Feasibility of a Limiting D Mechanism for Complex Formation and Ligand Substitution Reactions of Pentacyanoferrate(II)

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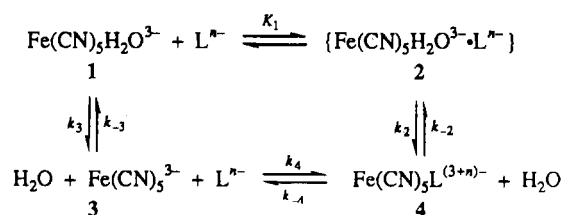Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Germany

The pressure dependence of a series of complex formation reactions of the type $Fe(CN)_5H_2O^{3-} + L^{n-} \rightarrow Fe(CN)_5L^{(3+n)-} + H_2O$ (where $n = 0, 1$) was investigated using stopped-flow techniques. The reported volumes of activation are all between +14 and +18 $cm^3\ mol^{-1}$ and strongly favor a limiting D mechanism. This is in good agreement with all the available data for the reverse ligand substitution reactions of $Fe(CN)_5L^{(3+n)-}$, which also occur according to a limiting D mechanism. Earlier arguments in favor of a dissociative interchange (I_d) or an ion-pair dissociative (D_{IP}) mechanism for the complex formation reactions are reanalyzed, and an overall discussion of ligand substitution processes on the $Fe(CN)_5^{3-}$ center is presented.

Introduction

The substitution behavior of pentacyanoferrate(II) complexes has been the subject of many mechanistic investigations.[2,3] It has been demonstrated that ligand substitution reactions of complexes of the type $Fe^{II}(CN)_5L^{(3+n)-}$ in general exhibit saturation kinetics with respect to the concentration of the entering ligand, in which case release of L becomes the rate-limiting step.[4-13] This means that ligand substitution involves the formation of an intermediate and is controlled by the nature of the leaving group L^{n-}. The limiting rate constant is characterized by significantly positive $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values,[8,9-13] in line with a limiting D mechanism. However, in the case of the complex formation reactions of $Fe^{II}(CN)_5H_2O^{3-}$, the mechanistic assignment seems controversial, since the kinetic and equilibrium data obtained at ambient pressure could be equally well explained in terms of either a dissociative interchange (I_d) or an ion-pair dissociative (D_{IP}) mechanism, i.e. route 1–2–4 in Scheme I, or a limiting D mechanism, i.e. route 1–3–4 in Scheme I.[2,8,14-17] The I_d or D_{IP} mechanism was favored by some groups[2,8,14,15] on the basis of the significant dependence of the overall second-order complex formation rate constant, viz. k_2K_1 or k_3k_4/k_{-3} for the two paths, respectively, on the nature of the entering ligand L^{n-}. In this

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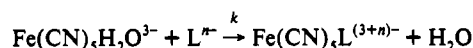(17) Burger, N.; Hankonyi, V.; Smeric, Z. *Z. Phys. Chem. (Leipzig)* **1990,** *271,* 787.

Scheme I.

respect it should be mentioned that arguments in favor of a D_{IP} mechanism, in which a limiting loss of the aqua ligand occurs within the ion pair, came from studies that involved positively charged entering ligands for which significant ion-pair formation was at hand and limiting rate constants were reached at high ligand concentrations.[2] In the case of neutral or negatively charged entering ligands no such rate saturation is observed[2,8] and it is more appropriate to think in terms of an I_d mechanism. However, the assignment of an I_d mechanism is apparently not in line with the $\Delta V^{\ddagger}$ value of $+13.5 \pm 1.5\ cm^3\ mol^{-1}$ reported for the reaction of $Fe(CN)_5H_2O^{3-}$ with CN^- to produce $Fe(CN)_6^{4-}$,[18] since this value is remarkably close to the limiting value calculated for the dissociation of a water molecule from an octahedral metal center, viz. 13.1 $cm^3\ mol^{-1}$,[19] thus suggesting the operation of a limiting D mechanism. Furthermore, due to the principle of microscopic reversibility, the reverse aquation reactions must then also follow an I_d mechanism, which is not in agreement with the kinetic observations referred to above.[4-13] This apparent mechanistic discrepancy between complex formation reactions of $Fe(CN)_5H_2O^{3-}$ and ligand substitution reactions of $Fe(CN)_5L^{(3+n)-}$ urged us to investigate the pressure dependence of a series of complex formation reactions. A systematic study of the effect of pressure on related reactions has contributed to the elucidation of the mechanisms of many inorganic and organometallic processes.[20,21] For this purpose we selected a series of complex formation reactions of $Fe(CN)_5H_2O^{3-}$ with neutral and negatively charged entering ligands in order to avoid significant ion-pairing effects and to distinguish between the limiting D or I_d nature of the mechanism; i.e. does the reaction involve the formation of an intermediate or not, respectively? The results of this study clearly demonstrate that all substitution processes on the pentacyanoferrate(II) center follow a limiting D mechanism.

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Table I. Rate Data as a Function of Pressure for the Complex Formation of $Fe(CN)_5H_2O^{3-}$ According to the Overall Reaction[a]

$$Fe(CN)_5H_2O^{3-} + L^{r-} \xrightarrow{k} Fe(CN)_5L^{(3+n)-} + H_2O$$

L^{r-}	P, MPa	k_{obs},[b] s^{-1}	k,[c] $M^{-1} s^{-1}$	ΔV^*, $cm^3 mol^{-1}$	remarks
imidazole	5	1.21 ± 0.11	242	$+15.5 \pm 0.7$	$\mu = 0.1$ M, neutral pH
	50	0.93 ± 0.07	186		
	75	0.80 ± 0.05	160		
	100	0.66 ± 0.04	132		
histidine	10	3.00 ± 0.30	300	$+17.0 \pm 0.4$	$\mu = 0.1$ M, pH = 7.5
	40	2.46 ± 0.23	246		
	70	1.97 ± 0.18	197		
	100	1.63 ± 0.15	163		
methionine	10	4.69 ± 0.70	469	$+17.9 \pm 0.6$	$\mu = 0.1$ M, pH = 6.5
	40	3.85 ± 0.58	385		
	70	3.07 ± 0.47	307		
	100	2.46 ± 0.35	246		
glutathione (glut⁻)	10	1.85 ± 0.10	185	$+14.1 \pm 0.4$	$\mu = 0.5$ M, pH = 6.0
	25	1.70 ± 0.08	170		
	50	1.49 ± 0.09	149		
	75	1.30 ± 0.07	130		
	100	1.10 ± 0.05	110		
glycine (gly⁻)	10	1.13 ± 0.09	45.2	$+16.4 \pm 0.6$	$\mu = 0.1$ M, pH = 11.7
	40	0.90 ± 0.06	36.0		
	70	0.75 ± 0.05	30.0		
	100	0.62 ± 0.03	24.8		
β-alanine (β-ala⁻)	10	1.51 ± 0.10	60.4	$+16.8 \pm 0.2$	$\mu = 0.1$ M, pH = 11.7
	40	1.24 ± 0.08	49.6		
	70	1.01 ± 0.07	40.4		
	100	0.82 ± 0.05	32.8		

[a] Temperature = 25.0 °C; $[L^{r-}]$ = 0.005 – 0.025 M; for further experimental conditions see text. [b] Mean value of between four and six kinetic runs. [c] $k = k_{obs}/[L^{r-}]$.
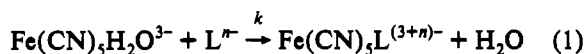
Experimental Section

Materials. β-Alanine, glycine, L-methionine, L-histidine, glutathione, and imidazole were obtained from Sigma and used as supplied. All other chemicals were of analytical reagent grade. Solutions of aquapentacyanoferrate(II) were freshly prepared by dissolving $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ in Ar-saturated deionized water or buffer (NaOH–citrate) to yield concentrations of 5×10^{-5} or 1×10^{-4} M. A ligand solution at the desired pH and ionic strength (0.1 or 0.5 M, adjusted with $LiClO_4$) was mixed with the $Fe(CN)_5H_2O^{3-}$ solution of the same pH and ionic strength. The final pH for the reactions with the anionic form of the amino acids was around 11.7, but for the other ligands it was between 6.0 and 7.5. All solutions were deoxygenated with Ar before use. Kinetic measurements were performed under pseudo-first-order conditions, i.e. at a 50–200-fold excess of the ligand.

Instrumentation. UV–vis absorption spectra were recorded on a Shimadzu UV-250 spectrophotometer. pH measurements were performed on a Metrohm 632 pH meter equipped with a Sigma glass electrode. Kinetic measurements at ambient pressure were performed on a Durrum D110 stopped-flow instrument and at pressures up to 100 MPa on a homemade high-pressure stopped-flow unit.[22] Both instruments were thermostated to within ±0.1 °C and attached to an on-line data acquisition system.[23] The complex formation reactions were followed at 440 nm (imidazole and glutathione), 450 nm (histidine and methionine), and 455 nm (glycine and β-alanine). Experimental conditions were selected according to those adopted before in the ambient pressure studies.[6-8]

Results and Discussion

Complex formation reactions of $Fe(CN)_5H_2O^{3-}$ with the series of ligands (glutathione, imidazole, and some amino acids) investigated in this study exhibit excellent pseudo-first-order behavior for at least 3 half-lives of the reaction. Thus the rate law for the overall reaction (1) is given by the expression $k_{obs} = k[L^{r-}]$. Preliminary experiments demonstrated that plots of k_{obs} versus $[L^{r-}]$ are indeed linear and go through the origin, in agreement with that reported in the literature.[6-8] The slopes of

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$$Fe(CN)_5H_2O^{3-} + L^{r-} \xrightarrow{k} Fe(CN)_5L^{(3+n)-} + H_2O \quad (1)$$

such plots at ambient pressure were in good agreement with the values of k reported elsewhere.[6-8] No saturation effect could be observed in plots of k_{obs} versus $[L^{r-}]$ at high $[L^{r-}]$. In addition, there is good reason to believe that $Fe(CN)_5H_2O^{3-}$ is the only reactive iron(II) species under our selected conditions: i.e. no deprotonation of the coordinated water molecule occurs (see ref 8 for a detailed account).

Subsequently, the pressure dependence of these reactions was studied and the experimental conditions were selected according to those adopted in the ambient-pressure studies.[6-8] Under these conditions the reactions do no exhibit a significant pH dependence, such that no complications due to a possible change in pH at elevated pressure are to be expected. In order to check this, some reactions were repeated in the absence and presence of the buffers employed, without any markable effect on the observed pressure dependencies. The results are summarized in Table I, and plots of ln k versus pressure were linear in all cases, such that ΔV^* could be calculated from the slope ($=-\Delta V^*/RT$) using a standard least-squares fitting routine. For all the studied systems, k decreases significantly with increasing pressure, which results in a significantly positive ΔV^* value between 14 and 18 $cm^3 mol^{-1}$. These values are summarized, along with the available rate and thermal activation parameters (ΔH^* and ΔS^*) taken from the literature,[6-8] in Table II.

The results in Table II reveal the trend referred to above,[8] namely that k decreases with increasing charge on L^{r-}. This is not accompanied by a specific trend in ΔH^* and ΔS^*. The latter value is positive (between 12 and 54 J K^{-1} mol^{-1}) for most of the reactions, but negative for two systems. The values of ΔV^* are substantially positive for all available systems. In terms of the I_d mechanism suggested before,[2,8,14,15] i.e. route 1–2–4 in Scheme I, $k = k_2K_1$ such that $\Delta V^*(k) = \Delta V^*(k_2) + \Delta \bar{V}(K_1)$. The decrease in k with increasing negative charge on L^{r-} must mainly be due to a decrease in K_1 expected for this mechanism. The values of K_1 and $\Delta \bar{V}(K_1)$ cannot be determined experimentally from the kinetic data due to the absence of a significant curvature in the

Table II. Activation Parameters for Complex Formation of $Fe(CN)_5H_2O^{3-}$

$$Fe(CN)_5H_2O^{3-} + L^{r-} \xrightarrow{k} Fe(CN)_5L^{(3+n)-} + H_2O$$

L^{r-}	k (25 °C), M^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$ (25 °C), cm^3 mol^{-1}	remarks	ref
CN^-	30	76.9	+42	+13.5 ± 1.5	μ = 1.0 M	24
imidazole	240	63.5	+13	+15.5 ● 0.7	μ = 0.1 M	7, b
glut$^-$	219	76.1	+54	+14.1 ± 0.4	μ = 0.5 M, pH = 6.0	6, b
histidine	315	64.4^a	+21^a	+17.0 ± 0.4	μ = 0.1 M, pH = 7.5	7, b
methionine	535	69.8^a	+42^a	+17.9 ± 0.4	μ = 0.1 M, pH = 6.5	8, b
gly$^-$	28	61.4	−13	+16.4 ± 0.6	μ = 0.1 M, pH = 11.7	7, b
β-ala$^-$	57	59.8	−10	+16.8 ± 0.2	μ = 0.1 M, pH = 11.7	8, b

^{a} pH = 8–9. ^{b} This work.

plots of k_{obs} versus [L^{r-}], and can only be calculated using the extended Fuoss equation (2)[25] and our eq 3,[26] which is an improvement of the Hemmes equation[27] to allow for ionic strength effects (in SI units). In these expressions a is the contact distance

$$K_1 = {}^4/_3\pi a^3 N_A \exp(-W/RT) \qquad (2)$$

where

$$W = Z_1 Z_2 e_0^2 N_A / 4\pi\epsilon_0\epsilon a(1 + \chi a)$$

and

$$\chi = (2e_0^2 N_A \mu / \epsilon_0 \epsilon k_B T)^{1/2}$$

$$\Delta\bar{V}(K_1) = -RT\left\{\frac{Z_1 Z_2 e_0^2[\delta + 0.5a\chi(\delta + \beta)]}{4\pi\epsilon_0\epsilon k_B Ta(1 + a\chi)^2} + \beta\right\} \qquad (3)$$

of the ions (sum of radii $a = r_1 + r_2$), Z_1 and Z_2 are the charges on the ions, e_0 is the electronic charge, ϵ_0 is the permittivity of vacuum, ϵ is the bulk dielectric constant, χ is the reciprocal Debye–Hückel length, and μ is the ionic strength. For aqueous solutions at 25 °C, ϵ = 78.5, χ = 3.29$\sqrt{\mu}$ nm^{-1} with μ in mol dm^{-3},[27] δ = $(\partial \ln \epsilon/\partial p)_T$ = 4.71 × 10^{-4} MPa^{-1},[28] β = $(\partial \ln \rho/\partial p)_T$ = 4.52 × 10^{-4} MPa^{-1},[29] and R = 8.314 MPa cm^3 mol^{-1} K^{-1}. Ionic radii of 0.45 nm for $Fe(CN)_5(H_2O)^{3-}$[30] and 0.25 nm for L^-[31] were used to calculate at 25 °C and 0.1 M ionic strength: electronic work W = 4.4 kJ mol^{-1}, K_1 = 0.15 M^{-1}, and $\Delta\bar{V}(K_1)$ = −4.7 cm^3 mol^{-1}. These values are quite reasonable since ion-pair formation between ions of the same sign should be very weak and accompanied by a volume contraction due to an increase in electrostriction resulting from charge concentration. Such calculated values are in general in good agreement with directly measured values.

For neutral ligands, $Z_1 Z_2$ = 0 and eqs 2 and 3 become formally K_1 = $4\pi a^3 N_A/3$ and $\Delta\bar{V}(K_1)$ = −$RT\beta$. In our case K_1 = 0.87 M^{-1} and $\Delta\bar{V}(K_1)$ = −1.1 cm^3 mol^{-1}. Which such a small (close to zero) value of $\Delta\bar{V}(K_1)$, the experimentally determined values of $\Delta V^{\ddagger}$ (Table II) should mainly represent $\Delta V^{\ddagger}(k_2)$. In the case of mononegative ligands, L^-, $\Delta V^{\ddagger}(k_2)$ must be a bit more positive than the experimental $\Delta V^{\ddagger}$ in order to compensate for the $\Delta\bar{V}(K_1)$ value of −4.7 cm^3 mol^{-1} given above. This means that the $\Delta V^{\ddagger}(k_2)$ will have values between +15 and +22 cm^3 mol^{-1} for the ligands given in Table I, which are too high[21,32] for an interchange reaction step that mainly involves the partial dissociation of a solvent molecule in terms of an I_d mechanism.[8]

The alternative, dissociative (D) reaction route 1–3–4 represents a more realistic fit of the data. For this mechanism $k = k_3 k_4/k_{-3}$ and the decrease in k with increasing negative charge on L^{r-} must mainly be due to a decrease in k_4 resulting from charge repulsion. The expression for k results in $\Delta V^{\ddagger}$ = $\Delta V^{\ddagger}(k_3)$ + $\Delta V^{\ddagger}(k_4)$ − $\Delta V^{\ddagger}(k_{-3})$, for which $\Delta V^{\ddagger}(k_3)$ will be a common contribution independent of L^{r-}. The degree of bond formation during the reactions of $Fe(CN)_5^{3-}$ with H_2O (k_{-3}) and L^{r-} (k_4) will to some extent determine the corresponding values of $\Delta V^{\ddagger}(k_{-3})$ and $\Delta V^{\ddagger}(k_4)$, but since both processes involve a coordinatively unsaturated complex, the reactions should be strongly associative and accompanied by significantly negative $\Delta V^{\ddagger}$ values. The difference $\Delta V^{\ddagger}(k_4)$ − $\Delta V^{\ddagger}(k_{-3})$ could then be close to zero, such that the experimental $\Delta V^{\ddagger}$ mainly represents $\Delta V^{\ddagger}(k_3)$. This is quite realistic since the experimental $\Delta V^{\ddagger}$ values exhibit no significant dependence on the nature of L^{r-} and are close to the theoretical value of +13 cm^3 mol^{-1} expected for the dissociation of a water molecule from the octahedral complex.[19] Thus the activation volumes reported in this study urge us to suggest that for neutral and monoanionic ligands all substitution reactions of pentacyanoferrate(II) complexes follow a limiting D mechanism.

We now turn to an analysis of the arguments presented earlier[6–8] in favor of an I_d (or D_{IP}) instead of a D mechanism for the substitution of a coordinated water molecule by neutral and monoanionic ligands.[2,8] A limiting D mechanism was discarded on the basis that an interaction distance of approximately 4 Å is required to explain a 10-fold decrease in specific rate in going from a neutral to a monanionic ligand on the basis that k_4 represents a diffusion-controlled process in the limiting situation.[2,8] The calculations for the distance of interaction in terms of an I_d mechanism resulted in 6–7 Å, which is much more reasonable than the value calculated on the basis of a diffusion-controlled process.[8] However, we do not support the claim that k_4 is a diffusion-controlled process. In addition, the reverse reaction step, k_{-2} or k_{-4}, must involve the formation of an intermediate since this step is independent of the nature of the entering ligand.[2,4,8,12,13] The large positive volumes of activation reported for the dissociation of $Fe(CN)_5L^{(3+n)-}$ [12,13] support the operation of a limiting D mechanism in which either $Fe(CN)_5^{3-}$ or $Fe(CN)_5H_2O^{3-}$ is the reactive intermediate, depending on the efficiency of the scavenging nucleophile and the lifetime of the five-coordinate $Fe(CN)_5^{3-}$ species. In terms of the reverse aquation reaction in Scheme I, the intermediate must be the $Fe(CN)_5^{3-}$ species since no scavenging ligand other than water is present. However, this conclusion is not in line with the principle of microscopic reversibility, since forward and reverse reaction steps cannot proceed according to different mechanisms involving different transition states. The only reasonable explanation is that all substitution processes of pentacyanoferrate(II) complexes follow a limiting D mechanism. The limiting rate constant (k_3) cannot be reached experimentally for the forward reaction in Scheme I (route 1–3–4), as for the reverse reaction (see above), since the leaving ligand (water) is present in a too large excess, as it is the solvent for the system.

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At this point we would like to refer to the present discussion in the literature concerning the differentiation between I_d and D mechanisms.[33] In terms of the accepted nomenclature, an I_d mechanism refers to a reaction sequence in which no intermediate is formed, whereas a D mechanism involves the formation of an intermediate. There are cases known where such an intermediate is short enough lived to feel the influence of the leaving group, and a D_l nomenclature has been suggested.[33] Nevertheless, the process is still basically D in character and should be characterized by significantly more positive ΔV^* values than in the case of an I_d mechanism. Finally, we see no realistic reason why the substitution reactions of $Fe(CN)_5H_2O^{3-}$ cannot follow a limiting D mechanism when the reactions of $Fe(CN)_5L^{(3+n)-}$, where L^{n-}

is a much stronger nucleophile than H_2O, do follow such a mechanism. Differentiation between a limiting D or a D_{IP} mechanism for complex formation (anation) reactions of $Fe(CN)_5H_2O^{3-}$ will only be possible for systems that show strong ion-pair formation, as mentioned above,[2,8] such that a limiting rate constant can be reached at high nucleophile concentrations. Whether ΔV^* measurements can throw more light on the differentiation between these two possibilities will be studied in more detail in a future investigation.

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