

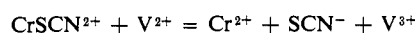
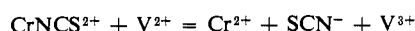
The Kinetics and Mechanism of the Oxidation of Hexaaquovanadium(II) by the Isothiocyanato- and Thiocyanatopentaaquochromium(III) Ions¹

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Abstract: The kinetics of the oxidation of hexaaquovanadium(II) ions by nitrogen-bonded and sulfur-bonded chromium(III) thiocyanate have been studied by the use of conventional and flow techniques. The rate law for the former reaction is $-d[\text{CrNCS}^{2+}]/dt = [\text{CrNCS}^{2+}][\text{V}^{2+}]\{k_1 + k_2/[\text{H}^+]\}$. At 25° and 3.0 *M* ionic strength, $k_1 = 4.41 \times 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$, $k_2 = 3.57 \times 10^{-4} \text{ sec}^{-1}$, $\Delta H_1^\ddagger = 23.1 \pm 2.5 \text{ kcal mol}^{-1}$, $\Delta S_1^\ddagger = -1 \pm 8 \text{ cal deg}^{-1} \text{ mol}^{-1}$, $\Delta H_2^\ddagger = 22.8 \pm 0.4 \text{ kcal mol}^{-1}$, and $\Delta S_2^\ddagger = 2.0 \pm 1.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The inverse-acid term in the rate law is interpreted as a reaction path involving hydroxide ion as the bridging group. The reaction of the sulfur-bonded chromium(III) complex with vanadium(II) proceeds by an inner-sphere mechanism with thiocyanate as the bridging group. The rate law for the oxidation-reduction reaction is $-d[\text{CrSCN}^{2+}]/dt = [\text{CrSCN}^{2+}][\text{V}^{2+}]\{k_3 + k_4/[\text{H}^+]\}$. At 25° and 1.0 *M* ionic strength, $k_3 = 8.0 \text{ M}^{-1} \text{ sec}^{-1}$, $k_4 = 1.8 \text{ M}^{-2} \text{ sec}^{-1}$, $\Delta H_3^\ddagger = 13.0 \pm 0.9 \text{ kcal mol}^{-1}$, and $\Delta S_3^\ddagger = -11.0 \pm 2.8 \text{ cal deg}^{-1} \text{ mol}^{-1}$, while at 25° and 3.0 *M* ionic strength, $k_3 = 16.2 \text{ M}^{-1} \text{ sec}^{-1}$, $k_4 = 2.5 \text{ M}^{-2} \text{ sec}^{-1}$, $\Delta H_3^\ddagger = 12.4 \pm 0.7 \text{ kcal mol}^{-1}$ and $\Delta S_3^\ddagger = -11.4 \pm 2.4 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The mechanisms of the reactions are discussed.

The formation of unstable linkage isomers in inner-sphere, electron-transfer reactions involving the transfer of an unsymmetrical bridging group has been a popular subject in recent years.³⁻⁷ We have found that the S-bonded monothiocyanate complex $(\text{H}_2\text{O})_5\text{CrSCN}^{2+}$ is an important product of the reduction of FeNCS^{2+} and of *trans*- $\text{Co}(\text{en})_2\text{OH}_2(\text{NCS})^{2+}$ by chromium(II).^{8,9} The aquation and isomerization of this complex to the N-bonded complex in the absence as well as in the presence of metal ions such as chromium(II) and mercury(II) have been described elsewhere.^{9,10} We are mainly concerned here with the kinetics and mechanisms of the reduction of the two linkage isomers by vanadium(II) ions.



Earlier, we reported briefly that the rate of reduction of CrSCN^{2+} by vanadium(II) is comparable to the rate of complex formation between vanadium(II) and thiocyanate, and we showed that the oxidation-reduction reaction proceeds by an inner-sphere mechanism.¹¹ The work reported here comprises more extensive data confirming the earlier observations. In addition, the kinetics of the oxidation of vanadium(II) by CrNCS^{2+} are presented, and the mechanisms of the reactions are discussed.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

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(3) R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **6**, 217 (1958).

(4) D. L. Ball and E. L. King, *J. Amer. Chem. Soc.*, **80**, 1091 (1958).

(5) J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965).

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(7) J. P. Birk and J. H. Espenson, *ibid.*, **90**, 1153 (1968).

(8) A. Haim and N. Sutin, *ibid.*, **87**, 4210 (1965).

(9) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

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Experimental Section

Materials. A stock solution of vanadium(IV) was prepared by electroreduction of a slurry of vanadium pentoxide (Fisher Scientific Co.) in perchloric acid at a platinum gauze electrode. The vanadium(II) was prepared by electroreduction of the vanadium(IV) perchlorate solution at a mercury pool electrode in an argon atmosphere and at ice temperature. Iron(III) perchlorate (G. F. Smith Chemical Co.) was recrystallized twice from perchloric acid and a stock solution 0.73 *M* in Fe(III) and 2.76 *M* in HClO_4 was prepared. A chromium(II) perchlorate solution containing 0.1 *M* chromium(II) and 1 *M* perchloric acid was prepared by reduction of chromium(III) perchlorate (G. F. Smith Chemical Co.) solution with amalgamated zinc and stored under argon. Magnesium perchlorate was precipitated by treating magnesium oxide (Baker analyzed reagent) with an appropriate amount of perchloric acid and a 2.0 *M* stock solution was prepared from the salt. Sodium thiocyanate (Fisher Chemical Co.) was used without further purification. Quadruply distilled water, distilled water purified by redistillation from acid dichromate, followed by a distillation from alkaline permanganate and a final redistillation, was used to prepare all the solutions.

The preparation and analysis of solutions containing the two isomers of chromium(III) thiocyanate has been described previously.⁸⁻¹¹

Analyses. The vanadium(II) concentration was determined by titrating with deoxygenated iron(III) perchlorate a solution containing 5 ml of $\sim 0.3 \text{ M}$ vanadium(II) perchlorate and 15 ml of $\sim 0.1 \text{ M}$ sodium thiocyanate in 1 *M* perchloric acid to the red color characteristic of iron(III) thiocyanate solutions. The above procedure was conducted in an argon atmosphere. The vanadium(II) concentration¹² measured with a Cary Model 14 spectrophotometer was always compared with the above result and they were reasonably close, within 0.3%. The hydrogen ion concentration in the vanadium(II) solution was determined by absorbing the vanadium(II) on an ion-exchange column prewashed with deoxygenated quadruply distilled water and in an argon atmosphere. The total hydrogen ion was titrated to phenolphthalein pink with standard 1.0 *M* sodium hydroxide solution. Allowance was made for the hydrogen ion released from the column when the vanadium(II) was adsorbed.

Iron(III) was analyzed by passing an iron(III) perchlorate solution through an amalgamated zinc column and the resulting iron(II) solution was then titrated with standard cerium(IV) sulfate solution using ferroin as an indicator. Vanadium(IV) concentration was determined by potentiometric titration with standard cerium(IV) sulfate solution. The Volhard method was used to determine the

(12) G. Gordon and P. H. Tewari, *J. Phys. Chem.*, **70**, 200 (1966); Table I of this reference listed ϵ_0 at 450 $\text{m}\mu$ as 2.31 which should be 2.13.

thiocyanate ion concentration. Magnesium ion was analyzed gravimetrically as magnesium sulfate.

The Kinetic Measurements of the V^{2+} -CrNCS $^{2+}$ Reaction. The slow oxidation-reduction reaction was studied in argon to prevent the oxidation of vanadium(II) by air. The two reactants were thermally equilibrated for 0.5 hr in separate vessels in a constant temperature bath. The reaction was started by introducing the degassed CrNCS $^{2+}$ solution into the vanadium solution. The concentration ranges used were $[V(II)] = 0.03$ – $0.22 M$, $(CrNCS^{2+}) = 2.0 \times 10^{-4}$ to $1.0 \times 10^{-3} M$, $(HClO_4) = 0.30$ to $2.40 M$, ionic strength adjusted to $3.0 M$ with magnesium perchlorate. The rate of reaction was followed by removal of 15 ml of the reacting solution and quenching the reaction on a Dowex 50W-X8 ion-exchange column. The free thiocyanate ion produced in the reaction was washed into a 200-ml volumetric flask containing 2 ml of $\sim 0.4 M$ iron(II) perchlorate solution. The iron(II) destroys an oxidizing species, possibly hydrogen peroxide, which is formed in the ion-exchange column when vanadium is adsorbed in the presence of air. This precaution was necessary to prevent the fading of the FeNCS $^{2+}$ formed in the subsequent step. The eluate was adjusted with concentrated perchloric acid and $0.73 M$ iron(III) to a final concentration $3.0 \times 10^{-2} M$ in iron(III) and $1.0 M$ in perchloric acid. The optical density of the reddish FeNCS $^{2+}$ complex formed was measured in a 5.0-cm cell on Cary Model 14 spectrophotometer at $460 m\mu$ and 25.0° .⁹ Since the vanadium(II) was always present in large excess over the CrNCS $^{2+}$, pseudo-first-order conditions obtained in all the kinetic runs. The rate constants were obtained from the slopes of plots of $\log(D_\infty - D_t)$ vs. time, where D_t and D_∞ are the absorbances at time t and at the end of the reaction, respectively.

The Kinetic Measurements of the V^{2+} -CrSCN $^{2+}$ Reaction. The oxidation-reduction reaction was studied with the flow apparatus which has been described previously.¹³ The two reactants were kept under argon pressure and were thermally equilibrated for 0.5 hr in the constant-temperature bath prior to the kinetic measurements. The disappearance of CrSCN $^{2+}$ was followed by observing the change in absorbance at $262 m\mu$ (an absorption maximum of CrSCN $^{2+}$). The kinetics of the reaction were studied at 1.0 and $3.0 M$ ionic strength, and at several temperatures. The concentration ranges used were $[V(II)] = 0.039$ to $0.10 M$, $(CrSCN^{2+}) = 5.9 \times 10^{-5}$ to $5.5 \times 10^{-4} M$, $(HClO_4) = 0.27 M$ to $1.0 M$, ionic strength adjusted to $1.0 M$ with magnesium perchlorate, and $[V(II)] = 0.01$ to $0.10 M$, $(CrSCN^{2+}) = 8.9 \times 10^{-5}$ to $2.4 \times 10^{-4} M$, $(HClO_4) = 0.42$ – $2.7 M$, ionic strength adjusted to $3.0 M$ with magnesium perchlorate. A large excess of vanadium(II) was present in all cases to ensure pseudo-first-order conditions. Although the CrSCN $^{2+}$ solutions also contained some CrNCS $^{2+}$, the reaction of the latter complex with vanadium(II) is too slow to interfere with the reaction of CrSCN $^{2+}$. The rate constants were obtained from the slopes of plots of $\log(D_\infty - D_t)$ vs. time, where D_t and D_∞ are the absorbances at time t and at the end of the reaction, respectively.

Results

The V^{2+} -CrNCS $^{2+}$ Reaction. The second-order rate constants for the oxidation of vanadium(II) by CrNCS $^{2+}$ are presented in Table I. These rate constants were calculated from

$$-d(CrNCS^{2+})/dt = k_N(V^{2+})(CrNCS^{2+}) \quad (1)$$

The rates were not affected by the addition of $1.0 \times 10^{-3} M$ SCN $^-$, of $0.03 M$ V(III), or of $5 \times 10^{-3} M$ Cr $^{2+}$ but increased with decreasing acidity. In the range $(HClO_4) = 0.30$ to $2.4 M$, the observed rate constant is given by

$$k_N = k_1 + k_2/(H^+) \quad (2)$$

The rate constants in eq 2 were replaced by the corresponding absolute rate theory expressions, and the various activation parameters were calculated using a nonlinear least-squares program.¹⁴ In this calculation

(13) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).

(14) The computer program for treatment of the kinetic data to obtain the activation parameters was adapted by W. Alexander and N. Sutin from the nonlinear least-squares program written by W. C. Hamilton.

Table I. Rate Constants for the Oxidation of Vanadium(II) by CrNCS $^{2+}$ at $3.0 M$ Ionic Strength

Temp, °C	(V $^{2+}$), M	(CrNCS $^{2+}$), $10^4 M$	(HClO $_4$), M	k_N , $10^4 M^{-1} sec^{-1}$
25.0	0.03	5.14	1.0	4.01
25.0	0.05	6.10	1.0	4.40
25.0	0.10	6.10	1.0	3.92
25.0	0.15	6.10	1.0	3.70
25.0	0.20	6.10	1.0	4.20
25.0	0.22	2.00	1.0	4.21
25.0	0.10	10.0	1.0	4.05
25.0	0.10	6.15	1.0	3.62 ^a
25.0	0.07	7.10	0.35	11.1
25.0	0.10	5.14	0.45	8.94
25.0	0.10	6.10	0.66	6.05
25.0	0.10	6.00	0.80	5.46 ^b
25.0	0.15	5.14	2.0	2.31
25.0	0.20	5.70	2.4	1.88
15.0	0.049	5.70	0.30	3.12
15.0	0.07	4.44	0.33	3.01
15.0	0.10	4.44	0.45	1.97
15.0	0.10	4.44	0.67	1.40
15.0	0.115	5.70	1.0	1.03
15.0	0.10	4.44	2.0	0.58
35.0	0.07	5.14	0.34	40.5
35.0	0.10	5.14	0.45	31.3
35.0	0.10	5.14	0.67	21.1
35.0	0.10	5.14	1.0	14.2
35.0	0.10	5.14	1.0	14.6 ^c
35.0	0.20	5.70	2.4	6.88
40.1	0.074	4.02	1.0	26.8
40.1	0.074	4.02	1.5	18.9
40.1	0.074	4.02	2.0	15.2
40.1	0.074	4.02	2.4	14.2
44.6	0.074	4.02	1.0	42.4
44.6	0.074	4.02	1.5	31.3
44.6	0.074	4.02	2.0	25.8

^a $0.03 M$ vanadium(III) added. ^b $1.0 \times 10^{-3} M$ thiocyanate added. ^c $0.005 M$ chromium(II) added.

each rate constant was weighted according to the reciprocal of its square since the per cent error in k_N was approximately constant. The calculated values of the rate constants agreed with the experimental values with an average deviation of 3.5%. The activation parameters calculated by the program are $\Delta H_1^\ddagger = 23.1 \pm 2.5$ kcal mol $^{-1}$, $\Delta S_1^\ddagger = -1 \pm 8$ cal deg $^{-1}$ mol $^{-1}$, $\Delta H_2^\ddagger = 22.8 \pm 0.4$ kcal mol $^{-1}$, and $\Delta S_2^\ddagger = 2.0 \pm 1.3$ cal deg $^{-1}$ mol $^{-1}$. At 25.0° and $3 M$ ionic strength $k_1 = (4.41 \pm 0.70) \times 10^{-5} M^{-1} sec^{-1}$ and $k_2 = (3.57 \pm 0.07) \times 10^{-4} sec^{-1}$.

The V^{2+} -CrSCN $^{2+}$ Reactions. The rate of oxidation of vanadium(II) by CrSCN $^{2+}$ is first order with respect to both reactants. The second-order rate constants calculated from

$$-d(CrSCN^{2+})/dt = k_S(V^{2+})(CrSCN^{2+}) \quad (3)$$

are presented in Table II. The rates were not affected by the addition of $2.55 \times 10^{-3} M$ V(III), but decreased with decreasing acidity. In the range $(HClO_4) = 0.42$ to $2.7 M$, the observed rate constant is given by

$$k_S = k_3 + k_4(H^+) \quad (4)$$

The values of k_3 and k_4 and of the corresponding activation parameters calculated by the least-squares program are $\Delta H_3^\ddagger = 12.4 \pm 0.7$ kcal mol $^{-1}$, $\Delta S_3^\ddagger = -11.4 \pm 2.4$ cal deg $^{-1}$ mol $^{-1}$, $\Delta H_4^\ddagger = 8.2 \pm 2.9$ kcal mol $^{-1}$, and $\Delta S_4^\ddagger = -29 \pm 10$ cal deg $^{-1}$ mol $^{-1}$. At 25.0° and $3 M$ ionic strength $k_3 = 16.2 \pm 0.4 M^{-1} sec^{-1}$ and $k_4 = 2.5 \pm 0.3 M^{-2} sec^{-1}$. The calculated

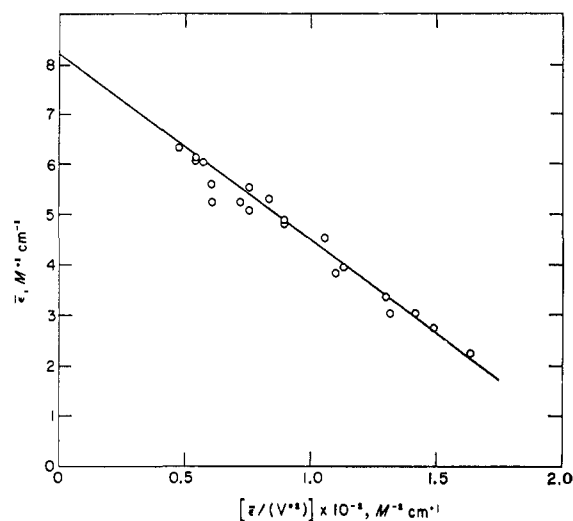


Figure 1. Plot of $\bar{\epsilon}$ vs. $\bar{\epsilon}/(V^{2+})$ at 710 $m\mu$, 25°, and 1.0 M ionic strength.

values of the rate constants agreed with the experimental values with an average deviation of 3.5%. Less extensive measurements at ionic strength 1.0 M gave $\Delta H_3^\ddagger = 13.0 \pm 0.9$ kcal mol $^{-1}$, $\Delta S_3^\ddagger = -11.0 \pm 2.8$ cal deg $^{-1}$ mol $^{-1}$, $\Delta H_4^\ddagger = 5.8 \pm 5.0$ kcal mol $^{-1}$, $\Delta S_4^\ddagger = -39 \pm 16$ cal deg $^{-1}$ mol $^{-1}$, $k_3 = 8.0 \pm 0.4$ M^{-1} sec $^{-1}$, and $k_4 = 1.8 \pm 0.7$ M^{-2} sec $^{-1}$ at 25.0°.

Table II. Rate Constants for the Oxidation of Vanadium(II) by $CrSCN^{2+}$ at 3.0 M Ionic Strength

Temp, °C	(V $^{2+}$), M	(CrSCN $^{2+}$), $10^4 M$	(HClO $_4$), M	k_3 , M^{-1} sec $^{-1}$
25.1	0.05	2.0	1.0	21.1
25.1	0.04	2.0	1.0	18.3
25.1	0.025	2.0	1.0	19.9
25.1	0.01	2.0	1.0	17.7
25.1	0.025	1.0	1.0	17.5
25.1	0.10	2.1	1.0	19.2
25.0	0.056	2.4	1.0	18.9
25.1	0.05	1.5	0.42	18.3
25.1	0.05	2.1	0.85	18.8
25.1	0.05	2.1	1.3	20.0
25.1	0.05	1.5	1.5	20.9
25.1	0.05	1.5	2.0	21.3
25.1	0.05	1.5	2.5	22.5
25.1	0.05	1.5	2.7	23.2
14.8	0.09	0.89	0.75	8.5
14.8	0.09	0.89	1.5	9.7
14.8	0.073	1.10	2.5	11.8
20.0	0.09	0.89	0.75	13.0
20.0	0.10	1.80	1.0	12.6
20.0	0.10	1.80	1.5	12.9
20.0	0.09	0.89	1.5	13.7
20.0	0.10	1.80	2.0	14.7
30.0	0.04	0.90	0.5	26.7
30.0	0.04	0.90	1.0	27.2
30.0	0.04	0.90	1.5	28.4
30.0	0.04	0.90	2.0	28.9
30.0	0.04	0.90	2.5	32.5
35.1	0.037	1.10	0.5	33.8
35.1	0.037	1.10	1.4	36.8
35.1	0.037	0.90	2.0	40.9
35.1	0.037	0.90	2.5	45.3

The Vanadium(II)-Thiocyanate Equilibrium. During the course of this work the equilibrium constant for reaction 5 was also determined



using a spectrophotometric method. Although the value of K_1 is not pertinent to the main theme of this paper, the results are of interest in view of the discrepancy in the values of K_1 which have recently been reported.^{15,16} These reports give $K_1 = 27 \pm 5$ M^{-1} at 25° and $\mu = 0.84$ M (determined spectrophotometrically)¹⁵ and $K_1 = 11$ M^{-1} at 24° and $\mu = 1.0$ M (determined from kinetic data).¹⁶ The difference between these values appears to be outside the experimental error of the measurements.

The absorbance at 710 $m\mu$ of solutions containing vanadium(II), thiocyanate, perchloric acid, and sodium perchlorate was measured in an argon atmosphere. The concentration ranges used were $[V(II)] = 0.015$ to 0.12 M , $(SCN^-) = 0.005$ to 0.02 M , and $(HClO_4) = 0.50$ M . The data were analyzed according to¹⁷

$$\bar{\epsilon} = \epsilon_1 - [\bar{\epsilon}/K_1(V^{2+})] \quad (6)$$

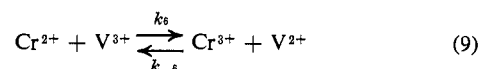
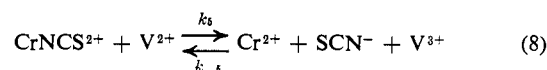
where $\bar{\epsilon} = [A - \epsilon_0(V^{2+})]/(SCN^-)_T$, and A , the absorbance per unit path length is given by

$$A = \epsilon_0(V^{2+}) + \epsilon_1(VNCS^+) \quad (7)$$

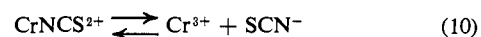
In the above equation, ϵ_0 and ϵ_1 are the molar absorptivities of V^{2+} and $VNCS^+$, respectively. The value of ϵ_0 used is 1.11 M^{-1} cm $^{-1}$ at 710 $m\mu$.¹⁵ A plot of $\bar{\epsilon}$ vs. $\bar{\epsilon}/(V^{2+})$ is shown in Figure 1. This plot gives $K_1 = 27 \pm 2$ M^{-1} and $\epsilon_1 = 8.2 \pm 0.5$ M^{-1} cm $^{-1}$ at 25° and ionic strength 1.0 M , in good agreement with the values reported in ref 15.

Discussion

The Mechanism of the V^{2+} - $CrNCS^{2+}$ Reaction. The kinetic data are consistent with the following reaction scheme



where the individual rate constants are functions of the acidity. Evidently the net effect of reactions 8 and 9 is the aquation of $CrNCS^{2+}$.



The equilibrium constant for reaction 10 is 5×10^{-3} M at 25° and ionic strength 0.5 M .¹⁸ Thermodynamic considerations show that the forward rate of reaction 10 is still more than ten times faster than the reverse rate even after 80% of the reaction is complete under typical reaction conditions. In other words

(15) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

(16) W. Kruse and D. Thusius, *ibid.*, **7**, 464 (1968).

(17) B. R. Baker, N. Sutin, and T. J. Welch, *ibid.*, **6**, 1948 (1967).

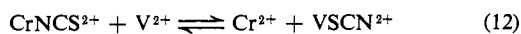
(18) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208, 1216 (1955).

$$\frac{(\text{CrNCS}^{2+})}{200(\text{Cr}^{3+})(\text{SCN}^-)} > 10 \quad (11)$$

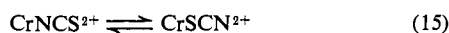
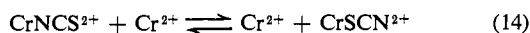
for $(\text{CrNCS}^{2+})_0 = 5 \times 10^{-4} M$ and $(\text{V}^{2+})_0 = 0.1 M$ even when $(\text{Cr}^{3+})/(\text{CrNCS}^{2+})_0 = 0.8$. Evidently the reverse rate does not contribute significantly to the observed rate during the first two half-lives of the reaction. The reverse rate has therefore been neglected in interpreting the data, a procedure justified by the lack of dependence of the rate constants on $(\text{CrNCS}^{2+})_0$.

The absence of inhibition by added thiocyanate as well as the linearity of the first-order plots indicate that the forward rate of reaction 9 is faster than the reverse rate of reaction 8. The observed rate constant may therefore be identified with k_5 , thus $k_5 = k_1 + k_2/(\text{H}^+)$. Now k_{-5} is equal to k_3/K_8 where K_8 is the equilibrium constant for reaction 8. This equilibrium constant is equal to the equilibrium constant for reaction 10 divided by the equilibrium constant for reaction 9 (1.9×10^3 at 25° and ionic strength $2.5 M$).¹⁹ Consequently $K_8 \approx 2.6 \times 10^{-6} M$ and $k_{-5} = k_{-1} + k_{-2}/(\text{H}^+)$ with $k_{-1} \approx 17 M^{-2} \text{ sec}^{-1}$ and $k_{-2} \approx 1.4 \times 10^2 M \text{ sec}^{-1}$ at 25° . A similar two-step mechanism has previously been proposed for the reaction of the chloropentaaquochromium(III) ion with vanadium(II).¹⁹ However in the latter case the rate of formation of Cr^{2+} and V^{3+} in the first step was higher than the rate at which these two species reacted, and a more complicated kinetic analysis was necessary.

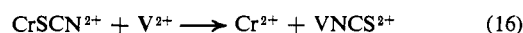
The rate law indicates that reaction 8 proceeds by two parallel paths, one acid independent and the other acid dependent. The acid-independent path (reaction 8 with $k_5 = k_1$ and $k_{-5} = k_{-1}$) may proceed by (a) an inner-sphere, thiocyanate-bridged mechanism



(b) an inner-sphere, water-bridged mechanism, which yields CrNCS^+ and V^{3+} , or (c) an outer-sphere mechanism, which may either yield CrNCS^+ and V^{3+} , or Cr^{2+} and $\text{V}^{3+} \cdot \text{SCN}^-$, where the latter represents an ion pair of $\text{V}(\text{H}_2\text{O})_6^{3+}$ and thiocyanate. Adjacent attack on coordinated thiocyanate is not considered to provide an important pathway, since recent experiments¹⁰ suggest that this mode of attack is less likely than previously believed.¹ The isomerization reactions



followed by



are also discounted, since these reactions would not

(19) J. H. Espenson and O. J. Parker, *J. Amer. Chem. Soc.*, **90**, 3689 (1968). The chloride-hydroxide criterion assumes that hydroxide and chloride are roughly equally effective bridging groups. The experimental evidence supporting this assumption comes mainly from reactions involving chromium(II). On the other hand there are some exceptions. For example, hydroxide is a much better bridging group than chloride in the Fe^{2+} - FeX^{2+} exchange reactions. It is thus necessary to apply the chloride-hydroxide criterion (as well as the chloride-thiocyanate criterion) with caution.

compete successfully with the direct reaction between CrNCS^{2+} and V^{2+} under the conditions used in these studies.

Some information about the mechanism of the acid-independent reaction can be obtained from a comparison of the rates of reaction of vanadium(II) with CrNCS^{2+} and with CrCl^{2+} . The relevant data are summarized in Table III. Evidently vanadium(II)

Table III. Comparison of the Effects of Chloride and Thiocyanate on Electron Transfer Rates^a

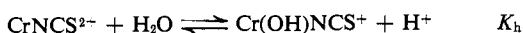
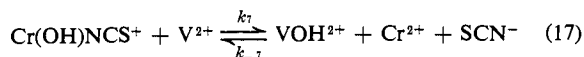
Reaction	$k_{\text{Cl}^-}/k_{\text{NCS}^-}$	Ref
$\text{V}^{2+} + \text{CrX}^{2+}$	$\sim 1 \times 10^3$	<i>b, c</i>
$\text{V}^{2+} + (\text{NH}_3)_5\text{CoX}^{2+}$	~ 17	<i>d</i>
$\text{V}^{2+} + \text{FeX}^{2+}$	~ 1	<i>e</i>
$\text{Cr}^{2+} + \text{CrX}^{2+}$	$\sim 1 \times 10^5$	<i>f, g</i>
$\text{Cr}^{2+} + (\text{NH}_3)_5\text{CoX}^{2+}$	3.2×10^4	<i>d, h, k</i>
$\text{Cr}^{2+} + \text{FeX}^{2+}$	~ 1	<i>i, j</i>

^a Rate constants at 25° . ^b Reference 19. ^c This work. ^d J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964). ^e Reference 11. ^f Reference 4. ^g R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964). ^h J. P. Candlin and J. Halpern, *ibid.*, **4**, 766 (1965). ⁱ Reference 10. ^j G. Dulz and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 829 (1964). ^k The value of $k_{\text{Cl}^-}/k_{\text{NCS}^-}$ for the reaction of $(\text{NH}_3)_5\text{CoX}^{2+}$ with $\text{Cr}(\text{dipy})_3^{2+}$ (which is outer-sphere) is 80.

reacts about 10^3 times more rapidly with CrCl^{2+} than with CrNCS^{2+} . By analogy with the azide-thiocyanate rate comparisons, it might be expected that chloride would be a much better bridging group than the (unsymmetrical) thiocyanate ion. To some extent this prediction is supported by the data in Table III. Thus chloride-thiocyanate ratios as high as 10^3 to 10^5 are found in some cases, while in none of the reactions is this ratio less than unity. It seems reasonable to conclude that chloride is acting as a bridging ligand in those systems in which a large discrimination in favor of chloride is observed, a conclusion confirmed by the identities of the products of the reactions involving chromium(II). The reaction of vanadium(II) with $(\text{NH}_3)_5\text{CoCl}^{2+}$ is probably also inner-sphere with the relatively low chloride-thiocyanate ratio being due to the fact that the rate of the chloride-bridged reaction is primarily determined by the rate of substitution of a water molecule coordinated to vanadium(II). The absence of discrimination between chloride and thiocyanate in the oxidation of vanadium(II) by FeX^{2+} is not unexpected since both these reactions are outer-sphere. By contrast, the absence of discrimination in the oxidation of chromium(II) by the iron(III) complexes (which proceeds by an inner-sphere mechanism) is consistent with the view that the rates of these reactions are primarily determined by the rate of substitution on chromium(II).¹⁰ The chloride-thiocyanate criterion places the reaction of vanadium(II) with CrCl^{2+} in the chloride-bridged category, an assignment opposite to the one previously made on the basis of a comparison of the effects of hydroxide and chloride on the rates of vanadium(II)-chromium(III) reactions.¹⁹ The chloride-thiocyanate comparison also suggests that the reaction

of vanadium(II) with CrNCS^{2+} proceeds by an inner-sphere mechanism with thiocyanate acting as the bridging ligand. However, in common with other mechanistic assignments made on the basis of relative rate comparisons, the above conclusions should be considered as tentative and need to be substantiated by more direct lines of evidence.

The inverse-acid term in the rate law may be interpreted in terms of the reaction of Cr(OH)NCS^+ with V^{2+} by an inner-sphere mechanism

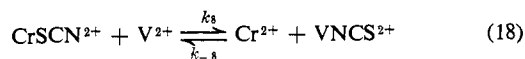


where k_2 is equal to k_7K_h . Although the value of K_h has not been reported, the hydrolysis constant of CrNCS^{2+} is probably not too different from the hydrolysis constant of CrCl^{2+} . The value of the latter is about $7 \times 10^{-6} M$.²⁰ Substitution of this value for K_h gives $k_7 \approx 51 M^{-1} \text{sec}^{-1}$, corresponding to a value of $k_7/k_1 \approx 1 \times 10^6$. Similarly, the value of k_{-7} is equal to k_{-2}/K_h' where K_h' is the hydrolysis constant of V^{3+} ($1.4 \times 10^{-3} M$ at 20° and ionic strength $1 M$).²¹

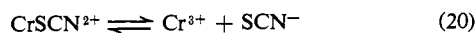


Substitution for k_{-2} and K_h' gives $k_{-7} \approx 1 \times 10^5 M^{-2} \text{sec}^{-1}$ and $k_{-7}/k_{-1} \approx 6 \times 10^3$ at 25° . The large values of k_7/k_1 and k_{-7}/k_{-1} are consistent with a hydroxide-bridged mechanism for reaction 17. Although the value of k_7 calculated above is somewhat uncertain because of the uncertainty in the value of K_h , it is of interest that the estimated value lies quite close to the value expected for a reaction in which substitution on vanadium(II) is rate determining.

The Mechanism of the V^{2+} - CrSCN^{2+} Reaction. As previously reported,¹¹ VNCS^{2+} is the immediate product of reaction of vanadium(II) and CrSCN^{2+} , indicating that the oxidation-reduction reaction proceeds by an inner-sphere, thiocyanate-bridged mechanism.



These steps are followed by the reaction of Cr^{2+} and V^{3+} (reaction 9). The net effect of the above reactions is the aquation of the chromium(III) complex.



The observed rate constant is equal to the rate constant for the forward rate of reaction 18, in other words, $k_8 = k_3 + k_4(\text{H}^+)$. The rate constant for the reverse rate of reaction 18 is equal to k_8/K_{18} where K_{18} is the equilibrium constant for reaction 18. In order to obtain K_{18} it is necessary to know the stability constant of CrSCN^{2+} . This stability constant may be estimated from the forward and reverse rates of reaction 14. The forward rate constant for reaction 14 is $1.4 \times 10^{-4} M^{-1} \text{sec}^{-1}$ at 25°

and ionic strength $1.0 M$,⁴ while the reverse rate constant is $40 M^{-1} \text{sec}^{-1}$ at 25° and ionic strength $1.0 M$.⁹ These rate constants give 3.5×10^{-6} for the equilibrium constant of reaction 14 (or reaction 15) at 25° .⁸ This value together with the equilibrium constant for reaction 10 gives $1.4 \times 10^3 M$ for the equilibrium constant for reaction 20 at 25° . Since the equilibrium constant for the formation of VNCS^{2+} is $117 M^{-1}$ at 25° and ionic strength $1.0 M$,¹⁷ we estimate that K_{18} is equal to 86 at 25° . Consequently $k_{-8} = k_{-3} + k_{-4}(\text{H}^+)$ where $k_{-3} = 9.3 \times 10^{-2} M^{-1} \text{sec}^{-1}$ and $k_{-4} = 2.1 \times 10^{-2} M^{-2} \text{sec}^{-1}$ at 25° and ionic strength $1.0 M$. Evidently the forward rate of reaction 19 is much more rapid than the reverse rate of reaction 18.

The rate constants for the reduction of CrSCN^{2+} and CrNCS^{2+} by vanadium(II) and chromium(II) are compared in Table IV. It is apparent that vanadium(II)

Table IV. Comparison of Rate Constants for the Reduction of CrSCN^{2+} and CrNCS^{2+} by Vanadium(II) and Chromium(II) at 25° and Ionic Strength $1.0 M$

Reaction	$k, M^{-1} \text{sec}^{-1}$	$k_{\text{NCS}^-}/k_{\text{SCN}^-}$	Ref
$\text{CrSCN}^{2+} + \text{V}^{2+}$	8.0, 16.2 ^a		<i>b</i>
$\text{CrNCS}^{2+} + \text{V}^{2+}$	4.41×10^{-6} ^a	2.7×10^{-6}	<i>b</i>
$\text{CrSCN}^{2+} + \text{Cr}^{2+}$	40		<i>c</i>
$\text{CrNCS}^{2+} + \text{Cr}^{2+}$	1.4×10^{-4} ^{d,e}	3.5×10^{-6}	<i>f</i>

^a Ionic strength $3.0 M$. ^b This work. ^c Reference 9. ^d Rate constant in $1.0 M$ perchloric acid. ^e Estimate from the rate constant at 27° . ^f Reference 4.

Table V. Comparison of Rates of Substitution and of Electron-Transfer Reactions Involving Vanadium(II)^a

Reaction	$k, M^{-1} \text{sec}^{-1}$	$\Delta H^\ddagger, \text{kcal mol}^{-1}$	$\Delta S^\ddagger, \text{cal deg}^{-1} \text{mol}^{-1}$	Ref
$\text{V}^{2+} + \text{SCN}^-$	28	13.5	-7	<i>b</i>
$\text{V}^{2+} + \text{SCN}^-$	15			<i>c</i>
$\text{V}^{2+} + \text{CrSCN}^{2+}$	8.0	13.0	-11	<i>d</i>
$\text{V}^{2+} + \text{VO}^{2+}$	1.6 ⁱ	12.3 ⁱ	-16.5 ⁱ	<i>e</i>
$\text{V}^{2+} + \text{cis-Co(en)}_2(\text{N}_3)_2^+$	32.9			<i>f</i>
$\text{V}^{2+} + \text{Co}(\text{NH}_3)_6\text{X}^{2+}$	2.1 to 45	11.0 to 12.2	-13 to -17	<i>g, h</i>

^a Rate constants at 25° and $1.0 M$ ionic strength. ^b Reference 15, ionic strength = $0.84 M$. According to ref 15 $\Delta S^\ddagger = -2$ eu. However we calculate $\Delta S^\ddagger = -7$ eu from the data reported there. ^c Reference 16, rate constant at 24° . ^d This work. ^e T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **68**, 228 (1964); ionic strength $2.0 M$. ^f J. H. Espenson, *J. Amer. Chem. Soc.*, **89**, 1276 (1967). ^g See Table III, footnote *d*. ^h Reference 23. ⁱ These are observed parameters and contain the contribution of an outer-sphere path. The outer-sphere path accounts for about 35% of the observed rate at 0° [T. W. Newton and F. B. Baker, *Inorg. Chem.*, **3**, 569 (1964)]. The value of ΔH^\ddagger for the inner-sphere path is $12.8 \text{ kcal mol}^{-1}$ if it is assumed that the extinction coefficient of the dinuclear complex is independent of temperature. ^j Where X = azide, binoxalate, oxalate, glyoxalate, pyruvate, trimethylpyruvate, and oxamate.

and chromium(II) react at similar rates with the chromium(III) complexes, indicating a common mechanism for the reactions. This suggests that the CrNCS^{2+} - V^{2+} reaction, in common with the other reactions in Table

(20) N. Bjerrum, *Z. Phys. Chem.*, **59**, 336 (1907).

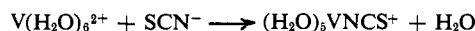
(21) L. Pajdowski, *J. Inorg. Nucl. Chem.*, **28**, 443 (1966).

IV, proceeds by an inner-sphere mechanism. This conclusion is consistent with the one reached earlier about the mechanism of the $\text{CrNCS}^{2+}-\text{V}^{2+}$ reaction. Since, as will be seen, there is good evidence that the rate of the $\text{CrSCN}^{2+}-\text{V}^{2+}$ reaction is controlled by the rate of substitution on vanadium(II), the above reasoning requires that the "redox-controlled" rate for the $\text{CrSCN}^{2+}-\text{V}^{2+}$ reaction not be much faster than the "substitution-controlled" rate. In any event, the similarity of the values of $k_{\text{NCS}}/k_{\text{SCN}}$ for the vanadium(II) and chromium(II) reductions is quite striking.

There is evidence that the rates of a number of oxidation-reduction reactions involving vanadium(II) are primarily controlled by the rate of replacement of a water molecule coordinated to the vanadium(II).^{11, 16, 22, 23} The relevant data are summarized in Table V. It is apparent that the rate constants and activation parameters for the oxidation-reduction reactions are very similar to the corresponding parameters for the substitution of vanadium(II) by thiocyanate.

(22) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(23) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).



Some of the faster oxidation-reduction rates may be due to electrostatic effects, while steric effects may be important in some of the slower reactions.²³ The identification of the products of the oxidation-reduction reactions has shown that the reactions of vanadium(II) with CrSCN^{2+} , VO^{2+} , *cis*- $\text{Co}(\text{en})_2(\text{N}_3)_2^+$, and $\text{Co}(\text{NH}_3)_5(\text{C}_2\text{O}_4)^+$ proceed mainly by inner-sphere mechanisms.

The rate law for the reaction of vanadium(II) with CrSCN^{2+} contains a term which is first order in acid. This term is small, and very probably represents a medium effect. The absence of an inverse acid term in the rate law is not surprising, since the rate of reaction of CrSCN^{2+} with vanadium(II) appears to be primarily determined by the rate of substitution on the vanadium(II), and under these conditions $\text{Cr}(\text{OH})\text{SCN}^+$ would not react much more rapidly than CrSCN^{2+} with vanadium(II). Such a term is found, for example, in the rate law for the reaction of CrSCN^{2+} with chromium(II),⁹ and of CrNCS^{2+} with vanadium(II), reactions in which substitution on the reducing agents is not rate determining.

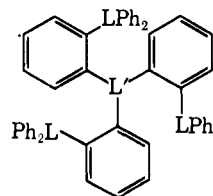
Phosphorus-31 Nuclear Magnetic Resonance Studies of Coordination Compounds. I. The Stereochemistry of Some Complexes with Multidentate Ligands

James W. Dawson and L. M. Venanzi¹

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford, England. Received July 2, 1968

Abstract: Phosphorus-31 nmr has been used to determine the structures of some diamagnetic complexes containing the potentially quadridentate ligands (*o*- $\text{Ph}_2\text{LC}_6\text{H}_4$)₃L' (L' = L = P, QP; L' = As, L = P, ASTP; L' = Sb, L = P, SBTP; L' = P, L = As, PTAS). The number, relative intensities, and chemical shifts of the resonances in the spectra of the five-coordinate complexes $[\text{MCl}(\text{ligand})]^+$ (M = Ni, Pd, or Pt, ligand = QP; M = Ni, ligand = ASTP, SBTP, or PTAS) and six-coordinate complexes $[\text{M}^{n+}\text{X}_2(\text{ligand})]^{(n-2)+}$ (M = Ru(II), X = Cl, ligand = QP, ASTP, or PTAS; M = Rh(III), X = Cl, ligand = QP; M = Fe(II), X = NCS, ligand = QP) confirm the structural assignments made on the basis of other physical measurements. The stereochemistry of the complex $[\text{IrHCl}(\text{QP})][\text{BPh}_4]$ has been determined. In the spectra of the complexes $[\text{M}(\text{CO})_3(\text{QP})]$ (M = Cr or W), peaks in the chemical shift region associated with the free ligand signals have been assigned to uncoordinated phosphorus atoms.

Recent studies^{2,3} have shown that phosphorus-31 nuclear magnetic resonance (³¹P nmr) can be used for structural assignment in coordination compounds. We have used this technique to study complexes of the potentially quadridentate ligands shown in the facing column. The complexing properties of these ligands have been extensively investigated⁴ and two main types of



L' = P, L = P, QP tris(*o*-diphenylphosphinophenyl)phosphine
 L' = As, L = P, ASTP tris(*o*-diphenylphosphinophenyl)arsine
 L' = Sb, L = P, SBTP tris(*o*-diphenylphosphinophenyl)stibine
 L' = P, L = As, PTAS tris(*o*-diphenylarsinophenyl)phosphine

complex are known: $[\text{M}^{n+}\text{X}(\text{ligand})]^{(n-1)+}$ with trigonal-bipyramidal structure (1) and $[\text{M}^{n+}\text{X}_2(\text{ligand})]^{(n-2)+}$ with octahedral structure (2).

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(2) S. O. Grim, D. A. Wheatland, and W. McFarlane, *J. Amer. Chem. Soc.*, **89**, 5573 (1967), and references therein.

(3) S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, **7**, 161 (1968).

(4) J. G. Hartley, D. G. E. Kerfoot, and L. M. Venanzi, *Inorg. Chim. Acta*, **1**, 145 (1967), and references therein.