

# Dynamics in the Hydrogen Cyanide – Water System. A Carbon-13 NMR Study

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Rate constants for proton exchange in aqueous solutions containing  $\text{CN}^-$  and HCN were determined by the  $^{13}\text{C}$  NMR line-broadening technique at two ionic strengths at 25 °C. The rate law is  $d[\text{HCN}]/dt = k_0[\text{HCN}] + k_1[\text{HCN}][\text{OH}^-] + k_2[\text{HCN}][\text{CN}^-]$ . The rate constants are  $k_0 = 38.7$  (32.9)  $\text{s}^{-1}$ ,  $k_1 = 3.5 \times 10^9$  ( $3.3 \times 10^8$ ),  $k_2 = 3.1 \times 10^6$  ( $2.0 \times 10^6$ )  $\text{M}^{-1} \text{s}^{-1}$ , in 1 M  $\text{NaClO}_4$  (in 3 M  $\text{LiClO}_4$ ). In the presence of phosphate buffer, three additional terms have to be added to the rate equation,  $k_{p0}[\text{HCN}][\text{PO}_4^{3-}] + k_{p1}[\text{HCN}][\text{HPO}_4^{2-}] + k_{p2}[\text{HCN}][\text{H}_2\text{PO}_4^-]$ , with  $k_{p0} = 1.3 \times 10^9$ ,  $k_{p1} = 3.7 \times 10^5$  and  $k_{p2} = 1.7 \times 10^3$   $\text{M}^{-1} \text{s}^{-1}$  in 1 M  $\text{NaClO}_4$ . The activation parameters for the reaction  $\text{HCN} + \text{H}_2\text{O} \xrightleftharpoons[\text{K}_{-0}]{k_0} \text{CN}^- + \text{H}_3\text{O}^+$  have been determined:  $\Delta H^\ddagger = 45 \pm 4$   $\text{kJ mol}^{-1}$  and  $\Delta S^\ddagger = -64 \pm 12$   $\text{J mol}^{-1} \text{K}^{-1}$ .

Kinetic and mechanistic information concerning complete schemes of ligand exchange reactions for metal-ion complexes is restricted to a few transition metal ions. For post-transition metals, only a few investigations of limited scope can be found in the literature.<sup>1</sup> During the last decade developments in the field of multinuclear NMR have led to a new approach to the study of the dynamics of chemical reactions in solution. Recently we have studied ligand exchange reactions in the systems thallium(III) chloride<sup>2</sup> and thallium(III) bromide<sup>3</sup> in aqueous solution by means of  $^{205}\text{Tl}$  NMR. These studies provided relatively detailed information on the main kinetic pathways of halide exchange processes. As an appropriate next step in our work in the field of equilibrium dynamics of Tl(III) halide and pseudohalide complexes,<sup>2,4</sup> we intend to carry out a kinetic investigation of the Tl(III) –  $\text{CN}^-$  system.

For studies of the ligand exchange kinetics of metal ion complexes with various ligands a knowledge of the equilibrium distribution of the complexes is extremely important. Therefore, we have determined the equilibrium constants for the  $\text{Tl}(\text{CN})_n^{3-n}$  species by means of  $^{205}\text{Tl}$  and  $^{13}\text{C}$  NMR.<sup>4</sup> We have also determined the protonation constant of the  $\text{CN}^-$  ligand in several ionic media using potentiometry and  $^{13}\text{C}$  NMR.<sup>5</sup>

The rate of ligand exchange for thallium(III) halide (Cl, Br) complexes was found to be fast,<sup>2,3</sup> but the correspond-

ing rate for the cyanide ion is slow on the actual NMR timescale.<sup>4</sup> This facilitates a kinetic study of the thallium (III) – cyanide ion system. On the other hand, the study is complicated by the presence of hydrogen cyanide in the investigated solutions. HCN can exchange protons with  $\text{CN}^-$ ,  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , and this can introduce a difficulty when the intricate kinetic system of five exchanging  $\text{Tl}(\text{CN})_n^{3-n}$  species ( $n = 0 - 4$ ) is to be studied.<sup>4</sup> Therefore, before starting the investigation of the thallium cyanide complexes, we decided to perform a kinetic study of the simpler system containing only HCN and  $\text{CN}^-$  in water. Proton transfer between HCN and a number of bases has been carefully studied by Bednar and Jencks<sup>6</sup> by means of  $^1\text{H}$  NMR in 1 M solutions of HCN. In the present work we have used  $^{13}\text{C}$  NMR in order to determine the exchange pathways and the kinetic parameters in dilute aqueous solutions of HCN –  $\text{CN}^-$  at 25 °C. Furthermore, because of the low buffer capacity and hence the instability of the equilibria in these solutions at about pH 7, solutions containing phosphate buffer were also studied.

## Experimental

The samples for the NMR measurements were made from solid sodium cyanide (enriched to 99 % in  $^{13}\text{C}$ ) dissolved in water containing the ionic medium. The total concentration of cyanide was 0.050 or 0.100 M, and the pH was adjusted to appropriate values by careful addition of 6 M  $\text{HClO}_4$ , sufficiently concentrated to prevent dilution of the solutions and thus to avoid significant changes in the total cyanide concentration. The hydrogen ion concentration was calculated from the measured pH using the method

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suggested by Irving.<sup>7</sup> Since the buffer capacity of the solutions is low between pH 6 and 8, the equilibria were very unstable in this region. Therefore, the pH values of the solutions were measured before and after recording the NMR spectra. When the difference between these two measurements was less than 0.05 pH unit, the measurement was accepted. Additionally, for two sets of data in the region  $5 < \text{pH} < 8$ , a phosphate buffer was added in order to obtain stable pH values. (In this case, 1 M NaClO<sub>4</sub> was used as the ionic medium; LiClO<sub>4</sub> could not be used because of the low solubility of lithium phosphate.)

The NMR spectra were recorded using Bruker AM400 and MSL200 spectrometers. Typical parameters (AM400): flip angle ca. 25° (3.5 μs), pulse repetition time 0.4–0.8 s, spectral window ca. 9000 Hz, number of scans 300–10000. A typical series of <sup>13</sup>C NMR spectra is shown in Fig. 1.

### Data treatment

As can be concluded from Fig. 1, the kinetic analysis of the NMR data cannot be carried out by using the simple approximate equations valid for the slow and the fast exchange part, respectively, in the case of a two-site exchange system.<sup>8</sup> This is due to two reasons: (1) At low pH values the HCN signal is a spin-spin coupled doublet. (2) A continuous transition between the slow and the fast exchange regimes takes place when the concentrations are varied. Therefore, the pseudo-first-order rate constant,  $k_{\text{HCN}}^{\text{obs}}$

(hereafter  $k_{\text{obs}}$ ), was extracted by complete bandshape analysis.<sup>8,9</sup>

Generally, the absorption lineshape,  $V$ , of an NMR spectrum can be described by eqn. (1) when adopting the formalism introduced by Reeves and Shaw,<sup>9</sup> where the con-

$$V = (\text{constant}) \times C^{-1} \cdot P \quad (1)$$

stant only affects the intensity of the peak, while the product,  $C^{-1} \cdot P$ , determines the shape and the position of the signal.  $P$  is the column vector of molar fractions and  $C$  is a matrix represented by eqn. (2) where matrix  $R_2$  is the sum

$$C = R_2 + w \cdot \epsilon_2 \cdot w \quad (2)$$

of a diagonal matrix of  $\Delta v_i^0(i)$  (the non-exchange linewidth for the  $i$ th site) and matrix  $K$ , which contains the pseudo-first-order rate constants (see below).  $\epsilon_2 = R_2^{-1}$ , and  $w$  is a diagonal matrix of the frequency variable,  $w_j = x - \Omega_j$ , where  $\Omega_j$  are the chemical shifts of the various species and  $x$  is the independent variable in Hz. The non-exchange linewidth for CN<sup>-</sup> was determined experimentally in highly alkaline solutions,  $\Delta v_1^0 \approx 2$  Hz. The non-exchange linewidth of the HCN signal was determined in a different way, because of the pH-independent contribution to the chemical exchange occurring in an acidic medium. Bednar and Jencks<sup>6</sup> observed a slight acid inhibition for the reaction between HCN and water. This observation was confirmed in our measurements. In ca. 6 M HClO<sub>4</sub> the linewidth of the HCN signal is 6 Hz at 25°C. At -6°C the linewidth is 5 Hz, but only 2.8 Hz when half of the water is replaced by D<sub>2</sub>O. Considering the series of these data a non-exchange linewidth for HCN of less than 2.8 Hz appears reasonable. On the other hand, it is probable that this signal is not much narrower than that of the free cyanide ion. A linewidth of 2 Hz was therefore assumed for the HCN doublet. This point is not crucial, since the line-broadening caused by the chemical exchange is one or two orders of magnitude larger.

The  $K$  matrix was constructed in the following way. The generally written reaction (3) is the exchange under study,



and  $k_{\text{obs}}$  and  $k_{-\text{obs}}$  are pseudo-first-order rate constants that are related by eqn. (4). In more complicated cases the

$$k_{\text{obs}} P_{\text{HCN}} = k_{-\text{obs}} P_{\text{CN}^-} \quad (4)$$

density matrix method is suitable for constructing the rate matrix,<sup>10</sup> but in our case a simpler, but still exact way, was chosen. The exchanging system was considered to consist of three sites, as shown in Scheme 1. The factor 2 originates from the fact that the 'population' attributed to one peak of the HCN doublet is equal to half of the real population of

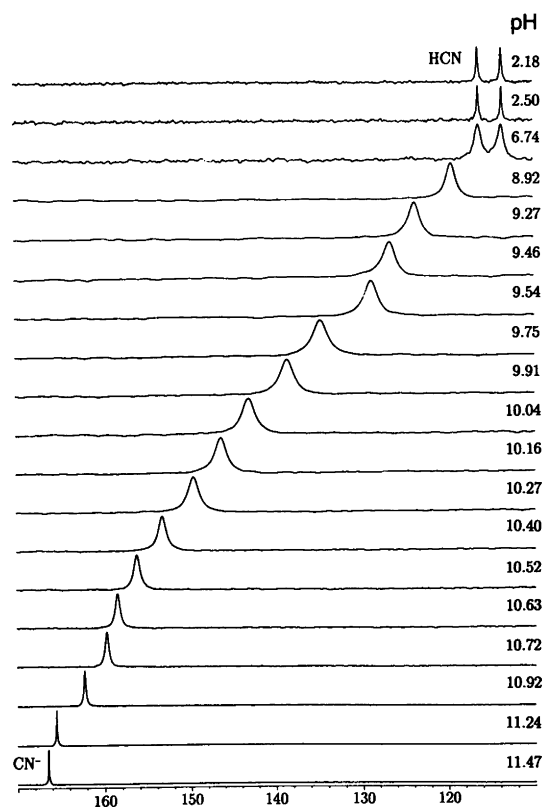
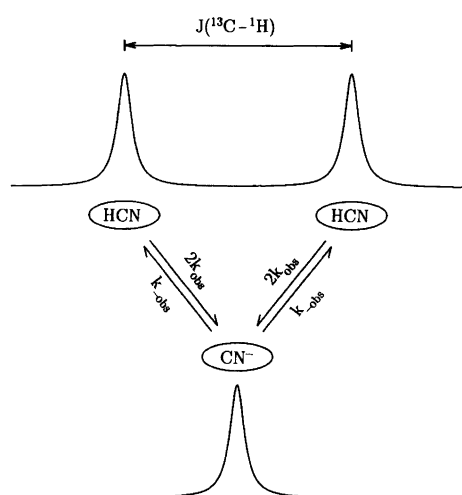


Fig. 1. 100.6 MHz <sup>13</sup>C NMR spectra of 0.1 M NaCN in water as a function of pH at 25°C;  $I = 3$  M LiClO<sub>4</sub>. The chemical shifts are reported in ppm toward higher frequency from TMS.



Scheme 1.

the HCN site. Therefore, the elements of the population vector  $P$  are  $\frac{1}{2}x_{\text{HCN}}$ ,  $x_{\text{CN}^-}$ ,  $\frac{1}{2}x_{\text{HCN}}$  in terms of molar fractions.

From scheme 1,  $K$  can be deduced as eqn. (5).

$$K = \begin{vmatrix} -2k_{\text{obs}} & k_{-\text{obs}} & 0 \\ 2k_{\text{obs}} & -2k_{-\text{obs}} & 2k_{\text{obs}} \\ 0 & k_{-\text{obs}} & -2k_{\text{obs}} \end{vmatrix} \quad (5)$$

Finally, the  $w$  matrix is given by eqn. (6), where  $J$  is the

$$w = \begin{vmatrix} x - \Omega_1 + \frac{1}{2}J & 0 & 0 \\ 0 & x - \Omega_2 & 0 \\ 0 & 0 & x - \Omega_1 - \frac{1}{2}J \end{vmatrix} \quad (6)$$

spin-spin coupling constant between  $^{13}\text{C}$  and  $^1\text{H}$  in HCN,  $\Omega_1$  is the chemical shift of HCN and  $\Omega_2$  is the chemical shift of  $\text{CN}^-$ . The model constructed above was tested for the very slow and very fast exchange regimes, and was found to lead to the same results as the approximate equations.<sup>8</sup> The NMR spectra were then calculated, and  $k_{\text{obs}}$  values leading to good agreement with the experimental spectra could be determined. The rate equations were deduced from the pH dependence of these  $k_{\text{obs}}$  values.

## Results

The spectra in Fig. 1 show that the rate of the overall exchange process decreases with increasing hydrogen ion concentration. In alkaline solutions a narrow single peak appears, which broadens at decreasing pH and the chemical shift moves toward lower frequency. This behaviour indicates fast chemical exchange on this timescale. At ca. pH 7 a proton-coupled HCN doublet appears which persists at lower pH.

In the pH range between 2 and 11 the following empirical rate equation given by eqn. (7) was found to be valid, as deduced from a least-squares analysis of the dependence of  $k_{\text{obs}}$  on  $[\text{H}^+]$  at various total cyanide concentrations and

$$k_{\text{obs}} = k_0 + k_1[\text{OH}^-] + k_2[\text{CN}^-] \quad (7)$$

ionic strengths. When a phosphate buffer was used the rate equation was given by eqn. (8). The stepwise dissociation

$$k_{\text{obs}} - (k_0 + k_1[\text{OH}^-] + k_2[\text{CN}^-]) = k_0[\text{PO}_4^{3-}] + k_{p1}[\text{HPO}_4^{2-}] + k_{p2}[\text{H}_2\text{PO}_4^-] \quad (8)$$

constants for the phosphate were taken from Ref. 11 and extrapolated graphically to 1 M  $\text{NaClO}_4$ :  $pK_1 = 1.8$ ,  $pK_2 = 6.4$ ,  $pK_3 = 11.2$ . The rate constants are given in Table 1. The phosphate dependence was studied in the ionic medium of 1 M  $\text{NaClO}_4$  using two concentrations of the phos-

Table 1. Rate constants of proton exchange in the HCN – water system at 25 °C in various ionic media (units  $\text{M}^{-1} \text{s}^{-1}$ ; errors are given as  $\pm 2\sigma$ ).

	1 M $\text{NaClO}_4^a$	1 M $\text{NaClO}_4^b$	3 M $\text{LiClO}_4^b$	1 M $\text{KCl}^c$
$k_0'^d$	$0.65 \pm 0.07$	$0.70 \pm 0.11$	$0.59 \pm 0.04$	0.72
$k_1$	$(1.8 \pm 0.3) \times 10^9$	$(3.5 \pm 0.7) \times 10^9$	$(3.3 \pm 0.4) \times 10^9$	$8.0 \times 10^9$
$k_2$	$(7.2 \pm 0.6) \times 10^6$	$(3.1 \pm 0.5) \times 10^6$	$(2.0 \pm 0.1) \times 10^6$	$\leq 10^5$
$k_{-0}$		$4.8 \times 10^{10}$	$3.3 \times 10^{11}$	
$k_{-1}$		$1.2 \times 10^3$	$1.5 \times 10^3$	
Phosphate buffer concentration <sup>b</sup>				
	0.046 M	0.023 M		
$k_{p0}$	$(1.7 \pm 0.2) \times 10^9$	$(1.3 \pm 0.2) \times 10^9$	–	–
$k_{p1}$	$(2.8 \pm 0.2) \times 10^5$	$(3.7 \pm 0.3) \times 10^5$	–	–
$k_{p2}$	$(1.1 \pm 0.6) \times 10^3$	$(1.7 \pm 0.5) \times 10^3$	–	–

<sup>a</sup>Total concentration of cyanide = 0.05 M, 200 MHz spectrometer, 10 %  $\text{D}_2\text{O}$ . <sup>b</sup>Total concentration of cyanide = 0.10 M, 400 MHz spectrometer. <sup>c</sup>20 °C, Ref. 6. <sup>d</sup> $k_0'[\text{H}_2\text{O}] = k_0$ .

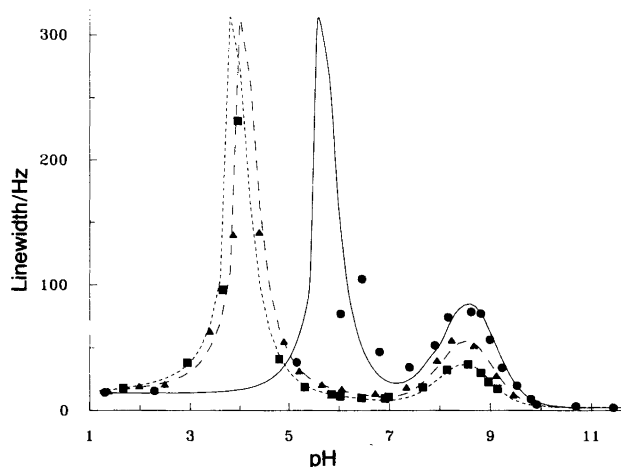


Fig. 2. Dependence of  $^{13}\text{C}$  NMR linewidths on the pH of the solution. Experimental (points) and calculated (lines): ●, no phosphate added; ▲, 0.023 M in phosphate; ■, 0.046 M in phosphate. Temperature 25 °C,  $(\text{HCN})_{\text{tot}} = 0.1 \text{ M}$ , in 1 M  $\text{NaClO}_4$ . In the case of the ( $^{13}\text{C}$ - $^1\text{H}$ ) spin-spin coupled doublet the linewidth in the figure was measured at half height of each of the components when they were well separated; otherwise measurements were at the half height of the entire signal.

phate buffer. Eqn. (7) is valid only above ca. pH 2. For more acidic solutions up to concentrated  $\text{HClO}_4$  some line-narrowing was found, indicating the possibility of a very slight proton inhibition of the exchange, as observed by Bednar and Jencks.<sup>6a</sup> A quantitative analysis of this contribution is very difficult because the medium and the activity of  $\text{H}^+$  are changed simultaneously.

Using the rate constants in Table 1 the linewidths were calculated (cf. section headed Data treatment) and compared with the experimental ones. Good agreement was found (Fig. 2), except for the unbuffered region  $5.5 < \text{pH} < 8.5$  (cf. Experimental section). The presence of the first maximum is caused by the presence and coalescence of the HCN doublet, while the second maximum is due to the usual two-site exchange between HCN and  $\text{CN}^-$ .

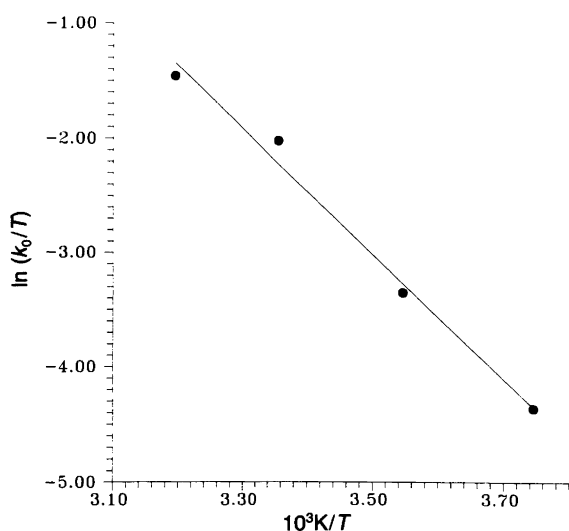
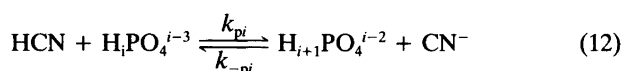
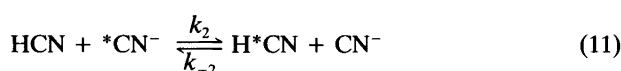
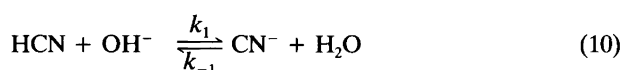
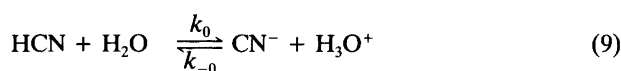


Fig. 3. Arrhenius plot for reaction (9);  $I = 3 \text{ M LiClO}_4$ , pH 2.2.

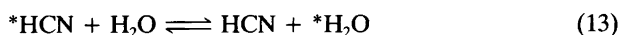
At pH 2.2,  $^{13}\text{C}$  NMR spectra were also recorded at  $-6$ , 9 and 40 °C in order to calculate the activation parameters (Fig. 3).

## Discussion

The terms in the rate eqns. (7) and (8) can be attributed to the parallel reaction paths (9)–(12).



As discussed by Bednar and Jencks,<sup>6a</sup> the reaction between HCN and water goes through pathway (9) rather than through reaction (13). The activation parameters for



reaction (9) could be determined at pH 2.2, where this reaction dominates the exchange (cf. Figs. 3 and 4):  $\Delta H^\ddagger = 45 \pm 4 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -64 \pm 12 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $I = 3 \text{ M LiClO}_4$ . Since we have not found strong acid inhibition we agree with Bednar and Jencks<sup>6a</sup> that the proton exchange may follow the Eigen mechanism.

A comparison of our results with the rate constants found in the literature (Table 1) shows that the numerical values of  $k_0$  and  $k_1$  are similar; the small differences may be due to differences in the temperature and in the ionic media. However, our value for  $k_2$  is an order of magnitude higher than the estimate by Bednar and Jencks<sup>6b</sup> ( $\leq 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ). We are not able to explain this difference, but our value for  $k_2$  is closer to the so-called Eigen curves on the Brönsted plot ( $\log k$  vs.  $\text{p}K$ ) of Bednar and Jencks [cf. Fig. 6 in Ref. 6(a)].

The  $k_{pi}$  values for proton removal by phosphate anions can also be fitted to the Brönsted plot and follow the so-called Eigen curves.<sup>6a</sup> This means that our results also show HCN behaves as a 'normal' acid rather than a 'carbon' acid.<sup>12</sup>

Since the protonation constants and ionic products for water were determined in both ionic media,<sup>5</sup> the value of the reverse rate constants could be calculated. In  $I = 1 \text{ M NaClO}_4$ ,  $\text{p}K_a = 9.09$  and  $\text{p}K_w = 13.8$ . Thus,  $k_{-0} = 4.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{-1} = 1.2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . In  $I = 3 \text{ M LiClO}_4$ ,  $\text{p}K_a = 10.00$  and  $\text{p}K_w = 13.6$ , yielding  $k_{-0} = 3.3 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$  and  $k_{-1} = 1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ . The difference between the dissociation constant in 3 M  $\text{LiClO}_4$  and in 1 M  $\text{NaClO}_4$  is

about one order of magnitude. The equilibrium constant is equal to the ratio between the forward and the backward reactions. Interestingly, in the present case this difference,  $\Delta K_a$ , can be entirely attributed to the decreased rate of removal of the proton from HCN by  $\text{OH}^-$  ( $k_1$ ) or to the increased rate of the diffusion-controlled formation of HCN from  $\text{H}_2\text{O}^+$  and  $\text{CN}^-$  ( $k_{-0}$ ), whereas all the other reaction rates remain unchanged when the ionic medium is changed from 1 M  $\text{NaClO}_4$  to 3 M  $\text{LiClO}_4$ . The two parallel paths are different: the reverse step of reaction (9) involves the proton ion, while the forward step of reaction (10) involves the hydroxide ion. It seems that the change in the ionic medium has a strong effect, especially on these two ions. It is hard to explain the effect of concentrated salt, since many solution parameters change when the concentration of electrolyte and/or its quality is altered. In the present case the rate of diffusion of the proton increases, while the rate of proton transfer from HCN to  $\text{OH}^-$  decreases. The latter observation is rather common.<sup>13</sup> It has been explained by a change in the water structure, by the Grotthuss mechanism<sup>14</sup> and by a decrease in the number of water molecules available.<sup>15</sup> We have no explanation as to why the proton moves slower in 1 M  $\text{NaClO}_4$  and in 1 M  $\text{KCl}^{6c}$  than in 3 M  $\text{LiClO}_4$ .

## Conclusions

$^{13}\text{C}$  NMR spectroscopy is a convenient tool for the determination of proton exchange dynamics of simple carbon-containing acids. The timescale defined by the difference between the chemical shifts of HCN and  $\text{CN}^-$  on a 400 MHz NMR spectrometer is sufficiently long for this kind of study, and hence informative spectra can be obtained from

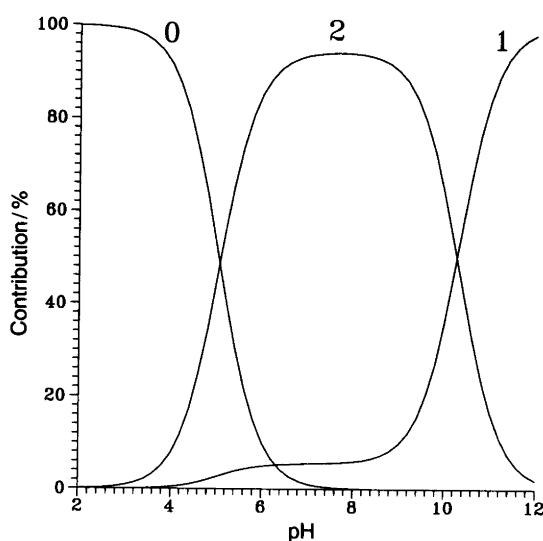


Fig. 4. Percentage contribution of parallel reaction paths to the total exchange rate calculated as  $k_0[\text{HCN}] + k_1[\text{HCN}][\text{OH}^-] + k_2[\text{HCN}][\text{CN}^-]$ . 0, 1 and 2 correspond to reaction paths denoted in the text by  $k_0$ ,  $k_1$  and  $k_2$ .  $I = 1 \text{ M NaClO}_4$ ,  $[\text{CN}]_{\text{tot}} = 0.050 \text{ M}$ ,  $25^\circ\text{C}$ .

which the rate data can be extracted in a convenient way. Moreover, the  $^{13}\text{C}$ - $^1\text{H}$  spin-spin coupling provides an additional timescale and further facilitates the interpretation of the data. Carbon-13 NMR appears to be a simpler method than  $^1\text{H}$  NMR with solvent saturation as used in the work of Bednar and Jencks,<sup>6</sup> and some inherent pitfalls in the latter method can be avoided. Concluding, the present work supplements the study by Bednar and Jencks<sup>6</sup> and, together with the latter, provides a relatively complete picture of the dynamic behaviour of hydrogen cyanide in aqueous solution.

*Supplementary Material.* A listing of primary experimental data in the form:  $\text{pH}_{\text{exp}}$ ,  $\text{pH}_{\text{calc}}$ ,  $p_{\text{HCN}} = [\text{HCN}]/[\text{CN}]_{\text{tot}}$ ,  $p_{\text{CN}}$ ,  $^{13}\text{C}$  linewidth,  $^{13}\text{C}$  chemical shift and  $(\text{pH}_{\text{exp}} - \text{pH}_{\text{calc}})$  in various ionic media, 7 pp, is available from one of the authors (J.G.) on request.

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