Kinetics and Mechanism of Replacement of Water in Aquapentacyanoferrate(II) Ion with a Variety of Entering Ligands in Ethylene Glycol Solvent †

By **Dušanka Pavlović, Dušan Šutić, and Smiljko Ašperger,*** Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

The kinetics of replacement of water in $[Fe(CN)_5(OH_2)]^{3-}$ with pyridine, 3-cyanopyridine, nicotinamide, 4-aminopyridine, and cyanide have been studied in ethylene glycol solvent containing $\geqslant$0.055 mol dm^{-3} water at 25 °C. The rate law obeyed is $-d[Fe(CN)_5(OH_2)^{3-}]/dt = k_2'[Y][Fe(CN)_5(OH_2)^{3-}]$. With excess of entering ligand Y, $k_{obs.}(= k_2'[Y])$ is practically independent of water concentration. Values of $\Delta H^‡$ and $\Delta S^‡$ for the replacement of water by Y in the aqua-complex are almost identical for water and ethylene glycol solvents, supporting the assertion that Y replaces water in both solvents. These results strongly support the I_d mechanism and make the *D* mechanism very unlikely.

The kinetics of replacements in pentacyano(ligand)-ferrate(II) ions have been extensively studied.[1-5] Limiting reaction rates, at sufficiently large concentrations of entering ligand Y, have been observed with all the leaving ligands, except water, where the replacements obey the second-order rate law [2,3,5] $d[Fe^{II}(CN)_5Y]/dt = k_Y[Fe(CN)_5(OH_2)^{3-}][Y]$. The body of data accumulated supports the dissociative mechanism but, as already pointed out,[5] the *D* (dissociative) [equations (1) and (2)] and I_d (interchange dissociative) mechanisms [6] [equations (3) and (4)] can equally well explain all the experimental data.

$$D\begin{cases} [Fe^{II}(CN)_5X] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + X & (1) \\ [Fe(CN)_5]^{3-} + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe^{II}(CN)_5Y] & (2) \end{cases}$$

$$I_d\begin{cases} [Fe^{II}(CN)_5X] + H_2O \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}} [Fe(CN)_5(OH_2)]^{3-} + X & (3) \\ [Fe(CN)_5(OH_2)]^{3-} + Y \underset{k_{-2}'}{\overset{k_2'}{\rightleftharpoons}} [Fe^{II}(CN)_5Y] + H_2O & (4) \end{cases}$$

If the reverse steps of reactions (2) and (4) are neglected because of the relative stability of the final reaction product, the application of the steady-state approximation to the hypothetical intermediates $[Fe(CN)_5]^{3-}$ and $[Fe(CN)_5(OH_2)]^{3-}$, respectively, will give the same rate law with the observed rate constants (5) and (6). Consequently, both the *D* and I_d mechanisms can explain the fact that, at sufficiently large concentrations of Y, limiting reaction rates are observed.

$$k_{obs.}{}^{D} = \frac{k_1k_2[Y]}{k_{-1}[X] + k_2[Y]} \qquad (5)$$

$$k_{obs.}{}^{I_d} = \frac{k_1'[H_2O]k_2'[Y]}{k_{-1}'[X] + k_2'[Y]} \qquad (6)$$

For $[Fe(CN)_5(OH_2)]^{3-}$, *i.e.* $X = H_2O$, Malin and his coworkers [2,3] assumed that $k_{-1}[H_2O] \gg k_2[Y]$ because the solvent concentration was 55.5 mol dm^{-3} and equation (5) for the *D* mechanism reduced to (7) in agreement with the observed second-order rate law. If the I_d mechanism is operating, the aqua-complex ($X = H_2O$) will react according to (4) and, neglecting its reverse, the second-order rate law is expected as we, in fact, observed.

$$k_{obs.}{}^{D} = \frac{k_1k_2[Y]}{k_{-1}[H_2O]} \qquad (7)$$

In this paper we show that the *D* and I_d mechanisms are distinguishable if the replacement of water by Y in $[Fe(CN)_5(OH_2)]^{3-}$ ion is carried out in a solvent which does not co-ordinate, or co-ordinates relatively slowly. The choice of solvents for this purpose appeared to be limited, but ethylene glycol seemed to be satisfactory. If the *D* mechanism is operating the gradients of the straight lines obtained on plotting $k_{obs.}{}^{D}$ against [Y] in ethylene glycol solvent should decrease with increasing water concentration [$X = H_2O$, equation (7)]. Moreover, in pure ethylene glycol, at a sufficiently high concentration of Y, the second-order rate law should not hold [equation (5), $X = H_2O$]. If, on the other hand, the I_d mechanism is operating, equation (3) ($X = H_2O$) reduces to a fast water exchange [2,3] at the $[Fe(CN)_5(OH_2)]^{3-}$ anion, a step irrelevant to the kinetics of formation of $[Fe^{II}(CN)_5Y]$ anion. Equation (4) requires that the second-order rate law applies in pure and mixed solvents, and this was strictly borne out by the results obtained. Apparently this is the only evidence available so far that can be used for distinguishing the two mechanisms in this system.

RESULTS AND DISCUSSION

The kinetics of replacement of water in $[Fe(CN)_5(OH_2)]^{3-}$ with pyridine (py), 3-cyanopyridine (3CN-py), nicotinamide (na), 4-aminopyridine ($4NH_2$-py), and cyanide were studied in ethylene glycol solvent under first-order conditions (excess of entering reagent Y).

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[1] D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1973, 602.

[2] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 2080.

[3] H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 1973, **12**, 2084.

[4] Z. Bradić, D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1974, 344.

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

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

The rate law obeyed was $-d[Fe(CN)_5(OH_2)^{3-}]/dt = k_2'[Y][Fe(CN)_5(OH_2)^{3-}]$, and $k_{obs.}/s^{-1} = k_2'[Y]$. The kinetics were followed spectrophotometrically using the stopped-flow technique. For py, 3CN-py, na, and $4NH_2$-py, respectively, the change in light absorption was followed at the wavelength corresponding to maximum absorption of the relevant reaction product in ethylene glycol (390, 460, 410, and 335 nm, respectively), whereas for cyanide the change in absorption was followed at 440 nm which is the wavelength of maximum absorption of $[Fe(CN)_5(OH_2)]^{3-}$ in ethylene glycol. The maximum absorption of the same complex in aqueous solution was also found at 440 nm, in good agreement with the literature[7] (445 nm). The py and 3CN-py complexes show bathochromic shifts of 30 and 36 nm in ethylene glycol compared to aqueous solution. The initial concentration of $[Fe(CN)_5(OH_2)]^{3-}$ was always 5.0×10^{-5} mol dm^{-3} and the temperature was 25 ± 0.1 °C.

When pyridine or nicotinamide, respectively, was the entering ligand the concentrations of water in ethylene glycol were 0.055, 0.333, and 0.166 mol dm^{-3}. The observed rate constant was independent of the water concentration (Figure 1). When 3CN-py, $4NH_2$-py, and cyanide, respectively, were the entering ligands the concentration of water in ethylene glycol was always 0.055 mol dm^{-3}. Strict linearity was obtained on plotting $k_{obs.}$ against the concentrations of these reagents (Figure 1). The maximum concentration of 3CN-py which could be used was 0.3 mol dm^{-3}. At higher concentrations the replacement rate was too rapid to be followed by the stopped-flow technique. Cyanide reagent was prepared by dissolving sodium cyanide in water or tetramethylammonium cyanide in ethylene glycol.

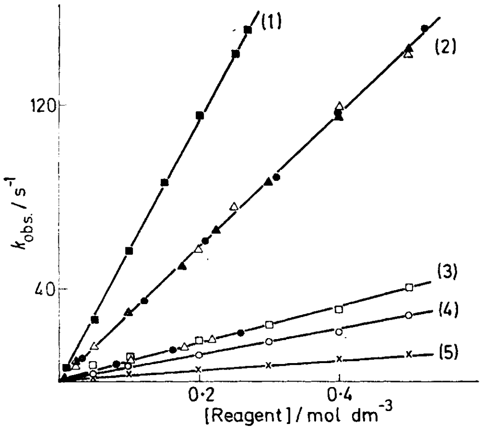

FIGURE 1 Linear dependence of $k_{obs.}$ on concentration of entering ligand for replacement of water in 5.0×10^{-5} mol dm^{-3} $[Fe(CN)_5(OH_2)]^{3-}$ in ethylene glycol solvent containing 0.055 mol dm^{-3} water at 25 ± 0.1 °C. Entering ligand: (1) 3CN-py; (2) py [water concentration: (●) 0.055, (△) 0.166, and (▲) 0.333 mol dm^{-3}]; (3) na [water concentration: (□) 0.055, (●) 0.166, and (△) 0.333 mol dm^{-3}]; (4) $4NH_2$-py; and (5) cyanide

Activation Parameters for the Replacement of Water in $[Fe(CN)_5(OH_2)]^{3-}$ *Ion by Entering Ligand* Y *in Aqueous and Ethylene Glycol Solution.*—The parameters $\Delta H^‡$ and $\Delta S^‡$ were determined from plots of log (k_2/T) against $1/T$, which were good straight lines. Tables 1 and 2 show the results obtained in water and ethylene glycol. A comparison of the $\Delta H^‡$ and $\Delta S^‡$ values in water and ethylene glycol shows that these parameters are very similar in both solvents.

TABLE 1

Activation parameters[a] for the replacement of water in 5.0×10^{-5} mol dm^{-3} $[Fe(CN)_5(OH_2)]^{3-}$ by Y in aqueous solution

Y	[Y] / mol dm^{-3}	θ_c / °C	$10^{-2}k_2'$ / dm^3 mol^{-1} s^{-1}	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal K^{-1} mol^{-1}
py	0.1	20.0	2.77	15.6 ± 0.7	6 ± 2
		25.6	4.08	(16.1)[b]	(7)[b]
		30.0	6.93		
		34.8	11.00		
3CN-py	0.05	20.0	4.62	16.0 ± 0.5	8 ± 2
		25.2	7.30		
		29.8	11.54		
		35.0	17.30		
CN^-	0.3	20.0	0.14	15.8 ± 0.8	0.5 ± 1.5
		25.2	0.21		
		30.0	0.42		
		35.0	0.58		
NO_2^-	0.4	20.3	0.17	14.5 ± 1.0	−4 ± 2
		25.0	0.24		
		29.8	0.36		
		34.9	0.58		
SCN^-	0.4	20.0	0.49	14.5 ± 0.9	−2 ± 2
		25.2	0.72		
		29.6	1.08		
		34.8	1.58		
SO_3^{2-}	0.2	20.2	0.02	16.3 ± 0.6	−2 ± 1.5
		25.0	0.03		
		29.9	0.049		
		34.8	0.078		

[a] 1 cal = 4.184 J. [b] From ref. 2.

TABLE 2

Activation parameters for the replacement of water in 5.0×10^{-5} mol dm^{-3} $[Fe(CN)_5(OH_2)]^{3-}$ by Y in ethylene glycol solvent

Y	[Y] / mol dm^{-3}	θ_c / °C	$10^{-2}k_2'$ / dm^3 mol^{-1} s^{-1}	$\Delta H^‡$ / kcal mol^{-1}	$\Delta S^‡$ / cal K^{-1} mol^{-1}
py	0.1	20.0	1.63	15.7 ± 0.8	5 ± 2
		25.0	2.47		
		29.5	3.65		
		34.3	5.78		
3CN-py	0.01	20.0	3.47	15.4 ± 0.7	5 ± 2
		25.0	4.95		
		29.5	7.70		
		34.3	11.50		
na	0.1	20.0	0.69	16.5 ± 0.8	6 ± 1.5
		25.0	1.10		
		29.5	1.73		
		34.3	2.77		
$4NH_2$-py	0.1	20.0	0.53	15.3 ± 0.6	2 ± 2
		25.0	0.81		
		29.5	1.26		
		34.3	1.87		
CN^-	0.1	20.0	0.17	16.5 ± 0.8	4 ± 2
		25.0	0.27		
		29.5	0.45		
		34.3	0.68		

Change of the Absorption Spectra of $[Fe(CN)_5(OH_2)]^{3-}$ *in Ethylene Glycol Solution.*—The spectra of the aqua-complex in ethylene glycol changed with time. Maximum absorption shifted from 440 to 406 nm (Figure 2).

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[7] G. Emschwiller, *Compt. rend.*, 1972, **C274**, 1500.

There was an isosbestic point at 433 nm, suggesting that during the interval of observation the absorption in this spectral region is essentially accounted for by two species. After several hours the isosbestic point was less well expressed, suggesting that new chemical species are being formed. The initial reaction might be the replacement of water in the aqua-complex by ethylene glycol. Dimerization and polymerization processes of $[Fe(CN)_5(OH_2)]^{3-}$ might also occur [7,8] as well as the partial oxidation of the $[Fe(CN)_5(OH_2)]^{3-}$ to $[Fe(CN)_5(OH_2)]^{2-}$. However, the observed spectral changes were much slower than replacement of water by Y in $[Fe(CN)_5(OH_2)]^{3-}$, and therefore did not interfere with the replacements studied.

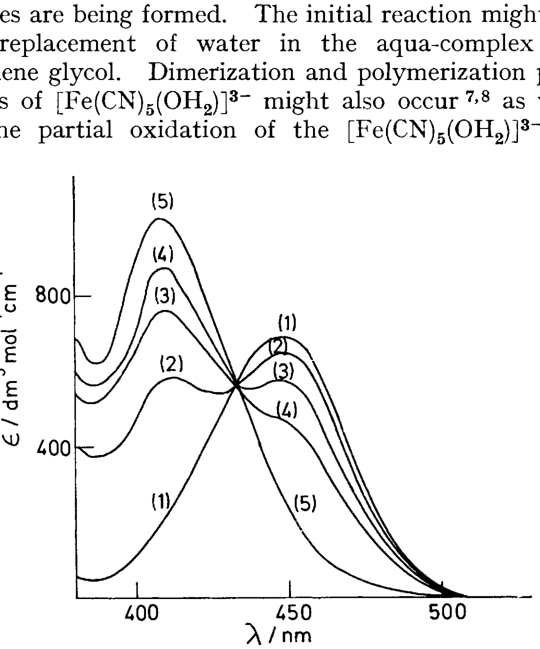

FIGURE 2 Change of the absorption spectra of 5×10^{-5} mol dm^{-3} $[Fe(CN)_5(OH_2)]^{3-}$ ion in ethylene glycol with time. Curves 1—5 correspond approximately to reaction times of 0, 15, 45, 90, and 120 min, respectively

The fact that the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the replacement of water in the aqua-complex are almost identical in water and ethylene glycol solvents (Tables 1 and 2) supports the assumption that the entering ligand Y replaces co-ordinated water regardless of solvent (providing that the free energies of activation for dissociation of water and ethylene glycol, respectively, from the pentacyano-complex ion are sufficiently different as to justify the assumption). Moreover, solvated pentacyano-complexes react relatively slowly at room temperature.* The only exception so far is the aqua-complex, the replacement reactions of which have rates with half-times of the order of milliseconds.

EXPERIMENTAL

Materials.—All the chemicals used were of E. Merck analytical purity, except sodium thiocyanate, 3-cyanopyridine, nicotinamide, and 4-aminopyridine which were twice recrystallized from water. Trisodium amminepentacyanoferrate(II) was prepared according to the procedure of Kenney *et al.*,[9] and was recrystallized several times from a saturated solution in ammonia at ice-bath temperature. Trisodium aquapentacyanoferrate(II) was prepared by a modified Hoffman procedure,[10] recrystallized several times from ice-cold water, and dried *in vacuo* (P_4O_{10}). The fresh aqua-complex, prepared in this way, gave the same replacement rates as the aqua-complex freshly prepared by dissolving $Na_3[Fe(CN)_5(NH_3)]$ in water.[2] Emschwiller [7,8] pointed out that the preparation of the aqua-complex yields at least two components, the mononuclear $[Fe(CN)_5(OH_2)]^{3-}$ and the binuclear $[Fe_2(CN)_{10}]^{6-}$ species. Since the mononuclear species reacts *ca.* 100 (or more) times faster than the binuclear species, the replacement rates of water in $[Fe(CN)_5(OH_2)]^{3-}$ could be readily measured.

Tetramethylammonium cyanide was prepared from tetramethylammonium iodide and potassium cyanide dissolved in methanol, on an ion-exchange column. Methanol was removed by vacuum distillation, and the tetramethylammonium cyanide was recrystallized twice from water and dried over $CaCl_2$. The product was free from potassium as shown by flame photometry. Cyanide was determined potentiometrically using a silver electrode. E. Merck analytical grade ethylene glycol was used without further purification. Its water content was determined by Karl Fischer's method.[10]

Kinetics.—Aqueous solutions of $[Fe(CN)_5(OH_2)]^{3-}$ were prepared from freshly prepared $Na_3[Fe(CN)_5(OH_2)]$ or $Na_3[Fe(CN)_5(NH_3)]$. Ethylene glycol solutions of the aqua-complex were made from freshly prepared $Na_3[Fe(CN)_5(OH_2)]$ only. The solutions of the complex and of the reagent were separately thermostatted (±0.05 °C) and after thermal equilibrium had been reached the solutions were mixed in a stopped-flow spectrophotometer.

Spectrophotometry.—Absorption spectra were recorded on a Cary 16 K spectrophotometer. Fast replacements of water in $[Fe(CN)_5(OH_2)]^{3-}$ were followed using a Durrum D-110 stopped-flow spectrophotometer.

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* Unpublished work from this laboratory obtained on studying the reactions : $[Fe(CN)_5{\cdot}HCONH_2]^{3-} + Y$ in formamide and $[Fe(CN)_5{\cdot}Me_2SO]^{3-} + Y$ in dimethyl sulphoxide.

[8] G. Emschwiller, *Compt. rend.*, 1954, **C238**, 341; 1964, **C259**, 4281; 1969, **C268**, 694; 1970, **C270**, 1362.

[9] D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nuclear Chem.*, 1961, **20**, 75.

[10] S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc. (A)*, 1969, 2044.