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Kinetics of Formation of the Violet $Fe^{III}Fe^{II}(CN)_5CO$ Mixed Valence Complex

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The reaction of ferric ions with cyanoferrate(II) and cyanoruthenate(II) complexes produces a series of Prussian blue type mixed valence complexes [1–3] of great interest in studies of electron transfer phenomena [4–6], in colloidal chemistry, in analytical chemistry, and also as inorganic pigments. Among these complexes, the $Fe^{III}Fe^{II}(CN)_5CO$ has attracted our attention by its deep red-violet color, which has been assigned [2] to the intervalence transition,

$$Fe^{III}Fe^{II}(CN)_5CO \xrightarrow{h\nu} Fe^{II}Fe^{III}(CN)_5CO$$

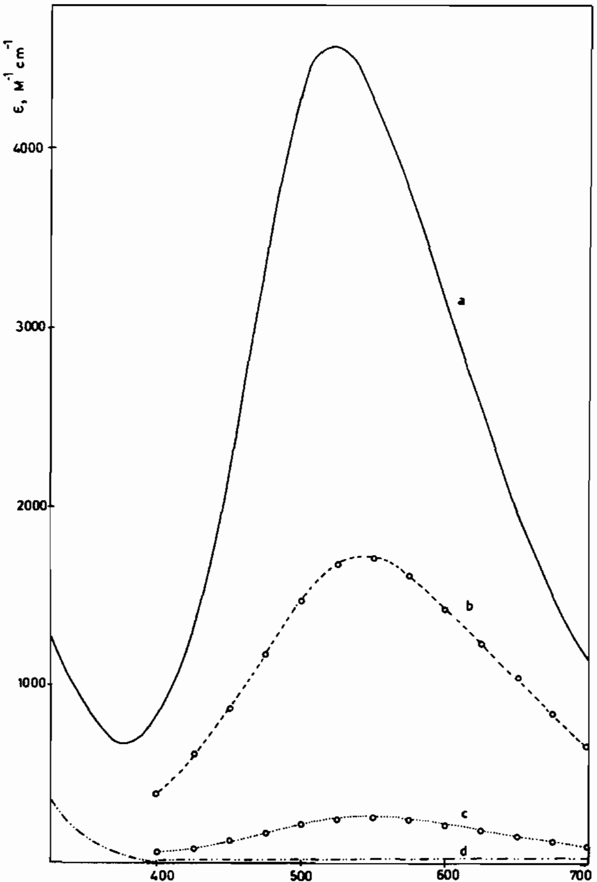

Fig. 1. Visible spectra of aqueous solutions of the Fe^{III}-$Fe^{II}(CN)_5CO$ mixed valence complex, (a) after 1 hour; (b) after 50 msec; (c) after 2 msec. Spectrum (d) refers to the $Fe(CN)_5CO^{3-}$ complex before the mixing with aqueous ferric ions.

The formation of the violet mixed valence complex from aqueous Fe^{3+} and $Fe(CN)_5CO^{3-}$ was observed to occur in two well defined steps. The first one is very rapid ($t_{1/2} < 20$ msec) and requires the use of fast reaction techniques, *e.g.* stopped-flow, to be detected. Since the $Fe(CN)_5CO^{3-}$ ion is quite inert and resistant [7] to oxidation in aqueous solution, this rapid step can be definitely assigned to a substitution reaction in the ferric ion, forming simple binuclear species like

$(H_2O)_5Fe^{III}$–NC–$Fe^{II}(CN)_4CO$,

or

$(H_2O)_5Fe^{III}$–OC–$Fe^{II}(CN)_5$

The second step is much slower and is preceded by an induction period, typical of polymerization and precipitation reactions.

Figure 1 illustrates the spectra of the species at the several steps of formation of the mixed valence complexes. The starting $Fe(CN)_5CO^{3-}$ and Fe^{3+} solutions are practically colorless; therefore, the changes in the visible spectra arise exclusively from the specific interactions between the two ions.

Spectrum *a*, in Figure 1, refers to the polymeric form of the mixed valence complex and can be compared with spectrum *b* of the monomer, obtained immediately after the first, rapid reaction (50 msec). The difference in the intensities of the intervalence bands is consistent with the monomeric and polymeric nature of the complexes, since it should be related to the number of interacting sites in the system. However, it is remarkable that the energy of the intervalence transition is little affected by the polymerization process. It is concluded that the successive substitution of water molecules in the aqueous Fe^{3+} ions by isocyanide groups should result in similar optical Franck–Condon barriers for this kind of mixed valence complexes. Spectrum *c* was measured at the limit of the mixing time of the stopped-flow instrument (2 msec) in an attempt to obtain evidence for outer-sphere, mixed valence complexes of the type $Fe^{3+}(aq)//Fe(CN)_5CO^{3-}$. This kind of complex is expected to exhibit weak intervalence transitions, characteristic of Day and Robin's class I systems.

The kinetics of the substitution process were investigated as a function of the concentration of the reactants and pH. The results are shown in the Table. The observed rate constants increase systematically with the pH, indicating the occurrence of a base catalysed substitution reaction with the ferric ions.

A systematic deviation from the expected second order behavior was observed at increasing concentrations of the ferric ions. This kind of behavior, as shown in Figure 2, can be interpreted in terms of formation of outer-sphere complexes between the reactants.

Thus, for the proposed mechanism,

$$\mathrm{Fe^{3+}(aq) + Fe(CN)_5CO^{3-}} \underset{}{\overset{K_0}{\rightleftharpoons}} \mathrm{Fe^{3+}(aq)//Fe(CN)_5CO^{3-}} \tag{1}$$

$$\mathrm{Fe^{3+}(aq)//Fe(CN)_5CO^{3-}} \xrightarrow{k_1} \mathrm{Fe^{III}{-}NC{-}Fe^{II}(CN)_4CO} \tag{2}$$

$$\mathrm{Fe(OH)^{2+}(aq) + Fe(CN)_5CO^{3-}} \overset{K_0'}{\rightleftharpoons} \mathrm{Fe(OH)^{2+}(aq)//Fe(CN)_5CO^{3-}} \tag{3}$$

$$\mathrm{Fe(OH)^{2+}(aq)//Fe(CN)_5CO^{3-}} \xrightarrow{k_2} \mathrm{Fe^{III}{-}NC{-}Fe^{II}(CN)_4CO} \tag{4}$$

$$\mathrm{Fe^{3+}(aq) + OH^-} \overset{K_b}{\rightleftharpoons} \mathrm{Fe(OH)^{2+}(aq)} \tag{5}$$

one can express the observed rate constant as

$$k_{obsd} = \frac{k_1.K_0[Fe^{3+}] + k_2.K_0'.K_b[Fe^{3+}][OH^-]}{1 + K_0[Fe^{3+}] + K_0'.K_b[Fe^{3+}][OH^-]} \tag{I}$$

In agreement with the theoretical behavior predicted from equation I, the plot of $1/k_{obsd}$ against $1/[Fe^{3+}]$ was linear, with an intercept of (1.30 ± 0.11) $\times 10^{-2}$ and a slope of (1.97 ± 0.12) $\times 10^{-5}$. Neglecting the contribution of the K_0' term, the association constant for the outer-sphere complex (K_0) was calculated as (6.6 ± 0.6) $\times 10^2$ M^{-1}. This value is consistent with that calculated using the Eigen–Fuoss equation [8] and an approximate internuclear distance of 6 Å.

For a constant $[Fe^{3+}]$ concentration, the plots of $k_{obsd}/[Fe^{3+}]$ against $[OH^-]$ were also linear (see internal plot in Figure 2) with an intercept of (1.54 ± 0.04) $\times 10^4$ and a slope of (2.57 ± 0.38) $\times 10^{16}$.

TABLE. Rate Constants[a] for the Reaction $Fe^{3+}(aq) + Fe(CN)_5CO^{3-}$.

$[Fe(CN)_5CO^{3-}]$ ($\times 10^{-5}$ *M*)	$[Fe^{3+}]$ ($\times 10^{-4}$ *M*)	$[H^+]$ ($\times 10^{-2}$ *M*)	k_{obsd} ($\times 10$ s^{-1})
2.70	2.50	1.00	1.10
4.80	7.0	1.00	2.28
4.80	1.25	1.00	3.48
4.80	2.00	1.00	4.5
4.80	2.50	1.00	4.6
4.80	3.50	1.00	5.5
4.80	4.00	1.00	5.9
25.0	0.50	1.00	1.09
4.80	2.50	2.00	7.4
4.80	2.50	3.20	5.3
4.80	2.50	0.32	24.6
4.80	2.50	0.40	18.8

[a] 25.0 °C, 0.100 *M* lithium perchlorate, 520 nm.

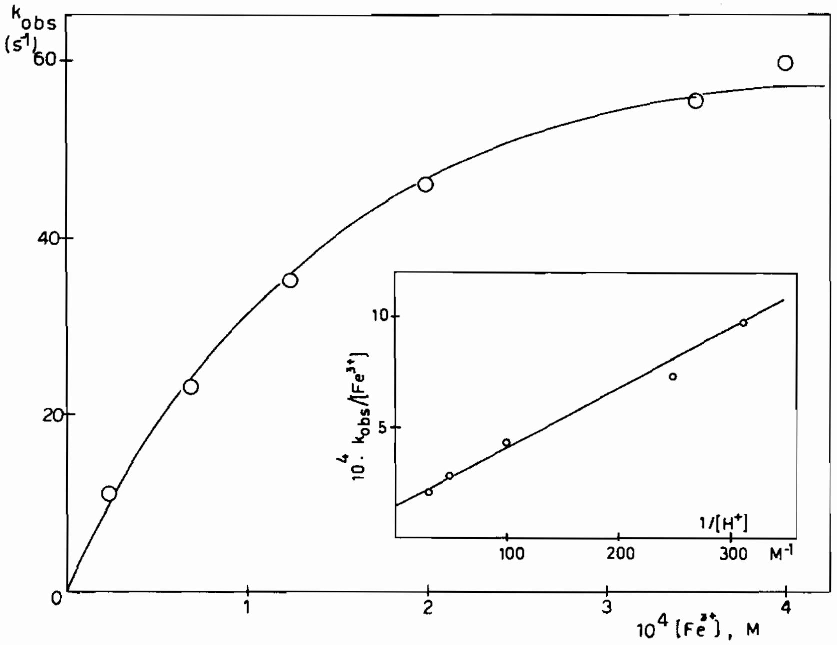

Fig. 2. Dependence of k_{obsd} with respect to the concentration of the ferric ions, or $1/[H^+]$ (internal plot), at 25 °C and 0.100 *M* lithium perchlorate.

Based on these values, the rate constant of substitution within the ion pair (k_1) was calculated as $27 \pm 8\ s^{-1}$.

Assuming for the equilibrium (5) a K_b value of $6 \times 10^{11}\ M^{-1}$, the base catalytic constant ($k_2.K'_0$) becomes $5 \times 10^4\ M^{-1}\ s^{-1}$, in agreement with the data previously reported [9] for the substitution reactions in the $Fe(H_2O)_5OH^{2+}$ ion.

The proposed mechanism can be extended to the general case of formation of Prussian blue complexes, except for the exclusion implicit in this work, of the $[H^+]$ dependence introduced by the protonation of the cyanoferrates. This kind of effect was ruled out for the $Fe(CN)_5CO^{3-}$ complex, which is known to display very weak basic properties in aqueous solution.

The mixed valence complex can be obtained in pure form from concentrated hydrochloric solutions by the slow diffusion of water into the system. The analysis of the solid is consistent with the composition $Fe[Fe(CN)_5CO]\cdot 5H_2O$ (Calcd for Fe, 31.04; C, 20.03; N, 19.46; H, 2.80. Found: Fe, 30.4; C, 20.1; N, 19.2; H, 2.3).

The electronic spectrum of the solid is comparable with those of the colloidal samples, with a broad intervalence band centered at 570 nm. The infrared spectrum of the mixed valence complex (in nujol) shows the vibrational bands of the water molecules at 3640 and 1600 cm^{-1}, and the characteristic CN and CO stretching bands at 2115 and 2045 cm^{-1}, respectively. A set of absorption bands associated with the deformation and stretching modes of the FeNC, FeOC, FeCN and FeCO groups were observed at 625, 590, 535, 500 and 475 cm^{-1}. The electronic and structural properties of the complex are being investigated in this laboratory.

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