Mechanism of Reaction of the Binuclear Dimer of $[Fe(CN)_5(OH_2)]^{3-}$ † with Uncharged Ligands in Aqueous Solution ‡

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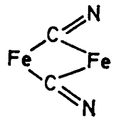
The kinetics of reactions of the binuclear dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with pyridine (py), nitrosobenzene (PhNO), 3CN-py, and 4CN-py, respectively, have been measured at pH 5.5—6.0. With a 20-fold, or larger, excess of the complexing ligand (no extra salt added) the average $k_{obs.}$ at 25 °C for all reagents used is $0.024 \pm 0.001\ s^{-1}$. The activation parameters for the reaction of the dimer with 3CN-py are $\Delta H^\ddagger = 70.3 \pm 3.0$ kJ mol^{-1} and $\Delta S^\ddagger = 29.7 \pm 4.0$ J K^{-1} mol^{-1}. Ratios of rate constants (competition ratios) for the reactions of various ligand pairs (Y^1 and Y^2) with $[Fe(CN)_5(OH_2)]^{3-}$ and its binuclear dimer have been determined. The competition ratios at 25 °C with Y^1,Y^2 defined as (*a*) py,PhNO, (*b*) 3CN-py,4CN-py, (*c*) 4CN-py,py, (*d*) 4CN-py,PhNO, and (*e*) 3CN-py,PhNO are: for the binuclear dimer, (*a*) 1.35, (*b*) 1.04, (*c*) 1.61, (*d*) 2.17, (*e*) 2.21; for $[Fe(CN)_5(OH_2)]^{3-}$, (*a*) 1.32, (*b*) 1.01, (*c*) 1.66, (*d*) 2.15, (*e*) 2.19. Almost equal competition ratios for identical pairs Y^1,Y^2 for the dimer and $[Fe(CN)_5(OH_2)]^{3-}$ suggest that the aqua-complex is the only intermediate in the replacements involving the binuclear complex, and that the binuclear complex is singly bridged, having the structure $[(NC)_5Fe(\mu\text{-}NC)Fe(CN)_4(OH_2)]^{6-}$.

In aqueous solution aquapentacyanoferrate(II) ions are in equilibrium with a binuclear complex, for which the structure $[(NC)_4Fe(\mu\text{-}CN)(\mu\text{-}NC)Fe(CN)_4]^{6-}$ (1), involving two non-linear cyano-bridges, has been proposed.[1,2] This structure was mainly based on the observation [1] that the dry lead(II)-induced precipitate, obtained from aqueous solutions rich in dimer, does not show the i.r. absorption band of water, which the singly bridged dimer $[(NC)_5Fe(\mu\text{-}NC)Fe(CN)_4(OH_2)]^{6-}$ (2) should show. A recent structure determination of $[(H_3N)_5Co^{III}(\mu\text{-}CN)\text{-}Co^{III}(CN)_5]$ has shown [3] that in singly bridged complexes the deviation from linearity of the bridging cyanide can be as much as 27.8° (Co–N–C and Co–C–N, 159.8 and 172.4°), respectively. But structure (1) requires about three times as large a deviation from linearity, and is therefore most unlikely. The assumption that the metal atoms are bonded to carbon atoms [4] as in (A), or to π electrons of the cyano-groups [4] (which will preserve linearity of the cyano-group), has no experimental support in the ferricyanide system.



(A)

It has been suggested [5-7] that (1) reacts with a nucleophile Y, yielding $[Fe^{II}(CN)_5Y]$, *via* the intermediate (2). Several equations were written [7] to show how $[Fe^{II}(CN)_5Y]$ might be formed from (1). These equations involve different intermediates reacting with Y. We determined the ratio of rate constants (competition ratios) for the reactions of various ligand pairs (Y^1 and Y^2) with the mononuclear aqua-complex and its binuclear dimer. Almost equal competition ratios for identical pairs Y^1 and Y^2 were obtained with the dimer and the $[Fe(CN)_5(OH_2)]^{3-}$ complex. This observation suggests that the aqua-complex is the only intermediate in the replacements involving the binuclear complex. Therefore, the binuclear complex should be singly bridged, and we ascribe to it the structure (2).

EXPERIMENTAL

Materials.—All the chemicals used were of E. Merck analytical purity, except 3-cyanopyridine (3CN-py) and 4-cyanopyridine (4CN-py) which were several times recrystallized from ethanol. Trisodium amminepentacyanoferrate(II) was prepared as previously described,[8] 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,[9] 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.[10] Emschwiller [11] observed that the preparation of $[Fe(CN)_5(OH_2)]^{3-}$ also yields the binuclear complex. Since the mononuclear species reacts *ca.* 100 (or more) times as fast as the binuclear species, the replacement rates in both complexes with Y, yielding $[Fe^{II}(CN)_5Y]$, could be readily measured.

Nitrosobenzene was prepared as described in the literature.[12] Water was redistilled and had a conductivity of *ca.* 1.2×10^{-4} S m^{-1}.

Kinetics.—The solution of the complex, prepared either by dissolving $Na_3[Fe(CN)_5(NH_3)]\cdot 3H_2O$ in water,[10] or by dissolving freshly prepared $Na_3[Fe(CN)_5(OH_2)]$ in water, was thermostatted (±0.05 °C) and after thermal equilibrium had been reached the solution was added as fast as possible to a thermally equilibrated solution of the reagent, quickly mixed, and the light absorption measured in thermostatted 5-cm quartz cells. For example, a 2.5×10^{-5} mol dm^{-3} aqueous solution of the dimer was prepared by quickly injecting 0.1 cm^3 of a thermally equilibrated 0.01 mol dm^{-3} solution of the aquapentacyanoferrate(II) into a thermostatted solution of the reagent. At reaction time zero, the quickly diluted solution contained virtually the same ratio of dimer to monomer as the concentrated solution. The reaction was followed by measuring the light absorption at

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† Aquapentacyanoferrate(II).

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the wavelength of the maximum absorption of the reaction product. The wavelengths used were 363, 415, 478, and 528 nm for the reaction products $[Fe(CN)_5(py)]^{3-}$, $[Fe(CN)_5(3CN\text{-}py)]^{3-}$, $[Fe(CN)_5(4CN\text{-}py)]^{3-}$, and $[Fe(CN)_5(ONPh)]^{3-}$, respectively.

All kinetic measurements were performed in the dark, or in diffuse dim light so as to prevent photoreaction.[13]

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.

RESULTS AND DISCUSSION

Davies and Garafalo observed [5,6] that the reactions of the dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with complexing ligands can be adequately followed at pH 11, but when the reactions were followed at pH 9.5—11 they obtained non-linear first-order plots. We measured the rates of reactions of 2.5×10^{-5} mol dm^{-3} dimer in aqueous solution, prepared as described in the Experimental section, with uncharged complexing ligands under first-order conditions. The observed first-order rate constants determined at *ca.* 20-fold or larger excesses of the complexing reagents py, 3CN-py, 4CN-py, and PhNO were constant, on average, up to *ca.* 90% completion of reaction. These measurements were made in buffered solutions, at pH 5—7 (potassium hydrogen phthalate + Na[OH] at pH 5, and $K[H_2PO_4]$ + Na[OH] at pH 6 and 7) and in unbuffered solutions at pH 5.5—6.0. No significant change of the rate constant was observed between pH 5 and 7. The rate constants at 25 °C, *e.g.* for the reaction of 2.5×10^{-5} mol dm^{-3} dimer with 5×10^{-4} mol dm^{-3} 3CN-py at ionic strength 9.5×10^{-4} mol dm^{-3} ($Na[ClO_4]$ added), were determined at pH 5, 6, and 7 as 0.025 8, 0.025 2, and 0.025 0 s^{-1}, respectively. Increase of ionic strength from 4.5×10^{-4} to 9.5×10^{-4} mol dm^{-3} had little effect on the rate constant, but at $I = 0.050$ and 0.450 mol dm^{-3} the rate constants at 25 °C decreased from 0.025 3 to 0.021 4 and 0.017 6 s^{-1}, respectively. It is interesting to note that Garafalo and Davies [5] determined the rate constant for the reaction of *ca.* 2.5×10^{-5} mol dm^{-3} dimer with 0.01 mol dm^{-3} isonicotinamide at 25 °C as 0.016 1 s^{-1} at $I = 1$ mol dm^{-3}, pH 11—12.3. This value agrees very well with our rate constant, obtained with the 3CN-py reagent and extrapolated to the same ionic strength (1.0 mol dm^{-3}, $k_{\text{extrap.}} = 0.016$ s^{-1}). James and Murray [7] studied the reaction of the dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with HCN, py, and Me-py reagents at pH 6.8 and $I = 1.0$ mol dm^{-3}, and obtained linear first-order plots of ln (absorbance) against time up to *ca.* 80—85% completion of reaction. These authors, also, encountered no difficulties when working at such low pH. They also observed no change of the rate constant between pH 5 and 7. In general, their rate constants are lower by a factor of 10 or more than those found by Davies and Garafalo and by us.

The rate constants for the reaction of 2.5×10^{-5} mol dm^{-3} dimer with a 20-fold excess of 3CN-py at 298.00, 292.85, and 289.32 K were 0.025 4, 0.012 1, and 0.007 64 s^{-1}. Each rate constant is an average value obtained from three independent kinetic runs. From the linear Arrhenius plot the enthalpy and entropy of activation were determined by a least-squares method as 70.3 ± 3.0 kJ mol^{-1} and 29.7 ± 4.0 J K^{-1} mol^{-1}, respectively. These activation parameters are in reasonable agreement with those determined by Garafalo and Davies [5] for the dissociation of the supposed dicyano-bridged intermediate ($\Delta H^\ddagger = 82.8$ kJ mol^{-1} and $\Delta S^\ddagger = 35.1$ J K^{-1} mol^{-1}).

Figure 1 shows typical kinetics of the reaction between the binuclear dimer of $[Fe(CN)_5(OH_2)]^{3-}$ and a reagent (4CN-py). The latter was present in only four-fold excess. It can be seen that the reaction rate remains practically constant for a period corresponding to *ca.* 76% completion of the reaction, suggesting that the concentration of the reaction intermediate, from which the product is formed, is almost constant during this period. The span of linearity can be made even larger than in Figure 1 if the reagent excess is further reduced. (Curves analogous to Figure 1 were also obtained with py, 3CN-py and PhNO reagents.)

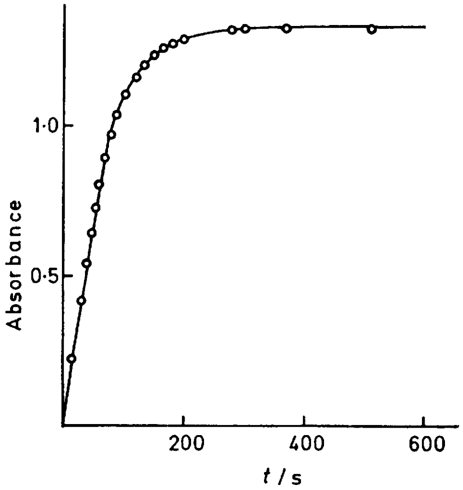

FIGURE 1 Kinetics of reaction of a 2.5×10^{-5} mol dm^{-3} solution of the dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with 1.0×10^{-4} mol dm^{-3} 4CN-py at 25 °C and pH 5.5—6.0 followed by change in light absorption at 478 nm

The mechanism we propose is as in equations (1) and (2). The dissociation of complex (2) is the rate-determining step in which the iron–nitrogen bond is broken, and

$$\underset{(2)}{[(NC)_5Fe^{II}(\mu\text{-}NC)Fe^{II}(CN)_4(OH_2)]^{6-}} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2[Fe(CN)_5(OH_2)]^{3-} \quad (1)$$

$$[Fe(CN)_5(OH_2)]^{3-} + Y \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe^{II}(CN)_5Y]^{3-} + H_2O \quad (2)$$

water co-ordinated yielding $[Fe(CN)_5(OH_2)]^{3-}$. We suggest that these changes follow an I_d (dissociative interchange) mechanism.[14-17]

The value of k_2 depends primarily on the charge of the reagent Y, since charge is the most important factor in determining the relative diffusion rate of the substituent towards the intermediate $[Fe(CN)_5(OH_2)]^{3-}$. James and

Ratios of rate constants for the reactions of various ligand pairs (Y^1 and Y^2) with $[Fe(CN)_5(OH_2)]^{3-}$ and its binuclear dimer in aqueous solutions at pH 5.5—6.0 (no buffer, no extra salt added); py = pyridine, PhNO = nitrosobenzene

Reaction	$\frac{\theta_c}{°C}$	Y^1,Y^2				
		(*a*) py, PhNO	(*b*) 3CN-py, 4CN-py	(*c*) 4CN-py, py	(*d*) 4CN-py, PhNO	(*e*) 3CN-py, PhNO
Dimer + Y *	25	1.36 ± 0.05	1.01 ± 0.03	1.59 ± 0.04	2.16 ± 0.13	2.21 ± 0.07
	25	1.34 ± 0.23	1.06 ± 0.27	1.63 ± 0.11	2.19 ± 0.06	
$[Fe(CN)_5(OH_2)]^{3-}$ + Y^1,Y^2	25	1.30 ± 0.07	1.01 ± 0.03	1.66 ± 0.09	2.15 ± 0.06	2.18 ± 0.09
$[Fe^{II}(CN)_5Y^1]$ + Y^2	35	1.33 ± 0.12				2.19 ± 0.15

* Upper row, ratios of initial rates; lower row, data obtained from equation (4). Uncertainties are standard deviations of the mean. They were determined from variances of the ratios of slopes of the straight lines (L. Saunders and R. Fleming, ' Mathematics and Statistics,' The Pharmaceutical Press, London, 1957, p. 227). Variances were calculated from the slopes and their standard deviations by the least-squares method.

Murray[18] studied the rate of replacement of water in $[Fe^{II}(CN)_5(OH_2)]^{3-}$ with $[Co^{III}(CN)_6]^{3-}$ and $[Fe^{II}(CN)_6]^{4-}$. From their rate data for these highly negatively charged ions, and the rate data for water replacement by neutral reagents,[10,19,20] it may be concluded that, in equations (1) and (2) k_2 for uncharged ligands is at least 100 times as large as k_{-1}. We determined k_2 (25 °C) for the reagents py, 3CN-py, 4CN-py, and PhNO at pH *ca.* 6 and $I = 6 \times 10^{-4}$—6×10^{-5} mol dm^{-3} to be 458, 769, 760, and 353 dm^3 mol^{-1} s^{-1}, respectively. The reversible step in (2) can be neglected because of the relative stability of $[Fe(CN)_5Y]^{3-}$ (k_{-2} is relatively small) and large concentration of Y used.

The ratios of rate constants k_2 (competition ratios) for the reactions of various ligand pairs (Y^1 and Y^2) with the dimer were determined in two ways. The first method was based on the ratios of initial rates which are easy to determine, because these remain constant up to *ca.* 70% completion of replacements under the described conditions (Figure 1). Using the known molar absorption coefficients for the $[Fe^{II}(CN)_5Y]^{3-}$ products, plots of absorbance against time were converted into plots of product concentration against time. The initial rates (slopes) for each reagent were determined by the least-squares method. The ratio of slopes for a pair of reagents was taken as the ratio of $k_2^{Y_1} : k_2^{Y_2}$. The result are collected in the first row of the Table.

The second method was based on application of the steady-state approximation to the $[Fe(CN)_5(OH_2)]^{3-}$ intermediate. Equations (3) and (4) can be derived for the observed rate constant from which, unfortunately, the $[Fe(CN)_5(OH_2)]^{3-}$ concentration is not eliminated.

$$k_{obs.} = \frac{k_{1'}k_2[Y]}{k_{-1}[Fe(CN)_5(OH_2)^{3-}] + k_2[Y]} \quad (3)$$

$$\frac{1}{k_{obs.}} = \frac{k_{-1}[Fe(CN)_5(OH_2)^{3-}]}{k_{1'}k_2} \times \frac{1}{[Y]} + \frac{1}{k_{1'}} \quad (4)$$

where $k_{1'} = k_1[H_2O]$

However, the experiments show that, under the reaction conditions described (Figure 1), the concentration of the intermediate is practically constant until the reaction is *ca.* 70% complete, as already mentioned. The limiting values for $k_{obs.} = k_{1'}$ which were obtained in the presence of excess of Y (Figure 2) did not depend on the nature of the entering ligand, as required by (3). The average $k_{1'}$ value, at pH 5.5—6.0 (no buffer, no extra salt added), for all reagents used is 0.024 ± 0.001 s^{-1} at 25 °C. The assumed constancy of the concentration of the reaction intermediate is in agreement with the linearity of the double reciprocal plot, $1/k_{obs.}$ against $1/[Y]$ (Figure 3). The rate constant ratios $k_2^{Y_1} : k_2^{Y_2}$ were determined from the ratios of slopes obtained by a least-squares method and are collected in the second row of the Table. It can be seen that the competition ratios determined by the two methods are in very reasonable agreement.

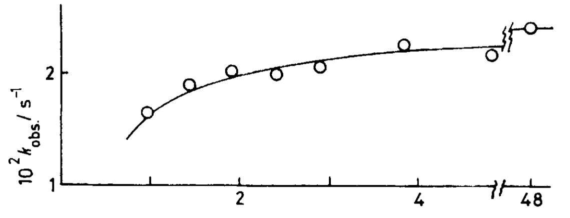

FIGURE 2 Dependence of $k_{obs.}$ on 4CN-py concentration in the reaction of a 2.5×10^{-5} mol dm^{-3} solution of the dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with 4CN-py at 25 °C and pH 5.5—6.0

The ratios of rate constants for the reactions of $[Fe(CN)_5(OH_2)]^{3-}$ with various ligand pairs Y^1 and Y^2 were determined: (*a*) from linear plots of $k_{obs.}/s^{-1}$ against reagent concentration[15,16] (neglecting the reverse reaction in the I_d scheme (2), the second-order rate law becomes valid, *i.e.* $k_{obs.} = k_2[Y]$); (*b*) from linear plots[21] of $1/k_{obs.}$ against $1/[Y^2]$ (or against $[Y^1]$) in the replacement of Y^1 by Y^2 in $[Fe^{II}(CN)_5Y^1]$, under first-order conditions at 35 °C. For the I_d replacement scheme in (5) and (6) the equation (7) is valid, as can be shown by application of the steady-state approximation to the $[Fe(CN)_5(OH_2)]^{3-}$ intermediate. The Table summarizes

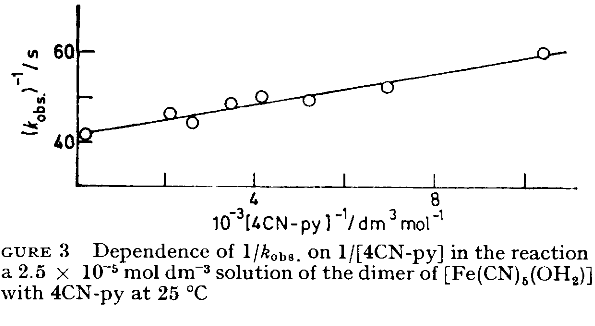

FIGURE 3 Dependence of $1/k_{obs.}$ on 1/[4CN-py] in the reaction of a 2.5×10^{-5} mol dm^{-3} solution of the dimer of $[Fe(CN)_5(OH_2)]^{3-}$ with 4CN-py at 25 °C

the competition ratios. The almost equal competition ratios with identical pairs Y^1 and Y^2, for the aqua-complex and its dimer, suggest that the aqua-complex is

$$[\mathrm{Fe^{II}(CN)_5Y^1}] + \mathrm{H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Fe(CN)_5(OH_2)}]^{3-} + \mathrm{Y^1} \quad (5)$$

$$[\mathrm{Fe(CN)_5(OH_2)}]^{3-} + \mathrm{Y^2} \xrightarrow{k_2} [\mathrm{Fe^{II}(CN)_5Y^2}] + \mathrm{H_2O} \quad (6)$$

$$\frac{1}{k_{\mathrm{obs.}}} = \frac{1}{k_1[\mathrm{H_2O}]} + \frac{k_{-1}[\mathrm{Y^1}]}{k_1[\mathrm{H_2O}]k_2[\mathrm{Y^2}]}$$

the only intermediate in the replacements involving the binuclear complex. If the dimer were doubly bridged [structure (1)], at least two intermediates {(2) and $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$} reacting with Y could be envisaged,[7] which should result in different competition ratios for $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ and its dimer.

Our results are partly in disagreement with those obtained by James and Murray [7] who found the rate ratios 1.0 : 1.03 : 1.06 for HCN, py, and Me-py, reacting with $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$, and 0.25 : 1.0 : 1.3 for the same reagents reacting with the intermediate in the reactions of the dimer.

It has been recently shown [22] that, in the reaction of $[\mathrm{Fe(CN)_5(OH_2)}]^{3-}$ with 3CN-py (and 4CN-py), an unstable nitrile-bound complex is first formed. This reaction is followed by rearrangement of the unstable isomer to the stable pyridine-bound isomer. This observation is of no kinetic relevance to the results presented.

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