Reactions of Copper(I) in Perchlorate Solution. Kinetics and Mechanisms of the Reduction of Cobalt(III) Complexes by Copper(I)[1a,b]

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Abstract: Cobalt(III) complexes are reduced by copper(I) in acidic perchlorate solutions according to a mixed second-order rate expression. The rate constants (M^{-1} sec^{-1}) at 25.0°, $\mu = 0.200\ M$ are: $Co(NH_3)_5Br^{2+}$, $4.46 \pm 0.15 \times 10^5$; $Co(NH_3)_5Cl^{2+}$, $4.88 \pm 0.17 \times 10^4$; *trans*- and *cis*-$Co(en)_2Cl_2^+$, $\geqslant 1 \times 10^7$ and $2.13 \pm 0.09 \times 10^4$; $Co(NH_3)_5N_3^{2+}$, $1.50 \pm 0.02 \times 10^3$; $Co(NH_3)_5OH^{2+}$, 3.8×10^2; $Co(NH_3)_5NCS^{2+}$, *ca.* 1–3; $Co(NH_3)_5F^{2+}$, 1.11 ± 0.02; *trans*-$Co(NH_3)_4(OH_2)CN^{2+}$, 0.47 ± 0.01; $Co(NH_3)_5CN^{2+}$, $3.3 \pm 0.2 \times 10^{-3}$; ROH_2^{3+}, 1.0×10^{-3}; and $Co(en)_3^{3+}$, $\leq 4 \times 10^{-4}$. Many of the reactions were studied as functions of temperature, and $Co(NH_3)_5Br^{2+}$ and $Co(NH_3)_5Cl^{2+}$ were also studied as a function of ionic strength. The reaction mechanisms are discussed, and arguments for an inner-sphere mechanism are advanced.

This paper reports on studies of the rates and mechanisms of the reactions of a series of Co(III) complexes with Cu(I) in perchlorate solution. A typical example is the reduction of pentaamminebromocobalt(III) ion shown in reaction I.

$$Co(NH_3)_5Br^{2+} + Cu^+ + 5H^+ = Co^{2+} + Cu^{2+} + 5NH_4^+ + Br^- \quad (I)$$

Among the redox reactions whose mechanisms have been widely studied are those of various reducing agents with ammonia or amine complexes of cobalt(III) that may also contain one or two halide, pseudohalide, or aquo ligands.[2,3] The reducing agents include the following: Cr^{2+}, V^{2+}, Fe^{2+}, Eu^{2+}, $Cr(bipy)_3^{2+}$, $Ru(NH_3)_6^{2+}$, and $Co(CN)_5^{3-}$.

Owing to the instability of Cu^+ with respect to disproportionation in perchlorate solution, reaction II, the rates

$$2Cu^+ = Cu^{2+} + Cu^0(s) \quad (II)$$

and mechanisms of its reactions have not received much previous attention. Endicott and Taube[4] reported approximate rate constants for the reduction of three Co(III) complexes by Cu(I) in perchlorate solution. These studies were based on the use of the very small Cu^+ concentrations in equilibrium[5] with the metal and high concentrations of Cu^{2+}. As noted later, our results, obtained by somewhat different methods, contradict theirs in two of the cases, nor could their findings in those reactions be duplicated by their methods.

In the present work we have employed perchlorate solutions of Cu^+ prepared from the reduction of Cu^{2+} by insufficient amounts of a one-electron reducing agent.[6] For most purposes, the reaction of Cu^{2+} and Cr^{2+} was employed. The metastable solutions of Cu^+, if protected from air and from metal surfaces (that appear to catalyze the disproportionation), can be preserved without change for an hour or more.

We have carried out kinetic studies on the following complexes ($R = Co(NH_3)_5$): RBr^{2+}, RCl^{2+}, RF^{2+}, RN_3^{2+}, $RNCS^{2+}$, ROH_2^{3+}, ROH^{2+}, RCN^{2+}, RNH_3^{3+}, $Co(en)_3^{3+}$, *cis*- and *trans*-$Co(en)_2Cl_2^+$, and *trans*-$Co(NH_3)_4(H_2O)(CN)^{2+}$. Cu(I) is a class b or soft-acid metal ion, and we wish to establish the pattern of its rates with various bridging ligands (if, indeed, inner-sphere mechanisms are involved). The recent correlation suggested by Haim[7] has stressed how the hardness or softness of a metal ion may affect the stabilities of the transition states involved, and thereby the relative rates. Previous work on soft-acid metal ions has dealt only with $Co(CN)_5^{3-}$ in which the most stable halide-bridged transition state was that containing iodide ion, as would be expected if Haim's[7] correlation is applicable. Data of this type for Cu^+ reactions will be helpful in extending the applicability of these ideas.

Copper(II) is labile with respect to substitution, preventing a direct confirmation of whether an inner-sphere mechanism operates for copper(I) reactions by the criterion of the immediate products of electron transfer. The indirect criteria available at present do enable some reasonable inferences concerning the detailed configuration of the transition states for electron transfer, and we shall consider their application to these previously unstudied reactions.

Experimental Section

Materials. Dilute solutions of Cu^+ were prepared by the reaction of Cu^{2+} and Cr^{2+}, which was allowed to proceed to at least 99% completion, as computed from the known rate constants[6b] under the conditions of each experiment. In a number of cases the formation of Cu^+ was monitored spectrally during the preparation to confirm its formation in the time allowed. Also, the rate constants for the $Cu^{2+} + Cr^{2+}$ reaction were evaluated at ionic

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[1] (a) Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission. (b) Based on the Ph.D. thesis of O. J. P., Iowa State University, Aug 1968. (c) Fellow of the Alfred P. Sloan Foundation.

[2] H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954).

[3] N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966), and references therein.

[4] J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964).

[5] The equilibrium constant for reaction II is $1.0\text{–}1.3 \times 10^6\ M^{-1}$ at 25.0° and $0.004 \leq \mu \leq 0.02\ M$ [J. F. Endicott and H. Taube, *Inorg. Chem.*, **4**, 437 (1965)].

[6] (a) J. H. Espenson, K. Shaw, and O. J. Parker, *J. Am. Chem. Soc.*, **89**, 5730 (1967); (b) K. Shaw and J. H. Espenson, *Inorg. Chem.*, **7**, 1619 (1968).

[7] A. Haim, *ibid.*, **7**, 1475 (1968).

Table I. Analyses and Absorption Spectra of Cobalt(III) Complexes

Compound	% Co		λ, nm (ε, M^{-1} cm^{-1})				Ref
	Calcd	Found	Max	Min	Max	Min	
$[RBr](ClO_4)_2$	13.9	13.0	550 (52)	429 (11)	253 (16,700)		15, 16
$[RCl](ClO_4)_2$	15.6	16.1	531 (50)	418 (9)	229 (17,800)		15, 16
$[RF](ClO_4)_2$	16.3	16.1	511 (45)	406 (8.5)	352 (40)		15
$[RN_3](ClO_4)_2$	15.3	14.2	516 (255)	442 (55)	302 (7830)	246 (660)	15, 17
$[RNCS](ClO_4)_2$	14.7	14.2	497 (180)	422 (42)	307 (1550)		15, 18
$[ROH_2](ClO_4)_3$	12.8	12.7	492 (49)	401 (9)	345 (46)	287 (6)	16, 18
$[RCN](ClO_4)_2 \cdot 0.5H_2O$	15.6	15.3	440 (57)	373 (11.5)	327 (53)		12, 15, 19
$[Co(NH_3)_4(OH_2)CN](ClO_4)_2$	15.9	15.7	446 (68)	375 (14)	330 (55)		12, 19
trans-$[Co(en)_2Cl_2]Cl$	20.6	19.9	619 (39)	525 (6)	246 (18,400)		20, 21, 22
cis-$[Co(en)_2Cl_2]Cl$	20.6	19.4	534 (74)	450 (18)	239 (14,900)		20, 21 22
$[Co(en)_3](ClO_4)_3$			465 (90)	387 (8.4)	378 (82)	287 (5)	15, 18

strengths different from 1.00 *M*, for use in preparations under such conditions.

The following complexes were prepared by standard methods: $[RBr]Br_2$,[8] which was recrystallized,[8] then converted to $[RBr](ClO_4)_2$ using $LiClO_4$ and recrystallized; $[RCl]Cl_2$, which was prepared from $[RCO_3](NO_3) \cdot H_2O$ by heating in concentrated HCl, and converted to $[RCl](ClO_4)_2$ with $HClO_4$ and recrystallized; $[RN_3]Cl_2$,[9] which was converted to $[RN_3](ClO_4)_2$ with $HClO_4$ and recrystallized twice; $[RNCS](ClO_4)_2$;[10] $[RF](NO_3)_2$,[11] which was converted to $[RF](ClO_4)_2$ with $HClO_4$, and recrystallized twice; $[ROH_2](ClO_4)_3$, which was prepared by the slow addition of $HClO_4$ to the carbonato complex, the solid so obtained being recrystallized twice; $[RCN](ClO_4)_2 \cdot 0.5H_2O$;[12] *trans*-$[Co(NH_3)_4(OH_2)CN]Cl_2$,[12] which was converted to the perchlorate in poor yield by adding $NaClO_4$ to a saturated solution at 50°; $[Co(en)_3](ClO_4)_3$[13] and *trans*- and *cis*-$[Co(en)_2Cl_2]Cl$,[14] which were used as the chlorides.

The identity and purity of each cobalt complex was established by analysis, and by its visible-uv absorption spectrum in comparison with literature values.[15-22] Our analytical and spectral results are summarized in Table I, which gives references to spectral data that, in every case, agree quantitatively with our findings.

The preparations and purification of other materials used in these studies have been described.[6,23] Conductivity water was used in all experiments.

Rate Procedures. The very rapid reactions were studied by the stopped-flow technique, using the apparatus and procedures described before.[24] In such experiments, Cu^+ was generated in one of the volumetric flasks used as a solution reservoir. Nitrogen gas, purified of traces of O_2 by passage through a succession of Cr^{2+} scrubbing towers, was continuously bubbled through the reactant flasks.

In the slower reactions, a Cary Model 14 recording spectrophotometer was used to follow the reaction rates. In these cases the reaction vessel was a cylindrical fused silica cell, usually of 5-cm optical path, which was sealed with a rubber serum cap. Copper(I) was generated in the cell, by injecting Cr^{2+} through the cap into an O_2-free solution of Cu^{2+}. The progress of the Cr(II)–Cu(II) reaction was usually monitored at 270 nm, and after it was completed and the cell thermostated,[25] the Co(III) complex was injected. The progress of the Cu^+–Co(III) reaction was monitored spectrophotometrically at one or more appropriate wavelengths where Cu^+ or Co(III), or both, had considerable absorption. Approximate molar absorptivities of Cu^+ in the uv are as follows: λ 280 nm (ε 170 M^{-1} cm^{-1}), 275 (210), 270 (240), 265 (260), 260 (290), 255 (310), 250 (350), 245 (390), 240 (450), 235 (550), 230 (770), and 225 (970).

Reaction Conditions. Most rate experiments were carried out with a sufficient excess of Cu^+ that its concentration remained essentially constant during each run. Likewise $[H^+]$ was high relative to the other concentrations, and remained effectively constant. The precise Cu^+ concentration in each run was needed to compute true rate constants. During the course of each stopped-flow run three to six samples of Cu^+ were removed from the solution reservoir for analysis.

Rate studies were carried out at various temperatures, 0–35°, with 25.0° being a temperature common to all the complexes. Ionic strength was maintained at a fixed value by addition of $LiClO_4$. The ionic strength of most runs was 0.200 *M*, although measurements on RBr^{2+} and RCl^{2+} were extended to cover other ionic strengths as well.

Kinetic Data. Absorbance values (*D*) were read at appropriate time intervals from the recording chart of the Cary spectrophotometer. Transmittance readings were read from the stopped-flow oscillograms, but the treatment of the data was the same in both cases since the total absorbance change in the stopped-flow experiments was small ($\Delta D \leq 0.1$ absorbance unit).[24]

In runs with a large excess of one reagent or the other, the reaction followed pseudo-first-order kinetics. Plots of log $(D - D_\infty)$ *vs.* time were linear, as were plots constructed by a Guggenheim treatment[26] of the data. The pseudo-first-order rate constant (eq 1) was

$$k_1 = -\mathrm{d}\ln(D_t - D_\infty)/\mathrm{d}t = -\mathrm{d}\,\mathit{ln}(D_t - D_{t+\tau})/\mathrm{d}t \qquad (1)$$

computed from the slope of one of these plots, usually that constructed according to the Guggenheim method. The second-order rate constant *k*, defined by eq 2, was computed from the expression $k = k_1/[Cu^+]_{av}$. In runs where initial concentrations were more

$$-\mathrm{d}[\mathrm{Co(III)}]/\mathrm{d}t = -\mathrm{d}[\mathrm{Cu}^+]/\mathrm{d}t = k[\mathrm{Co(III)}][\mathrm{Cu}^+] \qquad (2)$$

comparable, the second-order rate constant was evaluated from a plot made according to eq 3.

$$\log \frac{[B]_0 - [A]_0(D_0 - D)/(D_0 - D_\infty)}{[A]_0(D - D_\infty)/(D_0 - D_\infty)} = \log \frac{[B]_0}{[A]_0} + \frac{k([B]_0 - [A]_0)}{2.303}t \qquad (3)$$

Results

Reaction Stoichiometry. The reactions of Cu^+ and Co(III) complexes were shown to follow, in a quantitative

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manner, the 1:1 stoichiometry given by reaction I. The amount of Co(III) consumed was determined by analyzing the decrease in its concentration after it was brought into reaction with an insufficient quantity of Cu^+. In the case of RBr^{2+} the initial concentration of Cu^+ was established directly from the amount of Cr^{2+} used to generate it according to reaction III, the preparation being carried out in the presence of an excess of Cu^{2+}. The decrease in

$$Cu^{2+} + Cr^{2+} = Cu^+ + Cr^{3+} \qquad \text{(III)}$$

concentration of RBr^{2+} was determined from the absorbance at 253 nm of the solution produced upon reaction of Cu^+ with excess RBr^{2+}. At 253 nm RBr^{2+} has an intense absorption maximum (ε 16,700 M^{-1} cm^{-1}), and the other materials present are essentially transparent relative to it: Cu^{2+} (18), Cr^{3+} (4), and Co^{2+} (<0.4). The results on $Cu^+ + RBr^{2+}$ are shown in Table II, and indicate that the reaction follows a 1:1 stoichiometry within the limits of the analyses.

In the subsequent work on stoichiometry, and in all the rate studies, the reaction of Cu^+ and RBr^{2+} was used to analyze Cu^+ solutions. The procedure consisted in treating, under purified nitrogen, samples of Cu^+ with a 20–200% excess of a fresh RBr^{2+} solution in dilute $HClO_4$. The concentration of the RBr^{2+} solution was known only approximately, since an identical sample was diluted to the same final volume. The desired concentration was computed from the difference of the absorbances of the two solutions.

Stoichiometry experiments on the reduction of $RN_3{}^{2+}$ and RCl^{2+} were carried out, using the RBr^{2+} analysis for Cu^+. The decrease in $[RN_3{}^{2+}]$ was measured by the absorbance change at 302 nm (ε 7874), where the other species are essentially transparent. The decrease in $[RCl^{2+}]$ was evaluated at 260 nm (ε 1750), with a correction applied for the absorbance of Cu^{2+} (ε 18). The results are also summarized in Table II and confirmed the equation above, reaction I. In the case of the other Co(III) complexes the same 1:1 stoichiometry was assumed, and the kinetic data appeared to be in accord with this assumption.

Reaction Kinetics. Each of the Co(III) complexes obeyed the mixed second-order rate expression, given by eq 2. The rate studies are summarized below with the faster reactions described first.

The reduction of *trans*-$Co(en)_2Cl_2{}^+$ proceeded too rapidly for a rate study, even at optimum conditions. With the initial concentrations 9×10^{-6} M complex, 9×10^{-5} M Cu^+ the reaction was over before the time of first observation, which was *ca.* 0.003–0.004 sec after mixing. We set the lower limit $k \geq 1 \times 10^7$ M^{-1} sec^{-1}.

The reduction of RBr^{2+} proceeded at quite a high rate, but its large molar absorptivity at λ 253 nm permitted concentrations low enough to bring it in the measurable range. The most extensive variation of concentrations was made in the runs at 25°, as follows: $6.3 \times 10^{-6} \leq [Cu^+]_0 \leq 2.0 \times 10^{-4}$ M, $1.4 \times 10^{-5} \leq [RBr^{2+}]_0 \leq 9.3 \times 10^{-5}$ M. The reaction followed mixed second-order kinetics as shown in eq 2. The value of k_{RBr} remained independent of Cu^{2+} concentration, which was varied in the range $1.6 \times 10^{-4} \leq [Cu^{2+}] \leq 1.3 \times 10^{-3}$ M; it was also independent of $[H^+]$, as shown in the unchanged value of k as $[H^+]$ was lowered from 0.2 to 0.025 M. A run was also carried out using the reaction of V^{2+} and Cu^{2+} as a synthetic method for Cu^+ instead of Cr^{2+}; the same rate constant was obtained. Of particular note were runs carried out using the preparative method for Cu^+ given by Endicott and Taube,[4] whereby the reverse of reaction II was used at a high $[Cu^{2+}]$ to prepare a small concentration of Cu^+. Again, these runs gave essentially the same value of k. The reaction was

Table II. Stoichiometry of the Reduction of $Co(NH_3)_5X^{2+}$ Complexes by Cu^+ in Perchlorate Solution

Complex	Initial concn, $M \times 10^4$			ΔD[a]	$\Delta[RX^{2+}]/[Cu^+]_0$
	RX^{2+}	Cu^{2+}	Cu^+		
RBr^{2+}	0.472	1.71	0.408	1.349	0.99
RBr^{2+}	0.445	1.71	0.408	1.307	0.96
RBr^{2+}	0.461	0.78	0.184	0.618	0.99
RBr^{2+}	0.423	0.78	0.189	0.620	0.99
RBr^{2+}	0.457	0.78	0.184	0.612	1.00
$RN_3{}^{2+}$	0.678	1.15	0.276	0.438	1.01
$RN_3{}^{2+}$	0.788	1.48	0.341	0.546	1.02
$RN_3{}^{2+}$	0.783	1.48	0.341	0.537	1.04
RCl^{2+}	3.29	7.50	1.71	0.584	1.01
RCl^{2+}	3.28	7.50	1.71	0.586	1.01

[a] Absorbance decrease (optical path 2 cm) at λ 253 nm (RBr^{2+}), 302 ($RN_3{}^{2+}$), and 260 (RCl^{2+}).

Table III. Second-Order Rate Constants for the Reaction of RBr^{2+} and Cu^+ [a]

Temp, °C	$[H^+]$, M	Initial concn, $M \times 10^5$			$10^{-5}k$, M^{-1} sec^{-1}
		Cu^+	RBr	Cu^{2+}	
1.6	0.197	12.5	6.00	50.0	2.28[b]
1.6	0.197	12.5	2.97	50.0	2.58
1.6	0.199	2.33	1.33	30.8	2.25
15.8	0.196	10.9	1.05	24.1	3.44
15.8	0.199	2.32	1.34	30.8	3.65
25.0	0.197	19.8	3.42	128.0	4.18[c]
25.0	0.025	9.10	3.27	30.9	4.43
25.0	0.198	9.10	3.27	30.9	4.54
25.0	0.192	4.18	9.30	127.0	4.28[d,e]
25.0	0.199	2.51	1.37	30.5	4.44
25.0	0.198	1.34	2.28	51.7	4.55[d]
25.0	0.199	0.625	2.45	16.4	4.82[d]

[a] μ = 0.200 M ($LiClO_4$), λ 253 nm (except as noted). [b] λ 270 nm. [c] Cu^+ prepared by V^{2+} reduction. [d] Cu^+ prepared by reverse of II. [e] λ 274 nm.

Table IV. Second-Order Rate Constants for the Reaction of RCl^{2+} and Cu^+ [a]

Temp, °C	$[H^+]$, M	Initial concn, $M \times 10^5$			$10^{-4}k$, M^{-1} sec^{-1}
		Cu^+	RCl^{2+}	Cu^{2+}	
1.6	0.194	24.8	4.74	200.0	2.25
1.6	0.194	24.8	4.60	200.0	2.01[b]
1.6	0.197	13.3	1.32	98.4	2.18
15.8	0.194	48.5	4.90	153.0	3.14
15.8	0.194	47.0	3.37	156.0	3.16
15.8	0.194	45.8	9.80	158.0	3.10[b]
25.0	0.171	128.0	25.3	640.0	4.75[c]
25.0	0.188	56.5	4.47	243.0	4.84
25.0	0.190	47.0	2.10	153.0	4.75
25.0	0.195	23.2	2.10	79.5	4.68
25.0	0.197	19.80	1.30	127.0	5.16[d,e]
25.0	0.025	9.10	1.07	31.0	4.85[e]
25.0	0.198	9.10	1.07	31.0	5.11[e]
25.0	0.192	4.18	8.25	427.0	4.69[f]
25.0	0.198	1.34	2.32	51.5	5.07[f]

[a] μ = 0.200 M ($LiClO_4$), λ 245 nm (except as noted). [b] λ 260 nm. [c] λ 280 nm. [d] Cu^+ prepared by V^{2+} reduction. [e] λ 230 nm. [f] Cu^+ prepared by reverse of II.

Table V. Second-Order Rate Constants for the Reaction of *cis*-Co(en)$_2$Cl$_2^+$ and Cu$^+$ at 25.0° [a]

λ, nm	[H$^+$], *M*	Initial concn, *M* × 10^4 Cu$^+$	*cis*	Cu^{2+}	10^{-4}*k*, *M*$^{-1}$ sec^{-1}
275	0.171	12.8	1.19	64.1	2.17
265	0.171	12.8	1.00	64.1	2.22
250	0.198	5.65	0.477	24.3	2.10
245	0.190	4.81	0.477	15.2	1.98
255	0.021	4.51	0.502	8.00	2.04
240	0.025	2.19	0.210	8.05	2.27

[a] $\mu = 0.200\ M$ (LiClO$_4$).

Table VI. Second-Order Rate Constants for the Reaction of RN$_3^{2+}$ and Cu$^+$ [a]

Temp, °C	[H$^+$], *M*	Initial concn, *M* × 10^4 Cu$^+$	RN$_3^{2+}$	Cu^{2+}	10^{-3}*k*, *M*$^{-1}$ sec^{-1}
15.8	0.189	8.00	0.250	27.8	1.05
15.8	0.194	4.87	0.250	15.2	1.12
15.8	0.194	4.69	0.050	15.6	1.02[b]
25.0	0.171	12.8	1.00	54.2	1.51[c]
25.0	0.171	10.7	2.35	43.3	1.52[d]
25.0	0.179	10.7	0.500	43.3	1.52[e]
25.0	0.179	10.7	0.250	43.3	1.51
25.0	0.179	10.0	0.500	50.0	1.49[e]
25.0	0.021	4.51	0.500	20.5	1.50[e]
25.0	0.195	2.25	0.500	20.9	1.57[f]
25.0	0.195	2.11	0.148	21.0	1.46[f,g]
34.2	0.193	4.96	0.250	7.55	1.93
34.2	0.193	2.78	0.200	12.5	2.08
34.2	0.193	2.78	0.0500	12.5	1.95[b]

[a] $\mu = 0.200\ M$ (LiClO$_4$), λ 330 nm (except as noted). [b] λ 302 nm. [c] λ 355 nm. [d] λ 370 nm. [e] 340 nm. [f] 310 nm. [g] $[HN_3]_0 = 5.0 \times 10^{-4}\ M$.

Table VII. Second-Order Constants for the Reaction of RF^{2+} and Cu$^+$ [a]

Temp, °C	[H$^+$], *M*	Initial concn, *M* × 10^3 Cu$^+$	RF^{2+}	Cu^{2+}	*k*, *M*$^{-1}$ sec^{-1}
15.0	0.159	0.504	9.67	1.56	0.504
15.0	0.171	0.330	6.10	1.73	0.529
15.0	0.184	0.237	3.05	1.18	0.480[b]
25.0	0.141	1.00	12.8	3.12	1.06[c]
25.0	0.0187	0.500	12.8	1.56	1.09
25.0	0.171	0.494	6.10	1.57	1.11
25.0	0.180	0.380	3.05	1.68	1.12
25.0	0.180	0.360	3.05	1.70	1.11
25.0	0.0374	0.220	3.84	1.44	1.10[d]
25.0	0.0187	0.200	3.84	1.46	1.14[d]
25.0	0.0187	0.094	1.20	0.322	1.13[d]
35.0	0.159	0.504	9.94	1.56	2.33
35.0	0.171	0.504	6.10	1.56	2.10
35.0	0.184	0.237	3.05	1.82	2.30[d]

[a] $\mu = 0.200\ M$ (LiClO$_4$), λ 265 nm (except as noted). [b] 260 nm. [c] 285 nm. [d] 255 nm.

studied also at 1.6 and 15.8°. The data are summarized in Table III, the averages of $10^{-5}k$ (M^{-1} sec^{-1}) being: 2.37 ± 0.18 (1.6°), 3.55 ± 0.10 (15.8°), and 4.46 ± 0.15 (25.0°).

The rate constant for reduction of RCl^{2+} was about one-tenth that of RBr^{2+}, making possible more extensive concentration variations. The variations at 25.0°, for example, were $1.3 \times 10^{-5} \leq [Cu^+]_0 \leq 1.3 \times 10^{-3}\ M$, $1.1 \times 10^{-5} \leq [RCl^{2+}]_0 \leq 2.5 \times 10^{-4}\ M$. The rate constants proved independent of [Cu^{2+}] and [H$^+$], and the source of Cu$^+$ (Cr^{2+} reduction, V^{2+} reduction, or reproportionation) again proved immaterial to the rate constant. The individual runs are summarized in Table IV; the average values are $10^{-4}k$ (M^{-1} sec^{-1}) = 2.15 ± 0.09 (1.6°), 3.13 ± 0.02 (15.8°), and 4.88 ± 0.17 (25.0°).

A brief study of the reaction of *cis*-Co(en)$_2$Cl$_2^+$ and Cu$^+$ was undertaken; its rate proved considerably lower than that of the *trans* isomer. Kinetic studies were made at only 25.0°, and the average value is $10^{-4}k = 2.13 \pm 0.09\ M^{-1}$ sec^{-1}. The individual runs are presented in Table V.

The kinetics of reduction of RN$_3^{2+}$ by Cu$^+$ was subjected to a considerable variation of reaction conditions. Initial concentrations were $2.1 \times 10^{-4} \leq [Cu^+]_0 \leq 1.3 \times 10^{-3}$, $1 \times 10^{-4} \leq [RN_3^{2+}]_0 \leq 1 \times 10^{-3}\ M$. The possibility of the reaction of Cu$^+$ with the HN$_3$ liberated during the course of the Cu$^+$–RN$_3^{2+}$ reaction was investigated by adding to a run with $2 \times 10^{-4}\ M$ Cu$^+$, $5 \times 10^{-4}\ M$ HN$_3$, a concentration higher than that eventually formed in most runs. The rate constant was the same as in the absence of added HN$_3$, proving that this was not a problem during the time of the rate experiments. The stoichiometry experiments (Table II), where RN$_3^{2+}$ was always in excess, gave no indication of side reactions being important during the times needed to study the reaction rates. In fact, the equilibrium absorbance readings in runs with excess Cu$^+$ were apparently stable up to 20 sec, giving no indication of a subsequent reaction of HN$_3$ and Cu$^+$ in this length of time. The rate constants are as follows: $10^{-3}k$ (M^{-1} sec^{-1}) = 1.06 ± 0.04 (15.8°), 1.50 ± 0.02 (25.0°), and 1.99 ± 0.06 (34.2°). The individual kinetic experiments are summarized in Table VI.

An attempted study of the reaction of Cu$^+$ and RNCS^{2+} was complicated by the precipitation of CuSCN(s) even at the lowest concentrations (K_{sp} is $5 \times 10^{-15}\ M^2$). Under the conditions of the experiments the precipitate did not settle. Instead of the expected decrease in absorbance in experiments using the recording spectrophotometer, an increase was noted as the solution became increasingly cloudy. From this absorbance change, *k* for RNCS^{2+} was estimated to be 1–3 M^{-1} sec^{-1} at 25.0°.

The rate constants for RF^{2+} + Cu$^+$ and for other slower reactions were evaluated from conventional (non-stopped-flow) spectrophotometric rate studies as described in an earlier section. At 25.0°, the following concentration ranges were covered: $9.4 \times 10^{-5} \leq [Cu^+] \leq 1.0 \times 10^{-3}\ M$, $3.1 \times 10^{-3} \leq [RF^{2+}]_0 \leq 1.3 \times 10^{-2}\ M$. The rate proved independent of [Cu^{2+}], of [H$^+$], and of the wavelength used to follow the decreasing absorbance of Cu$^+$, which was generally the limiting reagent. Studies were made at 15.0, 25.0, and 35.0°, where the average rate constants are 0.506 ± 0.017, 1.11 ± 0.02, and 2.24 ± 0.10 M^{-1} sec^{-1}, respectively. The individual runs are shown in Table VII.

A limited study of the reactions of *trans*-Co(NH$_3$)$_4$(OH$_2$)CN^{2+} and RCN^{2+} with Cu$^+$ was carried out. In three experiments with the first complex, each with $[Cu^+]_0 = 5.04 \times 10^{-4}$, $[Co(III)]_0 = 3.77 \times 10^{-3}$, $[Cu^{2+}]_0 = 1.56 \times 10^{-3}\ M$, rate constants were 0.460 M^{-1} sec^{-1} ([H$^+$] = 0.0389), 0.449 (0.181), and 0.487 (0.181)). At 25.0° and $\mu = 0.200\ M$ (LiClO$_4$), the average is 0.47 ± 0.01 M^{-1} sec^{-1}.

Three runs were also carried out for RCN^{2+}, at 0.04–0.15 *M* H$^+$. Values of *k* lead to the average

Table VIII. Summary of Rate Constants and Activation Parameters at $\mu = 0.200\ M$

Co(III) complex	k, M^{-1} sec^{-1} [a] 1.6°	15.0°	25.0°	35.0°	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$,[b] cal/(mol deg)
trans-$Co(en)_2Cl_2^+$			$>1 \times 10^7$			
RBr^{2+}	$2.37 \pm 0.14 \times 10^5$	$3.55 \pm 0.10 \times 10^5$ [c]	$4.46 \pm 0.15 \times 10^5$		3.86 ± 0.24	-19.8 ± 0.8
RCl^{2+}	$2.15 \pm 0.09 \times 10^4$	$3.13 \pm 0.02 \times 10^4$ [c]	$4.88 \pm 0.17 \times 10^4$		5.33 ± 0.33	-19.4 ± 1.1
cis-$Co(en)_2Cl_2^+$			$2.13 \pm 0.09 \times 10^4$			
RN_3^{2+}		$1.06 \pm 0.04 \times 10^3$ [c]	$1.50 \pm 0.02 \times 10^3$	$1.99 \pm 0.06 \times 10^3$ [d]	5.42 ± 0.26	-25.8 ± 0.9
ROH^{2+}			3.8×10^2			
$RNCS^{2+}$			*Ca.* 1–3			
RF^{2+}		0.506 ± 0.017	1.11 ± 0.02	2.24 ± 0.10	12.4 ± 0.3	-16.6 ± 0.9
trans-$Co(NH_3)_4(OH_2)CN^{2+}$			0.47 ± 0.01			
RCN^{2+}			0.0033 ± 0.0002			
ROH_2^{3+}			0.001			
$Co(en)_3^{3+}$			$\leq 4 \times 10^{-4}$			

[a] The uncertainties represent the average deviation of the individual rate constants from the mean. [b] The uncertainties represent the standard deviation of the activation parameters. [c] 15.8°. [d] 34.2°.

$3.3 \pm 0.2 \times 10^{-3}\ M^{-1}\ \text{sec}^{-1}$, at 25.0°, $\mu = 0.200\ M$ ($LiClO_4$), independent of $[H^+]$.

The reduction of ROH_2^{3+} by Cu^+ was fairly slow (contrary to the published report[4]), and precise data were difficult to obtain since high Cu^+ concentrations could not be employed owing to its instability (reaction II). Kinetic data were obtained at 25.0° with the following initial concentrations: $Cu^+ = 5.04 \times 10^{-4}$, $ROH_2^{3+} = 1.93 \times 10^{-2}$, and $Cu^{2+} = 1.56 \times 10^{-3}\ M$. Six runs were performed at each of three $[H^+]$ in the range 0.018–0.075 M, with these results ($[H^+]_{av}$ (10^3k, $M^{-1}\ \text{sec}^{-1}$)): 0.0747 (3.7, 4.2), 0.0378 (6.8, 7.8), and 0.0183 (13.2, 13.4). The rate constants vary with $[H^+]$ according to the functional form given by eq 4. At 25.0°, $\mu = 0.200\ M$ ($LiClO_4$), $a = 0.0010\ M^{-1}\ \text{sec}^{-1}$, and $b = 0.00023\ \text{sec}^{-1}$.

$$k = a + b/[H^+] \qquad (4)$$

The rates of reduction of RNH_3^{3+} and of $Co(en)_3^{3+}$ were both very low. For the second reactant where the solubility permitted Co(III) concentrations considerably higher than with the hexaammine, an approximate value $4 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$ at 25.0° was noted, but this may contain a sizable contribution from side reactions and the true rate constant may be a good deal lower than this.

The kinetic data for all the cobalt complexes are summarized in Table VIII, along with activation parameters for those complexes whose rates were studied at more than one temperature.

Effect of Ionic Strength. The rate constant for a second-order reaction of two cations is expected to increase with increasing ionic strength. The reduction rates of RBr^{2+} and RCl^{2+} were measured at 25.0° as a function of ionic strength, covering the ranges μ = 0.00094–0.200 M (RBr^{2+}), and 0.00094–3.00 M (RCl^{2+}). In both cases, $LiClO_4$ was the electrolyte added to maintain ionic strength at the values desired. The rate constants are summarized in Tables IX (RBr^{2+}) and X (RCl^{2+}).

Plots of log k *vs.* $\mu^{1/2}$ were made, and are shown in Figures 1 and 2 for RBr^{2+} and RCl^{2+}, respectively. The linear portion of the graph at $\mu \leq 0.04$ is drawn with a slope in agreement with the Brønsted-Debye-Hückel slope for a reaction of 2 cations with 2+ and 1+ ionic charges (eq 5). At 25.0° $A = 0.509$, and the anticipated

$$\log k = \log k^0 + 2Az_1z_2\mu^{1/2} \qquad (5)$$

slope of +2.04 is in good agreement with our findings at $\mu \leq 0.04\ M$.

Table IX. Ionic Strength Dependence of the Rate Constant for the Reaction of RBr^{2+} and Cu^+ at 25.0° [a]

$10^2 \times \mu$, M	Initial concn, $M \times 10^4$ Cu^+	Cu^{2+}	RBr^{2+}	$10^{-5}k$, M^{-1} sec^{-1}
0.0934	0.322	0.87	0.0800	1.74
0.0935	0.320	0.87	0.0775	1.50
0.423	0.975	3.02	0.097	2.03
0.957	0.890	3.11	0.102	1.95
1.00	0.985	3.01	0.100	1.95
2.25	0.925	3.08	0.089	2.74
3.96	0.890	3.11	0.102	2.70
4.00	0.958	3.04	0.126	3.00
6.25	0.925	3.07	0.089	3.22
10.0	0.970	3.02	0.123	4.13
20.0	0.910	3.09	0.327	4.43
20.0	0.910	3.09	0.327	4.54

[a] Ionic strength maintained with $LiClO_4$.

Table X. Ionic Strength Dependence of the Rate Constant for the Reaction of RCl^{2+} and Cu^+ at 25.0° [a]

$10^2 \times \mu$, M	Initial concn, $M \times 10^4$ Cu^+	Cu^{2+}	RCl^{2+}	$10^{-4}k$, M^{-1} sec^{-1}
0.094	0.320	0.87	0.0765	1.49
0.094	0.322	0.87	0.0735	1.52
0.423	0.975	3.03	0.112	1.84
0.957	0.950	3.05	0.113	2.09
1.00	0.985	3.03	0.107	2.33
2.25	0.925	3.08	0.109	2.86
3.96	0.950	3.05	0.113	2.80
4.00	0.951	3.04	0.111	2.82
6.25	0.925	3.07	0.109	4.08
10.0	0.970	3.03	0.107	3.79
20.0	0.910	3.09	0.107	4.85
20.0	0.910	3.09	0.107	5.11
100	0.905		0.100	7.87
100	0.905		0.100	7.37
100	0.905		0.100	7.37
100	0.960		0.100	7.77
100	0.960		0.100	7.62
300	1.17		0.100	11.5
300	1.17		0.100	11.0

[a] Ionic strength maintained with $LiClO_4$.

Interpretation and Discussion

Characterization of Copper(I). Since Cu^+ is unstable with respect to disproportionation by reaction II, it seems useful to summarize here the various items documenting its existence under the conditions of our experiments. In particular, it is important to demonstrate that the species is not a supersaturated solution of the zerovalent metal,

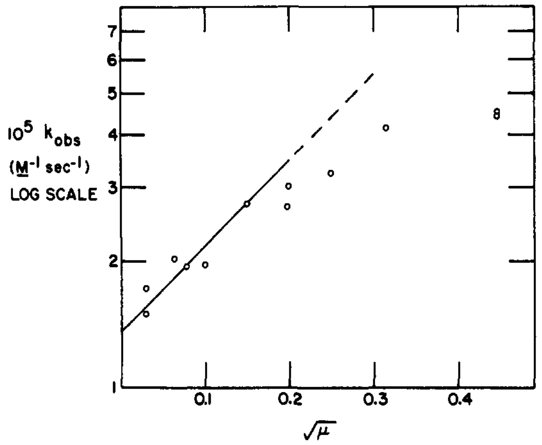

Figure 1. Plot of k (log scale) *vs.* $\mu^{1/2}$ for the reaction of RBr^{2+} and Cu^+ at 25.0°. The straight line is drawn with the limiting Brønsted–Debye–Hückel slope at 25.0°. Data from Table IX.

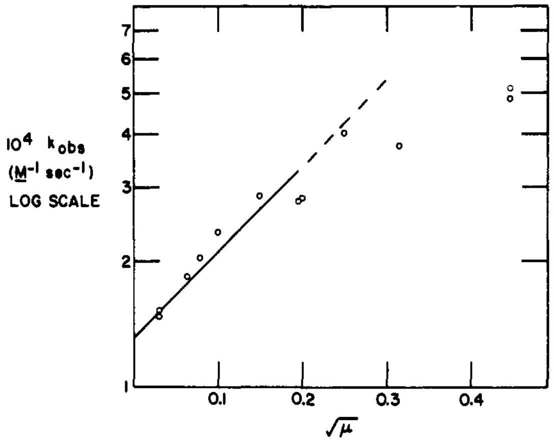

Figure 2. Same as Figure 1 for RCl^{2+} + Cu^+, data from Table X.

Cu^0(aq). The solutions of Cu^+ were prepared by reducing Cu^{2+} with an insufficient quantity of V^{2+} [23] or Cr^{2+}.[6] Manahan and coworkers[27,28] have also recently devised quite different procedures. The confirming lines of evidence for the production and existence of Cu^+ that we have obtained are these: (1) the stoichiometry of the reduction of Cu^{2+} with Cr^{2+} [6] and with V^{2+} [23] confirmed the production of Cu^+, and eliminated Cu^0(aq); (2) the kinetic data on the reaction of Cu^{2+} with Cr^{2+} [6] and with V^{2+} [23] confirmed the 1:1 stoichiometry; (3) the same rate constants were obtained when RBr^{2+} was reduced by Cu^+ prepared from Cu^{2+} + V^{2+} and Cu^{2+} + Cr^{2+}, as when it was prepared by reaction II; (4) the salt effect on the reaction of Cu^+ and RBr^{2+} (and RCl^{2+}) was quantitatively consistent with ions of this charge type, and quite inconsistent with that of an uncharged Cu^0(aq).

$Co(NH_3)_5OH_2^{3+}$. The rate of reduction of this complex by Cu^+ is dependent on $[H^+]$, as shown in eq 4. The second term probably corresponds to the rate-determining reaction of ROH^{2+} and Cu^+.

$$ROH_2^{3+} \overset{K_a}{\rightleftharpoons} ROH^{2+} + H^+ \qquad \text{(IV)}$$

$$ROH^{2+} + Cu^+ \xrightarrow{k_{OH}} Co(II) + Cu(II) \qquad \text{(V)}$$

The value of K_a given by Splinter, Harris, and Tobias[29] is 6.1×10^{-7} M at 25.0° in a medium with $[ClO_4^-] = 0.300$ M. Ignoring the difference in ionic strength, k_{OH} ($=b/K_a$) is computed to be 3.8×10^2 M^{-1} sec^{-1} at 25.0°, $\mu = 0.200$ M.

Reaction Mechanism. A question of central interest in this work is whether bridged (inner-sphere) activated complexes are formed. The possibility for obtaining a direct confirmation for these Cu^+ reductions appears slight for two reasons. First, the high substitution lability of Cu^{2+} prevents an examination of the ligands occupying its primary coordination sphere immediately after electron transfer. In this respect, the situation resembles that for V^{2+}, Eu^{2+}, and Fe^{2+} reductions where, except in a few special cases, a definitive proof of mechanism has not been made. Second, it seems unlikely that ligand transfer would accompany the decomposition of the potential ligand-bridged transition state being considered here: $[Co^{III}\text{-}X\text{-}Cu^{I}]$. Decomposition of this transition state would be governed largely by the relative substitution rates of Co(II) and Cu(II). The d^7 system will probably be less labile than the d^9,[3] suggesting that if ligand-bridged transition states are involved, the primary product may be a Co(II) complex in which the Co(II)–X bond remains intact.

Despite the limitations inherent in the system that prevent definitive studies, some indirect arguments concerning mechanism can be made. The evidence will consist of comparisons of relative reaction rates with similar reactions of known mechanism. The most useful are those where data are available for both inner-sphere and outer-sphere systems, and where the two general schemes show large differences. The comparisons to be considered here are the following rate ratios: ROH^{2+}/ROH_2^{3+}, $RN_3^{2+}/RNCS^{2+}$, along with a consideration of possible nonbridging ligand effects.

The value for k_{OH}/k_{H_2O} is 3.8×10^5 using $k_{OH} = b/K_a = 3.8 \times 10^2$ M^{-1} sec^{-1} as indicated above. A similar high reactivity for the hydroxo complex compared to the aquo was noted[30] in the inner-sphere reduction of the same complexes by Cr^{2+} ($k_{OH}/k_{H_2O} = 2 \times 10^6$), and it has been noted in the reactions of other hydroxo–aquo pairs with Cr^{2+}, Eu^{2+}, and Fe^{2+} for which inner-sphere mechanisms have been proposed.[31] In contrast, the reductions of ROH^{2+} and ROH_2^{3+} by $Ru(NH_3)_6^{2+}$ and by $Cr(bipy)_3^{2+}$ proceed by outer-sphere mechanisms, and have $k_{OH}/k_{H_2O} = 0.01$ and 0.6, respectively.[4,32,33]

The high reactivity of a bridging N_3^- compared to a bridging NCS^- has been invoked[34,35] as an indication of

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(27) J. A. Altermatt and S. Manahan, *Inorg. Nucl. Chem. Letters*, **4**, 1 (1968).

(28) J. A. Altermatt and S. E. Manahan, *Anal. Chem.*, **40**, 655 (1968).

(29) R. C. Splinter, S. J. Harris, and R. S. Tobias, *Inorg. Chem.*, **7**, 397 (1968).

(30) A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **81**, 1288 (1959).

(31) D. W. Carlyle and J. H. Espenson, *ibid.*, **90**, 2272 (1968), and references therein.

(32) A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 42 (1960).

(33) For a reaction where substitution into the primary coordination sphere is rate determining, the high reactivity of OH^- relative to H_2O as a bridging ligand may be leveled such that the rate appears to be independent of $[H^+]$, or nearly so. This may be the case in the reaction of ROH_2^{3+} and V^{2+} [3,23]

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

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

an inner-sphere mechanism. The ratio for RN_3^{2+} and $RNCS^{2+}$ in their reactions with Cu^+ is k_{N_3}/k_{NCS} = *ca.* 10^3, where the uncertainty arises from the use of an approximate rate constant for $RNCS^{2+}$. By way of comparison, the inner-sphere reactions[35] of CrN_3^{2+} and $CrNCS^{2+}$ with Cr^{2+} have a rate ratio of $k_{N_3}/k_{NCS} = 4 \times 10^4$; RX^{2+} with Cr^{2+}, 10^4; RX^{2+} with Fe^{2+}, $\geq 3 \times 10^3$; and RX^{2+} with Eu^{2+}, 3×10^2. The outer-sphere reaction of RX^{2+} with $Cr(bipy)_3^{2+}$ has a rate ratio of 4. These results support the assignment of an inner-sphere mechanism to the Cu^+ reactions.

The study of "nonbridging ligand effects" has given rise to several empirical rate trends that operate in inner-sphere reactions.[36-38] The presumption is that these effects are absent, or at least far less pronounced in outer-sphere reactions. The recent studies of Patel and Endicott[39] and the work of Bifano and Linck[38] indicate that some implications of the earlier studies that such effects were unique to inner-sphere reactions are not correct.

For the complexes *trans*- and *cis*-$Co(en)_2Cl_2^+$ the rate ratio for Cu^+ is $k_t/k_c \geq 5 \times 10^2$. In comparison, the rate ratio[36,40] for $Cr(en)_2Cl_2^+ + Cr^{2+}$ is $k_t/k_c = 26$, and that for $Co(en)_2Cl_2^+ + Fe^{2+}$ is 21. On the other hand, the corresponding ratio for $Co(en)_2Cl_2^+ + Ru(NH_3)_6^{2+}$ is 10 from the work of Endicott and Taube.[4] The Cr^{2+} reaction proceeds by an inner-sphere mechanism, and that of Fe^{2+} probably also does, whereas the $Ru(NH_3)_6^{2+}$ reaction necessarily proceeds outer-sphere. The ratio k_t/k_c is not particularly diagnostic of mechanism.

A second comparison of nonbridging ligand effects is afforded by the compounds *trans*-$Co(NH_3)_4(OH_2)CN^{2+}$ and RCN^{2+}. The potential bridging group, CN^-, is *trans* to H_2O and NH_3, respectively. The rate ratio found in this work was 140 for Cu^+, the aquo complex having the higher rate. Similar changes of one H_2O and NH_3 *trans* to the bridging ligand have been studied with other reducing agents. For example, the same complexes react with Cr^{2+} in inner-sphere mechanisms at rates differing by a factor of 40.[19] The rates of *trans*-$Co(en)_2(OH_2)Cl^{2+}$ and *trans*-$Co(en)_2(NH_3)Cl^{2+}$ with Fe^{2+} exhibit a ratio of 3.6×10^3, and those of *trans*-$Co(en)_2(OH_2)N_3^{2+}$ and *trans*-$Co(en)_2(NH_3)N_3^{2+}$ with the same reducing agent, 2.8×10^3.[36] These Fe^{2+} reactions have been interpreted as inner-sphere reactions.

Comparisons with Related Reactions. The various rate effects cited above support our contention that the reductions of Co(III) complexes by Cu^+ involve inner-sphere transition states. The wide spread of rates for the various complexes, which exceeds a factor of 10^{10}, also supports this proposal. The trends are generally greater for Cu^+ than noted for Cr^{2+}, where it has been suggested[41] that the higher rates may be partly limited by the rate of Cr(II)–H_2O exchange, an idea that finds support from $FeX^{2+} + Cr^{2+}$ rates.[41,42] A more obvious manifestation of this effect is the rate of V^{2+} reductions, where the V^{2+}–H_2O exchange rate effectively limits the rates of inner-sphere reactions to a narrow range.[43,44] The large spread of the values for Cu^+ (Table IX) reflects the very high H_2O exchange rate of the d^{10} configuration.

Haim[7] has suggested an interesting correlation of the stabilities of transition states for redox reactions of various metal ion complexes. The same computation for these reactions can be made for the hypothetical process shown in (VI) where one transition state is converted to another.

$$[(NH)_5CoFCu^{3+}]^{\ddagger} + Br^- = [(NH_3)_5CoBrCu^{3+}]^{\ddagger} + F^- \quad (Q^{\ddagger}) \quad \text{(VI)}$$

The value of $Q^{\ddagger}$ can be computed from the relevant rate and equilibrium constants;[7] its value is 1.9×10^3. The higher stability of the bromide transition state is consistent with the inner-sphere reduction reaction involving the soft-acid[45] Cu^+. It does not distinguish the inner-sphere model from an outer-sphere mechanism, however.[7]

The rate constant found for $RBr^{2+} + Cu^+$ (Table III) was the same irrespective of the source of Cu(I) used. In this study there were three such sources: Cr^{2+} reduction, V^{2+} reduction, and the reaction of Cu^{2+} and Cu^0. The rate constant at 25.0°, $4.46 \pm 0.15 \times 10^5\ M^{-1}\ sec^{-1}$, can be compared with the result of Endicott and Taube,[4] who report a preliminary value $k = 10^5$–$10^7\ M^{-1}\ sec^{-1}$. The results they report for ROH_2^{3+} and $Co(NH_3)_6^{3+}$ are $>10^2$ and $>2 \times 10^2$, respectively. The latter two values are in considerable disagreement with ours: $ROH_2^{3+} = 0.0010 + 0.00023/[H^+]$, $Co(NH_3)_6^{3+}$ very slow, and $Co(en)_3^{3+} \leq 4 \times 10^{-4}\ M^{-1}\ sec^{-1}$. These two rate constants were no different when different methods were used to synthesize Cu^+, including the method of Endicott and Taube. We are unable to explain the origin of this disagreement.

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