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The Kinetics of the Formation and Aquation of the Monothiocyanate Complex of Vanadium(III)[1a]

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The forward and reverse rates of the reaction $V^{3+} + SCN^- \rightleftharpoons VNCS^{2+}$ have been studied by the use of a flow technique. The approach to equilibrium is given by $k_{obsd} = k_d + k_f(V^{3+})$, where $k_d = 1.03 \pm 0.06$ sec^{-1} and $k_f = 114 \pm 10$ M^{-1} sec^{-1} at 25.0° and ionic strength 1.0 M. The rates are independent of the hydrogen ion concentration in the range $(H^+) = 0.025$–1.0 M. Studies at various temperatures between 5.0 and 37.0° yield the following activation parameters: $\Delta H_d^{\ddagger} = 10.7 \pm 0.5$ kcal mole^{-1}, $\Delta H_f^{\ddagger} = 7.6 \pm 0.6$ kcal mole^{-1}, $\Delta S_d^{\ddagger} = -22.6 \pm 1.5$ cal mole^{-1} deg^{-1}, and $\Delta S_f^{\ddagger} = -23.8 \pm 1.9$ cal mole^{-1} deg^{-1}. The equilibrium constant for the formation of $VNCS^{2+}$ determined spectrophotometrically is 117 ± 6 M^{-1} at 25.0° and ionic strength 1.0 M. Measurements of the variation of the equilibrium constant with temperature give $\Delta H°$ and $\Delta S°$ values of -3.5 ± 0.3 kcal mole^{-1} and -2.2 ± 1.3 cal mole^{-1} deg^{-1}, respectively. The results are discussed in terms of an SN2 mechanism.

Introduction

Although substitution reactions of hexaaquoiron(III) and hexaaquochromium(III) have been extensively studied,[2-4] very few investigations have dealt with substitution reactions of hexaaquovanadium(III). The paucity of data on the latter reactions is probably related to the instability of perchloric acid solutions of vanadium(III). Nevertheless, such solutions have been used in a number of investigations. Furman and Garner[5] have studied the equilibria obtaining in perchloric acid solutions containing vanadium(III) and thiocyanate. They showed that $VNCS^{2+}$ was the principal thiocyanate complex present in the solutions, at least at low thiocyanate concentrations. They also estimated the equilibrium constant for reaction 1.

$$V(H_2O)_6^{3+} + SCN^- \rightleftharpoons V(H_2O)_5NCS^{2+} + H_2O \qquad (1)$$

The forward rate of reaction 1 has been measured by Kruse,[6] but no kinetic data have been published. We have made a detailed study of the forward and reverse rates of reaction 1. We find that these rates differ in important respects from the rates of the corresponding iron(III) and chromium(III) reactions.

Experimental Section

Materials.—Solutions of vanadium(III) were prepared by two different methods, both involving the electrolysis of solutions of divanadium pentoxide (Baker Analyzed reagent) in perchloric acid. A bright platinum gauze cathode was used in the first method. The electrolysis was continued until the color of the solutions changed from deep blue to violet, indicating that vanadium(II) was being formed. Palladium black (Fischer Scientific Co.) was then added and the solution was allowed to stand with stirring (under an argon atmosphere) until hydrogen evolution ceased, indicating the completion of the oxidation of vanadium(II) to vanadium(III) by hydrogen ions. The solution was then filtered through a fritted disk under argon pressure into a storage vessel. In the second method a platinized platinum cathode was used and the electrolysis was continued until the solutions turned deep blue and no vanadium(IV) could be detected spectrophotometrically. Vanadium(IV) has an absorption maximum at 760 mμ and an extinction coefficient of 16.5, which is several hundred times larger than that for vanadium(III) at this wavelength.

Stock solutions of sodium perchlorate were prepared from sodium carbonate (Baker Analyzed reagent) and perchloric acid. Stock solutions containing thiocyanate were prepared from sodium thiocyanate (Matheson Coleman and Bell) without further purification and from ammonium thiocyanate (Baker Analyzed reagent) which had been recrystallized twice from 95% ethanol. All solutions for the equilibrium and kinetics measurements were prepared with triple-distilled water.

Analysis of Solutions.—The vanadium(III) concentration in the stock solutions was determined by titration at 80° of an aliquot of the solution with permanganate under an atmosphere of argon. The vanadium(V) produced in this titration was reduced to vanadium(IV) with sulfur dioxide, and the excess sulfur dioxide was then removed by boiling and bubbling argon through the solutions. The vanadium(IV) concentrations of the resulting solutions were determined by titration at 80° with permanganate. The vanadium(III) concentration was calculated from the difference in the amount of permanganate required for the two titrations. The vanadium(III) solutions generally contained <1% of vanadium(IV). The perchloric acid concentration of the vanadium(III) solutions was determined by passing an aliquot of the solution through a Dowex 50-W cation-exchange column in the hydrogen ion form (under an atmosphere of argon). The column was washed with deoxygenated water and the eluate was titrated with standard sodium hydroxide solution. The hydrogen ion concentration of the solution was calculated from the amount of base in excess of that required to neutralize the 3 moles of hydrogen ion released from the column per mole of vanadium(III). Thiocyanate was determined by the Volhard procedure.

Equilibrium Measurements.—The spectra of deoxygenated solutions containing thiocyanate, perchloric acid, and vanadium(III) were recorded at 5.0, 12.0, 25.0, and 37.0° on a Cary Model 14 spectrophotometer. The concentration ranges used were $[V(III)] = 2.0 \times 10^{-3}$ to 33.8×10^{-3} M, $(SCN^-) = 1.00 \times 10^{-3}$ or 2.00×10^{-3} M, and $(HClO_4) = 1.00$ M.

Kinetic Measurements.—The kinetic measurements were made at 5.0, 12.0, 25.0, and 37.0°, and at an ionic strength of 1.0 M, using the stopped flow apparatus previously described.[7] Solu-

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[1] (a) Research performed under the auspices of the U. S. Atomic Energy Commission; (b) Née Teresa J. Conocchioli.

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

[3] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

[4] For recent reviews, see, for example, M. Eigen and R. G. Wilkins, "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, and N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

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

[6] W. Kruse, unpublished observation quoted by Eigen and Wilkins.[4]

[7] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

tions containing perchloric acid and vanadium(III) were mixed with solutions containing perchloric acid and thiocyanate and the formation of the monothiocyanate complex of vanadium(III) was followed at 290 and at 350 mμ, which are absorption maxima of $VNCS^{2+}$. The concentration ranges used were $[V(III)] = 1.2 \times 10^{-3}$ to 24.6×10^{-3} M, $(SCN^-) = 5.0 \times 10^{-5}$ to 5.0×10^{-4} M, and $(HClO_4) = 2.5 \times 10^{-2}$ to 1.0 M. In a few runs 0.1 M chloride and 0.1 M vanadium(IV) were added to the above solutions to determine whether these ions had any kinetic effect on the reaction.[8] No effect ascribable to the added chloride or vanadium(IV) was observed.

Results

The Vanadium(III)–Thiocyanate Equilibrium.—The absorbance per unit path length, A, is related to the molar absorptivities ϵ_0 and ϵ_1 of V^{3+} and $VNCS^{2+}$, respectively, by the equation

$$A = \epsilon_0(V^{3+}) + \epsilon_1(VNCS^{2+}) \qquad (2)$$

Substitution for $(VNCS^{2+})$ from K_1 and for (SCN^-) from the mass balance expression gives

$$\bar{\epsilon} = \epsilon_1 - \frac{\bar{\epsilon}}{K_1(V^{3+})} \qquad (3)$$

where $\bar{\epsilon} = [A - \epsilon_0(V^{3+})]/(SCN^-)_T$ and $(SCN^-)_T$ is the total thiocyanate concentration. The values of ϵ_0 used are 1.0 and 4.0 at 290 and 350 mμ, respectively. These values were obtained from separate experiments without thiocyanate present and agree with previously published values.[5] It is apparent from eq 3 that a plot of $\bar{\epsilon}$ *vs.* $\bar{\epsilon}/(V^{3+})$ should yield a straight line with slope K_1^{-1} and intercept ϵ_1. Plots of $\bar{\epsilon}$ *vs.* $\bar{\epsilon}/(V^{3+})$ at 290 and 350 mμ are shown in Figures 1 and 2, respectively, for the equilibrium measurements made at 25.0°. The measurements made at 5.0, 12.0, and 37.0° gave similar plots. The equilibrium constants calculated from the slopes of these curves are 146 ± 8, 138 ± 7, 117 ± 6, and 87 ± 4 M^{-1} at 5.0, 12.0, 25.0, and 37.0°, respectively. The value of $\Delta H°$, calculated from the slope of a plot of log K_1 *vs.* $1/T$, is -3.5 ± 0.3 kcal mole^{-1} and the values of $\Delta G°$ and $\Delta S°$ are -2.8 ± 0.1 kcal mole^{-1} and -2.2 ± 1.3 cal mole^{-1} deg, respectively, at 25.0°.

The values of ϵ_1 determined from the intercepts of the plots are 1990 ± 100 and 580 ± 50 at 290 and 350 mμ, respectively.[9] These values are not in agreement with $\epsilon_1 = 3760$ at 290 mμ and $\epsilon_1 = 810$ at 350 mμ, reported by Furman and Garner.[5] However, the data reported by Furman and Garner indicate that higher complexes may have been present under the conditions used in their study and that these complexes may have made an appreciable contribution to the absorption, especially at the lower wavelengths. Thus the value of K_1 determined in the earlier work was found to depend upon the wavelength. Furman and Garner estimate that K_1 is approximately 100 M^{-1} at 25°. A correction of their data for the presence of higher complexes would tend to increase K_1 and decrease ϵ_1.

Kinetic Measurements.—Values of k_{obsd} calculated from

$$\frac{d(VNCS^{2+})}{dt} = k_{obsd}[(VNCS^{2+})_{eq} - (VNCS^{2+})] \qquad (4)$$

are plotted *vs.* (V^{3+}) in Figure 3. It is apparent from this figure that k_{obsd} is given by

$$k_{obsd} = k_d + k_f(V^{3+}) \qquad (5)$$

It is also apparent from Figure 3 that the rates are independent of the perchloric acid concentration in the range 0.025–1.0 M. The data are thus consistent with the rate law

$$\frac{d(VNCS^{2+})}{dt} = k_f(V^{3+})(SCN^-) - k_d(VNCS^{2+}) \qquad (6)$$

where the rate constants are defined by

$$V^{3+} + SCN^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} VNCS^{2+} \qquad K_1 \qquad (7)$$

The rate constants in eq 5 were replaced by the corresponding absolute rate theory expressions and the data for all the temperatures were treated simultaneously according to

$$k_{obsd} = \frac{kT}{h}\{e^{(\Delta S_d^{\ddagger}/R)-(\Delta H_d^{\ddagger}/RT)} + (V^{3+})e^{(\Delta S_f^{\ddagger}/R)-(\Delta H_f^{\ddagger}/RT)}\} \qquad (8)$$

A nonlinear least-squares program[10] was used to evaluate the activation parameters together with their

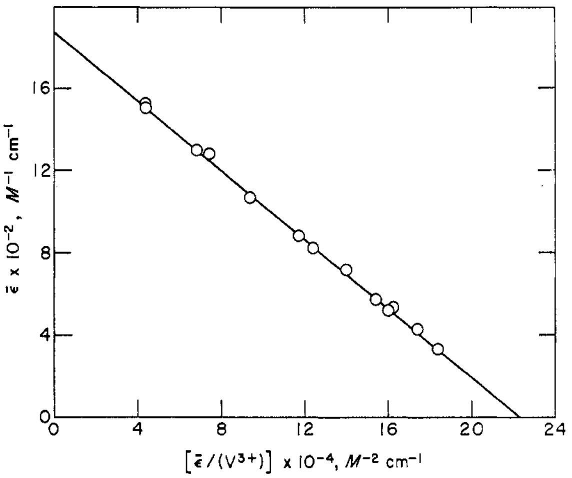

Figure 1.—Plot of $\bar{\epsilon}$ *vs.* $\bar{\epsilon}/(V^{3+})$ at 290 mμ, 25°, and 1.0 M ionic strength.

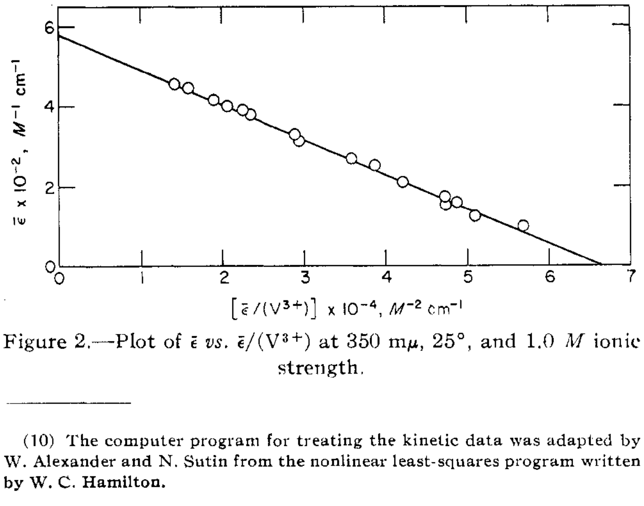

Figure 2.—Plot of $\bar{\epsilon}$ *vs.* $\bar{\epsilon}/(V^{3+})$ at 350 mμ, 25°, and 1.0 M ionic strength.

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(8) Chloride ions and vanadium(IV) are produced in the reaction of vanadium(III) with perchlorate ions.

(9) No dependence of the maximum molar absorptivities on the temperature was observed.

(10) The computer program for treating the kinetic data was adapted by W. Alexander and N. Sutin from the nonlinear least-squares program written by W. C. Hamilton.

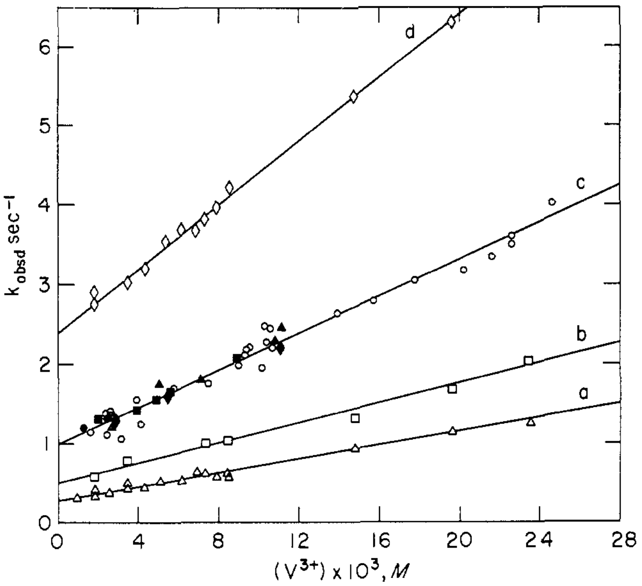

Figure 3.—Plots of k_{obsd} *vs.* (V^{3+}) at various temperatures and hydrogen ion concentrations; ionic strength 1.00 *M:* (a) 5.0°, $(H^+) = 1.00$ *M;* (b) 12.0°, $(H^+) = 1.00$ *M;* (c) 25.0° and $(H^+) = 1.00$ *M* (open circles), $(H^+) = 0.50$ *M* (closed triangles), $(H^+) = 0.25$ *M* (closed diamonds), $(H^+) = 0.15$ *M* (closed squares), and $(H^+) = 0.025$ *M* (closed circles); (d) 37.0°, $(H^+) = 1.00$ *M*.

standard deviations. In this calculation each rate constant was weighted according to the reciprocal of its square since the per cent error in k_{obsd} was approximately constant. The activation parameters calculated by the program are $\Delta S_d^{\ddagger} = -22.6 \pm 1.5$ cal mole^{-1} deg^{-1}, $\Delta H_d^{\ddagger} = 10.7 \pm 0.5$ kcal mole^{-1}, $\Delta S_f^{\ddagger} = -23.8 \pm 1.9$ cal mole^{-1} deg^{-1}, and $\Delta H_f^{\ddagger} = 7.6 \pm 0.6$ kcal mole^{-1}. These parameters give $k_d = 1.03 \pm 0.06$ sec^{-1} and $k_f = (1.14 \pm 0.10) \times 10^2$ M^{-1} sec^{-1} at 25.0°. The value of K_1 calculated from k_f/k_d and the values of $\Delta H°$ and $\Delta S°$ calculated from the activation parameters are in satisfactory agreement with the values determined spectrophotometrically. From the acid independence of the rate in the range $(H^+) = 0.025–1.0$ *M* we estimate that a path inversely proportional to (H^+) contributes no more than 10% to the over-all rate at $(H^+) = 0.025$ *M*.[11]

Discussion

The thermodynamic parameters for the formation of $VNCS^{2+}$ determined in this work are similar to those previously determined for $FeNCS^{2+}$. Thus, K_1 for the formation of $FeNCS^{2+}$ is 146 M^{-1} at 25.0° and ionic strength 0.40 *M*, while $\Delta H°$ and $\Delta S°$ are -1.6 kcal mole^{-1} and $+5.2$ cal mole^{-1} deg^{-1}, respectively.[2,12,13] On the other hand, the activation parameters for the iron(III) and vanadium(III) reactions are quite different. The values of these parameters are compared in Table I. It will be seen that the activation energies for the vanadium(III) reactions are lower and their entropies of activation more negative than the values for the corresponding iron(III) reactions.

Table I

Values of the Activation Parameters for the Acid-Independent Reactions of Monothiocyanate Complexes of Vanadium(III), Iron(III), and Chromium(III)

	Metal ion		
	V(III)	Fe(III)	Cr(III)
Ref	This work	2	3
Ionic strength, *M*	1.0[a]	0.40[a]	0.50[b]
k_f at 25.0°, M^{-1} sec^{-1}	114 ± 10	127 ± 10	1.79×10^{-6}
$\Delta H_f^{\ddagger}$, kcal mole^{-1}	7.6 ± 0.6	14.6 ± 1.4	25.1
$\Delta S_f^{\ddagger}$, cal mole^{-1} deg^{-1}	−23.8 ± 1.9	−10 ± 5	−0.7
k_d at 25.0°, sec^{-1}	1.03 ± 0.06	0.87 ± 0.07	9.2 ± 10^{-9}
$\Delta H_d^{\ddagger}$, kcal mole^{-1}	10.7 ± 0.5	13.0 ± 1.4	27.5
$\Delta S_d^{\ddagger}$, cal mole^{-1} deg^{-1}	−22.6 ± 1.5	−5 ± 5	−3

[a] The medium used in these studies was $HClO_4–NaClO_4$.
[b] The medium used in these studies was $HClO_4–NaClO_4–LiClO_4$.

This difference in the activation parameters can be rationalized by postulating that the vanadium(III) reactions have more S_N2 character than the corresponding iron(III) reactions. A considerable amount of evidence indicates that the iron(III) reactions are predominantly S$_N$1 in character. Rate comparisons have shown that, in common with the rates of complex formation of many divalent ions, the rates of formation of $(H_2O)_5FeX^{2+}$ complexes are primarily determined by the loss of a water molecule coordinated to the iron(III).[14] The entering ligand appears to have relatively little effect on the loss of the coordinated water molecule. While iron(III) has five d electrons, vanadium(III) has only two d electrons. Consequently, unlike spin-free iron(III), vanadium(III) has an orbital available for bond formation. The availability of an orbital for forming a bond to the entering ligand could account for the enhanced S$_N$2 character and lower activation energies for the vanadium(III) reactions.[15] Similarly, the increased order in the transition state resulting from the formation of a seven-coordinated structure could explain the relatively negative entropies of activation for the vanadium(III) reactions.

The effect of the number of d electrons on the crystal field stabilization of five-, six-, and seven-coordinated structures has been calculated by Basolo and Pearson.[16] They have shown that vanadium(III) and spin-free iron(III) complexes do not lose any crystal field stabilization energy in either an S$_N$1 or an S$_N$2 mechanism. Consequently both five- and seven-coordinated transition states can readily be formed in vanadium(III) and spin-free iron(III) reactions compared, for example, to d^3, spin-paired d^6, and d^8 systems. This is supported by the data presented in Table I. It is apparent that the activation energies for the reactions of the d^3 chromium(III) system are much higher than the activation energies for the vanadium(III) and

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[11] According to L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966), the hydrolysis constant of the vanadium(III) ion is 1.4×10^{-3} *M* at 20° and ionic strength 1 *M*. From these data we estimate that about 5–10% of the vanadium(III) exists as VOH^{2+} at $(H^+) = 0.025$ *M*.

[12] Somewhat different values of $\Delta H°$ and $\Delta S°$ have been reported by M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1572 (1955).

[13] Evidence has been previously presented that the monothiocyanate complex of iron(III) is nitrogen bonded: A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966); T. J. Conocchioli and N. Sutin, *ibid.*, **89**, 282 (1967). The similarity of the spectra of the monoazide and monothiocyanate complexes of vanadium(III) (both have absorption maxima at 350 mμ) strongly suggests that the latter complex is nitrogen bonded.

[14] D. E. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

[15] L. E. Orgel, *J. Chem. Soc.*, 4756 (1952).

[16] F. Basolo and R. G. Pearson, "Kinetics and Mechanism," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 108.

iron(III) systems. The increased activation energy for the chromium(III) reactions reflects the loss of a substantial amount of crystal field stabilization energy in forming the transition state in the d^3 system. This loss is somewhat smaller for an SN1 than for an SN2 mechanism. It is noteworthy that the entropies of activation for the chromium(III) reactions are also more positive than the entropies of activation for the vanadium(III) reactions. However, because of the importance of crystal field effects in the chromium(III) reactions, comparisons between the chromium(III) and vanadium(III) systems may be less valid than comparisons between the iron(III) and vanadium(III) systems.

The conclusion that the vanadium(III) reaction is predominantly SN2 in character is consistent with the decreased importance of the inverse acid path in the vanadium(III) system.[17] The inverse acid path in the iron(III) system has been interpreted in terms of the conjugate base mechanism

$$Fe(H_2O)_5X^{2+} \rightleftharpoons Fe(H_2O)_4(OH)X^+ + H^+ \qquad (9)$$

$$Fe(H_2O)_4(OH)X^+ + H_2O \rightleftharpoons Fe(H_2O)_5OH^{2+} + X^- \qquad (10)$$

in which the five-coordinated intermediate $Fe(H_2O)_4OH^{2+}$ is stabilized through π bonding of the hydroxide group. A similar five-coordinated intermediate could also be formed in the vanadium(III) system. Since the activation parameters for the inverse acid path are not known, it is not profitable to speculate whether such an intermediate is indeed formed in the vanadium(III) reaction. On the other hand, if an SN2 mechanism also operates in the inverse acid path, then the results obtained in the present study suggest that the seven-coordinated transition state formed by the addition of thiocyanate to $V(H_2O)_5OH^{2+}$ is not much more stable (and may well be much less stable) than the one formed by the addition of thiocyanate to $V(H_2O)_6^{3+}$. In any event the SN2 mechanism appears to provide such a favorable pathway for the acid-independent reaction that this reaction effectively masks the contribution of the inverse acid path.[18]

Finally, SN2 mechanisms have recently been proposed for the reactions of CH_3HgOH and of UO_2^{2+} with various anions.[19,20] In both cases no contribution from an acid-dependent pathway was discerned within the experimental error of the measurements. More significantly, however, the rate constants for complex formation depended upon the nature of the incoming ligand. Additional work on the substitution reactions of $V(H_2O)_6^{3+}$ is planned in order to determine the ligand dependence of the rate constants.

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(17) Whereas the rate of formation of $VNCS^{2+}$ is independent of the hydrogen ion concentration in the range 0.025–1.0 *M*, the rates of formation of $FeNCS^{2+}$ and $CrNCS^{2+}$ increase by factors of 5 and 1.2, respectively, when the hydrogen ion concentration is decreased from 0.40 to 0.025 *M* at 25.0°. However, in comparing these rate constant variations, it should be remembered that the hydrolysis constants of $V(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ are similar and are about ten times larger than the hydrolysis constant of $Cr(H_2O)_6^{3+}$ at 25.0°.

(18) The above argument assumes that the hydrolysis constants of $V(H_2O)_5NCS^{2+}$ and $Fe(H_2O)_5NCS^{2+}$ have similar values. Since the hydrolysis constants of $V(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ are not very different, there is no reason to believe that the hydrolysis constants of their thiocyanate complexes will not be similar.

(19) M. Eigen, G. Geier, and W. Kruse in "Essays in Coordination Chemistry," W. Schneider, G. Anderegg, and R. Gut, Ed., Birkhäuser Verlag, Basel, Switzerland, 1964, pp 164–178.

(20) P. Hurwitz and K. Kustin, *J. Phys. Chem.*, **71**, 324 (1967).

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The Hydrolysis of Beryllium(II) in 1 *m* NaCl

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The hydrolysis of beryllium(II) in 1 *m* NaCl was measured at 0, 25, and 60° to establish better the reactions which occur and their temperature coefficients. Potentiometric measurements were made with hydrogen electrodes at 0 and 60° and with a quinhydrone electrode at 25°. The beryllium concentration was varied in the range 0.002–0.05 *m* and the pH was varied in the range 2–7. The results at low $\bar{n}$, the hydroxyl number, are consistent with previous work suggesting the formation of $Be_2(OH)^{3+}$ and $Be_3(OH)_3^{3+}$. The third species previously proposed to account for data in nearly neutral solutions, $Be(OH)_2$, is incorrect. By computer analysis of the data at three temperatures, the most probable third species is $Be_5(OH)_7^{3+}$ which gives a slightly better fit than $Be_6(OH)_8^{4+}$. With careful consideration of the experimental error and the weighting of the data, there was no justification for adding more species to the scheme. The $-\log Q$ values for the most probable scheme are: 0°, (2, 1) 3.64, (3, 3) 10.08, (5, 7) 28.66; 25°, (2, 1) 3.43, (3, 3) 8.91, (5, 7) 25.33; and 60°, (2, 1) 2.93, (3, 3) 7.67, (5, 7) 22.11, where the numbers in parentheses are the subscripts (x, y) for the species $Be_x(OH)_y^{(2x-y)+}$ formed in the reaction $xBe^{2+} + yH_2O = Be_x(OH)_y^{(2x-y)+} + yH^+$. The $\Delta H°$ values at 25° for the formation of these species in the order of increasing polynuclearity are 5.0, 16.0, and 45.3 kcal/mole and the respective $\Delta S°$ values are 1.4, 15.3, and 35.2 eu. Relationships among the $\Delta H°$ and among the $\Delta S°$ terms for the polynuclear hydrolysis products of several different metal ions are discussed.

Introduction

The beryllium(II) ion is the lightest and smallest ion to produce polynuclear hydrolysis products—$(M_x(OH)_y^{(2x-y)+})$—in aqueous solutions. The unhydrolyzed ion is known to be tetrahedrally hydrated in water,[1] as would be expected from its uniquely small size, and

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(1) D. N. Fiat and R. E. Connick, *J. Chem. Phys.*, **39**, 1349 (1963); M. Alei and J. A. Jackson, *ibid.*, **41**, 3402 (1964).