quite different and can be adequately represented by the expression

$$\text{rate} = k[\text{Ti(IV)}][\text{H}_2\text{O}_2]$$

$$k = 1.2 \times 10^2 + 0.5 \times 10^2[\text{H}^+] + 0.09 \times 10^2[\text{H}^+]^2$$

at 25°, $I = 3.0\ M$. The agreement between experimental and calculated values is indicated in Table I. We hesitate to identify reaction paths with the various terms of the above expression because of the paucity of data on the reacting species. We are content to demonstrate acid catalysis and to determine that at $2.0\ M\,[\text{H}^+]$, $k = 1.6 \times 10^{10} \exp(-10{,}600/RT)$.

Discussion

The rapid formation of chromium, vanadium, and titanium peroxy species in acid solution has some similar characteristics. All reactions are first order in oxy ion and hydrogen peroxide. A rate term involving $[\text{H}^+]$ occurs in the three reactions involving the oxy ions in noncoordinating media. If this were associated with a very reactive H_3O_2^+, formed in a rapid preequilibrium, then the rather high over-all rate constants would lead to improbably high rate constants for the reaction between the transition metal ion and H_3O_2^+ ($\approx 10^8\ M^{-1}\ \text{sec}^{-1}$). It is believed rather that the acid catalysis arises from a reactive protonated (or possibly with titanium(IV) dehydroxylated) form of the oxy ion. A first-order dependence on C_{H^+} has been established for the reactions of many oxy anions[13] and in the reactions of VO_2^+ with inorganic (*e.g.*, Fe(II))[22] and organic (*e.g.*, cyclohexanol)[23] reductants. Little data on kinetic reactions of titanium(IV) appear available. Further evidence that this is a reasonable interpretation is afforded by the fact that the rate of reaction of VO_3^+ or the titanium(IV) sulfate species (with both of which protonation is less likely to occur or produce a particularly reactive species) with hydrogen peroxide is acid independent. It is particularly difficult to see why H_3O_2^+, if this was the active species in these reactions, would not react as well with the anionic (?) titanium sulfate complex ion as the cationic titanium species in perchloric acid. Obviously, these ideas, if correct, do not imply that in the acid-catalyzed reactions of hydrogen peroxide with other nucleophiles such as halide ions, etc., H_3O_2^+ cannot be the reactive species either. Indeed, Edwards[13] has presented strong evidence that this is the cause of the rate dependence on $[\text{H}^+]$ with those oxidation–reduction reactions.

The third-order rate constants for the formation of all monoperoxy species are remarkably similar, although, since these are composite values, particular significance may not necessarily be attached to this. The formation of the diperoxychromate in low acidities and monoperoxy- and diperoxyvanadate and monoperoxytitanate species in perchloric and sulfuric acids is accompanied by enthalpies of activation of 3.9, 9.3, 8.5, 10.0, and 10.9 kcal mole^{-1} and entropies of activation of −26, −9, −14, −14, and −9 eu, respectively. These low values are characteristic of many reactions of peroxides with nucleophiles. The negative values of $\Delta S^{\ddagger}$ have been ascribed to requirements of a precisely oriented transition state.[13]

Acknowledgment. We are indebted to the National Science Foundation, which supported this work (Grant GP 1963). We have incorporated helpful comments of the referees in this paper.

[22] N. A. Daugherty and T. W. Newton, *J. Phys. Chem.*, **67**, 1090 (1963).

[23] J. S. Littler and W. A. Waters, *J. Chem. Soc.*, 4046 (1959).

The Kinetics of the Iron(II)-Catalyzed Dissociation of the Monothiocyanate Complex of Iron(III)[1]

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Abstract: The kinetics of the iron(II)-catalyzed dissociation of FeNCS^{2+} have been studied by use of a flow technique. The approach to equilibrium is given by $k_{\text{obsd}} = [k_{\text{d}} + k_4(\text{Fe}^{2+})] + [k_{\text{d}} + k_4(\text{Fe}^{2+})]K_1(\text{Fe}^{3+})/[1 + K_2 \cdot (\text{Fe}^{2+})]$. The values of k_{d} and k_4 are 0.68 ± 0.04 sec^{-1} and 10.5 ± 0.6 M^{-1} sec^{-1}, respectively, at 25.0° and ionic strength 3.0 M. The equilibrium constant for the reaction $\text{Fe}^{2+} + \text{SCN}^- \rightleftharpoons \text{FeNCS}^+$ is 7.0 ± 0.5 M^{-1}. The results are discussed in terms of remote and adjacent attack on the coordinated thiocyanate.

Both inner-sphere and outer-sphere mechanisms have been proposed for the electron-transfer reactions between iron(II) and anion complexes of iron(III).[2–4] Recent studies of the iron(II)-catalyzed dissociation of the monochloro complex of iron(III) have shown that the FeCl^{2+}–Fe^{2+} exchange reaction proceeds mainly by an inner-sphere, chloride-bridged mech-

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] H. Taube, *Advan. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[3] J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961).

[4] N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

anism.[5] The success of this approach encouraged us to undertake the study of a system in which the anion complexed with the iron(III) was asymmetric. Under these conditions a group-transfer reaction could yield an unstable isomer in which the "wrong end" of the anion would be bonded to the iron(III) and which might be distinguishable from the stable isomer. Unstable isomers produced in this manner have recently been detected. For example, the reactions of $Co(NH_3)_5NO_2^{2+}$ and $Co(NH_3)_5CN^{2+}$ with $Co(CN)_5^{3-}$ produce the unstable species $Co(CN)_5ONO^{3-}$ and $Co(CN)_5NC^{3-}$, respectively,[6] while the reaction of $Co(NH_3)_5CN^{2+}$ with chromium(II) produces $CrNC^{2+}$.[7] Similarly, the reactions of $FeNCS^{2+}$ and *trans*-$Co(en)_2(OH_2)NCS^{2+}$ with chromium(II) produce the sulfur-bonded chromium(III) complex, $CrSCN^{2+}$.[8,9] We have made an extensive study of the iron(II)-catalyzed dissociation of the monoisothiocyanato complex of iron(III) in an attempt to detect the sulfur-bonded complex $FeSCN^{2+}$ If this complex were formed,

$$FeNCS^{2+} + Fe^{2+} \longrightarrow Fe^{2+} + FeSCN^{2+}$$

then the rates of dissociation of $FeNCS^{2+}$ and of $FeCl^{2+}$ could exhibit different iron(II) dependences. In particular, because of the reversal of the above group-transfer reaction, the dissociation of $FeNCS^{2+}$, unlike that of $FeCl^{2+}$, might reach a limiting rate at high iron(II) concentrations.

Experimental Section

Iron(III) perchlorate (G. Frederick Smith Chemical Co.) was purified by recrystallization from perchloric acid. Solutions of iron(II) perchlorate were prepared by electroreduction of perchloric acid solutions of iron(III). The sodium thiocyanate was obtained from Fisher Scientific Co. and the perchloric acid (70%) from J. T. Baker Chemical Co. The iron(III) concentration of the stock solution was determined by passing an aliquot through a Jones reductor and titrating the resulting iron(II) with cerium(IV). The free acid concentration was determined by adding excess standard alkali to an aliquot of iron(III) perchlorate, precipitating iron(III) hydroxide, then back-titrating with standard acid to the methyl red end point. The iron(II) solutions were standardized spectrophotometrically by forming the tris(1,10-phenanthroline) complex (ϵ_{max} 11,100 at 520 mμ). The free acid in the iron(II) solutions was determined as described for the iron(III) solutions except that 30% hydrogen peroxide was added initially to oxidize the iron(II) to iron(III). The ionic strength was maintained with magnesium perchlorate which was prepared from magnesium oxide (J. T. Baker Chemical Co.) and concentrated perchloric acid. All solutions were prepared with triply distilled water.

The kinetics were studied at 25.0°, at ionic strength 3.0 *M*, and at a constant acidity of 1.80 *M* using the flow techniques and apparatus previously described.[10] Solutions containing iron(III), iron(II), and perchloric acid were mixed with perchloric acid solutions containing thiocyanate and iron(II), and the formation of the iron(III) thiocyanate complex was followed at 460 mμ. The disappearance of the iron(III) thiocyanate complex was followed in runs where solutions of iron(III), thiocyanate, and perchloric acid were mixed with iron(II) and perchloric acid. The iron(III) concentration of the reactant solutions used in each run was determined polarographically by measuring the change in current resulting from the addition of excess ascorbic acid. The following concentration ranges were used: [Fe(III)] = 1.5 to 12.6 × 10^{-3} *M*, [Fe(II)] = 0.5 to 4.0 × 10^{-1} *M*, (SCN^-) = 1.0 to 2.5 × 10^{-4} *M*, ($HClO_4$) = 1.80 *M*.

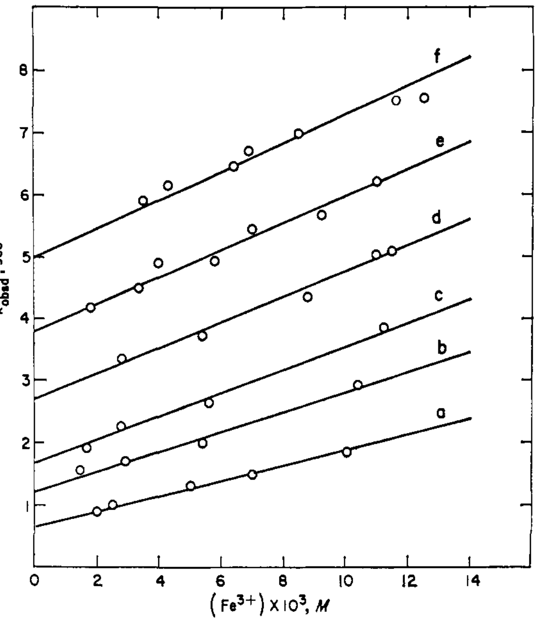

Figure 1. Plots of k_{obsd} *vs.* (Fe^{3+}) at 25.0° and ionic strength 3.0 *M*: (a) no added Fe^{2+}; (b) 0.05 *M* Fe^{2+}; (c) 0.10 *M* Fe^{2+}; (d) 0.20 *M* Fe^{2+}; (e) 0.30 *M* Fe^{2+}; (f) 0.40 *M* Fe^{2+}. $(SCN^-)_T$ = 1.0 to 2.5 × 10^{-4} *M*.

Results

Values of k_{obsd} calculated from

$$\frac{d(FeNCS^{2+})}{dt} = k_{obsd}[(FeNCS^{2+})_{eq} - (FeNCS^{2+})] \quad (1)$$

are presented in Table I. In Figure 1, the values of k_{obsd} are plotted *vs.* (Fe^{3+}) at various iron(II) concentrations. It is apparent that

$$k_{obsd} = k'' + k'(Fe^{3+}) \quad (2)$$

where k'' and k' are functions of the iron(II) concentration. The values of k'' and k' calculated from the intercepts and slopes of the plots in Figure 1 are presented in Table II. In the absence of iron(II), k_{obsd} is given by

$$k_{obsd} = k_d + k_f(Fe^{3+}) \quad (3)$$

where the rate constants are defined by the equation

$$Fe^{3+} + SCN^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} FeNCS^{2+} \qquad K_1 \quad (4)$$

The values of k_f and k_d are (1.22 ± 0.06) × 10^2 M^{-1} sec^{-1} and 0.68 ± 0.04 sec^{-1}, respectively, at 25.0° and ionic strength 3.0 *M*. These values may be compared with k_f = (1.27 ± 0.10) × 10^2 M^{-1} sec^{-1} and k_d = 0.88 ± 0.07 sec^{-1} at 25.0° and ionic strength 0.40 *M*.[11] The rate constants are in good agreement,

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(5) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).
(6) J. Halpern and S. Nakamura, *ibid.*, **87**, 3002 (1965).
(7) J. H. Espenson and J. P. Birk, *ibid.*, **87**, 3280 (1965).
(8) A. Haim and N. Sutin, *ibid.*, **87**, 4210 (1965).
(9) A. Haim and N. Sutin, *ibid.*, **88**, 434 (1966).
(10) G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963).
(11) J. F. Below, Jr., R. E. Connick, and C. P. Coppel, *J. Am. Chem. Soc.*, **80**, 2961 (1958).

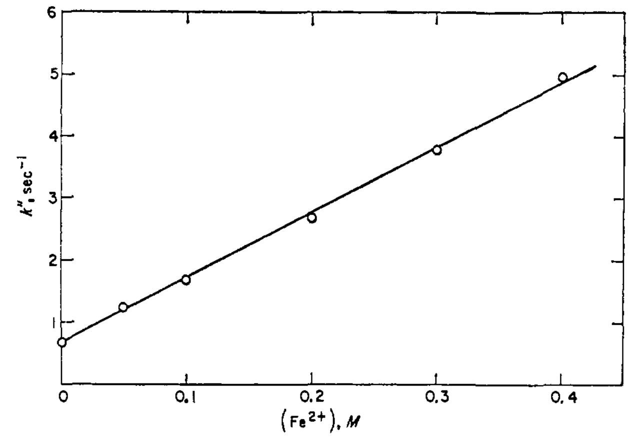

Figure 2. Plot of k'' vs. (Fe^{2+}) at 25.0° and ionic strength 3.0 M.

Table I. Rate Constants for the Approach to Equilibrium in the Iron(III), Iron(II), and Thiocyanate System at 25.0° and Ionic Strength 3.0 M^a

[Fe(III)] × 10^3, M	[Fe(II)] × 10^1, M	k_{obsd}, sec^{-1}
2.0[b]	. . .	0.92
2.5	. . .	1.01
5.0[c]	. . .	1.32
7.0[b]	. . .	1.50
10.0	. . .	1.86
1.5	0.50	1.61
2.9	0.50	1.73
5.4	0.50	2.03
10.4	0.50	2.96
1.7	1.0	1.93
2.8	1.0	2.27
5.6	1.0	2.66
11.2	1.0	3.87
2.8	2.0	3.36
5.4	2.0	3.75
8.8	2.0	4.36
11.0	2.0	5.10
11.5	2.0	5.06
1.8	3.0	4.20
3.4	3.0	4.50
4.0	3.0	4.91
5.8	3.0	4.95
7.0	3.0	5.46
9.2	3.0	5.63
11.0	3.0	6.24
3.5	4.0	5.92
4.3	4.0	6.18
6.4	4.0	6.48
6.9	4.0	6.73
8.5	4.0	7.00
11.6	4.0	7.53
12.5	4.0	7.56

[a] $(HClO_4)$ = 1.80 M. (SCN^-) = 1.0 × 10^{-4} M except where indicated. The range of thiocyanate concentrations that could be used in this work was limited by the formation of $Fe(NCS)_2^+$ [b] (SCN^-) = 2.0 × 10^{-4} M. [c] (SCN^-) = 2.5 × 10^{-4} M.

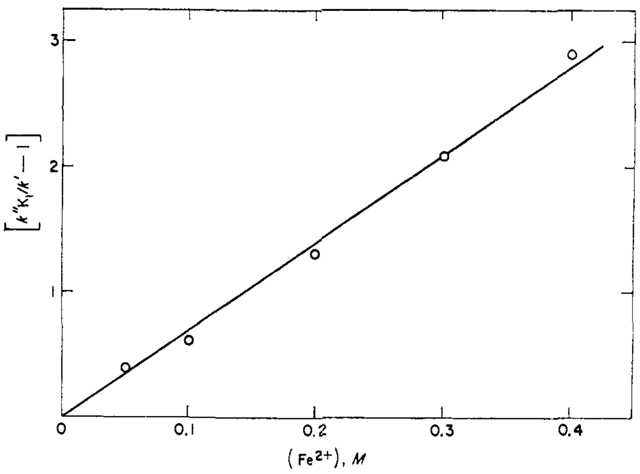

Figure 3. Plot of $k''K_1/(k' - 1)$ vs. (Fe^{2+}) at 25.0° and ionic strength 3.0 M.

considering the difference in ionic strength and the fact that the rate constants determined in this study may contain a small contribution from the hydrolyzed iron(III) path, while the data from ref 11 have been corrected for this path. The equilibrium constant $K_1 = k_f/k_d$ = 180 ± 10 M^{-1} is in excellent agreement with K_1 = 175 ± 8 M^{-1} at 25.0° and ionic strength 3.0 M determined by spectrophotometric measurements on solutions containing iron(III) and thiocyanate.[12]

Table II. Values of the Forward and Reverse Rate Constants at 25.0° and Ionic Strength 3.0 M^a

[Fe(II)], M	k'', sec^{-1}	k', M^{-1} sec^{-1}
0.0	0.68	122
0.05	1.25	158
0.10	1.70	186
0.20	2.70	207
0.30	3.80	218
0.40	5.00	230

[a] $(HClO_4)$ = 1.80 M.

The values of k'' are plotted vs. (Fe^{2+}) in Figure 2. It is seen that

$$k'' = k_d + k_4(Fe^{2+}) \tag{5}$$

The value of k_4 obtained from the slope of Figure 2 is 10.5 ± 0.6 M^{-1} sec^{-1} at 25.0° and ionic strength 3.0 M. Since k_{obsd} measures the rate of approach to equilibrium, k' is given by

$$k' = \frac{K_1k''}{1 + K_2(Fe^{2+})} \tag{6}$$

where K_2 is the equilibrium constant for the formation of $FeNCS^+$.

$$Fe^{2+} + NCS^- \rightleftharpoons FeNCS^+ \quad K_2 \tag{7}$$

Figure 3 is a plot of $k''K_1/(k' - 1)$ vs. (Fe^{2+}). The value of K_2 calculated from the slope of this plot is 7.0 ± 0.5 M^{-1}. This value is in very good agreement with K_2 = 6.5 ± 0.6 M^{-1} determined by spectrophotometric measurements on solutions containing iron(II), iron(III), and thiocyanate.[12]

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(12) J. K. Rowley and N. Sutin, unpublished observations.

Discussion

The Formation and Dissociation of $FeNCS^{2+}$ in the Absence of Iron(II). The kinetic data in the absence of iron(II) are consistent with the following reaction scheme.[13]

$$Fe^{3+} + SCN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} FeNCS^{2+} \qquad K_1 \tag{8}$$

$$Fe^{3+} + SCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} FeSCN^{2+} \tag{9}$$

$$FeSCN^{2+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} FeNCS^{2+} \tag{10}$$

This scheme includes the usual substitution step (eq 8)[14] and a path involving the formation and linkage isomerization of $FeSCN^{2+}$ (eq 9 and 10). If [Fe(III)] is constant, and the steady-state assumption for the concentration of $FeSCN^{2+}$ is valid, then

$$k_d = k_{-1} + \frac{k_{-2}k_{-3}}{k_{-2} + k_3} \tag{11}$$

and

$$k_f = k_1 + \frac{k_2k_3}{k_{-2} + k_3} \tag{12}$$

The values of the individual rate constants cannot be determined from the kinetic data. However, by analogy with the chromium(III)–thiocyanate system,[15] it is likely that k_1 is larger than k_2. Since $k_{-2}k_{-3}/k_3 = k_{-1}k_2/k_1$, it follows that $k_{-2}k_{-3}/k_3 < k_{-1}$ provided $k_1 > k_2$. In other words, the linkage isomerization reaction very probably does not provide the major pathway for the dissociation (and formation) of $FeNCS^{2+}$. Nevertheless this pathway cannot be excluded entirely, and a small fraction of the dissociation (and formation) reactions of $FeNCS^{2+}$ could involve the formation of $FeSCN^{2+}$ as an intermediate.[16]

The Iron(II)-Catalyzed Formation and Dissociation of $FeNCS^{2+}$. The rate constants for the formation and dissociation of $FeNCS^{2+}$ in the presence of iron(II) are linear in the iron(II) concentration (apart from the pseudo-inhibition arising from the equilibrium condition, eq 6). The results can be readily rationalized in terms of an "electron-transfer" path forming $FeNCS^+$

$$FeNCS^{2+} + Fe^{2+} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} FeNCS^{+} + Fe^{3+} \tag{13}$$

with $k_4 = 10.5 \pm 0.6\ M^{-1}\ sec^{-1}$ at 25.0° and ionic strength 3.0 M.[17] The results do not exclude a thiocyanate-transfer path forming $FeSCN^{2+}$ in steady-state concentrations.

$$FeNCS^{2+} + Fe^{2+} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Fe^{2+} + FeSCN^{2+} \tag{14}$$

The maximum contribution which this thiocyanate-transfer path can make to k_d is $k_{-2}k_5/k_{-5} = k_{-2}k_{-3}/k_3$. Since, as we have seen, there is good evidence that $k_{-2}k_{-3}/k_3 \leq 0.68\ sec^{-1}$, the above estimate of k_4 is relatively insensitive to the operation of a thiocyanate-transfer path.

The dissociation of $FeCl^{2+}$, like that of $FeNCS^{2+}$, is catalyzed by iron(II). Two paths were considered for the iron(II)-catalyzed dissociation of $FeCl^{2+}$.[5] These are an outer-sphere path with rate constant k_0, and an inner-sphere, water-bridged path with rate constant k_{H_2O}. The value of $(k_0 + k_{H_2O})$ is 12.1 ± 1.6 $M^{-1}\ sec^{-1}$ at ionic strength 3.0 M and 25.0°.[5] The above two paths, with rate constants k_0' and k_{H_2O}', respectively, are also available for the iron(II)-catalyzed dissociation of $FeNCS^{2+}$.[18] However, there is an additional path for forming $FeNCS^+$ from $FeNCS^{2+}$ which has no parallel in the chloride system.[19] This is the inner-sphere, thiocyanate-bridged path in which the iron(II) attacks the sulfur atom of the coordinated thiocyanate (remote attack), but the electron transfer following this reaction does not result in transfer of the thiocyanate group.[20] The rate constant k_4 is the sum of the rate constants for these three processes, *i.e.*, $k_4 = (k_0' + k_{H_2O}' + k_S')$.

The Thiocyanate-Catalyzed Iron(II)–Iron(III) Exchange Reaction. Additional information concerning the importance of the inner-sphere, thiocyanate-bridged path in the $FeNCS^{2+}$–Fe^{2+} reaction can be obtained by comparing the value of k_4 with the rate constant for the thiocyanate-catalyzed iron(II)–iron(III) exchange reaction. The rate constant for the $FeNCS^{2+}$–Fe^{2+} exchange reaction includes all the exchange paths involving Fe^{2+} and $FeNCS^{2+}$. It is given by[21]

$$k_{ex} = k_N + 2k_4 + 2k_5 \tag{15}$$

where k_N is the rate constant for adjacent attack on the coordinated thiocyanate.

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[13] It is assumed that the stable forms of the monothiocyanate complexes of iron(II) and iron(III) are nitrogen bonded. Evidence supporting the view that the monothiocyanate complex of iron(III) is nitrogen bonded has been presented.[8,9] Additional evidence is provided by the similarity of the spectra of the monothiocyanate and monoazide complexes of iron(III). The preference of iron(II) for the nitrogen end of the thiocyanate group may be even greater than that of iron(III): C. K. Jørgensen, *Inorg. Chem.*, **3**, 1201 (1964).

[14] The possibility that the aquation of $FeNCS^{2+}$ may proceed *via* linkage isomerization was not considered in ref 11.

[15] The formation of $CrSCN^{2+}$ from chromium(III) and thiocyanate proceeds about 1/100th as fast as the formation of $CrNCS^{2+}$.[8]

[16] From the data reported by Haim and Sutin[8] we calculate that about 1% of the formation and dissociation reactions of $CrNCS^{2+}$ involve the formation of $CrSCN^{2+}$ as an intermediate.

[17] The rate constants k_4 and k_5 are composite rate constants and include acid-independent as well as any acid-dependent paths. Since the studies were made at constant acidity, the general conclusions do not depend upon any assumptions concerning the magnitudes of the acid-dependent and acid-independent paths.

[18] The value of k_0' is probably somewhat smaller than k_0 because the $FeCl^{2+}$–Fe^{2+} reaction has a more favorable free energy change than the $FeNCS^{2+}$–Fe^{2+} reaction does. Similarly, k_{H_2O}' is probably smaller than k_{H_2O} since there is some evidence that chloride is a "better" nonbridging ligand than thiocyanate: P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965). These considerations suggest that $(k_0' + k_{H_2O}') < (k_0 + k_{H_2O})$.

[19] Because of the symmetry of the chloride system it is likely that chloride transfer occurs in the inner-sphere, chloride-bridged reaction.

[20] A reason for the absence of thiocyanate transfer in the thiocyanate-bridged path is the greater stability of the products of the nontransfer reaction ($FeNCS^+ + Fe^{3+}$) compared to the products of the thiocyanate-transfer path ($Fe^{2+} + FeSCN^{2+}$).

[21] In deriving eq 15 it is assumed that equilibrium between Fe^*NCS^{2+}, Fe^*SCN^{2+}, Fe^{*3+}, and thiocyanate is maintained throughout the course of the exchange reaction. The exchange reaction will cease to be first order in iron(II) when the equilibrium assumption breaks down.

$$\mathrm{FeNCS^{2+}} + \mathrm{Fe^{2+}} \underset{}{\overset{k_N}{\rightleftharpoons}} \mathrm{Fe^{2+}} + \mathrm{FeNCS^{2+}} \qquad (16)$$

The reactants and products of the adjacent attack path are identical, and consequently this path is not detected spectrophotometrically.[22] The $FeNCS^{2+}$–Fe^{2+} exchange reaction has been studied by Horne[23] and also by Laurence.[24] According to Horne $k_{ex} = 27.8$ M^{-1} sec^{-1} at 25.0° and ionic strength 0.5 M. This value of k_{ex} is about 30% lower than the value reported by Laurence. The value reported by Horne is preferred, since the rate constants for the iron(II)–iron(III) exchange reaction in the absence of thiocyanate reported by Laurence are in poor agreement with the values reported by other workers.[25] Provided the rate constant for the $FeNCS^{2+}$–Fe^{2+} reaction determined by Horne is not in serious error, and the rates of the $FeNCS^{2+}$–Fe^{2+} and $FeCl^{2+}$–Fe^{2+} reactions have similar ionic strength dependences, then k_{ex} for the former reaction is calculated to be 51.6 M^{-1} sec^{-1} at 25.0° and ionic strength 3.0 M. Subtraction of $2k_4$ (21.0 M^{-1} sec^{-1}(from k_{ex} (51.6 M^{-1} sec^{-1}) leads to the important result that $(k_N + 2k_5) = 30.6$ M^{-1} sec^{-1} at 25.0° and ionic strength 3.0 M. These studies do not give the relative contributions of adjacent and remote attack. However, by analogy with the $FeNCS^{2+}$–Cr^{2+} and $Co(en)_2(OH_2)NCS^{2+}$–Cr^{2+} reactions[8,9], it is likely that the rate constants for adjacent and remote attack [k_N and $(k_5 + k_S')$, respectively] are of the same order of magnitude.

Finally, it should be noted that, while thiocyanate appears to be at least as "good" a bridging ligand as chloride in the FeX^{2+}–Fe^{2+} and FeX^{2+}–Cr^{2+} reactions,[8,26] thiocyanate is a much poorer bridging ligand than chloride in other reactions.[27,28] Although we cannot offer an explanation for these effects, the results obtained in the present investigation suggest that the $FeNCS^{2+}$–Fe^{2+} reaction, like the $FeCl^{2+}$–Fe^{2+}, $FeNCS^{2+}$–Cr^{2+}, and $FeCl^{2+}$–Cr^{2+} reactions,[5,8,26] proceeds predominantly *via* an inner-sphere mechanism.

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(22) It is assumed that thiocyanate transfer occurs in the reaction proceeding by adjacent attack.

(23) R. A. Horne, Ph.D. Thesis, Columbia University, 1955.

(24) G. S. Laurence, *Trans. Faraday Soc.*, **53**, 1326 (1957).

(25) According to J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952), the rate constants (in M^{-1} sec^{-1}) for the iron(II)–iron(III) exchange reaction are 3.55 (0°), 11.2 (9.8°), and 61.6 (25°) at $(H^+) = 9.67 \times 10^{-2}$ M, and 1.34 (0°), 3.34 (10°), and 8.78 (20°) at $(H^+) = 0.55$ M. These values may be compared with the rate constants reported by Laurence[24] at $(H^+) = 9.67 \times 10^{-2}$ M [3.15 (0°), 8.5 (9.8°), 34.6 (25°)] and by Horne[23] at $(H^+) = 0.55$ M [1.31 (0°), 3.43 (10°), and 8.22 (20°)]. It will be seen that the rate constants for the iron(II)–iron(III) exchange reaction determined by Horne are in better agreement with the Silverman and Dodson values than are those determined by Laurence. However, the dependence of the exchange rate in the presence of thiocyanate on the concentrations of iron(II) and iron(III) was not extensively studied by either Laurence or Horne. For this reason the effect of thiocyanate on the iron(II)–iron(III) exchange reaction warrants further study.

(26) G. Dulz and N. Sutin, *J. Am. Chem. Soc.*, **86**, 829 (1964).

(27) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958).

(28) J. P. Candlin, J. Halpern, and D. L. Trimm, *ibid.*, **86**, 1019 (1964).