energies in both the M(*trans*[14]diene)$^{n+}$ and the M(teta)$^{n+}$ complexes. The relatively low molar absorptivity of the ligand→metal transitions in Cu(teta)$^{2+}$ [7,21] and Cu(*trans*[14]diene)$^{2+}$ (where this transition appears to be mixed with a metal→ligand transition) complexes is to be noted.

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Reactions Involving Copper(I) in Perchlorate Solution. A Kinetic Study of the Reduction of Iron(III) by Copper(I)[1]

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Rate studies were carried out on the oxidation–reduction reaction of iron(III) and copper(I) ions in perchlorate solutions which produces quantitative yields of iron(II) and copper(II). The rate law is first order in each metal ion, with an inverse dependence on hydrogen ion concentration. The values (sec^{-1} × 10^{-4}, μ = 1.00 *M*) are 2.48 ± 0.11 (1.6°), 7.67 ± 0.38 (15.8°), and 16.1 ± 0.3 (25.0°), with activation parameters $\Delta H^{\ddagger}$ = 12.4 ± 0.2 kcal/mol and $\Delta S^{\ddagger}$ = 6.7 ± 0.7 eu. The reactions of FeN_3^{2+} and FeF^{2+} with Cu^+ are immeasurably rapid by the techniques used, the lower limits at 1.6° and at μ = 1.00 *M* being 10^8 and 5 × 10^6 M^{-1} sec^{-1}, respectively. The mechanism is discussed in comparison with related reactions, and it is concluded that an inner sphere process is probably involved.

Introduction

The reaction of iron(III) and copper(I) has not been studied previously. The reaction occurring in acidic perchlorate solution is that shown by

$$Fe^{3+} + Cu^{+} = Fe^{2+} + Cu^{2+} \qquad \text{(I)}$$

Recent studies[2-6] have concerned the preparation and reactions of the metastable Cu^+ ion. Reduction of Cu^{2+} with an insufficient quantity of strong 1-equiv reducing agents such as V^{2+} and Cr^{2+} affords dilute solutions of Cu^+ which, if protected from oxygen and metal surfaces, survive several hours without disproportionation. Such solutions exhibit strong reducing properties, reacting with VO^{2+},[4] Co(III) complexes,[6] and a number of other oxidizing agents,[2] including Fe^{3+}.

One particular point of interest is the role claimed for the reaction of Fe^{3+} and Cu^+ in the studies of Higginson and Sykes.[7] The reaction of V^{3+} and Fe^{3+} is catalyzed by Cu^{2+}, and the following scheme was proposed[7] to account for the observed kinetics

$$V^{3+} + Cu^{2+} \rightleftharpoons V(IV) + Cu^{+} \qquad \text{(II)}$$

$$Fe^{3+} + Cu^{+} \longrightarrow Fe^{2+} + Cu^{2+} \qquad \text{(I)}$$

The rate of reaction II is given[4] by the expression

$$d[Cu^+]/dt = \{k_1[V^{3+}][Cu^{2+}]/[H^+]\} - k_2[VO^{2+}][Cu^+][H^+] \qquad (1)$$

where the hydrogen ion dependence is as shown except for a small medium effect[4b] on k_1. Provided the reaction of the Cu^+ intermediate with Fe^{3+} is sufficiently rapid compared to its reaction with VO^{2+}, the forward rate of II will be the measured catalytic rate. This was the claim made,[7] and one point of interest in these studies is the validity of this approximation.

The reduction of Fe^{3+} to Fe^{2+} by one-electron reducing agents has been the subject of a number of rate studies. The reducing agents studied include V^{2+},[8] Cr^{2+},[9,10] Eu^{2+},[11] Ti^{3+},[12] V^{3+},[7] and Fe^{2+} (electron exchange).[13] A comparison with these cases is most helpful in settling the question of whether an inner-sphere transition state is involved in the present reaction. This is a particularly relevant point for Fe^{3+}, since established cases of inner-sphere (Cr^{2+}) and outer-sphere (V^{2+}) reactions are known, and those reactions not subject to a direct answer (Eu^{2+}, Fe^{2+}) have several features strongly suggesting they are of the inner-sphere type.

Experimental Section

Materials.—Solutions of Cu^+ were prepared by the reaction[3] of Cr^{2+} and Cu^{2+}. These solutions were prepared immediately before use in one of the volumetric flasks used as a solution reservoir. The reaction of Cu^{2+} and Cr^{2+} was allowed to proceed to at least 99% completion, the time required (5–35 min) being computed from the known rate constant[3] for the conditions of that experiment. At intervals during the course of the experiment, samples of Cu^+ were removed for analysis.[6]

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[1] (a) Work performed in the Ames Laboratory under the auspices of the U. S. Atomic Energy Commission. Contribution No. 2465. (b) Based on the Ph.D. thesis of O. J. P., Iowa State University, Sept 1968.

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The other reagents included iron(III), copper(II), chromium(III) and -(II), lithium perchlorates, perchloric acid, sodium azide, and hydrofluoric acid which were prepared, purified, and analyzed by procedures described previously.[4,6,10,11,14]

Reaction Stoichiometry.—A solution containing a known quantity of Fe^{3+} was freed of dissolved oxygen by purging for at least 30 min with nitrogen, which had been purified by passage through successive Cr^{2+} scrubbing towers. A carefully measured volume of Cu^- in perchloric acid, containing Cu^{2+} also, was added under the surface of the Fe^{3+}. During these operations the solutions were continuously purged with nitrogen.

The quantitative determination of the reaction occurring was made spectrophotometrically using the absorbance of Fe^{3+} at its uv maximum, 240 nm (ϵ 4230 M^{-1} cm^{-1}), to measure its concentration. These experiments were carried out with an excess of Fe^{3+} and employed known and insufficient quantities of Cu^+.

Rate Measurements.—The high reaction rates dictated the use of a spectrophotometric stopped-flow technique, the instrumentation for which has been described previously.[9,14] The rate measurements were made at wavelengths in the ultraviolet region, at or near the 240-nm maximum for Fe^{3+} where Cu^+ also absorbs (ϵ ~450), but where Cu^{2+}, Fe^{2+}, and Cr^{3+} are relatively transparent. All of the rate measurements were performed at ionic strength 1.00 *M*, maintained with lithium perchlorate.

The kinetic data were read from Polaroid photographs of the traces of transmittance (photomultiplier voltage) *vs.* time. These values were used to construct the rate plot appropriate to the concentration conditions of the run in question.

Results

Stoichiometry.—The quantity of Fe^{3+} reduced upon reaction with an insufficient quantity of Cu^+ was measured spectrophotometrically. The absorbances of Fe^{3+} solutions treated with Cu^+ as described above were measured after the volumetric flasks containing the reacted solutions were diluted to their capacities with conductivity water. Identical solutions of Fe^{3+} were prepared at the same time but were not allowed to react with Cu^+. The difference in the absorbance readings of the two was computed. From this difference, under the assumption that Beer's law is obeyed by Fe^{3+} solutions in 1 *F* $HClO_4$ at 240 nm as proved here and as published,[15] the change in Fe^{3+} concentration was computed.

Four repeat measurements were made of a reaction with the following initial concentrations ($\times 10^{-4}$): Fe^{3+}, 2.36 *M;* Cu^+, 0.98 *M;* Cu^{2+}, 3.33 *M*. The stoichiometric ratios in the four trials were $\Delta[Fe^{3+}]/[Cu^+]_0$ = 0.93, 0.95, 0.96, and 0.97. The results are within experimental error of 1.00 considering the likely errors of the Cu^+ analysis and of the method for determining the change in Fe^{3+} concentration, thus confirming reaction I as written.

Kinetics.—Rate studies were carried out over a wide range of concentrations. In all of the rate experiments $LiClO_4$ was added to maintain 1.00 *M* ionic strength. In runs at 1.6° with $[H^+] = 0.98$ *M*, for example, the ranges were $[Cu^+]_0 = (2.4\text{–}6.1) \times 10^{-4}$ *M* and $[Fe^{3+}]_0 = (0.275\text{–}11.3) \times 10^{-4}$ *M*. In experiments where the excess of Cu^+ was sufficiently high ($\geq 10[Fe^{3+}]_0$), plots of log $(D - D_\infty)$ *vs.* time were linear for at least 3 half-lives, indicating pseudo-first-order behavior with respect to the Fe^{3+} concentration and allowing evaluation of a pseudo-first-order rate constant k_1. The reaction was studied also under conditions where the excess of Cu^+ was smaller, and in addition some runs in which Fe^{3+} was in excess were performed. In these cases second-order kinetic plots were linear, suggesting the rate expression

$$-d[Fe^{3+}]/dt = -d[Cu^+]/dt = k_2[Fe^{3+}][Cu^+] \qquad (2)$$

The values of k_2 at 1.6° are summarized in Table I. Typical rate plots are shown in Figure 1.

Table I

Rate Constants for the Reaction of Fe^{3+} and Cu^+ in Perchlorate Solution at 1.6° and μ = 1.00 *M*

$[H^+]$, *M*	λ, nm	Initial concn × 10^4, *M*			$10^{-4}k_2$, M^{-1} sec^{-1}	$10^{-4}k_3 = 10^{-4}k_2[H^+]$, sec^{-1}
		Cu^+	Fe^{3+}	Cu^{2+}		
0.980	240	2.36	0.275	0.790	2.57	2.52
0.995	240	2.50	0.275	0.775	2.85	2.84
0.985	255	6.05	0.455	2.64	2.46	2.42
0.980	275	2.36	0.550	0.790	2.67	2.62
0.980	300	2.36	11.3	0.790	2.56	2.51
0.750	240	2.50	0.275	0.775	3.70	2.78
0.750	255	6.05	0.455	2.64	2.89	2.17
0.500	240	2.50	0.275	0.775	4.88	2.44
0.500	255	3.51	0.455	2.88	4.81	2.41
0.400	280	1.17	5.00	0.388	5.79	2.32
0.350	240	1.13	0.275	0.405	7.20	2.52
0.350	240	1.16	0.319	0.403	6.91	2.42
0.260	240	1.13	0.319	0.405	9.30	2.42
0.200	240	0.97	0.275	0.421	12.3	2.46
0.200	240	1.11	0.319	0.408	12.0	2.40
0.100	240	0.82	0.275	0.436	24.9	2.49
0.075	240	0.66	0.275	0.453	32.1	2.41
					$10^{-4}k_3$(av) =	2.48 ± 0.11

Studies were carried out over a wide range of hydrogen ion concentration, 0.075–1.00 *M*. The lower limit was set by the excessively high rates, being the lowest $[H^+]$ at which k_2 could be evaluated with sufficient precision.

A plot of k_2 *vs.* $1/[H^+]$ was made for the data at 1.6°, as shown in Figure 2. Within experimental error the plot is a straight line with zero intercept, suggesting the rate expression

$$-d[Fe^{3+}]/dt = -d[Cu^+]/dt = k_3[Fe^{3+}][Cu^+]/[H^+] \qquad (3)$$

where $k_3 = k_1[H^+]/[Fe^{3+}] = k_2[H^+]$. The constancy of the product $k_2[H^+]$ is illustrated by the last column in Table I. The average value is $10^{-4}k_3 = 2.48$ sec^{-1} at 1.6° and $\mu = 1.00$ *M* ($LiClO_4$), with an average deviation of the individual rate constants from the mean of 4.4%.

Temperature Dependence.—The rate constant was also evaluated by the stopped-flow technique at higher temperatures, 15.8 and 25.0°. In these studies the hydrogen ion concentration was also varied, but the rather large temperature dependence limited the range covered, with 0.200 *M* H^+ being the lowest concentration at these two temperatures.

The initial concentration conditions and rate constants for these experiments are summarized in Tables II (15.8°) and III (25.0°). The average rate constants

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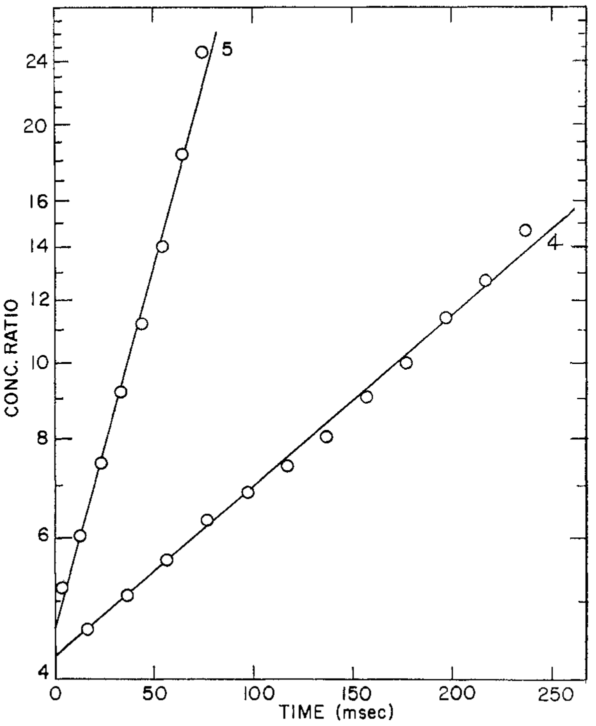

Figure 1.—Typical second-order rate plots for $Fe^{3+} + Cu^+$. The reactions depicted are runs 4 and 5 of Table I.

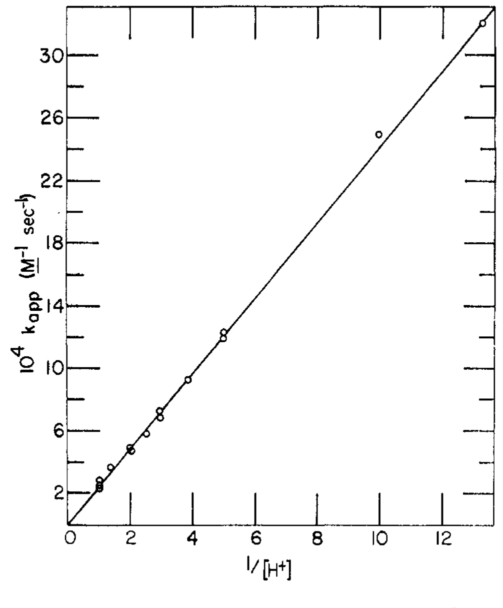

Figure 2.—A plot of the second-order rate constant k_2 vs. $1/[H^+]$ at 1.6°, illustrating the correctness of eq 3.

TABLE II

RATE CONSTANTS FOR THE REACTION OF Fe^{3+} AND Cu^+ IN PERCHLORATE SOLUTION AT 15.8° AND $\mu = 1.00\ M^{a,b}$

$[H^+]$, M	Initial concn × 10^4, M^b Cu^+	Cu^{2+}	$10^{-4}k_2$, M^{-1} sec^{-1}	$10^{-4}k_3 = 10^{-4}k_2[H^+]$, sec^{-1}
0.995	2.50	7.76	7.25	7.21
0.750	2.43	7.84	10.2	7.65
0.500	2.43	7.84	14.7	7.35
0.350	1.12	8.14	20.9	7.32
0.260	1.09	8.21	32.0	8.32
0.200	1.09	8.21	40.8	8.16
			$10^{-4}k_3$(av) =	7.67 ± 0.38

[a] λ 240 nm. [b] $[Fe^{3+}]_0 = 2.75 \times 10^{-5}\ M$ throughout.

TABLE III

RATE CONSTANTS FOR THE REACTION OF Fe^{3+} AND Cu^+ IN PERCHLORATE SOLUTION AT 25.0° AND $\mu = 1.00\ M^{a,b}$

$[H^+]$, M	Initial concn × 10^4, M^b Cu^+	Cu^{2+}	$10^{-4}k_2$, M^{-1} sec^{-1}	$10^{-4}k_3 = 10^{-4}k_2[H^+]$, sec^{-1}
0.995	2.36	7.91	16.4	16.3
0.750	2.36	7.91	20.9	15.7
0.500	2.36	7.91	33.0	16.5
0.350	1.06	4.12	45.0	15.8
0.200	1.06	4.12	81.2	16.2
			$10^{-4}k_3$(av) =	16.1 ± 0.3

[a] λ 240 nm. [b] $[Fe^{3+}]_0 = 3.19 \times 10^{-5}\ M$ throughout.

are $10^{-4}k_3$ (sec^{-1}) = 7.67 (15.8°) and 16.1 (25.0°), with mean deviations of 4.5 and 1.9%, respectively.

Reactions of $Cu^+ + (H_2O)_5FeX^{2+}$.—Only in the case of FeF^{2+} and FeN_3^{2+} were experiments deemed worthwhile, for the concentration of other anions needed to form the Fe(III) species would precipitate or complex Cu^+. The reaction with FeN_3^{2+} was attempted with the initial concentration conditions $[Cu^+]_0 = 1.4 \times 10^{-5}\ M$, $[Cu^{2+}]_0 = 4.9 \times 10^{-4}\ M$, $[FeN_3^{2+}]_0 = 4.4 \times 10^{-6}\ M$, at 1.6° and $\mu = 1.00\ M$, and was studied at 460 nm where FeN_3^{2+} (ϵ 4400) absorbs. The reaction was complete before the first observation, 3.5 msec after mixing. From this observation a lower limit $k \geq 1 \times 10^8\ M^{-1}$ sec^{-1} at 1.6° was set for the rate constant of the reaction of FeN_3^{2+} and Cu^+.

The reaction of FeF^{2+} and Cu^+ was also extremely rapid. An experiment was performed at 1.6° and $\mu = 1.00\ M$ ($LiClO_4$), with $[Cu^+]_0 = 1.2 \times 10^{-4}\ M$, $[FeF^{2+}]_0 = 5.0 \times 10^{-5}\ M$, and $[Cu^{2+}]_0 = 8.9 \times 10^{-4}\ M$. The reaction was complete within the mixing time, and a lower limit $k \geq 5 \times 10^6\ M^{-1}$ sec^{-1} for $FeF^{2+} + Cu^+$ was set.

Interpretation and Discussion

Activation Parameters.—The values of k_3 were fit to the equation

$$k_3 = (\kappa RT/Nh) \exp[(-\Delta H_3^{\ddagger}/RT) + (\Delta S_3^{\ddagger}/R)] \qquad (4)$$

The individual observed rate constants k_3 at each temperature were weighted as k_3^{-2} and fit by a nonlinear least-squares program[16] taking $\kappa = 1$ and using a standard state of 1 mol/l. On this basis the activation parameters are $\Delta H_3^{\ddagger} = 12.4 \pm 0.2$ kcal mol^{-1} and $\Delta S_3^{\ddagger} = 6.7 \pm 0.7$ cal mol^{-1} deg^{-1}, where the uncertainties given represent the standard deviation.

Reaction Mechanism.—The reaction proceeds by a single path along which the transition state has the composition $[Fe(OH)Cu(H_2O)_n{}^{3+}]^{\ddagger}$. The formation of this transition state from the predominant form of the reactants is indicated by the net activation process[17]

$$Fe(H_2O)_6{}^{3+} + Cu_{aq}{}^{+} + H_2O = [Fe(OH)Cu(H_2O)_n{}^{3+}]^{\ddagger} + H^+ \qquad (III)$$

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(16) The computer program was based on Report LA 2367 + addenda from Los Alamos Scientific Laboratory. We are grateful to Drs. T. W. Newton and R. H. Moore for supplying copies of these programs.

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One reasonable detailed mechanism for the reaction involves the acid dissociation of Fe^{3+} and the rate-determining reaction of its conjugate base

$$\mathrm{Fe(H_2O)_6{}^{3+}} \rightleftharpoons \mathrm{(H_2O)_5FeOH^{2+}} + \mathrm{H^+} \qquad (K_{\mathrm{Fe}}) \quad \mathrm{(IV)}$$

$$\begin{tikzcd}
\mathrm{(H_2O)_5FeOH^{2+}} + \mathrm{Cu^+} \arrow[r] & {[\mathrm{Fe(OH)Cu(H_2O)}_n{}^{3+}]^{\ddagger}} \arrow[d] & (k_4) \quad \mathrm{(V)} \\
 & \mathrm{Fe_{aq}{}^{2+}} + \mathrm{CuOH^+} \arrow[d, shift right] & \\
 & \mathrm{Cu_{aq}{}^{2+}} \arrow[u, shift right] &
\end{tikzcd}$$

According to this mechanism $k_4 = k_3/K_{\mathrm{Fe}}$. At the temperatures studied $10^{-7}k_4$ (M^{-1} sec^{-1}) = 6.50 (1.6°), 8.09 (15.8°), and 9.77 (25.0°) using the published values[18] of K_{Fe} appropriate to $\mu = 1.00\ M$ and the temperatures in question. The corresponding activation parameters of k_4 are $\Delta H_4^{\ddagger} = 2.2 \pm 0.5$ kcal mol^{-1} and $\Delta S_4^{\ddagger} = -14.8 \pm 1.7$ cal mol^{-1} deg^{-1}. Step V involves an inner-sphere transition state in which OH^- serves as a bridging ligand. Inner-sphere mechanisms are common among metal complexes, and recent evidence[19] indicates they may constitute the preferred pathway in all situations where unfavorable substitution rates do not prevent their contribution.[5,8]

The chief supporting evidence[4,10,20,21] for an inner-sphere mechanism comes from the predominance of the inverse acid path to the acid-independent path, the latter being insignificant within the error of the rate measurements. The reactivity of the hydroxo complex exceeds that of Fe^{3+} by a factor of $\geq 5 \times 10^3$, indicative of a role for this anion most reasonably attributed to a bridging ligand.

An alternative sequence, involving the same hydroxide-bridged transition state, is

$$\mathrm{Cu_{aq}{}^+} + \mathrm{H_2O} = \mathrm{CuOH_{aq}} + \mathrm{H^+} \qquad (K_{\mathrm{Cu}}) \quad \mathrm{(VI)}$$

$$\mathrm{CuOH_{aq}} + \mathrm{Fe(H_2O)_6{}^{3+}} \longrightarrow [\mathrm{Fe(OH)(Cu(H_2O)}_n{}^{3+}]^{\ddagger} \qquad (k_5) \quad \mathrm{(VII)}$$

This mechanism gives $k_5 = k_3/K_{\mathrm{Cu}}$. With the value K_{Cu} estimated[22] as *ca.* 10^{-11}, $k_5 \approx 10^{15}\ M^{-1}$ sec^{-1} which is higher than the encounter-controlled limit in water at 25°. These arguments eliminate eq VI and VII from further consideration. The relatively low rate of $Fe(H_2O)_6{}^{3+}$–solvent exchange[23] makes any mechanism involving a substitution in the primary coordination sphere of Fe(III) an unlikely one.

Related Reactions.—The reductions of Fe^{3+} by other 1-equiv reducing agents have received considerable attention, the studies including Cr^{2+},[9,10] Eu^{2+},[11] V^{2+},[8] Ti^{3+},[12] Fe^{2+},[13] and V^{3+}.[7] Table IV summarizes the rate expressions and rate constants at 25.0°. Each of the reactions except that of V^{2+} has a major rate term varying as $1/[H^+]$ that carries the bulk of the reaction, even at high $[H^+]$. The reaction of V^{2+} proceeds by an outer-sphere mechanism as shown unequivocally since its rate exceeds the exchange rates of both $Fe(H_2O)_6{}^{3+}$ and $V(H_2O)_6{}^{2+}$ with solvent.[8] Aside from this reaction, the high reactivity of $FeOH^{2+}$ supports the assignment of an inner-sphere mechanism.

TABLE IV

RATE EQUATIONS AND RELATIVE RATES OF REDUCTION OF IRON(III) IN PERCHLORATE SOLUTION

$-d[Fe^{3+}]/dt = (a + (b/[H^+]))[Fe^{3+}]$[reducing agent]

Reaction	b/a, M^a	Ref
$Cr^{2+} + Fe^{3+} = Cr^{3+} + Fe^{2+}$	2.3^b	9, 10
$Eu^{2+} + Fe^{3+} = Eu^{3+} + Fe^{2+}$	2.3^c	11
$Fe^{2+} + Fe^{3+} = Fe^{3+} + Fe^{2+}$	1.9^d	13
$V^{2+} + Fe^{3+} = V^{3+} + Fe^{2+}$	≤ 0.037	8
$V^{3+} + Fe^{3+} + H_2O = VO^{2+} + Fe^{2+} + 2H^+$	2.4^e	7
$Cu^+ + Fe^{3+} = Cu^{2+} + Fe^{2+}$	$\geq 7^c$	This work
$Np^{3+} + Fe^{3+} = Np^{4+} + Fe^{2+}$	17^f	*g*

[a] At 25.0° and $\mu = 1.00\ M$ ($NaClO_4$). [b] b/a is 13 M when $LiClO_4$ was used[10] to maintain ionic strength 1.00 M. [c] $\mu = 1.00\ M$ ($LiClO_4$). [d] At 0° and $\mu = 0.50\ M$ ($LiClO_4$). [e] $\mu = 3.00\ M$ ($NaClO_4$). [f] $\mu = 2.0\ M$ ($LiClO_4$). [g] T. W. Newton and N. A. Daugherty, *J. Phys. Chem.*, **71**, 3768 (1967).

The entropy of the activated complex is given by $\Delta S_3^{\ddagger} + S°(Fe^{3+}) + S°(Cu^+) + S°(H_2O)$, where the molar entropies are based on the standard state of 1 mol/l. with $S°(H^+)$ taken as 0. The values for Cu^+ and H_2O given by Latimer[24] and the estimate $S°(Fe^{3+}) = -70$ eu were used. The entropy of the activated complex so computed is $S^{\ddagger} = -53 \pm 5$ eu, which lies in the range of values (−25 to −52 eu) cited by Newton and Baker[25] for activated complexes of 3+ charge. In this respect the activated complex appears perfectly normal.

The present reaction would be an interesting one in which to consider the possible application of Marcus' theory of electron-transfer reactions.[19,26–28] The electron-exchange rate for Cu^+ and Cu^{2+} hydrated cations is, however, unknown. When one attempts to estimate this value on the basis of the observed Cu^+ and Cu^{2+} reaction rates, it appears it may be considerably smaller than the value found by McConnell and Weaver[29] for electron exchange between Cu(I) and Cu(II) chloro complexes in 12 F HCl. The question of the Cu^+ and Cu^{2+} aquo ion exchange rate remains unresolved, however, in the absence of direct experimental data.

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