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The Kinetic and Equilibrium Properties of the Vanadium(II) Thiocyanate Complex in Aqueous Solution

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The thermodynamics and kinetics of the aqueous equilibrium $V^{2+} + NCS^- = VNCS^+$ have been studied. The association concentration quotient, enthalpy of formation, and entropy of formation at $\mu = 0.84$ were found to be 27 ± 5 M^{-1} at 25°, -5.2 ± 0.7 kcal/mole, and -11 ± 3 eu, respectively. The rate of formation of the complex from the reactants was measured by the stopped-flow technique. At 25°, $[H^+] = 0.50$ M, and $\mu = 0.84$, the bimolecular rate constant for complex formation is 28 ± 3 M^{-1} sec^{-1}. The enthalpy and entropy of activation are 13.5 ± 0.8 kcal/mole and -2 ± 4 eu, respectively.

Introduction

Studies of the rate with which a ligand replaces a water molecule in the first coordination sphere of a metal ion have found continuing interest.[1-4]

On the basis of crystal field theory it has been predicted that among the divalent first-row transition metal ions those having three or eight d electrons should undergo replacement of solvent molecules by ligands more slowly than do those of other electronic configurations.[1,2] Therefore complexation reactions of the d^3 ion vanadium(II) are of interest. A convenient ligand for the study of such a reaction is the thiocyanate ion, NCS^-. Previous descriptions of this system have not included its equilibrium properties, nor have activation parameters been reported.[5,6]

Experimental Section

Materials.—J. T. Baker reagent grade ammonium thiocyanate was dried for 1 hr at 80° and used without further purification. Analysis by titration with standardized silver nitrate using dextrin and dichlorofluorescein showed the NH_4NCS to be 99.8% pure. Ammonium thiocyanate solutions were prepared by dissolving weighed amounts of ammonium thiocyanate in solutions of perchloric acid and lithium perchlorate of appropriate concentration. The spectra of these solutions were taken and showed no measurable contribution to the absorbance in the concentration and wavelength ranges studied.

Vanadium(IV) perchlorate solutions were prepared by adding stoichiometric amounts of barium perchlorate to filtered solutions of vanadium(IV) sulfate (purified, Fisher Scientific Co.). The barium sulfate precipitate was removed by centrifugation and filtration. Barium perchlorate was produced by adding perchloric acid (Baker and Adamson, 70%) to solutions of barium hydroxide (J. T. Baker, 98.0%). To make lithium perchlorate, lithium carbonate (Mallinckrodt, 99.5%) was added to perchloric acid. The lithium perchlorate produced was recrystallized twice. Saturated lithium perchlorate solutions, 4.47 M,[7] were made by maintaining a saturated solution of lithium perchlorate in equilibrium with solid $LiClO_4$ for a period of 4 hr at 25.0 ± 0.2°. This $LiClO_4$ solution was added to experimental solutions to maintain the ionic strength.

All equilibrium experiments were performed using electrolytically produced vanadium(II). Kinetic measurements were performed using vanadium(II) which had been produced by electrolysis and subsequently stored in contact with zinc amalgam for periods not exceeding 8 hr. Rates of reaction were found to be independent of storage times. Vanadium(II) solutions were produced and maintained under a positive pressure of purified nitrogen. Any residual oxygen in the nitrogen was removed by passing the nitrogen stream through a chromium(II) scrubbing solution which was kept in contact with zinc amalgam. Vanadium(II) concentrations were determined spectrophotometrically.

To determine hydrogen ion concentration in vanadium(II) solutions aliquots of vanadium(II) solution were added under nitrogen to water which had been deoxygenated by bubbling with nitrogen for at least 0.5 hr. The resulting solutions were titrated potentiometrically with standardized ethylenediamine solution using a pH meter with glass and calomel electrodes. Distilled, deionized water was used throughout.

In acid solutions a slow decomposition of thiocyanate occurs. Changes in the absorbance of vanadium(II) thiocyanate solutions are apparent after periods of about 1 hr. Therefore all spectra involving these two reagents were taken as quickly as possible after mixing (10 min near room temperature and up to 20 min at higher and lower temperatures). When necessary, vanadium(II) spectra were taken in spectrophotometric cells which had been sealed with Parafilm, capped with rubber septum caps, and then vented with purified nitrogen. To minimize contributions to the absorbance by $VNCS^{2+}$, which absorbs more strongly than $VNCS^+$ at shorter wavelengths,[8] all spectral measurements were performed between 700 and 800 mμ.

Measurements.—A Beckman Expandomatic pH meter, Beckman general purpose glass electrode, and Leeds and Northrup calomel electrode were used for pH measurements. The saturated KCl solution of the calomel electrode was removed and replaced with 4 M LiCl.

Spectrophotometric data were obtained using a Cary Model 14 recording spectrophotometer (Applied Physics Corp.). The instrument was equipped with a variable-temperature cell holder in which the cell could be totally immersed in water. Accuracy of the temperature control was ±0.3°. Reaction rates were followed spectrophotometrically using a Gibson–Durrum stopped flow device whose characteristics have been described elsewhere.[9]

Extinction Coefficients of Vanadium(II) in Acidic Perchlorate Solutions.—The extinction coefficients of vanadium(II) were calculated from the absorbances of solutions of known concentrations of vanadium(II). Vanadium(II) concentrations were

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(1) H. Taube, *Chem. Rev.*, **50**, 69 (1952).

(2) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Chapter 3.

(3) M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, Chapter 3.

(4) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

(5) W. Kruse, unpublished results (quoted in ref 3).

(6) B. R. Baker and N. Sutin, unpublished results quoted by B. R. Baker, M. Orthanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89**, 722 (1967).

(7) J. P. Simmons and C. D. L. Ropp, *ibid.*, **50**, 1650 (1928), in A. Seidell, "Solubilities of Inorganic and Metal–Organic Compounds," Vol. 2, 4th ed, American Chemical Society, Washington, D. C., 1965, p 408.

(8) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **73**, 4528 (1951).

(9) P. A. Rock and J. H. Swinehart, *Inorg. Chem.*, **5**, 1078 (1966).

determined by two methods. In the first method, solutions of known concentrations of vanadium(IV), determined spectrophotometrically,[10] were reduced with zinc amalgam. In the second method measured volumes of vanadium(II) solutions were added to solutions of excess iron(III). The iron(II) produced was titrated with standardized Ce(IV). The results from these methods differed by 2%. The extinction coefficient obtained for vanadium(II) at 558 mμ was 4.40 ± 0.05 M^{-1} cm^{-1}. Values (in M^{-1} cm^{-1} and mμ) at other wavelengths were: 2.1_1 (350), 1.5_8 (380), 0.5_3 (410), 0.5_1 (440), 0.9_1 (470), 2.1_5 (500), 3.8_2 (530), 4.40 (558), 3.7_3 (590), 2.4_4 (620), 1.4_0 (650), 1.0_0 (680), 1.1_1 (710), 1.6_1 (740), 2.2_1 (770), and 2.7_3 (800). The extinction coefficients were independent of hydrogen ion concentration over the range $0.1 \leqslant [H^+] \leqslant 0.7$ M. The rather large discrepancy between these extinction coefficients and those published by King and Garner[11] was probably caused by the presence of vanadium(III) in the solutions of those workers.

Results and Discussion

Composition of the Complex.—Job's method of continuous variations[12] as extended by Vosburgh and Cooper[13] has been applied to the vanadium(II)–thiocyanate system. This method establishes a 1:1 mole ratio of vanadium(II) to thiocyanate.

The excess absorbance, Y, is defined as the measured absorbance per centimeter of light path minus the absorbance expected for a solution in which no complex is formed. Figure 1 shows Y at two wavelengths as a function of X, which is [total V(II)]/[total V(II) + total NCS$^-$], in mixtures of equimolar solutions of vanadium(II) perchlorate and ammonium thiocyanate. The perchloric acid concentration was held at 0.50 M throughout and the total initial concentration of vanadium(II) plus thiocyanate was held constant at 0.087 M. In this experiment Y is accurate to no more than 10%. The mole fraction of vanadium(II), X, at which the absorbance difference Y is a maximum can be related to the number of vanadium(II) ions per thiocyanate ion in the complex, n, by the equation $n = X/(1 - X)$. The existence of the maximum in the curve at $X \approx 0.45$ indicates that the VNCS$^+$ species is the main complex formed. The asymmetry of the curve is probably due to contributions to Y by a higher complex. The broadness of the maximum indicates that the 1:1 complex is not particularly stable.

Association Quotient and Heat of Formation of VNCS$^+$.—The association concentration quotient for the formation of VNCS$^+$ has been determined by studying solutions of varying vanadium(II) and thiocyanate concentrations. In these experiments the vanadium(II) concentration was always greater than the thiocyanate concentration by a factor of at least 4. The treatment of data was, in this case, identical with that of Furman and Garner[8] in their study of the association constant of VONCS$^+$.

The function

$$ab/(D - a\epsilon_{V^{2+}}) = [(a + b)/(\epsilon_{VNCS^+} - \epsilon_{V^{2+}})] - [1/(\epsilon_{VNCS^+} - \epsilon_{V^{2+}})K_{VNCS^+}]$$

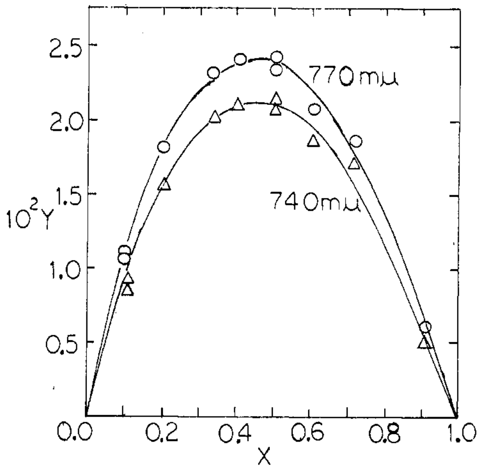

Figure 1.—Plot of excess absorbance, Y, *vs.* mole fraction of vanadium(II), X. $[V^{2+}] + [NCS^-] = 0.087$ M; $[HClO_4] = 0.50$ M.

defined by Furman and Garner, where the total concentrations of vanadium(II)- and thiocyanate-containing species are represented by a and b, and D is the total absorbance, has been used. In Figure 2, $ab/(D - a\epsilon_{V^{2+}})$ has been plotted against $(a + b)$ at 770 mμ and at 740 mμ. In these solutions a varied from 0.0900 to 0.0200 M. A least-squares straight line has been drawn through the experimental points. From the slopes of the curves $(\epsilon_{VNCS^+} - \epsilon_{V^{2+}})$ was calculated. The values (in M^{-1} cm^{-1} and mμ) obtained for ϵ_{VNCS^+} at several wavelengths are: 6.6 (500), 10.5 (530), 10.8 (560), 7.8 (590), 4.9 (620), 4.7 (650), 4.8 (680), 7.0 (710), 9.6 (740), 12.8 (770), and 12.9 (800). Values of K_{VNCS^+} determined at two wavelengths are given in Table I. No dependence of K_{VNCS^+} on the relative concentration of thiocyanate to vanadium(II) is evident.

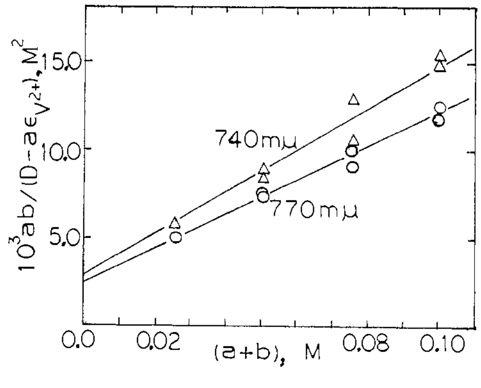

Figure 2.—Plot of $ab/(D - a\epsilon_{V^{2+}})$ *vs.* $(a + b)$; temperature 25 ± 1°.

Such a dependence would be expected in the case where the extinction coefficient, ϵ_{VNCS^+}, was in error. There is a tendency of increasing K_{VNCS^+} as the wavelength decreases. This is probably due to contributions to the absorbance by VNCS^{2+} at shorter wavelengths. Another source of error in K_{VNCS^+} is the large correction of the absorbance for uncomplexed vanadium(II).

Thermodynamic Parameters.—Assuming no temperature dependence of the extinction coefficients and including corrections for changes in density of the

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[10] $\epsilon_{VO^{2+}} = 17.17 \pm 0.01$ M^{-1} cm^{-1} at 758 mμ; determined by potentiometric titration with Ce(IV) at 75°: M. Barrett, unpublished results.

[11] W. R. King and C. S. Garner, *J. Phys. Chem.*, **58**, 29 (1954).

[12] P. Job, *Ann. Chim.*, [9] **9**, 113 (1928); [10] **6**, 97 (1936).

[13] W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

Table I

Determination of K_{VNCS^+} [a]

ϵ, mμ	D [b]	$10^2[\mathrm{V}^{2+}]$, [c] M	$10^3[\mathrm{NCS}^-]$, [c] M	K_{VNCS^+}, M^{-1}
770	0.272	9.00	9.95	31.6
	0.266	9.00	9.71	25.8
	0.205	6.50	10.05	25.1
	0.147	4.00	10.81	31.5
	0.142	4.00	10.30	29.4
	0.064	2.00	5.22	32.6
740	0.203	9.00	9.95	35.7
	0.200	9.00	9.71	31.9
	0.155	6.50	10.05	30.1
	0.114	4.00	10.81	41.7
	0.110	4.00	10.30	37.5
	0.049	2.00	5.22	38.7

[a] $[\mathrm{H}^+] = 0.50\ M$, $\mu = 0.84$, and temperature is 25 ± 1°. [b] Total absorbance. [c] Initial concentrations.

solutions K_{VNCS^+} was determined at 770 mμ at several temperatures. The results are presented in Table II. The least-squares-fit straight line of the ln K_{VNCS^+} *vs.* $1/T$ plot yields $\Delta H = -5.2 \pm 0.7$ kcal/mole and $\Delta S = -11 \pm 3$ eu. At 25° K_{VNCS^+} is $27 \pm 5\ M^{-1}$. In view of the high ionic strength used and the uncertainty in K_{VNCS^+} no physical significance can be attached to the calculated ΔS value.

Table II

Data for Temperature Dependence of K_{VNCS^+} [a]

Temp, °C	D [b]	$10[\mathrm{V}^{2+}]$, [c] M	$10[\mathrm{NCS}^-]$, [c] M	K_{VNCS^+}, M^{-1}
10.8	0.151	0.401	0.103	41
15.5	0.147	0.398	0.100	38
19.6	0.141	0.397	0.101	30
24.7	0.140	0.400	0.103	27
25.5	0.138	0.397	0.100	28
29.8	0.138	0.394	0.102	25
29.8	0.135	0.397	0.101	24
35.4	0.134	0.398	0.098	23
36.8	0.137	0.399	0.101	25
37.2	0.130	0.396	0.100	20
40.0	0.130	0.395	0.101	19
45.0	0.118	0.397	0.087	15

[a] $[\mathrm{H}^+] = 0.5$, $\mu = 0.84$, and $\lambda = 770$ mμ. [b] Total absorbance. [c] Initial concentrations.

The Rate of Formation of VNCS$^+$.—The kinetics of the forward reaction of the equilibrium

$$\mathrm{V}^{2+} + \mathrm{NCS}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{VNCS}^+ \qquad (1)$$

in excess vanadium(II) were studied using the stopped-flow technique. The reaction was followed by observing the rate of formation of VNCS$^+$ at 770 mμ. Vanadium(II) concentrations varied from 0.029 to 0.178 M. Vanadium(II) was present in at least tenfold excess over thiocyanate.

The mechanism for the reaction was assumed to be as shown in eq 1. Using the relationship $K_{\mathrm{VNCS}^+} = k_1/k_{-1}$, it follows that

$$\frac{d[\mathrm{VNCS}^+]}{dt} = k_1[\mathrm{V}^{2+}][\mathrm{NCS}^-] - \frac{k_1}{K_{\mathrm{VNCS}^+}}[\mathrm{VNCS}^+]$$

If $[\mathrm{V}^{2+}]$ is essentially constant during the course of an experiment, $[\mathrm{NCS}^-]$ is expressed in terms of $[\mathrm{VNCS}^+]$ and $[\mathrm{V}^{2+}]$, and $[\mathrm{VNCS}^+]_0$ and $[\mathrm{VNCS}^+]_\infty$ are defined as the concentrations of the complex at the start of the reaction, and after attainment of the final equilibrium value the rate law may be integrated yielding[14]

$$k_1t = \frac{1}{[\mathrm{V}^{2+}] + (1/K_{\mathrm{VNCS}^+})} \ln \frac{[\mathrm{VNCS}^+]_\infty - [\mathrm{VNCS}^+]_0}{[\mathrm{VNCS}^+]_\infty - [\mathrm{VNCS}^+}$$

k_1 is the bimolecular forward rate constant.

The absorbance change involved in the reaction was quite small. Therefore it was possible to assume the differences in voltage observed on the oscilloscope were proportional to differences in absorbance. Since the concentration of vanadium(II) was essentially constant throughout a run and $\epsilon_{\mathrm{VNCS}^+}$ is much larger than $\epsilon_{\mathrm{V}^{2+}}$ at 770 mμ, it could be assumed that changes in $[\mathrm{VNCS}^+]$ were responsible for the observed absorbance change. Thus changes in voltage were proportional to changes in $[\mathrm{VNCS}^+]$. A plot of log $(V_\infty - V)$, where V_∞ and V are the voltages observed at infinite time and at other times, *vs.* time yielded a straight line. Table III summarizes the kinetic runs made for the purpose of testing the rate law and obtaining the temperature dependence of the rate constants. Runs 9 through 13 show that the rate constant is independent of hydrogen ion concentration over the range $0.17\ M \leqslant [\mathrm{H}^+] \leqslant 0.69\ M$. It is evident that there is no important hydrogen or hydroxide ion catalyzed path operating in this range of hydrogen ion concentrations.

Table III

Summary of Kinetic Data

Expt	Temp, °C	10^2 $[\mathrm{V}^{2+}]$, M	10^3 $[\mathrm{NCS}^-]$, [a] M	$[\mathrm{H}^+]$, M	μ, M	k_{obsd}, sec^{-1}	k_1, M^{-1} sec^{-1}
1	5.5	5.40	4.09	0.50	0.84	.358	4.9
2	7.5	4.93	5.63	0.50	0.84	.354	5.1
3	15.7	5.39	4.08	0.50	0.84	1.02	12.7
4	18.4	4.93	4.21	0.50	0.84	1.39	17.9
5	24.3	5.20	3.99	0.50	0.84	2.44	28.4
6	27.8	5.38	4.07	0.50	0.84	2.84	33.7
7	35.2	5.39	4.06	0.50	0.84	5.21	52.2
8	37.0	4.90	4.19	0.50	0.84	6.39	65.5
9	23.9	4.92	5.27	0.17	0.84	2.38	28.7
10	24.2	5.38	5.33	0.22	0.83	2.51	28.6
11	24.0	4.92	5.61	0.50	0.84	2.63	29.9
12	24.2	5.38	5.52	0.68	0.84	2.20	25.0
13	23.8	4.92	5.96	0.69	0.84	2.42	29.1
14	23.9	4.92	4.56	0.17	0.32	2.12	25.5
15	23.9	5.38	5.64	0.50	1.34	2.63	29.9
16	23.9	4.92	6.98	0.17	1.66	2.62	31.5
17	24.0	2.90	2.58	0.50	0.84	1.75	27.7
18	24.7	17.8	4.06	0.36	0.84	5.76	27.0

[a] Initial concentration.

Experiments 14, 15, and 16 indicate a small increase in rate constant with ionic strength. Because of the uncertainty in K_{VNCS^+} and in the vanadium(II) concentration the increase in rate constant is comparable in magnitude to the experimental uncertainty in k_1. Runs 17 and 18 may be compared with runs 11 and 5 to show that varying the concentration of vanadium(II) by a factor of 6 has no measurable effect on the calculated bimolecular forward rate constant. This together with the results of the thiocyanate ion and hydrogen ion dependence studies substantiates the assumed rate law.

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(14) J. F. Below, R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958).

Experiments were run at temperatures covering the range from 5.5 to 37°. A plot of log (k_1/T) *vs.* $1/T$ yields $\Delta H^{\ddagger} = 13.5 \pm 0.8$ kcal/mole and $\Delta S^{\ddagger} = -2 \pm 4$ eu. The value of k_1 at 25° is $28 \pm 3\ M^{-1}\ \text{sec}^{-1}$.

Reverse Reaction.—The rate constant for the reverse reaction can be calculated from the concentration association constant, K_{VNCS^+}, and the bimolecular forward rate constant using eq 13. At 25° $k_{-1} = 1.0\ \text{sec}^{-1}$. From ΔH and ΔS for the equilibrium process and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the forward reaction $\Delta H^{\ddagger}$ for the reverse reaction is 18.7 kcal/mole and $\Delta S^{\ddagger}$ is 9.0 eu.

A check on the consistency of the rate and equilibrium measurements can be performed using the pseudo-first-order rate constants, k_{obsd}, obtained in runs 5, 17, and 18. A plot of these rate constants *vs.* $[V^{2+}]$ gives a straight line yielding k_1 and k_{-1} as slope and intercept. From these values, respectively, $27\ M^{-1}\ \text{sec}^{-1}$ and $1\ \text{sec}^{-1}$, K_{VNCS^+} is computed as $27\ M^{-1}$ at 25 ± 1° in good agreement with the spectrophotometrically determined value for the association concentration quotient.

Mechanism.—A mechanism for the formation of metal ion complexes has been postulated by Eigen.[3,15] In this mechanism the formation of the VNCS^+ complex is preceded by the rapid preequilibrium formation of an outer-sphere association complex or ion pair, eq 2. In the following slow step, eq 3, a water molecule is

$$V(H_2O)_6^{2+} + NCS^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} V(H_2O)_6^{2+}NCS^- \qquad (2)$$

$$V(H_2O)_6^{2+}NCS^- \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} (H_2O)_5VNCS^+ + H_2O \qquad (3)$$

lost from the first coordination sphere and the thiocyanate ion is inserted. The bimolecular rate constant, k_1, would then be the product of the ion-pairing constant, K_{ip} ($K_{\text{ip}} = k_{12}/k_{21}$), and the rate constant k_{23}, $k_1 = K_{\text{ip}}k_{23}$. If the rate-determining step in the formation of products from the ion pair is the loss of a water molecule from the first coordination sphere, k_{23} approximates the first-order rate constant for water exchange, k_{w}. Making this assumption the rate constant for water exchange of vanadium(II) can be estimated. From the data of Davies and Smith[16] the bimolecular rate constant, k_1, for the formation of NiNCS^+ is $6.3 \times 10^3\ M^{-1}\ \text{sec}^{-1}$ at 25°, $\mu = 0.5$. Swift and Connick[17] have found the rate constant k_{w} for water exchange by Ni^{2+} at 25° and at $\mu = 0.3$ to be $2.7 \times 10^4\ \text{sec}^{-1}$. From these data K_{ip} is $2.3 \times 10^{-1}\ M^{-1}$. Applying the same K_{ip} to the vanadium(II) thiocyanate system the water-exchange rate constant is estimated to be $122\ \text{sec}^{-1}$.

It is interesting to consider the enthalpy and entropy of formation of the ion pair. Swift and Connick found the enthalpy and entropy of activation for nickel(II)–water exchange to be 11.6 kcal/mole and 0.6 eu, respectively. If $k_1 = K_{\text{ip}}k_{\text{w}}$, then $\Delta H^{\ddagger} = \Delta H_{\text{ip}} + \Delta H_{\text{w}}^{\ddagger}$. From the data of Davies and Smith for the nickel(II)–thiocyanate reaction $\Delta H^{\ddagger} = 9.8$ kcal/mole and $\Delta S^{\ddagger} = -10.9$ eu. For K_{ip} we can calculate $\Delta H_{\text{ip}} = 9.8$ kcal/mole $-$ 11.6 kcal/mole $= -1.8$ kcal/mole and $\Delta S_{\text{ip}} = -10.9$ eu $-$ 0.6 eu $= -11.5$ eu.

Although the significance of these values is questionable, ΔH_{ip} and ΔS_{ip} can be used to estimate $\Delta H_{\text{w}}^{\ddagger}$ and $\Delta S_{\text{w}}^{\ddagger}$ for water exchange by vanadium(II): $\Delta H_{\text{w}}^{\ddagger} = 13.5$ kcal/mole $-$ (-1.8 kcal/mole) $= 15.3$ kcal/mole, $\Delta S_{\text{w}}^{\ddagger} = -2$ eu $-$ (-11.5 eu) $= 9.5$ eu. To calculate these activation parameters for water exchange of vanadium(II) we have assumed small ionic strength effects and a similarity in mechanism between the nickel(II)–thiocyanate and vanadium(II)–thiocyanate reactions. These assumptions, while reasonable, can be justified only in that they allow a prediction of the activation parameters and of the rate constant for water exchange.

All these considerations have been based on the mechanism shown in eq 2 and 3. An alternative is a one-step mechanism in which no ion pair is formed. The rate of substitution for a water molecule by a ligand in such a mechanism is governed partly by the displacing ability of the ligand and partly by the lability of the metal ion. However, a wide variation in rates of complexing among metal ions and a relative invariance among ligands has been noted.[3] Sound absorption experiments[15] also indicate the existence of ion pairs. Therefore the ion-pair mechanism is probably more important.

There is disagreement between the value of the bimolecular rate constant for complex formation, $k_1 = 28\ M^{-1}\ \text{sec}^{-1}$, reported here and the values of 40[5] and $9 \pm 1\ M^{-1}\ \text{sec}^{-1}$ [6] recorded in the literature. Depending on the experimental method used, the values of K_{VNCS^+} and/or ϵ_{VNCS^+} are important in determining k_1. A difference in these values could account for the discrepancies noted.

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[17] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).