of the acid dissociation rate was one-fifth the limiting value of the neutral dissociation rate. This they took to indicate that partial predissociation of one TPTZ moiety takes place before protonation of the complex. The evidence for a moderately stable $Fe(TPTZ)_2H^{3+}$ species may alter Pagenkopf and Margerum's conclusions. Our results indicate that a second process for the acid dissociation of $Fe(TPTZ)_2H^{3+}$ involving direct attack of $Fe(TPTZ)_2^{2+}$ by a proton should also be considered, although the observed evidence may only be a manifestation of the partially predissociated protonated complex proposed by Pagenkopf and Margerum.[8] No definitive conclusion can be drawn from the equilibrium analysis presented in this study; nevertheless, the formation of $Fe(TPTZ)_2H^{3+}$, partially dissociated or not, must be considered to rationalize the experimental data.

The value for $\beta_2 = (2.8 \pm 1.2) \times 10^{11}$ was determined by a technique which is independent of the molar absorbance. The molar absorbance is reported[3,9] to be 22,400 ± 200, and it may vary with the ligand concentration.[9] The two values for β_2 previously reported by Buchanan, *et al.*[9] ($\beta_2 = 1.75 \times 10^{10}$), and by Pagenkopf and Margerum[8] ($\beta_2 = (3.0 \pm 1.8) \times 10^{12}$) were determined with the aid of the molar absorbance. The use of the normalization of absorbances proposed by Momoki, *et al.*,[11] in the method described by Likussar and Boltz[13] for the determination of β', and thus β_2, eliminates the molar absorbance from the problem, which enhances the reliability of the method presented in this study. Pagenkopf and Margerum[8] used a value of 21,600 for ϵ in their determination of β_2.

The reliability of the formation constant for $Fe(TPTZ)_2H^{3+}$, $(2.5 \pm 1.1) \times 10^2$, is dependent upon the assumptions concerning the equilibria present in the problem. Any contribution of $Fe(TPTZ)^{2+}$ to the formation equilibrium was dismissed because of the observed linearity of the Job plot (Figure 2); thus only $Fe(TPTZ)_2^{2+}$ was considered to contribute to the absorbance at 593 nm. The value of K_{2H} is known,[10] $(6.58 \pm 0.01) \times 10^2$, but K_H had to be numerically optimized. The value of 9.5×10^2 for K_H was observed to give a well-behaved pH dependence of $\beta' \cdot A_{Fe}A_{TPTZ}^2$ (Figure 3). Variation of K_H over its uncertainty limits had a negligible effect on β_2 at pH >3 and only a 10% effect at pH <2. Ultimately, the value for $\beta_{Fe(TPTZ)_2H^{3-}}$ was numerically found, and this value is highly dependent upon the value of K_H for TPTZ used.

Absorbance measurements were hindered by ligand insolubility above pH 4.5. The reported solubility of TPTZ at pH 4.5 is 9.2×10^{-5} mol/l.,[9] which is three times the concentration of TPTZ present in the solutions for the determination of β'. A marked decrease in the solubility of TPTZ must occur above a pH of 5, since $Fe(TPTZ)_2^{2+}$ solutions above this pH rapidly became turbid. Absorbance measurements made at a pH >4.5 were considered unreliable; therefore, the evaluation of β' was restricted to the pH region between 1.5 and 4.5.

Conclusion

The formation of a protonated complex ion, $Fe(TPTZ)_2H^{3+}$, was attributed to a spectral shift in the spectrum of $Fe(TPTZ)_2^{2+}$ at low pH. A value of $\beta_2 = (2.8 \pm 1.2) \times 10^{11}$ for $Fe(TPTZ)_2^{2+}$ was determined with the assumption that $\beta_{Fe(TPTZ)_2H^{3+}} = (2.5 \pm 1.1) \times 10^2$.

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Kinetics and Mechanisms of Some Substitution Reactions of Pentacyanoferrate(III) Complexes[1]

BY JAMES H. ESPENSON* AND STEPHEN G. WOLENUK, JR.

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A procedure for the synthesis and purification of the monomeric complex $Fe(CN)_5H_2O^{2-}$ was devised. The following reactions were studied, with data at 25.0°, $\mu = 1.00$ M, as indicated: (1) the equilibrium $Fe(CN)_5H_2O^{2-} + SCN^- = Fe(CN)_5SCN^{3-} + H_2O$ has $K = 257 \pm 15$ M^{-1} and a forward rate given by $\{a + b[H^+]^{-1}\}[Fe(CN)_5H_2O^{2-}][SCN^-]$, with $10^2a = 1.96 \pm 0.19$ M^{-1} sec^{-1} and $10^3b = 5.2 \pm 0.3$ sec^{-1}; (2) the reaction $Fe(CN)_5SCN^{3-} + OH^- = Fe(CN)_5OH^{3-} + SCN^-$ proceeds quantitatively to the right at $[OH^-]/[SCN^-] > 0.2$ with a pseudo-first-order rate constant given by $A + B[OH^-]/\{[OH^-] + C[SCN^-]\}$ (the values at 25°, $\mu = 1.00$ M, are $10^3A = 2.78 \pm 0.05$ M^{-1} sec^{-1}, $10^2B = 1.32 \pm 0.09$ M^{-1} sec^{-1}, and $C = 3.1 \pm 0.4$); (3) the reaction of the dimer $Fe_2(CN)_{10}^{4-}$ with SCN^- occurs in two stages

$$Fe_2(CN)_{10}^{4-} \xrightarrow{k_1\ [SCN^-]} [Fe_2(CN)_{10}SCN^{5-}] \xrightarrow{k_2\ [SCN^-]} 2Fe(CN)_5SCN^{3-}$$

with $k_1 = 0.010$ and $k_2 \cong 10^{-4}$ M^{-1} sec^{-1}. The kinetic data for all of these reactions are interpreted in terms of proposed reaction mechanisms.

Introduction

At the beginning of this century Hofmann[2] prepared complexes of the empirical formula $Na_3Fe(CN)_5(H_2O)_x$ and $Na_2Fe(CN)_5(H_2O)_y$. Subsequent work on these supposed "aquo" complexes, largely by Emschwiller and coworkers,[3] has established the dimeric

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[1] (a) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 3198. (b) Based on the M.S. thesis of S. G. W., Jr., Iowa State University, Dec 1971.

[2] K. Hofmann, *Ann. Chem.*, **312**, 1 (1900).

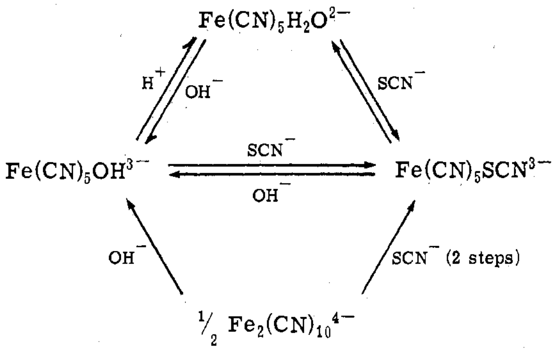
[3] (a) G. Emschwiller, *C. R. Acad. Sci.*, **247**, 1115 (1958); (b) *C. R. Acad. Sci., Ser. C*, **265**, 281 (1967); (c) *ibid.*, **268**, 692 (1969); (d) G. Emschwiller and C. K. Jørgensen, *Chem. Phys. Lett.*, **5**, 561 (1970).

nature of the anions $Fe_2(CN)_{10}^{6-}$ and $Fe_2(CN)_{10}^{4-}$. The monomer and dimer of the Fe(III) complex come to equilibrium very slowly, and their direct interconversion as shown in reaction I is not an important process under any of the conditions studied.

$$\tfrac{1}{2}Fe_2(CN)_{10}^{4-} + H_2O = Fe(CN)_5H_2O^{2-} \qquad (I)$$

In the present study we have considered a related family of reactions involving the interconversion of the species $Fe_2(CN)_{10}^{4-}$, $Fe(CN)_5OH^{3-}$, $Fe(CN)_5H_2O^{2-}$, and $Fe(CN)_5SCN^{3-}$ as shown in Scheme I.

SCHEME I



The particular reactions studied and our goals in choosing these systems for investigation are as follows. First, the anation reaction between the aquo complex and thiocyanate ions[4-6]

$$Fe(CN)_5H_2O^{2-} + SCN^- = Fe(CN)_5SCN^{3-} + H_2O \qquad (II)$$

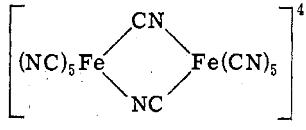
is analogous to the corresponding anation reactions[7] of $Co(CN)_5H_2O^{2-}$. Reactions such as eq II provide particularly useful systems in which to study octahedral substitution mechanisms because outer-sphere association between the reactants is minimized in the case of anionic complexes. The Co(III) complex provides the classic, definitive example of the limiting SN1 mechanism for octahedral substitution. Still to be resolved, however, is the question of whether this limiting mechanism provides the preferred pathway for complexes of metal ions having different electronic configurations. An unanticipated *base catalysis* was noted in these experiments in strongly acidic solution, pH ≤ 2.

Second, we studied the base hydrolysis of the thiocyanato complex as in reaction III. This reaction was

$$Fe(CN)_5SCN^{3-} + OH^- = Fe(CN)_5OH^{3-} + SCN^- \qquad (III)$$

among those whose equilibrium constant was evaluated by Jaselskis.[8,9] The reaction is of an unusual type, because the complex lacks any protons, ruling out the SN1 CB mechanism, which is the generally preferred mechanism of base hydrolysis in octahedral complexes.[10,11] In contrast to the situation found[7d] when OH^- was added to $Co(CN)_5I^{3-}$, reaction III does not occur simply by aquation of the $Fe(CN)_5SCN^{3-}$ complex but rather shows dependences upon OH^- and SCN^- concentrations requiring a more complicated process.

Finally, we considered the monomerization reactions of the dimeric anion $Fe_2(CN)_{10}^{4-}$, whose structure was suggested by Emschwiller and Jørgensen[3d] to be



Both OH^- and SCN^- convert $Fe_2(CN)_{10}^{4-}$ to the respective $Fe(CN)_5X^{3-}$ complex, as in reactions IV and V. Our studies indicate the occurrence of two discrete steps, which were studied spectroscopically and kinetically.

$$Fe_2(CN)_{10}^{4-} + 2OH^- = 2Fe(CN)_5OH^{3-} \qquad (IV)$$

$$Fe_2(CN)_{10}^{4-} + 2SCN^- = 2Fe(CN)_5SCN^{3-} \qquad (V)$$

Experimental Section

Materials.—Sodium "aquopentacyanoferrate(III)," which in fact is a hydrate of the decacyanodiferrate(III) ion, was prepared by the method of Hofmann,[2] oxidizing the dimeric iron(II) complex $Fe_2(CN)_{10}^{6-}$ with bromine, forming the intensely blue $Fe_2(CN)_{10}^{4-}$. The production of the pale greenish yellow monomeric complex $Fe(CN)_5H_2O^{2-}$ was mentioned briefly by Emschwiller and Jørgensen,[3d] who oxidized the monomeric iron(II) complex in a similar manner. In the course of the present work, the following method was developed for preparing and purifying $Fe(CN)_5H_2O^{2-}$. A solution of $Fe_2(CN)_{10}^{4-}$ (*ca.* 5 m*M* in Fe(III)) in 0.25 *M* sodium hydroxide was allowed to stand in the dark at room temperature for 1–2 hr, until the deep blue solution became a clear, pale yellow.[12] The solution was then placed directly on a column of Sephadex G25 which was prepared in the usual way.[13] The dinuclear species passed directly through the column, followed by pure $Fe(CN)_5OH^{3-}$ which was eluted with water and collected directly in a solution of dilute perchloric acid at 0°.

Such solutions of $Fe(CN)_5H_2O^{2-}$ which also contained $HClO_4$ and $NaClO_4$ were stable for several hours if kept cold. The iron content of this solution, and of other iron complexes, was determined by conversion to $Fe(H_2O)_6^{3+}$ by fuming in perchloric acid and was analyzed using the 238-nm peak of Fe^{3+}.[14] Attempts to precipitate salts of $Fe(CN)_5H_2O^{2-}$ were frustrated by its decomposition as well as by the onset of dimerization when attempts were made to concentrate the solutions.

Solutions of $Fe(CN)_5SCN^{3-}$ used for studying reaction III and also for studying the reverse rate of reaction II were prepared by mixing SCN^- (0.02 *M*) and $Fe(CN)_5H_2O^{2-}$ (0.001 *M*), which results in *ca.* 91% conversion to $Fe(CN)_5SCN^{3-}$. These solutions are stable for a considerably longer period of time than those of the aquo complex.

Sodium thiocyanate and sodium perchlorate were recrystallized twice from water; other materials were the reagent grade chemicals. Conductivity water was used for all stock solutions and kinetic runs.

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[4] R. Stasiw and R. Wilkins, *Inorg. Chem.*, **8**, 156 (1969).

[5] D. Gutterman, Ph.D. Thesis, Columbia University, 1970; D. F. Gutterman and H. B. Gray, *Inorg. Chem.*, **11**, 1727 (1972).

[6] The question of whether this complex in aqueous solution is bonded Fe–SCN or Fe–NCS has not been settled, although the former seems probable based on work in solution.[4] The infrared spectrum of $(Et_4N)_3[Fe(CN)_5NCS]$ indicates that this compound, at least in the solid state and in certain aprotic solvents, is N bonded.[5] Our use of the formula $Fe(CN)_5SCN^{3-}$ for the more stable isomer in solution follows the suggestion[4] that the S-bonded form predominates, but no evidence bearing directly on that point was obtained here; further consideration is given to this issue in the Discussion.

[7] (a) A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962); (b) *ibid.*, **1**, 583 (1962); (c) A. Haim, R. Grassi, and W. K. Wilmarth, *Advan. Chem. Ser.*, **No. 49**, 31 (1965); (d) R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 237 (1967).

[8] B. Jaselskis, *J. Amer. Chem. Soc.*, **83**, 1082 (1961).

[9] The blue complex Jaselskis[8] refers to as "$Fe(CN)_5H_2O^{2-}$" is the dimeric species $Fe_2(CN)_{10}^{4-}$ as is the "aquo" complex of Stasiw and Wilkins.[4]

[10] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2d ed, Wiley, New York, N. Y., 1967, pp 177–193, 261–265.

[11] M. L. Tobe, *Accounts Chem. Res.*, **3**, 377 (1970).

[12] At this point the complex is largely $Fe(CN)_5OH^{3-}$, with small amounts of unreacted dimer, often a small amount of ferric hydroxide, and possibly $Fe_2(CN)_{10}OH^{5-}$. A longer time or a higher $[OH^-]$ increases the amount of ferric hydroxide formed.

[13] "Sephadex, Gel Filtration in Theory and Practice," Pharmacia Fine Chemicals, Piscataway, N. J. 08854.

[14] R. Bastian, R. Weberling, and F. Pallilla, *Anal. Chem.*, **28**, 459 (1956).

Methods.—The reaction rates were determined using a Cary 12 recording spectrophotometer. Some dilution experiments on reaction II had small absorbance changes; for those reactions we used a Cary 14 instrument with an expanded-scale recorder reading 0–0.1 absorbance unit full scale.

The spectra of the relevant species are shown in Figures 1 and 2. The intensely blue solutions of $Fe_2(CN)_{10}^{4-}$ show characteristic absorption maxima at λ 568 nm (ε 1600 M^{-1} cm^{-1}), 407 nm (ε 1976), and 358 nm (ε 2135), whereas the pale yellow solutions of monomeric $Fe(CN)_5H_2O^{2-}$ have absorption maxima at 394 nm (ε 743) and 340 nm (ε 748). Freshly prepared solutions of the dimer $Fe_2(CN)_{10}^{4-}$ and of the monomeric $Fe(CN)_5H_2O^{2-}$ both obey Beer's law indicating the presence of only a single species in either solution. The peak of $Fe(CN)_5SCN^{3-}$ at λ 590 nm was used to evaluate the equilibrium constant for reaction II as well as for most of the kinetic experiments on reactions II and III. The reaction between thiocyanate ion and $Fe_2(CN)_{10}^{4-}$ was studied at several wavelengths, with most of the kinetic data on the first stage based on measurements at 423 nm.

The reaction of $Fe(CN)_5SCN^{3-}$ with OH^- (eq III) proceeded to $\geq 96\%$ completion under all the concentration conditions considered. Pseudo-first-order rate constants were evaluated from the usual semilog (absorbance)–time plots, log $(D_\infty - D_t)$ *vs.* *t*; the resulting k^{III}_{obsd} values were then considered as a function of the variables ($[OH^-]$, $[SCN^-]$) which were constant during a given experiment.

Two different types of kinetic experiments[15] were performed on the reaction of $Fe(CN)_5H_2O^{2-}$ with SCN^-, eq II. In the first instance, "mixing" experiments were performed, following the formation of $Fe(CN)_5SCN^{3-}$ after addition of SCN^- to the aquo complex. The concentration-jump method provided the alternative process. In these "dilution" experiments, a solution in which reaction II was at equilibrium was suddenly diluted with water (and perhaps $HClO_4$ or $NaClO_4$) such that the resulting solution had the desired concentrations and unit ionic strength.

In both cases these rate measurements correspond to the same kinetic pattern. All the experiments were performed with a large excess of SCN^-, and the reaction followed the anticipated pseudo-first-order kinetic pattern, plots of log $|D_t - D_{eq}|$ *vs.* time being linear. A pseudo-first-order rate constant designated k^{II}_{obsd} was evaluated from the slopes of such plots. It represents a rate constant which describes the rate of approach to equilibrium in reaction II and consequently is a summation of the apparent rate constants for the forward and reverse reactions at particular $[SCN^-]$ and $[H^+]$. Experiments were carried out to evaluate k_{obsd} over wide ranges of concentration, 3.3×10^{-3} to 0.35 *M* SCN^- and 2×10^{-3} to 0.61 *M* H^+.

Two purposes were served by the dilution experiments: to measure the rate of approach to equilibrium starting from the opposite direction and to extend the evaluation of k^{II}_{obsd} to thiocyanate concentrations too low for the mixing experiments because they would correspond to a very small equilibrium extent of anation of the starting aquo complex.

Results

Equilibrium Studies.—The equilibrium constant for reaction II was evaluated spectrophotometrically at λ 590 nm. Solutions used for these studies contained SCN^- in large excess. The absorbance (*D*) is related to the independent variable $[SCN^-]$ by the relation

$$\bar{\epsilon} = \epsilon_1 - K_{II}\{(\bar{\epsilon} - \epsilon_0)/[SCN^-]\} \qquad (1)$$

where $\bar{\epsilon}$ is the apparent molar absorptivity, $(D/b[Fe]_T)$, ϵ_0 is the molar absorptivity of the aquo complex, *b* is the optical path, ϵ_1 is the molar absorptivity of $Fe(CN)_5SCN^{3-}$, and $[Fe]_T$ is the sum $[Fe(CN)_5H_2O^{2-}] + [Fe(CN)_5SCN^{3-}]$. Measurements were made at 18.3, 25.0, and 34.6° at $\mu = 1.00$ *M*. Plots of the data according to eq 1 are shown in Figure 3. The least-squares fit gave the parameters summarized in Table I. The average value of ϵ_1 is 2710 M^{-1} cm^{-1}, in good agreement with the literature value of 2680 M^{-1} cm^{-1}.[8] Assuming $\Delta H°_{II}$ is not a function of temperature, the

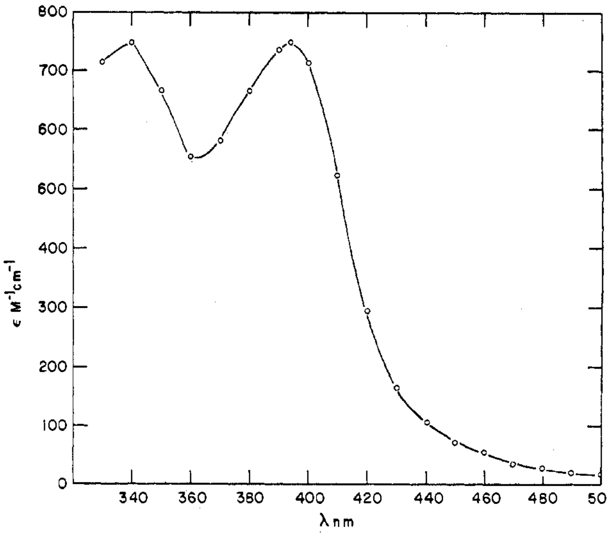

Figure 1.—The spectrum of monomeric $Fe(CN)_5H_2O^{2-}$.

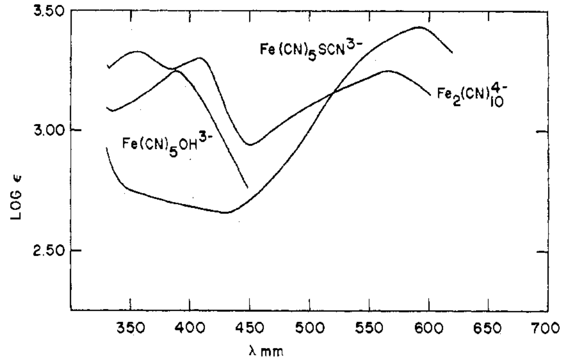

Figure 2.—The spectra of $Fe_2(CN)_{10}^{4-}$, $Fe(CN)_5SCN^{3-}$, and of $Fe(CN)_5OH^{3-}$.

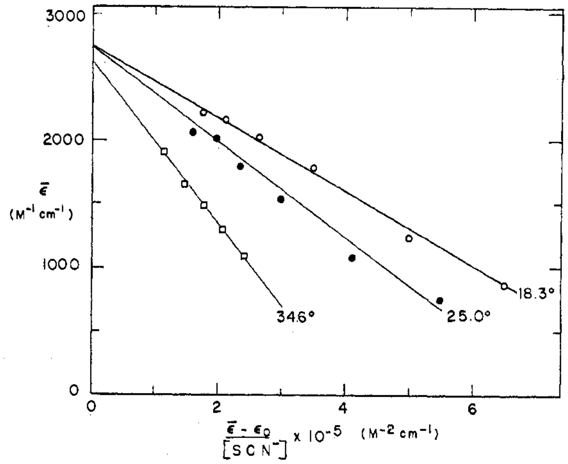

Figure 3.—Plots for the determination of the equilibrium constant for reaction II at various temperatures, according to eq 1.

TABLE I

EQUILIBRIUM STUDIES OF REACTION II[a]

Temp, °C	K_{II},[b] M^{-1}	ϵ_1,[b] M^{-1} cm^{-1}
18.3	345 ± 8	2756 ± 27
25.0	257 ± 15	2740 ± 70
34.6	155 ± 5	2625 ± 37

[a] Evaluated at λ 590 nm in solutions having $\mu = 1.00$ *M* and $[H^+] = 0.100$ *M*. [b] The values of K_{II} and ϵ_1 are those resulting from a least-squares fit of the data to eq 1; the indicated uncertainties represent one standard deviation.

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[15] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, **6**, 1370 (1967).

thermodynamic parameters associated with reaction II are $\Delta H°_{II} = -8.8 \pm 0.6$ kcal mol^{-1}, $\Delta S°_{II} = -18.7 \pm 1.8$ cal mol^{-1} K^{-1}, and $\Delta G°_{II,298} = -3.29 \pm 0.05$ kcal mol^{-1}. The corresponding equilibrium constant for the formation of $Co(CN)_5SCN^{3-}$ from $Co(CN)_5H_2O^{2-}$ is 1460 M^{-1} at 40° and $\mu = 1.0$ M,[7a] compared to the extrapolated 40° value of 120 M^{-1} for reaction II.

The acidity constant corresponding to the reaction

$$Fe(CN)_5H_2O^{2-} \rightleftharpoons Fe(CN)_5OH^{3-} + H^+ \qquad (VI)$$

was determined by a spectrophotometric titration of the monomeric aquo complex with OH^-. The data were plotted as suggested by an equation similar to that of eq 1 and gave the value $K_{VI} = (4 \pm 1) \times 10^{-9}$ M, which can be compared to the analogous value for $Co(CN)_5H_2O^{2-}$, reported in the literature[7a] as 2×10^{-10} M at 40°, $\mu = 1$ M.

The equilibrium constant for reaction III was determined by Jaselskis[8] as $K_{III} = (1.50 \pm 0.15) \times 10^3$ at 25° and $\mu = 0.95$ M. This value can be calculated independently from the values determined here for reactions II and VI together with K_w according to the relation

$$K_{III} = K_{VI}/K_{II}K_w \qquad (2)$$

Using $K_w = 1.4 \times 10^{-14}$ M^2 at 25.0° and $\mu = 1.00$ M,[16] the calculated value of K_{III} is $(1.1 \pm 0.3) \times 10^3$, in satisfactory agreement with the direct determination.

Kinetics of the Reaction of $Fe(CN)_5H_2O^{2-}$ with SCN^-.—The rate experiments based on mixing the aquo complex with thiocyanate ions encompassed a concentration range of 0.010–0.346 M SCN^-, which was always present in large excess. The dilution experiments extend this range down to 0.0034 M SCN^-. The values of k^{II}_{obsd} showed a linear dependence upon $[SCN^-]$ as illustrated in Figures 4 and 5 and expressed by the equation

$$k^{II}_{obsd} = k_{aq} + k_{an}[SCN^-] \qquad (3)$$

where k_{aq} and k_{an} are the apparent rate constants referring to a particular constant $[H^+]$. The quotient k_{an}/k_{aq} at each $[H^+]$ corresponds to K_{II}. At the three $[H^+]$ depicted in Figure 5, this quotient has the values 277 M^{-1} (0.0197 M H^+), 244 M^{-1} (0.0395 M H^+), and 244 M^{-1} (0.105 M H^+), which agree satisfactorily with the directly determined value, 257 M^{-1}.

As illustrated in Figure 5, both k_{an} and k_{aq} increase with decreasing $[H^+]$, although the overall equilibrium does not involve H^+. These dependences take the form of a linear dependence upon $[H^+]^{-1}$

$$k_{an} = a + b[H^+]^{-1} \qquad (4a)$$

$$k_{aq} = c + d[H^+]^{-1} \qquad (4b)$$

such that the overall rate expression for reaction II is

$$d[Fe(CN)_5SCN^{3-}]/dt = \{a + b[H^+]^{-1}\}[Fe(CN)_5H_2O^{2-}][SCN^-] - \{c + d[H^+]^{-1}\}[Fe(CN)_5SCN^{3-}] \qquad (5)$$

The most meaningful method of considering the rate expression is to relate the experimentally determined values of k^{II}_{obsd} to $[SCN^-]$ and $[H^+]$ simultaneously. The principle of microscopic reversibility provides the following relation.

$$K_{II} = k_{an}/k_{aq} = a/c = b/d \qquad (6)$$

Using these expressions, eq 3 becomes

$$k^{II}_{obsd} = \{c + d[H^+]^{-1}\} + \{a + b[H^+]^{-1}\}[SCN^-]$$

which further simplifies to

$$k^{II}_{obsd}/\{[SCN^-] + K_{II}^{-1}\} = a + b[H^+]^{-1} \qquad (7)$$

The application of eq 7 to all 27 kinetic runs[17] is illustrated in Figure 6, where the left-handed side, calculated using $K_{II} = 257$ M^{-1}, is plotted *vs.* $[H^+]^{-1}$. Alternatively, the value of K_{II} in eq 7 may be left as an adjustable parameter. The least-squares values of the

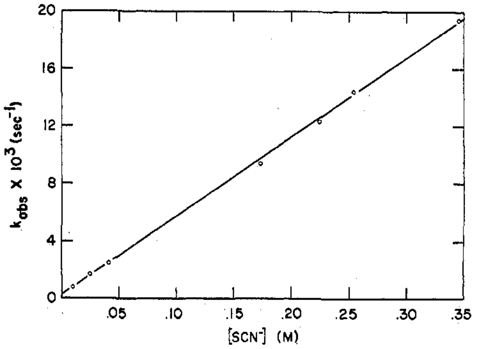

Figure 4.—The linear variation of k^{II}_{obsd} with $[SCN^-]$ at relatively high thiocyanate concentrations (0.160 M H^+).

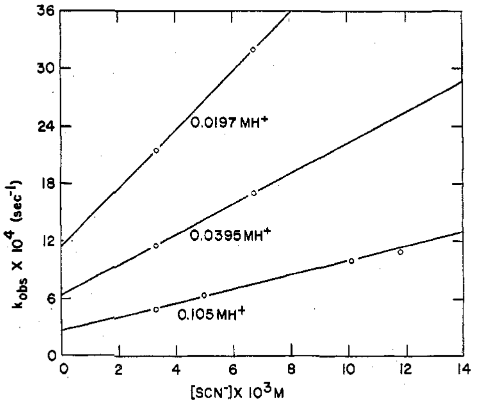

Figure 5.—The variation of k^{II}_{obsd} with $[SCN^-]$ at low $[SCN^-]$ and various $[H^+]$.

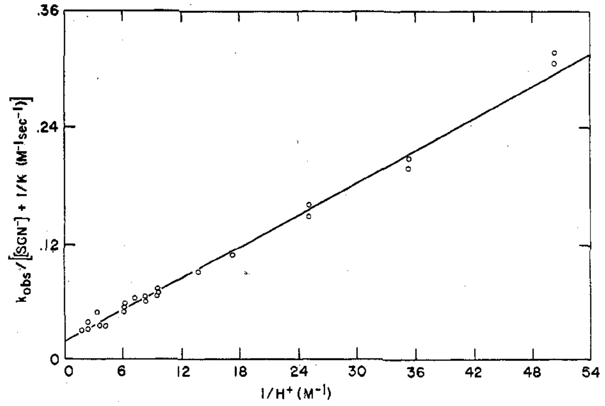

Figure 6.—The correlation of all the kinetic data for reaction II with $[SCN^-]$ and $[H^+]$ variations according to eq 7 using $K_{II} = 257$ M^{-1}.

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[16] R. Näsänen and P. Moriläinen, *Suom. Kemistilehti B*, **33**, 149 (1960).

[17] The original data are given in the thesis cited.[1b]

parameters from both computations are summarized in Table II and are seen to be in reasonable agreement.

TABLE II

RATE CONSTANTS[a] FOR THE REACTION

$Fe(CN)_5H_2O^{2-} + SCN^- = Fe(CN)_5SCN^{3-} + H_2O$

K_{II}, M^{-1}	257 (fixed)	218 ± 27 (variable)
10^2a, M^{-1} sec^{-1}	1.96 ± 0.19	2.02 ± 0.20
10^3b, sec^{-1}	5.17 ± 0.26	4.88 ± 0.33
10^5c, sec^{-1}	7.6 ± 1.2	9.2 ± 2.0
10^5d, M sec^{-1}	2.0 ± 0.2	2.2 ± 0.4

[a] 25.0°, $\mu = 1.00\ M$. The values of c and d are computed from the other parameters according to eq 6.

Considering the nature of the equilibrium and kinetic determinations, the values with K_{II} constrained to the spectrophotometric value appear the more reliable.

Kinetics of the Reaction of $Fe(CN)_5SCN^{3-}$ with OH^-.—The addition of OH^- to a solution of $Fe(CN)_5SCN^{3-}$ prepared from reaction II results in the formation of $Fe(CN)_5OH^{3-}$, because the aquo complex is readily neutralized as implied by reaction VI. The mechanism by which this occurs, however, proved not to be simply an aquation process, the reverse of reaction II, as was the case, for instance, when OH^- was added to $Co(CN)_5SCN^{3-}$. Rather, the Fe(III) complex reacted by a considerably more complicated process, dependent upon $[SCN^-]$ as well as $[OH^-]$.

At the concentration of OH^- and SCN^- employed, the conversion of $Fe(CN)_5SCN^{3-}$ to $Fe(CN)_5OH^{3-}$ went to ≥96% completion. This result was anticipated on the basis of the K_{III} value and was confirmed by spectrophotometric analysis of the final solutions. A total of 21 rate experiments were performed, covering the concentration ranges 0.0087–0.875 M SCN^- and 0.005–0.10 M OH^-, with the results given in Table III.

TABLE III

PSEUDO-FIRST-ORDER RATE CONSTANTS[a] (k^{III}_{obsd}, sec^{-1} × 10^3) FOR REACTION III

	$[OH^-]$, M			
$[SCN^-]$, M	0.00500	0.0200	0.0500	0.0700
0.00866	3.35[b]	7.20	11.5	12.7[c]
0.0238				9.65
0.0456	3.25	4.58	6.60	7.75
0.0888	3.07	3.58	4.79	5.65
0.219				3.90
0.435	2.95	3.03	3.15	3.40
0.442				3.35
0.875				3.03

[a] At 25.0°, $\mu = 1.00\ M$. [b] Excluded from the analysis of the data; calculated value, 5.2×10^{-3} sec^{-1}. [c] Also, at 0.00866 M SCN^- and 0.100 M OH^-, $k^{III}_{obsd} = 0.0130$ sec^{-1}.

Three parameters are needed to account for the dependence of k^{III}_{obsd} upon $[OH^-]$ and $[SCN^-]$, which can be realized by the expression[18]

$$k^{III}_{obsd} = A + B[OH^-]/\{[OH^-] + C[SCN^-]\} \quad (8)$$

The data in Table III were treated according to eq 8, excluding one widely deviant value with the result $A = (2.78 \pm 0.07) \times 10^{-3}$ sec^{-1}, $B = (1.32 \pm 0.09) \times 10^{-2}$ sec^{-1}, and $C = 3.10 \pm 0.43$. The average deviation between the calculated and observed values of k^{III}_{obsd} was 3.5%.[19]

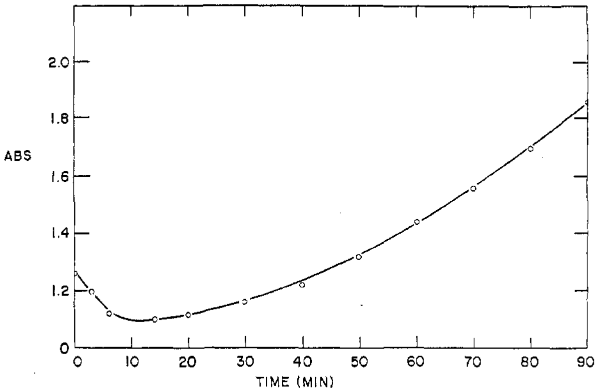


Figure 7.—A typical kinetic experiment indicating the two-stage reaction. Data taken at λ 590 nm, b = 2 cm, $\mu = 1.00\ M$, at 25°; the final absorbance in this experiment would be 3.16.

Kinetics of the Reaction of $Fe_2(CN)_{10}^{4-}$ with SCN^-.—Reaction V occurs in two steps. A sample kinetic run at λ 590 nm is shown in Figure 7. At 423 nm, the intermediate produced in the first stage has the same molar absorptivity as the product, so that the first-stage can be studied by itself. The rate is given by

$$-d[Fe_2(CN)_{10}^{4-}]/dt = k_V[Fe_2(CN)_{10}^{4-}][SCN^-] \quad (9)$$

with $k_V = 0.0102 \pm 0.0004\ M^{-1}$ sec^{-1} (25°, $\mu = 1.00\ M$).

A detailed kinetic study of the second stage was not carried out, but the rate does increase with $[SCN^-]$. Assuming a second-order rate expression, the approximate constant is *ca.* $10^{-4}\ M^{-1}$ sec^{-1}.

Interpretation and Discussion

The dominant monomeric species in acidic solution is $Fe(CN)_5H_2O^{2-}$; it is not further protonated to an appreciable extent at $[H^+] \leq 1\ M$,[20] as its absorption spectra were identical in strongly acidic and approximately neutral solutions. On the other hand, the coordinated water molecule of $Fe(CN)_5H_2O^{2-}$ ought to be appreciably acidic; the K_a value is $4 \times 10^{-9}\ M$. This number appears reasonable on two counts: it is comparable to that for $Co(CN)_5H_2O^{2-}$ ($K_a = 2 \times 10^{-10}\ M$[7a]) and for $Cr(CN)_5H_2O^{2-}$ ($K_a \cong 10^{-9}\ M$[21a]); and for cationic complexes charge effects would cause a far greater extent of acid dissociation (*e.g.*, for $Fe(H_2O)_6^{3+}$, $K_a = 1.4 \times 10^{-3}\ M$[21b]).

The dimeric ion $Fe_2(CN)_{10}^{4-}$ has identical spectra in strongly acidic and basic solutions, which is consistent with the absence of a coordinated water molecule.

The mechanistic interpretations of the various kinetic results will be based on those species which are predominant forms, but not necessarily the most reactive.

The interconversion of the species $Fe(CN)_5SCN^{3-}$ and $Fe(CN)_5H_2O^{2-}$ in acid solution is related to that

---

(18) An equivalent three-parameter expression takes the form $\{P[OH^-] + Q[SCN^-]\}/\{[OH^-] + C[SCN^-]\}$; the data were cast in the form of eq 8 for the convenience of the mechanistic interpretation.

(19) Inclusion of the omitted value changed the parameters to $A = (2.83 \pm 0.14) \times 10^{-3}$ sec^{-1}, $B = (1.5 \pm 0.2) \times 10^{-2}$ sec^{-1}, and $C = 4.4 \pm 1.3$; the average deviation was 6.1%.

(20) Considering that $Fe(CN)_6^{3-}$ is not appreciably basic under similar conditions [J. Jordan and G. J. Ewing, *Inorg. Chem.*, **1**, 387 (1962)], the ion $Fe(CH)_5H_2O^{2-}$ with one unit less of negative charge would not likely add H^+ appreciably.

(21) (a) L. Jeftić and S. W. Feldberg, *J. Phys. Chem.*, **75**, 2381 (1971); (b) R. M. Milburn and W. C. Vosburgh, *J. Amer. Chem. Soc.*, **77**, 1352 (1955).

involving $Fe(CN)_5SCN^{3-}$ and $Fe(CN)_5OH^{3-}$ in basic solution. The principle of microscopic reversibility and thermodynamic considerations impose certain restrictions on mechanistic steps which can be proposed to account for these opposing reactions. For example, consider the pathway for reaction II represented by the rate law term

$$d[Fe(CN)_5SCN^{3-}]/dt = b[H^+]^{-1}[Fe(CN)_5H_2O^{2-}][SCN^-] - d[H^+]^{-1}[Fe(CN)_5SCN^{3-}] \quad (10)$$

for which the following, in itself, appears to be a suitable mechanism

$$Fe(CN)_5H_2O^{2-} \rightleftharpoons Fe(CN)_5OH^{3-} + H^+ \quad (K_{VI}) \quad (VI)$$

$$Fe(CN)_5OH^{3-} + SCN^- \rightleftharpoons Fe(CN)_5SCN^{3-} + OH^- \quad (k_f, k_r) \quad (VII)$$

according to which $b = K_{VI}k_f$ and $d = K_wk_r$. The computed second-order rate constants for VII are thus $k_f = 1.3 \times 10^6\ M^{-1}\ sec^{-1}$ and $k_r = 1.4 \times 10^9\ M^{-1}\ sec^{-1}$. *The latter is clearly inconsistent with the results on the direct study of the reaction of* $Fe(CN)_5SCN^{3-}$ *with* OH^-, *where no bimolecular path was noted and a very rapid reaction was not observed* (k_r is very close to the diffusion-controlled limit). Thus the simple sequence shown above which includes the nucleophilic displacement reaction VII *cannot* be invoked to explain the rate law term shown in eq 10.

Complexities are added in the present situation by the necessity of considering microscopic reversibility and thermodynamic arguments. To clarify the mechanistic arguments we shall set forth the mechanism we believe operative, considering the interrelation of the processes in acidic and basic solutions and demonstrating that the proposals do not violate the restrictions referred to above.

Mechanisms of Reactions II and III.—The rate expression in eq 5 indicates that reaction II proceeds by two parallel pathways, with transition states having the respective compositions $\{Fe(CN)_5(H_2O)SCN^{3-}\}^{\ddagger}$ and $\{Fe(CN)_5(OH)SCN^{4-}\}^{\ddagger}$. The proposed mechanism invokes two seven-coordinated species as reaction intermediates, having the same compositions as these transition states. The second such intermediate yields the products of the reaction upon reaction with H^+. The suggested mechanism is summarized in Scheme II. The empirical parameters from eq 5 are related to the rate constants as follows: $a = k_1$, $b = k_3/K_{VI}$, $c = k_{-1}(k_{-2}/k_2)$, and $d = k_{-3}(k_{-4}/k_4)$. Numerical values are $k_1 = 0.020\ M^{-1}\ sec^{-1}$ and $k_3 = 1.3 \times 10^6\ M^{-1}\ sec^{-1}$. The value of k_3 is strikingly large in relation to k_1. A possible reason for this related to the structures and chemistry of the reaction intermediate will be advanced in a subsequent section.

SCHEME II

$$\begin{tikzcd}
Fe(CN)_5H_2O^{2-} \arrow[rr, shift left, "K_{VI}"] \arrow[d, shift right, "k_1{[SCN^-]}"'] & & Fe(CN)_5OH^{3-} \arrow[ll, shift left, "H^+"] \arrow[d, shift right, "k_3{[SCN^-]}"'] \\
Fe(CN)_5(H_2O)SCN^{3-} \arrow[u, shift right, "k_{-1}"'] \arrow[dr, shift right, "k_2"'] & & Fe(CN)_5(OH)SCN^{4-} \arrow[u, shift right, "k_{-3}"'] \arrow[dl, shift right, "k_4{[H^+]}\ fast"'] \\
& Fe(CN)_5SCN^{3-} + H_2O \arrow[ul, shift right, "k_{-2}"'] \arrow[ur, shift right, "k_{-4}"'] &
\end{tikzcd}$$

The rate expression for reaction III shown in eq 8 suggests the operation of two parallel pathways, of which that represented by the parameters B and C shows two alternative rate-determining steps corresponding to the transition states $\{Fe(CN)_5SCN^{3-}\}^{\ddagger}$ and $\{Fe(CN)_5OH^{3-}\}^{\ddagger}$ and an intermediate $Fe(CN)_5^{2-}$. The pathway having a rate simply $A[Fe(CN)_5SCN^{3-}]$, on the other hand, does not involve this intermediate. The suggested mechanism is shown in Scheme III,

SCHEME III

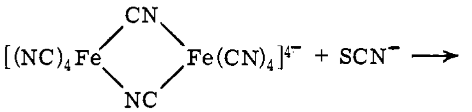
$$\begin{tikzcd}
Fe(CN)_5SCN^{3-} \arrow[r, shift left, "k_6"] \arrow[d, "k_5"'] & Fe(CN)_5^{2-} \arrow[l, shift left, "k_{-6}{[SCN^-]}"] \arrow[d, "k_7{[OH^-]}"] \\
{[intermediate]} \arrow[r, "OH^-", "fast"'] & Fe(CN)_5OH^{3-}
\end{tikzcd}$$

according to which the parameters of eq 8 are $A = k_5$, $B = k_6$, and $C = k_{-6}/k_7$. The one pathway involves the five-coordinate intermediate $Fe(CN)_5^{2-}$, in a limiting SN1 mechanism, the competition between SCN^- and OH^- controlling its fate. The undesignated intermediate has an unknown structure; possible formulations will be considered in a later section.

Some consequences of the proposed mechanisms are noted. In Scheme II the pathway involving the intermediate $Fe(CN)_5(OH)SCN^{4-}$ does not make an important contribution to base hydrolysis in hydroxide solution because the rate constants k_5 and k_6 are both considerably larger than k_{-4}.

The intermediate $Fe(CN)_5^{2-}$ in Scheme III indicates that an important pathway for base hydrolysis is simply a nucleophilic substitution process occurring by the limiting SN1 mechanism. The same intermediate $Fe(CN)_5^{2-}$ is not involved in the anation reaction in acidic solution; the kinetic results (eq 5) are completely inconsistent with a SN1 mechanism under such conditions.

The Mechanism of Reaction V.—The formation of $Fe(CN)_5SCN^{3-}$ from $Fe_2(CN)_{10}^{4-}$ and SCN^- proceeds by way of an intermediate. Based on the structure of the dimer we suggest the mechanism



$$\longrightarrow [(NC)_5FeCNFe(CN)_4(SCN)]^{5-} \quad (VIII)$$

$$[(NC)_5FeCNFe(CN)_4(SCN)]^{5-} + SCN^- \longrightarrow 2Fe(CN)_5SCN^{3-} \quad (IX)$$

Attack of SCN^- at the less stable (Fe–N) end of the bridging cyano group seems a reasonable process to suggest as the first step. Moreover, this is not a reversible process because the rate constant extrapolates to *ca.* zero at $[SCN^-] = 0$. The fact that the intermediate shows considerable absorption at λ >500 nm suggests its retention of a dimeric structure. Singly bridged μ-cyano-diferrate(III) species analogous to the intermediate produced by reaction VIII are known.[3c] A few qualitative observations were made in the reaction of $Fe_2(CN)_{10}^{4-}$ with OH^- (reaction IV), and these also suggest that this process also occurs in two steps.[22]

Chemical Interpretations of Schemes II and III.—The rate constants for the formation of seven-coordinated intermediates by reaction of SCN^- with, respectively, $Fe(CN)_5OH^{3-}$ and $Fe(CN_5)H_2O^{2-}$ are designated in Scheme II as k_3 and k_1. Their ratio is $k_3/k_1 \approx 10^8$, which implicates $Fe(CN)_5OH^{3-}$ as a species much more reactive toward SCN^- than $Fe(CN)_5H_2O^{2-}$. Considering the charges on the aquo and hydroxo complexes this is a surprising result, yet the pronounced $[H^+]^{-1}$ rate dependence (terms *b*, *d* of eq 5) forces such an interpretation. We suggest that the unusually high reactivity of the hydroxo complex is caused by the labilizing effect of OH^-, permitting easier entry of SCN^- into the primary coordination sphere.

The usual operation of this effect is somewhat different. In $Cr(H_2O)_6^{3+}$ complexes,[23] for example, the pronounced $[H^+]^{-1}$ terms are attributed to an enhanced *dissociative* reaction: $Cr(H_2O)_5OH^{2+} \rightarrow Cr(H_2O)_4OH^{2+} + H_2O$ (or the equivalent bond-breaking feature in a concerted reaction). In the present case, however, the CN^- groups are too stable to act as leaving groups. Consequently, we suggest that the main feature of these reactions is bond making, involving intermediates of expanded coordination number.

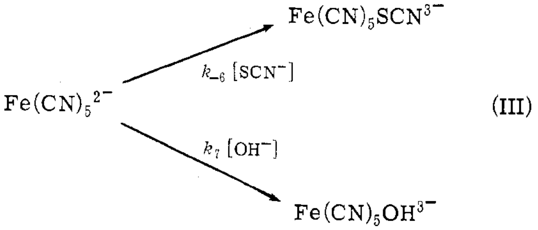
The intermediate formed by addition of SCN^- to the hydroxo complex is $Fe(CN)_5(OH)SCN^{4-}$. The reaction cannot be completed simply by loss of OH^-, however, as this would lead to contradictions when considered in conjunction with the results of base hydrolysis in hydroxide solution (see the discussion of reaction VII). Rather, product formation requires reaction of H^+, in a relatively fast process

$$Fe(CN)_5(OH)SCN^{4-} + H^+ \longrightarrow Fe(CN)_5SCN^{3-} + H_2O \quad (X)$$

The reaction of $Fe(CN)_5SCN^{3-}$ with OH^- is suggested to proceed *via* the mechanism shown in Scheme III. We shall consider two aspects of this process, the limiting SN1 pathway and the chemical nature of the second intermediate indicated in that scheme.

The usual mechanism[10,11] for base hydrolysis of an octahedral complex ML_5X involves the conjugate base, formed by dissociation of an acidic proton from one of the nonleaving ligand groups, $ML_4(L-H)X$. Because $Fe(CN)_5SCN^{3-}$ has no protons, the CB mechanisms are obviously precluded. In fact, the existence of base catalysis for the reverse of reaction II was a surprising result; the conversion of $Co(CN)_5SCN^{3-}$ to $Co(CN)_5OH^{3-}$, for example, occurs simply by a mechanism which is the reverse of the anation process, showing no dependence upon $[OH^-]$.

The rate depends upon $[OH^-]$ and $[SCN^-]$ corresponding to one pathway for base hydrolysis, leading to competitive rate constants for $Fe(CN)_5^{2-}$



(III)

with the ratio $k_{-6}/k_7 = 3.1 \pm 0.4$. Thiocyanate ion is therefore a somewhat better nucleophile toward $Fe(CN)_5^{2-}$ than OH^- is. The overall driving force for replacement of SCN^- by OH^- in reaction III resides then in a different consideration. The formation of $Fe(CN)_5^{2-}$ from $Fe(CN)_5SCN^{3-}$ and $Fe(CN)_5OH^{3-}$ is controlled by bond-breaking factors. The specific rates are 0.013 and $\sim 4 \times 10^{-6}$ sec^{-1}, respectively.[24] Clearly, OH^- is a much poorer leaving group than SCN^-, by a factor of *ca.* 3×10^{-4}.

We offer two suggestions concerning the possible detailed chemistry of the second intermediate shown in Scheme III, simply designated there as "intermediate." This substance is formed directly from $Fe(CN)_5SCN^{3-}$ without intervention of any reagent other than possibly solvent molecules, and yet it cannot be the dissociation product $Fe(CN)_5^{2-}$ as this substance was well characterized by the kinetic competition terms also shown in Scheme III.

A possible detailed mechanism associated with this step is shown by the equations

$$Fe(CN)_5SCN^{3-} + H_2O \xrightleftharpoons[k_4]{k_{-4}} Fe(CN)_5(OH)SCN^{4-} + H^+ \quad (XI)$$

$$Fe(CN)_5(OH)SCN^{4-} \xrightleftharpoons[k_3]{k_{-3}} Fe(CN)_5OH^{3-} + SCN^- \quad (XII)$$

in which case k_{-4} of Scheme II woud be the same as k_5 of Scheme III.[25] The numerical values involved in eq 8 would, at the same time, not provide an additional important pathway for base hydrolysis by reversing the other part of Scheme II.[26]

The intermediate under discussion might also be the linkage isomer $Fe(CN)_5NCS^{3-}$, as in eq XIII-XIV.

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[22] The following is not a suitable mechanism for reaction V

$$Fe_2(CN)_{10}^{4-} + SCN^- + H_2O \longrightarrow Fe(CN)_5SCN^{3-} + Fe(CN)_5H_2O^{2-}$$

$$Fe(CN)_5H_2O^{2-} + SCN^- \longrightarrow Fe(CN)_5SCN^{3-}$$

because the spectrum of the intermediate does not correspond even approximately to the substance shown and because the observed rate of the second step in the reaction of the dimer is far slower than the known anation rate of the aquo complex.

[23] J. H. Espenson, *Inorg. Chem.*, **8**, 1554 (1969).

[24] The latter value refers to k_{-7} of Scheme III and was calculated from parameters *B* and *C* of eq 8.

[25] According to eq XI–XII, the rate of anation in acidic solution is given by $k_3K_{VI}k_4[Fe(CN)_5H_2O^{2-}]/\{k_3 + k_4[H^+]\}$, which reduces to a form consistent with Scheme II, $k_3K_{VI}[Fe(CN)_5H_2O^{2-}]/[H^+]$, when $k_4[H^+] \gg k_{-3}$. The rate of base hydrolysis would be given by $k_{-3}k_{-4}[Fe(CN)_5SCN^{3-}]/\{k_{-3} + k_4[H^+]\}$ which reduces to $k_{-4}[Fe(CN)_5SCN^{3-}]$ when $k_4[H^+] \ll k_{-3}$. The relative requirements on k_4 and k_{-3} are consistent with the results in anation experiments (carried out at pH ≤ 2) as well as base hydrolysis (at pH ≥ 10.5). Microscopic reversibility applied to this scheme gives $k_4 \cong 140k_{-3}$, which is clearly consistent with the necessary condition in basic solution, but only barely so in the acid experiments.

[26] This additional pathway

$$Fe(CN)_5SCN^{3-} + H_2O \xrightleftharpoons[k_2]{k_{-2}} Fe(CN)_5(H_2O)(SCN)^{3-}$$

$$Fe(CN)_5(H_2O)(SCN)^{3-} \xrightleftharpoons[k_1]{k_{-1}} Fe(CN)_5H_2O^{2-} + SCN^-$$

gives $k_{an} = k_1/k_2/(k_{-1} + k_2)$, which is 0.013 sec^{-1} (parameter *a* of eq 5), from which we calculate the pseudo-first-order rate constant for base hydrolysis, $k_{-1}k_{-2}/(k_{-1} + k_2)$, to be $k_{an}/K_{II} = 5.2 \times 10^{-5}$ sec^{-1}, a value so small as to contribute inappreciably to *A* of eq 8.

$$\mathrm{Fe(CN)_5SCN^{3-}} \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} \mathrm{Fe(CN)_5NCS^{3-}} \qquad \text{(XIII)}$$

$$\mathrm{Fe(CN)_5NCS^{3-} + OH^-} \overset{\text{(fast)}}{\rightleftarrows} \mathrm{Fe(CN)_5OH^{3-} + NCS^-} \qquad \text{(XIV)}$$

If such a scheme applies, $k_5 = A = 0.0028\ \text{sec}^{-1}$. The value of k_{-5} can be determined as described in the literature,[4] for which we determined $k_{-5} = 0.036\ \text{sec}^{-1}$.[27] This would give for the linkage isomerization reaction K_{XIII} the value of 0.08, which does not seem unreasonable considering the undoubtedly softer acidity of $\mathrm{Fe(CN)_5^{2-}}$ compared to that of $\mathrm{Fe(H_2O)_5^{3+}}$.

Further work on these complexes is planned, to study directly the immediate reactions of the complex $\mathrm{(Et_4N)_3Fe(CN)_5NCS}$, known to be N bonded in the solid state,[5] when dissolved in aqueous solution, to attempt to provide further evidence for the generality of Schemes II and III by the study of other members of the $\mathrm{Fe(CN_5)X^{3-}}$ series, and to study in considerably greater detail the novel two-step process by which the dimer $\mathrm{Fe_2(CN)_{10}^{4-}}$ undergoes substitution and monomerization.

[27] Although they ascribed a N → S isomerization to the two-step reaction observed, Stasiw and Wilkins[4] did not carry out a study sufficient to characterize the system and did not cite a value for k_{-5}. The value given in the text was determined in the course of this study by repeating their measurements.

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The Diastereomers of Tris[(+)-3-acetylcamphorato]ruthenium(III). Separation and Assignment of Absolute Configurations

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Separation of the four diastereomers of tris[(+)-3-acetylcamphorato]ruthenium(III) was accomplished by thin-layer chromatography on silica gel. Proton and deuteron nuclear magnetic resonance spectra are used to distinguish the cis and trans diastereomers. Complete configurational assignments are based on the isomorphism of two of the diastereomers with two diastereomers of the analogous chromium(III) complex for which absolute configurations are known. The relative signs of Cotton effects in the circular dichroism spectra of the individual diastereomers are consistent with the configurational assignments.

The four diastereomers possible for tris complexes of chiral, bidentate ligands having inequivalent donor atoms may be designated Δ-cis, Δ-trans, Λ-cis, and Λ-trans. Here cis and trans refer to facial and meridional arrangements of like donor atoms in the octahedral coordination sphere, and Δ and Λ indicate right- and left-hand helicities about the C_3 or pseudo-C_3 axis of the complex.[1] These four diastereomers have been separated and characterized for a few α-amino acid and β-diketone complexes. Most work has involved cobalt(III) as the metal ion. For example, all twelve diastereomers of the Co(III) complexes of L-alanine, L-valine, and L-leucine have been isolated, and absolute configurations of the isomers have been assigned from CD and nmr data.[2] The configurational assignments are supported by an X-ray study of one diastereomer of the alanine complex.[3]

More recently the diastereomers of tris(β-diketonato)cobalt(III) complexes, where β-diketone = (+)- and (−)-hydroxymethylenecarvone ((+)- and (−)-Hhmcar),[4] (+)-hydroxymethylenepulegone ((+)-Hhmpul),[4] and (+)-3-acetylcamphor ((+)Hatc),[5,6] have been separated chromatographically and investigated by ORD, CD, and nmr methods. The diastereomers of $\mathrm{Cr((+)atc)_3}$ may also be separated by thin-layer chromatography (tlc) on silica gel, and X-ray powder diffraction data demonstrate the isomorphism of three of these diastereomers with three diastereomers of $\mathrm{Co((+)atc)_3}$.[6] A single-crystal X-ray structural determination[7] of one of the diastereomers of $\mathrm{Cr((+)atc)_3}$ confirmed the configurational assignment made earlier and, combined with the X-ray powder diffraction studies, established absolute configurations of all eight diastereomers of $\mathrm{Co((+)atc)_3}$ and $\mathrm{Cr((+)atc)_3}$.[6] Paramagnetic vanadium(III) complexes of the above β-diketones show well-resolved, isotropically shifted pmr signals in solution.[4,8] The diastereomers present in a mixture can be identified by analysis of the pmr spectra in some cases, and signal integration provides a measure of the relative diastereomer abundances. For $\mathrm{V((+)atc)_3}$ the relative proportions of diastereomers depend somewhat on the solvent used. However, all four isomers are clearly present in some solvents.[9]

The present work concerns the ruthenium(III) complex of (+)-3-acetylcamphor, $\mathrm{Ru((+)atc)_3}$, I. This complex is unique in the series of acetylcamphor complexes studied thus far in that the diastereomers are sufficiently nonlabile to allow their separation and measurement of their individual CD spectra as was done for the Co(III) and Cr(III) complexes, yet the

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(7) W. DeW. Horrocks, Jr., D. L. Johnston, and D. MacInnes, *J. Amer. Chem. Soc.*, **92**, 7620 (1970).

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