Aquation of Fe–N Bonds in Pentacyano(ligand)ferrate(2—) Ions: Electronic and Medium Effects

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The rate of Fe–N bond breakage in $[Fe(CN)_5L]^{n-}$ (L = aromatic amine) ions has been determined for several neutral, anionic, and cationic amines. The results, together with previously reported values for related systems, are used to discuss the mechanism of substitution on $[Fe(CN)_5L]^{n-}$ systems. The contributions of inner (electronic and electrostatic) and solvent effects to the activation process are discussed.

The aquation of aromatic amine ligands in pentacyano(ligand)ferrate(2−) systems has been extensively studied since the first report by Toma and Malin.[1–11] It is currently accepted that the basic mechanism is dissociative, in the sense that extensive bond breaking takes place to reach the activated state, without much bond formation with the incoming ligand. The distinction however between a dissociative (*D*) mechanism and a dissociative interchange (I_d) according to the classification by Langford and Gray[12] is not easy, difficulties mainly arising from the very basis of the classification; one of the purposes of the present work is to clarify this aspect of the substitution kinetics in $[Fe(CN)_5L]^{n-}$ ions.

In these systems, it has been possible to measure both the rate of aquation and the rate of substitution on $[Fe(CN)_5(H_2O)]^{3-}$ of various ligands:[13,14] a definite lack of sensitivity to ligand basicity has been demonstrated, and this in turn allows the discussion of rather subtle effects exhibited when the nature of L is changed; it has thus been contended previously by us that solvational changes to reach the activated complex can be detected in some favourable cases.[5,15,16] On the other hand, high-pressure studies have not shown any detectable solvent participation in the measured $\Delta V^{\ddagger}$ values.[7]

In the present paper further rates of aquation of aromatic ligands are reported, and the results used to illustrate the influence of inner (electronic and electrostatic) and hydration effects in the energetics of activation.

Experimental

Unless otherwise stated, all reagents used were analytical grade or better. The following ligands were used, and their $[Fe(CN)_5L]^{n-}$ complexes synthesized, either in aqueous solution or as the sodium salt: nicotinamide, nicotinic acid and its anion, isonicotinic acid and its anion, *NN*-diethylnicotinamide (nikethamide, coramine), pyrazine mono-*N*-oxide, nicotinoylglycinate anion, and pyridylpyridinium cation. The complexes in solution were prepared by mixing the sodium salt of aminopentacyanoferrate(II) ion with an appropriate amount of the ligand (ten-fold excess) or by first preparing the sodium salt (according to procedures previously described).[4,8]

The visible spectra of the complex ions in aqueous solution were recorded on a Shimadzu 210A spectrophotometer.

Kinetic measurements were performed spectrophotometrically, by following the decrease in absorbance at the maximum of the metal-to-ligand charge-transfer band[1] when dimethyl sulphoxide (dmso) was added to the solution containing *ca.* 10^{-4} mol dm^{-3} complex, adequate buffering mixtures, and sodium chloride to fix the ionic strength at 1 mol dm^{-3}. The mechanism of replacement of L by dmso is well known,[17] and the present paper will discuss only the values obtained at high dmso concentrations, which have been proven to be identifiable with k_{-L}, the first-order rate constant of release of the ligand L.[1] Kinetic measurements were performed in the temperature range 10—35 °C, and at various pH in the case of ligands which enter into protolytic equilibria in water.[5,18] Different values of dmso concentrations up to 0.15 mol dm^{-3} were employed to ensure that saturation values were measured; these were determined in triplicate runs. Both k_{-L} and the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined by least-squares fitting of the data. Errors quoted in the Table (see later) correspond to 90% confidence limits.

Results and Discussion

The accepted equilibria involved in the interchange of two ligands L and L′ are given by equations (1) and (2). No

$$[Fe(CN)_5L]^{n-} + H_2O \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + L^{(n-3)-} \quad (1)$$

$$[Fe(CN)_5(H_2O)]^{3-} + L'^{(m-3)-} \rightleftharpoons [Fe(CN)_5L']^{m-} + H_2O \quad (2)$$

evidence has been found for direct substitution of L′ for L without mediation of the aquopentacyano-complex. At high L′ concentrations a limiting rate is achieved; the experimental rate constant thus obtained is the first-order k_{-L} corresponding to forward reaction (1). Water mediates the replacement of L by L′ through reactions (1) and (2); in this case the distinction between *D* and solvent-mediated I_d mechanisms is ambiguous. Thus, the demonstration of the existence of the species $[Fe(CN)_5]^{3-}$ (see ref. 19) has not been achieved and it is probably impossible to distinguish it from solvent-equilibrated $[Fe(CN)_5(H_2O)]^{3-}$. The probable stability of outer-sphere associated species such as $[Fe(CN)_5 \cdots L]^{n-3}$ has been proposed also as a criterion for classification. It has thus been argued that if L is negatively charged, it would not be retained in the outer co-ordination sphere, and the mechanism should be termed *D*;[19] however, even this as an *a priori* criterion is dangerous when it is realized that the similarly charged methylpyrazinium cation and penta-amineruthenium(II) have been reported to have a rather large outer-sphere association constant.[20] In the following, therefore, we shall label the mechanism I_d. An interesting general critique to the Langford and Gray classification can also be found in ref. 21.

Trends in the Values of k_{-L}.—In the Table we have collected the values of the rate constant k_{-L} obtained in this work, together with those previously available. The data are for 25 °C and 1 mol dm^{-3} ionic strength, except as noted. We have also included the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. As

Table. Rate constants at 25 °C and $I = 1$ mol dm^{-3}, activation parameters, and wavelengths of the band maximum of the charge-transfer transition for several pentacyano(ligand)ferrate(2−) complex ions

Ligand	10^4k_{-L}/s^{-1}	$\lambda_{max.}$/nm	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	Ref.
(1) Nicotinate anion	4.8	380	116 ± 4	82 ± 13	5, this work
(2) Nicotinic acid	14.2	392	96 ± 9	21 ± 27	5, this work
(3) Isonicotinoylhydrazide	7.2	437	109 ± 2	61 ± 5	4, 5
(4) Isonicotinoylhydrazide anion	2.6	415	120 ± 3	80 ± 10	5
(5) Isonicotinate	2.9	418	114 ± 4	70 ± 9	This work
(6) Isonicotinic acid	7.1	427	97 ± 4	17 ± 8	This work
(7) Nicotinamide	9.0	392	106 ± 3	53 ± 7	This work
(8) Pyridine	11.0	362	104	46	1
(9) Nikethamide	5.8	392	106 ± 3	51 ± 5	This work
(10) Pyridylpyridinium	17.8	482	110 ± 3	76 ± 8	This work
(11) Nicotinoylglycinate	7.6	395	118 ± 3	93 ± 8	This work
(12) Methylpyrazinium	2.8	655	115	75	1
(13) Isonicotinamide	7.3	435	109	58	1
(14) Pyrazine mono-*N*-oxide	9.0	518	111 ± 4	70 ± 10	This work
(15) Pyrazine	4.2	452	110	58	1
(16) 4-Methylpyridine	11.5	356	100 ± 2	38 ± 8	1
(17) 4-Cyanopyridine	10.2 *	419			30

* Measured at 0.1 mol dm^{-3} ionic strength.

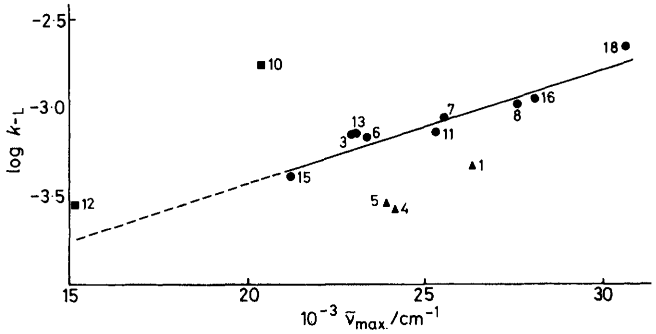

Figure 1. Log k_{-L} as a function of the wavenumber of the maximum of the t_{2g}→π* band. For key see Table; 18 = 4-aminopyridine

expected for a dissociative mechanism, there is an approximately linear relationship in these systems between log k_{-L} and −log Q with unitary slope, which implies that the rate constant for the reverse reaction, k_L, is essentially constant.[19] Other related linear free-energy relationships can be expressed in a more indirect fashion, as has been done by Toma and coworkers,[8,9] who have shown that there is a linear relationship between log k_{-L} and the energy of the lowest *d–d* transition, for a wide variety of ligands including water, aromatic and aliphatic amines, and inorganic anions. Restricting ourselves to aromatic amines, another linear free-energy relationship can be established, as shown in Figure 1, where log k_{-L} has been plotted against the energy of the t_{2g}→π* transition typical of these complexes. The qualitative relationship between this energy and the energy of the broken bond can be seen in Figure 2, which shows that electronic changes in L which produce a red shift in the band maximum will also produce an increase in the π-bonding energy; usually, such changes will also bring about a decrease in the σ-bonding energy, and the existence of the relationship shown in Figure 1 therefore implies that either σ bonding is irrelevant in the activation process because it does not change appreciably from ligand to ligand,[15] or that σ- and π-bonding changes are geared in such a way that the π-energy change is a fixed fraction of the total change.

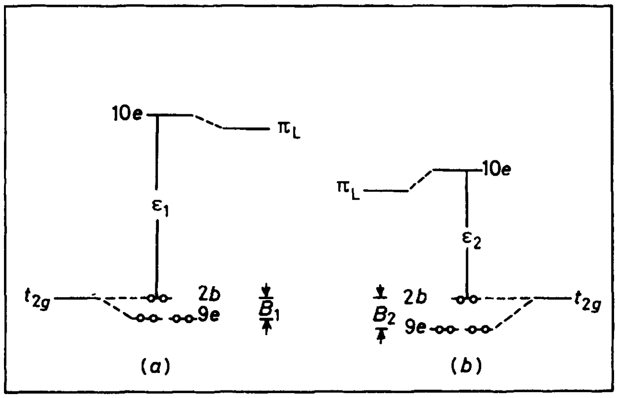

Figure 2. Relationship between the energy of the charge-transfer transition (ε) and the stabilization energy arising from π bonding (*B*). Energy levels have been labelled according to M. Braga, A. C. Pavao, and J. R. Leite, *Phys. Rev. B.*, 1981, **23**, 4328. The energy of the 2*b* level has been arbitrarily taken as equal to the energy of the original t_{2g} level. Only the 2*b*→10 *e* transition is indicated, although other sublevels are involved

It is apparent on inspection of Figure 1 that non-neutral ligands fall rather apart of the drawn line. A situation similar to that found for the pyridylpyridinium ion in Figure 1 has been analysed by Haim,[22] in the aquation of mononegative and dinegative ligands from $[Co(NH_3)_5X]^{n+}$ ions. He attributes the deviation, in the sense of an increased rate of release with increasing charge for a given value of the stability of the complex, to electrostatic interactions in the ion pair involved in the detailed mechanism, which in our case would be as in equations (3) and (4) (L = pyridylpyridinium). Calling Q the

$$[Fe(CN)_5L]^{2-} + H_2O \rightleftharpoons [Fe(CN)_5(H_2O)^{3-} \cdots L^+] \quad (3)$$

$$[Fe(CN)_5(H_2O)^{3-} \cdots L^+] \rightleftharpoons [Fe(CN)_5(H_2O)]^{3-} + L^+ \quad (4)$$

overall stability constant (*i.e.* $K_3^{-1}K_4^{-1}$) and noting that $(k_{-L}/k_{-3}) = K_3$, the relationship (5) ensues and a new line is

$$\log k_{-L} = \log(k_{-3}K_4^{-1}) - \log Q \quad (5)$$

defined through the ion-pair equilibrium (4) which changes the intercept but not the slope in the log k_{-L} *vs.* $-\log Q$ plot. The value for methylpyrazinium cation is rather low according to this picture but the basic ideas seem to represent qualitatively well the behaviour of cationic ligands. Alternatively, a completely equivalent interpretation [22] focuses on the differences in the stabilization of the activated complex by electrostatic interactions, thus lowering the free energy of activation. Also, solvation effects may contribute in the way pointed out in ref. 16 for the release of α,ω-diamines in an acidic medium.

Deprotonation of a ligand is logically expected to decrease the extent of π bonding and increase the extent of σ bonding; in agreement with this, the band maximum in such cases shifts to lower wavelengths, as can be seen in the case of nicotinic and isonicotinic acids and their anions, and also of isonicotinoylhydrazide and its monoanion, included in the Table.

When examining the kinetic data (Table) it is obvious that the rate constants of the negatively charged ligands change in the wrong direction, *i.e.* they are released more slowly than their conjugate acids. If outer-sphere pairs are involved, similar reasoning to that of positively charged ligands could explain the trends; however, we feel that an examination of the solvation changes accompanying the activation process provides a better route to understanding the observations.

In a previous paper we have used the model of Caldin and Bennetto [23] to explain the trends observed in the activation parameters for the release of aliphatic amines. In this model, the solvent accommodates concertedly to ligand movement in the activation process; it is interesting that this model is more likely to be of application to negatively charged ions such as the pentacyanoferrates under study. An important feature of the results which suggests the operation of solvent effects is the increase, well beyond error limits, in both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ when the ligand is deprotonated; in fact, the resulting decrease in the rate at 25 °C arises from the lack of exact compensation of $\delta(\Delta H^\ddagger)$ and $\delta(T\Delta S^\ddagger)$, and it would be expected that at temperatures higher than 50 °C the order would be inverted. We shall discuss the data therefore in terms of $\Delta S^\ddagger$ rather than in terms of $\Delta G^\ddagger$.

In the processes discussed here, we may equate the activated state to the reaction products $[\mathrm{Fe(CN)_5(H_2O)}]^{3-}$ and $\mathrm{L(aq)}^{(n-3)-}$. This is reasonable whether the mechanism is either truly dissociative (*D*) or a dissociative interchange (I_d). For the release of two ligands L and L′ the difference $\delta(\Delta S_s^\ddagger)$ will therefore be given by $-\delta\{\Delta S_s^\ominus[\mathrm{Fe(CN)_5}]\} + \delta[\Delta S_s^\ominus(\mathrm{L})]$, where the subscript s refers to solvation, and we confine ourselves to this contribution, with exclusion of electronic effects. If L and L′ are both neutral, $\delta(\Delta S_s^\ddagger)$ should not be substantially different from zero. If L′ is mononegatively charged, the corresponding $[\mathrm{Fe(CN)_5L'}]^{4-}$ will be more strongly solvated than $[\mathrm{Fe(CN)_5L}]^{3-}$, whilst no noticeable differences are expected in the solvation of the released L′⁻ and L, in view of the lack of influence of the charge on the solvation of organic anions.[5,24] Therefore, for negatively charged ligands, there is an increase in both the entropy and the enthalpy of activation. It is interesting that the difference in hydration entropy between $[\mathrm{Fe(CN)_5L}]^{3-}$ and $[\mathrm{Fe(CN)_5L'}]^{4-}$ calculated according to Cobble's rules [25,26] is at least as large (in fact larger) than the differences actually observed in $\Delta S^\ddagger$.

It is also interesting that solvent effects, which could in principle also be detected through changes in $\Delta V^\ddagger$ with pressure, were not apparent in high-pressure measurements;[27] in general, as pointed out by Burgess and co-workers,[7] it is always possible that the different activation parameters may yield different (hopefully complementary) information on the same system.

Some ligands included in the Table have not been plotted in Figure 1, because they were expected to deviate. Thus, *NN*-diethylnicotinamide falls below the neutral ligand line. Steric effects in the reverse reaction are clearly implicit in the difficult synthesis of its solid complex salt $\mathrm{Na_3[Fe(CN)_5L]\cdot 4H_2O}$,[28] and on the basis of the above reasoning this deviation was therefore to be expected. Carboxylate-protonated nicotinic acid is released [5] faster than expected for a neutral ligand; however, k_{-L} in this case was measured at very low pH values (*ca.* 1.1), and cyanide protonation [29] may play an important role under these conditions. The release of 4-cyanopyridine was measured in 0.1 mol dm^{-3} ionic strength medium,[30] and the data are therefore not directly comparable. Pyrazine mono-*N*-oxide exhibits very peculiar behaviour, which has already been observed in the complex it forms with the $[\mathrm{Ru(NH_3)_5}]^{2+}$ moiety.[31,32] The oxidation of the terminal nitrogen, N(A), gives rise to changes that are in many ways comparable to the changes brought about by protonation of pyrazine;[31] this is in agreement with the electronic structure calculations reported for these molecules.[33] In our studies with pyrazine mono-*N*-oxide it appears as if a substantial stabilization of an outer-sphere species with $[\mathrm{Fe(CN)_5(H_2O)}]^{3-}$ is operative.

In Figure 1, the anionic nicotinoylglycinate is shown to behave as a neutral ligand; again, this is exactly the expected behaviour, as previous work [16] has shown that the deceleration brought about by a decrease in the charge decreases steadily as the charged centre in the ligand molecule moves away from the metallic moiety.

In conclusion, it is felt that both inner and solvation effects must be considered in any effort to explain trends in the reactivity of these complexes.

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