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## Reactions Involving Copper(I) in Perchlorate Solution. A Kinetic Study of the Reaction of Chromium(II) and Copper(II) Ions<sup>1</sup>

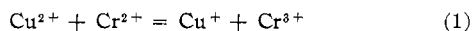
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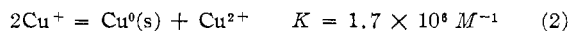
Chromium(II) reduces copper(II) in perchloric acid solution, forming copper(I) which decomposes to the metal only very slowly in dilute (<0.01 *M*) solution. The rate equation is  $d[\text{Cu}^+]/dt = \{a + (b/[\text{H}^+])\}[\text{Cr}^{2+}][\text{Cu}^{2+}]$ ; at 24.6° and 1.00 *M* perchlorate concentration,  $a = 0.17 \text{ M}^{-1} \text{ sec}^{-1}$  and  $b = 0.587 \text{ sec}^{-1}$ . Activation parameters were evaluated for each rate constant. The reaction is postulated to proceed by an inner-sphere mechanism, largely on the basis of the pattern of reactivity toward hydroxide ion.

### Introduction

It was found that chromium(II) in dilute acidic solution containing perchlorate as the only anion was slowly oxidized by copper(II). The net reaction was shown to be that given by eq 1 provided  $[\text{Cu}^{2+}]_0 > [\text{Cr}^{2+}]_0$ .

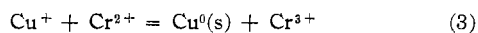


In the absence of complexing anions, copper(I) is thermodynamically unstable with respect to disproportionation (eq 2), but we found that considerable

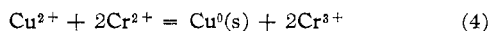


time may elapse before any metallic copper is formed under certain conditions. The most favorable circumstances for retaining  $\text{Cu}^+$  appear to be low concentration, high acidity, and the absence of oxygen or other oxidizing agents.

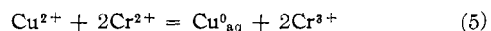
In the presence of excess chromium(II), copper(I) is readily reduced to the metal (eq 3); under those cir-



cumstances the net reaction is that shown in eq 4. The question that arose in the course of these studies was not whether eq 4 occurred when the starting concentra-



tion of copper(II) exceeded that of chromium(II), for it clearly did not, but whether the product could be a metastable  $\text{Cu}(0)$  species. The latter would, in effect, be a supersaturated solution of the metal that had failed to precipitate presumably for lack of an appropriate nucleation site. Were that the case the net reaction would be that given by eq 5; the evidence presented here establishes that a process such as eq 5



does not occur appreciably and that under most of the conditions employed eq 1 represents the exclusive process.

Altermatt and Manahan<sup>2</sup> have recently published an electrochemical procedure for generating aqueous solutions of copper(I) perchlorate and have also shown that  $\text{Cu}^+$  solutions may be prepared by the careful dissolu-

tion of the freshly precipitated hydroxide in perchloric acid.

Our interest in this reaction arose from several factors: (1) its uniqueness in producing  $\text{Cu}_{\text{aq}}^+$  in a metastable situation in perchlorate solution, (2) the question it posed of an inner-sphere or outer-sphere reaction mechanism, and (3) the subsequent studies allowed on the reduction mechanisms of copper(I). Since copper(II) is remarkable for its catalytic activity toward a wide variety of processes, further and direct information on copper(I) will enable a greater understanding of its role in catalytic phenomena. A preliminary report of some of these findings has been published.<sup>3</sup>

### Experimental Section

**Materials.**—Copper(II) perchlorate was obtained from two independent sources which gave indistinguishable kinetic data. First, reagent grade material supplied by G. F. Smith Chemical Co. was used without further purification. Second, analytical grade copper(II) carbonate was dissolved in concentrated perchloric acid and boiled for 5 min. The solution was filtered to remove undissolved carbonate, and the copper(II) perchlorate was crystallized and then recrystallized from conductivity water.

Solutions of copper(II) were analyzed by the standard volumetric procedure in which potassium iodide is added and the liberated iodine titrated with sodium thiosulfate using starch indicator. The total cation content of the solution was also analyzed by passing aliquots of the solution through a column of Dowex 50W cation-exchange resin in the hydrogen ion form, followed by titration of the washings with sodium hydroxide. The analysis of copper(II) and of total cation content always agreed to within 1%, assuming that each copper ion released two hydrogen ions from the resin column.

Chromium(II) perchlorate solutions in perchloric acid were prepared by the electrolytic reduction of chromium(III) perchlorate and stored under nitrogen. They were analyzed by reaction with a slight excess of pentaamminechlorocobalt(III) chloride followed by spectrophotometric determination of the cobalt(II) produced, as its thiocyanate complex in 50 vol % acetone. The details of these procedures have been given previously.<sup>4</sup>

Reagent grade lithium perchlorate, used to maintain constant ionic concentration, was recrystallized two times before use. Solutions were analyzed by displacement of hydrogen ions from a cation-exchange column followed by titration of the washings with sodium hydroxide. Reagent grade perchloric acid was

(1) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2294.

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

(3) J. H. Espenson, K. Shaw, and O. J. Parker, *J. Am. Chem. Soc.*, **89**, 5730 (1967).

(4) J. H. Espenson, *Inorg. Chem.*, **4**, 1025 (1965).

used without further purification. All solutions were made up using a double redistillate of distilled water from alkaline permanganate in a tin-lined Barnstead still.

**Rate Studies.**—The progress of the reaction was followed spectrophotometrically using a Cary Model 14 recording spectrophotometer, by monitoring the increase of absorbance at wavelengths 2700–3000 Å (primarily copper(I) absorption) or 5740 Å (chromium(III) absorption). The solutions were made up volumetrically using lithium perchlorate to maintain a total perchlorate concentration of 1.00 *M*.

The reactant solution, omitting chromium(II), was contained in a 5- or 10-cm cylindrical optical cell fitted with a serum cap. A stream of nitrogen, purified by successive passage through two Cr(II) wash solutions, dilute sodium hydroxide, and water, was bubbled through the solution in the cell for 30 min by means of a Teflon needle passing through a wider steel needle which pierced the serum cap. The cell was then placed in a thermostated cell compartment of the spectrophotometer,<sup>5</sup> and after allowing it to reach temperature, the reaction was begun by adding the appropriate quantity of chromium(II) solution from a volumetric syringe.

At temperatures below room temperature it was necessary to sweep the cell compartment continuously with dry air to prevent condensation of moisture on the optical windows.

### Results and Interpretation

**Rate Equation and Stoichiometry.**—When copper(II) was in at least 10-fold excess over chromium(II), the reaction followed pseudo-first-order kinetics as evidenced by the excellent linearity of the appropriate rate plots. Values of the absorbance were read at appropriate time intervals from the recording chart of the spectrophotometer. The progress of the chart, which was driven by a synchronous motor, was used to time the reaction. A pseudo-first-order rate constant  $k'$  was evaluated from the slopes of such plots (eq 6), in which  $D_\infty$  and  $D_t$  represent the absorbance

$$k' = -\frac{d \ln [D_\infty - D_t]}{dt} = -\frac{d \ln [Cr^{2+}]}{dt} \quad (6)$$

values at the end of the reaction and at time  $t$ , respectively. A second-order rate constant  $k$  was computed from the value of  $k'$  and the average copper(II) concentration in the run

$$k = \frac{-d[Cr^{2+}]/dt}{[Cr^{2+}][Cu^{2+}]} = \frac{k'}{[Cu^{2+}]_{av}} \quad (7)$$

Experiments were also carried out under conditions where the excess of copper(II) over chromium(II) was much smaller. In part, the point of such experiments was to verify that the second-order rate law was applicable over wide ranges of concentrations with the rate constant so computed remaining invariant.

Considering all of the concentrations studied, the total variation of copper(II) concentration covered a factor of 84 ( $0.0006 \leq [Cu^{2+}]_0 \leq 0.05 M$ ), and that of chromium(II), a factor of 45 ( $0.00012 \leq [Cr^{2+}]_0 \leq 0.0054 M$ ). The data at one particular hydrogen ion concentration are summarized in Table I. Except for the values at the very lowest excess of copper(II), where the long time needed for the reaction of  $Cu^{2+}$  and  $Cr^{2+}$  to come to completion allowed time for a second stage of reduction of  $Cu^+$  by  $Cr^{2+}$  to affect the absorbance readings late in the run, the values of  $k$  ap-

pear to be constant. In that one set of runs at the lowest  $[Cu^{2+}]$  the values of  $D_\infty$  were about 10% lower than in the other runs and it is probable that a competing reaction, a second reduction step or disproportionation, resulted in some loss of  $Cu^+$ . Considering all 16 entries in Table I the average of the deviation of the individual values from the mean is 8.0%, and if the four runs with  $[Cu^{2+}]_0 = 3.07 \times 10^{-3} M$  are omitted, it is 2.6%; *i.e.*,  $k = 0.990 \pm 0.080$  and  $0.936 \pm 0.025$ , respectively. These data also establish that the rate constant is independent of the wavelength used and independent of  $[Cr^{3+}]$ .

TABLE I  
KINETIC DATA FOR  $Cu^{2+}$ - $Cr^{2+}$  REACTIONS AT 24.6°,  
[ $H^+$ ] = 0.762 *M*, [ $ClO_4^-$ ] = 1.00 *M* ( $LiClO_4$ ), AND  $\lambda$  3000 Å  
(EXCEPT AS NOTED)

$10^2[Cu^{2+}]_0$ , <i>M</i>	$10^3[Cr^{2+}]_0$ , <i>M</i>	$k$ , $M^{-1}$ $sec^{-1}$	$10^2[Cu^{2+}]_0$ , <i>M</i>	$10^3[Cr^{2+}]_0$ , <i>M</i>	$k$ , $M^{-1}$ $sec^{-1}$
51.2	1.37	0.965	3.07	1.37	(1.12)
51.2	1.37	0.960	3.07	1.37	(1.15)
38.4	1.37	0.915	3.07	1.37	(1.23) <sup>a</sup>
25.6	1.37	0.950	12.8	5.43	0.954
12.8	1.37	0.962	12.8	5.43	0.916 <sup>b</sup>
12.8	1.37	0.946	12.8	5.43	0.918 <sup>b</sup>
7.67	1.37	0.922	12.8	5.43	0.862 <sup>b,c</sup>
3.07	1.37	(1.11)	5.12	0.504	0.965 <sup>d</sup>

<sup>a</sup>  $-1.6 \times 10^{-3} M$   $Cr^{3+}$  present. <sup>b</sup> 5740 Å. <sup>c</sup>  $-4.0 \times 10^{-3} M$   $Cr^{3+}$  present. <sup>d</sup> 2800 Å.

The experiments where the excess of copper(II) was small provided, in addition, a confirmation that reaction 1 correctly described the stoichiometry. The principle of this method is as follows. Were the net reaction  $Cu^{2+} + \alpha Cr^{2+}$  (*e.g.*,  $Cu^{2+} + 2Cr^{2+}$  as in eq 5 where  $Cu_{aq}^0$  is listed as a product), the value of  $[Cu^{2+}]$  at a given time would be a function of the stoichiometry, *i.e.*, a function of  $\alpha$ . The kinetics in such circumstances would be described by

$$\ln \{[Cu^{2+}]/[Cr^{2+}]\} = \ln \{[Cu^{2+}]_0/[Cr^{2+}]_0\} + k \{[Cu^{2+}]_0 - [Cr^{2+}]_0/\alpha\} t \quad (8)$$

in which the concentration of copper(II) at each point during the run was computed from the relation  $[Cu^{2+}] = [Cu^{2+}]_0 - ([Cr^{2+}]_0/\alpha) + ([Cr^{2+}]/\alpha)$  with  $[Cr^{2+}] = [Cr^{2+}]_0(D_\infty - D)/(D_\infty - D_0)$ . Equation 8 corresponds to a rate constant  $k$  defined by the relation  $-d[Cr^{2+}]/dt = -\alpha d[Cu^{2+}]/dt = k[Cu^{2+}][Cr^{2+}]$ .

Runs with  $[Cu^{2+}]_0/[Cr^{2+}]_0 \leq 10$  were treated according to eq 8 with two values of  $\alpha$ , 1 and 2. Runs with an initial concentration ratio of 2.3 were decisive in distinguishing the alternatives. With  $\alpha$  taken as 2, the rate plots diverged from linearity. On the other hand, when  $\alpha = 1$  was used, the appropriate plots were linear and the value of  $k$  so computed agreed with that obtained at higher ratios where the issue of stoichiometry did not enter the treatment of the kinetic data. A typical experiment is depicted in Figure 1, for a run with an initial ratio  $[Cu^{2+}]_0/[Cr^{2+}]_0 = 2.3$ , in which the data were treated by both alternatives.

A second test of the reaction stoichiometry came from experiments in which the excess Cu(II) was analyzed. In one experiment with the initial concentrations

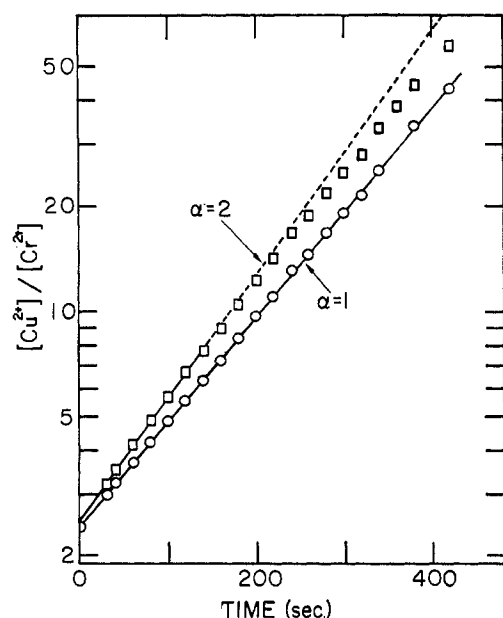


Figure 1.—Plots illustrating the use of kinetic data to substantiate stoichiometry. Run 14 of Table I was plotted assuming the stoichiometry  $\text{Cu}^{2+} + 2\text{Cr}^{2+}$  (upper curve) and  $\text{Cu}^{2+} + \text{Cr}^{2+}$  (lower curve), each with a rate  $k[\text{Cu}^{2+}][\text{Cr}^{2+}]$ . The last point shown represents 96.5% reaction.

0.011 M  $\text{Cu}^{2+}$ , 0.010 M  $\text{Cr}^{2+}$ , and 0.97 F  $\text{HClO}_4$  the absorbance was followed with time at 7500 Å, where  $\text{Cu}^{2+}$  had an absorption maximum ( $\epsilon$  11) and  $\text{Cr}^{2+}$  also absorbed ( $\epsilon$  2) but where  $\text{Cr}^{3+}$  ( $\epsilon < 0.4$ ) and  $\text{Cu}^+$  ( $\epsilon \sim 0$ ) were nearly transparent. The expected over-all decrease in absorbance in a cell with a 10-cm optical path is  $(10)(0.010)(2 + (11/\alpha))$  which is 1.30 for  $\alpha = 1$  and 0.75 for  $\alpha = 2$ . The observed absorbance decrease was 1.29, in excellent agreement with a stoichiometry producing  $\text{Cu}^+$  as given in reaction 1.

The spectrum of copper(I) obtained by subtracting the contribution of copper(II) and chromium(III) from the spectrum of the products showed no maxima; an increasing absorbance with decreasing wavelength was noted below 3500 Å. It was not possible to construct an accurate spectrum because of the presence of small quantities of impurities of high absorbance, such as  $\text{Cr}_2(\text{OH})_2^{4+}$  arising from the reactant chromium(II) solution. Approximate molar absorbances of copper(I) at the wavelengths used in the reactions 3000, 2800, and 2700 Å were 80,  $2.2 \times 10^2$ , and  $3.0 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. No independent spectrum of hydrated copper(I) is available for comparison, and no conclusive spectral identification of the product could be made.

A spectrophotometric study of the chromium(III) produced in the reaction solution and after ion-exchange chromatography produced no evidence for any Cr(III) product other than the simple hydrated cation  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ . In particular, the 4+ dimer, known to be the product of a number of Cr(II) oxidations particularly by 2-equiv reagents,<sup>6</sup> was not present in these solutions in a quantity that could be detected by ion-exchange chromatography.

(6) M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3197 (1959).

**Hydrogen Ion and Temperature Dependences.**—The second-order rate constant was studied as a function of hydrogen ion concentration, covering the range  $0.011 \leq [\text{H}^+] \leq 0.99 \text{ M}$ ; the data are summarized in Table II.

TABLE II  
KINETIC DATA FOR  $\text{Cu}^{2+}$ - $\text{Cr}^{2+}$  REACTIONS,  
AT  $[\text{ClO}_4^-] = 1.00 \text{ M}$ , MAINTAINED  
WITH LITHIUM PERCHLORATE

$10^4[\text{Cu}^{2+}]_0$ , M	$10^4[\text{Cr}^{2+}]_0$ , M	$[\text{H}^+]$ , M	Wave- length, Å	$k$ , $\text{M}^{-1} \text{ sec}^{-1}$	
				Obsd	Calcd
24.6°					
128	13.7	0.972	3000	0.809	0.773
128	13.7	0.972	3000	0.788	0.773
128	13.7	0.610	3000	1.15	1.13
128	13.7	0.510	3000	1.32	1.32
128	13.7	0.358	3000	1.76	1.81
128	13.7	0.257	3000	2.35	2.45
51.2	6.05	0.170	2800	3.75	3.62
51.2	5.49	0.100	2800	6.33	6.03
51.2	5.04	0.100	2800	6.67	6.03
25.6	2.52	0.100	2800	6.37	6.03
25.6	2.52	0.0700	2800	8.76	8.54
25.6	2.52	0.0500	2800	11.8	11.9
25.6	2.52	0.0500	2800	11.7	11.9
13.3	1.21	0.0309	2700	18.8	19.1
13.3	1.21	0.0207	2700	26.7	28.4
6.12	1.21	0.0106	2700	51.2	55.6
6.12	1.21	0.0106	2700	51.0	55.6
34.2°					
64.0	5.66	0.986	2800	1.77	1.85
38.4	3.40	0.700	2800	2.53	2.47
38.3	3.40	0.500	2800	3.25	3.33
25.6	2.27	0.300	2700	5.31	5.32
12.8	1.13	0.100	2700	15.3	15.3
6.40	1.13	0.0500	2700	32.8	30.2
15.6°					
154	14.2	0.967	3000	0.314	0.324
154	14.2	0.700	3000	0.400	0.415
154	14.2	0.500	3000	0.575	0.547
38.4	3.40	0.100	2800	2.52	2.39
25.6	3.40	0.0502	2700	4.86	4.77
25.6	2.27	0.0200	2700	11.2	11.6

The predominant rate term was inversely proportional to  $[\text{H}^+]$  as noted by the excellent linearity of plots of  $k$  vs.  $1/[\text{H}^+]$  at each of the three temperatures studied. Such plots all had nonzero intercepts, the probable interpretation being that the rate law consists of two independent terms, as represented by

$$-d[\text{Cu}^{2+}]/dt = -d[\text{Cr}^{2+}]/dt = k[\text{Cu}^{2+}][\text{Cr}^{2+}] = \{a + (b/[\text{H}^+])\}[\text{Cu}^{2+}][\text{Cr}^{2+}] \quad (9)$$

Since the rate term  $b/[\text{H}^+]$  carries the bulk of the reaction, the interpretation of the less important rate term  $a$  cannot necessarily be made in terms of a genuine reaction pathway with the transition state  $(\text{CrCu}^{4+})^\ddagger$ . We shall also consider whether this rate term could arise from a reasonable medium effect on the rate constant  $b$ .

Consider the changes in activity coefficients that may occur when equal concentrations of  $\text{H}^+$  and  $\text{Li}^+$  are traded for one another in a medium that is otherwise constant and that contains  $\text{ClO}_4^-$  as the only anion. Following Harned's rule and assuming only a single rate

term varying as  $1/[\text{H}^+]$  is important, the relation becomes.

$$k = b^0[\text{H}^+]^{-1}e^{\beta[\text{H}^+]} \cong b^0\beta + (b^0/[\text{H}^+]) \quad (10)$$

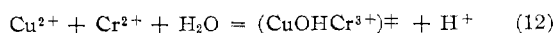
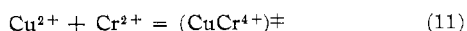
where  $b^0$  represents an intrinsic rate constant in the absence of such medium effects. This relation has the same form as the empirical rate law, eq 9, and the constant  $a = b^0\beta$ . The values at  $24.6^\circ$  yield  $a = 0.17 M^{-1} \text{sec}^{-1}$  and  $b = 0.587 \text{sec}^{-1}$ ; the parameters based on eq 10 are  $\beta = 0.29 M^{-1}$  and  $b = 0.587 \text{sec}^{-1}$ . This value of  $\beta$  appears to be nearly three times as large a medium effect as one generally finds in situations similar to this. For a replacement of  $\text{H}^+$  by  $\text{Li}^+$  in 1.00  $M$  perchlorate solution, a value of 0.1 for  $\beta$  would represent a reasonable medium effect. For that reason we reject the interpretation that the rate term  $a[\text{Cr}^{2+}][\text{Cu}^{2+}]$  represents a medium effect exclusively. We readily admit, however, that a substantial part of this kinetic term may (and probably does) arise from medium effects on  $b$  rather than a reaction pathway.

The rate was studied as a function of temperature. Values of  $k$  were fit for their simultaneous dependence upon  $[\text{H}^+]$  and temperature.<sup>7</sup> The former variation was of the form in eq 9, and the temperature dependence of each of the rate constants  $a$  and  $b$  was described by the Eyring absolute rate theory expression. On that basis the activation parameters are as follows, with the indicated uncertainties representing one standard deviation

Rate constant	$\Delta S^\ddagger$ , eu	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>
$a$	$-20.2 \pm 8.4$	$12.5 \pm 2.5$
$b$	$-2.1 \pm 1.2$	$17.1 \pm 0.4$

These four parameters reproduce the 44 observed rate constants with an rms deviation<sup>8</sup> of 4.1%.

**Reaction Mechanism.**—The formation of the transition state along each of the parallel and independent pathways from the predominant species involved can be represented by the net activation processes<sup>9</sup> as shown in



From the known molar ionic entropies and the observed values of  $\Delta S^\ddagger_a$  and  $\Delta S^\ddagger_b$ , one can calculate the molar entropy of each transition state, a quantity which has been found to correlate closely with its ionic charge.

(7) The nonlinear least-squares program for this computation was supplied by Drs. R. H. Moore and T. W. Newton. The program is based on a report from the Los Alamos Scientific Laboratory, LA 2367 + addenda.

(8) Rms deviation =  $(100/n)[\sum(k_{\text{obsd}} - k_{\text{calcd}})^2/k_{\text{obsd}}^2]^{1/2}$

(9) T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).

For  $(\text{CuCr}^{4+})^\ddagger$  and  $(\text{CuOHCr}^{3+})^\ddagger$  the values are  $S^\ddagger_a = -67 \pm 10$  and  $S^\ddagger_b = -32 \pm 4$  eu (on the scale  $S^0([\text{H}^+]) = 0$ ). Comparing these values with those in the extensive summary of Newton and Baker,<sup>10</sup> each is found to lie in the middle of the typical range of values for the two charge types under consideration. The reasonable value of  $S^\ddagger_a$  for  $(\text{CuCr}^{4+})^\ddagger$  provides a further confirmation of the conclusion that this term largely represents a genuine reaction pathway.

That the main reaction term varies as  $1/[\text{H}^+]$  may be a strong indication that the reaction is proceeding by an inner-sphere mechanism in which hydroxide ion is playing the role of a bridging ligand. The evidence that the hydrogen ion dependence of the rate of an oxidation-reduction reaction can provide information on its mechanism has been summarized in earlier publications<sup>11,12</sup> that gave the examples and references on which this hypothesis is based.

Regardless of whether the reaction occurs by an inner-sphere mechanism the true second-order rate constant can be computed, depending on whether the reaction is assumed to occur between  $\text{CuOH}^+$  and  $\text{Cr}^{2+}$ , or  $\text{Cu}^{2+}$  and  $\text{CrOH}^+$ . Since the acid dissociation quotient of  $\text{Cu}^{2+}$  is  $\sim 10^{-7} M^{13}$  and that of  $\text{Cr}^{2+}$  has not been measured but is undoubtedly very near  $10^{-7} M$ , the second-order rate constant with either of the above reacting species is ca.  $10^6 M^{-1} \text{sec}^{-1}$  at  $25^\circ$ ; lack of precise acidity constants prevents a better value at this time.

That the second stage of reduction, eq 3, is unimportant under most of the conditions encountered, except perhaps at the lowest  $\text{Cu}^{2+}/\text{Cr}^{2+}$  starting ratios, was not anticipated. Other factors being equal, it was expected that  $\text{Cu}^+$ , being a stronger oxidizing agent than  $\text{Cu}^{2+}$ , would oxidize  $\text{Cr}^{2+}$  at a higher rate. The result that the rate constant for eq 1 is higher than that for eq 3 by a factor that is  $\geq 10^2$  probably arises from the nucleation barrier for forming metallic copper encountered in the latter reaction. The same factor appears to be largely responsible for the low rate of the very favorable disproportionation reaction of  $\text{Cu}^+$ ; if the reaction must proceed by prior formation of  $\text{Cu}_{\text{aq}}^0$ , the first step of both reactions would then probably be rather unfavorable thermodynamically and kinetically.

(10) T. W. Newton and F. B. Baker, *Advances in Chemistry Series*, No. 71, American Chemical Society, Washington, D. C., 1967, p 268.

(11) D. W. Carlyle and J. H. Espenson, *J. Am. Chem. Soc.*, **90**, 2272 (1968).

(12) J. H. Espenson and O. J. Parker, *ibid.*, **90**, 3689 (1968).

(13) A. E. Martell and L. G. Sillén, "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, p 59.