The Kinetics of the Spontaneous and Mercury(II)-Catalyzed Aquation and Isomerization of the Sulfur-Bonded Monothiocyanate Complex of Chromium(III)[1]

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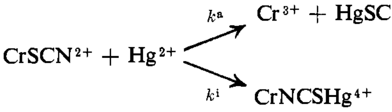
Abstract: The rate of the spontaneous aquation and isomerization of the sulfur-bonded monothiocyanate complex of chromium(III) is given by the rate law $-[d(\mathrm{CrSCN^{2+}})]/dt = \{(k_0^a + k_0^i) + (k_{-1}^a + k_{-1}^i)/(\mathrm{H^+})\}(\mathrm{CrSCN^{2+}})$. At 25.0° in perchloric acid–sodium perchlorate solutions of ionic strength 1.0 *M* the rate constants are $k_0^a = 1.7 \times 10^{-5}$ sec^{-1}, $k_0^i = 4.2 \times 10^{-5}$ sec^{-1}, $k_{-1}^a = 2.7 \times 10^{-6}$ *M* sec^{-1}, and $k_{-1}^i = 6.9 \times 10^{-6}$ *M* sec^{-1}. The rate of the mercury(II)-catalyzed aquation and isomerization of the sulfur-bonded monothiocyanate complex of chromium(III) is given by the rate law $-[d(\mathrm{CrSCN^{2+}})]/dt = \{(k_0^a + k_0^i) + (k_{-1}^a + k_{-1}^i)/(\mathrm{H^+})\}(\mathrm{CrSCN^{2+}})(\mathrm{Hg^{2+}})$. At 25.0° in perchloric acid–sodium perchlorate solutions of ionic strength 1.0 *M* the rate constants are $k_0^a = 3.1 \times 10^2$ M^{-1} sec^{-1}, $k_0^i = 2.3 \times 10^2$ M^{-1} sec^{-1}, $k_{-1}^a = 3.1 \times 10^2$ sec^{-1}, and $k_{-1}^i = 2.3 \times 10^2$ sec^{-1}. The activation parameters for the spontaneous and mercury(II)-catalyzed reactions were determined and their mechanisms are discussed.

The sulfur-bonded monothiocyanate complex of chromium(III) has been recently prepared by the reaction of chromium(II) with $\mathrm{FeNCS^{2+}}$ and with *trans*-$\mathrm{Co(en)_2OH_2(NCS)^{2+}}$.[3,4] The complex undergoes chromium(II)-catalyzed isomerization

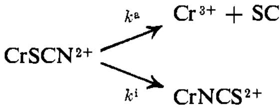
$$\mathrm{CrSCN^{2+} + Cr^{2+} \longrightarrow Cr^{2+} + CrNCS^{2+}}$$

mercury(II)-catalyzed isomerization and aquation[5]



$$\mathrm{CrSCN^{2+} + Hg^{2+}} \begin{cases} \xrightarrow{k^a} \mathrm{Cr^{3+} + HgSCN^+} \\ \xrightarrow{k^i} \mathrm{CrNCSHg^{4+}} \end{cases}$$

as well as spontaneous isomerization and aquation[3,4]



$$\mathrm{CrSCN^{2+}} \begin{cases} \xrightarrow{k^a} \mathrm{Cr^{3+} + SCN^-} \\ \xrightarrow{k^i} \mathrm{CrNCS^{2+}} \end{cases}$$

We have studied the kinetics and stoichiometry of the spontaneous and of the mercury(II)-catalyzed isomerization and aquation reactions as a function of temperature and acidity. In this paper we wish to report the results of these studies and to discuss the mechanisms of these reactions.

Experimental Section

Materials. The iron(III) perchlorate (G. F. Smith Chemical Co.) was purified by recrystallization from perchloric acid. A stock solution approximately 0.5 *M* in iron(III) and 2.5 *M* in perchloric acid was prepared from the recrystallized iron(III) perchlorate. The stock solution of sodium thiocyanate (Fisher Chemical Co.) was approximately 0.5 *M*. Stock solutions approximately 0.1 *M* in chromium(II) and 1 *M* in perchloric acid were prepared by the reduction of chromium(III) perchlorate (G. F. Smith Chemical Co.) solutions with amalgamated zinc. Sodium perchlorate solution was prepared by neutralizing sodium carbonate (Baker analyzed reagent) with perchloric acid (Baker analyzed reagent). A stock solution approximately 0.2 *M* in mercury(II) and 1 *M* in perchloric acid was prepared by dissolving mercury(II) oxide (Matheson Coleman and Bell) in perchloric acid. The concentration of mercury(II) was determined by titration with thiocyanate using iron(III) as the indicator. The perchloric acid concentration of the mercury(II) solution was determined by titration with sodium hydroxide in the presence of excess potassium iodide.

Solutions containing both $\mathrm{CrSCN^{2+}}$ and $\mathrm{CrNCS^{2+}}$ were prepared in the following manner. A solution approximately 0.1 *M* in chromium(II) and 1 *M* in perchloric acid was gradually added to a well-stirred mixture of 8 ml of 0.5 *M* sodium thiocyanate and 9 ml of 0.5 *M* iron(III) perchlorate until the mixture started to turn green. The iron(II) produced in this reaction was oxidized with sodium peroxydisulfate. $\mathrm{CrSCN^{2+}}$ and $\mathrm{CrNCS^{2+}}$ were absorbed on a Dowex 50W-X8 ion-exchange column, and the column was washed with 0.2 *M* perchloric acid. The chromium(III) thiocyanate complexes were then eluted with 1 *M* perchloric acid. The ion-exchange procedure was carried out with chilled solutions. The solutions containing $\mathrm{CrSCN^{2+}}$ and $\mathrm{CrNCS^{2+}}$ were stored at −10° and their composition was determined prior to use.

Analysis of Solutions of $\mathrm{CrSCN^{2+}}$ and $\mathrm{CrNCS^{2-}}$. Total chromium(III) was determined spectrophotometrically as chromate ion (ϵ 4.83 × 10^3 at 372 mμ) after oxidation with alkaline peroxide.[6] The thiocyanate produced during the storage of the stock solution at −10° was determined spectrophotometrically as $\mathrm{FeNCS^{2+}}$ after the addition of excess iron(III) (ϵ 3.6 × 10^3 at 460 mμ when $[\mathrm{Fe(III)}] = 3.12 \times 10^{-2}$ *M*, $[\mathrm{SCN^-}] \sim 10^{-5}$ *M*, and $[\mathrm{HClO_4}] = 1.0$ *M*).[4] Total thiocyanate was determined in the same manner after the bound thiocyanate was released by making the solution slightly alkaline.

Two methods were used to determine the amounts of $\mathrm{CrSCN^{2+}}$ and $\mathrm{CrNCS^{2+}}$ in the mixture. In the first method, vanadium(II) was added to the mixture. Conditions were chosen to ensure that the reaction of vanadium(II) with $\mathrm{CrSCN^{2+}}$ was complete while the reaction with $\mathrm{CrNCS^{2+}}$ was negligible.[7,8] Cationic species were then absorbed on a Dowex 50W-X8 ion-exchange column in the $\mathrm{H^+}$ form, and the thiocyanate formed in the reaction (in an amount equal to the concentration of $\mathrm{CrSCN^{2+}}$) was determined spectrophotometrically as $\mathrm{FeNCS^{2+}}$. In the second method advantage was taken of the difference in the rates at which the two linkage isomers react with mercury(II). The reaction of $\mathrm{CrNCS^{2+}}$ with mercury(II) to yield the $\mathrm{CrNCSHg^{4+}}$ complex is accompanied by a large change in absorbance at 292 mμ. This reaction is too rapid to be followed on the stopped-flow apparatus. On the other hand, the reaction of $\mathrm{CrSCN^{2+}}$ with mercury(II) is much slower.[5] Thus, $\mathrm{CrNCS^{2+}}$ concentrations in the mixtures could be determined from the change in absorbance measured at 292 mμ on the stopped-flow apparatus[9]

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[2] On leave of absence from Rudjer Boskovic Institute, Zagreb, Yugoslavia.

[3] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 4210 (1965).

[4] A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).

[5] M. Orhanović and N. Sutin, *ibid.*, **90**, 538 (1968).

[6] G. W. Haupt, *J. Res. Natl. Bur. Stand.*, **48**, 2331 (1952).

[7] B. R. Baker, M. Orhanović, and N. Sutin, *J. Amer. Chem. Soc.*, **89**, 722 (1967).

[8] M. Orhanović and N. Sutin, unpublished results.

under conditions which ensured complete reaction of mercury(II) with $CrNCS^{2+}$, while the reaction with $CrSCN^{2+}$ did not occur. A solution containing a 8.6×10^{-4} to 1.4×10^{-3} M mixture of the two linkage isomers was first mixed on the stopped-flow apparatus with a 1 M perchloric acid solution at 1°, and the absorbance of the mixture was measured on the oscilloscope. The solution containing the linkage isomers was then mixed with a solution containing 0.16 M mercury(II) perchlorate in 1 M perchloric acid and the absorbance of the mixture was measured on the oscilloscope before any reaction of mercury(II) with $CrSCN^{2+}$ occurred. The amount of $CrNCS^{2+}$ present in the original solution was then calculated using a calibration plot giving the change in absorbance at 292 mμ which occurred when known amounts of $CrNCS^{2+}$ were mixed with 0.16 M mercury(II) solution at 1°. The relative amounts of $CrSCN^{2+}$ and $CrNCS^{2+}$ in the mixture were about 75 and 25%, respectively. The extinction coefficient of $CrSCN^{2+}$ at 262 mμ was found to be $(8.0 \pm 0.3) \times 10^3$.

Kinetic Measurements and the Determination of Product Ratios. The spontaneous aquation and isomerization of $CrSCN^{2+}$ were followed on a Cary Model 14 recording spectrophotometer by measuring the absorbance at 262 mμ of aliquots of the thermostated reaction mixture. Some experiments were performed by determining the amount of thiocyanate released in the aquation reaction. The reaction was first order and the rate constants were calculated from the slopes of plots of $\log (D_t - D_\infty)$ *vs.* time, where D_t and D_∞ are the optical densities at time t and at 10 half-lives of the reaction, respectively. Ionic strength was kept constant in all the kinetic experiments by the addition of $NaClO_4$ and $HClO_4$. At the completion of reaction the concentration of $CrNCS^{2+}$ was calculated from the absorbance at 292 mμ in order to obtain the amount of isomerization.

The product ratio was also determined by preparing $CrSCN^{2+}$ with S^{35}-labeled thiocyanate and measuring the activity in the SCN^- and $CrNCS^{2+}$ formed in the reaction. Some kinetic experiments were carried out with nonlabeled $CrSCN^{2+}$ in the presence of labeled ammonium thiocyanate. After 10 half-lives of the reaction, thiocyanate was separated from $CrNCS^{2+}$ by a Dowex 50W-X8 ion-exchange column and the activities of the two fractions were measured on a Beckman liquid scintillation counter.

The kinetics of the mercury(II)-catalyzed aquation and isomerization of $CrSCN^{2+}$ were studied by the use of the stopped-flow technique.[9] Mercury(II) was present in sufficient excess to ensure pseudo-first-order conditions. The reaction was followed at 262 mμ where a decrease of absorbance due to the disappearance of $CrSCN^{2+}$ was observed, and also at 235 mμ where an increase in absorbance due to the formation of $HgSCN^+$ and $CrNCSHg^{4+}$ occurred. The rate constants calculated from the absorbance changes at the two wavelengths were identical within the experimental error of the measurements.

The yields of the products of the reaction between mercury(II) and $CrSCN^{2+}$ were determined in the following manner. Hydrochloric acid was added to an aliquot of the reaction mixture in order to decompose the $CrNCSHg^{4+}$ complex into $CrNCS^{2+}$. The concentration of $CrNCS^{2+}$ was then determined spectrophotometrically at 292 mμ.[10] Hexaaquochromium(III) was determined spectrophotometrically as chromate ion,[6] after separating the products on a Dowex 50W-X8 ion-exchange column.

Table I. First-Order Rate Constants for the Spontaneous Aquation and Isomerization of $CrSCN^{2+}$ at $\mu = 1.0$ M ($HClO_4 + NaClO_4$)

($HClO_4$), M	Temp, °C	k_{obsd}, $10^4 \times sec^{-1}$	($HClO_4$), M	Temp, °C	k_{obsd}, $10^4 \times sec^{-1}$
1.0	14.9	0.162	0.046	25.0	2.76
0.99	14.9	0.159	0.032	25.0	3.66[a]
1.0	15.0	0.162	0.020	25.0	5.50
0.61	15.0	0.175	0.020	25.0	5.47
0.31	15.0	0.208	0.018	25.0	6.28
0.12	15.0	0.306	0.0092	25.0	11.1
0.098	15.0	0.329	1.0	35.0	2.64
0.058	15.0	0.430	0.10	35.0	6.68
0.045	15.0	0.546	0.043	35.0	13.0
0.033	15.0	0.684	0.031	35.0	17.0
0.018	15.0	1.15	0.017	35.0	28.6
0.013	15.0	1.58	0.016	35.0	29.6
1.0	25.0	0.694	0.012	35.0	40.6
0.11	25.0	1.50			

[a] In the presence of 1.7×10^{-2} M NaCl.

Results

The Spontaneous Aquation and Isomerization of $CrSCN^{2+}$. The over-all rate constants observed for the spontaneous aquation and isomerization of $CrSCN^{2+}$ at different hydrogen ion concentrations and different temperatures are presented in Table I. The rate constants at a particular temperature increase with decreasing perchloric acid concentration. These observations are consistent with a rate law having both acid-independent and inverse-acid terms

$$-\frac{d(CrSCN^{2+})}{dt} = \{(k_0^a + k_0^i) + (k_{-1}^a + k_{-1}^i)/(H^+)\}(CrSCN^{2+})$$

where k_0^a and k_0^i are the rate constants for the aquation and isomerization of $CrSCN^{2+}$, k_{-1}^a/K_h and k_{-1}^i/K_h are the rate constants for the aquation and isomerization of $Cr(SCN)OH^+$, and K_h is the equilibrium constant for the reaction

$$CrSCN^{2+} + H_2O \rightleftharpoons Cr(SCN)OH^+ + H^+$$

Thus $k_{obsd} = (k_0^a + k_0^i) + (k_{-1}^a + k_{-1}^i)/(H^+)$.

Using a high-speed computer, the observed rate constants given in Table I were treated simultaneously for all temperatures according to the expression

$$k_{obsd} = \left(\frac{kT}{h}\right)\sum_i (H^+)^i e^{\Delta S_i^{\ddagger}/R} e^{-\Delta H_i^{\ddagger}/RT} \qquad (1)$$

with $i = 0$ and -1. A nonlinear least-squares program[11] was used to obtain the best values of the enthalpy and entropy of activation as well as the values of the rate constants at 25° for the two terms in the rate law. 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 calculated values of the rate constants agreed with the experimental values with an average deviation of 1.7%. The activation parameters calculated by the program are $\Delta H_0^{\ddagger} = 23.5 \pm 0.3$ kcal mole^{-1}, $\Delta S_0^{\ddagger} = 1.0 \pm 0.9$ cal mole^{-1} deg^{-1}, $\Delta H_{-1}^{\ddagger} = 27.8 \pm 0.2$ kcal mole^{-1}, and $\Delta S_{-1}^{\ddagger} = 11.7 \pm 0.5$ cal mole^{-1} deg^{-1}. At 25.0° $k_0 = (k_0^a + k_0^i) = (5.9 \pm 0.1) \times 10^{-5}$ sec^{-1} and $k_{-1} = (k_{-1}^a + k_{-1}^i) = (9.6 \pm 0.1) \times 10^{-6}$ M sec^{-1}.[12]

The ratios of SCN^- to $CrNCS^{2+}$ formed in the spontaneous aquation and isomerization of $CrSCN^{2+}$ are presented in Table II. The ratio does not depend on either the temperature or the hydrogen ion concentration, and it has an average value of 0.39 ± 0.03. In the experiment with S^{35}-labeled $CrSCN^{2+}$, where the amount of labeled SCN^- and $CrNCS^{2+}$ formed in the

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

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

(11) 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.

(12) The values of k_{-1} reported earlier are about 50% higher than those obtained in this work. The reason for this discrepancy is not known. However, the results of kinetic measurements recently performed by A. Haim at the State University of New York at Stony Brook are in very good agreement with the data presented in this paper.

reaction was determined, the product ratio is equal to 0.5 ± 0.1. The agreement between the two methods is satisfactory, considering the higher experimental error inherent in the labeling measurements. Individual rate constants and corresponding activation parameters are presented in Table IV.

Table II. The Ratio of SCN^- to $CrNCS^{2+}$ Formed in the Spontaneous Aquation and Isomerization of $CrSCN^{2+}$ at $\mu = 1.0\ M$

Temp, °C	$(HClO_4)$, M	$(SCN^-)/(CrNCS^{2+})$
15.0	1.0	0.40
15.0	0.02	0.40
25.0	1.0	0.36
25.0	0.02	0.41
35.0	1.0	0.34
35.0	0.02	0.40

The kinetic measurements performed in the presence of 0.01 and 0.1 M labeled thiocyanate showed that 0.2 and 1.1%, respectively, of the $CrNCS^{2+}$ produced in the isomerization reaction had incorporated thiocyanate from the solution.

The Mercury(II)-Catalyzed Aquation and Isomerization of $CrSCN^{2+}$. The rate of this reaction is first order with respect to both of the reactants. The second-order rate constants obtained are presented in Table III.

Table III. Second-Order Rate Constants for the Mercury(II)-Catalyzed Aquation and Isomerization of $CrSCN^{2+}$ at $\mu = 1.0\ M$

$(CrSCN^{2+})$, $10^4 M$	(Hg^{2+}), $10^3 M$	$(HClO_4)$, M	Temp, °C	k, $10^{-3} \times$ $(M^{-1}\ sec^{-1})$
1.5	2.0	1.0	25.0	1.3
2.2	5.0	1.0	25.0	1.1
3.8	16	1.0	25.0	1.1
5.4	50	1.0	25.0	1.1
3.8	100	1.0	25.0	1.0
0.30	6.0	0.40	25.0	1.8
0.30	6.0	0.20	25.0	3.3
0.30	6.0	0.10	25.0	5.9
0.30	3.0	0.077	25.0	7.6
0.30	3.0	0.062	25.0	9.5
0.30	3.0	0.053	25.0	10.8
1.0	3.0	1.0	15.4	0.54
1.0	3.0	0.20	15.4	1.5
1.0	3.0	0.10	15.4	2.7
1.0	3.0	0.064	15.4	4.0
1.0	3.0	0.050	15.4	5.0
1.0	6.0	1.0	6.1	0.23
1.0	6.0	0.20	6.1	0.54
1.0	6.0	0.10	6.1	1.2
1.0	6.0	0.065	6.1	1.8
1.0	6.0	0.050	6.1	2.1

The rate constants increase as the concentration of hydrogen ion decreases. The observation is consistent with the rate law

$$-d(CrSCN^{2+})/dt = \{(k_0{}^a + k_0{}^i) + (k_{-1}{}^a + k_{-1}{}^i)/(H^+)\}(CrSCN^{2+})(Hg^{2+})$$

where $k_0{}^a$ and $k_0{}^i$ are the rate constants for the aquation and isomerization proceeding by the acid-independent reaction path, while $k_{-1}{}^a$ and $k_{-1}{}^i$ are the rate constants for the aquation and isomerization proceeding by the inverse-acid reaction path. Using eq 1 (with $k_{obsd} = k$) the results reported in Table III were treated simultaneously for all temperatures in the same way as the results reported in Table I. The calculated values for the rate constants agreed with the experimental values with an average deviation of 4.0%. The activation parameters calculated by the program are $\Delta H_0{}^{\ddagger} = 11.9 \pm 1.3$ kcal mole^{-1}, $\Delta S_0{}^{\ddagger} = -6.1 \pm 4.4$ cal mole^{-1} deg^{-1}, $\Delta H_{-1}{}^{\ddagger} = 14.5 \pm 0.5$ kcal mole^{-1}, $\Delta S_{-1}{}^{\ddagger} = 2.5 \pm 1.8$ cal mole^{-1} deg^{-1}. At 25.0° $(k_0{}^a + k_0{}^i) = (5.4 \pm 0.4) \times 10^2\ M^{-1}\ sec^{-1}$ and $(k_{-1}{}^a + k_{-1}{}^i) = (5.4 \pm 0.2) \times 10^2\ sec^{-1}$.

The ratio of Cr^{3+} to $CrNCS^{2+}$ formed in the mercury(II)-catalyzed aquation and isomerization of $CrSCN^{2+}$ was found to be independent both of the hydrogen ion concentration and the temperature and it is equal to 1.32 ± 0.12. Individual rate constants and corresponding activation parameters are presented in Table IV.

Table IV. The Rate Constants and the Activation Enthalpies[a] for the Spontaneous and Mercury(II)-Catalyzed Aquation and Isomerization of $CrSCN^{+2}$ at 1.0 M Ionic Strength

Rate constant	Value, 25°	$\Delta H^{\ddagger}$, kcal mole^{-1}
	Spontaneous Reaction	
$k_0{}^a$	$1.7 \times 10^{-5}\ sec^{-1}$	23.5
$k_0{}^i$	$4.2 \times 10^{-5}\ sec^{-1}$	23.5
$k_{-1}{}^a$	$2.7 \times 10^{-6}\ M\ sec^{-1}$	27.8
$k_{-1}{}^i$	$6.9 \times 10^{-6}\ M\ sec^{-1}$	27.8
	Mercury(II)-Catalyzed Reaction	
$k_0{}^a$	$3.1 \times 10^2\ M^{-1}\ sec^{-1}$	11.9
$k_0{}^i$	$2.3 \times 10^2\ M^{-1}\ sec^{-1}$	11.9
$k_{-1}{}^a$	$3.1 \times 10^2\ sec^{-1}$	14.5
$k_{-1}{}^i$	$2.3 \times 10^2\ sec^{-1}$	14.5

[a] The values calculated for the entropies of activation depend upon the mechanism assumed for the reaction. If reaction 2 is rate determining, then the aquation and isomerization reactions proceed *via* the same activated complex. Under these conditions the entropies of activation for the aquation and isomerization reactions are identical and are equal to the values presented in the text for $(k_a + k_i)$. On the other hand, if reaction 2 is at equilibrium and reaction 3 is rate determining (or if the aquation and isomerization reactions proceed independently), then $\Delta S^{\ddagger} = -1.6$, 0.3, 9.1, and 11.0 cal mole^{-1} deg^{-1} for the $k_0{}^a$, $k_0{}^i$, $k_{-1}{}^a$, and $k_{-1}{}^i$ paths, respectively. These values of $\Delta S^{\ddagger}$ are composite values and are equal to the sum of $\Delta S°$ for reaction 2 and the entropy of activation for the appropriate path in reaction 3. In addition, in this case the equality of the enthalpies of activation for the aquation and isomerization reactions would be fortuitous.

Discussion

The Spontaneous Aquation and Isomerization of $CrSCN^{2+}$. Some information concerning the mechanism of aquation of $CrSCN^{2+}$ can be obtained from a comparison of the entropy of activation for this reaction with the entropies of aquation for other CrX^{2+} reactions. The entropies of activation for the acid-independent aquation of CrX^{2+} complexes, where X = Cl, NO_3, Br, NCS, and I, show a linear correlation with the partial molal entropies of the anions once the latter have been corrected for the loss of rotational freedom upon complex formation.[13,14] The slope of

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(13) T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).
(14) T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 4338 (1967).

the line is 0.53 indicating that solvation of the anions is about half complete in the transition state. The entropy of activation for the acid-independent aquation of $CrSCN^{2+}$ (+1.0 or −1.6 cal mole^{-1} deg^{-1} depending upon the mechanism assumed) is not too different from the value for the acid-independent aquation of $CrNCS^{2+}$ (−3.5 cal mole^{-1} deg^{-1})[15] suggesting that similar solvation obtains in the transition states for the aquation reactions of the two complexes. Accordingly, it appears that the aquation of $CrSCN^{2+}$ proceeds by a transition state in which the 3+ charge of chromium(III) ions and the 1− charge of the ligand are being separated, as has been suggested for the CrX^{2+} complexes with X = Cl, NO_3, Br, NCS, and I.[16]

Two mechanisms were previously considered[4] for the spontaneous isomerization of $CrSCN^{2+}$. The first mechanism involves bending of the thiocyanate group to form a seven-coordinated transition state. The second mechanism involves formation of an intimate ion pair $Cr(H_2O)_5{}^{3+}\cdot SCN^-$ which undergoes dissociation into $Cr(H_2O)_5{}^{3+}$ and SCN^- relatively slowly compared to the rate of internal return, and in which the thiocyanate group is not bent to a significant extent. The second mechanism was favored because of the large amount of energy required to bend the linear thiocyanate group. The second mechanism finds further support in the present studies. The observation that only a very small amount of labeled $CrNCS^{2+}$ is produced when the aquation–isomerization is carried out in the presence of labeled thiocyanate supports the assumption that dissociation of the ion pair is relatively slow. A similar conclusion has been previously reached[4] on the basis of the formation of only very low yields of $CrCl^{2+}$ when the aquation–isomerization is carried out in the presence of 0.8 *M* Cl^-. Moreover, the similarity of the rate laws and activation enthalpies for the aquation and isomerization reactions suggests that the transition states for the two reactions are identical, or, at least, that they have very similar structures. Since there is no reason to believe that the aquation of $CrSCN^{2+}$ involves bending of the thiocyanate group, it is likely that bending of thiocyanate does not occur to a significant extent in the isomerization reaction either.

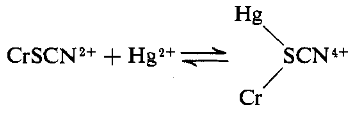
The simplest reaction scheme embodying the above features involves the formation of a common intermediate in the aquation and isomerization reactions.

$$(H_2O)_5CrSCN^{2+} \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} Cr(H_2O)_5{}^{3+}\cdot SCN^- \qquad (2)$$

$$Cr(H_2O)_5{}^{3+}\cdot SCN^- \begin{array}{l} \xrightarrow[H_2O]{k_w} Cr(H_2O)_6{}^{3+} + SCN^- \\ \xrightarrow{k_x} (H_2O)_5CrNCS^{2+} \end{array} \qquad (3)$$

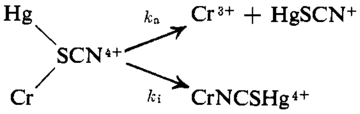
The values of k_x and k_w are of the same order of magnitude since comparable amounts of Cr^{3+} and $CrNCS^{2+}$ are formed in the aquation–isomerization. The relative magnitudes of k_x and k_{-d} are less certain. It might be argued that k_x should be larger than k_{-d} since internal return of the ion pair to form the more stable isomer should occur more readily than internal return to form the less stable isomer. This argument assumes that rotation of the thiocyanate can readily occur in the ion pair. However, the formulation of the intermediate as $Cr(H_2O)_5{}^{3+}\cdot SCN^-$ should not be taken too literally for bond formation between $Cr(H_2O)_5{}^{3+}$ and the π system of thiocyanate may be important in stabilizing the intermediate. Finally, it has also been proposed that the isomerization of $(Et_4dien)PdSCN^+$ proceeds by an intermolecular process rather than one involving bending of the thiocyanate group.[18]

The Mercury(II)-Catalyzed Aquation and Isomerization of $CrSCN^{2+}$. The relatively slow rate of the reaction between mercury(II) and $CrSCN^{2+}$ indicates that the rate-determining step is not substitution on mercury(II). We propose therefore that this reaction proceeds by a rapid preequilibrium step which involves the formation of a sulfur-bonded binuclear complex



$$CrSCN^{2+} + Hg^{2+} \rightleftharpoons \begin{array}{l} Hg \\ \quad\diagdown \\ \quad\; SCN^{4+} \\ \quad\diagup \\ Cr \end{array} \qquad (4)$$

followed by the decomposition of this complex *via* two parallel paths



$$\begin{array}{l} Hg \\ \quad\diagdown \\ \quad\; SCN^{4+} \\ \quad\diagup \\ Cr \end{array} \begin{array}{l} \xrightarrow{k_a} Cr^{3+} + HgSCN^+ \\ \xrightarrow{k_i} CrNCSHg^{4+} \end{array}$$

The value of the equilibrium constant for the preequilibrium step is not large enough to cause departure from the second-order kinetics under the experimental conditions used ($K < 1\ M^{-1}$ at 25° and $\mu = 1\ M$). A mechanism involving attack of the mercury(II) at the nitrogen atom of $CrSCN^{2+}$ is also consistent with the kinetic data.

The ratio of aquation to isomerization in the mercury(II)-catalyzed path may be compared with the corresponding ratio for the spontaneous reaction. Not surprisingly, the addition of mercury(II) to $CrSCN^{2+}$ favors the aquation path although a significant amount of isomerization still occurs.

The Spectrum and Primary Yield of $CrSCN^{2+}$. The existence of the mercury(II)-catalyzed isomerization was not recognized in the earlier study of the linkage isomers.[4] Consequently, it is necessary to revise some of the conclusions reached in the earlier work.

Two methods were previously employed for the analysis of solutions containing both $CrSCN^{2+}$ and $CrNCS^{2+}$. In the first method, chlorine was bubbled through the solution and it was found that Cr^{3+} and $CrCl^{2+}$ were produced. Since control experiments showed that the oxidation of $CrNCS^{2+}$ by chlorine produced Cr^{3+}, it was assumed that the $CrCl^{2+}$ resulted from the oxidation of $CrSCN^{2+}$. In the second

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

(16) Notable exceptions here are the aquations of CrF^{2+} and $CrN_3{}^{2+}$. In these cases it was found that the entropies of activation are much too positive, and also that there is a hydrogen ion catalyzed reaction path, which was not observed in the aquation of the above CrX^{2+} complexes. It was suggested therefore[13,17] that the acid-independent aquation of CrF^{2+} and $CrN_3{}^{2+}$ proceeds by a transition state in which 2+ charge of hydroxochromium(II) and neutral acid are being separated.

(17) F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964).

(18) F. Basolo, W. H. Baddley, and K. J. Weidenbaum, *J. Amer. Chem. Soc.*, **88**, 1576 (1966).

method, mercury(II) was added to the solution containing both $CrSCN^{2+}$ and $CrNCS^{2+}$, and it was found that $CrNCSHg^{4+}$ and Cr^{3+} were produced. Since the reaction of $CrNCS^{2+}$ with Hg^{2+} produces $CrNCSHg^{4+}$, it was assumed that Cr^{3+} resulted from the reaction of $CrSCN^{2+}$ with Hg^{2+}. However, we now know that Cr^{3+} is not the sole chromium-containing product of the reaction of Hg^{2+} with $CrSCN^{2+}$; instead $CrNCSHg^{4+}$ is also produced in this reaction. Consequently, the amount of $CrSCN^{2+}$ calculated from the amount of $CrNCSHg^{4+}$ produced upon the addition of mercury(II) to the reaction mixture will be too low if allowance is not made for the amount of the binuclear complex formed from the reaction of mercury(II) with $CrSCN^{2+}$. Similarly, the amount of $CrSCN^{2+}$ in the reaction mixture calculated from the amount of $CrCl^{2+}$ produced upon the addition of chlorine will be too low if, as now seems to be the case, the reaction of $CrSCN^{2+}$ with Cl_2 produced Cr^{3+} in addition to $CrCl^{2+}$. Accordingly, the extinction coefficients of $CrSCN^{2+}$ determined in this work are 72% of those previously reported[4] (the new values are ϵ 8.0 × 10^3 at 262 mμ, 20 at 435 mμ, and 26 at 620 mμ).

The evidence for adjacent attack of chromium(II) on the oxidizing agents, *trans*-$Co(en)_2OH_2(NCS)^{2+}$ and $FeNCS^{2+}$, was the observation that the yields of $CrSCN^{2+}$ were relatively low and could not readily be accounted for by other mechanisms.[4] It appears now that the yields of $CrSCN^{2+}$ in the above oxidation–reduction reactions are ~100 and ~75%, respectively. Consequently, these studies do not provide evidence for adjacent attack by chromium(II) on thiocyanate. The yields of ~25% of $CrNCS^{2+}$ in the oxidation of chromium(II) by $FeNCS^{2+}$ could result from the oxidation of $CrNCS^+$ since the oxidation is carried out in the presence of relatively high concentrations of free thiocyanate. The latter is absent during the oxidation of *trans*-$Co(en)_2OH_2(NCS)^{2+}$, and 100% of $CrSCN^{2+}$ is observed with this oxidizing agent.

Although not pertinent to the main theme of this paper, it is of interest to note that the oxidation of chromium(II) by $FeNCS^{2+}$ and by FeN_3^{2+} proceeds at rates which are not significantly different. The rate constants for the oxidation of chromium(II) by $FeNCS^{2+}$ and FeN_3^{2+} are $(2.8 \pm 0.7) \times 10^7$ and $(2.9 \pm 0.7) \times 10^7$ M^{-1} sec^{-1}, respectively, at 25.0° and 1.0 M ionic strength.[19,20] The similarity in the rates of oxidation is surprising in view of the large difference in rates usually observed in inner-sphere reactions involving azide and thiocyanate as bridging groups.[21,22] The absence of any discrimination between azide and thiocyanate (and also chloride[19,20]) suggests that a similar rate-determining step obtains in these oxidations. This step may be substitution on chromium(II) or some other reorganization process.[23]

Acknowledgment. We wish to thank Dr. Albert Haim for helpful discussions.

(19) R. C. Barile and N. Sutin, unpublished results.

(20) The rate constant for the oxidation of chromium(II) by $FeCl^{2+}$ is $(1.0 \pm 0.2) \times 10^7$ M^{-1} sec^{-1} at 25.0° and 1.0 M ionic strength.

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

(22) J. H. Espenson, *Inorg. Chem.*, **4**, 766 (1965).

(23) The value of the rate constant for the formation of the dinuclear intermediate $[(H_2O)_5FeXCr(H_2O)_5]^{4+}$ may be estimated from the rate constant for water exchange of $Cr(H_2O)_6^{2+}$. The lower limit of the latter rate constant is 7.4×10^9 sec^{-1} (G. W. Merideth and R. E. Connick, Paper 106, Division of Inorganic Chemistry, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965). Consequently the second-order rate constant for water exchange of $Cr(H_2O)_6^{2+}$ is $\geq 8 \times 10^8$ M^{-1} sec^{-1}, where any one of the six coordinated water molecules may be replaced. (Although these six water molecules are not equivalent, they become equivalent through the very rapid inversion of the distorted octahedron.) Because of the electrostatic repulsion between FeX^{2+} and Cr^{2+} as well as the less favorable steric factor, the rate constant for the formation of the dinuclear intermediate is expected to be smaller than the second-order rate constant for water exchange of $Cr(H_2O)_6^{2+}$. The possibility that substitution on chromium(II) is rate-determining in certain isotopic fractionation experiments is discussed in a paper by M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).