameters at 25°: $\Delta H^{\ddagger} = 21$ kcal mol^{-1} and $\Delta S^{\ddagger} = -30$ cal deg^{-1} mol^{-1}. From the observed temperature coefficient, the rate coefficient for the second-order reaction with water at 25° is calculated as $k = 9 \times 10^{-10}\ M^{-1}\ \text{sec}^{-1}$.

Hydroxide Ion Catalyzed Detritiation. Since the hydroxide ion catalyzed detritiation of *p*-nitrobenzyl cyanide is a rapid reaction only low hydroxide ion concentrations could be employed. At 25.0° from measurements in 1.0×10^{-3} and 2.0×10^{-3} *M* sodium hydroxide (with ionic strength, $I = 0.100$) the catalytic coefficient $k_{\text{OH}^-} = 26 \pm 1\ M^{-1}\ \text{sec}^{-1}$ was determined. Rate coefficients, in M^{-1} sec^{-1} units, from measurements at three other temperatures gave the following activation parameters for the hydroxide ion catalyzed reaction: $E_a = 12.3$ kcal mol^{-1}; $\Delta H^{\ddagger} = 11.7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -12.9$ cal deg^{-1} mol^{-1}.

Detritiation in Buffer Solutions. The detritiation of *p*-nitrobenzyl cyanide was studied in six different amine buffers. The choice of amine buffers was dictated by the extraction procedure used to follow the reaction in that when phenol buffers were used, phenol was extracted along with *p*-nitrobenzyl cyanide and greatly reduced the counting efficiency. For each amine, the rate was measured for about five different buffer concentrations at one buffer ratio. Plots of rate coefficient against buffer concentration were accurately linear: the gradient corresponding to the catalytic coefficient of the amine and the intercept to the hydroxide ion-catalyzed reaction. In all cases this latter was predicted, within experimental error, by the value calculated from reaction in sodium hydroxide solutions. For diethylamine since only low buffer concentrations could be used owing to the high rate of reaction, and because hydroxide ion was present in relatively high concentration, the buffer ratio and therefore the hydroxide ion concentration varied as the buffer was diluted. Hence, the catalytic coefficient for diethylamine was evaluated for each buffer concentration, using the known value for the hydroxide ion reaction, and the average taken.

Catalytic coefficients for six amines together with those for water and hydroxide ion are shown in Table I.

Table I. Base Catalytic Coefficients in the Detritiation of *p*-Nitrobenzyl Cyanide[a]

Base catalyst	pK° [b]	k, M^{-1} sec^{-1}	Statistical p	q
Water	−1.744	9×10^{-10}	3	1
Hydroxide ion	15.74	26	2	1
Diethylamine	11.01	1.7	2	1
Diethanolamine	8.883	0.085	2	1
Morpholine	8.492	0.101	2	1
Imidazole	6.95	0.0036	2	1
3,4-Lutidine	6.46	0.00131	1	1
Pyridine	5.21	0.00045	1	1

[a] 25° and I = 0.100. [b] D. D. Perrin, "Dissociation Contants of Organic Bases in Aqueous Solution," Butterworths, London, 1965.

Figure 1 shows a Brønsted plot for these base catalysts in the detritiation reaction; log k/q is plotted against log $(q/p)(1/K^\circ)$ where k is the base catalytic coefficient, p and q are statistical factors to account for the number of acidic and basic sites on the catalysts, and K° is the thermodynamic dissociation constant of the conjugate acid of the general base catalyst. A line with gradient $\beta = 0.61$ is drawn through the points based on a least-squares calculation which excluded hydroxide ion and water. It is clear that hydroxide ion shows a much lower catalytic coefficient than expected.

Strictly, rate coefficients for detritiation should be plotted against the dissociation constants of the tritium substituted acids since there will be a slight change of isotope effect with base strength. A correction of this sort is relatively unimportant however.

Proton Transfer from Bromomalononitrile. These data are best discussed in two sections, referring to the studies in phosphate and in morpholine buffer solutions.

Phosphate Buffer Solutions. For this system it can easily be shown that for the concentration and pH range investigated, the relaxation time (τ) is given by eq 1 where RCH and B^{2-} represent bromomalononitrile and orthophosphate dianion, respectively, and $\bar{c}$ refers to equilibrium concentrations (25°).

$$\frac{1}{\tau} = k_1(\bar{c}_{\text{RCH}} + \bar{c}_{\text{B}^{2-}}) + k_{-1}(\bar{c}_{\text{RC}^-} + \bar{c}_{\text{HB}^-}) \qquad (1)$$

This is the reciprocal relaxation time for (2).

$$\text{RCH} + \text{B}^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{RC}^- + \text{HB}^- \qquad (2)$$

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[13] J. E. Erman and G. G. Hammes, *Rev. Sci. Instrum.*, 37, 746 (1966). See also E. Faeder, Ph.D. Thesis, Cornell University, 1970.

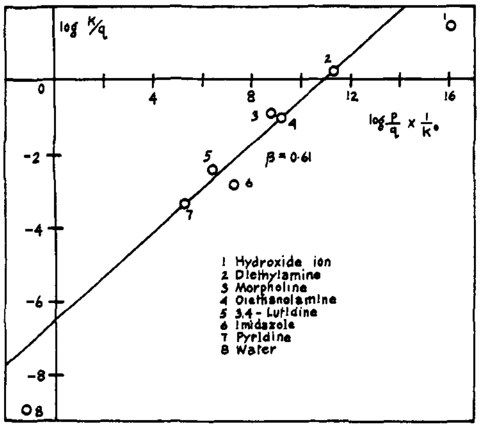


Figure 1. Brønsted plot for *p*-nitrobenzyl cyanide.

Since phosphate buffer was always kept in at least a tenfold excess over carbon acid, the equation further simplifies.

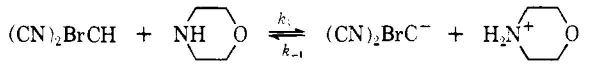
$$\frac{1}{\tau} = k_1\bar{c}_{\mathrm{B}^{2-}} + k_{-1}\bar{c}_{\mathrm{HB}^-} \tag{3}$$

If $K^{0.1}{}_{\mathrm{RCH}}$ and $K^{0.1}{}_{\mathrm{H_2PO_4^-}}$ are the dissociation constants of bromomalononitrile and orthophosphate anion, respectively, at 25° and an ionic strength of 0.100 M we have

$$\frac{1}{\tau} = k_{-1}\{1 + \text{buffer ratio}(K^{0.1}{}_{\mathrm{RCH}}/K^{0.1}{}_{\mathrm{H_2PO_4^-}})\}[\mathrm{H_2PO_4^-}] \tag{4}$$

The phosphate buffer was varied through a tenfold concentration range and the carbon acid through a threefold range. Figure 2 shows the expected linear variation of the reciprocal relaxation time against buffer concentration for two buffer ratios: $C_{\mathrm{B}^{2-}}/C_{\mathrm{HB}^-} = 2.50$, pH = 7.263; and $C_{\mathrm{B}^{2-}}/C_{\mathrm{HB}^-} = 5.0$, pH = 7.564. The rate coefficient (k_{-1}) in the reverse direction for eq 2 calculated from the gradients of these two lines had the values 4.0×10^7 and 4.6×10^7 M^{-1} sec^{-1}. The corresponding values of k_1 were 7.6×10^6 and 8.7×10^6 M^{-1} sec^{-1}. The following average values were therefore obtained: $k_{-1} = 4.3 \pm 0.3 \times 10^7$ M^{-1} sec^{-1}; $k_1 = 8.2 \pm 0.6 \times 10^6$ M^{-1} sec^{-1}. Relaxation times were independent of carbon acid concentration.

Morpholine Buffer Solutions. These data are less reliable than those obtained for proton exchange in phosphate buffers. Since the latter system was so well behaved, however, we have assumed that the studies in morpholine, though less precise, also refer to a simple proton transfer between carbon acid and morpholine.



(5)

Buffer concentrations (at a buffer ratio of 0.19, pH = 7.71) were varied through a threefold range and carbon acid concentrations adjusted to give measureable effects. Since the carbon acid concentration was not negligible compared with that of the morpholine, the buffer ratio was not precisely constant for all these solutions. For this system the assumptions leading to (3) are no longer valid and the overall equation (1) was applied. The equilibrium concentrations were calculated from the stoichiometric concentrations using the measured pK for bromomalononitrile and a value p$K^{0.1}$ = 8.435 for morpholine.[14] For the solutions studied, even though the buffer ratio was not constant, the ratio of the two concentration terms in (1) was practically constant and equal to 4.8 ± 0.1. For eq 1 we can therefore write

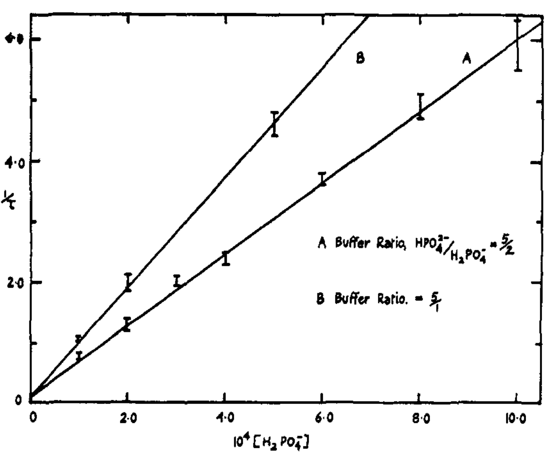


Figure 2. Plot of reciprocal relaxation time against buffer concentration for bromomalononitrile in phosphate buffer. Error bars are twice the average deviation.

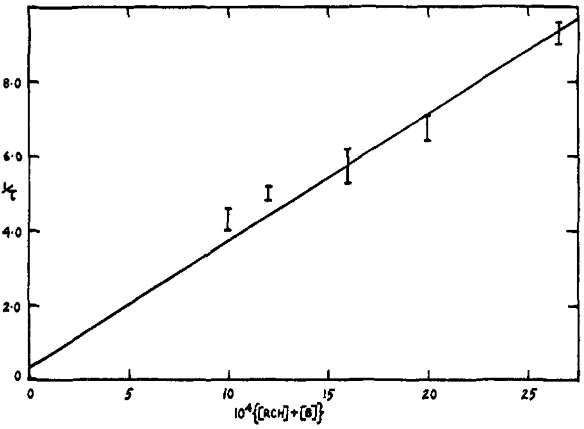


Figure 3. Plot of reciprocal relaxation time against buffer concentration for a morpholine buffer.

$$\frac{1}{\tau} = k_1(\bar{c}_{\mathrm{RCH}} + \bar{c}_{\mathrm{B}}) + \frac{k_1}{7.1} \times 4.8(\bar{c}_{\mathrm{RCH}} + \bar{c}_{\mathrm{B}}) = k_1 \times 1.68(\bar{c}_{\mathrm{RCH}} + \bar{c}_{\mathrm{B}}) \tag{6}$$

$K^{0.1}{}_{\mathrm{CHBr(CN)_2}}/K^{0.1}{}_{\mathrm{morpholine}} = 7.1$ and $\bar{c}_{\mathrm{B}}$ refers to morpholine concentration.

A plot of the reciprocal relaxation time against the sum of concentrations of morpholine and bromomalononitrile is shown in Figure 3. The following rate coefficients at 25° were calculated: $k_1 = 2.1 \times 10^7$ and $k_{-1} = 3.0 \times 10^6$ M^{-1} sec^{-1}. As an alternative method of approach, k_1 and k_{-1} were calculated from the complete expression (1) for each relaxation time. The average values were $k_1 = 2.3 \pm 0.3 \times 10^7$ and $k_{-1} = 3.2 \pm 0.4 \times 10^6$ M^{-1} sec^{-1}.

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(14) H. B. Hetzer, R. G. Bates, and R. A. Robinson, *J. Phys. Chem.*, 70, 2869 (1966).

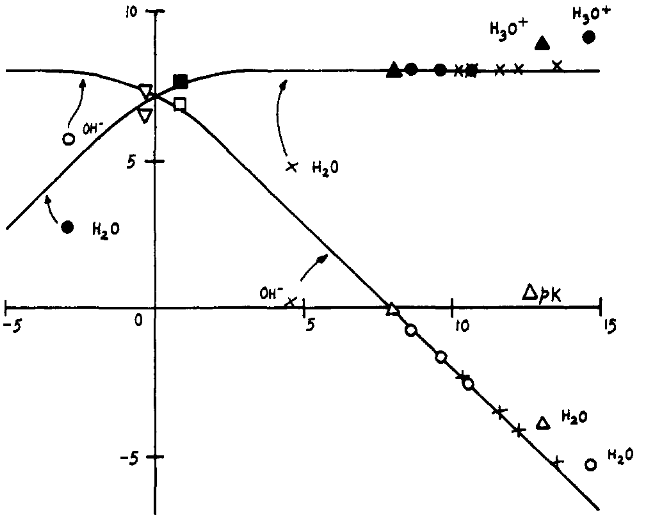


Figure 4. Forward and reverse rates of proton transfer from cyanocarbon acids. Open and closed points represent forward and reverse rate coefficients, respectively, for: *tert*-butylmalononitrile, ○ and ●; malononitrile, △ and ▲; 1,4-dicyano-2-butene, × and ✱; bromomalononitrile, □ and ■ and ▽.

Discussion

In the previous papers of this series it was found that the proton transfer data for three aliphatic cyano-substituted carbon acids were well represented by an Eigen plot of log k *vs.* ΔpK (see Figure 3 in ref 6) although in fitting the data for 1,4-dicyano-2-butene a value for the pK of this weak acid was assumed; the assumed value, however, was within the range of the approximate experimental measurement. The success of ΔpK as a correlating agent and the observed Brønsted coefficients of $\alpha = 0$ and $\beta = 1$ at large ΔpK identify these cyanocarbon acids as belonging to the class of acids showing "normal" proton transfer behavior and involving virtually complete proton transfer in the transition state. A possible reservation is that the limiting reverse rates at large ΔpK are about an order of magnitude below those that might be anticipated from simple diffusion control. Figure 4 shows this Eigen plot with the addition of two sets of points for bromomalononitrile. The new data show good agreement with the earlier results. Actually, for the phosphate and morpholine catalyzed ionization of bromomalononitrile, the differences in charge type should result in a difference of about a factor of 4 in the rates of the two reactions 7 and 8 if these were diffusion controlled.

$$RC^- + BH^+ \longrightarrow RCH + B \tag{7}$$

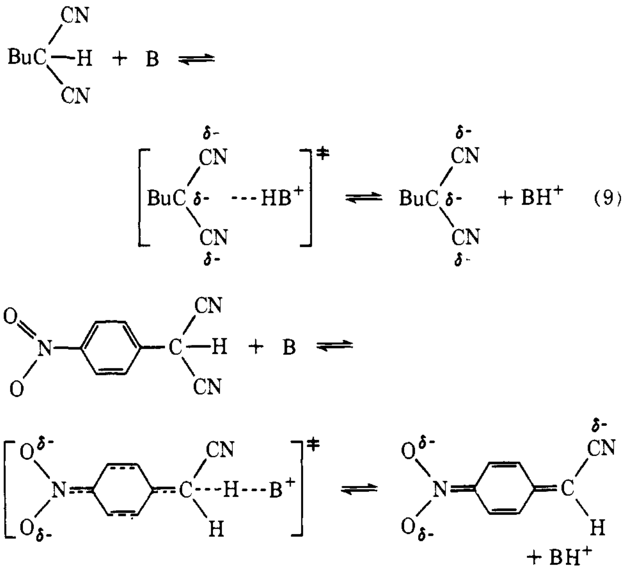
$$RC^- + BH^- \longrightarrow RCH + B^{2-} \tag{8}$$

No attempt has been made to correct for this difference in charge type although statistical corrections to allow for the different numbers of acidic and basic sites in the reactant molecules have been made. All these effects, however, are relatively unimportant in making general conclusions about the Eigen plot.

These new results for the ΔpK = 0 region confirm simple cyanocarbons as examples of carbon acids to be classed as normal in the Eigen sense. There are important differences between this behavior of cyanocarbons and that of most other carbon acids, where Brønsted β coefficients even for large values of ΔpK remain substantially below unity and where the diffusion limiting rate is not approached even for the thermodynamically favorable situations. We shall return to a discussion of this difference after a consideration of the remaining experimental data.

The aromatically substituted species, *p*-nitrobenzyl cyanide, was selected as a cyanocarbon acid which would perhaps *not behave* similarly to the simple malononitriles and dicyanobutene. The experimental results with this species are in accord with this expectation. Even though the pK of *p*-nitrobenzyl cyanide (p$K°$ = 13.4) is very close to that for *tert*-butylmalononitrile (p$K°$ = 13.10), its proton removal shows quite different behavior in that the Brønsted β is only 0.6 as compared to 1.0 for the malononitriles. It follows that the Brønsted α for the reverse reaction is 0.4 compared to 0. It also follows that for *p*-nitrobenzyl cyanide the calculated rates for the reverse reaction are quite considerably slower than the diffusion limit. All of these results are similar to those observed with such carbon acids as diketones and nitroparaffins and the implication is that with *p*-nitrobenzyl cyanide as with these others, the proton is only partially transferred in the transition state.[15]

In seeking an explanation of the difference between the simple cyanocarbons with their essentially normal behavior and *p*-nitrobenzyl cyanide as well as most other carbon acids,[5] the obvious place to turn is to differences in electronic rearrangements which occur in the proton transfer process. In the case of a simple cyanocarbon acid, as for example malononitrile, it is reasonable to suppose that the removal of the proton to form the carbanion is accomplished with negligible changes in bond lengths. The situation with the *p*-nitrobenzyl cyanide (and with most other carbon acids) is almost surely quite otherwise as the structures below imply (9).



Consider the case where reaction in the reverse direction is thermodynamically favorable. As the carbon-hy-

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[15] The rates of the phenolate ion catalyzed proton transfer from *p*-nitrobenzyl cyanide have previously been measured at −77° in ether–ethanol solvent [E. F. Caldin and E. Harbron, *J. Chem. Soc.*, 2314 (1962); E. F. Caldin and G. Tomalin, *Trans. Faraday Soc.*, **64**, 2814 (1968)]. A Brønsted exponent β = 0.51 was calculated. This, together with the value of the primary isotope effect in this solvent, is compatible with the proposition that the proton is about half transferred in the transition state.

drogen bond is formed, the electrons which in the anion are delocalized must be returned to the basic carbon atom. With *p*-nitrobenzyl as the activating group, since several bond length changes are involved, considerable activation energy is required. With cyano as the activating group, however, this process contributes negligibly to the activation energy and the reverse reaction is virtually diffusion controlled. In the ionizing reaction the activating *p*-nitrobenzyl or cyano groups are required to delocalize the electrons *from* the acidic carbon as the carbon–hydrogen bond is broken. For *p*-nitrobenzyl cyanide considerable bond length changes are again involved in this process.

These effects imply different shapes for the potential energy curves for carbon–hydrogen bond breakage in malononitrile and *p*-nitrobenzyl cyanide. The curve for *p*-nitrobenzyl cyanide would be steeper and as a result intersection of these curves with that for bond breakage of B–H$^+$ occur at different points. The two processes therefore have different activation energies and transition states with different degrees of proton transfer.

While our results indicate that malononitriles belong to the normal class of acids, the reverse rates are about a factor of 10 slower than would be expected for a diffusion limited process.[5] They are however independent of the pK of the base catalyst and in this resemble diffusion controlled rates. The difference in rates for the reactions of hydronium ion and carboxylic acids with the malononitrile anions is also suggestive of diffusion control. A possible explanation of why the rates are slightly lower than those expected for diffusion involves restructuring of solvation shells. One way in which this could possibly operate is shown in (10) where I$_1$ is a solvated ion pair and I$_2$ an encounter complex between the solvated ions.

$$\mathrm{RCT} + \mathrm{B} \underset{-1}{\overset{1}{\rightleftharpoons}} \mathrm{RC^-\cdots TB^+} \underset{-2}{\overset{2}{\rightleftharpoons}} \mathrm{RC^-(aq)\cdots BT^+(aq)} \xrightarrow{3} \mathrm{RC^-(aq)} + \mathrm{BT^+(aq)} \xrightarrow{4} \mathrm{RCH} \qquad (10)$$

$$-\frac{\mathrm{d(RCT)}}{\mathrm{d}t} = \frac{k_1k_2k_3\mathrm{(RCT)(B)}}{k_{-1}(k_{-2}+k_3)+k_2k_3} \qquad (11)$$

Since tritium is present in tracer amounts step 4 effectively renders step 3 irreversible. Treating the concentrations of the intermediates by the steady state approximation we obtain (11). If we assume step 2 to be a relatively slow solvent reorganization and $k_2 > k_{-1}$,[16] the specific rate coefficient for detritiation is k_1. The calculated reverse rate coefficient for the *proton* transfer in which step 3 must now be considered reversible is $k_{-3}(k_{-1}/k_2)(k_{-2}/k_3)$. The process corresponding to k_{-3} is diffusion controlled. We have already assumed $k_{-1} < k_2$ and $k_{-2} < k_3$; hence it follows that the calculated reverse rate coefficient will have a value lower than that for the diffusion controlled process, k_{-3}. For oxygen acids, proton transfer can perhaps take place without this solvent reorganization so that intermediates like I are unnecessary.

Hydroxide Ion as a Base Catalyst in Proton Transfers. In the general base-catalyzed detritiation of *tert*-butylmalononitrile and of 1,4-dicyano-2-butene it was concluded that hydroxide ion showed anomalously low reactivity relative to the other base catalysts (see Figure 4). As a catalyst in the detritiation of *p*-nitrobenzyl cyanide, hydroxide ion is again less reactive than one would have predicted from its pK and the Brønsted plot (Figure 1). It was noted by Bell[17] that hydroxide ion is anomalous in proton transfers from carbon acids. Its behavior with cyanocarbon acids, therefore, is not unexpected. The anomaly cannot simply be explained by the incorrect use of p$K° = 15.74$ for water. To rationalize the rate coefficient for hydroxide ion with those of the catalysts, pK values for water of 10, 12.5, and 12 would be required in the reactions with 1,4-dicyano-2-butene, *p*-nitrobenzyl cyanide, and *tert*-butylmalononitrile, respectively. Further studies of this hydroxide ion anomaly are in progress[18] and will be discussed in a subsequent publication.

Acknowledgment. We have benefited greatly from discussion with Dr. Zafra Margolin and acknowledge with gratitude the technical assistance of Mrs. Diane Parchomchuk.

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[16] This is equivalent to assuming that there is no "return" from the ion pair: D. J. Cram, *et al.*, *J. Amer. Chem. Soc.*, 83, 3688 (1961).

[17] R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, 1941, p 92.

[18] F. A. Long and Z. Margolin, unpublished work.