

fragments; however, the molecule ion was not observed. The ion corresponding to $m/e = 84$ exhibiting a high relative intensity may be a protonated phosphonitrilic fluoride monomer, $\text{PF}_2=\text{NH}^+$. It is further observed from this table that ions containing the NH_2 group are more stable than those with one hydrogen less. The exception is that presumed to be the phosphonitrilic derivative which shows a considerably higher relative abundance than PF_2NH_2^+ .

Acknowledgment.—The authors are grateful to Mr. Joseph West at Rohm & Haas Co., Redstone Research Laboratories, Huntsville, Ala., for the nmr spectra and to Dr. Domenick Bertelli for the computed spectra. A part of this work was funded by the Memphis State University Research Foundation.

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The Kinetics and Mechanism of the Oxidation of Iron(II) by Thiocyanatopentaamminecobalt(III) Ions. Comparisons with Related Systems¹

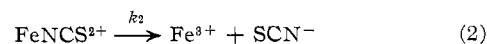
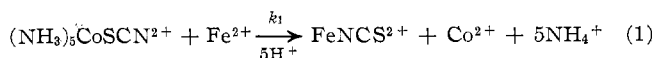
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Comparisons of the effect of azide and thiocyanate on the rates of electron-transfer reactions involving metal ions and their complexes have been widely used as a basis for determining whether a particular reaction proceeds by an inner- or an outer-sphere mechanism.²⁻⁴ If the metal centers of the oxidizing and reducing agents are hard and if transfer of the bridging group occurs during the reaction, then an inner-sphere reaction should proceed faster when the bridging group is azide than when it is isothiocyanate. This is principally due to the increased stability of a metal-nitrogen bond over a metal-sulfur bond.⁴ Similar free energy considerations show that an inner-sphere reaction should proceed faster when the bridging group is thiocyanate than when it is either azide or isothiocyanate. This study is concerned with the kinetics and mechanism of the reaction of $(\text{NH}_3)_5\text{CoSCN}^{2+}$ with Fe^{2+} at 25.0° and 1.0 *M* ionic strength and comparisons of this reaction with other systems. Because of the favorable free energy change, it was expected that the rate of oxidation of iron(II) by $(\text{NH}_3)_5\text{CoSCN}^{2+}$ would be relatively rapid. This could allow identification of the primary iron(III) reaction product and thus establish the mechanism of the reaction. Because the rates of dissociation of FeX^{2+} complexes are rapid, an inner-sphere mechanism for reductions by iron(II)

has only been unambiguously established in very few instances.⁵

Perchloric acid solutions containing $(\text{NH}_3)_5\text{CoSCN}^{2+}$ were prepared according to the procedure of Buckingham, Creaser, and Sargeson.⁶ The concentrations of the cobalt(III) complex were determined spectrophotometrically using the known extinction coefficients.⁶ The kinetics of the reduction of the $(\text{NH}_3)_5\text{CoSCN}^{2+}$ by iron(II) were studied under pseudo-first-order conditions with the iron(II) present in large excess. It was found that the reaction proceeds in two stages



The first stage corresponds to the reduction of the cobalt(III) complex and was studied at relatively low iron(II) concentrations on a Cary 16K spectrophotometer. Two types of measurements were performed. In the first type the disappearance of $(\text{NH}_3)_5\text{CoSCN}^{2+}$ was followed at 288 nm, an absorbance maximum of the cobalt(III) complex ($\epsilon 1.56 \times 10^4$ at 288 nm).⁶ Excess iron(III) was added in the second type of measurement and the formation of FeNCS^{2+} was followed at 460 nm, an absorbance maximum of the iron(III) complex ($\epsilon 4.60 \times 10^3$ at 460 nm).⁷ The solution concentrations and observed rate constants are summarized in Table I. The value of k_1 obtained from these measurements is $0.12 \pm 0.01 \text{ M}^{-1} \text{ sec}^{-1}$ at 25.0° and 1.0 *M* perchloric acid.⁸ It is also apparent from the data presented in Table I that the value of k_1 decreases with decreasing acidity. A similar dependence of the rate on the perchloric acid concentration has previously been found for the reaction of CrSCN^{2+} with vanadium(II) and was ascribed there to a medium effect.⁹ This medium effect could arise from the use of sodium perchlorate instead of lithium perchlorate to maintain the ionic strength.

The second stage of the reaction was studied at high iron(II) concentrations on the stopped-flow apparatus previously described.¹⁰ In these experiments the formation of FeNCS^{2+} and its subsequent decay were followed at 440 nm, the wavelength of the maximum ratio of the absorbance of FeNCS^{2+} to that of $(\text{NH}_3)_5\text{CoSCN}^{2+}$. At $\lambda 440 \text{ nm}$, $[\text{Fe(II)}] = 0.478 \text{ M}$, and $[\text{HClO}_4] = 1.55 \text{ M}$, a maximum in the absorbance *vs.* time curve was observed at $t = 0.6 \pm 0.1 \text{ sec}$.¹¹ Ac-

(5) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 5343 (1966).

(6) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(7) The iron(III) concentration used in these measurements ($3.53 \times 10^{-2} \text{ M}$) was sufficiently large so that $[\text{Fe}^{3+}]$ remained essentially constant during a run, and the equilibrium between Fe^{3+} , SCN^- , and FeNCS^{2+} was maintained throughout the course of the reaction.

(8) The data in Table I indicate that there may be a slight dependence of the rate constants on the iron(III) concentration. Such a dependence could occur if the aquation of $(\text{NH}_3)_5\text{CoSCN}^{2+}$ was catalyzed by iron(III). The $(\text{NH}_3)_5\text{CoH}_2\text{O}^{3+}$ produced in the catalyzed aquation would not react with iron(II) to any significant extent during the course of the $\text{Fe(II)}-(\text{NH}_3)_5\text{CoSCN}^{2+}$ reaction.

(9) M. Orhanovic, H. N. Po, and N. Sutin, *J. Am. Chem. Soc.*, **90**, 7224 (1968).

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

(11) The position of the maximum in the absorbance-time curve is very sensitive to traces of iron(III) in the iron(II).

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

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

(3) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

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

TABLE I
SECOND-ORDER RATE CONSTANTS^a FOR THE REACTION BETWEEN
THIOCYANATOPENTAAMMINECOBALT(III) AND IRON(II)
AT 25.0° AND 1.0 M IONIC STRENGTH

10 ³ [Fe(II)], M	10 ³ [Co(III)], M	λ, nm	10k ₁ , M ⁻¹ sec ⁻¹
0.114	7.01	288	1.12
0.226	6.93	288	1.19
0.334	6.84	288	1.17
0.440	6.76	288	1.21
0.841	4.59	288	1.18
1.03	4.49	288	1.23
1.03	4.21 ^b	288	1.12
1.03	4.21 ^b	288	1.11
1.21	4.39	288	1.33
1.85	4.04	288	1.25
0.330	4.51	460 ^c	1.36
0.330	9.01	460 ^c	1.25
0.991	4.51	460 ^c	1.33
0.991	9.01	460 ^c	1.33
47.8	125.0	330 ^d	1.11
1.03	5.65	288 ^e	1.03
1.03	5.65	288 ^f	1.03
1.03	5.65	288 ^g	1.04
1.03	5.65	288 ^h	1.09

^a Results obtained from Cary 16K spectrophotometer unless otherwise indicated. ^b Cobalt(III) solution prepared from the solid sample provided by Dr. A. M. Sargeson. ^c In the presence of 0.0353 M iron(III). ^d Reaction studied on the stopped-flow apparatus; ionic strength 3.0 M, [HClO₄] = 1.55 M. ^e [HClO₄] = 0.044 M. ^f [HClO₄] = 0.0889 M. ^g [HClO₄] = 0.1975 M. ^h [HClO₄] = 0.4444 M.

According to the proposed mechanism the maximum in this curve is given by

$$t_{\max} = \frac{1}{k_2 - k_1(\text{Fe}^{2+})} \ln \frac{\epsilon_2 k_2}{\epsilon_1 [k_2 - k_1(\text{Fe}^{2+})] + \epsilon_2 k_1(\text{Fe}^{2+})} \quad (3)$$

where ϵ_2 and ϵ_1 are the molar absorptivities of FeNCS²⁺ (ϵ 4.32 × 10³ at 440 nm) and of (NH₃)₅CoSCN²⁺ (ϵ 38 at 440 nm), respectively. From previous work¹² the value of k_2 is calculated to be 5.72 sec⁻¹ under the above conditions. The value of t_{\max} calculated from eq 3 is 0.70 sec, in satisfactory agreement with the observed value, thus confirming the formation of the intermediate FeNCS²⁺ and demonstrating that the reaction of (NH₃)₅CoSCN²⁺ with iron(II) is inner sphere. Less extensive measurements on the reaction between (NH₃)₅CoSCN²⁺ and vanadium(II) indicate that this reaction, too, proceeds by an inner-sphere mechanism with $k_1 = 30 \pm 5$ M⁻¹ sec⁻¹ in 1.0 M perchloric acid at 25°.

The effect of X on (NH₃)₅CoX²⁺ + Fe²⁺ and CrX²⁺ + Cr²⁺ reactions, where X = thiocyanate, azide, or isothiocyanate, is compared in Table II. In each case it is evident that the rate constants are in the order: thiocyanate > azide > isothiocyanate. This reactivity pattern is expected on the basis of free energy considerations.

In the simplest model the rate constants for a series of related reactions are directly proportional to the square roots of their equilibrium constants.^{13,14} This

(12) T. J. Conocchioni and N. Sutin, *J. Am. Chem. Soc.*, **89**, 282 (1967).

(13) R. A. Marcus, *J. Phys. Chem.*, **67**, 853 (1963).

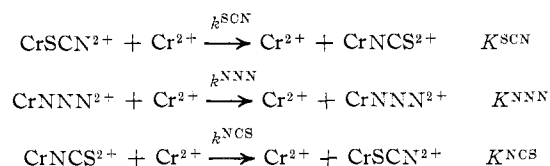
(14) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966).

TABLE II
COMPARISON OF RATE CONSTANTS FOR THE REDUCTION OF
NITROGEN- AND SULFUR-BONDED Cr(III) AND Co(III)
COMPLEXES BY Cr(II), V(II), AND Fe(II) AT 25.0°

Reaction	k ₁ , M ⁻¹ sec ⁻¹	Ref
(NH ₃) ₅ CoSCN ²⁺ + Fe ²⁺	1.2 × 10 ⁻¹	a
(NH ₃) ₅ CoN ₃ ²⁺ + Fe ²⁺	8.8 × 10 ⁻³	b
(NH ₃) ₅ CoNCS ²⁺ + Fe ²⁺	<3 × 10 ⁻⁶	c
CrSCN ²⁺ + Cr ²⁺	40	d
CrN ₃ ²⁺ + Cr ²⁺	6.1	e
CrNCS ²⁺ + Cr ²⁺	1.4 × 10 ⁻⁴	f
CrSCN ²⁺ + V ²⁺	8.0	g
CrNCS ²⁺ + V ²⁺	4.4 × 10 ⁻⁵	g
(NH ₃) ₅ CoSCN ²⁺ + V ²⁺	30	a
(NH ₃) ₅ CoN ₃ ²⁺ + V ²⁺	13	h
(NH ₃) ₅ CoNCS ²⁺ + V ²⁺	0.3	h

^a This work. ^b A. Haim, *J. Am. Chem. Soc.*, **85**, 1016 (1963). ^c Reference 3. ^d Reference 14. ^e R. Snellgrove and E. L. King, *Inorg. Chem.*, **3**, 288 (1964). ^f Reference 2. ^g Reference 9. ^h J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

relationship leads to a particularly simple expression when applied to the CrX²⁺ + Cr²⁺ reactions



According to the simple model

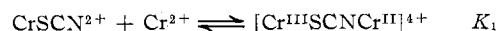
$$\begin{aligned} k^{\text{SCN}} &= k_0(K^{\text{SCN}})^{1/2} \\ k^{\text{NNN}} &= k_0(K^{\text{NNN}})^{1/2} \\ k^{\text{NCS}} &= k_0(K^{\text{NCS}})^{1/2} \end{aligned}$$

where k_0 , the intrinsic exchange rate constant, is assumed to be the same for all three reactions, and the equilibrium constants refer to the overall reactions. Since $K^{\text{NNN}} = 1$ and $K^{\text{SCN}} = 1/K^{\text{NCS}}$, it follows that

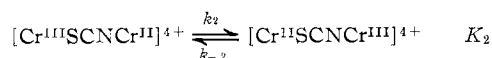
$$k^{\text{NNN}} = (k^{\text{SCN}} k^{\text{NCS}})^{1/2}$$

In other words, the simple model predicts that the rate constant for the azide-mediated reaction should be equal to the geometric mean of the rate constants for the other two reactions. The data in Table II show that this is not the case and that the azide-mediated reaction proceeds more rapidly than predicted by this model.

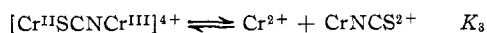
The simple model neglects any differences in the stabilities of the precursor complexes. In a more detailed treatment it is necessary to allow for the fact that the overall reaction proceeds in a number of steps and that $k_{\text{obsd}} = K_1 k_2$, where K_1 is the stability constant for the formation of the precursor complex and k_2 is the rate constant for the subsequent electron transfer. These steps may be represented as follows: (a) formation of the precursor complex



(b) the electron transfer



(c) dissociation of the successor complex



It can readily be shown that

$$\begin{aligned} (k^{\text{SCN}}k^{\text{NCS}})^{1/2} &= (K_1^{\text{SCN}}K_1^{\text{NCS}})^{1/2}(k_2^{\text{SCN}}k_2^{\text{NCS}})^{1/2} \\ &= (K_1^{\text{SCN}}K_1^{\text{NCS}})^{1/2}[k_2^{\text{CNS}}(K_2^{\text{SCN}})^{1/2}k_2^{\text{CNS}}(K_2^{\text{NCS}})^{1/2}]^{1/2} \\ &= (K_1^{\text{SCN}}K_1^{\text{NCS}})^{1/2}k_2^{\text{CNS}} \end{aligned}$$

where k_2^{CNS} is the hypothetical rate constant for electron transfer with zero free energy change in a thiocyanate-bridged intermediate. It seems reasonable to assume that this rate constant is equal to the rate constant for electron transfer within the symmetrical azide-bridged intermediate, *i.e.*, that $k_2^{\text{CNS}} = k_2^{\text{NNN}}$.¹⁵ Because $k^{\text{NNN}} = K_1^{\text{NNN}}k_2^{\text{NNN}}$, it follows that

$$\frac{k^{\text{NNN}}}{(k^{\text{SCN}}k^{\text{NCS}})^{1/2}} = \frac{K_1^{\text{NNN}}}{(K_1^{\text{SCN}}K_1^{\text{NCS}})^{1/2}}$$

Since K_1^{NNN} and K_1^{SCN} both involve formation of a N-Cr^{II} bond, it seems likely that they will be quite similar. Hence k^{NNN} will be equal to $(k^{\text{SCN}}k^{\text{NCS}})^{1/2}$ only if $K_1^{\text{SCN}} = K_1^{\text{NCS}}$. The experimental data indicate that $K_1^{\text{SCN}}/K_1^{\text{NCS}} \approx 7 \times 10^3$. This value seems reasonable and indicates that chromium(II) is behaving as a hard metal center toward azide and isothiocyanate.¹⁶ Inspection of Table II suggests that iron(II), too, is acting as a hard metal center in the $(\text{NH}_3)_5\text{CoX}^{2+} + \text{Fe}^{2+}$ reactions.

In the four systems presented in Table II the ratio of $k^{\text{SCN}}/k^{\text{NCS}}$ is of the order of 10^4 – 10^5 in all but the series of reactions of vanadium(II) with $(\text{NH}_3)_5\text{CoX}^{2+}$ where it is 10^2 . This comparison supports the view that the reaction of vanadium(II) with $(\text{NH}_3)_5\text{CoSCN}^{2+}$ (and probably also the reaction of vanadium(II) with CrSCN^{2+}) is limited by the rate of water replacement on vanadium(II)^{4,17,18} in contrast to the other systems where the rate-determining step is that of electron transfer. The similarity in the rate constants for the oxidation of vanadium(II) by CrSCN^{2+} and by $(\text{NH}_3)_5\text{CoSCN}^{2+}$ is particularly striking in view of the large difference in the driving force for the two reactions. This similarity provides further evidence for the interpretation that the rates of these reactions are primarily controlled by the rate of loss of a water molecule coordinated to the vanadium(II).^{4,17}

Acknowledgment.—The authors are grateful to Dr. A. M. Sargeson for the gift of a sample of $[(\text{NH}_3)_5\text{CoSCN}]\text{Cl}_2 \cdot 1.5\text{H}_2\text{O}$. They have also benefited from helpful discussions with Dr. A. Haim.

(15) The assumption that $k_2^{\text{CNS}} = k_2^{\text{NNN}}$ is supported by the observation that $k^{\text{NCS}}/k^{\text{NNN}}$ is about unity for outer-sphere reactions. See, for example, ref. 4.

(16) For comparison with the value of $K_1^{\text{SCN}}/K_1^{\text{NCS}}$ estimated above, it may be noted that the ratio of the equilibrium constants for the reactions $\text{Cr}^{3+} + \text{NCS}^- \rightleftharpoons \text{CrNCS}^{2+}$ and $\text{Cr}^{3+} + \text{SCN}^- \rightleftharpoons \text{CrSCN}^{2+}$, which is equal to the equilibrium constant for the isomerization reaction $\text{CrSCN}^{2+} \rightleftharpoons \text{CrNCS}^{2+}$, is 3×10^5 at 25° and 1.0 M ionic strength. Evidently the preference for bonding to nitrogen (rather than to sulfur) is much more marked for chromium(III) than for chromium(II). This conclusion is not unexpected since a Cr^{3+} ion is almost certainly harder than a Cr^{2+} ion.

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

(18) M. V. Olson, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, **51**, 289 (1969).

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trans-Bis(fluoroxy)tetrafluoroselenium [SeF₄(OF)₂]

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Fluoroxypentafluoroselenium, SeF₅OF, has been obtained in high yield by the action of fluorine upon seleninyl fluoride, SeOF₂, in the presence of potassium fluoride catalyst.¹ While refining the principal product by fractional codistillation, it was observed that a small amount of another compound was present which had a longer retention time than SeF₅OF. By combining the material from several preparative runs, a sufficient amount of the new compound was obtained to allow its identification as *trans*-bis(fluoroxy)tetrafluoroselenium. It is possible that the compound resulted from the action of fluorine upon potassium fluoroselenite, KSeO₂F, which could have been formed by the hydrolysis of some SeOF₂ and subsequent reaction of the SeO₂ with the potassium fluoride catalyst. The reaction of KSeO₂F with fluorine at -78° was later shown to be a method for the preparation of SeF₄(OF)₂.

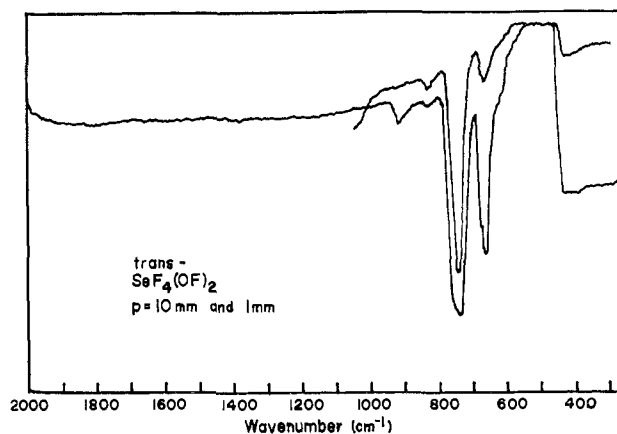


Figure 1.—Infrared spectrum of SeF₄(OF)₂.

Preparations

KSeO₂F.—Potassium fluoroselenite, KSeO₂F, was prepared using a method similar to that described by Paetzold and Aurich.² Equimolar quantities of potassium fluoride and selenium dioxide were mixed and heated until molten under a stream of nitrogen in a nickel crucible. A small stainless steel spatula was placed in the salt to facilitate removal after cooling. The crucible was then placed in a desiccator and allowed to cool. The salt was powdered in a mortar before use and was handled in a dry bag.

SeF₄(OF)₂.—Approximately 1.1 g of powdered potassium fluoroselenite was placed in a Hoke 4HS30 stainless steel sampling cylinder fitted with a brass valve having a stainless steel needle. A 10-mmol quantity of fluorine was then condensed into the cylinder. The liquid nitrogen was then removed from the dewar vessel surrounding the cylinder, and the cylinder was allowed to

(1) J. E. Smith and G. H. Cady, *Inorg. Chem.*, in press.

(2) R. Paetzold and K. Aurich, *Z. Anorg. Allgem. Chem.*, **335**, 281 (1965).