Kinetics and Mechanism of Replacements in Pentacyano(ligand)ferrate(II) Ions. An Attempt to Distinguish between the D and I_d Mechanisms †

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The kinetics of replacements of 3-cyanopyridine (3CN-py) by pyridine (py) in $[\mathrm{Fe(CN)_5(3CN\text{-}py)}]^{3-}$ at 25 °C, and of nitrosobenzene by $[\mathrm{CN}]^-$ in $[\mathrm{Fe(CN)_5(ONPh)}]^{3-}$ at 50 °C, have been studied in solutions containing various water concentrations achieved by the addition of sorbitol, glucose, sucrose, glycerol, and ethylene glycol. The observed rate constants pertain to a $\geqslant$200-fold excess of the entering ligand, and a 10-fold excess of the leaving ligand, over the concentration of the starting complexes (5×10^{-5} mol dm^{-3}). Under the reaction conditions used, sorbitol, glucose, sucrose, and even glycerol do not enter the complexes to any significant degree, but, it seems, ethylene glycol does. A large and analogous reduction in rate with decreasing water concentration occurs in both replacement reactions, which suggests that this is a general effect. The results are interpreted in terms of an I_d mechanism *via* a $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ reaction intermediate in aqueous solutions.

THE mechanism of ligand replacements in pentacyano(ligand)ferrate(II) ion has been extensively studied,[1] but as already pointed out [2,3] the D (dissociative) and I_d (dissociative interchange) mechanisms [4] can equally well explain the main kinetic observations. These can be summarized as follows: limiting reactions rates, at sufficiently large concentrations of entering ligand Y, were observed with all leaving ligands X, except water, when the replacements in aqueous solution obeyed the second-order rate law: $d[\mathrm{Fe^{II}(CN)_5Y}]/dt = k_Y[\mathrm{Fe(CN)_5(OH_2)}^{3-}][\mathrm{Y}]$. Neglecting the reverse replacement of Y by X, because of the large excess of Y over X ($\geqslant$200-fold), and because of the relative stability of the final reaction product $[\mathrm{Fe^{II}(CN)_5Y}]$, application of the steady-state approximation to the hypothetical intermediates $[\mathrm{Fe(CN)_5}]^{3-}$ (D mechanism), and $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ (I_d mechanism), respectively, will give the same rate law with the observed rate constants $k_{\mathrm{obs.}}{}^{D} = k_1k_2[\mathrm{Y}]/(k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}])$ and $k_{\mathrm{obs.}}{}^{I_d} = k_1'[\mathrm{OH_2}]k_2'[\mathrm{Y}]/(k_{-1}'[\mathrm{X}] + k_2'[\mathrm{Y}])$ {k_1 and k_{-1}, and k_1' and k_{-1}' being the rate constants for the formation, and its reverse, of the hypothetical intermediates $[\mathrm{Fe(CN)_5}]^{3-}$ and $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$, respectively, and k_2 and k_2' the rate constants of formation of $[\mathrm{Fe^{II}(CN)_5Y}]$ from these potential intermediates}.

In a previous paper [1] the replacement of water in $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ by a variety of entering ligands Y was studied in ethylene glycol solvent at varying water concentrations. The observed rate constant was independent of water concentration, which supported the I_d mechanism and made the D mechanism unlikely. In this paper further arguments are presented in favour of the I_d mechanism for the replacement reactions $[\mathrm{Fe^{II}(CN)_5X}] + \mathrm{Y}$ {X = 3-cyanopyridine (3CN-py) or nitrosobenzene (PhNO); Y = py or $[\mathrm{CN}]^-$}. The replacements were carried out in the presence of a large excess of the entering ligand Y. Under these conditions, rate constants for the D and I_d mechanisms reduce to $k_{\mathrm{obs.}}{}^{D} \simeq k_1$, and $k_{\mathrm{obs.}}{}^{I_d} \simeq k_1'[\mathrm{H_2O}]$. Consequently, in the case of an I_d mechanism, $k_{\mathrm{obs.}}{}^{I_d}$ should depend on the water concentration. This was true in aqueous solutions in which the water concentration was reduced by addition of sorbitol, sucrose, glucose, glycerol, and ethylene glycol.

RESULTS

Kinetics of Replacement of 3-*Cyanopyridine by Pyridine in Pentacyano*(3-*cyanopyridine*)*ferrate*(II) *Ion in Solutions containing Different Water Concentrations.*—The kinetics of replacement were monitored spectrophotometrically at 370 nm {the maximum absorption of the reaction product $[\mathrm{Fe(CN)_5(py)}]^{3-}$, ε 3 400 dm^3 mol^{-1} cm^{-1}; the starting complex, $[\mathrm{Fe(CN)_5(3CN\text{-}py)}]^{3-}$, has a maximum at 415 nm, ε 4 650 dm^3 mol^{-1} cm^{-1}}. The concentration of the $\mathrm{Na_3[Fe(CN)_5(3CN\text{-}py)]}$ complex was *ca.* 5×10^{-5} mol dm^{-3} and that of pyridine was 0.12 mol dm^{-3}. Because of the large excess of entering reagent over the starting complex, the reverse reaction (replacement of py by 3CN-py) could be

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[1] D. Pavlović, D. Šutić, and S. Ašperger, *J.C.S. Dalton*, 1976, 2406 and refs. therein.

[2] Z. Bradić, M. Pribanić, and S. Ašperger, *J.C.S. Dalton*, 1975, 353.

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

[4] Symbolism given by C. H. Langford and H. B. Gray, ' Ligand Substitution Processes,' W. A. Benjamin, New York, 1965.

neglected. Reactions were allowed to proceed at (25 ± 0.05 °C.

(*a*) *Addition of sorbitol, sucrose, and glucose to the reaction mixture.* By addition of sorbitol the concentration of water was decreased from 55.55 to 21.75 mol dm^{-3}. The maximum concentration of sorbitol which could be attained was 70% by weight. Absorption spectra of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ in solutions containing sorbitol did not change with time, and we concluded that sorbitol does not enter the complex under these reaction conditions. The addition of sucrose and glucose exhibited a similar effect on the replacement rate. Both compounds do not co-ordinate during the replacements studied. Observed rate constants decreased almost linearly with decreasing water concentration in all the three cases (Figure 1). The percentage decrease in the observed rate constants is about twice as large as the percentage decrease in the water concentration, which is most probably due to the large decrease in water activity in these solutions.

(*b*) *Addition of glycerol.* In aqueous glycerol mixed solvents the water concentration could be reduced to *ca.* 11 mol dm^{-3}, in which case the observed rate constant was reduced by *ca.* 25-fold (Figure 1).

(*c*) *Addition of ethylene glycol.* In aqueous ethylene glycol mixed solvents the water concentration could be reduced to *ca.* 1 mol dm^{-3}, and the solubility of the complexes was still satisfactory. Under the reaction conditions used, ethylene glycol seems to enter the complex, but less efficiently than water, which explains why $k_{obs.}$ is still appreciable at this small water concentration (Figure 1).

Kinetics of Replacement of Nitrosobenzene by Cyanide in Pentacyano(nitrosobenzene)ferrate(II) *Ion in Solutions containing Various Water Concentrations.*—The kinetics of replacements were followed spectrophotometrically at 528 nm (maximum absorption of the violet nitrosobenzene complex,[5] ε 6 400 $dm^3\ mol^{-1}\ cm^{-1}$). At this wavelength the absorption of the hexacyanoferrate(II) ion is negligible. The concentration of $Na_3[Fe(CN)_5(ONPh)]$ was 5.25×10^{-5}—10^{-4} mol dm^{-3}, and that of Na[CN] was 0.01 mol dm^{-3}. The temperature was kept at 50 ± 0.1 °C. The decrease in water concentration on addition of sucrose, sorbitol, glycerol, and even ethylene glycol resulted in a decreased reaction rate. The gradients of plots obtained for these reagents (Figure 2) suggest that, at 50 °C, ethylene glycol enters the complex. Even glycerol seems to show some tendency to co-ordinate (which was not observable at 25 °C, Figure 1). On the other hand, sorbitol and sucrose do not enter the complex at all. The effect of the decrease in rate on decreasing water concentration is similar in both replacement reactions studied {replacement of 3CN-py by py, and of PhNO by $[CN]^-$ in pentacyano(ligand) complex ion}, and is obviously a general effect.

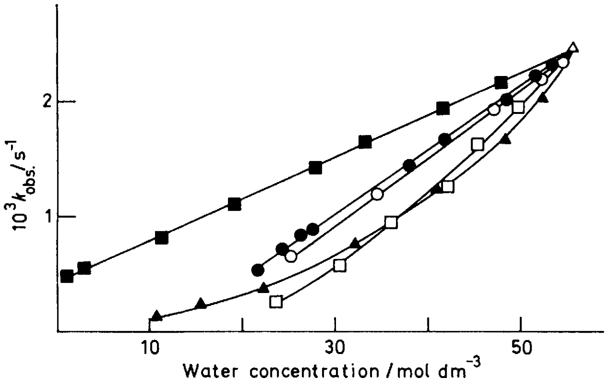

FIGURE 1 Dependence of $k_{obs.}$ on water concentration in the replacement of 3-cyanopyridine by 0.12 mol dm^{-3} pyridine in 5×10^{-5} mol dm^{-3} $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ in the presence of 5×10^{-4} mol dm^{-3} 3-cyanopyridine, in aqueous solutions containing: (■) ethylene glycol, (●) sorbitol, (○) glucose, (□) sucrose, and (▲) glycerol at 25 ± 0.05 °C; (△) is for the replacement in pure water

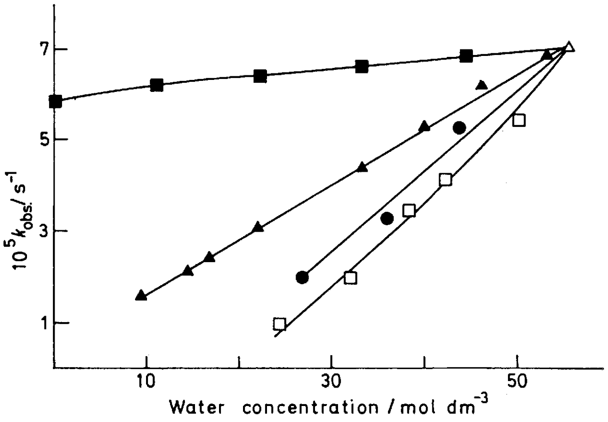

FIGURE 2 Dependence of $k_{obs.}$ on water concentration in the replacement of nitrosobenzene by 0.01 mol dm^{-3} Na[CN] in 5.25×10^{-5}–10^{-4} mol dm^{-3} $Na_3[Fe(CN)_5(ONPh)]$, in aqueous solutions at 50 ± 0.1 °C. See Figure 1 for key

The observed decrease in rate on addition of polyhydric alcohols and saccharides is not caused by an increase in viscosity of these solutions. It was previously found [1] that the rate of replacement of water in $[Fe(CN)_5(OH_2)]^{3-}$ by various ligands is practically the same in aqueous and ethylene glycol solutions, although the viscosity of these solutions is different. We have now measured by the stopped-flow technique the rate of replacement of water by 0.005 mol dm^{-3} 3CN-py in 5×10^{-5} mol dm^{-3} $[Fe(CN)_5(OH_2)]^{3-}$ in aqueous solution (k 630 ± 10 $dm^3\ mol^{-1}\ s^{-1}$), and in aqueous solution containing 48% (w/w) glycerol (water concentration reduced to 25.7 mol dm^{-3}; k 620 ± 10 $dm^3\ mol^{-1}\ s^{-1}$), at 25 °C. The difference in viscosity of the two solutions is *ca.* 5.4-fold, but the difference in rate is negligible. It can be concluded that, under the reaction conditions used, viscosity has little effect on the rate. The decrease in rate on addition of polyalcohols and saccharides is therefore caused by a decrease in water concentration in the reaction of $[Fe^{II}(CN)_5X] + Y$, because water is needed to form the $[Fe(CN)_5(OH_2)]^{3-}$ intermediate. On the other hand, when $[Fe(CN)_5(OH_2)]^{3-}$ is the starting complex ($X = H_2O$) the rate should be independent of water concentration in an I_d mechanism, as is actually observed in solutions of ethylene glycol [1] and now also in glycerol.

DISCUSSION

The dependence of rate constants on such properties of the mixed solvents as their dielectric constants or their Grunwald–Winstein Y values has been used in distinguishing between dissociative and associative types of

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[5] S. Ašperger, I. Murati, and O. Čupahin, *J. Chem. Soc.*, 1953, 1041.

mechanism,[6] but the D and I_d mechanisms could not be differentiated.

The question of whether pentacyano(ligand)ferrate(II) ion undergoes replacement reactions by a D or I_d mechanism is still under debate. If the D mechanism operates the reaction intermediate should live long enough to discriminate between reagents. The most thoroughly investigated replacement is that when $X = H_2O$, *i.e.* the reaction $[Fe(CN)_5(OH_2)]^{3-} + Y^{n-} \xrightarrow{k_f} [Fe^{II}(CN)_5Y]^{(3+n)-} + H_2O$. If one tries to interpret the mechanism of this reaction in terms of a D mechanism then the expression for $k_{obs.}$ reduces to $k_1k_2[Y]/(k_{-1}[H_2O])$ (since the term $k_2[Y] \ll k_{-1}[H_2O]$, it can be neglected [1]). Indeed, the linearity of the plot of $k_{obs.}$ against [Y] was reported by all investigators in cases where the leaving ligand was water.[1,7,8] The forward rate constant would then be $k_f = k_1k_2/k_{-1}[H_2O]$ dm^3 mol^{-1} s^{-1}. The observed variation of k_f with various entering reagents [2] might be attributed formally to changes of k_2 {the rate constant for the reaction of the intermediate $[Fe(CN)_5]^{3-}$ with Y}. If this were true, the reaction intermediate would discriminate between reagents, and the D mechanism would be ensured. On the other hand, it was pointed out [2] that uncharged ligands react at almost the same rates (although the basicity of these reagents is different), and that the differences in rates are due to differences in the charges on Y. This observation was recently supported by James and Murray.[9] In a previous paper [2] we discussed the changes in k_2 with the nature of the reagents in terms of a D mechanism, where k_2 is very near to the diffusion-controlled limit [7,8] and therefore very much influenced by interionic forces.[10] The alternative explanation is in terms of an I_d mechanism. The entering reagent does not contribute energetically to the transition state (accidental bimolecularity), but its chance of filling the position vacated by dissociation of water depends on its charge. Therefore, only uncharged entering ligands should react at roughly the same rates. Consequently, the I_d mechanism explains equally well the kinetic data, as does the D mechanism. It appears that the only means of distinguishing between these two mechanisms is by variation of the solvent composition, as was previously done [1] for the $[Fe^{II}(CN)_5(OH_2)]^{3-}$, and has now been done for $[Fe^{II}(CN)_5(3CN\text{-}py)]^{3-}$ and $[Fe^{II}(CN)_5(ONPh)]^{3-}$ complexes.

It has been observed that $[Fe(CN)_6]^{4-}$ is a much stronger electron-pair donor than $[Fe(CN)_6]^{3-}$, which causes a large shift of the redox potential in organic solvents due to the interaction between iron(II) species and the solvent molecules.[11] However, it appears that this solvent effect is not a dominant factor governing the replacement rates studied. If it were it would influence analogously the rates of replacement in both $[Fe(CN)_5(OH_2)]^{3-}$ and $[Fe(CN)_5X]^{3-}$ (X = 3CN-py or PhNO). This is not the case. The rates of replacement of water in $[Fe(CN)_5(OH_2)]^{3-}$ are practically the same in water, aqueous ethylene glycol, and aqueous glycerol solutions, as already mentioned.

EXPERIMENTAL

Materials.—All the chemicals were obtained from E. Merck (analytical purity). Trisodium pentacyano(pyridine)ferrate(II) was prepared according to the literature [12] (ε 3 400 dm^3 mol^{-1} cm^{-1} at maximum absorption, 365 nm, in aqueous solution; in ethylene glycol solution there is a bathochromic shift of 25 nm). Trisodium pentacyano(3-cyanopyridine)ferrate(II) was prepared by addition of $Na_3[Fe(CN)_5(NH_3)]$ to an aqueous solution of 3-cyanopyridine, which was in 100-fold excess (molar) over the complex. The reaction mixture was then warmed at *ca.* 35 °C for *ca.* 20 min, ethanol was added, the product was filtered off, washed several times with ethanol, and dried *in vacuo* over calcium chloride (ε 4 650 dm^3 mol^{-1} cm^{-1} at 414 nm in aqueous solution; in ethylene glycol solution there is a bathochromic shift of 36 nm). Trisodium pentacyano(nitrosobenzene)ferrate(II) was prepared as previously described,[13] and by the procedure of Dezsi *et al.*[14] Both procedures give a good product, but the yield by the latter is larger. The amounts of water of crystallization depended on the manner of drying.

Kinetics.—Reagent solutions (pyridine and sodium cyanide, respectively) were prepared by addition of these substances to aqueous solutions containing various concentrations of polyhydric alcohols (ethylene glycol, glycerol, or sorbitol) or saccharides (glucose or sucrose). Solutions of $Na_3[Fe(CN)_5(3CN\text{-}py)]$ or $Na_3[Fe(CN)_5(ONPh)]$, were freshly prepared in separate flasks. 3-*Cyanopyridine* (10-*fold molar* excess) was added to the solution of 3CN-py complex to suppress aquation. At zero time the previously thermostatted solutions were mixed and rapidly transferred to optical cells (1 or 2 cm). The latter were inserted into the chamber of a Cary-16 K spectrophotometer, kept at 25 ± 0.05 or 50 ± 0.1 °C. Some measurements were made with a Unicam SP 500 spectrophotometer. The rate of replacement of water by 3CN-py in $[Fe(CN)_5(OH_2)]^{3-}$ was monitored at 415 nm {maximum absorption of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$} using a Durrum D-110 stopped-flow spectrophotometer.

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