Solute–Water Interactions in the Aquation of Isonicotinohydrazide and Nicotinic Acid Complexes of Pentacyanoferrate(II) at Various pH

By **Miguel A. Blesa,*** **Irene A. Funai,** and **Pedro J. Morando,** Comisión Nacional de Energía Atómica and Departamento de Fisicoquímica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Junín 956, Buenos Aires, Argentina
José A. Olabe, Departamento de Política Científica, Universidad de Luján, Argentina

Changes in the rate constants and activation parameters of the title reactions, as the state of protonation of the outgoing ligand and cyanides changes, seem to reflect solely changes due to the different charge type, *i.e.* the different contribution from water structuring around the activated complex. Rate constants for the title and related reactions are remarkably insensitive to changes in Fe–N bonding.

MUCH data has now accrued on the substitution reactions of $[Fe(CN)_5L]^{n-}$ ions. In most of the work presented so far, the emphasis has been on ' inner ' effects, *i.e.* changes in bond-breaking rates as the ligand is varied have been related to changes in the σ- and/or π-bonding strength of the Fe–L bond.[1-4] However, some recent observations have focused attention on the contribution of solvation energetics to the activation process, at least when small changes are to be interpreted.[5,6]

In this paper, we report another piece of evidence pointing in the same direction, *i.e.* changes in bond-breaking rates when the state of protonation of a basic ligand is changed. In a previous paper[3] we measured the rates of release of ethylenediamine (en) and of its conjugated acid (Hen^+) and attributed the ratio $k_{-Hen} : k_{-en} = 2 : 1$ to nearly compensating basicity and charge effects. Now we have determined the pH profile of the rate constant for the release of nicotinic acid (Hnic) and isonicotinohydrazide (Hinh), which show similar changes, and this fact together with the activation data seems to provide a good case for solvation influence.

EXPERIMENTAL

Reagents.—The salt $Na_3[Fe(CN)_5(Hinh)]\cdot6H_2O$ was prepared as described before;[4] $Na_4[Fe(CN)_5(nic)]\cdot6H_2O$ was prepared following essentially the technique of Toma and Malin.[1] Analytical data and the i.r. spectrum of the latter salt were in good accord with the proposed formula. In aqueous solution, this complex shows the characteristic $t_{2g}\rightarrow\pi^*$ transition of $[Fe(CN)_5L]^{n-}$ ions containing an aromatic amine.[1] For L = nic^-, $\lambda_{max.} = 380$ nm and $\varepsilon = 4.05 \times 10^3$ dm^3 mol^{-1} cm^{-1}.

Potentiometric Titrations.—These were carried out at 25 °C under nitrogen using a Radiometer M 52 digital pH-meter with G-202 C and calomel electrodes. The ionic strength was 1 mol dm^{-3} (NaCl).

Kinetic Experiments.—The rates of release of (H)inh and (H)nic were measured spectrophotometrically using pyridine (py) or dimethyl sulphoxide (dmso) as scavengers for $[Fe(CN)_5(OH_2)]^{3-}$. The stoicheiometry is shown in equation (1), where X = py or dmso. For L = (H)nic and for

$$[Fe(CN)_5L]^{n-} + X \longrightarrow [Fe(CN)_5X]^{3-} + L^{(n-3)-} \tag{1}$$

L = Hinh at low pH, dmso was chosen, while either scavenger was employed in neutral or alkaline (H)inh solutions. The absorbance was monitored at 380 [(H)nic], 437 (Hinh),[4] or 360 nm (py)[1] using a Hitachi–Perkin-Elmer 139 spectrophotometer. The ionic strength was 1 mol dm^{-3} NaCl, and buffer solutions of various compositions were employed. No dependence was detected on the type of buffer. The temperature was varied between 10 and 35 °C. All the measurements were made at high X concentration, where first-order kinetics are found (see below).

Individual rate constants given below are the averages from duplicate runs, and are believed to be correct to within ±5 %. No deviation from linearity in the first-order kinetic plots was apparent (except at the lowest pH values) up to at least 80% completion of reaction.

RESULTS

The basic mechanism governing the reactions studied is dissociative, probably I_d [equations (2)—(4)]. At high

$$[Fe(CN)_5L]^{n-} \underset{k_L}{\overset{k_{-L}}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + L^{(n-3)-} \tag{2}$$

$$[Fe(CN)_5]^{3-} + H_2O \overset{K}{\rightleftharpoons} [Fe(CN)_5(OH_2)]^{3-} \tag{3}$$

$$[Fe(CN)_5]^{3-} + X \underset{k_{-X}}{\overset{k_X}{\rightleftharpoons}} [Fe(CN)_5X]^{3-} \tag{4}$$

[X] the experimental rate constant is simply $k_{expt.} = k_{-L}$.[1-4,7] All our measurements were carried out under these conditions.

TABLE 1

Rate constants for the release of Hinh at 25.2 °C, various pH, and I = 1 mol dm^{-3} (NaCl)

pH	10^4k_{-L}/s^{-1}	pH	10^4k_{-L}/s^{-1}
3.60	7.75 *	9.64	7.02
4.31	7.28 *	9.82	6.66
5.17	6.86 *	10.08	6.45
6.11	6.88 *	10.26	5.76
7.21	6.63 *	10.36	4.50
8.05	7.25	10.53	4.19
8.65	7.13	10.69	4.05
8.88	7.68	11.48	3.07
9.11	7.50	11.86	2.66
9.31	7.61	12.14	2.71
9.44	7.21	12.33	2.69
		12.48	2.50

* 0.1 mol dm^{-3} dmso was used as scavenger. In all the other cases, 0.1 mol dm^{-3} py was employed.

Hinh as a Ligand.—Table 1 shows the pH dependence of $k_{-(H)inh}$ at 25 °C. The data, plotted in Figure 1, show clearly

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[1] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.

[2] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1974, **13**, 1772.

[3] M. A. Blesa, J. A. Olabe, and P. J. Aymonino, *J.C.S. Dalton*, 1976, 1196.

[4] M. A. Blesa, I. A. Funai, P. J. Morando, J. A. Olabe, P. J. Aymonino, and G. Ellenrieder, *J.C.S. Dalton*, 1977, 845.

[5] A. R. Garafalo and G. Davies, *Inorg. Chem.*, 1976, **15**, 1101.

[6] N. E. Katz, P. J. Aymonino, M. A. Blesa, and J. A. Olabe, *Inorg. Chem.*, in the press.

[7] Z. Bradic, D. Pavlovic, I. Murati, and S. Asperger, *J.C.S. Dalton*, 1974, 344.

that deprotonation of co-ordinated Hinh takes place with pK_a 10.4 in our medium (I 1 mol dm^{-3} NaCl). Potentiometric titration of free Hinh and $[Fe(CN)_5(Hinh)]^{3-}$ also showed similar pK_a values (10.5 for both uncomplexed and co-ordinated Hinh). Literature values for the pK_a of Hinh in other ionic media are also similar.[8,9] The insensitivity of pK_a to co-ordination is remarkable, although by no means an isolated fact (see below), and implies similar stabilities for the complexes of Hinh and inh$^-$ in view of relation (5) where the left-hand K values are the stability constants of the respective complexes.

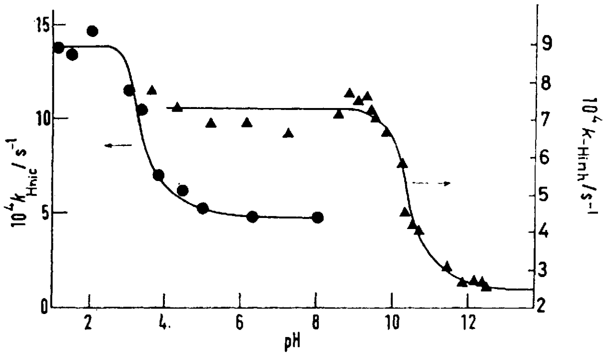

FIGURE 1 pH Profiles for the specific rate of release of Hinh (▲) and Hnic (●). Plateau values chosen are the averages from all the measurements in each saturation region. Lines are drawn simply as a visual aid and do not have any special meaning

$$\frac{K(\text{Hinh})}{K(\text{inh}^-)} = \frac{K_a(\text{co-ordinated Hinh})}{K_a(\text{free Hinh})} \qquad (5)$$

Deprotonation of co-ordinated Hinh is also attended by spectral changes; a hipsochromic shift puts the $t_{2g}\rightarrow\pi^*$ band maximum at *ca.* 415 nm in Na[OH]–NaCl buffer of pH 12.1 and I = 1 mol dm^{-3}, against a blank of free inh$^-$ under the same conditions (ε 5×10^3 dm^3 mol^{-1} cm^{-1}). The rate constants for the release of Hinh and inh$^-$ can be taken as equal to the upper and lower plateau values in Figure 1; from these, a factor $k_{-Hinh} : k_{-inh} = 2.7 : 1$ is obtained at 25 °C. It is noteworthy that the decrease in rate constant attending deprotonation is accompanied by a hipsochromic shift; in systems of constant charge type it is well known that the strength of π bonding, as measured by the position of the charge-transfer band, governs the magnitude of k_{-L}.[1] In the present case such a correlation does not hold.

Table 2 shows the dependence of k_{-Hinh} and k_{-inh} on the temperature. From these data the following values are obtained for the activation parameters: $\Delta H^\ddagger_{-Hinh} = 109.2 \pm 1.5$ kJ mol^{-1}; $\Delta S^\ddagger_{-Hinh} = 61 \pm 5$ J K^{-1} mol^{-1}; $\Delta H^\ddagger_{-inh} = 120 \pm 3$ kJ mol^{-1}; $\Delta S^\ddagger_{-inh} = 80 \pm 10$ J K^{-1} mol^{-1}. Uncertainties quoted are 80% confidence limits calculated using a least-squares regression analysis. It is seen that the small change in rate constant is the result of large and nearly compensating changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

As shown in Figure 1 and Table 1, measurement of the rate of release of H_2inh^+ was also attempted at pH 1.2. The complex $[Fe(CN)_5(H_2inh)]^{2-}$, however, could not be characterized. At this pH the charge-transfer band shows a hipsochromic shift to *ca.* 410 nm, indicative of protonation at cyanide.[1] No noticeable changes in reactivity are found at low pH, and this is rather surprising as the reacting species should be $[Fe(CN)_4(CNH)(Hinh)]^{2-}$.

(H)nic *as a Ligand.*—Due to the zwitterionic nature of nicotinic acid, complex formation by Hnic with $[Fe(CN)_5(OH_2)]^{3-}$ takes place only with the nicotinate anion. The co-ordinated ligand however is easily protonated at low pH, and the same type of k–pH profile is found as for Hinh (see Figure 1 and Table 3). From the kinetic data the pK_a is 3.3 which is close to the value deduced from the first and second pK_a values for Hnic and assuming that pK_a values for (6) and (7) are equal.[10]

TABLE 2

Rate constants for the release of Hinh and inh$^-$ at various temperatures and I = 1 mol dm^{-3} (NaCl). 0.1 mol dm^{-3} py was used as scavenger

pH	θ_c/°C	10^4k_{-L}/s^{-1}
12.2	10.0	0.171
	15.2	0.505
	20.1	1.06
12.5	25.2	2.50
12.2	29.9	5.65
	35.1	12.07
8.1	11.0	0.768
	14.9	1.44
	19.9	3.30
	25.0	7.25
	30.5	15.4
	35.5	28.9

TABLE 3

Rate constants for the release of Hnic at 25.2 °C, various pH, and I = 1 mol dm^{-3} (NaCl)

pH	10^4k_{-L}/s^{-1}
1.10	13.8
1.47	13.4
2.02	14.6
2.46	13.8
3.00	11.5
3.30	10.5
3.78	7.1
4.41	6.2
4.93	5.3
6.27	4.8
7.98	4.8

TABLE 4

Rate constants for the release of Hnic and nic$^-$ at various temperatures and I = 1 mol dm^{-3} (NaCl). 0.1 mol dm^{-3} dmso was used as scavenger

pH	θ_c/°C	10^4k_{-L}/s^{-1}
1.1	15.5	3.39
	20.4	7.46
	25.1	13.8
	30.0	25.3
	35.0	41.8
8.0	15.3	0.92
	20.3	2.06
	25.2	4.79
	29.9	10.7
	34.8	20.3

$$H\overset{+}{N}C_5H_4CO_2H \rightleftharpoons NC_5H_4CO_2H + H^+ \qquad (6)$$

$$H\overset{+}{N}C_5H_4CO_2Me \rightleftharpoons NC_5H_4CO_2Me + H^+ \qquad (7)$$

Table 4 collects the results of measurements at various temperatures. From these, $\Delta H^\ddagger_{-nic} = 116 \pm 4$ kJ mol^{-1},

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[8] A. Albert, *Nature*, 1956, **177**, 525.

[9] K. Nagano, H. Tsukahara, H. Kinoshita, and Z. Tamura, *Chem. Pharm. Bull.* (*Tokyo*), 1963, **11**, 797.

[10] E. Klingsberg, 'Heterocyclic Compounds,' Interscience, New York, 1960, vol. 14, p. 75.

$\Delta S^{\ddagger}_{-nic} = 82 \pm 13$ J K^{-1} mol^{-1}, $\Delta H^{\ddagger}_{-Hnic} = 96 \pm 9$ kJ mol^{-1}, and $\Delta S^{\ddagger}_{-Hnic} = 21 \pm 27$ J K^{-1} mol^{-1}. At 25 °C, the ratio $k_{-Hnic} : k_{nic} = 3.0 : 1$. As before, the first three figures are least-square values with 80% confidence limits. The scatter of data and uncertainties at higher temperatures were higher for Hnic, and a 50% confidence limit is quoted. The large interval given does not affect our conclusions, as even the worst case is in line with our reasoning.

The band maximum for $[Fe(CN)_5(Hnic)]^{3-}$ is at 380 nm (pH >5). At lower pH, two different changes occur: in the range $3.0 < pH < 4.0$ a bathochromic shift puts the maximum at 393 nm, and further lowering of pH (pH *ca.* 1) is attended by a shift in the opposite direction to 365 nm. Figure 2 shows these spectra, on an arbitrary scale of absorbance: no absolute absorption coefficients are reported in view of the irreversibility of aquation at low pH; only the species $[Fe(CN)_5(nic)]^{4-}$ can be rendered stable by adding an adequate excess of free nic$^-$. The spectral changes reflect the existence of $[Fe(CN)_5(nic)]^{4-}$, $[Fe(CN)_5(Hnic)]^{3-}$, and $[Fe(CN)_4(CNH)(Hnic)]^{2-}$ as the major species at the various pH values.

TABLE 5

Rate parameters for the release of basic ligands and their conjugate acids

Ligand	10^3k (25 °C)/s^{-1}		$k_{-HL} : k_{-L}$ (25 °C)	$\Delta H^{\ddagger}$/kJ mol^{-1}		$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}		Ref.
	HL^{n+}	$L^{(n-1)+}$		HL^{n+}	$L^{(n-1)+}$	HL^{n+}	$L^{(n-1)+}$	
en	10.4	5.15	2.0	100	97	50	38	3
pd [a]	8.17	5.07	1.6	101	103	54	59	6
hd [b]	5.3	4.1	1.3					6
Hinh	0.725	0.260	2.8	109	120	61	80	4, *c*
Hnic	1.42	0.479	3.0	96	116	21	82	*c*
HCN	9.7	0.40	24	113	127	7.9	29	*d*
$[SO_3]^{2-}$	0.63	0.057	11	117	125	84	100	*e*

[a] pd = propane-1,3-diamine. [b] hd = hexane-1,6-diamine. [c] This work. [d] Data at 40 °C from J. Legros, *J. Chim. phys.*, 1964, **61**, 909. [e] Data at 20 °C from J. Legros, *J. Chim. phys.*, 1964, **61**, 923.

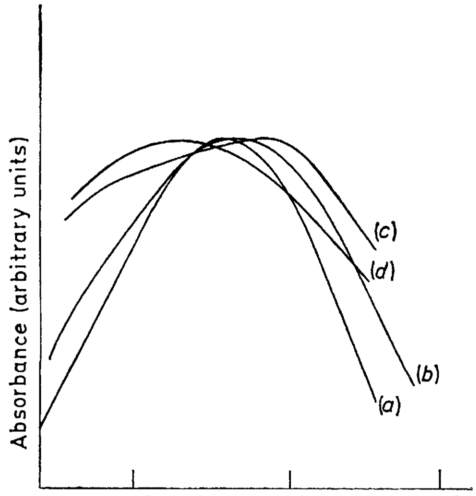

FIGURE 2 Absorption spectra of $[Fe(CN)_5(Hnic)]^{3-}$ at pH 8.0 (*a*), 3.33 (*b*), 3.30 (*c*), and 1.47 (*d*)

DISCUSSION

In Table 5 we have collected data for a series of basic ligands. It is clearly seen that in almost every case the acidic form of the ligand is released faster than the basic form and that the ratio $k_{-L} : k_{-LH}$ is usually small whilst the activation parameters for the release of the basic form are both noticeably higher. The hipsochromic shift attending deprotonation of both ligands is in agreement with the expected decrease in π-bonding strength. The parallel decrease in k_{-L} is therefore remarkable, as all previous work suggests that decreasing π-bonding strength should be attended by an increase in reaction rate.[1] Therefore, unless an exception is postulated in the sense that in the present case σ rather than π bonding governs the rate of release, which is contrary to previous work,[1] the increase in $\Delta H^{\ddagger}$ should not be traced to Fe–N bond effects, and should in fact show the importance of hydration of the reactants and activated complex. In a dissociative I_d process like the one under study, when we compare the activation steps (8) and (9), the additional structuring of water around

$$[Fe(CN)_5(HL)]^{3-}(aq) \longrightarrow [Fe(CN)_5{}^{3-} \cdots HL]^{\ddagger}(aq) \qquad (8)$$

$$[Fe(CN)_5L]^{4-}(aq) \longrightarrow [Fe(CN)_5{}^{3-} \cdots L^-]^{\ddagger}(aq) \qquad (9)$$

the second, more highly charged, reactant ion should be reflected in higher $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ values for reaction (9). (For these comparisons to be meaningful, the cationic environment should be, as in our case, kept rigorously constant, otherwise specific ion-pairing effects vitiate any conclusion.) The influence of the charge type is in complete accordance with the well known effects operating in the kinetics of ionization of weak acids.[11]

Previously,[6] we have shown that for the series $[Fe(CN)_5L]^{3-}$ (L = aliphatic amine) the changes in reactivity are governed by solvation effects. Thus, log k_{-L} is not noticeably related to the pK_a of the conjugated ammonium ion, whilst good correlations are found with quantities reflecting the hydration of the released amine (for example, $\Delta H^{\ominus}$ for the phase transfer from gas to aqueous solution). These effects also show up in a series of aliphatic diamines [12] where the ratio $k_{-HL^+} : k_{-L}$ decreases from 2 : 1 for ethylenediamine to *ca.* 1 : 1 for hexane-1,6-diamine, suggesting that, as the proton attached to the far end of the ligand is situated farther from the metallic moiety, solvent structure changes attending charge separation become less important.

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[11] F. Basolo and R. G. Pearson, ' Kinetics and Mechanism,' 1st edn., Wiley, New York, 1961.

[12] N. E. Katz, P. J. Aymonino, M. A. Blesa, and J. A. Olabe, unpublished work.

Published values of the activation parameters for (H)en release are, however, anomalous and are being re-investigated.[3]

Also, the changes in the presence of a strong polymeric cation, such as poly[trimethyl(vinylbenzyl)ammonium ion], are reasonably interpreted on the same grounds.[13] Garafalo and Davies [5] also pointed out the importance of solvent effects in the equilibria of these ions.

Summing up, the rates of release of aliphatic and aromatic amines from $[Fe(CN)_5L]^{3-}$ ions are remarkably insensitive to 'inner' effects, the highest rate constant reported being *ca.* 2×10^{-2} s^{-1} for cyclohexylamine [6] at 25 °C and the lowest being 2.8×10^{-4} s^{-1} for methylpyrazinium cation,[1] even though several pK_a units are spanned together with changes in π bonding, charge type, *etc.* The reverse processes are also little affected by these changes, and thus the stability constants are all similar.[14] This insensitivity to inner effects allows solvent effects, which are rather minor, to emerge without being swamped out by larger changes from other sources. Much caution must be exerted therefore in trying to attach 'inner' structural significance to small changes in rates, or even to large changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$.

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[7/078 *Received, 17th January,* 1977]

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[13] M. A. Blesa, J. A. Olabe, and R. Fernandez-Prini, unpublished work.

[14] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080.