Effect of Solvent Structure on the Kinetics of Ligand Substitution in Pentacyano(*N,N*-dimethylethylenediamine)ferrate(II)

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The rate constants and activation parameters for the dissociation of *N,N*-dimethylethylenediamine from its complex with the pentacyanoferrate(II) moiety have been determined in aqueous methanol mixtures from a methanol mole fraction $x_2 = 0$ to 0.114. There is a negative correlation between the logarithm of the rate constant and Grunwald–Winstein *Y* values. Changes in the excess Gibbs free energy of mixing are reflected in the Gibbs free energy of activation, indicating a transition state more hydrophobic than the initial state. The increase in enthalpy and entropy of activation with increasing mole fraction of methanol is interpreted by considering the greater requirements for exchanging a ligand for a water molecule in a more structured solvent, thus pointing to an I_d mechanism. Entropy variations seem to control the free-energy changes as in the case of the excess thermodynamic parameters of mixing.

THE role of the solvent in the kinetics of ligand-substitution processes has been studied by several authors.[1-4] Caldin and Bennetto [1] showed how far the structural changes in bulk solvent are reflected in the variation of rate constants with solvent composition for some metal + ligand recombinations. More recently, Burgess and co-workers [2] found a quite general correlation between thermodynamic data for a variety of solvent mixtures and kinetic parameters for the aquation of tris(5-nitro-1,10-phenanthroline)iron(II). A similar result was obtained for the reactions of pentacyano(3,5-dimethylpyridine)ferrate(II) and related anions with a range of groups in mixed aqueous solvents.[5]

We are currently interested in the operation of solvation [6] and salt [7] effects on the kinetics of ligand replacements in pentacyano(ligand)ferrate(II) complexes. In this paper we report the results of a study on the kinetics of aquation of pentacyano(*N,N*-dimethylethylenediamine)ferrate(II), $[Fe(CN)_5(dmen)]^{3-}$, in aqueous methanol mixtures. An aliphatic ligand was chosen so that solute–solvent interactions would not be swamped out by π-bonding effects, while a ' typically aqueous ' (t.a.) mixture was included to allow comparisons with previous results for similar systems.[5]

EXPERIMENTAL

Sodium pentacyano[2-aminoethyl(dimethyl)ammonium]-ferrate(II), $Na_2[Fe(CN)_5(Hdmen)]\cdot 2H_2O$ (1), was prepared by dissolving $Na_3[Fe(CN)_5(NH_3)]\cdot 3H_2O$ (obtained as in ref. 8; 1 g) in the minimum amount of water. Immediately after dissolution, a 100-fold excess of *N,N*-dimethylethylenediamine (Fluka) was added at 0 °C. After standing for 30 min in the dark, precipitation was accomplished by adding cold ethanol (200 cm³) saturated with NaI. The solid was collected in a sintered-glass filter, washed with ethanol and diethyl ether, and stored in a desiccator over KOH.

Complex (1) was characterized by its visible spectrum (in solution in excess of dmen to prevent aquation), $\lambda_{max.} = 395$ nm and $\varepsilon_{max.} = 500$ dm³ mol⁻¹ cm⁻¹, which compared well with data for the Hen^+ complex (en = ethylenediamine) ($\lambda_{max.} = 402$ nm and $\varepsilon_{max.} = 365$ dm³ mol⁻¹ cm⁻¹).[9] Its water content was checked by adding excess of pyridine (py) and comparing the final absorbance value with that expected for complete formation of the $[Fe(CN)_5(py)]^{3-}$ complex.[10]

The i.r. spectrum of (1) was obtained using a KBr disc and recorded on a Perkin-Elmer 457 spectrophotometer in the 4 000—250 cm⁻¹ range. It showed characteristic bands (*cf.* refs. 9 and 11) at 2 825 and 2 440 [vibrations of $\overset{+}{N}H(CH_3)_2$], 2 030 [ν(C≡N)], 1 360 (CH_2 wag), 1 260 (NH_2 wag), 1 030 [ν(C–N)], and 575 cm⁻¹ [δ(Fe–C)].

The kinetics of reaction (1) were followed under pseudo-first-order conditions and at a pH high enough to ensure deprotonation of the diamine.

$$[Fe(CN)_5(dmen)]^{3-} + py \longrightarrow [Fe(CN)_5(py)]^{3-} + dmen \quad (1)$$

The increase in absorbance at 365 nm {maximum for the $[Fe(CN)_5(py)]^{3-}$ complex} [10] was monitored by using a Metrolab RC325 visible spectrophotometer provided with thermostatted cells. Concentrations in the cell at time $t = 0$ were [complex] = 2×10^{-4}, [dmen] = 5×10^{-3}, and [py] = 0.1 mol dm⁻³. The ionic strength *I* was fixed at 1 mol dm⁻³ with NaCl. The pH was *ca.* 12 (Na_2HPO_4–NaOH buffer) and methanol (Merck *pro analysi*) was added at mole fractions 0, 0.010, 0.053, and 0.114. We could not pursue this study to higher mole fractions of methanol because of the low solubility of NaCl. Deionized water was used throughout. The temperature was maintained to within ±0.3 °C. Duplicate or triplicate runs were made at each mole fraction and temperature. The rate constants were determined to within ±3% by plotting $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ against *t*. The plots were linear up to three half-lives and a least-squares method was used to evaluate the slopes. The reaction proceeded to completion at all mole fractions. The enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation were calculated by a least-squares method, using Eyring's equation. Errors in $\Delta H^\ddagger$ and in $\Delta S^\ddagger$ were estimated to be ±2 kJ mol⁻¹ and ±8 J K⁻¹ mol⁻¹ respectively (*cf.* ref. 12).

RESULTS

The Table shows the limiting rate constants obtained at different mole fractions and temperatures. For a dissociative mechanism, $k_{obs.}$ for reaction (1) equals k_{-L}, the rate constant for the release of dmen.[6a] The present complex behaves kinetically in a similar way to that displayed by other diamines of general formula $NH_2(CH_2)_nNH_2$ (n = 2—

Rate constants k_{-L} at different temperatures T and mole fractions of methanol x_2 for the release of N,N-dimethylethylenediamine from its complex with pentacyanoferrate(II) at pH = 12 and I = 1 mol dm^{-3}

$x_2 = 0$		$x_2 = 0.010$		$x_2 = 0.053$		$x_2 = 0.114$	
T/K	10^3k_{-L}/s^{-1}	T/K	10^3k_{-L}/s^{-1}	T/K	10^3k_{-L}/s^{-1}	T/K	10^3k_{-L}/s^{-1}
289.3	1.47	289.0	1.17	289.1	1.35	289.1	1.51
293.7	2.8	294.2	2.6	293.9	2.9	293.2	3.3
298.2	4.4	298.2	4.7	298.2	5.3	298.2	6.4
304.2	10.9	303.6	9.9	303.8	11.5	303.2	12.5

6, see ref. 6*b*): experiments performed at pH 6 in pure water showed that the rate constant for the release of protonated diamine, k_{-HL}, is almost double that for the release of unprotonated diamine, k_{-L}. The rate constants in the Table correspond to values of k_{-L}.

The variation of k_x/k_0 with x_2 at 298.2 K is shown in Figure 1, where k_x is the rate constant k_{-L} at a mole fraction x_2 of methanol and k_0 is the rate constant k_{-L} at $x_2 = 0$.

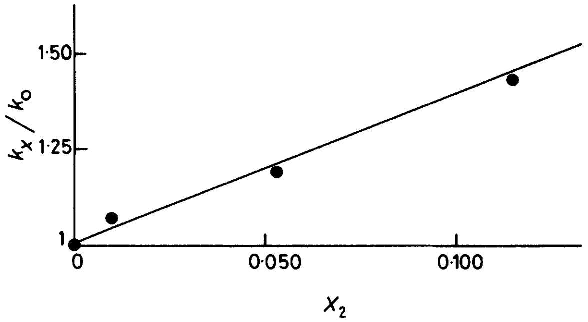

FIGURE 1 Ratio of limiting rate constants for dmen substitution at $[Fe(CN)_5(dmen)]^{3-}$ in water + methanol mixtures (k_x) and in pure water (k_0) plotted against mole fraction of methanol x_2 at 298.2 K

Figure 2 shows the correlation of log k_x with Grunwald–Winstein Y values (obtained from ref. 13). From the slope of the line a value of $m = -0.3$ is obtained.

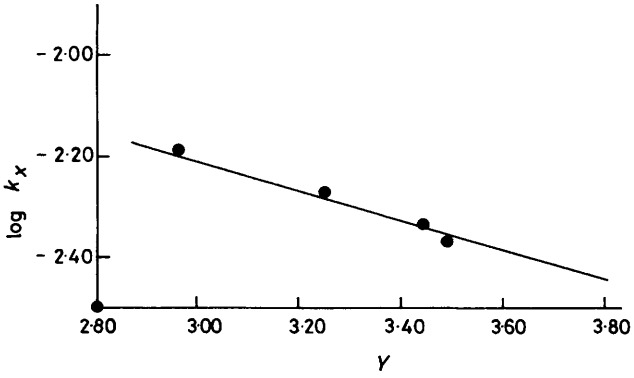

FIGURE 2 Dependence of the logarithm of the limiting rate constant for dmen substitution at $[Fe(CN)_5(dmen)]^{3-}$ in water + methanol mixtures on Grunwald–Winstein Y values at 298.2 K

A correlation between $\delta_m\Delta G^‡$ and G^E at 298.2 K is shown in Figure 3; $\delta_m\Delta G^‡$ is defined as $\Delta G^‡(x_2) - \Delta G^‡(x_2 = 0)$, *i.e.* the difference between the Gibbs free energy of activation (obtained from the corresponding rate constant) at mole fraction x_2 of methanol and that in pure water, while G^E is the excess Gibbs free energy of mixing (obtained for each value of x_2 by interpolation of data reported in ref. 2).

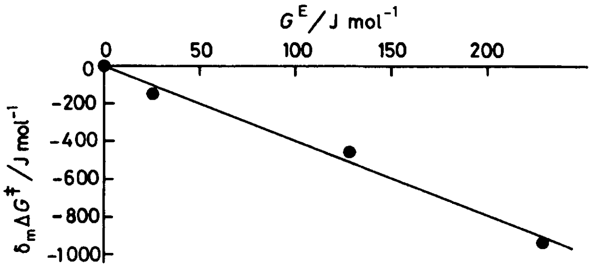

FIGURE 3 Relation between the difference in activation free energies ($\delta_m\Delta G^‡$) and excess free energies of mixing (G^E)

The variations of $T\Delta S^‡$, $\Delta H^‡$, and $\Delta G^‡$ (at 298.2 K) with increasing x_2 are displayed in Figure 4 [curves (*a*), (*b*), and (*c*) respectively].

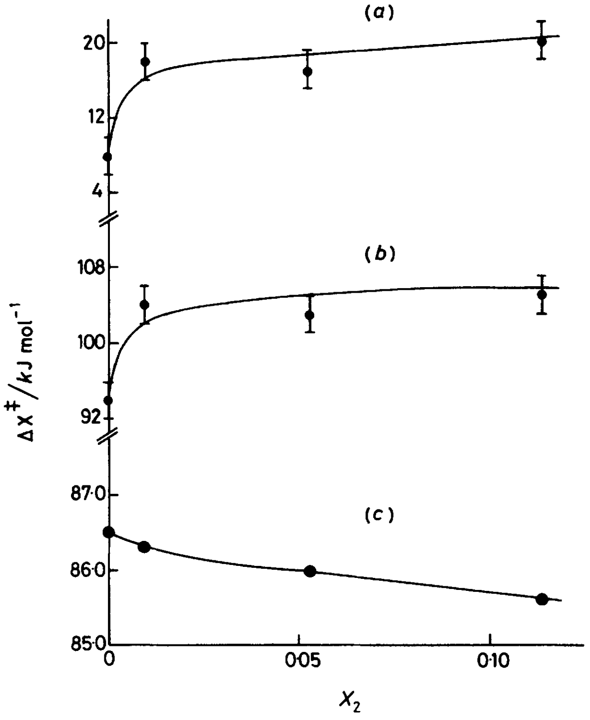

FIGURE 4 Variation of entropy of activation $T\Delta S^‡$ (*a*); enthalpy of activation $\Delta H^‡$ (*b*); and free energy of activation $\Delta G^‡$ at 298.2 K (*c*) with mole fraction of methanol for the release of dmen from $[Fe(CN)_5(dmen)]^{3-}$

DISCUSSION

The dissociative mechanism (D or I_d) for ligand substitutions at pentacyano(ligand)ferrate(II) complexes has been demonstrated by several workers.[14] The ratio obtained for k_{-HL}/k_{-L} (= 2.0) for the present reaction compares well with that for the en complex (= 1.9)[14c] and confirms that differences in solvation of the $[Fe(CN)_5(HL)]^{2-}$ and $[Fe(CN)_5L]^{3-}$ complexes seem to control the kinetics of substitution of diamines in pentacyano(diamine)ferrate(II) anions.[6b] When the chain length of the diamine increases and its free end ' dips ' more into bulk solvent the solvation differences are lessened and the ratio k_{-HL}/k_{-L} decreases. Replacing two hydrogens attached to the free N of en by methyl groups seems to be of no kinetic relevance in view of the similar ratios obtained for the en and the dmen complexes.

The limiting rate constant at 298.2 K for reaction (1) corresponding to the departure of neutral *N,N*-dimethylethylenediamine increases on addition of methanol (see Figure 1). This reaction is more sensitive to solvent variation than the reaction of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ (3,5-Me_2py = 3,5-dimethylpyridine) with cyanide.[5] Indeed, the ratio of the rate constant at $x_2 = 0.100$ and that at $x_2 = 0.050$ is 1.21 : 1 for the former reaction and 1.07 : 1 for the latter. It is possible that π-bonding effects may swamp out solvation effects (*cf.* ref. 6*a*) so that a higher sensitivity to solvent modifications is found for the dissociation of aliphatic ligands from the $[Fe(CN)_5]^{3-}$ moiety. However, this aliphatic–aromatic difference is rather small. What is more interesting, these systems are much less sensitive to solvent nature than in the case of solvolysis of t-butyl chloride.[5]

There is a negative correlation between log k_x and Grunwald–Winstein empirical *Y* values,[13] as observed in Figure 2. The value of $m = -0.3$ obtained from the slope can be associated with a separation of a negatively charged group containing several hydrophilic groups, such as CN^-, as already observed for the release of 3,5-Me_2py from the $[Fe(CN)_5]^{3-}$ group.[5] Indeed, negative *m* values have been found for reactions where small inorganic ions are transferred from water to mixed solvents, such as in the mercury(II)-catalyzed aquation of $[Co(NH_3)_5Cl]^{2+}$. (For further discussion, see ref. 15.) On the other hand, the negative correlation existing between $\delta_m\Delta G^\ddagger$ and G^E (see Figure 3) indicates a transition state more hydrophobic than the initial state,[2,5] which may be due to the greater exposure of the hydrophobic methylene groups of dmen to bulk solvent when the Fe–N bond is stretched on activation.

A thermodynamic cycle such as proposed by Wells[4] for the anation of cations in mixed aqueous solvents leads to equation (2) for the present reaction if we

$$\Delta G_x^\ddagger = \Delta G_0^\ddagger - \Delta G_t^\ominus\{[Fe(CN)_5(dmen)]^{3-}\} + \Delta G_t^\ominus\{[Fe(CN)_5]^{3-}\} + \Delta G_t^\ominus(dmen) \quad (2)$$

consider almost complete dissociation of the leaving ligand in the transition state, where $\Delta G_x^\ddagger$ and $\Delta G_0^\ddagger$ are the activation free energies in the solvent mixture and in pure water respectively, while $\Delta G_t^\ominus$ (X) refers to the free energy of transfer of species X between pure water and the mixture. If we consider that solvation of the initial complex is determined by the hydrophilic nature of the five cyanide groups (the sixth group is not so exposed to solvent as it is in the transition state), then the values of $\Delta G_t^\ominus\{[Fe(CN)_5(dmen)]^{3-}\}$ and $\Delta G_t^\ominus\{[Fe(CN)_5]^{3-}\}$ will nearly compensate each other in equation (2) and the value of $\Delta G_t^\ominus$(dmen) will control $\log(k_x/k_0)$, *i.e.* the difference $\Delta G_0^\ddagger - \Delta G_x^\ddagger$. As the departing ligand is more soluble in methanol [$\Delta G_t^\ominus(\text{dmen}) < 0$] there is a marked stabilization of the transition state with increasing mole fraction of methanol, and so the rate constant increases [$\log(k_x/k_0) > 0$]. That ligand solvation in the transition state affects the free energy of activation agrees with previous results obtained for the dissociation of various ligands from the $[Fe(CN)_5]^{3-}$ group in pure water.[6a] Also, it is to be noted that if Wells' assumptions are valid [and given the correct sign and magnitude for $\Delta G_t^\ominus$ (X)] then transition-state solvation seems to dominate over initial-state solvation for S_N1 type aquation reactions of anionic complexes.[16]

Figure 4 shows that $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ for the present reaction tend to increase with increasing mole fraction of methanol. As pointed out before,[17] these parameters must include terms for the variations of solvent structure with temperature. Nonetheless, they can be neglected by assuming that they are also included for aquation in pure water and must be very similar to those terms corresponding to aquation in water-rich mixtures. The trend in $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ is significant and demonstrates how variations in water structure with increasing x_2 are reflected in the activation parameters. Addition of methanol to water from $x_2 = 0$ to 0.3 enhances water structure, *i.e.* produces a ' structure-making ' effect.[18] The greater $\Delta H^\ddagger$ obtained for the present ligand dissociation when x_2 increases can be attributed to the greater expenditure of energy necessary for transfer of a ligand molecule from the inner co-ordination sphere of the complex to a more structured solvent and its replacement by a water molecule. The increased basicity of water in methanol + water mixtures[18,19] (which makes water more readily available for ligand substitution) would promote an I_d mechanism. Evidence in support of this has recently been obtained[20] from the kinetics of replacements in pentacyano(ligand)ferrate(II) ions. A concomitant increase in $T\Delta S^\ddagger$ can be associated with a greater freedom corresponding to the ligand replacement as the ordering of the bulk solvent increases. The observed typical compensation in $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ (see ref. 1) gives a less varying $\Delta G^\ddagger$ (see Figure 4). Moreover, the variations in $T\Delta S^\ddagger$ determine the variations in $\Delta G^\ddagger$, just as the value of TS^E (excess entropy of mixing) determines the value of G^E (excess Gibbs free energy of mixing).[19] For the reaction of pentacyano(piperidine)ferrate(II) with pyridine in acetonitrile + water mixtures, trends in H^E are reflected in $\Delta H^\ddagger$.[21]

To summarize, we can say that for a dissociative interchange mechanism such as is found for diamine dissociation from the pentacyano(*N,N*-dimethylethylenediamine)ferrate(II) complex, the transition state is larger than the initial state and so enhanced interaction between the leaving ligand and the bulk solvent will stabilize the transition state in aqueous methanol mixtures, thus making the reaction more rapid in such mixtures than in pure water. Correlations between kinetic parameters and excess thermodynamic data for the solvent mixtures lead to the conclusion that structural changes in solvent water introduced by an organic co-solvent determine the kinetics of ligand replacement.

We thank UNT and CONICET for financial support, Cátedra de Química Inorgánica, F.C.E., U.N.L.P., for the i.r. spectra, and Lic. J. C. Rodríguez for help in computation programs.

[1/1826 *Received, 23rd November*, 1981]

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