Notes

Salt Effects on the Kinetics of Substitution of the Pentacyano(pyrrolidine)ferrate(II) Ion

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Rate constants at 298.2 K for the release of pyrrolidine from pentacyano(pyrrolidine)ferrate(II) have been measured under pseudo-first-order conditions and the effect of inert inorganic and alkylammonium salts on the kinetics were investigated. The observed order can be explained considering solute–solvent interactions which turn out to be operative in dissociative processes.

RECENT kinetic studies on the substitution of ligands in complexes of pentacyanoferrate(II) have verified a mechanism of dissociative activation.[1-5] The influence of solvation in these processes has been assessed for complexes of the pentacyanoferrate(II) ion with aliphatic mono- and di-amines.[3,4]

Blandamer *et al.*[6] have analysed the salt effects on the kinetics of aquation of tri(5-nitro-1,10-phenanthroline)iron(II) in terms of the variations in ' water structure ' when the ionic strength is modified.

In this work we report the results of a study of the effects of inert salts on the kinetics of substitution of pyrrolidine by pyridine in the ion pentacyano(pyrrolidine)ferrate(II). This reaction has not been previously investigated. In order to examine the effect of added salts on the rate constant, three inorganic salts and three alkylammonium salts were chosen.

We discuss the influence of the medium on this reaction by considering the possible interactions between the reactant and the activated complex with some aqueous salt solutions.

EXPERIMENTAL

The pentacyano(pyrrolidine)ferrate(II) ion was prepared by adding an excess of pyrrolidine to a freshly prepared aqueous solution of amminepentacyanoferrate(II) obtained as in ref. 7.

The visible spectrum of the complex at 25 °C was determined at [complex] = 0.1 mol dm^{-3} with a Spekol ZV EK5 spectrophotometer. The data for $\lambda_{max.}$ and $\varepsilon_{max.}$ (385 nm and 580 dm^3 mol^{-1} cm^{-1} respectively) confirmed the formation of the complex $[(NC)_5Fe{-}NH(CH_2)_4]^{3-}$ in view of the similarity with $\lambda_{max.}$ and $\varepsilon_{max.}$ for $[(NC)_5Fe{-}NH_3]^{3-}$ (398 nm and 450 dm^3 mol^{-1} cm^{-1} respectively).

A typical kinetic experiment was carried out as follows: to an aqueous solution of pentacyano(pyrrolidine)ferrate(II), pyridine (Baker) was added so that the final concentrations in the cell were 1 mol dm^{-3} in pyridine, 2×10^{-4} mol dm^{-3} in pentacyano(pyrrolidine)ferrate(II), and 3.3×10^{-2} mol dm^{-3} in pyrrolidine (Fluka). The increase of absorbance with time was measured at $\lambda = 365$ nm [maximum of pentacyano(pyridine)ferrate(II)].[1] The pH of the solution was *ca.* 11 and did not change during the reaction. The temperature was held at 25 ± 0.1 °C throughout.

To examine the salt effects, aqueous solutions of KCl, KBr, KI (Merck) and $[NMe_4]Br$, $[NEt_4]Br$, and $[NBu_4]Br$ (Fluka) were added to the pyridine solution so that the final concentrations in the cell were 0.5, 1.0, and 2.0 mol dm^{-3} (see above), except for $[NBu_4]Br$, for which the maximum concentration was 1.5 mol dm^{-3} because of low solubility. In all cases, doubly distilled water was used.

RESULTS

For the reaction under study [equation (1)] the observed

$$[Fe(CN)_5(pyrrolidine)]^{3-} \xrightarrow{k_{-1}} [Fe(CN)_5]^{3-} + pyrrolidine \quad (1)$$

rate constant $k = k_{-1}$ for high concentrations of pyridine, where k_{-1} is the rate of release of pyrrolidine.[1-5] The experimental results confirm a pseudo-first-order reaction. Guggenheim's method [8] was applied to find in each case an average value of k for at least three determinations.

In the Table values of the rate constant k at each salt concentration c are shown. The estimated error in k is 5%.

It is to be noted that the value of k_0 is in good agreement with the values observed for the release of aliphatic monoamines.[3]

The Figure shows the dependence of log (k/k_0) on concentration of added salts.

DISCUSSION

According to the Brønsted–Bjerrum theory for a reaction of an ion with a neutral molecule, the relation between the rate constants with and without added salts is that shown in (2) where γ_i and γ_t are the activity

$$k/k_0 = \gamma_i/\gamma_t \quad (2)$$

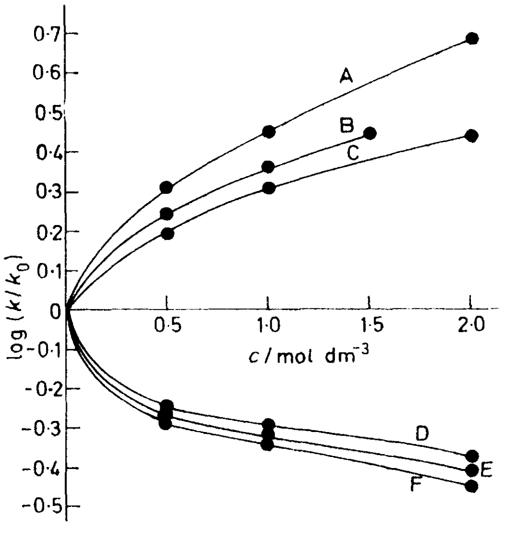
coefficients of the initial complex and the transition state respectively. A modified Debye–Hückel equation [6] predicts that the rate constant k will be lower than k_0 if $a_t > a_i$ (where a_t and a_i are the minimum distances of closest ionic approach for the transition and the initial state respectively). The reverse is also true.

Rate constants at 298.2 K for substitution of pyrrolidine by pyridine in pentacyano(pyrrolidine)ferrate(II)

Salt	c/mol dm^{-3}	10^3k/s^{-1}
None	0	3.72 (k_0)
KI	0.5	1.91
	1.0	1.72
	2.0	1.27
KBr	0.5	2.01
	1.0	1.83
	2.0	1.48
KCl	0.5	2.10
	1.0	1.88
	2.0	1.58
[NMe$_4$]Br	0.5	5.85
	1.0	7.61
	2.0	10.22
[NBu$_4$]Br	0.5	6.55
	1.0	8.52
	1.5	10.30
[NEt$_4$]Br	0.5	7.45
	1.0	10.44
	2.0	18.02

As shown in the Figure, the rate constant increases with alkylammonium salt concentration and decreases with added potassium halide.

When analysing the effects of the alkylammonium salts we suggest, in analogy to Blandamer *et al.*,[6] that the pyrrolidine which dissociates from the pentacyanoferrate(II) moiety is accommodated in the cavities that exist in aqueous solutions of alkylammonium salts. These voids are due to a reinforcement of the water structure.[9] The volume is thus diminished on approaching the transition state; that is, $a_t < a_i$ and so, the rate constant increases, in agreement with experiment.



Variation of log (k/k_0) with salt concentration c. Added salts are: [NEt$_4$]Br (A); [NBu$_4$]Br (B); [NMe$_4$]Br (C); KCl (D); KBr (E); and KI (F)

The trend in k for the alkylammonium salts differs from that observed in the aquation of tri(5-nitro-1,10-phenanthroline)iron(II), probably because of a high degree of association between the anionic complex considered here and the alkylammonium cation. However, the observed order: $k_{NEt_4} > k_{NBu_4} > k_{NMe_4} > k_{K^+}$ follows that observed in the reaction of depolymerization of diacetone.[10]

On the other hand, it has been suggested [10] that the variation of k with salt concentration is given by equation (3) where $B_{i,c}$ = coefficient of interaction between

$$\log(k/k_0) = (B_{i,c} - B_{t,c})c \qquad (3)$$

the initial complex and inert salt and $B_{t,c}$ = coefficient of interaction between activated complex and inert salt. In the so called α sequence, $B_{i,c}$ becomes more positive when cation size increases (considering only one type of anion); in this case, for a dissociative activation, k must follow the sequence of $B_{i,c}$ because the activated complex has a more dispersed negative charge and so the $B_{t,c}$ coefficients must have a less pronounced α sequence. In fact, the observed values of k increase with cation size.

The effect of inorganic salts, contrary to that of the alkylammonium salts, can be explained by considering that the inorganic ions, being ' structure breakers ',[11] produce a greater stabilization of the initial state with respect to the transition state and so, the rate constant k decreases in relation to k_0 (*cf.* ref. 6).

If we take into account the influence of the anions, the observed sequence is: $k_{Cl^-} > k_{Br^-} > k_{I^-}$. The changes are small but significant. The halide anions are ' structure breakers ' in the order $I^- > Br^- > Cl^-$, according to the size of the anion. We propose than when an anion with a more intense effect of ' structure breaking ' is added to solvent water, the number of cavities diminishes, the volume of the transition state becomes greater than that of the initial state, and so k decreases in the observed order.

Our results are in good agreement with those observed in the kinetics of dissociation of the tris(2,2'-bipyridine)-iron(II) complex.[12]

We conclude that the dissociation of pyrrolidine from the pentacyanoferrate(II) moiety is favoured by the greater ' structuring ' of water in the sequence KI < KBr < KCl < [NMe$_4$]Br < [NBu$_4$]Br < [NEt$_4$]Br. On approaching the transition state, the re-ordering of solvent water will be less demanding when there is more ' structure ' (*i.e.* when there are more voids which allow accommodation of the the releasing ligand) and consequently the $\Delta G^\ddagger$ values decrease in the above order.

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