Solvation Effects on the Kinetics of Diamine Replacement in Pentacyano(diamine)ferrate(II) Complexes †‡

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The rates of release of ligand L from $[Fe^{II}(CN)_5L]^{n-}$ complexes {L = unidentate terminal diamines $NH_2[CH_2]_nNH_2$ (n = 3—6) unprotonated or monoprotonated} have been measured in aqueous solutions at various pH and temperatures. The kinetic parameters are interpreted on the basis of solvation effects.

LIGAND-SUBSTITUTION processes in $[Fe^{II}(CN)_5L]^{n-}$ have been investigated by several workers [1-4] and the mechanism shown to be dissociative (I_d or D).§ Recently [5] we found that for the release of aliphatic monoamines the process of ligand solvation was operative, as indicated by the random influence of the ligand basicity on the limiting rate. The present work is intended to give further support to this argument and provide additional information about the effect of protonation of one of the donor sites of bifunctional ligands on the kinetics of substitution.[3]

We report the results of a study on the kinetics of release of ligand L from $[Fe^{II}(CN)_5L]^{n-}$ complexes in aqueous solution, where the ligands L are unidentate, unprotonated, or monoprotonated, terminal diamines of general formula $NH_2[CH_2]_nNH_2$ (n = 3—6). Our previous results [3] with ethylenediamine (n = 2) were repeated as an internal check, enabling us to attribute real significance to small changes (the new results do not differ greatly from the previous values).

TABLE 1

pH Dependence of the limiting rate constants k_{-L} for ligand exchange in $[Fe^{II}(CN)_5L]^{n-}$ at 25 °C and I = 1 mol dm^{-3} (NaCl) *

L = pd		L = bd		L = ptd		L = hxd	
pH	$10^3k_{-L}/s^{-1}$	pH	$10^3k_{-L}/s^{-1}$	pH	$10^3k_{-L}/s^{-1}$	pH	$10^3k_{-L}/s^{-1}$
8.00	8.15	8.30	6.78	9.60	6.85	9.25	5.39
9.00	8.39	9.50	6.83	9.80	6.07	9.85	5.39
9.25	8.35	10.45	6.65	10.15	6.19	10.90	4.81
9.40	8.12	10.65	6.71	10.50	6.32	11.20	4.47
9.60	7.60	10.75	6.50	10.65	6.53	11.40	4.69
9.90	7.75	10.90	6.17	10.70	6.25	11.60	4.39
10.00	7.75	11.00	6.32	10.90	6.57	11.70	4.45
10.20	7.29	11.05	6.36	11.20	6.50	11.80	4.58
10.40	7.19	11.30	5.78	11.45	6.00	12.20	4.25
10.50	6.55	11.80	5.33	11.80	5.93	12.70	4.13
10.70	7.20	13.50	4.80	11.90	4.87	13.35	4.24
11.00	6.43					13.40	4.09
11.10	6.40						
11.35	6.17						
11.60	5.81						
11.80	5.73						
12.15	5.53						
12.75	5.15						

* See also Table 2. For L = en see ref. 3.

EXPERIMENTAL

The sodium salts of the complexes $[Fe(CN)_5L]^{2-}$ (L = $[Hen]^+$, $[Hpd]^+$, $[Hbd]^+$, $[Hptd]^+$, or $[Hhxd]^+$,¶ were prepared from $Na_2[Fe(CN)_5(NO)]$ (Merck) by a method previously described.[6] They were characterized by chemical analyses, and i.r. and u.v.–visible spectra.[7] Except for the $[Hen]^+$ complex, the complexes are new.

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† A communication on this and related subjects was presented at the 18th International Conference on Co-ordination Chemistry, Saõ Paulo, Brazil, 18th–23rd July, 1977.

‡ No reprints available.

§ Recent evidence (S. Ašperger, 18th International Conference on Co-ordination Chemistry, Saõ Paulo, Brazil, 18th–23rd July, 1977) confirms our previous postulations (see ref. 3) that the mechanism is more likely to be I_d.

¶ en = Ethylenediamine, pd = propane-1,3-diamine, bd = butane-1,4-diamine, ptd = pentane-1,5-diamine, hxd = hexane-1,6-diamine, and py = pyridine.

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

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[6] J. A. Olabe and P. J. Aymonino, *J. Inorg. Nuclear Chem.*, 1974, **36**, 1221.

[7] N. E. Katz, J. A. Olabe, and P. J. Aymonino, unpublished work.

Propane-1,3-diamine (Aldrich) was used as available. Butane-1,4-diamine was obtained by neutralization of the corresponding dihydrochloride (Fluka). Pentane-1,5-diamine was prepared by a modified Gabriel synthesis.[8] Hexane-1,6-diamine was used as supplied (71% aqueous solution, Ducilo).

The kinetic studies were carried out in a thermostatted 1-cm optical cell of a Spectronic 600 E spectrophotometer. In a typical experiment, to an aqueous solution containing a small amount of the complex (final concentration 2×10^{-4} mol dm^{-3}) and an excess of free ligand (final concentration 5×10^{-3} mol dm^{-3}) was added pyridine in sufficiently high concentration (final value 0.1 mol dm^{-3}) to ensure first-order conditions and to obtain the limiting value $k_{\text{obs.}} = k_{-\text{L}}$ for the loss of ligand.[1-3] The pH was controlled by sodium tetraborate–phosphate or phosphate–sodium hydroxide buffers and measured with a Sargent–Welch model LSX pH meter. Temperatures were maintained to ±0.1 °C. Sodium chloride was used to maintain constant ionic strength at $I = 1$ mol dm^{-3}. The rate constants were measured at pH 8—14 and between 10 and 35 °C. Experiments were monitored at 365 nm ($\lambda_{\text{max.}}$ for the py complex) and in all cases the reaction proceeded to completion as deduced from the experimental A_∞ values. The $k_{-\text{L}}$ values were calculated from plots of log $[(A_\infty - A_t)/(A_\infty - A_0)]$ against t, which were linear up to at least 3 half-lives. Duplicate runs were performed for each experimental condition; the rate constants were found to be reproducible to within 1%. The activation parameters were determined from Eyring plots of $\log(k_{-\text{L}}/T)$ against $(1/T)$ by a least-squares method; an analysis of the variance about regression was used to obtain the confidence limits with 90% probability.[9]

TABLE 2

Temperature dependence of the saturation rate constants $k_{-\text{L}}$ for the monoprotonated and unprotonated forms of L at $I = 1$ mol dm^{-3} (NaCl)

L = en *			L = pd			L = bd		
pH	θ_c/°C	$10^3k_{-\text{L}}$/s^{-1}	pH	θ_c/°C	$10^3k_{-\text{L}}$/s^{-1}	pH	θ_c/°C	$10^3k_{-\text{L}}$/s^{-1}
7.9	14.5	2.09	8.45	11.9	1.13	8.0	20.3	3.49
7.9	20.0	4.94	8.45	15.0	1.99	8.0	25.0	6.97
7.9	25.0	9.87	8.45	20.0	4.04	8.0	29.3	13.5
7.9	29.0	18.1	8.45	25.0	8.17	8.0	33.8	23.7
7.9	33.8	31.1	8.45	29.3	14.1	13.0	20.3	2.23
13.8	14.5	1.17	12.4	15.3	1.23	13.0	25.0	4.38
13.8	20.0	2.52	12.4	21.5	2.90	13.0	29.3	8.85
13.8	25.0	5.21	12.4	22.0	2.96	13.0	33.8	14.6
13.8	29.0	9.29	12.4	25.0	5.07			
13.8	33.8	17.8	12.4	29.1	8.59			
			12.4	33.6	16.9			
L = ptd			L = hxd					
10.0	15.4	1.67	9.0	16.9	2.03			
10.0	20.5	3.71	9.0	20.9	3.71			
10.0	25.0	6.77	9.0	25.0	6.39			
10.0	29.1	11.8	9.0	29.3	11.5			
10.0	33.3	21.5	9.0	34.3	21.0			
14.0	15.4	1.18	14.0	16.9	1.33			
14.0	20.5	2.39	14.0	20.9	2.36			
14.0	25.0	4.57	14.0	25.0	4.13			
14.0	29.1	8.61	14.0	29.3	7.83			
14.0	33.3	15.5	14.0	34.3	14.8			

* Data are improved values with respect to ref. 3.

RESULTS

Tables 1 and 2 present the results obtained for the limiting rate constants $k_{-\text{L}}$ at different pH and temperature. At 25 °C there are two limiting values when pH is varied; the higher one at lower pH evidently corresponds to the release of the monoprotonated diamine and the value at high pH corresponding to the release of the unprotonated diamine. As shown in Table 3, $k_{-\text{HL}}$ decreased regularly from [Hen]$^+$ to [Hhxd]$^+$ and the difference between the rate constants $k_{-\text{HL}}$ and $k_{-\text{L}}$ becomes progressively smaller as the chain length of the diamine increases. In all cases, the inflection point nearly coincides with the first pK_a of the corresponding conjugate acid of the diamine.[10]

This behaviour can be explained by equations (1)—(4): [3]

$$[\text{Fe(CN)}_5(\text{HL})]^{2-} \xrightleftharpoons{k_{-\text{HL}}} [\text{Fe(CN)}_5]^{3-} + [\text{HL}]^+ \quad (1)$$

$$[\text{Fe(CN)}_5(\text{HL})]^{2-} \xrightleftharpoons{K_a} [\text{Fe(CN)}_5\text{L}]^{3-} + \text{H}^+ \quad (2)$$

$$[\text{Fe(CN)}_5\text{L}]^{3-} \xrightleftharpoons{k_{-\text{L}}} [\text{Fe(CN)}_5]^{3-} + \text{L} \quad (3)$$

$$[\text{Fe(CN)}_5]^{3-} + \text{py} \xrightleftharpoons{k_{\text{py}}} [\text{Fe(CN)}_5(\text{py})]^{3-} \quad (4)$$

$$k_{\text{obs.}} = (k_{-\text{HL}}[\text{H}^+] + k_{-\text{L}}K_a)/([\text{H}^+] + K_a) \quad (5)$$

The experimental data fit equation (5) which can easily be deduced from reactions (1)—(3) when [py] is large. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were derived from the temperature dependence of $k_{-\text{HL}}$ and $k_{-\text{L}}$ (Table 4).

DISCUSSION

The low sensitivity of the rate constants to the basicity of the ligands is shown by the small gradient of a plot of log $k_{-\text{HL}}$ against second pK_a (= 0.10 ± 0.03), in agreement with the behaviour of aliphatic monoamines [5] and

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[8] H. Raymond and H. Manske, *J. Chem. Soc.*, 1926, **128**, 2348.

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[10] 'The Chemistry of the Amino Group,' ed. S. Patai, Interscience, London, 1968, p. 177.

the 'soft' or 'b' character of this particular metal centre.[4,11] Thus, changing K_a by a factor of 10^3 merely doubles the rate constant. This lack of sensitivity to ligand basicity seems to be a general phenomenon in the aqueous chemistry of $[Fe^{II}(CN)_5L]^{n-}$ ions.[5,12] The fact that the rate constants for the reverse reaction (*i.e.* formation) are also relatively independent of the ligand donor properties causes the stability constants for the complexes of substituted amines to be rather insensitive to the nature of substituent groups;[1] with the present ligands the constancy of the pK_a of the ligand on co-ordination also emphasizes[3] the similarity of the stability constants of $[Fe(CN)_5(HL)]^{2-}$ and $[Fe(CN)_5L]^{3-}$. In this respect, aqueous $[Fe(CN)_5]^{3-}$ behaves rather peculiarly, since protonated and unprotonated ligands generally show very different affinities towards other metallic moieties.[13] Thus, solvation effects are evident.

TABLE 3

Comparison of the limiting rate constants for the release of monoprotonated and unprotonated forms of diamines from $[Fe^{II}(CN)_5L]^{n-}$ at 25 °C and I = 1 mol dm^{-3} (NaCl)

Ligand	$10^3k_{-HL}/s^{-1}$	$10^3k_{-L}/s^{-1}$	$k_{-HL} : k_{-L}$
en	10.4	5.6	1.9
pd	8.3	5.4	1.5
bd	6.9	4.6	1.5
ptd	6.4	4.5	1.4
hxd	5.3	4.1	1.3

TABLE 4

Activation parameters for ligand substitution in $[Fe^{II}(CN)_5L]^{n-}$

	Monoprotonated diamine		Unprotonated diamine	
Ligand	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}	$\Delta H^‡$/ kJ mol^{-1}	$\Delta S^‡$/ J K^{-1} mol^{-1}
en	101 ± 5	54 ± 17	102 ± 4	50 ± 13
pd	101 ± 6	54 ± 21	103 ± 6	59 ± 21
bd	105 ± 8	63 ± 25	103 ± 15	59 ± 50
ptd	102 ± 3	54 ± 13	104 ± 5	59 ± 17
hxd	97 ± 3	38 ± 8	101 ± 3	46 ± 13

Table 3 shows clearly that in all cases $k_{-HL} > k_{-L}$, a result which is also obtained for other ligands[12] and which can be related to differences in the activation free energies of processes (1) and (3), due to the different solvation of the anions $[Fe(CN)_5(HL)]^{2-}$ and $[Fe(CN)_5L]^{3-}$, the former being destabilized in water with respect to the latter. In going to the activated complex, less desolvation of the 2− ion must be reflected in a higher rate of substitution. The operation of such a solvation effect is frequently observed in the form of rather large and almost cancelling changes in $\Delta H^‡$ and $\Delta S^‡$.[12] In the present case, however, the activation parameters do not yield much information, since they are all similar, *viz.*: $\Delta H^‡$ = *ca.* 100 kJ mol^{-1} and $\Delta S^‡$ = *ca.* 55 J K^{-1} mol^{-1} (see Table 4). There seems to be a trend in the right direction (except for bd) but the changes are in any case very small. Higher $\Delta G^‡$ values seem to be associated with higher $\Delta H^‡$ and $\Delta S^‡$ values, as expected from previous work.[12]

On the other hand, in making vertical comparisons in Table 4, we can try to demonstrate the influence of solvation of the outgoing ligand on the rate of substitution. The free energy of solvation for the substituted ammonium ions increases by a nearly constant amount for each CH_2 group, while the free energy of solvation for the free amines increases only slightly (due to an almost exact balancing of entropy and energy effects).[14] We observed a similar trend in the rate constants (and consequently in $\Delta G^‡$) for the release of the monoprotonated and unprotonated diamines. Table 3 shows that the rate of release of the monoprotonated ligands decreases regularly with increasing chain length, while the unprotonated ligands are released at nearly the same rate and the numerical value is very close to that of monoamines.[5]

For the longest protonated diamines, since the charged end of the co-ordinated diamine already 'dips' into the bulk solvent, only the solvation of the co-ordinated end which is released upon activation will contribute to the energetics of the process and the $\Delta G^‡$ value which results is again similar to that of monoamines. Also, since the positive charge on the terminal N is more separated from the $[Fe(CN)_5]^{3-}$ moiety, smaller solvation differences are expected between the complexes $[Fe(CN)_5(HL)]^{2-}$ and $[Fe(CN)_5L]^{3-}$. This fact explains the decrease in the $k_{-HL} : k_{-L}$ ratio as the chain length increases.

The importance of the contribution of the solvent medium to $\Delta G^‡$ for ligand-substitution processes has already been established by Caldin and Bennetto[15] in their work on exchange reactions of bivalent transition-metal cations in various solvents. Recently[16] the kinetics of substitution of pentacyano(ligand)ferrate(II) complexes was investigated in mixed aqueous solvents, and the importance of the $[Fe(CN)_5]^{3-}$ moiety was assessed. Thus, the ratio of substitution rates in water and in 40% aqueous t-butyl alcohol was found to be very similar for leaving groups having great differences in solvation. Consequently, the solvation of the remaining $[Fe(CN)_5]^{3-}$ moiety, rather than that of the departing ligand, determined the difference in rates when the solvent was varied. In the present work the solvent is fixed and the structure of the ligands is varied in a systematic way. Since the solvation of the $[Fe(CN)_5]^{3-}$ moiety is expected to be the same for all our complexes (if the cationic environment is maintained constant) other effects are shown to be operative; namely, the solvation

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of the leaving ligand and/or the solvation of the initial complex (*i.e.* the charge type of the reactant ion). We can therefore conclude that solvation effects in these reactions can be observed even in water due to the constancy of all the other relevant parameters.

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