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Complex Formation between the Aquopentacyanoferrate(II) Ion and Thiourea and Its N-Substituted Derivatives

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Received March 28, 1979

The results of a kinetic investigation of the substitution reactions of pentacyanoaquoferrate(II) with thiourea and N-substituted thioureas are presented. The substitution rate constants, measured in the pH range 2.8–9.0, show a hydrogen ion dependence $k_f = (k_{AH_2}[H^+]^2 + k_{AH_1}K_{AH_2}[H^+] + k_AK_{AH_1}K_{AH_2})/([H^+]^2 + K_{AH_2}[H^+] + K_{AH_1}K_{AH_2})$, which is consistent with the presence of three reacting species: $HFe(CN)_5OH_2^{2-}$, $Fe(CN)_5OH_2^{3-}$, and $Fe(CN)_5OH^{4-}$. The acid dissociation constant for the aquo species has been determined ($K_{AH_1} = (1.37 \pm 0.20) \times 10^{-8}$ M). The aquo species is found to be more reactive toward thiourea (k_{AH}(25 °C) = 202 $M^{-1}\ s^{-1}$) than the hydroxy species (k_A(25 °C) = 100 $M^{-1}\ s^{-1}$) while the protonated aquo species (k_{AH_2}(25 °C) = 2 $M^{-1}\ s^{-1}$) is much less reactive. The dissociation rates of the $Fe(CN)_5TU^{3-}$ (TU = thiourea) species are larger than those of complexes with N-donor ligands, indicating labile Fe–S bonds. An isokinetic plot of the activation parameters suggests different mechanisms operating in the formation (I_d mechanism) and dissociation (D mechanism) reactions of $Fe(CN)_5TU^{3-}$ species.

Introduction

The reactions of pentacyanoferrate(II), $Fe(CN)_5L^{n-}$, complexes are currently the subject of considerable interest, for several reasons. Mechanistic aspects[1–8] have been studied by using a variety of ligands and solvent systems since there is evidence for a dissociative, D, mechanism in the substitution of these complexes. In studies of complexes of this type where the volumes of activation have been measured, the data are consistent with this proposed mechanism. Also, these low-spin iron species represent models for active sites in biological systems, and reactions with imidazole have been investigated[10] in this regard. Another feature of these complexes is their use as the reducing center is the identification of precursor complexes in inner-sphere electron transfer.[11,12]

To date, most of the studies have been undertaken for N-donor ligands, and relatively few data are available for sulfur-bonded complexes. In aqueous media, complexes are formed between $Fe(CN)_5(OH_2)^{3-}$ and thiols or thioureas, the rates of formation being pH dependent. There is also a need for the study of the comparative reactivities of the pH-related forms of the pentacyanoferrate(II) ion. Davies[8] has reported a value of ~2 × 10^{-7} M for the aquo–hydroxo equilibrium

$$Fe(CN)_5(OH_2)^{3-} \rightleftharpoons H^+ + Fe(CN)_5OH^{4-} \quad K_{AH_1} \quad (1)$$

Malin[13] has shown that at low pH, protonation occurs (at cyanide)

$$H[Fe(CN)_5OH_2]^{2-} \rightleftharpoons H^+ + Fe(CN)_5OH_2^{3-} \quad K_{AH_2} \quad (2)$$

with a dissociation constant $K_{AH_2} = (2.35 \pm 0.6) \times 10^{-3}$ M at 25 °C. The protonated species was found to be much less reactive than the aquo form.[13] There are no rate constants available for the reaction of the hydroxo form. In this paper, we wish to report details of a kinetic study of the reaction with thiourea and several N-substituted thioureas. These ligands are particularly useful for identifying pH effects since there is no evidence for protonation[14] over a wide (1–10) pH range, and the relative reactivities of the interrelated complex ions may be determined.

Experimental Section

Reagents. Sodium pentacyanoammineferrate(II) was prepared from sodium nitroprusside by the standard procedure.[15] The product was recrystallized from aqueous ammonia at 0 °C and washed with cold methanol. The dried yellow powder was stored under nitrogen in the dark at 5 °C. Thiourea (Fisher), allylthiourea (BDH), and *N,N′*-dimethylthiourea (Ralph-Emanuel) were used after repeated recrystallization from water.

Kinetic Measurements. Studies were made by using a stopped-flow apparatus described previously.[16] The apparatus was thermostated to ±0.05 °C. Formation reactions were monitored at 440 nm and dissociation reactions at 400 nm. The pentacyanoaquoferrate(II) ion was generated in solution by dissolving solid $Na_3[Fe(CN)_5NH_3]$ in deoxygenated distilled water. Freshly prepared solutions of low concentration ((2–4) × 10^{-5} M) were used to prevent dimerization of the anion.[17,18] In order to control the reaction pH, we used phosphate, phthalate, or borax buffers, since these were observed to have no effect on the reactant solutions and have in some instances been used in other studies.[13] The ionic strength was maintained at 0.50 M by using sodium chloride.

All measurements were made under pseudo-first-order conditions with ligand in excess. Plots of ln $(A_\infty - A_t)$ against time derived from photographic traces of photomultiplier output were linear for at least 3 half-lives.

Spectra. The spectra of pentacyanoferrate(II) solutions (1.5 × 10^{-4} M) were measured at various pH values by using a Varian Techtron 635 spectrophotometer over the range 350–500 nm. The sample cell holder was thermostated at the appropriate temperature (between 10 and 30 ± 0.1 °C). Freshly prepared solutions of low complex concentration, adjusted to pH ~4, were deoxygenated and allowed to thermostat prior to each run. The hydrogen ion concentration was changed by addition of small volumes (0.01 mL) of 0.1 M NaOH, and after equilibration the shift in the spectrum was monitored. Measurements were made over the range pH 4–10, the pH values

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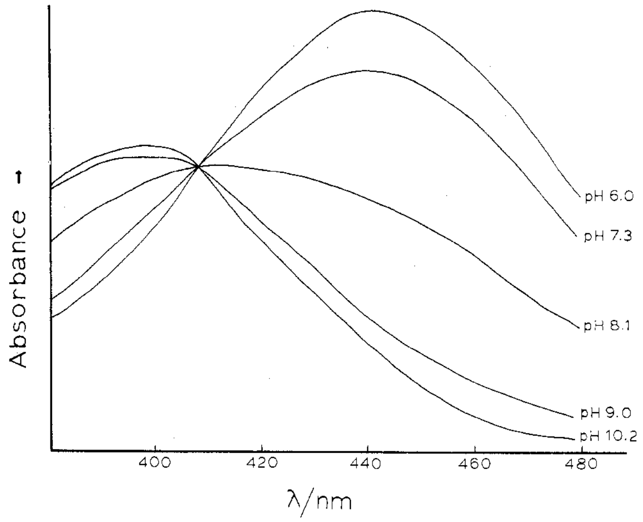


Figure 1. Variation of the visible spectrum of $Fe(CN)_5OH_2^{3-}$ with pH.

being measured by use of a Radiometer 26 instrument with a Radiometer GK2311C combination electrode. In the lower pH range 1–4, there is considerable evidence for the presence of two species (including an isosbestic point at 382 nm), but precise data on the hydrolysis constant could not be obtained owing to the instability of the complexes in solution.

Results

Nature of the Reactant Complexes. The visible spectrum of the pentacyanoaquoferrate(II) ion varies with pH as shown in Figure 1. The aquo complex, $Fe(CN)_5OH_2^{3-}$, has a maximum absorbance at 440 nm (ϵ = 700 M^{-1} cm^{-1}) while the hydroxy species, $Fe(CN)_5OH^{4-}$, has its absorbance maximum at 395 nm (ϵ = 495 M^{-1} cm^{-1}), on the basis of complete deprotonation of the aquo ligand at pH 10.6. An isosbestic point is observed at 408 nm (ϵ = 465 M^{-1} cm^{-1}) at pH $\geq$4. From the changes in optical density with pH it is possible to derive values for K_{AH_1} by using the equation

$$\frac{a}{\Delta OD} = \frac{b}{K_{AH_1}\Delta\epsilon} + \frac{1}{\Delta\epsilon} \qquad (3)$$

where $a = [Fe(CN)_5OH_2^{3-}]$, $b = [H^+]$, and ΔOD is the difference in optical density between the solution with 100% $Fe(CN)_5OH_2^{3-}$ and a solution at a given pH. Figure 2 shows the results of treatment of the data at 10 °C for the two wavelengths of maximum absorbance where the agreement is seen to be good ($K_{AH_1} = 1.05 \times 10^{-8}$ M, λ 395 nm; $K_{AH_1} = 1.19 \times 10^{-8}$ M, λ 440 nm). Measurements were made in the temperature range 10–30 °C, and calculations using eq 3 gave the following values of K_{AH_1}: 10 °C, $(1.12 \pm 0.20) \times 10^{-8}$ M; 18 °C, $(1.25 \pm 0.20) \times 10^{-8}$ M; 25 °C, $(1.37 \pm 0.20) \times 10^{-8}$ M; 30 °C, $(1.54 \pm 0.20) \times 10^{-8}$ M. From the data it is possible to compute ΔH, but the spread of the equilibrium constant values is too low for more than an estimate of enthalpy of dissociation ($\Delta H \approx 3$ kcal mol^{-1}). Davies[8] has reported a slightly larger value for K_{AH_1} of $\sim 2 \times 10^{-7}$ M. This latter constant, however, was computed from a kinetic rate dependence and at a different ionic strength (1.0 M). The value of K_{AH_2} used in this study was that of Malin.[13] Using these equilibrium constants, it is possible to determine the concentration profile of these species over the pH range 1–10. This profile is shown in Figure 3.

The values of $\Delta\epsilon$ computed from eq 3 for the two absorbance maxima, 395 and 440 nm, are 140 ± 25 and 375 ± 25 M^{-1} cm^{-1}, respectively. These values agree with the measured spectra of the pentacyanoaquoferrate(II) ion.

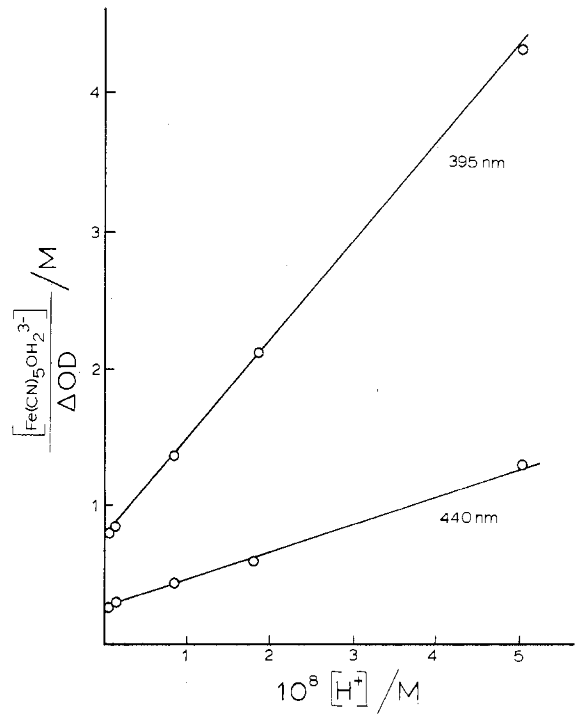


Figure 2. Plot of $[Fe(CN)_5OH_2^{3-}]/\Delta OD$ against $[H^+]$ at 395 and 440 nm from eq 3 (T = 10 °C).

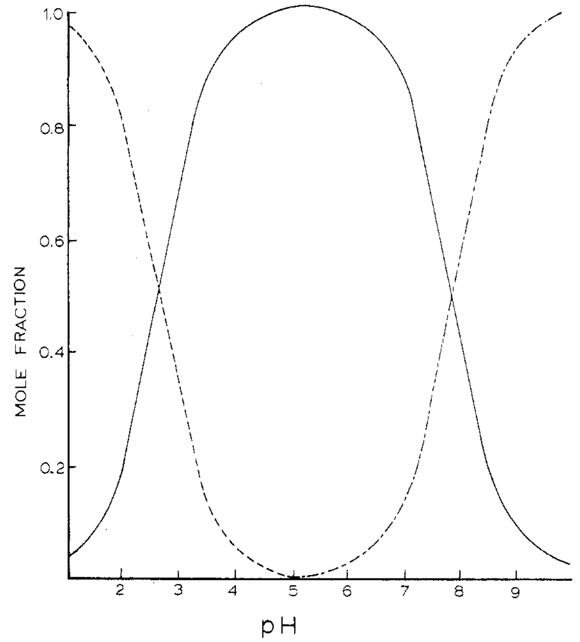


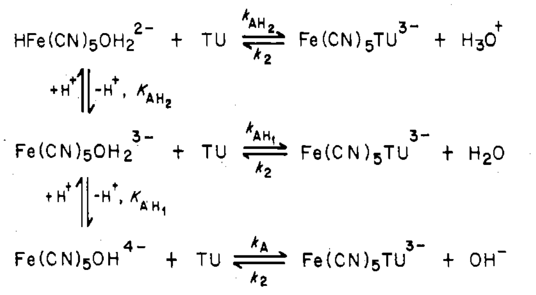
Figure 3. pH profile of pentacyanoferrate(II) species in solution: (---) $HFe(CN)_5OH_2^{2-}$, (—) $Fe(CN)_5OH_2^{3-}$, (···) $Fe(CN)_5OH^{4-}$ (measured at $[Fe(CN)_5OH_2^{3-}]_t = 1.5 \times 10^{-4}$ M).

Kinetics of Complex Formation. On reaction of pentacyanoaquoferrate(II) species with thiourea and its N-substituted derivatives, a rapid complex formation is observed with a shift of λ_{max} in the visible region to 406 nm. These reactions were readily studied by using the stopped-flow technique. Under pseudo-first-order conditions of excess ligand, the rate of formation may be expressed in the form

$$d[Fe(CN)_5TU^{3-}]/dt = k_{obsd}[Fe(CN)_5OH_2^{3-}] \qquad (4)$$

Good first-order behavior was observed in all cases to at least 80% of reaction. Plots of k_{obsd} against [TU], where TU is thiourea (ATU = allylthiourea and DMTU = *N,N'*-dimethylthiourea), were linear with positive intercepts. These

Scheme I



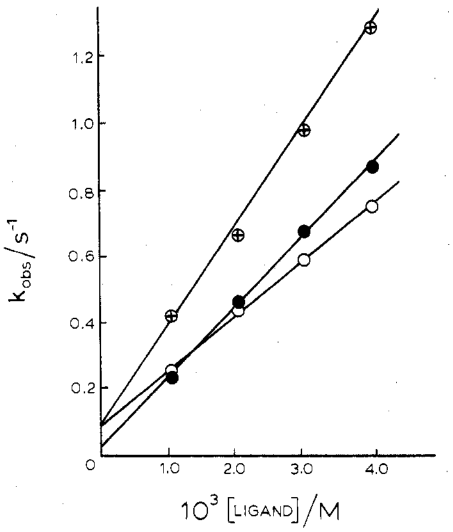


Figure 4. Plots of observed formation rate constants against ligand concentration at 25 °C: ⊕, dimethylthiourea; ●, thiourea; ○, allylthiourea.

Table I. Second-Order Rate Constants for the Reaction of $Fe(CN)_5OH_2^{3-}$ with Thiourea Ligands at Various pHs[a]

pH	$10^{-2}k_1$, $M^{-1}\,s^{-1}$	pH	$10^{-2}k_1$, $M^{-1}\,s^{-1}$
	Thiourea Ligand		
2.82	1.13	6.54	2.01
3.72	1.81	7.30	1.76
4.68	1.98	8.14	1.32
5.57	2.03	8.76	1.13
	Allylthiourea Ligand		
3.33	1.48	7.15	1.73
5.11	1.63	8.22	1.47
	Dimethylthiourea Ligand		
3.33	1.94	7.15	2.67
5.11	2.88	8.22	1.88

[a] $T = 25$ °C, $[Fe(CN)_5OH_2^{3-}] = 2.0 \times 10^{-5}$ M, $I = 0.50$ M (NaCl).

kinetic observations are consistent with the reactions of Scheme I, leading to the equation

$$k_{obsd} = k_1[TU] + k_2 \qquad (5)$$

where

$$k_1 = \frac{k_{AH_2}[H^+]^2 + k_{AH_1}k_{AH_2}[H^+] + k_A K_{AH_1}K_{AH_2}}{[H^+]^2 + K_{AH_2}[H^+] + K_{AH_1}K_{AH_2}} \qquad (6)$$

Details of the rate constants at 25 °C are presented in Table I, and conformity with eq 5 is shown in Figure 4 for the three substrates involved. From the knowledge of the acid dissociation constants it is possible to determine the rate constants for the individual paths in the reaction scheme. Profiles of k_1 against pH were compiled and are shown in Figure 5, where the correlation of observed and calculated (eq 6) values for thiourea is seen to be good at 18, 25, and 30 °C. Similar profiles were observed for allyl- and dimethylthiourea. Rate constants for the individual aquo and hydroxo paths in the overall scheme are presented in Table II. It may be noted that the aquo form reacts about twice as fast as the hydroxo form while the protonated aquo form has a negligible rate. This latter difference in reactivity was observed previously by Malin,[13] and on the basis of his rate data, the rate constants for the protonated-aquo pathway can be estimated to be about 1–2 $M^{-1}\,s^{-1}$ at 25 °C.

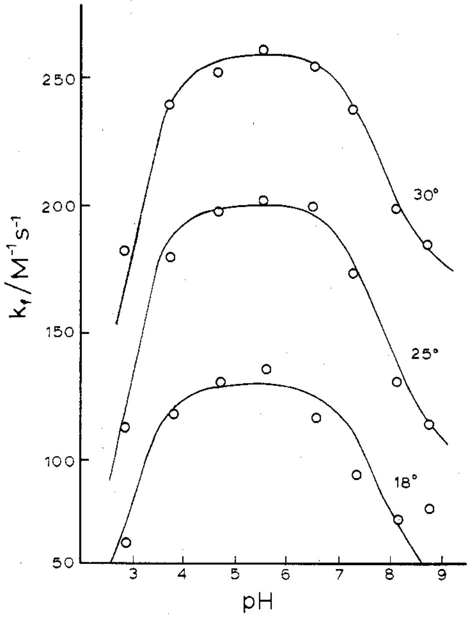


Figure 5. Variation of forward rate constant, k_1, with pH and temperature for the reaction of $Fe(CN)_5OH_2^{3-}$ with thiourea. Solid curves are calculated lines using eq 6 based on rate (Table II) and equilibrium constants.

Table II. Rate Constants for Reactions of $Fe(CN)_5OH_2^{3-}$ and $Fe(CN)_5OH^{4-}$ with Thiourea Ligands at Various Temperatures

ligand	T (±0.1), °C	$10^{-2}k_{H_2O}$, $M^{-1}\,s^{-1}$	$10^{-2}k_{OH^-}$, $M^{-1}\,s^{-1}$
thiourea	18	1.30	0.48
	25	2.02	1.00
	30	2.60	1.71
allylthiourea	18	1.15	0.66
	25	1.80	1.25
	30	2.30	1.87
dimethylthiourea	18	1.40	0.60
	25	2.80	1.44
	30	4.02	2.45

Table III. Activation Parameters for Reactions of $Fe(CN)_5OH_2^{3-}$ and $Fe(CN)_5OH^{4-}$ with Thiourea Ligands (298 K)

ligand	$\Delta H^\ddagger_{H_2O}$ (±0.5), kcal mol^{-1}	$\Delta S^\ddagger_{H_2O}$ (±2), cal deg^{-1} mol^{-1}	$\Delta H^\ddagger_{OH^-}$ (±0.5), kcal mol^{-1}	$\Delta S^\ddagger_{OH^-}$ (±2), cal deg^{-1} mol^{-1}
thiourea	10.8	−12	19.1	15
allylthiourea	11.0	−11	15.8	4
dimethylthiourea	16.1	−7	21.3	23

The activation parameters for the aquo and hydroxo pathways are presented in Table III. These parameters along with those for other ligands form an isokinetic relationship which is shown in Figure 7 and discussed below.

Kinetics of Dissociation Reactions. Unlike the case of previous studies of pentacyanoferrate(II) systems, intercepts

Table IV. Rate Constants and Activation Parameters for the Reaction of $Fe(CN)_5TU^{3-}$ with Pyridine (0.20 M)[a]

	10^2k_3, s^{-1}		
T (±0.05), °C	thiourea	allyl-thiourea	dimethyl-thiourea
16.8	1.66	2.24	3.14
21.2	2.32	3.80	4.42
25.0	3.90	4.51	8.13
30.4	5.52	7.95	11.46
$\Delta H^{\ddagger}$ (±1), kcal mol^{-1}	16.6	16.3	18.0
$\Delta S^{\ddagger}$ (±3), cal deg^{-1} mol^{-1}	−9	−10	−3

[a] pH 8.18, I = 0.05 M (NaCl).

were observed in the plots of k_{obsd} against [TU]. This implies that there is a measurable dissociation rate, k_2, for these complexes. Values of k_2 derived from the plots (Figure 4) using eq 5 show little variation with pH. More accurate determinations of k_2 were made by measuring the rate of the reaction

$$Fe(CN)_5TU^{3-} + py \rightarrow Fe(CN)_5py^{3-} + TU \qquad (7)$$

where py is pyridine.

It has been postulated from volume of activation[9] data that the dissociation of $Fe(CN)_5X^{3-}$ species occurs via a D mechanism, e.g.

$$Fe(CN)_5TU^{3-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Fe(CN)_5^{3-} + TU \qquad (8)$$

$$Fe(CN)_5^{3-} + py \xrightarrow{k_5} Fe(CN)_5py^{3-} \qquad (9)$$

In the present system, the observed rate constant k'_{obsd} may be written in the form

$$k'_{obsd} = \frac{k_3k_5[py]}{k_4[TU] + k_5[py]} \qquad (10)$$

From this equation it can be shown that at high [py] k'_{obsd} tends to a limiting value. In Table IV are reported limiting rate values for the dissociation of the three thiourea complexes along with the activation parameters. Rearrangement of eq 10 yields

$$\frac{1}{k'_{obsd}} = \frac{1}{k_3} + \frac{k_4[TU]}{k_3k_5[py]}$$

Plots of k'_{obsd} against $[py]^{-1}$ were linear as shown for the dissociation of $Fe(CN)_5TU_3^-$ in Figure 6. Values of k_3 were obtained for all three complexes and in most cases correlate well with the k_2 values from eq 5.

Discussion

In comparison with systems studied previously, it appears that these sulfur-bonded complexes have equilibrium constants (10^3 M^{-1}) somewhat smaller than for the nitrogen-bonded species (10^5 M^{-1}). This difference arises from a much larger dissociation rate, suggesting a labile Fe–S bond. It is of interest that in the corresponding reaction with dimethyl sulfoxide, the spectroscopic evidence is heavily in favor of a sulfur-bonded complex. In this system, however, the donor sulfur atom is considered to participate in dπ–dπ back-bonding with the iron center. The presence of an electronegative oxygen atom bonded to the donor sulfur may increase the positive charge and so allow for a greater degree of electron delocalization from the metal. In the current study, the sulfur donor, being a thioketone, is less likely to interact as strongly in this manner, and so a somewhat weaker bond may be expected. This would be reflected in the rate of dissociation (a D mechanism), and the dissociation of the thiourea complex is observed to be about 10 times as fast as that for the dimethyl sulfoxide species. Further studies with thiols, particularly RS^- ligands, may help to resolve this aspect.

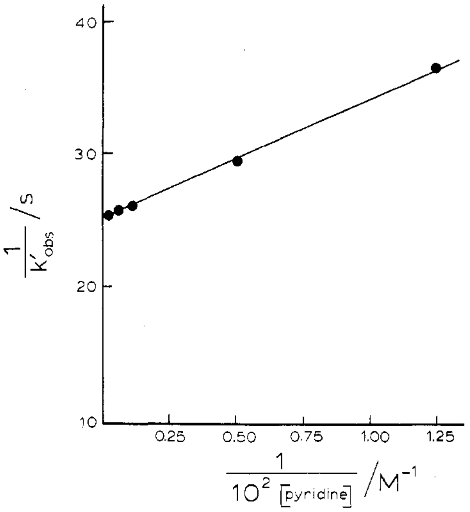


Figure 6. Plot of $1/k'_{obsd}$ against 1/[pyridine] for the dissociation of $Fe(CN)_5TU^{3-}$ at 25 °C.

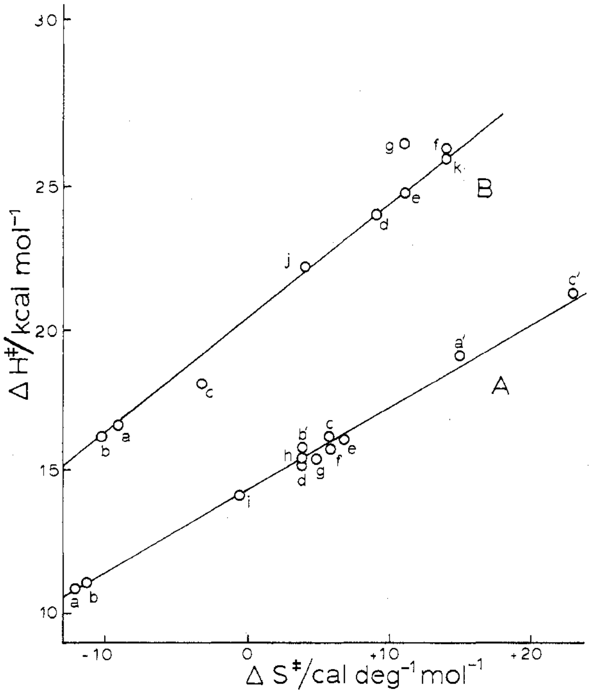


Figure 7. Isokinetic plots for the formation (line A) and dissociation (line B) reactions of $Fe(CN)_5X^{3-}$ where ligand X is (a) thiourea (this work), (b) allylthiourea (this work), (c) dimethylthiourea (this work), (d) 4-dimethylpyridine,[1] (e) pyridine,[1] (f) isonicotinamide,[1] (g) pyrazine,[1] (h) dimethyl sulfoxide,[19] (i) benzonitrile,[20] (j) 3-cyanopyridine,[9] and (k) isonicotinohydrazide.[21] Points a′, b′, and c′ refer to reactions of ligands a, b, and c with $Fe(CN)_5OH^{4-}$ (this work).

The reactivities of the three pH-related pentacyanoferrate(II) ions toward the thiourea ligands are in the order aquo > hydroxy ≫ protonated aquo. The low reactivity of the protonated aquo species has previously been noted by Malin.[13] In the reaction of a neutral ligand, such as thiourea, with pentacyanoferrate(II), the electrostatic effect of reducing the charge of the ion upon protonation would be less pronounced than with the *N*-methylpyrazinium cation.[13] The protonation of a cyanide would increase the positive charge carried by the iron(II) center which would strengthen the iron–oxygen bond. The iron–oxygen bond would also be expected to be stronger in the hydroxy species than in the aquo species because of the negative charge of the hydroxy ligand. In either a D or an I_d mechanism, the strength of this iron–oxygen bond would affect the rate of dissociation of the pentacyanoaquoferrate(II) ion.

A study[9] of $\Delta V^‡$ for the reaction of $Fe(CN)_5X^{3-} + Y$ has resulted in the conclusion that the reaction proceeds by a D mechanism. Correlations of $\Delta H^‡$ and $\Delta S^‡$ in an isokinetic plot (line B in Figure 7) are consistent with this mechanism for other reactions of closely related pentacyanoferrate(II) complexes with nitrogen- and sulfur-donor ligands. It is of interest, however, that for comparable reactions of both the aquo and hydroxy complexes, the values of $\Delta H^‡$ are significantly lower (by ~5–6 kcal mol^{-1}) and lie on a separate line (A in Figure 7), in an isokinetic plot. One interpretation of this finding is that there is a change in mechanism from a D to an I_d process in the case of these oxygen donors. The I_d mechanism has been postulated[22] for dissociation reactions of $Fe(CN)_5X^{3-}$ especially in the case where X is H_2O.

Acknowledgment. D.H.M. wishes to thank the University of Victoria for a Graduate Fellowship. Assistance from the National Research Council of Canada is also acknowledged.

Registry No. Sodium pentacyanoammineferrate(II), 14099-05-9; TU, 62-56-6; ATU, 109-57-9; DMTU, 534-13-4; $Fe(CN)_5OH_2^{3-}$, 18497-51-3; $Fe(CN)_5OH^{4-}$, 42859-22-3; $HFe(CN)_5OH^{2-}$, 70912-43-5.

Supplementary Material Available: A more complete table of kinetic data (5 pages). Ordering information is given on any current masthead page.

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Kinetics of Complexing of a Tridendate Nickel(II) Complex by Histidine Derivatives and Glycine

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Received May 14, 1979

The kinetics of complexing of the nickel(II) tridendate Schiff-base complex triaquo(tribenzo[*b,f,j*][1,5,9]triazacyclododecine)nickel(II) $\{(TRI)Ni(OH_2)_3^{2+}\}$ by histidine, 3-methylhistidine, histamine, histidine methyl ester, and glycine have been studied. For the first three ligands the observed pseudo-first-order rate constant is given by $k_{exptl} = \{A[\text{total ligand}]/(K_a + (H^+)) + B(H^+)\}/(C(H^+) + 1)$. This is shown to be consistent with the mechanism

$$\mathrm{Ni} + \mathrm{HL} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Ni{-}LH} \underset{k_{32}(H^+)}{\overset{k_{23}}{\rightleftharpoons}} \mathrm{Ni{-}L} \underset{k_{53}}{\overset{k_{35}}{\rightleftharpoons}} \mathrm{Ni{=}L}$$

with $A = k_{12}K_{a_1}$, $B = k_{21}k_{53}/k_{35}K_{23}$, and $C = k_{21}/k_{35}K_{23}$ where $K_{23} = k_{23}(H^+)/k_{32}$. Further work shows that the $Ni(OH_2)_6^{2+}$–histidine system conforms to the same rate law. The rate law with the other ligands is found to be simpler, and analysis indicates this is the case because of the higher acidity of the ester and unfavorable equilibrium for complexing of the carboxylate group for glycine.

The reactions of monodendate ligands with hexaaquonickel(II) are thought generally to proceed by a dissociative ion-pair mechanism.[1,2] This information can be used to elucidate the details of reaction pathways for complexing by multidendate ligands such as the amino acids. For this family of ligands earlier work[2] had assumed that initial bond formation between the amino acid and metal ion was rate limiting and concluded that only the anionic form of an α-amino acid is reactive. A recent reanalysis[3] has shown that the kinetics are equally consistent with a reaction scheme which essentially involves monodendate intermediate complex formation in a rapid preequilibrium, followed by rate-controlling chelate ring closure. It has been shown[4] that with two pyridine-2-carboxylic acids the mechanism changes rate-controlling steps as the pH changes from 2.5 to 6.5. In addition, the variation in rate constant for various α-amino acid–$Ni(OH_2)_6^{2+}$ systems can be explained in terms of steric effects on dissociation of the monodendate intermediate.[4]

The present work was designed to further explore the reaction pathways and reactivities of amino acid–nickel(II) systems by studying a tridendate Schiff-base complex of nickel(II) [$(TRI)Ni(OH_2)_3^{2+}$, Figure 1] reacting with histidine and its derivatives. The TRI complex was chosen for several reasons: (i) it exists as two resolvable, stable optical isomers so that stereoselectivity can be studied; (ii) its water-exchange rate[5] is almost the same as that of $Ni(OH_2)_6^{2+}$, so that a dissociative mechanism should yield similar rates for the two systems, and differences will reflect steric effects of the (TRI) ligand and probability effects because there are half the reactive sites present compared with $Ni(OH_2)_6^{2+}$.

0020-1669/79/1318-2895$01.00/0