but stirring was continued for 20 hr at 25° before removal of solvent and excess triethylphosphine under vacuum. The residues were extracted with methylene chloride, followed by acetone, followed by water. Evaporation of the organic extracts and addition of silver nitrate to the acidified aqueous extract gave $[PdCl(Et_3P)_3][BPh_4]$ (0.39 g, 0.48 mmole) from the methylene chloride, sodium tetraphenylborate (0.15 g, 0.44 mmole) from the acetone, and silver chloride (0.07 g, 0.49 mmole) from the water.

A second reaction under reflux for 5 hr gave similar results.

(b) ***trans*-$[PdCl(Et_3P)_2(Ph_3P)][BPh_4]$.** By the same procedure triphenylphosphine (0.127 g, 0.48 mmole), *trans*-$[PdCl_2(Et_3P)_2]$ (0.200 g, 0.5 mmole), and sodium tetraphenylborate (0.166 g, 0.5 mmole) gave silver chloride (0.068 g, 0.5 mmole) and *trans*-$[PdCl(Et_3P)_2(Ph_3P)][BPh_4]$ (0.48 g, 0.5 mmole). This complex was somewhat air sensitive, particularly in solution, and was best handled in a nitrogen atmosphere.

(c) **$[PtCl(Et_3P)_3][BPh_4]$.** By the same procedure triethylphosphine (0.08 ml, 0.54 mmole) and *cis*-$[PtCl_2(Et_3P)_2]$ (0.201 g, 0.40 mmole) gave silver chloride (0.057 g, 0.40 mmole) and $[PtCl(Et_3P)_3][BPh_4]$ (0.365 g, 0.40 mmole).

(d) **$[PtH(Et_3P)_3][BPh_4]$.** By the same procedure triethylphosphine (0.07 ml, 0.44 mmol) and sodium tetraphenylborate (0.149 g, 0.44 mmole) gave silver chloride (0.062 g, 0.43 mmole) and $[PtH(Et_3P)_3][BPh_4]$ (0.38 g, 0.44 mmole).

(e) **$[PtH(Ph_3P)_3][BPh_4]$.** By the same procedure triphenylphosphine (0.077 g, 0.3 mmole), *trans*-$[PtHCl(Ph_3P)_2]$ (0.221 g, 0.3 mmole), and sodium tetraphenylborate (0.100 g, 0.3 mmole) gave silver chloride (0.039 g, 0.3 mmole) and $[PtH(Ph_3P)_3][BPh_4]$ (0.39 g, 0.3 mmole).

4. Preparation of *trans*-$[PtH(CO)(Et_3P)_2][BPh_4]$. A procedure similar to 3d above but using carbon monoxide (1 atm) instead of triethylphosphine gave *trans*-$[PtH(CO)(Et_3P)_2][BPh_4]$ (0.321 g, 0.412 mmole).

5. Ligand-Exchange Reactions. (a) A procedure similar to 3a above but using triethylphosphine (0.2 ml, 1.4 mmole), *trans*-$[PdCl_2(Ph_3P)_2]$ (0.200 g, 0.285 mmole), and sodium tetraphenylborate (0.098 g, 0.286 mmole) gave silver chloride (0.040 g, 0.279 mmole) and a methylene chloride extract. Evaporation of this extract to small bulk followed by addition of diethyl ether gave $[PdCl(Et_3P)_3][BPh_4]$ (0.222 g, 0.258 mmole). *Anal.* Calcd for $C_{42}H_{65}BClP_3Pd$: C, 61.8; H, 8.0. Found: C, 61.7; H, 8.2. The mother liquor contained triphenylphosphine (0.148 g, 0.564 mmole), identified by infrared spectroscopy and melting point with a genuine sample).

(b) A procedure similar to 3a above but using triethylphosphine (0.05 ml, 0.34 mmole) and *cis*-$[PtCl_2(Ph_3P)_2]$ (0.107 g, 0.137 mmole) gave a light petroleum extract containing triphenylphosphine (0.072 g, 0.274 mmole). The residue was *cis*-$[PtCl_2(Et_3P)_2]$ (0.068 g, 0.135 mmole). Both products were identified by infrared spectroscopy and mixture melting points with genuine samples.

A similar reaction using triphenylphosphine (0.506 g, 1.9 mmoles) and *cis*-$[PtCl_2(Et_3P)_2]$ (0.093 g, 0.185 mmole) gave quantitative recovery of starting materials.

6. Reaction of *cis*-$[PtCl_2(Et_3P)_2]$ with $NaBPh_4$. *cis*-$[PtCl_2(Et_3P)_2]$ (0.211 g, 0.420 mmole) was heated under reflux in 15 ml of dry tetrahydrofuran with $NaBPh_4$ (0.288 g, 0.842 mmole) for 40 hr. Solvent was removed under vacuum and the residue extracted with methylene chloride, washed with acetone, and extracted with water.

Addition of silver nitrate to the acidified aqueous extract gave silver chloride (0.118 g, 0.824 mmole).

The methylene chloride extract was evaporated and the resulting residue reextracted with cyclohexane Evaporation of the cyclohexane followed by washing of the solid obtained with small volumes of methanol left *trans*-$[PtPh_2(Et_3P)_2]$ (0.229 g, 0.39 mmole) as a white residue.

A repeat reaction, in which the reaction mixture after removal of tetrahydrofuran was heated under vacuum at 70°, gave a white sublimate with infrared spectrum identical with that reported[23] for triphenylboron.

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Kinetic Studies of the Reduction of Monosubstituted Iron(III) Complexes by Europium(II) and Chromium(II) in Acidic Solution[1]

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Abstract: Rates have been measured for the oxidation–reduction reactions occurring between various Fe(III) complexes of the type $(H_2O)_5FeX^{2+}$ and Cr^{2+} and Eu^{2+}. The order of reduction rates differs, being $Br > Cl > F$ for Cr(II) reductions and the reverse for Eu(II). The Cr(II) reactions proceed by inner-sphere mechanisms, with transfer of the bridging ligand. Indirect arguments for Eu(II) are advanced in favor of inner-sphere mechanisms, but ligand transfer probably does not take place owing to the greater substitution lability of Eu(III) compared to Fe(II). Some complexation equilibria and rates are evaluated, notably for $FeNCO^{2+}$. The products of the reduction of this complex by Cr^{2+} have also been examined.

This paper represents a further report of work related to the question of the details of one-equivalent oxidation–reduction reactions. A number of studies on related reactions have been published recently.[2,3]

One question of current interest is whether particular electron-transfer reactions proceed by either inner- or

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(1) (a) Work was performed in the Ames Laboratory, under the auspices of the U. S. Atomic Energy Commission. (b) Based on the Ph.D. thesis of D. W. C., Iowa State University, Ames, Iowa; (c) NASA graduate trainee, 1967–1968.

(2) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968), and references cited therein.

(3) Recent reviews of this area have appeared: (a) N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966); (b) *Accounts Chem. Res.*, **1**, 225 (1968); (c) A. G. Sykes, *Advan. Inorg. Chem. Radiochem.*, **10**, 153 (1968).

outer-sphere mechanisms. The problem is not that the two mechanisms have a region of overlap, for they remain distinct, but that evidence for ligand transfer, the most useful criterion of an inner-sphere mechanism, is not generally obtainable.

The solution of this problem is resolved into two approaches: a search for model reactions where ligand transfer or its absence can be noted with certainty, and the development of criteria for indirect inference of detailed mechanism. For example, the reductions by V^{2+} of the compounds $(H_2O)_5CrSCN^{2+}$,[4] *cis*-$Co(en)_2(N_3)_2^+$,[5] and $Co(NH_3)_5C_2O_4^+$ [6] all give rise to the well-characterized ions $VNCS^{2+}$, VN_3^{2+}, and $VC_2O_4^+$. Likewise, the reaction of Fe^{2+} and $Co(C_2O_4)_3^{3-}$ [7] produces $FeC_2O_4^+$, establishing an inner-sphere mechanism for this case as well. In contrast, the reduction of $(H_2O)_5FeN_3^{2+}$ by V^{2+} [4] does not give rise to any VN_3^{2+}, although the latter is easily detectable[5] under the conditions employed. An outer-sphere mechanism is thereby established, in agreement with the latter reaction rate exceeding the rate of substitution[4,8] on V_{aq}^{2+}, preventing ligand bridging.

Among the indirect approaches that have been considered are activation volumes,[9] $\Delta S^{\ddagger}$ values,[10] and the pattern of reaction rates[2,11] in various reactions or series of reactions. The comparisons include the relative reaction rates of aquo, hydroxo, halo, azido, and thiocyanato complexes.

The main difficulty with these criteria in their present state is the absence of complete data on reactions where the mechanism is known with certainty. A further difficulty that has perhaps been less widely recognized is the question of the reliability with which parameters such as the ones considered reflect the type of mechanism. The latter point is particularly applicable to a number of the Eu(II) reactions studied in this work.

In a previous paper[2] we considered the kinetics of Eu(II) reductions of some Fe(III) complexes, namely $Fe(H_2O)_6^{3+}$, $(H_2O)_5FeOH^{2+}$, and $(H_2O)_5FeCl^{2+}$. Similar studies have been carried out for Cr^{2+} reductions by Dulz and Sutin.[12] The present paper reexamines the reactions of Cr^{2+} and Fe^{3+} in a lithium perchlorate–perchloric acid medium and extends the studies on reduction of the halide and pseudo-halide complexes $(H_2O)_5FeX^{2+}$ by Cr^{2+} and Eu^{2+}.

Experimental Section

Materials. Preparation and analyses of the following solutions have been described previously:[2,13] chromium(II) perchlorate iron(III) perchlorate, sodium azide, perchloric acid, lithium perchlorate, and europium(II) perchlorate. Sodium thiocyanate was prepared from two successive recrystallizations of the reagent grade salt from water. Lithium thiocyanate solution was prepared from sodium thiocyanate by cation exchange using Dowex 50W-X8 resin in the Li^+ form. A flame test revealed that a small concentration of sodium ions remained after the exchange procedure. Thiocyanate solutions were analyzed by passing samples through a column of Dowex 50W-X8 cation-exchange resin in the hydrogen ion form and titrating the protons so released with sodium hydroxide.

Reagent grade potassium cyanate was dried at 65°, stored in a desiccator, and measured by weighing. A sodium cyanate solution was made by adding silver cyanate crystals to an analyzed solution of sodium chloride at *ca.* 0°. Silver chloride and excess silver cyanate were removed by filtration; the number of moles of sodium cyanate in the solution was taken as the number of moles of sodium chloride present initially. The silver cyanate crystals were made from silver nitrate and urea, both recrystallized from the reagent grade compounds, in an aqueous solution at 70–90°. Sodium cyanate was also prepared by titrating a solution of the dry potassium salt with sodium perchlorate at *ca.* 0°, until potassium perchlorate failed to precipitate.

Reagent grade hydrofluoric acid was used without further purification. The water used for kinetic and preparative solutions was redistilled from alkaline permanganate in a tin-lined Barnstead still.

Chromium(III) Product Analysis. The Cr(III) complexes of 2+ ionic charge, which were produced in the oxidation of Cr^{2+} by FeF^{2+} and $FeNCO^{2+}$, were separated from other metal species by the following cation-exchange technique. The reaction products were treated with hydrogen peroxide to oxidize Fe^{2+} and were then taken up on Dowex 50W-X8 resin. The 2+ ions were eluted from the resin with 1 *F* electrolyte. The separation procedure was checked by separating known quantities of independently prepared CrF^{2+} from iron solutions; recovery exceeded 97%, independent of the presence of Cr^{3+}, Fe^{3+}, and Fe^{2+}.

Rate Measurements. All the experiments were carried out in solutions of 1.00 *M* ionic strength; lithium perchlorate was the electrolyte used to maintain ionic strength.

Most of the kinetic measurements utilized the stopped-flow technique, as described previously.[2,13] The rate of substitution of thiocyanate on Fe(III), the rates of reduction of thiocyanatoiron(III), and the rates of reduction of azidoiron(III) were monitored at 4600 Å, where the molar absorptivities of $FeNCS^{2+}$ and FeN_3^{2+} are 4700 and 4400 M^{-1} cm^{-1}, respectively. The rates of reduction of cyanatoiron(III) were measured at 3500 Å, where the molar absorptivities of $FeNCO^{2+}$ and Eu^{2+} are $\sim 2 \times 10^3$ and 4.0×10^2 M^{-1} cm^{-1}, respectively.

The rate of the Cr(II)–Fe(III) reaction was measured at 2400–2600 Å, where $\epsilon(Fe^{3+})$ is 4200–2800 M^{-1} cm^{-1}. The rate of formation and aquation of $FeNCO^{2+}$ was measured with a Cary Model 14 recording spectrophotometer, in a thermostated cell.[14] The wavelength range 3500–3900 Å was employed.

Competition Experiments. The spectrum of FeF^{2+} was not sufficiently different from that of Fe^{3+} to provide a convenient direct measurement of its rates. Studies of some reactions of FeF^{2+} employed FeN_3^{2+} as an "indicator." The rate of reduction of FeF^{2+} by Eu^{2+} was estimated in experiments involving competition between FeF^{2+} and FeN_3^{2+} for an insufficient quantity of Eu^{2+}. The experiments were carried out with the stopped-flow apparatus to measure the fraction of $[FeN_3^{2+}]_0$ that did not react with Eu^{2+}. Azidoiron(III) was the only species in these experiments that absorbed appreciably at 4600 Å, the wavelength used for these measurements.

The equilibrium constant for formation of FeF^{2+} was calculated from measurements of the absorbance at 4600 Å of equilibrium solutions containing Fe(III), HF, and HN_3.

Results and Interpretation

The Cr(II)–Fe(III) Reaction in Perchlorate Solution. The reduction of aquoiron(III) by chromium(II) is represented by reaction I. A kinetic study of this reaction was carried out by Dulz and Sutin[12] at 25.0°, in a $NaClO_4$–$HClO_4$ medium of unit ionic strength.

$$Fe(H_2O)_6^{3+} + Cr(H_2O)_6^{2+} = Fe(H_2O)_6^{2+} + Cr(H_2O)_6^{3+} \quad (I)$$

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[4] B. R. Baker, M. Orhanovic, and N. Sutin, *J. Am. Chem. Soc.*, **89** 722 (1967).

[5] J. H. Espenson, *ibid.*, **89**, 1276 (1967).

[6] H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

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[9] J. Candlin and J. Halpern, *ibid.*, **4**, 1086 (1965).

[10] See, for example, (a) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961); (b) W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discussions Faraday Soc.*, **29**, 49 (1960).

[11] See, for example, (a) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964); (b) J. H. Espenson and O. J. Parker, *ibid.*, **90**, 3689 (1968); (c) J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965). Considerable reliance is placed on the reactivity trends established in instances of known mechanism; see, for example, (d) J. P. Birk and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 1153 (1968); (e) D. L. Ball and E. L. King, *ibid.*, **80**, 1091 (1958); (f) D. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966); (g) J. P. Candlin, J. Halpern, and S. Nakamura, *J. Am. Chem. Soc.*, **85**, 2517 (1963).

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Further studies were carried out in the course of this work to obtain data in a medium where lithium perchlorate was the added electrolyte. The change from one supposedly indifferent cation to another in a medium of the same ionic strength is not necessarily a trivial one, owing to several observations[15-21] of failure of the "constant ionic strength principle." In many instances changes in rate of 10-20% have been realized on replacing Na^+ by Li^+.

Dulz and Sutin[12] reported reaction I followed the rate law shown in eq 1. Their studies revealed that the hydrogen-ion dependence of k' was described by the expression in eq 2. In the present studies we obtained

$$-d[Fe^{3+}]/dt = k'[Fe(III)][Cr^{2+}] \qquad (1)$$

$$k' = k_1 + k_2/[H^+] \qquad (2)$$

good rate plots when the data were treated by an integrated second-order expression. The rate constants are summarized in Table I. The values are different from those obtained in earlier work,[12] but the magnitude of the change does not seem unexpected[15-21] for the change in the supporting electrolyte.

Table I. Rate Constants for the Reaction of Cr^{2+} and Fe^{3+} as a Function of Temperature and $[H^+]$

Temp, °C	$[H^+]$, M	10^5-$[Fe^{3+}]_0$, M	10^4-$[Cr^{2+}]_0$, M	λ, Å	$10^{-4}k'$, M^{-1} sec^{-1} Obsd	Calcd[a]
1.6	0.02857	3.00	6.34	2400	2.92	2.81
1.6	0.0300	2.00	3.41	2400	2.82	2.68
1.6	0.0500	3.00	4.81	2400	1.64	1.63
1.6	0.0700	2.00	3.24	2400	1.10	1.17
1.6	0.100	3.00	8.23	2400	0.794	0.829
1.6	0.500	5.00	15.8	2400	0.179	0.186
1.6	1.00	5.00	16.1	2400	0.108	0.105
15.8	0.0500	2.40	2.60	2500	6.53	6.36
15.8	0.100	3.00	4.55	2400	3.42	3.23
15.8	1.00	7.15	15.3	2600	0.381	0.363
25.0	0.0500	3.00	1.77	2400	13.8	14.3
25.0	0.100	2.40	2.65	2500	7.55	7.30
25.0	0.100	3.00	2.48	2400	7.18	7.30
25.0	1.00	7.5	14.7	2600	0.756	0.792

[a] From the activation parameters summarized in Table II.

The variation of k' with hydrogen ion concentration is illustrated in Figure 1, where linear plots of k' *vs.* $1/[H^+]$ were obtained at each temperature. The small intercepts suggest that the term independent of the hydrogen ion may arise from a medium effect rather than from a genuine reaction pathway.

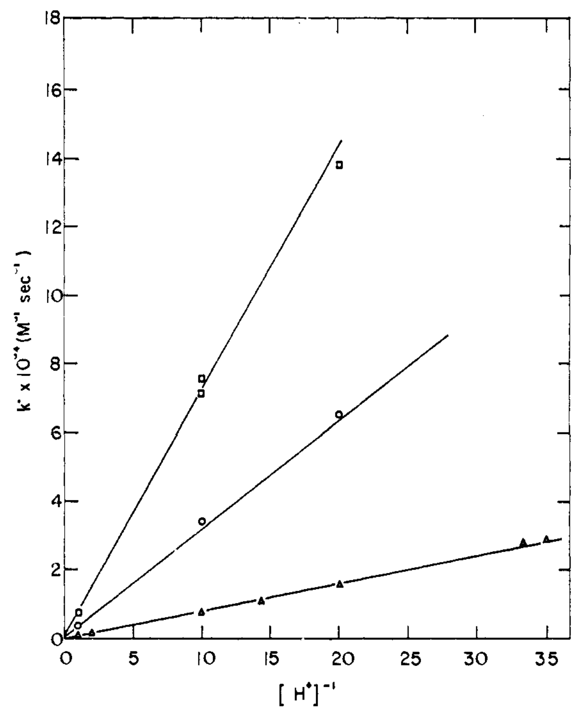

Figure 1. Temperature and hydrogen ion dependence of the rate constant for the reaction of Cr^{2+} and Fe^{3+} in perchlorate solution. The temperatures 1.6, 15.8, and 25.0° are denoted by △, ○, and □, respectively.

Assuming first that both k_1 and k_2 represent genuine reaction pathways, the values were fit to the Eyring relation, thereby deriving $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for each rate constant. This computation was carried out by a simultaneous fitting of the experimental values to the hydrogen-ion dependence of eq 2 and to the temperature dependence of the Eyring equation. The results are presented in Table II. The large standard deviations associated with k_1 reflect its small contribution to the observed rate expression.

Alternatively, one can consider that the small intercepts in Figure 1 arise from activity effects and are not true rate constants. Assuming that the effect of trading Li^+ for H^+ can be represented by a correction in the form suggested by Harned,[22] the data were fit to the following relation.

$$k' = (k_2^0/[H^+]) \exp(\beta[H^+]) \qquad (3)$$

In this relation k_2^0 is an intrinsic rate constant, in effect the value in a medium of $HClO_4 + LiClO_4$ at $\mu = 1.00$ in which all activity coefficients have the same values as in 1 F $LiClO_4$. The parameter β accounts for the different activity coefficients in the two media. A least-squares fit of the data at the three temperatures gives the values k_2^0 (sec^{-1}) = 802 ± 15, 3300 ± 70, and 7170 ± 180 with corresponding values of β = 0.217 ± 0.043, 0.144 ± 0.037, and 0.055 ± 0.050. The two computations will be considered critically in the discussion section, but it should be noted that the specific rate of the term varying as $[H^+]^{-1}$ is comparable in the two treatments.

Table II compares the data obtained in Na^+ and Li^+ media. The conditions of this work and of earlier studies were identical at $[H^+]$ = 1.00 M, 25.0°. In this limit the values of k' are in good agreement, being 7.9 × 10^3 and 7.7 × 10^3 M^{-1} sec^{-1}, respectively. The data in Na^+ medium contain a considerably larger contri-

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Table II. Temperature Dependence of the Rate Constants for Reaction of Cr^{2+} and Fe^{3+} in Perchlorate Solution[a]

	Rate constants 1.6°	15.8°	25.0°	25.0°	$\Delta H^{\ddagger}$,[b] kcal $mole^{-1}$	$\Delta S^{\ddagger}$,[b] eu
k_1, M^{-1} sec^{-1}	250	420	570	2330[c]	5.2 ± 4.4	−28 ± 16
k_2, sec^{-1}	800	3210	7330	5400[c]	14.8 ± 0.3	8.8 ± 0.9
$10^{-6}k_{FeOH}$,[d] M^{-1} sec^{-1}	2.1	3.4	4.4	3.3[c]	4.6 ± 0.6	−13 ± 2

[a] At μ = 1.00 M ($HClO_4$–$LiClO_4$, except as noted). [b] Uncertainties are the standard deviations. [c] $HClO_4$–$NaClO_4$ medium of μ = 1.00 M: ref 12. [d] Calculated as described in the text using values of Q_a given in ref 23.

bution from k_1, with a correspondingly lower value of k_2.

The major rate term, $k_2[Fe^{3+}][Cr^{2+}]/[H^+]$, corresponds to a transition state $[FeOHCr^{4+}]^{\ddagger}$. We shall assume for the moment that the reactants are $FeOH^{2+}$ and Cr^{2+}, which is not, however, the only formulation to be considered. The apparent rate constant k_2 is related to the acid dissociation constant[23] of Fe^{3+} (reaction II) and the second-order rate constant k_{FeOH} for the reaction of $FeOH^{2+}$ and Cr^{2+}; the expression is $k_2 = Q_ak_{FeOH}$. Values of k_{FeOH} are also presented in Table II, along with activation parameters corresponding to this formulation.

$$Fe(H_2O)_6^{3+} = (H_2O)_5FeOH^{2+} + H^+ \quad (Q_a) \qquad (II)$$

Reactions of $(H_2O)_5FeN_3^{2+}$. Equilibrium and rate studies for reaction III at 25.0° have been published.[13] A value of the equilibrium quotient at 1.6° was needed

$$Fe(H_2O)_6^{3+} + HN_3 = (H_2O)_5FeN_3^{2+} + H^+ \quad (Q_{N_3}) \qquad (III)$$

in order to compute concentrations of the azido complex in solutions at the start of a rate run. The absorbance of a solution 8.13 × 10^{-3} F Fe(III), 0.0208 F HN_3, and 0.790 F $HClO_4$ at μ = 1.00 M and 1.4° was 1.692 at 4600 Å for an optical path of 5.00 cm. On the assumption that the molar absorptivity of FeN_3^{2+} is the same as at 25.0°, 4.4 × 10^3 M^{-1} cm^{-1},[13] the value is Q_{N_3} = 0.36 at 1.6°.

Experiments to measure k_{FeN_3} for oxidation of Eu^{2+} by FeN_3^{2+} (reaction IV) were accomplished by mixing a Eu^{2+} solution with a solution containing FeN_3^{2+}, Fe^{3+},

$$FeN_3^{2+} + Eu^{2+} + H^+ = Fe^{2+} + Eu^{3+} + HN_3 \qquad (IV)$$

and HN_3, at equilibrium. The disappearance of FeN_3^{2+} was attributed to reaction IV according to the rate law shown in eq 4, since reaction III is virtually frozen in the time of this measurement.

$$-d[FeN_3^{2+}]/dt = k_{FeN_3}[FeN_3^{2+}][Eu^{2+}] \qquad (4)$$

The value of k_{FeN_3} was near the limit of stopped-flow measurability, leading to scatter in the results, which are listed in Table III. The initial concentration of Eu^{2+} was not varied sufficiently to confirm the second-order rate law, but the data are consistent with such an expression and have been so interpreted. Comparison of the result of the first experiment in Table III to the others indicates that k_{FeN_3} is not noticeably dependent upon $[H^+]$ in the range 0.050–0.65 M.

Table III. Kinetic Data for the Reaction of Eu^{2+} with FeN_3^{2+} at 1.6° and μ = 1.00 M

10^5-$[Eu^{2+}]_0$, M	10^5-$[FeN_3^{2+}]_0$,[a] M	10^5-$[Fe(III)]_0$, M	$[H^+]$, M	$10^{-7}k_{FeN_3}$, M^{-1} sec^{-1}
3.17	0.96	11.5	0.050	1.1
4.52	1.92	25.7	0.613	0.91
2.60	0.96	5.25	0.650	1.8
3.10	0.96	16.8	0.650	1.2
3.67	1.92	12.5	0.650	0.85
			Av	1.2 ± 0.3

[a] Calculated, using Q_{N_3} = 0.364.

Haim and Sutin[24] reported that k_{FeN_3} for the reaction of Cr^{2+} and FeN_3^{2+} is too high for measurement by stopped-flow methods and set a limit ≥2 × 10^7 M^{-1} sec^{-1} at 25°. A more recent study[24b] gave the value 2.9 × 10^7 at 25.0°, established by a competition method with $FeCl^{2+}$ rather than by direct measurement. Only a lower limit of 2 × 10^7 M^{-1} sec^{-1} was established by our attempts at a direct measurement at 1.6° in an experiment with $[Cr^{2+}]_0$ = 2.66 × 10^{-5}, $[FeN_3^{2+}]_0$ = 1.44 × 10^{-5}, and $[H^+]$ = 1.0 M; the reaction was complete before the first observation at *ca.* 0.004 sec after mixing.

Reactions of $(H_2O)_5FeNCS^{2+}$. The stability constant for formation of $FeNCS^{2+}$ in reaction V was needed for the studies of its reduction. The absorbances of Fe(III)–NCS^- solutions were measured under the desired con-

$$Fe(H_2O)_6^{3+} + NCS^- = (H_2O)_5FeNCS^{2+} + H_2O \quad (Q_{NCS}) \qquad (V)$$

ditions, and the equilibrium quotients computed using the molar absorptivity of Lister and Rivington.[25] The values are Q_{NCS} = 216, 163, and 138 M^{-1} at 1.6, 15.8, and 25.0°, respectively.[26–29]

Attempts were made to measure the third-order rate constant k_{NCS} for the pathway involving Eu(III), Fe(III), and thiocyanate ions. It was immeasurably small,[26] the total rate being accounted for within the precision of the measurements by the reaction of the aquo ions[2] or by the formation of the inner complex $FeNCS^{2+}$ and its subsequent rapid reduction.

The latter process, represented by reaction VI, was the subject of an independent rate study. Solutions of Fe(III) containing thiocyanate ion were mixed with so-

$$FeNCS^{2+} + Eu^{2+} = Fe^{2+} + Eu^{3+} + SCN^- \qquad (VI)$$

lutions of Eu^{2+}, and the rate of disappearance of

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(23) R. M. Milburn, *J. Am. Chem. Soc.*, **79**, 537 (1957).

(24) (a) A. Haim and Sutin, *ibid.*, **87**, 4210 (1965); (b) M. Orhanović and N. Sutin, *ibid.*, **90**, 4286 (1968).

(25) M. W. Lister and D. E. Rivington, *Can. J. Chem.*, **33**, 1572 (1955).

(26) The original data are given in ref 1b.

(27) The values of Q_{NCS} lead to $\Delta H°$ = −3.1 kcal $mole^{-1}$ for reaction V. This is not in particularly good agreement with earlier results[25,28,29] of −1.5 to 0.8 kcal $mole^{-1}$ although the latter refer to studies using $NaClO_4$ as the added electrolyte at ionic strengths other than 1 M.

(28) G. S. Laurence, *Trans. Faraday Soc.*, **52**, 236 (1956).

(29) R. H. Betts and F. S. Dainton, *J. Am. Chem. Soc.*, **75**, 5721 (1953).

$FeNCS^{2+}$ was measured. The initial concentrations were varied by factors of 27, 10, and 20 for Eu^{2+}, $FeNCS^{2+}$ and H^+, respectively. One experiment was done with $[FeNCS^{2+}] > [Eu^{2+}]$; the others were done with $[FeNCS^{2+}] < [Eu^{2+}]$. The rate behavior was described by eq 5 throughout these concentration variations. The results of the measurements are presented in Table IV.

$$-\mathrm{d}[\mathrm{FeNCS}^{2+}]/\mathrm{d}t = k_{\mathrm{FeNCS}}[\mathrm{FeNCS}^{2+}][\mathrm{Eu}^{2+}] \quad (5)$$

Table IV. Kinetic Data for the Reaction of Eu^{2+} with $FeNCS^{2+}$ [a]

Temp, °C	10^5-$[Eu^{2+}]_0$, M	10^5-$[FeNCS^{2+}]$, M	10^5-$[Fe(III)]$, M	10^3-$[NCS^-]$, M	$10^{-5}k_{FeNCS}$, M^{-1} sec^{-1}
1.6	9.50	1.2	3.05	0.750	3.1[b]
1.6	5.75	0.75	2.50	1.00	2.9[c]
1.6	0.5	7.5	30.5	0.750	3.1
1.6	4.02	1.2	2.25	3.00	3.8
1.6	4.77	0.95	2.50	1.50	3.5
1.6	8.28	0.47	1.91	0.750	2.5
1.6	13.5	4.7	19.1	0.750	3.0
15.8	3.28	0.85	4.28	0.750	5.2
15.8	3.28	1.0	5.35	0.750	4.9
15.8	5.55	1.0	5.35	0.750	5.4
15.8	6.10	0.85	4.28	0.750	4.4
25.0	4.57	0.76	4.40	0.750	6.5
25.0	5.10	1.1	6.30	0.750	6.5
25.0	9.55	1.1	3.18	1.50	5.6
25.0	4.78	1.5	8.80	0.750	6.5

[a] At $\mu = 1.00$ M, $[H^+] = 1.00$ M, except as noted. [b] $[H^+] = 0.050$. [c] $[H^+] = 0.100$ M.

The observed second-order rate constant at 1.6° was not dependent on $[H^+]$ in the range 0.050–1.00 M. Activation parameters, computed from the data using a least-squares computer program, are $\Delta H^{\ddagger} = 4.4 \pm 0.4$ kcal mole^{-1} and $\Delta S^{\ddagger} = -17.3 \pm 1.5$ eu.

It has been reported[24a] that k_{FeNCS} for the reaction between Cr^{2+} and $FeNCS^{2+}$ is $\geq 2 \times 10^7$ M^{-1} sec^{-1} at 25°, but the value 2.8×10^7 has more recently been claimed indirectly.[24b] The value for k_{FeNCS} was found to be $\geq 2 \times 10^7$ M^{-1} sec^{-1} in this study at 1.6°.

Reactions of $(H_2O)_5FeF^{2+}$. The formation of the monofluoroiron(III) cation is represented by reaction VII. The numerical value of Q_F under the conditions of this study was required for the design of experiments

$$\mathrm{Fe(H_2O)_6}^{3+} + \mathrm{HF} = \mathrm{(H_2O)_5FeF}^{2+} + \mathrm{H}^+ + \mathrm{H_2O} \quad (Q_F) \quad \text{(VII)}$$

to measure the rate of reduction of FeF^{2+}. Since the spectrum of FeF^{2+} is similar to that of Fe^{3+}, a measurement procedure using the absorbance of FeN_3^{2+} in Fe(III), HN_3, and HF solutions was devised. Absorbances were measured at 4600 Å, where only FeN_3^{2+} absorbs. Complexation of Fe(III) by HF caused the measured absorbance to be lower than if HN_3 were the only complexing agent. The concentrations of FeN_3^{2+} were computed from measured absorbances, and the concentrations of Fe^{3+} were calculated from the known equilibrium quotient Q_{N_3}. The concentration of FeF^{2+} was calculated by difference. A small correction for FeF_2^+ was made ($Q_2 = [FeF_2^+][H^+]/[FeF^{2+}][HF] = 12.6$[30] at 1.6°). The value[26] is $Q_F = 166 \pm 4$, which can be compared with the value of 202 at 1.6°, 0.50 M ionic strength ($NaClO_4$), extrapolated from the data of Connick, *et al.*[30]

No evidence was found for a fluoride-catalyzed pathway for reduction of Fe(III) by Eu(II) other than that involving the inner complex FeF^{2+}. In an experiment at 1.6° with the initial concentrations Eu(II) = 29.6×10^{-4} F, Fe(III) = 2.20×10^{-4} F, HF = 0.050 F, and $H^+ = 1.00$ M, the Fe(III) not being in contact with HF until the moment of mixing, the observed rate constant was 5.68×10^3 M^{-1} sec^{-1}, which is the same as the value in perchlorate solution.[2]

The reduction of FeF^{2+} by Eu^{2+} is represented by reaction VIII, and its rate was too high to measure by the direct procedure employed for other complexes, owing largely to the small differences in molar absorptivities.

$$\mathrm{FeF}^{2+} + \mathrm{Eu}^{2+} + \mathrm{H}^+ = \mathrm{Fe}^{2+} + \mathrm{Eu}^{3+} + \mathrm{HF} \quad \text{(VIII)}$$

The competition procedure described in the Experimental Section was used to evaluate k_f at 1.6°. The expression given in eq 6 describes the rate of change

$$\frac{\mathrm{d}[\mathrm{FeN_3}^{2+}]}{\mathrm{d}[\mathrm{FeF}^{2+}]} = \frac{k_{\mathrm{FeN_3}}[\mathrm{FeN_3}^{2+}]}{k_{\mathrm{FeF}}[\mathrm{FeF}^{2+}]} \quad (6)$$

of one complex with respect to the other in the presence of Eu^{2+}, assuming a second-order expression for each. This equation was integrated with the result given by eq 7, where the subscript x denotes concentrations immediately after all the Eu(II) has been oxidized, but before the Fe(III) complexes appreciably change in concentration from subsequent aquation or re-formation.

$$k_{\mathrm{FeF}} = k_{\mathrm{FeN_3}}\{\ln([\mathrm{FeF}^{2+}]_0/[\mathrm{FeF}^{2+}]_x)/\ln([\mathrm{FeN_3}^{2+}]_0/[\mathrm{FeN_3}^{2+}]_x)\} \quad (7)$$

The concentration of the azido complex was established from the oscilloscope deflection upon mixing, and that of the fluoro complex established from the mass balance relation

$$[\mathrm{FeF}^{2+}]_x = [\mathrm{FeF}^{2+}]_0 + [\mathrm{FeN_3}^{2+}]_0 - [\mathrm{Eu}^{2+}]_0 - [\mathrm{FeN_3}^{2+}]_x$$

The data are given in Table V and lead to the value $k_{FeF} = 1.9 \pm 0.3 \times 10^7$ M^{-1} sec^{-1} at 1.6°, $\mu = 1.00$ M. A single experiment at $[H^+] = 0.15$ indicated there was no large effect of hydrogen ion variation, although the low precision obtained for this very fast reaction really leaves that question open.

Table V. The Competitive Oxidation of Eu^{2+} by FeF^{2+} and FeN_3^{2+} [a]

10^5-$[Eu^{2+}]_0$, M	10^5-$[FeF^{2+}]_0$, M	10^5-$[FeN_3^{2+}]_x$, M	10^5-$[FeF^{2+}]_x$, M	$10^{-7}k_{FeF}$,[b] M^{-1} sec^{-1}
6.05	7.58	1.82	3.35	1.4[c]
2.43	3.35	2.73	1.83	2.5
2.84	1.69	1.82	0.67	1.6
3.35	3.35	2.23	1.41	2.1
6.13	6.75	1.82	2.44	1.8
			Av	1.9 ± 0.3

[a] Conditions: 1.6°, $\mu = 1.00$ M, $[H^+] = 0.50$ M, except as noted, with $[FeN_3^{2+}]_0 = 3.64 \times 10^{-5}$ M. [b] Computed according to eq 7, using $k_{FeN_3} = 1.2 \times 10^7$ M^{-1} sec^{-1}. [c] $[H^+] = 0.15$ M.

The reduction of FeF^{2+} by Cr^{2+}, reaction IX, was con-

$$\mathrm{FeF}^{2+} + \mathrm{Cr}^{2+} = \mathrm{Fe}^{2+} + \mathrm{CrF}^{2+} \quad \text{(IX)}$$

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(30) R. E. Connick, L. G. Hepler, Z Z. Hugus, J. W. Kury, W. M. Latimer, and M. S. Tsao, *J. Am. Chem. Soc.*, 78, 1827 (1956).

siderably slower than that by Eu^{2+}, and it could be studied directly. The initial concentrations of Cr^{2+}, FeF^{2+}, and H^+ were varied by factors of 3, 3, and 10, respectively. The results are summarized in Table VI, and lead to a value $k_{FeF} = 7.6 \pm 1.1 \times 10^5\ M^{-1}\ sec^{-1}$ at 1.6°, $\mu = 1.00\ M$, apparently independent of $[H^+]$.

Table VI. Kinetic Data for the Reaction of Cr^{2+} with FeF^{2+} at 1.6°, $\mu = 1.00\ M$

10^5-$[Cr^{2+}]_0$, M	10^5-$[FeF^{2+}]_0$, M	10^5-$[Fe(III)]_0$, M	$[H^+]_0$, M	$10^{-5}k_{FeF}$, $M^{-1}\ sec^{-1}$
6.66	2.55	10.4	0.10	8.7[a]
6.40	3.50	10.4	0.985	5.5
6.24	2.55	10.4	1.00	7.0
5.42	7.00	12.3	1.00	7.4
5.20	3.00	5.26	1.00	6.2
5.20	2.55	10.4	1.00	9.0
3.63	3.50	6.15	1.00	7.7[b]
2.12	5.35	13.5	1.00	9.3
			Av	7.6 ± 1.1

[a] Estimated from initial rates, using an estimate for D_∞; the uncatalyzed reduction of Fe(III) interfered. [b] The rate constant was evaluated assuming $[Cr^{2+}]_0 = [FeF^{2+}]_0 = 3.56 \times 10^{-5}\ M$.

The product of the reaction of Cr^{2+} and FeF^{2+} was proved to be CrF^{2+}, as written in reaction IX, by ion-exchange procedures. An experiment was performed with $[FeF^{2+}] = 0.00400$, $[Cr^{2+}] = 0.00296$, $[Fe^{3+}] = 0.00362$, $[H^+] = 0.65\ M$, $\mu = 1.00$ at 1.6°. The ion-exchange separation yielded CrF^{2+}, identified by its known[31] visible spectrum; 0.219 mmole of CrF^{2+} was obtained from 0.222 mmole of Cr^{2+}, for a 98.5% yield. The expected yield, assuming reaction IX occurred quantitatively as written, was 99.4%, in good agreement with the observed.

Reactions of $(H_2O)_5FeNCO^{2+}$. A complexation reaction first occurred when solutions of Fe^{3+} and HNCO were mixed, as given by reaction X, which illustrates the similarity of cyanate, azide, and thiocyanate ions. The complexes of $-NCO^-$ have been little studied, however, owing to the decomposition of HNCO to NH_4^+ and CO_2 which is especially pronounced at high acidity. This decomposition complicates a study of the kinetics and equilibrium of reaction X, since the total cyanate concentration decreases with time. Conditions were chosen to minimize the effect of the decomposition, and which did not require using the cyanate concentration in the computations.

$$Fe(H_2O)_6^{3+} + HNCO = (H_2O)_5FeNCO^{2+} + H_2O + H^+ \quad (Q_{NCO}) \quad (X)$$

The rate of approach to equilibrium in reaction X occurs sufficiently slowly that it was studied by conventional spectrophotometry. The studies described here were carried out at 2° under conditions of low $[H^+]$, low total cyanate, and high and varying Fe(III) concentrations. The experiments were done by adding perchloric acid to an equilibrium mixture (dilution), or by adding NaNCO to an Fe(III) solution (mixing), and recording the absorbance changes arising from net aquation or formation of $FeNCO^{2+}$. The absorbance changes did not appear to represent only pseudo-first-order processes; the absorbance continued to decrease slowly after the principal absorbance increase or decrease was over. The decrease, presumably due to hydrolysis of HNCO, was assumed to be a uniform component of all the observed changes; after correction for it, satisfactory first-order plots were obtained. The pseudo-first-order rate constants so computed are listed in Table VII. A plot of k_{obsd} *vs.* $[Fe^{3+}]/[H^+]$ was linear within experimental error, suggesting the rate expression[32] in eq 8 with the values $k_f = 0.60\ sec^{-1}$ and $k_{aq} = 0.051\ sec^{-1}$ at 2.0° and $\mu = 1.00\ M$. These results give an equilibrium quotient[33] $Q_{NCO} = 11.8$, and a molar absorptivity of $FeNCO^{2+}$ of $2 \times 10^3\ M^{-1}\ cm^{-1}$ at 3500 Å, a maximum.

$$d[FeNCO^{2+}]/dt = k_f[Fe^{3+}][HNCO]/[H^+] - k_{aq}[FeNCO^{2+}] \quad (8)$$

Table VII. Rate Constants for the $FeNCO^{2+}$ Substitution Reaction at 2.0° and $\mu = 1.00\ M$

		k,[b] sec^{-1}	
$10^3[Fe^{3+}]$,[a] M	$[H^+]$, M	Obsd	Calcd[c]
2.11	0.0218	0.131	0.109
4.01	0.0261	0.125	0.143
3.96	0.104	0.074	0.074
7.18	0.104	0.086	0.093
10.8	0.104	0.117	0.113
2.11	0.131	0.069	0.061
1.06	0.133	0.052	0.056
2.12	0.133	0.057	0.061

[a] C_{HNCO} was *ca.* $9 \times 10^{-5}\ M$ throughout. [b] This is the pseudo-first-order rate constant for the rate of approach to equilibrium. [c] The values are those computed from eq 8 using the values of k_f and k_{aq} given in the text.

Kinetic studies were carried out on the reduction of $FeNCO^{2+}$ by Eu^{2+} and by Cr^{2+}. The second-order rate constant for Eu^{2+} is[26] $10^{-6}k_{FeNCO}$ $(M^{-1}\ sec^{-1}) = 1.59 \pm 0.06$ (five runs) at 1.6°, $\mu = 1.00\ M$. The rate constant did not vary appreciably over the range $0.05 \leq [H^+] \leq 0.5\ M$.

The rate constants for the reaction of Cr^{2+} and $FeNCO^{2+}$ at various temperatures are as follows: 1.6°, $10^{-5}k_{FeNCO}$ $(M^{-1}\ sec^{-1}) = 4.4 \pm 0.4$; 15.8°, 5.8 ± 0.4; 20.0°, 5.9; and 25.0°, 7.2 ± 0.9. These values give $\Delta H^{\ddagger} = 2.9 \pm 0.7$ kcal mole^{-1} and $\Delta S^{\ddagger} = -22 \pm 63$ eu. The rate constant at 1.6° did not vary noticeably over the region $0.05 \leq [H^+] \leq 0.5\ M$. The stoichiometry of the Cr^{2+} reaction was examined since it offered the possibility[11d,34-36] that the linkage isomer $Cr-OCN^{2+}$ rather than $Cr-NCO^{2+}$ was produced. The product solution was passed through a column of Dowex 50W-X8 resin in the Na^+ form, and ions of charge $^{2+}$ were then eluted from the resin with 1 F $LiClO_4$ and 0.02 F $HClO_4$.

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(31) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 527 (1965).

(32) The derivation of this equation and the method of treating the experimental data for a similar situation can be found in ref 13.

(33) The value $Q = 11.8$ is in poor agreement with the result of A. Lodzinska [*Roczniki Chem.*, 40, 1369 (1966)], who gave $[Fe^{3+}] \cdot [NCO^-]/[FeNCO^{2+}] = 7 \times 10^{-3}\ M$ at $\mu = 0.7\ M$. Our data expressed in this manner give $2.5 \times 10^{-5}\ M$; the cause for the discrepancy is not known, but it may lie in possible changes during the longer times needed for the direct equilibrium experiments.

(34) J. P. Birk and J. H. Espenson, *J. Am. Chem. Soc.*, 87, 3280 (1965).

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

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

The freshly eluted product (A) was not stable; the visible–ultraviolet spectrum changed with time in a first-order process catalyzed by Cr^{2+} and by H^+; the product (B) of this reaction was not eluted from a resin column by 1 *F* electrolyte and presumably had an ionic charge of 3+ (or higher). Both products had spectra characteristic of Cr(III) complexes, with maxima at 5780 Å (ϵ 21.0) and 4010 (20.0) for A and 5720 (18.7) and 4110 (18.3) for B. Material B undergoes still further small spectral changes that occur quite slowly and were still occurring after 1 week at room temperature forming a third product (C) which appears to be $Cr(H_2O)_6^{3+}$.

Interpretation and Discussion

The Fe^{3+}–Cr^{2+} Reaction. This reaction proceeds chiefly by a pathway with the transition state $[FeOHCr^{4+}]^{\ddagger}$. If one assumes that the reaction of $FeOH^{2+}$ and Cr^{2+} is responsible, a second-order rate constant can be computed, as shown in Table II. The arguments we advance in favor of this formulation are as follows. If one considers the alternative pathway $CrOH^+ + Fe^{3+}$ the rate constant so calculated[37] is 7×10^9 M^{-1} sec^{-1} at 25.0°. If it is assumed that hydroxide ion is a bridging ligand, this rate constant is not reasonable since it greatly exceeds the substitution rate of $Fe(H_2O)_6^{3+}$, the latter being ~2–127 M^{-1} sec^{-1} for anionic nucleophiles.[13,38] Were the assumption of an inner-sphere mechanism removed, the process becomes analogous to the third order reaction $Fe(H_2O)_6^{3+} + Cl^- + M^{2+}$ (with $M^{2+} = Eu^{2+}$ [2] and Cr^{2+}[12]). Regardless of whether the latter processes are formulated as $Fe(H_2O)_6^{3+} \cdot X^- + M^{2+}$ or as $Fe(H_2O)_6^{3+} + MX^+$, the reactivity of hydroxide ion in this capacity appears unreasonably large compared to chloride ion.

We conclude that the most plausible rate-determining step is the reaction of $FeOH^{2+}$ and Cr^{2+}, and that the analogy to the $FeX^{2+} + Cr^{2+}$ reactions is valid, perhaps even to the conclusion that OH^- functions as a bridging ligand. The reactivity of OH^- as a bridging ligand is known[2,4,11b,13,39–42] to be comparable to that of Cl^-; their similarity of rates when the present reaction is interpreted on this basis supports our contention that an inner-sphere mechanism operates.

The acid-independent rate constant decreased by a factor of 4 when $LiClO_4$ rather than $NaClO_4$ was used to maintain ionic strength. The large rate change accompanying the replacement of one supposedly inert electrolyte by another suggests that changes in activity coefficients constitute the major, and perhaps the only, contribution to the observed intercepts in plots of k *vs.* $1/[H^+]$. The values of β obtained on the assumption that activity effects can be correlated by the Harned relation, and account for the entire effect, are sufficiently small to support this contention.

It should be noted that the details of the major path are not significantly altered by the model chosen for the acid-independent term. The computed entropy of the transition state $[Fe(OH)Cr^{4+}]^{\ddagger}$ is −62 eu, which is reasonable[43] considering the value of −70 for the analogous case with Eu^{2+}.[2]

Reactions of $(H_2O)_5FeX^{2+}$ with Cr^{2+} and Eu^{2+}. The second-order rate constants for the reactions studied are summarized in Table VIII, which includes data on $FeBr^{2+}$.[44] Perhaps the most striking feature of these data is the reversal in the reactivity pattern of the halide complexes toward Cr^{2+} and Eu^{2+}. The reactivity order of Cr^{2+} (Br > Cl > F) parallels that for the reductions of $(NH_3)_5CoX^{2+}$,[45] $(NH_3)CrX^{2+}$,[46] and $(H_2O)_5CrX^{2+}$ [11e] by Cr^{2+} and for the first of these oxidizing agents by V^{2+} [11e] and $Co(CN)_5^{3-}$ [11g] as well; this has been termed by Sutin[3a] the "normal" reactivity order. The reactions of $(H_2O)_5FeX^{2+}$ and Eu^{2+} follow an "inverted" order (F > Cl > Br), as do the rates of the reductions of $(NH_3)_5CoX^{2+}$ by Eu^{2+} [11a] and Fe^{2+}.[11c] As pointed out by Haim,[47] one would expect that fluoride ion would provide the most stable transition state (relative to other transition states, but not necessarily relative to the reactants) for class a or hard metal ions, and the available rates and thermodynamic data indicate this is the case.[47]

Table VIII. Summary of Rate Constants for the Reactions of $(H_2O)_5FeX^{2+}$ with Cr^{2+} and Eu^{2+}

$(H_2O)_5FeX^{2+}$ X =	k, M^{-1} sec^{-1} [a] Cr^{2+}	Eu^{2+}
OH	2.1×10^6	6.0×10^6
F	7.6×10^5	1.9×10^7
Cl	1×10^7 [b,c]	2.0×10^6
Br	$\geq 2 \times 10^7$ [d]	1.4×10^6 [d]
–NCS	2.8×10^7 [b,e]	3.2×10^5
N_3	2.9×10^7 [b,e]	1.2×10^7
–NCO	4.4×10^5	1.6×10^6

[a] At 1.6°, μ = 1.00 *M* ($LiClO_4$), except as noted. [b] 25.0°, μ = 1.00 *M* ($NaClO_4$). [c] Reference 12. [d] Reference 44. [e] Reference 24b.

The point remains, however, that different patterns of reactivity emerge despite the parallel stabilities of one transition state relative to another. Scheme I[48] illustrates the schematic free-energy profiles. On this basis the effect of changing the bridging halide ion on the Eu^{2+} reduction rates arises from a larger stabilization by F than by Br in the transition states than in the FeX^{2+} reactants, whereas the relative stabilization effects are reversed for Cr^{2+}. One must thus account for why the halides affect the transition states containing Eu more than those containing Cr.

The difference may arise from the greater substitution lability of Eu^{3+} and Eu^{2+} compared to first-row transition metal ions of the same ionic charges,[49] which largely determines the position of bond breaking in the inner-

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(37) The second-order rate constant for $CrOH^+ + Fe^{3+}$ is given as the quotient of the observed rate constant k_2 and the acid dissociation quotient of Cr^{2+}, the latter being *ca.* 10^{-6} *M*.

(38) D. Seewald and N. Sutin, *Inorg. Chem.*, **2**, 643 (1963).

(39) K. Shaw and J. H. Espenson, *ibid.*, **7**, 1619 (1968).

(40) T. W. Newton, G. E. McCrary, and W. G. Clark, *J. Phys. Chem.*, **72**, 4333 (1968).

(41) P. Dodel and H. Taube, *Z. Physik. Chem.* (Frankfurt), **44**, 92 (1965).

(42) M. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(43) T. W. Newton and F. B. Baker, Advances in Chemistry Series, No. 71, American Chemical Society, Washington, D. C., 1968, p 268.

(44) The reactions of $FeBr^{2+}$ will be published separately.

(45) J. P. Candlin and J. Halpern, *Inorg. Chem.*, **4**, 766 (1965).

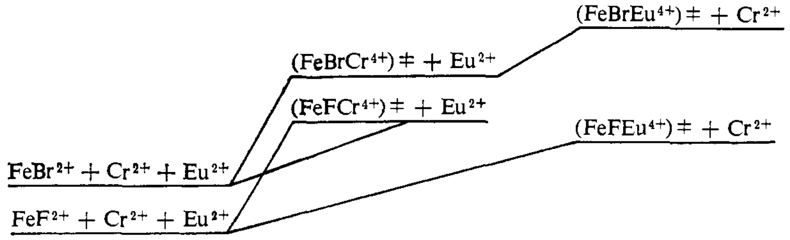
(46) A. E. Ogard and H. Taube, *J. Am. Chem. Soc.*, **80**, 1084 (1958).

(47) A. Haim, *Inorg. Chem.*, **7**, 1475 (1968).

(48) The authors are grateful to a referee for suggesting the use of the free energy profile as depicted.

(49) M. Eigen, *Rev. Pure Appl. Chem.*, **6**, 105 (1963).

Scheme I



sphere transition state subsequent to electron transfer.[50] Assuming inner-sphere mechanisms in the present cases, the configurations after electron transfer are Fe^{II}–X–Cr^{III} and Fe^{II}–X–Eu^{III}. In the first of these, breaking of the Fe^{II}–X bond occurs, and Cr^{III}–X^{2+} results. The position of bond breaking in the second instance we presume is also decided by the relative substitution rates, making Eu^{III}–X bond breaking the more probable fate of this transition state. The energy differences cited above for the two transition states can be rationalized on this basis.[51] The Fe–X bond in the Cr^{II} reactions lengthens prior to its being broken, thus narrowing the energetic difference between F and Br. The high reaction rates suggest that the transition states resemble the reactants more than the products, and thus the incipient Cr–X bonds do not compensate the effect of Fe–X bond breaking. On the other hand, in the transition states $(FeXEu^{4+})^{\ddagger}$ the effect of the FeX bond (which is to be retained) is *not* lessened as it was for Cr^{2+} *aud may perhaps increase* owing to a lesser discrimination of F over Br for Fe^{2+} compared to Fe^{3+}.

For slower reactions, *e.g.*, $(NH_3)_5CoX^{2+} + Fe^{2+}$,[11c] the inverted reactivity pattern owes its origin to other causes, and an explanation might be sought in the stabilities of transition states resembling the products. The high rate for fluoride is understood on this basis as originating in the stability of FeF^{2+}, the primary product of an inner-sphere reaction.

The rate of water exchange of $V(H_2O)_6^{2+}$ limits the rate of inner-sphere electron transfer,[4–6] these rates being clustered near the solvent exchange rate. The same factor may operate in the very fast reactions of Cr^{2+}, such as those with FeX^{2+}, and may account for the grouping of rate constants at the higher values,[3b,24b] particularly the remarkably small difference between FeN_3^{2+} and $FeNCS^{2+}$.

The recent review of Sutin[3b] has pointed out the effect of intrinsic and thermodynamic contributions to the rate of electron transfer. The trends in reactivity reflected in the observed rate constants contain contributions from factors of both types, and the factors do not necessarily complement one another.

Reactions of $FeNCO^{2+}$. Our studies on this complex are quite limited. Throughout, the decomposition of cyanic acid introduced complications in the experiments and their interpretation. We offer the following interpretation for our findings, admitting that additional studies are needed.

The single transition state for the substitution reaction is $(FeNCO^{2+})^{\ddagger}$. As was the case in the reaction of Fe(III) and hydrazoic acid,[13,38] the question of whether the mechanism involves $Fe^{3+} + NCO^-$ or $FeOH^{2+} + HNCO$ cannot be answered rigorously from kinetic data. Following the same line of argument presented in the work on FeN_3^{2+}, the second-order rate constants (M^{-1} sec^{-1}) at 1.6° by each formulation are computed to be 2.1×10^3 and 1.6×10^3, respectively. Extrapolated to 25° using $\Delta H^{\ddagger} = 20.2$ kcal for the first mechanism (this is the value of $\Delta H^{\ddagger}$ for $Fe^{3+} + NCS^-$) and 16.7 kcal for the second (the value of $\Delta H^{\ddagger}$ for $FeOH^{2+} + HN_3$), these rate constants become 4×10^4 and 2×10^4 M^{-1} sec^{-1}. The first clearly lies outside the range (2–127 M^{-1} sec^{-1}) for substitution on Fe^{3+}, whereas the second agrees quite closely with that expected for displacement of a coordinated water molecule in $(H_2O)_5FeOH^{2+}$. These arguments parallel those[13,38] in the Fe(III)–azide case, as do the conclusions, and will not be considered further here. On the basis of the obvious mechanistic and spectral similarities of the cyanate complex to FeN_3^{2+} and $FeNCS^{2+}$, we propose the ligand is N-bonded, but no direct structure proof can be cited.

The immediate species upon reaction of $FeNCO^{2+}$ and Cr^{2+} (designated A above) is apparently the cyanate complex of Cr(III). The question of whether it is Cr–NCO^{2+} or Cr–OCN^{2+} or a mixture of the two has not been settled; indeed, the presumed existence of a linkage isomerism phenomenon was not confirmed. By analogy with the chemistry of the $Co(NH_3)_5OH_2^{3+}$–HNCO system,[52] the subsequent spectral changes could arise from carbamate formation of the O-bonded complex to give a chelated complex $CrO_2CNH_3^{3+}$ (species B). The reaction sequence would then be completed by hydrolysis of the ligand resulting in CO_2, NH_4^+, and $Cr(H_2O)_6^{3+}$ (C).

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(50) This possibility was recognized in the early work on inner-sphere reactions: H. Taube and H. Myers, *J. Am. Chem. Soc.*, 76, 2103 (1954).

(51) It is helpful to consider an inner-sphere reaction as consisting of three steps: ligand reorganization of reactants, electron transfer, and ligand reorganization of products. The points we are making rely on the presumption that the reorganizations needed to equalize energies for electron transfer reflect the subsequent fate of the transition state, *i.e.*, that bond breaking may play an important role.

(52) A. M. Sargeson and H. Taube, *Inorg. Chem.*, 5, 1094 (1966).