most likely factor directly affecting changes in the rate of electron transfer.

According to theory, the heterogeneous electron-transfer rate constant, k_s, is independent of the polarizer concentration.[9] Thus, the concentration dependence of k_s observed in Table II seems to imply that the measured rate of electron transfer is only a conditional rate constant that has incorporated into it rates of both the spin conversion process and the actual heterogeneous electron transfer. This is further implied by the constancy of the term $k_s/\%\ \mathrm{Fe(III)}_{hs}$ for four of the five compounds studied.

The trend of the rate constant increase with the increase in high-spin population strongly points to an overall electron-transfer mechanism that involves a partially rate-determining spin conversion of Fe(III) prior to electron transfer, i.e. reaction 3, and not reaction 2. It is somewhat surprising, however, that the mechanism appears to be identical for all of the complexes of the $[\mathrm{Fe^{III}(X\text{-}Sal)_2trien}]^+$ series. However, this apparent rate-determining spin-conversion step does not seem consistent with the known relative rates of spin crossover and electron transfer measured in these systems, since rate constants for spin conversion are in the range of 10^7–10^8 s^{-1} in the bulk of solution while those for electron-transfer are 2.4 × 10^{-2} to 4.7 × 10^{-2} cm/s. (With the assumption of a reaction-layer thickness of 10 Å this corresponds to an electron-transfer rate constant of 2.4 × 10^5 to 4.7 × 10^5 s^{-1}.) Clearly this ~10^5-s^{-1} electron-transfer rate is much slower than the measured spin-conversion process, which, therefore, should not be rate determining. For this to be competitive with spin-conversion rates in the bulk of solution, a measured heterogeneous rate constant of 1–10 cm/s would be necessary.

Rates for spin conversion were measured in the absence of supporting electrolyte, and it is possible that the addition of 0.1 M TBAP as supporting electrolyte slows down the rate under our electrochemical conditions. This change, however, should not be large. A more plausible explanation is that the rate of spin conversion is slower at the electrode surface than in the bulk of solution. This decrease in the rate could possibly occur if there were an interaction between the electrical field in the Helmholtz reaction layer and the magnetic field of the diffusing species.[13] Since the data in Table II clearly suggest that spin conversion at the electrode surface is slower than in the bulk of the solution, it is reasonable to conclude that the CE mechanism as shown in reaction 3 is the actual mechanism in the electrochemical reduction of these spin-equilibrium complexes.

In conclusion, it appears from this study that the actual rate of spin conversion may be slowed down at the electrode surface such that the rates become competitive with the heterogeneous electron-transfer rates. If this is generally true, this should enable the electrochemical study of a large number of spin-equilibrium systems in which, at first thought, the spin-conversion rates appear to be too fast for observation by electrochemical methodologies. Several of these systems are now under further investigation.

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Registry No. $[\mathrm{Fe^{III}(5\text{-}OCH_3\text{-}Sal)_2trien}]^+$, 74111-31-2; $[\mathrm{Fe^{III}(3\text{-}OCH_3\text{-}Sal)_2trien}]^+$, 60371-34-8; $[\mathrm{Fe^{III}(Sal)_2trien}]^+$, 60351-91-9; $[\mathrm{Fe^{III}(3\text{-}NO_2\text{-}Sal)_2trien}]^+$, 74111-33-4; $[\mathrm{Fe^{III}(5\text{-}NO_2\text{-}Sal)_2trien}]^+$, 74111-29-8.

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Contribution from the Istituto di Chimica Analitica ed Elettrochimica, University of Pisa, 56100 Pisa, Italy, and the Istituto di Chimica Analitica, University of Turin, 10125 Turin, Italy

Complex Formation between Iron(III) and Highly Charged Ligands: Equilibria and Reaction Mechanisms

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The kinetics and equilibria of the complexation of iron(III) by the highly charged nonbasic ligands $\mathrm{Fe(CN)_6}^{3-}$, $\mathrm{Co(CN)_6}^{3-}$, and $\mathrm{Mo(CN)_8}^{4-}$ have been investigated in aqueous solution at 25 °C. The stability constants of the 1:1 complexes have been measured and found to be independent of the hydrogen ion concentration but highly sensitive to ionic strength effects. For the system involving octacyanomolybdate ion also a dinuclear complex $\mathrm{Fe_2Mo(CN)_8}^{2+}$ has been detected from both equilibria and kinetics and its stability constant has been measured. This study provides a rather rare example of kinetic evaluation of the equilibrium constants for the formation of outer-sphere complexes from labile aquo ions (K_{os}) and of the ratios between the species associated in the inner-sphere and in the outer-sphere state (K_{is}). The reaction mechanism is discussed in terms of associative interchange and the hypothesis that this mode of activation could be characteristic of all complex formation processes involving tervalent aquo cations is advanced.

Introduction

The basic mechanism for the formation of complexes from solvated cations and ligands is represented in (1), where K_{os}

$$\mathrm{M(H_2O)}_x + \mathrm{L} \overset{K_{os}}{\rightleftharpoons} \mathrm{M(H_2O)}_x,\ \mathrm{L} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{M(H_2O)}_{x-1}\mathrm{L} + \mathrm{H_2O} \quad (1)$$

is an outer-sphere association constant and k_1 is the specific rate at which the ligand changes place with a solvent molecule in the inner coordination shell of the metal ion.[1] k_{-1} is the rate constant for the (reverse) step of aquation.

Provided that the first of the two equilibria in (1) is fast in comparison with the second, the system exhibits only one relaxation time which is given by relationship[2] 2. In most

$$\frac{1}{\tau} = \frac{K_{os}k_1(|\mathrm{M}| + |\mathrm{L}|)}{1 + K_{os}(|\mathrm{M}| + |\mathrm{L}|)} + k_{-1} \quad (2)$$

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* To whom correspondence should be addressed at the University of Pisa.

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of the systems investigated the experimental conditions are such that the inequality, $K_{os}(|M| + |L|) << 1$, holds and (2) is thus reduced to (3). When rate laws of the form of (3)

$$\frac{1}{\tau} = K_{os}k_1(|M| + |L|) + k_{-1} \qquad (3)$$

are found (and this happens frequently), there is no hope of obtaining the value of K_{os} from kinetic experiments[3] and the only way to estimate this quantity is to calculate it by using some equation based on the theory of electrolyte solutions.[4,5] This procedure suffers from the restrictions due to the arbitrary choice of *a* and *d*, the distances from the central ion which limit the field of existence of the ion pairs.[6]

On the other hand, when highly charged reactants are involved, the value of K_{os} may well become so high that the full rate law (2) might hold. When this is the case, a kinetic evaluation of the stability constant of outer-sphere complexes is made possible.[7-9]

Finally when the inequality $K_{os}(|M| + |L|) >> 1$ is applicable,[10,11] the reciprocal relaxation time is made independent of the concentration of the reactants and (2) is reduced to $1/\tau = k_1 + k_{-1}$.

With this study on the complexation of iron(III) by highly charged nonbasic ligands, we have intended to obtain a kinetic evaluation of K_{os} and, in the mean time, to throw more light on the kinetics of complex formation at iron(III) which, though one of the most widely investigated, is still one of the least well understood.[12]

Experimental Section

Chemicals. A stock solution of iron(III) perchlorate was prepared by dissolving a weighed amount of the pure metal into a known excess of perchloric acid. Complete oxidation was achieved by dropwise addition of hydrogen peroxide to the solution containing a mixture of iron(II) and iron(III). The unreacted H_2O_2 was removed by decomposition at boiling temperature. The resulting $Fe(ClO_4)_3$ solution was analyzed by titration with EDTA and Tiron as indicator. The content in iron was found in excellent agreement with the value derived from the weight of dissolved metal.

Potassium hexacyanocobaltate (later referred as HCC) was prepared according to the procedure described by Bigelow[13] and twice recrystallized from water.

Potassium octacyanomolybdate (OCM) was prepared as reported in the literature[14] and twice recrystallized from water.

Potassium hexacyanoferrate (HCF) and other chemicals (Erba) were of analytical grade and were used without further purification.

Conductivity water was used to prepare the solutions and used as a reaction medium. The desired acidities were obtained by addition of $HClO_4$, and the ionic strength was adjusted with $NaClO_4$.

Instrumentation. Spectrophotometric equilibrium data were obtained with a Perkin-Elmer E 200 spectrophotometer.

Kinetic measurements were performed on a Durrum stopped-flow apparatus. Mean values of at least four replicated runs were taken, and the maximum spread was within 10%, usually much less. The temperature was 25.0 ± 0.1 °C throughout.

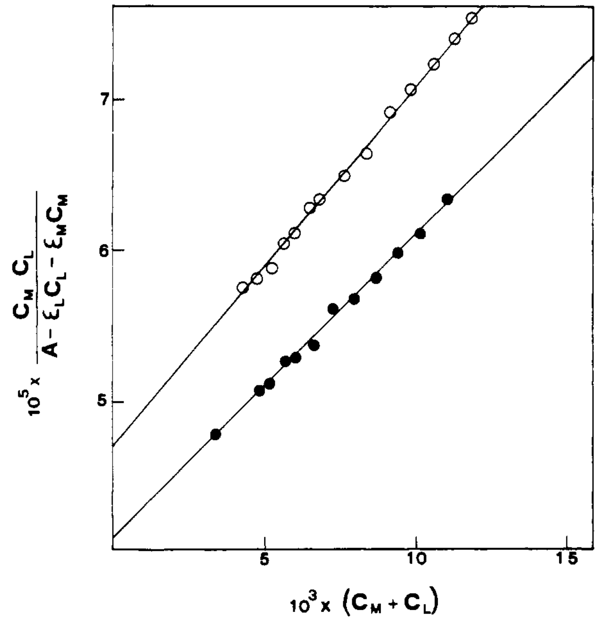

Figure 1. Plots of $C_MC_L/(A - \epsilon_LC_L - \epsilon_MC_M)$ as a function of $(C_M + C_L)$ for Fe/L systems at 25 °C and I = 0.5 M ($HClO_4$): $L^{3-} = Fe(CN)_6^{3-}$, λ = 500 nm (●); $L^{3-} = Co(CN)_6^{3-}$, λ = 380 nm (○).

Table I. Spectrophotometric Values of Equilibrium Constants K_1 (M^{-1}) for the Reaction $Fe^{3+} + Fe(CN)_6^{3-} \rightleftharpoons FeFe(CN)_6$ at Different Acidities and Ionic Strength (λ = 500 nm, T = 25 °C)

	I		
$|H^+|$	0.3	0.5	1.0
0.1			21[a]
0.3	81 ± 4		
0.5		48 ± 2	24 ± 1
1.0			26 ± 1

[a] T = 26 °C, from ref 17.

Table II. Spectrophotometric Values of the Equilibrium Constant K_1 (M^{-1}) for the Reaction $Fe^{3+} + Co(CN)_6^{3-} \rightleftharpoons FeCo(CN)_6$ at Different Acidities and Ionic Strengths (λ = 380 nm, T = 25 °C)

	I		
$|H^+|$	0.3	0.5	1.0
0.3	163 ± 10		
0.5		64 ± 4	47 ± 2
1.0			42 ± 2

Results

Equilibrium Studies. Absorbance measurements were performed to determine the stability constants of complexes of iron(III) with hexacyanoferrate (HCF), hexacyanocobaltate (HCC), and octacyanomolybdate (OCM). These ligands are unprotonated in the range of acidity (0.3–1 M) of our experiments and their formulas and charges are $Fe(CN)_6^{3-}$, $Co(CN)_6^{3-}$, and $Mo(CN)_8^{4-}$. Reactions of iron(III) with HCF and HCC lead to formation of 1:1 complexes. Since the classical methods of determination of equilibrium constants do not enable us to distinguish between outer-sphere and inner-sphere associated species, only an overall constant K_1 as defined in (4) can be determined[10-12] from absorbance measurements of systems as in (1). By keeping the analytical concentrations of metal and ligand (C_M and C_L) sufficiently

$$K_1 = \frac{|ML|_T}{|M||L|} = \frac{|M,L| + |ML|}{|M||L|} \qquad (4)$$

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(3) In principle K_{os} can be obtained as a ratio of the forward to the reverse rate constant relevant to the first association step in (1). Ultrasonic experiments can be operated on a sufficiently short time scale to detect the fast preassociation of the reactants and to measure the relaxation time pertinent to such a process (Burgess, J. "Metal Ions in Solution"; Ellis Horwood: Chichester, England, 1978; p 349).

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(14) Furman, N. H.; Miller, C. O. *Inorg. Synth.* **1950**, *3*, 160.

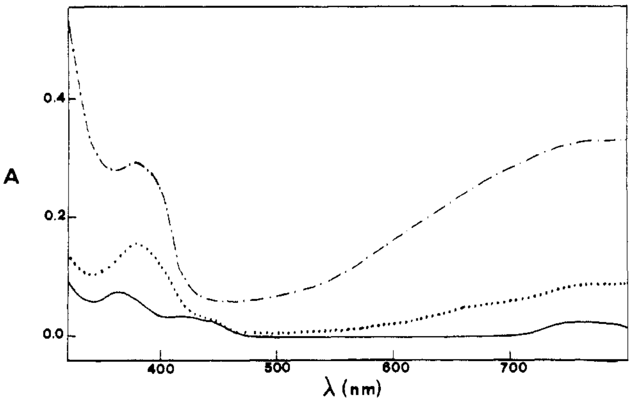

Figure 2. Spectral characteristics of the Fe/Mo(CN)$_8^{4-}$ system: $C_L = 4 \times 10^{-4}$ M, $C_M = 0$ (—); $C_L = 4 \times 10^{-4}$ M, $C_M = 4 \times 10^{-4}$ M (…); $C_L = 4 \times 10^{-4}$, $C_M = 10^{-2}$ M (-·-).

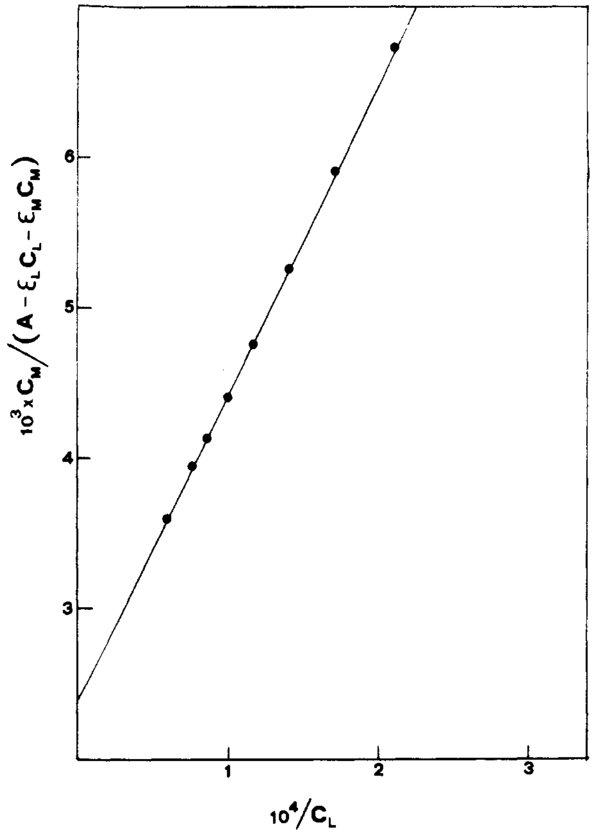

Figure 3. Plot of $C_M/(A - \epsilon_M C_M)$ as a function of $1/C_L$ for the Fe/Mo(CN)$_8^{4-}$ system ($I = 0.3$ M (HClO$_4$), $T = 25$ °C, $\lambda = 600$ nm).

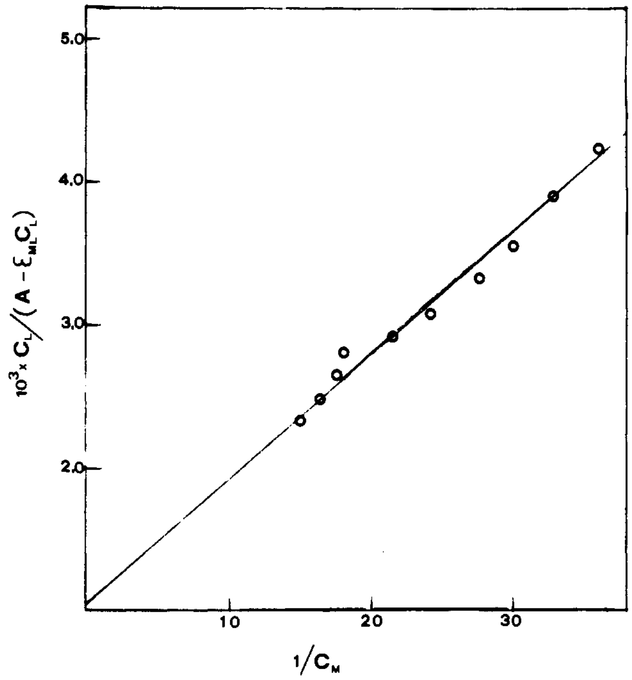

Figure 4. Plot of $C_L/(A - \epsilon_L C_L - \epsilon_{ML} C_L)$ against $1/C_M$ for the Fe/Mo(CN)$_8^{4-}$ system ($T = 25$ °C, $\lambda = 600$ nm).

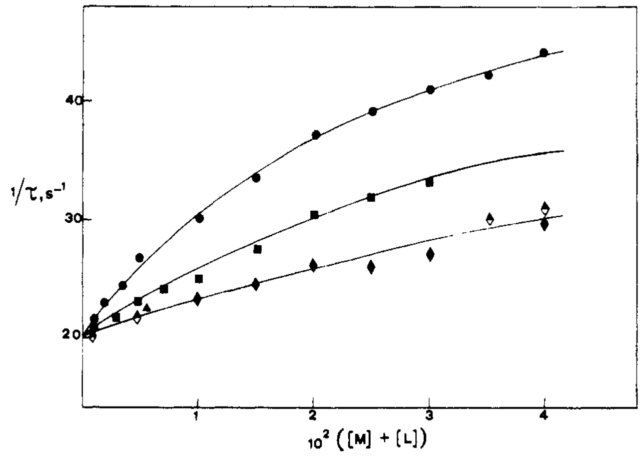

Figure 5. Plot of $1/\tau$ as a function of (|M| + |L|) for the Fe/Fe(CN)$_6^{3-}$ system ($T = 25$ °C): (solid circle) $I = 0.3$ M (HClO$_4$), (solid square) $I = 0.5$ M (HClO$_4$), (solid diamond) $I = 1$ M (HClO$_4$), and (half-solid diamond) $I = 1$ M (0.5 M HClO$_4$ + 0.5 M NaClO$_4$). The data at (|M| + |L|) < 0.01 M have been obtained under conditions of concentration or ionic strength jump.

low in order to avoid a large extent of complexation, the variation of absorbance, A, with the reactant concentration is given by expression[15] 5 where $\Delta\epsilon = \epsilon_{ML_T} - \epsilon_M - \epsilon_L$. Values

$$\frac{C_M C_L}{A - \epsilon_M C_M - \epsilon_L C_L} = \frac{1}{K_1 \Delta\epsilon} + \frac{1}{\Delta\epsilon}(C_M + C_L) \qquad (5)$$

of K_1 are obtained from the ratios of slope to intercept of straight lines as those of Figure 1 for the Fe/HCF and Fe/HCC systems and are reported in Tables I and II.

The reaction of iron(III) with octacyanomolybdate is more complex. The spectral features of this system, which are shown in Figure 2, indicate that a complex of higher nuclearity is also formed. From both static and kinetic experiments, we have inferred that the two equilibria (6) and (7) are operating except

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad (6)$$

$$\mathrm{ML} + \mathrm{M} \rightleftharpoons \mathrm{M_2L} \qquad (7)$$

when $C_L >> C_M$. In this case, of course, equilibrium 7 is suppressed. The data in Figure 3 have been obtained under these conditions and are plotted according to the method of Hildebrand and Benesi.[16] From the ratio of intercept to slope one obtains $K_1 = (1.15 \pm 0.06) \times 10^4$ M^{-1} and from the intercept $\epsilon_{ML} = 418$ M^{-1} cm^{-1}.

In Figure 4 an analogous plot is shown for data obtained at $C_M >> C_L$. Under these conditions only equilibrium 7 is operating. From the ratio of the intercept to slope of the straight line of Figure 4 one obtains $K_2/K_1 = 12 \pm 1$ M^{-1}, and

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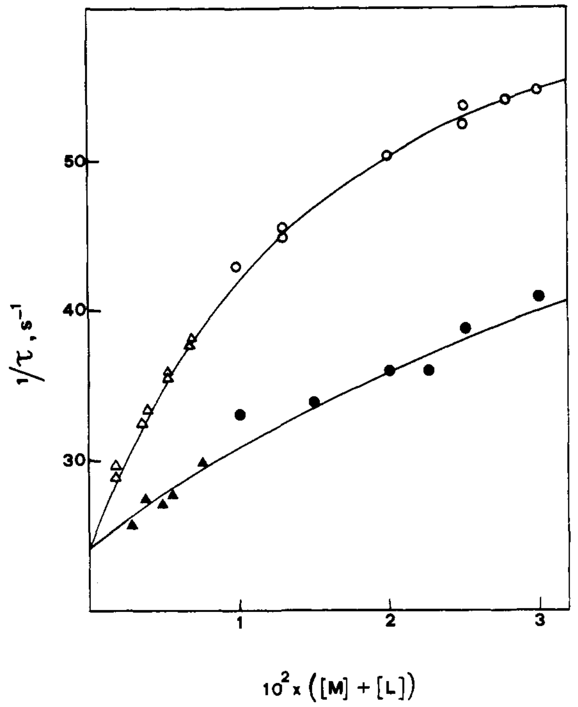

Figure 6. Plot of $1/\tau$ as a function of ($|M| + |L|$) for the Fe/Co(CN)$_6^{3-}$ system (T = 25 °C): △, ○, I = 0.3 M (HClO$_4$); ▲, ●, I = 1 M (HClO$_4$). Triangles refer to concentration-jump experiments.

Table III. Rate Constants (k_1, k_{-1}) and Stability Constants of Outer-Sphere Complexes for Reactions of Iron(III) with Highly Charged Ligands (T = 25 °C)

ligand	I	k_1, s^{-1}	k_{-1}, s^{-1}	K_{OS}, M^{-1}	K_1,^{b} M^{-1}	K_2, M^{-2}
Fe(CN)$_6^{3-}$	0.3	42	20	33	102	
	0.5	42	20	16	50	
	1.0	42	20	8	25	
	0.5^a	50^a	15^a	35^a		
Co(CN)$_6^{3-}$	0.3	51	24	55	172	
	1.0	51	24	15	47	
Mo(CN)$_8^{4-}$	0.3	410	10	260	1.1 × 10^4	1.4 × 10^5

^{a} I = 0.5 M. Reference 8. ^{b} Values obtained from (9).

from the known value of K_1 one derives $K_2 = (1.4 \pm 0.2) \times 10^{+5}$ M^{-2} and ϵ_{M_2L} 1.4 × 10^3 M^{-1} cm^{-1}.

Kinetic Studies. The experiments were carried out under conditions of concentration jump, ionic strength jump, and pseudo first order. Some experiments of complex decomposition were also performed, and the agreement between the different techniques was excellent. Figure 5 shows the results for the Fe/HCF system at different ionic strengths, and Figure 6 shows the results for the Fe/HCC system. In both cases the rates tend to a constant value at high concentrations of the reactants according to the rate law (2). Values of k_1, k_{-1}, and K_{os} are collected in Table III. It should be noted that (2) does not include the contribution of the hydrolized ion FeOH^{2+} despite its high reactivity. In the Appendix is shown that, since the ratio of the equilibrium constant of a 2–3 to a 3–3 outer-sphere complex is about 0.1, the path involving FeOH^{2+} represents only a small fraction of the overall reaction. Table III shows that k_1 and k_{-1} are independent of the ionic strength as expected for the interchange steps. The only parameter sensitive to changes in the ionic strength is K_{os}. Therefore plots of $1/\tau$ as a function of $K_{os}(|M| + |L|)/(1 + K_{os}(|M| + |L|)$ at the three ionic strengths must lie on a single straight line as shown in Figure 7. From slope and intercepts one obtains $k_1 = 42.2 \pm 0.2$ s^{-1} and $k_{-1} = 19.9 \pm 0.1$ s^{-1} for the system Fe/HCF whereas $k_1 = 49.5 \pm 0.2$ s^{-1} and $k_{-1} = 24.6 \pm 0.1$ s^{-1} for the system Fe/HCC.

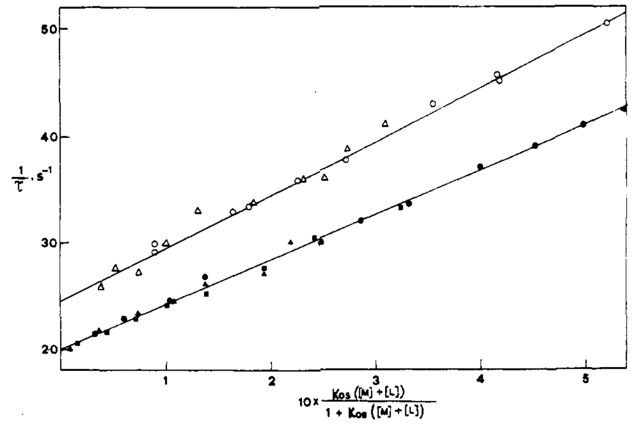

Figure 7. Plots of $1/\tau$ as a function of $K_{os}(|M| + |L|)/(1 + K_{os}(|M| + |L|))$ for the Fe/HCF system at ionic strengths 0.3 (●), 0.5 (■), and 1 M (▲) and for the Fe/HCC system at ionic strengths 0.3 (○) and 1 M (△).

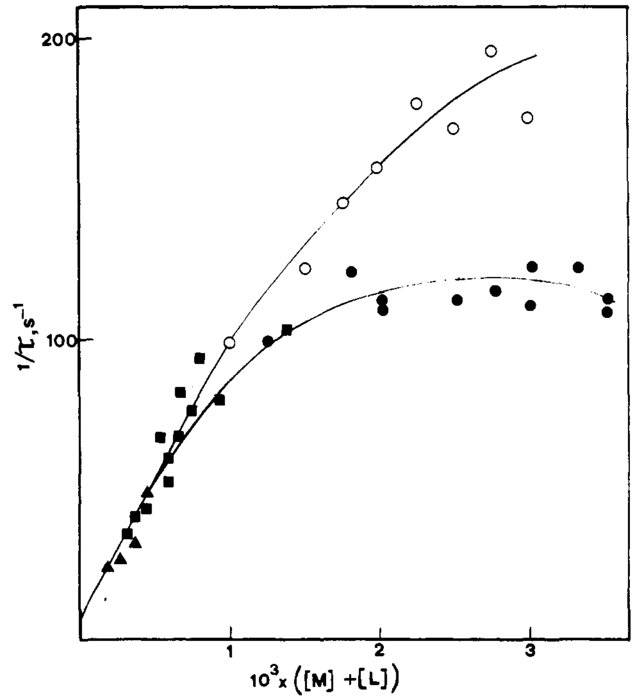

Figure 8. Plot of $1/\tau$ as a function of ($|M| + |L|$) for the Fe/Mo(CN)$_8^{4-}$ system (T = 25 °C, I = 0.3 M (HClO$_4$)): ○, $C_L >> C_M$; ●, $C_M >> C_L$; ■, concentration jump; ▲, ionic strength jump.

The reaction of iron(III) with OCM exhibits a more complex behavior as shown in Figure 8. At comparatively low values of ($|Fe^{3+}| + |L^{4-}|$) the results lie on the same curve both for $C_L > C_M$ and $C_M > C_L$. At higher concentrations of the reactants the rate tends to level off as in the other two system for $C_L > C_M$ whereas for $C_M > C_L$ the rate reaches a maximum value and then decreases.

This behavior can be rationalized if the formation of a triple ion is taken into account as in eq 3A of the Appendix. The relaxation treatment according to eq 3A leads to the kinetic equation (8). The values of the parameters have been computed by a least-squares analysis and are quoted in Table III.

$$\frac{1}{\tau} = \frac{k_1 K_{os}(|M| + |L|)}{1 + K_{os}(|M| + |L|) + K_2|M|^2} + k_{-1} \qquad (8)$$

Discussion

This study provides two pieces of information. The first is related to the chemistry of electrolyte interactions in the sense that the formation constant, K_{os}, of a solvent-separated ion pair is experimentally determined together with the ratio of concentrations of the inner- to outer-sphere complexes as obtained from k_1/k_{-1}. The second, which is of interest mainly to the kineticist, is concerned with the still unsettled question relevant to the mode of activation in complex-formation reactions involving tervalent cations.

Equilibrium Constants. As far as the overall equilibrium constants, K_1, are concerned, only the value obtained by Ibers and Davison[17] for the Fe/HCF system was available before the present study. This value, in excellent agreement with our results, is quoted in Table I.

A comparison between the results summarized in Tables I and II shows that the two ligands display a common behavior. The stability constants of both complexes $FeFe(CN)_6$ and $FeCo(CN)_6$ are similar and independent of $|H^+|$, whereas they change with ionic strength in the direction expected for interactions between appositely charged ions. The stability constant of $FeMo(CN)_8^-$ exceeds by ca. 2 orders of magnitude those of the above mentioned complexes. Such a difference cannot be entirely ascribed to the increase from 9 to 12 of the charge product. This change, at $I = 0.3$ M, makes the value of K_{os} for a 3–4 electrolyte only 5 times large than K_{os} for a 3–3 electrolyte.[4,5] The enhanced stability of $FeMo(CN)_8^-$ can be explained by assuming that the inner-sphere association is more extended in the system Fe/OCM than in Fe/HCF or Fe/HCC. This idea is confirmed by the kinetic results. Inner-sphere interaction is important also in the triple ion. In fact the formation constant of $Fe_2Mo(CN)_8^{2+}$ from Fe^{3+} and $FeMo(CN)_8^-$, K_2/K_1, exceeds by ca. 1 order of magnitude the value derived from electrostatic theories.[4,5]

As far as the equilibrium constants of the *individual* steps of complexation are concerned, these are related to the overall equilibrium constants through relationship[10–12] 9, where K_1 is defined by (4) whereas K_{os} and $K_{is} = k_1/k_{-1}$ are defined by (1).

$$K_1 = K_{os}(1 + K_{is}) \tag{9}$$

Singleton and Swinehart[8] derived from *T*-jump experiments a value of K_{os}, for the Fe/HCF system at $I = 0.5$ M, which is about twice our value (Table III). Our kinetic values of K_{os} agree with the electrostatic theory if the distance of closest approach, *a*, in the Fuoss equation is set at 7.6 Å for HCF, 6.8 Å for HCC, and 6.6 Å for OCM. These values of *a*, which are remarkably larger than the usual value of 5 Å, are nevertheless reasonable owing to the large sizes of the anions. In support to our finding we recall that conductance measurements give *a* values of 6.4–7.2 Å for[6] $LaFe(CN)_6$ and of 7.3 Å for[19] $LaCo(CN)_6$.

In Table III are also quoted values of K_1 computed with the help of (9). These are in excellent agreement with the spectrophotometric values despite the entirely different method of determination. The dynamic method, being able to distinguish between outer-sphere and inner-sphere association, must be considered far superior to the classical static methods in the study of solution equilibria. Considerable progress in the development of instruments for transient detection and recording has been made in recent years. As a consequence the dynamic technique promises to become a powerful new tool in analytical chemistry.[18]

Rate Constants. Singleton and Swinehart[8] derived for the Fe/HCF system at 25 °C and $I = 0.5$ M $k_1 = 50$ s^{-1} and $k_{-1} = 15$ s^{-1}. Contrary to our observation, they stated that the relaxation times are independent of the ionic strength. Walker and Watkins[20] in a subsequent study of the same system derived a value of 800 M^{-1} s^{-1} for the product $K_{os}k_1$. This, with $K_{os} = 35$ M^{-1} measured[8] under similar conditions, yields $k_1 = 22$ s^{-1}. For an interchange dissociative process at a given metal ion, k_1 must be independent of the nature of the ligand and corresponds to k^*, the rate constant for the process of water loss from the coordination shell of the metal ion.[1] According to Neely and Connick,[21] $k^* = {}^3/_4k_{\mathrm{H_2O}}$, where $k_{\mathrm{H_2O}}$ is the rate constant for the exchange of water between inner shell and bulk water. The more recent value[22] of $k_{\mathrm{H_2O}}$ is ca. 150 s^{-1}; therefore, k^* should be ca. 110 s^{-1}. The values of k_1 quoted in Table III do not agree with k^*. They are lower than k^* and close together for the two reactions involving HCF and HCC, whereas for the reaction with the larger OCM ion an enhancement of the rate of ligand penetration is observed.

The dependence of the rates of Fe^{3+} ion complexation on the ligand nature is not a novelty. For basic ligands the rate of substitution was found to be higher the more basic the ligand. It was suggested by Eigen[1] that the phenomenon was due to internal hydrolysis. Another explanation was that, owing to the "proton ambibuity",[23] the alternative path involving $FeOH^{2+}$ and the conjugate acid of the ligand cannot be ruled out and in such a case the experimental rate parameter *must* depend[24] on the p*K* of the entering group.[25] In reactions with nonbasic ligands both the above arguments break down and a rate constant for Fe^{3+} can be unambiguously obtained. In this case however no attempt has been made to draw a clear-cut correlation between reactivity and ligand properties. Yanasuga and Harada[26] explained the finding that Cl^- and Br^- react at $Fe(H_2O)_6^{3+}$ with rates different and both lower than that of water exchange by postulating the formation of a pentacoordinated intermediate $Fe(H_2O_5)^{3+}$ by fast loss of a water molecules. This may react selectively with different ligands in the rate-determining step. This picture requires that the rate of water exchange *should be* always higher than the rate of complexation, contrary to the evidence here given by the Fe/OCM system. In addition the energy for the bond Fe^{3+}–OH_2 is 116 kcal,[27] a value that, even taking account for solvation effects, makes the formation of $Fe(H_2O)_5^{3+}$ greatly disfavored. The most reasonable explanation of the different reactivities at $Fe(H_2O)_6^{3+}$ ion lies in the *associative* character of its mode of activation. If this is the case, a dependence of interchange rate constants k_1 on some property reflecting the nucleophilicity of the ligand must be observed.

In Figure 9 values of log k_1 for reactions of[26,28] Fe^{3+} with Cl^-, Br^-, and SCN^- are plotted against E_n, the electron donor constant,[30] and against *P*, the ligand polarizability.[31] For comparison the same plots have been drawn for reactions of V^{3+}, an ion whose tendency to react through an associative mechanism is well assessed.[29] The rates for both metal ions are well correlated.[32] The values of E_n for the three cyano-

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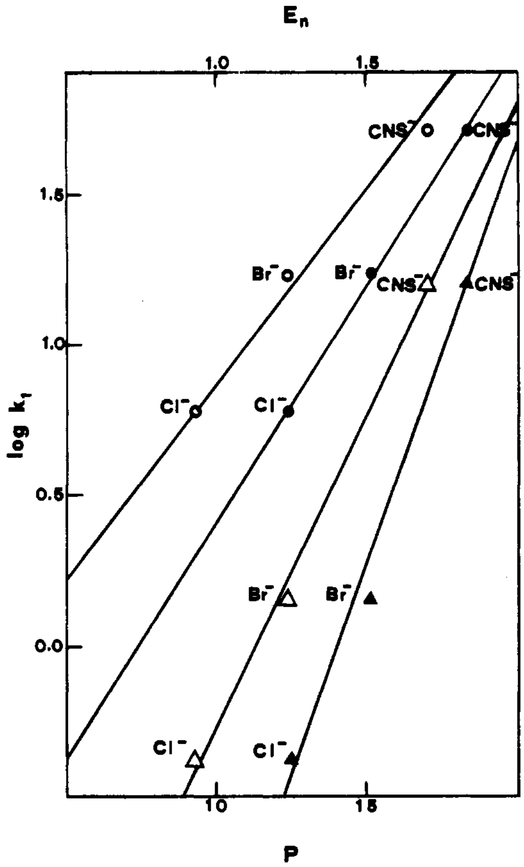


Figure 9. Plots of log k_1 for reactions of Fe(III) and V(III) with Cl⁻, Br⁻, and SCN⁻ against the electron-donor constant E_n (upper abscissa: ●, Fe(III); ▲, V(III)) and against the polarizability P (lower abscissa: ○, Fe(III); △, V(III)).

metalates are not available and are, on the other hand, hardly calculable since they should be based on the standard potentials for the half-reactions

$$2M(CN)_n^{x-} \rightleftharpoons M_2(CN)_{2n}^{2x-2} + 2e^-$$

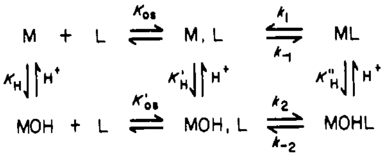
in which formations of dimers with highly improbable oxidation numbers are involved. Moreover, the species $Fe(CN)_6^{3-}$ and $Co(CN)_6^{3-}$, contrary to the halides, do not display any electron-donating ability, in case HCF and HCC are electron acceptors. For this reason we believe that the E_n scale is not suitable to represent the nucleophilicity of this class of ligand. On the other hand the polarizability, which generally increases as size increases, can be taken as a measure of the nucleophilic strength of these anions. Therefore, it is quite justified that the more polarizable OCM penetrates into the coordination shell of the $Fe(H_2O)_6^{3+}$ ion more rapidly than HCF and HCC which, being of about the same size, react at comparable rates.

In conclusion, from the analysis of the above presented results we infer that, in contrast with reactions of divalent metal ions (including $FeOH^{2+}$) whose mechanism of complexation is a dissociative interchange,[1] complex formation at Fe^{3+} undergoes an associative-interchange mode of activation. This conclusion is also supported by $\Delta S^{\ddagger} = -26$ eu for the Fe/HCF system[8] and by recent measurements of activation volumes for the binding of Cl⁻ and SCN⁻ to Fe^{3+}, which are[33] -4.5 and[34] 0 cm^3 mol^{-1}, respectively.

An inspection of the more recent literature shows that complex formation kinetics at tervalent cations such as Al(III),[35] Ga(III),[36] V(III),[29] Cr(III),[29] Mo(III),[29] and Ti(III)[29] are described, with various arguments and with rising enthusiasm, on the basis of associative interchanges. Particularly instructive is the shift from I_d to I_a mechanism when changing from $FeOH^{2+}$ to Fe^{3+}. The higher charge density of M^{3+} raises the energy required to dissociate the metal cation–water bond; hence, the dissociative mechanism becomes energetically less favored than the associative, in which the energy barrier is lowered through the formation of the new M^{3+}–L bond. This simple explanation, that has been given in some specific cases,[33,37] seems now to gain a general validity.

Appendix

(A) The reaction scheme given in (1) has to be extended to (1A) when the reaction path involving the hydrolyzed



$$\begin{tikzcd}
M + L \arrow[r, shift left, "K_{os}"] \arrow[d, shift right, "K_H"'] & M,L \arrow[l, shift left] \arrow[r, shift left, "k_{-1}"'] \arrow[d, shift right, "K_H'"'] & ML \arrow[l, shift left, "k_1"'] \arrow[d, shift right, "K_H''"'] \\
MOH + L \arrow[r, shift left, "K_{os}'"] \arrow[u, shift right, "H^+"'] & MOH, L \arrow[l, shift left] \arrow[r, shift left, "k_2"] \arrow[u, shift right, "H^+"'] & MOHL \arrow[l, shift left, "k_{-2}"] \arrow[u, shift right, "H^+"']
\end{tikzcd} \qquad (1A)$$

species MOH makes itself felt. The rate law for the scheme of (1A) is (2A), where $\alpha = 1 + K_H/|H^+|$, $\beta = 1 + K_H'/|H^+|$,

$$\frac{1}{\tau} = \frac{(k_1 + k_2(K_{os}'K_H/K_{os}|H^+|))K_{os}(|M| + |L|/\alpha)}{1 + K_{os}(|M| + |L|/\alpha)\beta} + \frac{k_{-1} + k_{-2}(K_H''/|H^+|)}{\gamma} \qquad (2A)$$

and $\gamma = 1 + K_H''/|H^+|$. The values of the first hydrolysis constant of the aquo cation $Fe(H_2O)_6^{3+}$, K_H, are 2.5, 1.98 and 2.0×10^{-3} at $I = 0.1$, 0.5, and 1 M, respectively.[38] Therefore, even at the lower investigated acidity (0.3 M) $\alpha \simeq 1$. On the other hand the ratio K_{os}'/K_{os}, calculated with the Fuoss equation, is ca. 0.1 at $I = 0.3$ M. Therefore, $K_H' = (K_{os}'/k_{os})K_H$ is ca. $0.1K_H$ and $\beta \simeq 1$.

In order to calculate the contribution of the path involving $FeOH^{2+}$, one can take $k_2 = 1.3 \times 10^3$ s^{-1}, which has been obtained for the iron(III)/HCF system,[20] and assume the same value also for the iron(III)/HCC system. Thus the term $k_2K_{os}'K_H/K_{os}|H^+|$ in (2A) gives a contribution to the forward reaction of only 2% at $|H^+| = 0.3$ M and less than 2% at $|H^+| = 0.5$ or 1 M. As far as the reverse path is concerned, plots of Figures 5 and 6 show that the intercept values are acidity independent. This means that, according to (2A), the intercept gives k_{-1} if $K_H''/|H^+| << 1$ and gives k_{-2} if the reverse is true. We do not have the possibility of evaluating K_H''; however, this cannot be very different from K_H'.

As an example, for the aluminum(III)/HCF system[10] $K_H'' = K_H' < 0.1K_H$. We can conclude that $\gamma \simeq 1$ and $k_{-2}K_H''/|H^+| << k_{-1}$ so that (2A) is reduced to (2). The above argument applies even more so to the system Fe/OCM, where the higher charge on the OCM ion makes the ratio $K_{os}'/K_{os} < 0.1$.

(B) With only the pathway involving Fe^{3+} taken into account, the relaxation time, τ, for the iron(III)/OCM system is derived for the reaction scheme of eq 3A. We call δ the

$$M + L \overset{K_{os}}{\rightleftharpoons} M,L \underset{k_{-1}}{\overset{k_{-1}}{\rightleftharpoons}} ML \qquad 2M + L \overset{K_2}{\rightleftharpoons} M_2L \qquad (3A)$$

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net change of concentration occurring during the relaxation process in the system of (3A). By use of the conservation and equilibrium equations, the rate law (4A) can be derived:

$$-\frac{d\delta}{dt} = \left[k_1\left(-\frac{\delta_{M,L}}{\delta_{ML}}\right) + k_{-1}\right]\delta \qquad (4A)$$

where

$$-\delta_{M,L}/\delta_{ML} = [K_{os}(|M| + |L|) + K_{os}K_2|M|^2|L|]/[1 + K_{os}(|M| + |L|) + K_2|M|^2 + 2K_2|M||L| + K_{os}K_2|M|^2|L|] \qquad (5A)$$

Being under the conditions of this work, $K_{os}K_2|M|^2|L| << K_{os}(|M| + |L|)$ and $2K_2|M||L| + K_{os}K_2|M|^2|L| << 1 + K_{os}(|M| + |L|) + K_2|M|^2$, eq 5A is reduced to (6A). Introduction of (6A) into (4A) and subsequent integration yield the relationship (8).

$$-\frac{\delta_{M,L}}{\delta_{ML}} = \frac{K_{os}(|M| + |L|)}{1 + K_{os}(|M| + |L|) + K_2|M|^2} \qquad (6A)$$

Registry No. Fe, 7439-89-6; $Fe(CN)_6^{3-}$, 13408-62-3; $Co(CN)_6^{3-}$, 14897-04-2; $Mo(CN)_8^{4-}$, 17923-49-8.

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Complexation Kinetics of Copper(II) with the Cryptand (2,2,1) in Dimethyl Sulfoxide

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The complexation kinetics of the cryptand (2,2,1), a macrobicyclic diaza polyether, with Cu^{2+} have been measured in dimethyl sulfoxide (Me_2SO) with stopped-flow methods. This system is one of a few cryptate systems where not only the rate constant of dissociation but also the rate constant of complex formation can be determined independently. The ratio of the rate constants for $Cu(2,2,1)^{2+}$ is found to be in agreement with the stability constant measured by calorimetric titration. As a result of the strong solvation of Cu^{2+} by Me_2SO, the formation rate constant is strikingly small, its value being unparalleled by those of other cryptand complexes. The thermodynamic quantities of the copper complex suggest that (2,2,1) forms with Cu^{2+} an inclusion complex. The changes of the dissociation rate and of the stability constant with temperature have also been studied, and activation parameters have been derived from the experimental data.

Introduction

The selective complexation of alkali- and alkaline-earth metal ions by polyether crown and cryptand molecules has been studied extensively,[2-5] and kinetic aspects of such complexation processes have also received increasing interest.[6-9] This is partly attributable to the fact that the complexes are considered as model systems for metal ion transportation in biological systems.[10,11] However, transition-metal ion complexation has been studied predominantly with open-chain and macrocyclic tetraaza and higher polyaza ligands.[12,13] These complexes are extraordinarily stable and can be regarded as simple models for naturally occurring structures found in proteins.[14] Replacement of the nitrogen-binding sites by oxygen sites decreases the stability of corresponding transition-metal ion complexes considerably.[15-17] Therefore, in only a few studies the complex formation of transition-metal ions with cryptands (2,1,1), (2,2,1), and (2,2,2) has been determined in water and in methanol. To our knowledge the present paper reports the first kinetic study on transition-metal ion complexation with a cryptand molecule in a nonaqueous solvent. Because of serious interference by hydrolysis of transition-metal ions in aqueous cryptand solutions, we have measured the rate constants for the formation and dissociation of $Cu(2,2,1)^{2+}$ in dimethyl sulfoxide (Me_2SO).

Table I. Stability Constant (log K_c) and Heat and Entropy of Complex Formation for $Cu(2,2,1)^{2+}$ in Me_2SO from Calorimetry and Activation Enthalpy and Entropy for the Cryptate Dissociation Reaction, Also at 25 °C

log K_c	ΔH_c, kJ mol^{-1}	ΔS_c, J K^{-1} mol^{-1}	$\Delta H_d^{\ddagger}$, kJ mol^{-1}	$\Delta S_d^{\ddagger}$, J K^{-1} mol^{-1}
2.7 ± 0.1	−17.9 ± 2.1	−8.4 ± 9.1	49.9 ± 4.2	−99 ± 17

Experimental Section and Results

(a) Materials. Cryptand (2,2,1) was purchased from Merck and used without further purification. Its purity of 98% given by Merck

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