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Kinetics of Formation and Stability Constants of Some Pentacyanoferrate(II) Complexes of Aromatic Nitrogen Heterocycles

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An investigation is presented of the kinetics of complexation of aqueous pentacyanoaquoferrate(II), generated on dissolution of sodium pentacyanoammineferrate(II), with the aromatic nitrogen heterocycles 4-methylpyridine, pyridine, isonicotinamide, pyrazine, and *N*-methylpyrazinium ion. In the presence of excess ligand, varied over a large range of concentrations, each reaction was found to obey the rate law $d[Fe(CN)_5L^{n-}]/dt = k_f[Fe(CN)_5H_2O^{3-}][L]$ with k_f varying from 3.6×10^2 to 5.5×10^2 M^{-1} sec^{-1} (25°, $\mu = 0.5$ M ($LiClO_4$), pH range 6–8.5) according to the ligand studied. Measured values of the enthalpy of activation varied from 15 to 17 kcal/mol. To calculate the formation constants of the complexes, the specific rates of formation were used together with the known kinetic parameters of dissociation. The relative values obtained follow the expected order of $d\pi$–$p\pi$ back-donation in the complexes.

Introduction

The reactivity of low-spin iron(II) complexes with respect to substitution by monodentate ligands has received surprisingly little attention, in comparison with the large number of data available for other octahedral, low-spin complexes such as those of Co(III),[1] Rh(III),[1] and Ru(II).[2-6]

Recently, Vaska and Yamagi[7] suggested a dissociative mechanism for monosubstitution in spin-paired Fe(II) complexes of the general formula $Fe(DPGH)_2L_2$ (DPGH is the bidentate diphenylglyoximato anion, L is pyridine, substituted pyridines, or triphenylphosphine) on reaction with carbon monoxide in nonaqueous solution. In our work[8] concerning the properties and reactivity of some pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles, we reported evidence for a limiting SN1 mechanism of ligand exchange in aqueous solution. We also found that the optical and chemical properties of those pentacyanoferrate(II) complexes show a striking similarity to the properties of the pentaammineruthenium(II) complexes.[9,10]

To investigate further the processes of substitution in low-spin iron(II) complexes and also to extend the interesting correlation with the chemistry of octahedral ruthenium(II), we have studied the kinetics of formation of the pentacyanoferrate(II) complexes of 4-methylpyridine, pyridine, isonicotinamide, pyrazine, and the *N*-methylpyrazinium ion.

Experimental Section

Materials. Sodium pentacyanoammineferrate(II) from Eastern Chemical Corp. was recrystallized several times from saturated ammonia solution at ice-bath temperature. This salt was also prepared by the conventional procedure[11] from sodium nitroprusside (Carlo Erba) and recrystallized several times as above. Sodium "pentacyanoaquoferrate(II)" was prepared using Hofmann's method[12] and recrystallized twice.

Pyridine (Riedel de Haen) and pyrazine (Aldrich) of high purity were used in the kinetic experiments as supplied. 4-Methylpyridine (Aldrich) was purified by double distillation from barium oxide. Isonicotinamide (Aldrich) was recrystallized twice from aqueous solution and kept under vacuum in the presence of anhydrous calcium chloride for several weeks. *N*-Methylpyrazinium iodide was prepared according to the procedure of Bahner and Norton[13] and recrystallized from absolute ethanol solution several times. *Anal.* Calcd for $C_5H_7N_2I$: C, 27.04; N, 12.6; H, 3.18; I, 57.2. Found: C, 27.11; N, 12.8; H, 3.22; I, 57.2.

Kinetic Measurements. The rate measurements were performed using a Durrum Model D-150 stopped-flow instrument to observe the formation of the $Fe(CN)_5L^{n-}$ products ($n = 2$, L = *N*-methylpyrazinium ion (MPz); $n = 3$; L = pyridine (py), 4-methylpyridine (pic), pyrazine (pz), and isonicotinamide (isonic)), at the wavelengths of the maxima in the complexes' electron-transfer absorption bands.

For each measurement an aqueous solution of the iron(II) reagent, maximum concentration 10^{-5} M, was freshly prepared by dissolving sodium pentacyanoammineferrate(II) in previously thermostated lithium perchlorate solution. Subsequently the reagent solutions were maintained in darkness in the stopped-flow instrument's thermostated drive syringe for 15 minutes to ensure thermal equilibrium.

The ligand concentration, [L], which was employed always greatly exceeded the total initial pentacyanoammineferrate(II) concentration. Under these conditions formation of $Fe(CN)_5L^{n-}$ was shown by spectrophotometry to be quantitative.[8] The pseudo-first-order rate constants, k_{obsd} (sec^{-1}), were obtained by plotting ln $|A_\infty - A_t|$ *vs.* time, where A_t is the measured absorbance at time *t*. Values of k_{obsd} given in this work are mean values of at least three measurements. These were found to be reproducible with a precision of better than 2%. However, because of systematic errors inherent in the stopped-flow method, the measured k_{obsd} values are considered accurate to within approximately 4%.

Each second-order rate constant (k_f) reported in the results was obtained as the slope of a plot of k_{obsd} *vs.* [L] with points at seven or more ligand concentrations, which ranged from approximately 1×10^{-3} to 4×10^{-1} M.

Temperature and ionic strength dependences of the rate constants were determined within the ranges 10–30° (±0.1°) and 0.1–1.5 M (lithium perchlorate), respectively. Some kinetic experiments were performed in argon atmosphere, yielding results identical with those performed without that precaution.

Results

Rate Studies. The rates of formation of the heterocycle-substituted pentacyanoferrate(II) anions were measured spectrophotometrically by the stopped-flow technique at the wavelengths corresponding to the λ_{max} of the complexes' electron-transfer bands. Because of their high extinction coefficients[8] (>3×10^3 M^{-1} cm^{-1}) extremely low concentrations (10^{-5} M and below) of the iron(II) reagent were employed.

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, pp 124–246.

(2) (a) R. J. Allen and P. C. Ford, *Inorg. Chem.*, **11**, 679 (1972); (b) R. E. Shepherd and H. Taube, to be submitted for publication.

(3) E. M. Elson, I. J. Itzkovitch, and J. A. Page, *Can. J. Chem.*, **48**, 1639 (1970).

(4) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **92**, 6170 (1970).

(5) H. E. Toma and J. M. Malin, *J. Amer. Chem. Soc.*, **94**, 4039 (1972).

(6) J. N. Armor and H. Taube, *J. Amer. Chem. Soc.*, **91**, 6874 (1969).

(7) L. Vaska and T. Yamagi, *J. Amer. Chem. Soc.*, **93**, 6673 (1971).

(8) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).

(9) P. C. Ford, *Coord. Chem. Rev.*, **5**, 75 (1970).

(10) P. C. Ford, D. F. P. Rudd, R. G. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 1187 (1968).

(11) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, Academic Press, New York, N. Y., 1965, p 1511.

(12) K. A. Hofmann, *Justus Liebigs Ann. Chem.*, **312**, 1 (1900).

(13) C. T. Bahner and L. L. Norton, *J. Amer. Chem. Soc.*, **72**, 2881 (1950).

Some preliminary experiments with sodium "pentacyanoaquoferrate(II)" prepared according to Hofmann's procedure[12] gave non-first-order kinetic behavior showing in addition to the main, fast reaction a second, slower absorbance increase. These kinetic measurements were, in general, not reproducible and seemed to depend upon the time of storage of the aqueous solution of pentacyanoferrate(II) and also on its concentration.

As Emschwiller[14] has pointed out, the material prepared by Hofmann's method consists of at least two components, the mononuclear $Fe(CN)_5H_2O^{3-}$ ion and the binuclear $Fe_2(CN)_{10}{}^{6-}$ species. Evidence for their coexistence in aqueous solution has been obtained by chromatographic and polarographic experiments[15] and through kinetic studies.[16] Emschwiller observed that the mononuclear pentacyanoaquoferrate(II) species is complexed readily by nitrosobenzene[17] while the binuclear complex reacts slowly. This behavior is quite similar to the two-step complexation process encountered in the authors' initial experiments. These irregularities, as well as the known thermal and photochemical sensitivity[15,18] of the starting material in question, precluded its further use.

To eliminate the difficulties which we have described, the salt sodium pentacyanoammineferrate(II) was used in the kinetic experiments. Substitution reactions employing 10^{-5} *M* solutions of pentacyanoammineferrate(II) were found to occur readily, giving defined and reproducible first-order kinetic plots, linear over at least 3 half-lives. From the slopes of these plots we have calculated the pseudo-first-order rate constants at several ligand concentrations. Two examples of the dependence of k_{obsd} on the concentrations of the entering ligands are shown in Table I.

For each pyridine and pyrazine ligand investigated k_{obsd} proved to be a linear function of the ligand concentration, giving a zero intercept. Plots of the observed rate constants *vs.* ligand concentration are shown in Figure 1. From the slopes of these plots we have calculated the second-order rate constants for the substitution processes. The rate data were taken in aqueous solution at pH values sufficiently basic (pH 6-8.5, unbuffered) to maintain the various ligands in their free-base forms. The rate was found not to vary with changing pH within the range investigated.

When the solutions were stored for more than 20 min a small but continuous variation of the final absorbance was observed in the stopped-flow traces. This effect was more pronounced at higher temperatures and was probably caused by thermal decomposition of the pentacyanoaquoferrate(II) ion.

Temperature Dependence. The temperature dependence of the rate constants of the substitution process was studied in the 10-30° range. The maximum useful temperature was governed by the onset of the above-noted variation in the final absorbance. The second-order rate constants at several temperatures and the activation parameters for the reactions studied are presented in Table II.

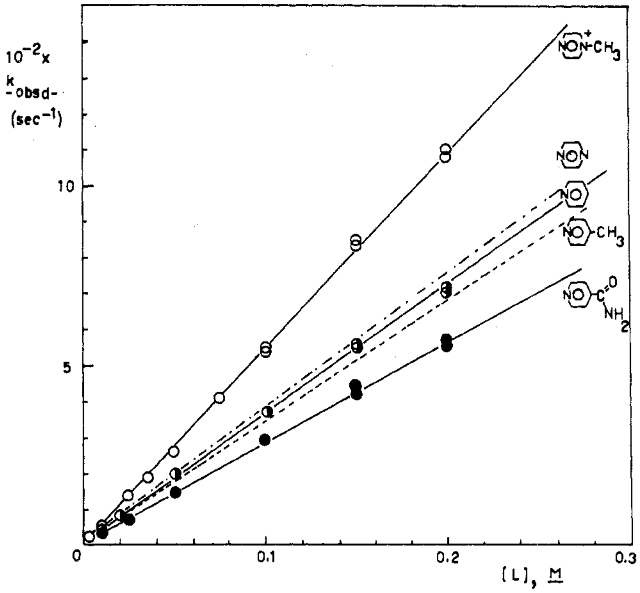

Figure 1. Plots of the observed rate constants *vs.* ligand concentration at 25° and $\mu = 0.50\,M$ (lithium perchlorate) for all reactions except that of the MPz ion, for which $\mu = 1.00\,M$. The experimental points for the pyrazine and 4-methylpyridine ligands are omitted for clarity.

Table I. Pseudo-First-Order Rate Constants of Formation of $Fe(CN)_5L^{n-}$

L = pyridine[a]		L = *N*-methylpyrazinium[b]			
[L], *M*	k_{obsd}, sec^{-1}	[L], *M*	k_{obsd}, sec^{-1}	[L], *M*	k_{obsd}, sec^{-1}
0.0050	1.7_0	0.0012	0.60	0.075	$41._0$
0.0100	3.7_0	0.0025	1.2	0.100	$54._0$
0.0200	7.4_0	0.0050	2.5	0.150	$87._0$
0.0500	18.4	0.010	5.6	0.200	118
0.100	37.0	0.025	14.0		
0.150	56.0	0.036	19.0		
0.200	71.0	0.050	$25._5$		

[a] $\mu = 0.50\,M$ ($LiClO_4$); $T = 25°$. [b] $\mu = 1.00\,M$; $T = 25°$.

Ionic Strength Dependence. The ionic strength dependences of two of the reactions were studied in the range $\mu = 0.10\text{-}1.50\,M$ (lithium perchlorate), with $[L] = 5.0 \times 10^{-2}$ *M*, $T = 25.0°$, using both a neutral ligand (pyridine) and a positively charged one (MPz). The second-order specific rates obtained at several ionic strengths are given in Table III.

Discussion

Rate Law. Three salient features emerge from the data describing the kinetics of formation of the substituted pentacyanoferrate(II) complexes: (1) when care is taken to avoid polynuclear ferrate(II) species, the rate law for complex formation is rigorously a second-order one, first order in the ligand concentration and first order in the concentration of the reacting complex; (2) the measured specific rates for all the reactions studied in this work are fairly high in comparison with those involving other low-spin, d^6 octahedral complexes;[1-6] (3) the calculated second-order rate constants show a notable insensitivity to the nature (in terms of charge and basicity) of the entering ligand.[19]

It has been shown recently[20] that under the conditions employed in this study the ammonia ligand is lost from the pentacyanoammineferrate(II) complex with a half-life of less than 40 sec. Therefore our subsequent discussion will

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(14) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **268**, 694 (1969).
(15) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **259**, 4281 (1964).
(16) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **238**, 341 (1954).
(17) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **270**, 1362 (1970).
(18) G. Emschwiller, *C. R. Acad. Sci., Ser. C*, **274**, 1500 (1972).

(19) The specific rate of formation of the pentacyano(dimethyl sulfoxide)ferrate(II) complex in aqueous solution is 2.4×10^2 M^{-1} sec^{-1} (25°, 1 *M* $LiClO_4$). This value, which is quite close to those found in this work, is a further example of the relative independence of the rate of the substitution process on the nature of the attacking ligand in these systems: H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 12, 2084 (1973).

(20) H. E. Toma and J. M. Malin, submitted for publication in *Inorg. Chem.*

Table II. Temperature Dependence of Specific Substitution Rates

Ligand	T, °C	$10^{-2}k_f$,[a] M^{-1} sec^{-1}	pK_a[b]	$\Delta H^{\ddagger}$,[c] kcal/mol	$\Delta S^{\ddagger}$, eu
4-Methylpyridine	11.4	1.11	6.11	15.1	4
	15.4	1.57			
	19.6	2.2_5			
	25.0	3.5			
	29.2	5.2			
Pyridine	10.5	0.79	5.30	16.1	7
	16.1	1.25			
	20.1	2.0_0			
	25.0	3.7			
	29.3	5.2			
Isonicotinamide	11.4	0.78	3.65	15.8	6
	14.8	1.17			
	20.0	2.1_7			
	25.0	3.0			
	29.6	4.4			
Pyrazine	10.0	0.83	0.6[d]	15.4	5
	14.8	1.34			
	19.4	2.1_0			
	25.0	3.8			
	30.1	5.2			
N-Methylpyrazinium	10.4	1.20	<0	16.8	10
	14.8	1.75			
	19.0	2.7_0			
	25.0	5.5			
	29.8	8.3			

[a] $\mu = 0.50\ M$ (lithium perchlorate) for all reactions except $\mu = 1.00\ M$ for *N*-methylpyrazinium. [b] K. Schofield, "Hetero Aromatic Nitrogen Compounds," Plenum Press, New York, N. Y., 1967. [c] Errors in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are ±0.5 kcal/mol and ±2 eu, respectively. [d] R. M. Acheson, "An Introduction to the Chemistry of Heterocyclic Compounds," Interscience, New York, N. Y., 1960, p 299.

Table III. Ionic Strength Dependence of Specific Substitution Rates at 25°

L = pyridine		L = *N*-methylpyrazinium ion	
μ, M	$10^{-2}k_f$, M^{-1} sec^{-1}	μ, M	$10^{-2}k_f$, M^{-1} sec^{-1}
0.100	3.8	0.100	$24._1$
0.250	3.8	0.250	$14._6$
0.500	3.7	0.500	9.2
0.750	3.7	0.750	7.3
1.00	3.6	1.00	5.6
1.50	3.6	1.50	3.1

be based on the consideration that the reactant iron(II) species is the ion $Fe(CN)_5H_2O^{3-}$, generated on rapid aquation of $Fe(CN)_5NH_3{}^{3-}$. Using the association quotient $Q = 80\ M^{-1}$ [15] for the dimerization process, the concentration of the binuclear pentacyanoferrate(II) species, $Fe_2(CN)_{10}{}^{6-}$ is expected to be totally negligible at the concentrations (less than $10^{-5}\ M$) used in this work.

The observed rate law (eq 1) could be explained either by a direct displacement mechanism, as shown in eq 2, or by a

$$\frac{d[Fe(CN)_5L^{n-}]}{dt} = k_f[Fe(CN)_5H_2O^{3-}][L] \tag{1}$$

$$Fe(CN)_5H_2O^{3-}(aq) + L(aq) \xrightarrow{k_f} Fe(CN)_5L^{n-}(aq) \tag{2}$$

dissociative SN1 mechanism (eq 3, 4) whose rate law, derived using the steady-state approximation, is given in eq 5.

$$Fe(CN)_5H_2O^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Fe(CN)_5{}^{3-} + H_2O \tag{3}$$

$$Fe(CN)_5{}^{3-} + L \xrightarrow{k_2} Fe(CN)_5L^{n-} \tag{4}$$

$$\frac{d[Fe(CN)_5L^{n-}]}{dt} = \frac{k_1k_2[Fe(CN)_5H_2O^{3-}][L]}{k_{-1} + k_2[L]} \tag{5}$$

Considering that the term k_{-1} in this mechanism incorporates the concentration of the solvent (55.5 M) and assuming that water and the heterocycle are approximately equal in their efficiency as attacking ligands, we note that, for $k_2[L]$ to be comparable with k_{-1}, [L] must be extremely high. Under the conditions of this study k_{-1} is probably much larger than $k_2[L]$, with the result that eq 5 is reduced to the simple, second-order form. Thus, the observed rate law does not allow a choice between the two mechanisms.

A relative invariance among the specific rates of attack of a number of entering ligands upon a given aqueous metal center is considered as indicative of a common, predominantly SN1 complexation mechanism.[21] The interpretation is consistent with the observations described in this work. If eq 3 and 4 adequately represent an SN1 reaction mechanism, then k_f (Tables II and III) equals k_2k_1/k_{-1}. The fraction k_1/k_{-1} is expected to be identical for all incoming ligands. The variations observed in k_f as a function of the ligand properties must therefore be caused by proportional changes in k_2. From the small variation in k_f seen among the ligands in Table II we note that k_2 must be remarkably independent of ligand basicity. This would be expected if k_2 were near the diffusion-controlled limit.

Activation Parameters. The activation parameters shown in Table II are practically identical for all the systems studied, within the limits of error. The positive activation entropies, $\Delta S^{\ddagger}$, fall into a range which is usually interpreted as indicating a dissociative pathway.[7]

A very striking comparison is found between the rate constants and activation parameters of the pentacyanoaquoferrate(II) complexation processes and those of the corresponding pentaammineaquoruthenium(II) reactions. For a number of substituted pyridines (3-chloropyridine, 3-methylpyridine, 4-methylpyridine, 3,5-dimethylpyridine) Allen and Ford[2a] found second-order rate constants ranging from 0.064 to 0.117 M^{-1} sec^{-1} with nearly identical sets of activation parameters $\Delta H^{\ddagger} = 15.3 \pm 0.6$ kcal/mol and $\Delta S^{\ddagger} = -13 \pm 2$ eu at 25°, at 0.20 M ionic strength (*p*-toluenesulfonate). Shepherd and Taube[2b] obtained similar results, although with slightly higher $\Delta H^{\ddagger}$ values and slightly less negative values of $\Delta S^{\ddagger}$, for a number of related substitution reactions of pentaammineaquoruthenium(II). On comparing the Ru(II) results with those obtained in this study one notes immediately that, small differences in the enthalpies of activation nonwithstanding, the main factor determining the considerable difference (of three orders of magnitude) in lability between the iron(II) and the ruthenium(II) systems resides in the entropic term.

Because of the lack of ionic strength dependence in the substitution reactions of both the pentacyanoaquoferrate(II) and the pentaammineaquoruthenium(II) ions with neutral ligands, this kind of effect is ruled out as responsible for the contrasting entropies of activation.

One interpretation of the differences in $\Delta S^{\ddagger}$ is that the pentacyanoferrate(II) substitution reactions may involve a greater degree of bond breaking (SN1 character) in the activated complex than the pentaammineaquoruthenium(II) reactions. Certainly, as Basolo and Pearson[1] have pointed out for an analogous Co(III) system, σ donation from the cyanide ligands to iron(II) in the $Fe(CN)_5H_2O^{3-}$ ion should cause an accumulation of negative charge on the metal which is probably only partly removed by π back-donation. This would weaken the iron(II)–H_2O bond, promoting an SN1

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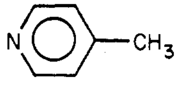
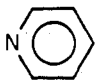
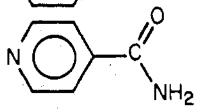
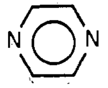
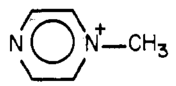
(21) M. L. Tobe, *Advan. Chem. Ser.*, No. 49, 17 (1965); M. Eigen and R. G. Wilkins, *ibid.*, No. 49, 55 (1965).

Table IV. Kinetic and Equilibrium Parameters[a] for $Fe(CN)_5L^{n-}$

L	λ_{max}, kK	$10^{-2}k_f$, M^{-1} sec^{-1}	$\Delta H_f^‡$, kcal/mol	$\Delta S_f^‡$, eu	$10^4 k_d$,[8] sec^{-1}	$\Delta H_d^‡$, kcal/mol	$\Delta S_d^‡$, eu	$10^{-5}K$, M^{-1}
	28.1	3.60	15.1	4	11.5	24.0	9	3.1
	27.6	3.65	16.1	7	11.0	24.8	11	3.3
	23.0	2.96	15.8	6	7.3	26.0	14	4.0
	22.2	3.80	15.4	5	4.2	26.4	14	9.0
	15.1	5.50	16.8	10	2.8	27.5	18	20

[a] $\mu = 0.50\ M$ (lithium perchlorate) for all reactions except $\mu = 1.00\ M$ for N-methylpyrazinium; $T = 25°$.

mechanism. Furthermore, it may be possible that a comparatively greater degree of bond formation (increased SN2 character) takes place in pentaammineaquoruthenium(II) substitution. There exists evidence that an associative intermediate is formed in at least one complexation reaction of that ion.[5]

A second explanation is that the different $\Delta S^‡$ values found for the iron(II) and ruthenium(II) substitution reactions both refer to predominantly SN1 mechanisms but that pentacoordinate intermediates of different configurations are involved. Allen and Ford[2] cited Tobe's hypothesis[22] that for octahedral complexes, dissociative pathways involving trigonal-bipyramidal intermediates give positive $\Delta S^‡$ values while for square-pyramidal intermediates more negative $\Delta S^‡$ values are observed. Allen and Ford also quoted stereochemical evidence[23] against formation of a trigonal-bipyramidal intermediate in octahedral ruthenium(II) substitution. On the other hand, in the pentacyanoaquoferrate(II) case we suggest that a hypothetical five-coordinate intermediate might easily rearrange from square-planar to trigonal-bipyramidal geometry for two reasons. First, a configuration of reduced electrostatic repulsion would be obtained. Second, as Basolo and Pearson suggested for the pentacyanocobalt(III) intermediate, π-bonding effects might allow rearrangement to a trigonal bipyramid with little or no loss of ligand field stabilization energy.

To summarize these arguments, it seems that both the increasing tendency toward an SN1 dissociative mechanism in the pentacyanoaquoferrate(II) case and the formation of pentacoordinate intermediates of different configurations (square pyramidal for Ru(II), trigonal bipyramidal for Fe(II)) could occur in these systems. Thus the contrasting sets of $\Delta S^‡$ values obtained in this work and in the Ru(II) studies might both be consistent with nonlimiting SN1 mechanisms.

Equilibrium Constants. Evidence for limiting SN1 ligand exchange was found in our recent work[8] concerning the substitution reactivity of the pentacyanoferrate(II) complexes of aromatic nitrogen heterocycles. The kinetics of ligand exchange in those systems showed the typical rate saturation curves expected for processes where the loss of a coordinated ligand completely determines the rate of substitution.

From the limiting specific rates of loss of the coordinated aromatic N heterocycles (k_d) measured in that work and from the specific rates of formation of the same complexes given in this article, we have calculated the association constants with respect to the aqueous pentacyanoaquoferrate(II) complex and the free ligand using the relationship $K = k_f/k_d$. The set of kinetic data and equilibrium constants is shown in Table IV.

The calculated values of K increase only slightly on moving down the series of complexes in Table IV. This reflects the relative independence on ligand properties of both k_f and k_d. The fourfold *decrease* in k_d, as the leaving ligands become progressively poorer bases by a factor of 10^6 overall, is noteworthy. This decrease is accompanied by an increase in the ligands' π-acceptor capacities[8] and is consistent with an increase in stabilization of the complexes by dπ-pπ back-donation. Comparing the two conflicting trends, of decreasing ligand basicity and increasing back-bonding ability, we suggest that the latter is slightly more important for this series of complex ions. This causes the observed ordering of k_d and K values.

Registry No. $Fe(CN)_5(pic)^{3-}$, 37475-65-3; $Fe(CN)_5(py)^{3-}$, 37475-75-5; $Fe(CN)_5(isonic)^{3-}$, 40299-77-2; $Fe(CN)_5(pz)^{3-}$, 40299-78-3; $Fe(CN)_5(MPz)^{2-}$, 40299-79-4; $Na_3[Fe(CN)_5NH_3]$, 14099-05-9; $Fe(CN)_5H_2O^{3-}$, 18497-51-3; pyridine, 110-86-1; 4-methylpyridine, 108-89-4; N-methylpyrazinium iodide, 6277-35-6.

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(22) M. L. Tobe, *Inorg. Chem.*, 7, 1260 (1968).
(23) P. C. Ford and C. Sutton, *Inorg. Chem.*, 8, 1544 (1969).