Kinetics of the Aquation of Amminepentacyanoferrate(II). A Volume Profile Analysis

Iwona Maciejowska,[†] Rudi van Eldik,*[,‡] Grazyna Stochel,[†] and Zofia Stasicka[†]

Department of Inorganic Chemistry, Jagiellonian University,
30 060 Kraków, Poland, and Institute for Inorganic
Chemistry, University of Erlangen-Nürnberg,
91058 Erlangen, Germany

Received November 18, 1996

Introduction

Pentacyanoferrate complexes are often used as models in fundamental and applied studies. The numerous kinetic investigations involving these complexes have contributed considerably to the understanding of the mechanisms of ligand substitution and electron transfer processes.[1−3] The common precursor employed in the synthesis of substituted pentacyanoferrate(II) complexes is $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$, which can in aqueous solution undergo aquation to yield the aquapentacyanoferrate(II) ion. Although this reaction has in many investigations been used as the source of the $Fe(CN)_5H_2O^{3-}$ ion, its kinetics and thermodynamics are still not well described. Several side reactions such as dimerization and/or polymerization, oxidation, and photochemical decomposition, as well as outer-sphere interactions with other species in solution,[4−8] can occur when reaction conditions are selected incorrectly, and can thus lead to an incorrect interpretation of the obtained data.

Our interest in the catalytic and photocatalytic conversion of nitric oxides into dinitrogen, using pentacyanoferrate complexes as catalysts, has led us to reexamine the substitution behavior of $Fe(CN)_5L^{3-}$ (where L = NH_3 or H_2O) in aqueous solution. In contrast to earlier studies,[9−14] we have now performed a detailed kinetic and thermodynamic study of the overall system at ambient and high pressure, which enables us to report not only activation parameters but also a complete volume profile analysis.

Experimental Section

Materials. $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ was prepared from sodium nitroprusside (Merck, reagent grade) according to standard procedures[15] and characterized by UV−vis and IR spectroscopy. The purified and dried yellow crystalline sample was stored under nitrogen in the dark at 5 °C to prevent oxidation and any light-induced reactions. All other chemicals were of analytical grade. Demineralized and doubly distilled water was used throughout this study.

Procedure and Instrumentation. Solutions of $Fe(CN)_5NH_3^{3-}$ were freshly prepared for each experiment by dissolving $Na_3[Fe(CN)_5NH_3]\cdot3H_2O$ in Ar-saturated water to yield a concentration of 2×10^{-3} M. The reaction pH was maintained by the use of Britton−Robinson buffers or by addition of NaOH, HCl, and ascorbic acid. Its value was determined before and after each reaction using an N517 (Meratronik) pH-meter and an appropriate glass electrode.

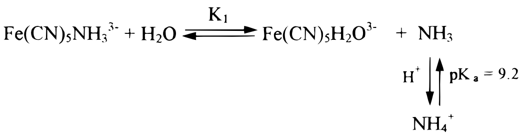
The UV−vis spectra were recorded and spectrophotometric titrations were carried out in normal or tandem optical cells of 1 cm and 0.88 cm path length, respectively, thermostated at 298 K (±0.1), using Shimadzu UV-2100 or Hewlett Packard HP 8453 spectrophotometers.

The equilibrium constant (K_2) for the formation of the ammine complex, $Fe(CN)_5NH_3^{3-}$, was determined from the spectrophotometric titration of $Fe(CN)_5H_2O^{3-}$ with aqueous NH_3. These experiments were done using a pH jump technique. The $Fe(CN)_5H_2O^{3-}$ solution was prepared by the addition of ascorbic acid (pH = 5) to the deoxygenated solution of $Fe(CN)_5NH_3^{3-}$ in the presence of an appropriate concentration of NH_4Cl. The pH of the solution was then jumped to the desired value in the range 6.5−9.0 by mixing rapidly with an appropriate buffer. Ascorbic acid was added to prevent possible oxidation of the aqua complex. Blank experiments indicated that there was no reaction between ascorbic acid and the aqua complex within the time scale of these experiments. The concentration of NH_3 was calculated from the equilibrium $NH_4^+ \leftrightarrow NH_3 + H^+$, $pK_a = 9.2$. The observed change in absorbance at λ_{max} of either $Fe(CN)_5H_2O^{3-}$ or $Fe(CN)_5NH_3^{3-}$ with change in concentration of added NH_3 was analyzed as described in the Supporting Information. No evidence for dimerization, oxidation or any other disturbing side reactions was observed under the selected conditions and time scale of the experiments.

Kinetic measurements at ambient pressure were performed on a stopped-flow spectrophotometer SX-17MV from Applied Photophysics, and on a home-made high-pressure stopped-flow unit[16,17] at pressures up to 150 MPa. Both instruments were thermostated to within ±0.1 °C in the range 288−313 K and attached to an on-line data acquisition system using Pro/Kineticist or Olis Kinfit programs. The formation of aquapentacyanoferrate(II) was followed at 440 nm, whereas the formation of $Fe(CN)_5NH_3^{3-}$ was followed at 400 nm.

Results and Discussion

Spectral Properties and Thermodynamics. The visible spectrum of deoxygenated aqueous solutions of amminepentacyanoferrate(II) ion varies with pH as shown in Figure S1 (Supporting Information). The spectral changes are consistent with the overall equilibrium (1). The aqua complex has a



$$Fe(CN)_5NH_3^{3-} + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} Fe(CN)_5H_2O^{3-} + \begin{array}{c} NH_3 \\ H^+ \downarrow\uparrow pK_a = 9.2 \\ NH_4^+ \end{array} \qquad (1)$$

maximum absorbance at 444 nm ($\epsilon = 660\ M^{-1}\ cm^{-1}$) and the $Fe(CN)_5NH_3^{3-}$ ion at 400 nm ($\epsilon = 450\ M^{-1}\ cm^{-1}$). These

---

* To whom correspondence should be addressed. E-mail: VANELDIK@ANORGANIK.CHEMIE.UNI-ERLANGEN.DE.

[†] Jagiellonian University.

[‡] University of Erlangen-Nürnberg.

(1) Norris, P. R.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1995**, 3643.

(2) Stochel, G. *Coord. Chem. Rev.* **1992**, *114*, 269 and references cited therein.

(3) Macartney, D. H. *Rev. Inorg. Chem.* **1988**, *9*, 101 and references cited therein.

(4) Asperger, S.; Murati, I.; Pavlovic, D. *J. Chem. Soc.* **1960**, 730.

(5) Kenney, D. J.; Flyn, T. P.; Gallin, J. B. *J. Inorg. Nucl. Chem.* **1961,** *20*, 75.

(6) Emschwiller, G. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 4333.

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

(8) Davies, G.; Garafalo, A. R. *Inorg. Chem.* **1976**, *15*, 1101.

(9) Bal Reddy, K.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 596.

(10) Sullivan, T. R.; Stranks, D. R.; Burgess, J.; Haines, R. I. *J. Chem. Soc., Dalton Trans.* **1977**, 1460.

(11) Stochel, G.; van Eldik, R.; Hejmo, E.; Stasicka, Z. *Inorg. Chem.* **1988**, *27*, 2767.

(12) Macartney, D. H.; McAuley, A. *Inorg. Chem.* **1979**, *18*, 2891.

(13) Blesa, M. A.; Borghi, E. B.; Fernandez-Prini, R. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 3021.

(14) Toma, H. E.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 176.

(15) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; Ferdinand Enke Verlag: Stuttgart, 1981; Vol. 3.

(16) van Eldik, R.; Palmer, D. A.; Schmidt, R.; Kelm, H. *Inorg. Chim. Acta* **1981**, *50*, 131.

(17) van Eldik, R.; Gaede, W.; Wieland, S.; Kraft, J.; Spitzer, M.; Palmer, D. A. *Rev. Sci. Instrum.* **1993**, *64*, 1355.

S0020-1669(96)01375-4 CCC: $14.00

values as well as the isosbestic point observed at 412 nm are in good agreement with that reported by other authors.[12,18,19] The degree of conversion of the ammine complex to the aqua complex as a function of pH is presented in the inset in Figure S1. The influence of pH on the spectra of deoxygenated solutions of $\mathrm{Fe(CN)_5H_2O^{3-}}$ ion (containing ascorbate) revealed the existence of a second reversible pH dependent equilibrium ($\mathrm{p}K_a \approx 2.9$). This equilibrium is characterized by an isosbestic point at 424 nm and the formation of a new species with $\lambda_{\max}$ at 413 nm (see Figure S2, Supporting Information). The observed pK_a value (see inset in Figure S2) agrees with the reported pK_a (2.6[20]) that was assigned to the protonation of a coordinated cyanide ion to form the $\mathrm{HFe(CN)_5H_2O^{2-}}$ complex.

The stoichiometry and equilibrium constant K_2 for the formation of the ammine complex (eq 2) were determined

$$\mathrm{Fe(CN)_5H_2O^{3-} + NH_3 \overset{K_2}{\rightleftharpoons} Fe(CN)_5NH_3^{3-} + H_2O} \qquad (2)$$

quantitatively by spectrophotometric titration of a 10^{-3} M deoxygenated solution of aquapentacyanoferrate(II) with $\mathrm{NH_3}$ in the pH range 6.5−9.0 at 298 K. Analysis of the data at pH < 7.5 showed deviations presumably due to ion-pair formation with $\mathrm{NH_4^+}$, such that the values of K_2 could only be determined approximately (see Figure S3, Supporting Information). Nevertheless, the results established a stoichiometry of 1:1 with log $K_2 = 4.7$ (pH = 6.5), log $K_2 = 4.6$ (pH = 7.0), and log $K_2 = 4.4$ (pH = 7.5). These values agree quite well with those determined in an indirect way[21] (log $K_2 = 4.3$ at pH = 7.0 and log $K_2 = 4.2$ at pH = 7.5). At pH > 7.5 the data were more accurate and, for instance, log $K_2 = 3.9$ at pH = 9.0 (see Figure S4, Supporting Information).

Kinetics. It has been shown[14,18,19,22] that ligand substitution reactions in complexes of the type $\mathrm{Fe(CN)_5L^{n-}}$ in general exhibit saturation kinetics with respect to the concentration of the entering ligand (L′), in which case the release of L becomes the rate-limiting step. The kinetics of the aquation reactions of $\mathrm{Fe(CN)_5L^{n-}}$ (eq 3) have up to now been studied in an indirect

$$\mathrm{Fe(CN)_5L^{n-} + H_2O \rightleftarrows Fe(CN)_5H_2O^{3-} + L} \qquad (3)$$

way from the rate of displacement of L by a stronger coordinating base L′ (often the methylpyrazinium cation). The rate constant for the dissociation of ammonia from $\mathrm{Fe(CN)_5\ NH_3^{3-}}$ determined in this way was reported to be $17.5 \times 10^{-3}\ \mathrm{s^{-1}}$ (pH = 7.2, $I = 1.0$ M, $T = 298$ K).[19]

In this study we followed the kinetics of the aquation and reverse complex formation reactions in (1) directly, by monitoring the changes in concentration of aquapentacyanoferrate(II). The reaction was investigated in a wide range of pH, [$\mathrm{NH_3}$], temperature, and pressure. The observed first-order rate constant, k_{obs}, strongly depends on the pH (see Figure 1) and the concentration of the added ammonium salt (i.e., $\mathrm{NH_4Cl}$) (see Figures 1a and 2). The observed rate constant turned out to be pH independent in the range 3−6 (the upper pH limit depends on the $\mathrm{NH_4Cl}$ concentration, see Figure 1a). In the lower pH range (pH < 3), k_{obs} decreases slightly with increasing [$\mathrm{H^+}$] probably due to the protonation of the cyano ligand on $\mathrm{Fe(CN)_5H_2O^{3-}}$. The p$K_a$ value estimated from Figure 1a lies between 2.5 and 2.7, which is in good agreement with our spectrophotometric result (compare Figure S2), as well as with the data reported by other authors[18] for the formation of $\mathrm{HFe(CN)_5H_2O^{2-}}$. At pH > 6.5, k_{obs} increases significantly with increasing pH (Figure 1) and increasing [$\mathrm{NH_4Cl}$] (Figure 2).

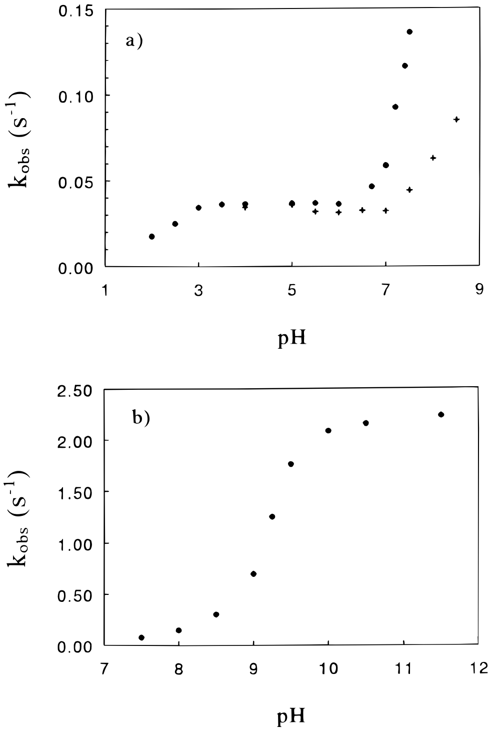


Figure 1. Plots of k_{obs} versus pH for the reaction $\mathrm{Fe(CN)_5NH_3^{3-} + H_2O \Leftrightarrow Fe(CN)_5H_2O^{3-} + NH_3}$ at $T = 298$ K, $I = 0.1$ M, in the pH range 1−9 (a) and 7−12 (b): (●) in the presence of 5×10^{-3} M $\mathrm{NH_4Cl}$; (+) without added $\mathrm{NH_4Cl}$.

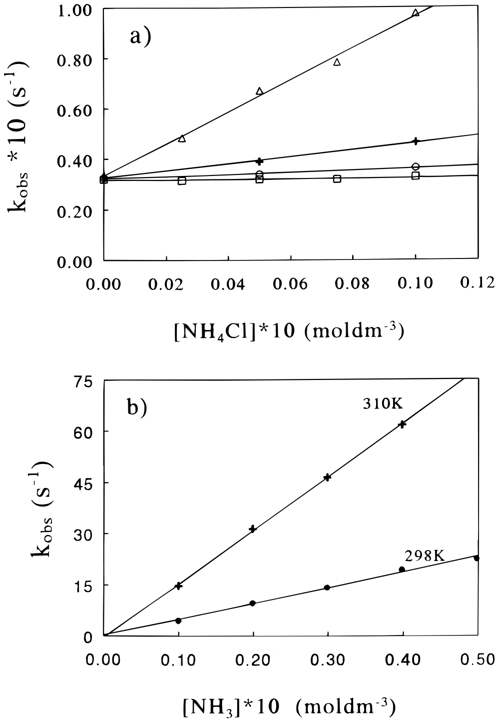
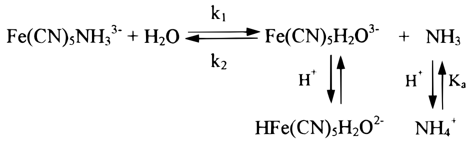


Figure 2. (a) Plots of k_{obs} versus [$\mathrm{NH_4Cl}$] for the reaction $\mathrm{Fe(CN)_5NH_3^{3-} + H_2O \Leftrightarrow Fe(CN)_5H_2O^{3-} + NH_3}$ as a function of pH: (□) pH 4.0, (○) pH 6.0, (+) pH 6.7, (△) pH 7.0; $T = 298$ K, $I = 0.1$ M. (b) Plots of k_{obs} versus [$\mathrm{NH_3}$] for the reaction $\mathrm{Fe(CN)_5H_2O^{3-} + NH_3 \Leftrightarrow Fe(CN)_5NH_3^{3-} + H_2O}$ at pH 11.5, $I = 0.1$ M, $T = 298$ K.

---

(18) Toma, H. E.; Batista, A. A.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 7509.
(19) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1974**, *13*, 1772.
(20) Malin, J. M.; Koch, R. C. *Inorg. Chem.* **1978**, *17*, 752.
(21) Norris, P. R.; Pratt, J. M. *J. Chem. Soc., Dalton Trans.* **1995**, 3651.
(22) Katz, N. E.; Aymonino, P.; Blesa, M. A.; Olabe, J. A. *Inorg. Chem.* **1978**, *17*, 556.

The observed pH and [NH_4Cl] dependences of k_{obs} suggest the following reaction scheme depicted in eq 4.



$$\begin{tikzcd}Fe(CN)_5NH_3^{3-} + H_2O \arrow[r, shift left, "k_1"] & Fe(CN)_5H_2O^{3-} \arrow[l, shift left, "k_2"] \arrow[d, shift left] & + & NH_3 \arrow[d, shift left, "K_a"] \\ & HFe(CN)_5H_2O^{2-} \arrow[u, shift left, "H^+"] & & NH_4^+ \arrow[u, shift left, "H^+"]\end{tikzcd} \quad (4)$$

For pH > 3 this scheme can be simplified to eq 1 and k_{obs} can be expressed by

$$k_{obs} = k_1 + k_2[NH_3] \quad (5)$$

where

$$[NH_3] = \frac{K_a}{K_a + [H^+]}[NH_x]_T \quad \text{and} \quad [NH_x]_T = [NH_3] + [NH_4^+] \quad (6)$$

Figure 1a shows that k_{obs} increases significantly with increasing pH at pH > 7, especially in the presence of NH_4Cl. With increasing pH, k_{obs} becomes much larger whereas the overall absorbance change becomes smaller due to the more efficient back reaction. At high pH (pH > 8), the reaction progress cannot be followed by conventional spectrophotometric methods anymore since it is totally controlled by the back reaction. Under these conditions it should be possible to follow the overall process by starting from $Fe(CN)_5H_2O^{3-}$ and adding NH_3/NH_4^+, thus studying directly the back reaction. There will be a small contribution of the forward reaction, but it will become less important at higher pH; in fact one would expect k_{obs} to reach a maximum at pH > 9.2 (the pK_a value of NH_4^+), where all NH_4^+ is converted to NH_3. We performed such experiments by using the pH jump technique. A typical set of spectra recorded for the back reaction are presented in Figure S5(Supportin Information). Combining the data for the forward and back reactions enabled us to construct the complete pH profile for the overall process (see Figure 1). A fit of the data in Figure 1b to eq 7 resulted in pK_a = 9.20 and $k_2 = 452 \pm 5$ $M^{-1}s^{-1}$, which is in excellent agreement with available literature data[23] (pK_a = 9.24 for $NH_4^+ \leftrightarrow NH_3 + H^+$)

$$k_{obs} = k_1 + k_2\frac{K_a}{K_a + [H^+]}[NH_x]_T \quad (7)$$

At the low-pH limiting condition (pH < 6), no complex-formation reaction occurs, whereas at the high-pH limiting condition (pH > 11), the forward aquation reaction can be neglected. Therefore rate constants for the aquation (k_1) and complex-formation reactions (k_2) were measured at pH = 5 and pH = 11.5 as a function of [NH_3], temperature and pressure, respectively, for which the data are summarized in Tables 1 and 2. As mentioned before, k_{obs} is independent of [NH_3] at pH = 5, such that $k_{obs} = k_1$ according to eq 5. The linear dependence of k_{obs} on [NH_3] at pH = 11.5 (see Figure 2b) results in a k_2 value of 460 ± 21 M^{-1} s^{-1} at 298 K, which is in excellent agreement with a value of 452 ± 5 M^{-1} s^{-1} obtained from Figure 1b under these conditions. The overall equilibrium constant, $K_2 = k_2/k_1 = (1.4 \pm 0.1) \times 10^4$ M^{-1} (log K_2 = 4.2), calculated from the kinetic data is in good agreement with that determined spectrophotometrically in this and earlier studies.[21]

Table 1. Rate and Activation Parameters for the Reaction[a]

$$Fe(CN)_5NH_3^{3-} + H_2O \xrightarrow{k_1} Fe(CN)_5H_2O^{3-} + NH_3$$

		$k_{obs} \times 10^2$ (s^{-1})	
T (K)	p (MPa)	[NH_4Cl] = 0	[NH_4Cl] = 0.01M
288.0	0.1	0.72	
290.5		1.06	1.11
293.0		1.56	1.62
295.5		2.32	2.30
298.0		3.12	3.20
		1.60[b]	
		1.75[c]	
		2.15[d]	
	10		2.90
	35		2.50
	55		2.29
	80		2.15
	105		1.77
	130		1.46
300.5	0.1	4.33	4.46
303.0		5.90	6.78
308.0		13.0	13.3
313.0		23.6	23.8
$\Delta H^‡$ (kJ mol^{-1})		102 ± 1	101 ± 1
		102 ± 1[b]	
		93 ± 5[c]	
$\Delta S^‡$ (J mol^{-1} K^{-1})		68 ± 4	67 ± 4
		63 ± 5[b]	
		34 ± 17[c]	
$\Delta V^‡$ (cm^3 mol^{-1})		16.4 ± 0.6[e]	13.5 ± 1.1[a,f]

[a] This work, pH = 5.0, I = 0.1 M (NaCl). [b] See ref 19, pH ≈ 9.2, I = 1.0 M (NaCl), reaction with pyridine. [c] See ref 22, pH = 7.2, I = 1.0 M ($NaClO_4$), reaction with *N*-methylpyrazinium iodide. [d] See ref 9, pH 9.4, I = 1.0 M (NaCl). [e] See ref 9, pH 9.4, I = 1.0 M (NaCl),T = 313 K. [f] T = 298 K.

The thermal activation parameters ($\Delta H^‡$ and $\Delta S^‡$) were determined in the usual way, whereas the pressure parameter ($\Delta V^‡$) was calculated from the slope (= $-\Delta V^‡/RT$) of a plot of ln k_{obs} *vs* pressure. The latter plot was linear within the experimental error limits (see Figure S6, Supporting Information). The values of $\Delta H^‡$ and $\Delta S^‡$ for both aquation (k_1) and complex-formation (k_2) reactions found in the present study are in good agreement with the values obtained in an indirect way[19,22] (see Tables 1 and 2).

For both substitution reactions (aquation and complex-formation) the activation entropy and activation volume are significantly positive, which underline the operation of a dissociative mechanism. $\Delta V^‡$ (k_2) must be corrected for the influence of pressure on the equilibrium $NH_4^+ \leftrightarrow NH_3 + H^+$, since this will affect the concentration of NH_3 in solution and in consequence the values of k_2 and $\Delta V^‡$ (k_2). According to available partial molar volumes

$$\Delta\bar{V} = \bar{V}(NH_4^+) - \bar{V}(NH_3) - \bar{V}(H^+) = 17.9 - 24.8 - 0 = -6.9\ cm^3\ mol^{-1}$$

(see refs 9 and 25).

Thus increasing pressure will cause a decrease in [NH_3], accompanied by a decrease in k_{obs} under such conditions. It follows that the corrected $\Delta \mathbf{V}^‡$ (k_2) = (21.3 ± 1.0)−6.9 = 14.4 ± 1.0 cm^3 mol^{-1}, which is indeed remarkably close to the limiting value expected for the dissociative release of a

---

(23) Fasman, G. D. *Handbook of Biochemistry and Molecular Biology, Physical and Chemical Data*; CRC Press: Cleveland, OH, 1976; Vol. 1.

(24) Millero, F. J. In *Water and Aqueous Solutions; Structure, Thermodynamics, and Transport Processes;* Horne, R. A., Ed.; Wiley Interscience: London, 1972; Chapter 13.

(25) Swaddle, T. W. *Inorg. Chem.* **1983**, *22*, 2663.

Table 2. Rate and Activation Parameters for the Reaction[a]

$$Fe(CN)_5H_2O^{3-} + NH_3 \xrightarrow{k_2} Fe(CN)_5NH_3^{3-} + H_2O$$

T (K)	p (MPa)	$[NH_4Cl]$ (M)	$k_{obs} \times 10^{-2}$ (s^{-1})	k_2 (M^{-1} s^{-1})
288.0	0.1	0.030	4.86	163
293.0	0.1	0.030	8.33	279
298.0	0.1	0.010	4.55	460 ± 21
		0.020	9.71	
		0.030	14.3	
		0.040	19.4	
		0.050	22.6	
		0.010		452 ± 5[b]
		0.00		365[c]
	5	0.030	9.79	
	30	0.030	8.81	
	60	0.030	6.33	
	90	0.030	4.65	
	120	0.030	3.79	
	150	0.030	2.98	
303	0.1	0.030	24.3	815
310		0.010	14.8	1436 ± 82
		0.020	31.4	
		0.030	46.5	
		0.040	61.8	
		0.050	71.1	
$\Delta H^‡$ (kJ mol^{-1})			78 ± 2	
			61.5[c]	
$\Delta S^‡$ (J mol^{-1} K^{-1})			67 ± 7	
			10.1[c]	
$\Delta V^‡$ (cm^3 mol^{-1})			21.3± 1.0	

[a] This work, pH = 11.5, I = 0.1 M (NaCl). [b] This work, calculated from Figure 1b. [c] See ref 18, pH 8−9, I = 0.1 M ($LiClO_4$).

coordinated water molecule in an octahedral complex,[26] viz., +13.1 cm^3 mol^{-1}. Similar $\Delta V^‡$ values were reported for a series of related complex-formation reactions.[27]

A volume profile (see Figure 3) can now be constructed for reaction 1. The very similar volumes of activation for both the forward and reverse reactions result from the rather close partial molar volumes of NH_3 (24.8 cm^3 mol^{-1}) and H_2O (18.0 cm^3 mol^{-1}) and the insensitivity of $\Delta V^‡$ for a limiting D mechanism toward the size of the leaving group.[9] The overall reaction volume of 1 ± 2 cm^3 mol^{-1} can be considered to be practically zero.

In the present study it was possible to investigate the substitution reactions of $Fe(CN)_5L^{3-}$ ($L = NH_3, H_2O$) in a direct way and to obtain a correlation between thermodynamic and kinetic data. In general a good agreement with available literature data exists, except in the case of the aquation rate constant k_1. The deviations with the literature values of k_1 (see Table 1) depend on the direct or indirect way in which the aquation was studied, and on the composition of the reaction medium (especially the ionic components and ionic strength). In general, aquation reactions measured in the presence of pyridines, isonicotinamide, and *N*-methylpyrazinium iodide are slower than those measured directly in this study. We have repeated some of the experiments and found data similar to that reported in the literature.[22] We and others[26,28] have observed that the reactivity of such cyanide complexes can depend significantly on specific medium effects. The aquation is sensitive toward the presence of different cations (Li^+, K^+, Na^+, Cs^+, and R_4N^+) in solution as demonstrated by some preliminary measurements performed in this study. Finally, the reported volume profile presents the first such analysis for ligand substitution reactions of pentacyanoferrate(II) complexes and clearly supports the operation of a limiting dissociative (D) mechanism.

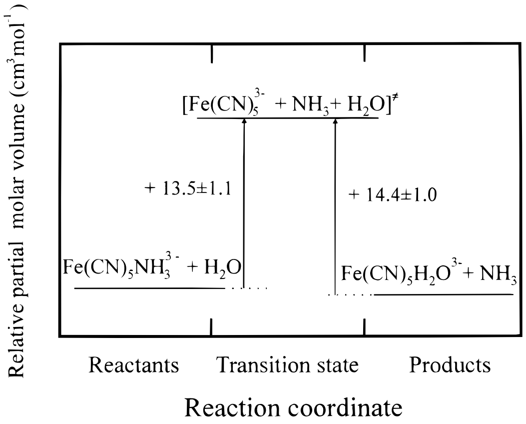


Figure 3. Volume profile for the overall reaction $Fe(CN)_5NH_3^{3-} + H_2O \Leftrightarrow Fe(CN)_5H_2O^{3-} + NH_3$.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Tempus Project JEP 8169, and Polish National Research Committee (KBN) (Grant PB 147/T09/95/09) for financial support.

Supporting Information Available: Information on the spectrophotometric determination of K_2 demonstrated with two figures and figures depicting spectral changes observed for the protonation of $Fe(CN)_5H_2O^{3-}$ and the pressure dependence of k_{obs} for the aquation and complex formation (8 pages). Ordering information is given on any current masthead page.

IC961375H

---

(26) Estrin, D. A.; Baraldo, L. M.; Slep, L. D.; Barja, B. C.; Olabe, J. A.; Paglieri, L.; Corongiu, G. *Inorg. Chem*. **1996**, *35*, 3897 and references cited therein.

(27) Stochel, G.; Chatlas, J.; Martinez, P.; van Eldik, R. *Inorg. Chem* **1992**, *31*, 5480.

(28) Szacilowski, K.; Stochel, G.; Stasicka, Z.; Kisch, H. *New J. Chem*., in press, and references cited therein.