ground state may be at least partially compensated by the destabilization of the activated complex due to steric inhibition of solvation. The leaving picoline group coupled with the bulky *t*-butyl groups can effectively shield the approach of solvent to the reaction site. Such an interpretation is in agreement with the more positive activation parameters observed for this exchange.

Finally, the kinetics of the corresponding cobalt(II) analog of I [$R_1 = R_2 = CH_3$] was studied. The rate of exchange of this complex is approximately an order of magnitude larger than that for the corresponding nickel complex, and this rate difference is associated with a large difference in activation energy. Such differences for Ni(II) and Co(II) complexes have been observed in other systems.[4] They are predicted by the crystal field model for a square-pyramidal or trigonal-bipyramidal intermediate and also expected from the greater Co–N bond lengths in the *trans* 2:1 complex.[14]

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY COLLEGE, NEW PALTZ, NEW YORK 12561

A Kinetic Study of the Reduction of Copper(II) by Tin(II) Chloride

BY THOMAS L. NUNES

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The reduction of Cu(II) by Sn(II) in aqueous hydrochloric acid yields kinetics and stoichiometry consistent with the reaction

$$\mathrm{Cu(II)} + \mathrm{Sn(II)} \rightleftharpoons \mathrm{Cu(I)} + \mathrm{X}$$
$$\mathrm{Cu(II)} + \mathrm{X} \longrightarrow \mathrm{Cu(I)} + \mathrm{Sn(IV)}$$

where X represents a species containing trivalent tin. The overall reaction rate is particularly sensitive to the chloride concentration, the steady state approximation failing in systems prepared with sulfuric acid instead of hydrochloric acid. A numerical curve fitting computer program was used to gain order of magnitude estimates of the separate rate constants for the nonsteady-state reactions at 25°.

Introduction

The presence of trace amounts of Cu(I) in aqueous acidic Sn(II) chloride solutions has been shown to enhance the reactivity of the solution toward dissolved nitric oxide[1] and Fe(III).[2] The identity of the reactive species does not appear to have been determined, although Powell and Nunes suggested the existence of a Cu(II) complex containing the $SnCl_3^-$ ion as a ligand. Experiments indicate that the reactive species in the nitric oxide reduction is not one of the stable oxidation states of copper or tin.[1,3]

If the reactive species in the Sn(II)–Cu(I) system is an active intermediate existing at low concentrations during a reduction, then a kinetic study of the reduction of Cu(II) by Sn(II) in hydrochloric acid solution might shed some light on the question of the nature of this intermediate. To the author's knowledge, this work represents the first such study.

Experimental Section

Apparatus.—The absorbance of reacting solutions was followed on a Beckman DB uv–visible spectrophotometer equipped with a thermostated sample compartment and a Beckman Model B spectrophotometer without thermostating. The reaction cell was constructed from a 3.6-cm length of Pyrex tubing equipped with two side arms to allow its use as a flow cell. The ends were ground parallel, and optical-quality cell windows were affixed with either polyester casting resin or Canada Balsam. A Beckman 1.0-cm optical path length flow cell was used for some runs at high Cu(II) concentration.

A stopped-flow technique was used employing a mixing system constructed from two three-way stopcocks, two 5-ml ground-glass syringes, and a "Y" cell designed for efficient mixing. Two 25-ml burets were used as reservoirs. A schematic of the system appears in Figure 1.

Both syringes could be emptied through the mixing cell simultaneously in less than 1 sec. The volume of the mixing cell was approximately 1 ml while the tube from the mixing cell to the reaction cell contained another 1.5 ml. Consequently, the maximum time between mixing and observing was approximately 0.25–0.5 sec. The time required for the Beckman DB meter to indicate 90% of a full-scale deflection was approximately 1 sec. The first half-life of all runs was 10 sec or longer with succeeding half-lives growing progressively longer for each second-order reaction. It was felt that the response time of the system was short enough compared to the reaction rates to allow meaningful measurements to be made.

Reagents.—Fisher Certified ACS reagents were used without purification except stannous chloride dihydrate, which was boiled in hydrochloric acid solution in the presence of tin pellets and recrystallized under nitrogen. All solutions were prepared with boiled distilled water and stored under nitrogen. Sulfuric and hydrochloric acid solutions were standardized by accepted procedures.[4]

Copper(I) chloride was prepared by boiling a hydrochloric acid solution of copper(II) chloride in the presence of copper pellets.

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[1] T. L. Nunes and R. E. Powell, to be submitted for publication.

[2] B. E. Reznik, N. A. Bidnyak, and M. V. Pchelkina, *Izv. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, **6**(2), 209–11 (1963); *Chem. Abstr.*, **59**, 5834*d* (1963).

[3] T. L. Nunes, Dissertation, University of California, Berkeley, Calif., 1967; available from University Microfilms, Ann Arbor, Mich. (Order No. 68-10,384).

[4] L. F. Hamilton and S. G. Simpson, "Quantitative Chemical Analysis," The Macmillan Co., New York, N. Y., 1958, p 157 ff.

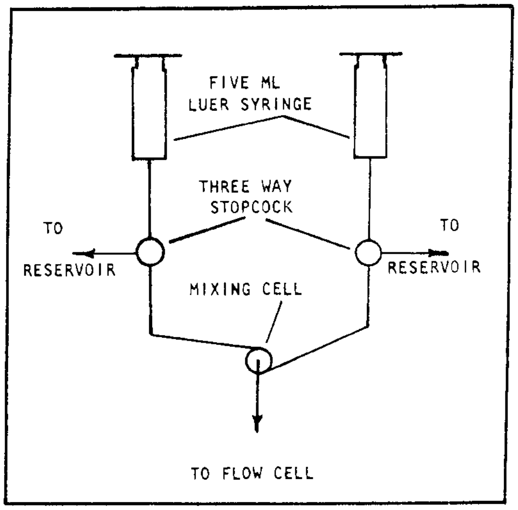

Figure 1.—Schematic of mixing apparatus.

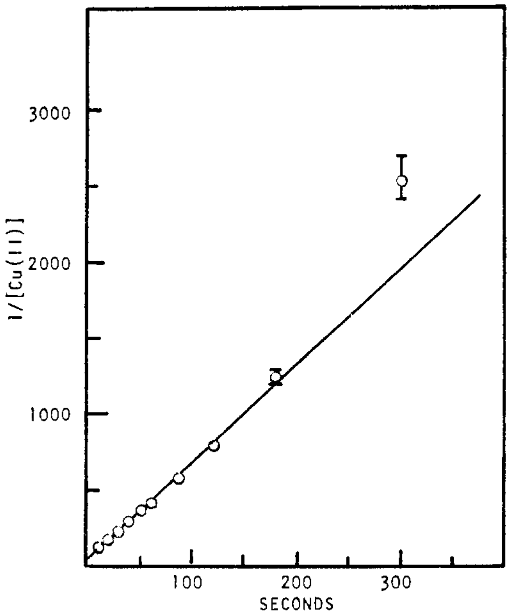

Figure 2.—Plot of 1/[Cu(II)] *vs.* time: circles, data; ———, least-squares fit to first 400 sec. Conditions: 25°, 0.75 M HCl, 0.25 M KCl, 0.50 M $SnCl_2$, $[Cu(II)]_0 = 0.035$ M.

The precipitated copper(I) chloride was filtered and rinsed with ethyl ether under nitrogen and stored under nitrogen in a desiccator until use.

Calculations.—All least-squares fits and numerical integrations were run on IBM 1130 computer. FORTRAN IV programs written by the author and subroutines from the IBM Scientific Subroutine Package were used exclusively.

Procedure.—The absorbance of the reacting solution compared to an air blank was read directly from the meter of the Beckman DB. The absorbance due to Cu(II) was obtained by subtracting the final absorbancy reading (reading at infinite time) from the reading of interest. The conversion factor between Cu(II) absorbance and concentration was determined from the slope of a plot of absorbance of known solutions of Cu(II) in hydrochloric acid against Cu(II) concentration. The free chloride concentrations in the reference solutions were adjusted to the same values as in the reacting solutions by varying the hydrochloric acid concentration.

The same flow cell was used for all measurements except those with an initial Cu(II) concentration of 0.10 M, in which a shorter flow cell (1.0 cm) was used to keep readings within the sensitive region of the instrument. All runs were made with a large excess of Sn(II), whose concentration remained essentially constant during the course of each reaction.

Most runs were followed at a wavelength of 7200 Å. A series of runs between 8000 and 10,000 Å was made on a Beckman Model B with an unthermostated cell.

Results and Discussion

Absence of Colored Intermediate.—Identical kinetic runs were followed between wavelengths of 6400 and 7200 at 200-Å intervals, while another set of identical runs was followed between wavelengths of 7200 and 8000 Å at 200-Å intervals and between 8000 and 10,000 Å at 500-Å intervals. Plots of log ($A - A_\infty$) against time (A is absorbance) were identical for each group within experimental error except for displacement along the log ($A - A_\infty$) axis.

The formation of a significant concentration of colored intermediate, such as a Cu(II) complex, cannot have taken place slowly, as the functional dependence of absorbance with time should be different in regions where the complex absorbs strongly. The wavelength region covered includes the region where copper(II)–ammine complexes absorb more strongly than the hexaaquo complex[5] and where the $CuCN^+$ ion is known to absorb.[6]

Rate Law in Chloride System. (a) Cu(II) Dependence.—For all runs, a second-order plot (namely, 1/[Cu(II)] *vs.* time) proved linear for at least 4 half-lives. Figure 2 contains such a plot for a typical experiment.

As indicated in Table I and Figure 3, the pseudo-second-order rate constants for each run show an inverse dependence upon the initial Cu(II) concentration.

TABLE I

INITIAL Cu(II) CONCENTRATION DEPENDENCE[a]

$[Cu(II)]_0$, M	Pseudo-second-order rate const, M^{-1} sec^{-1}	$[Cu(III)]_0$, M	Pseudo-second-order rate const, M^{-1} sec^{-1}
0.0010	114 ± 36	0.010	19.7 ± 0.7
0.0020	96 ± 15	0.035	5.98 ± 0.2
0.0035	42 ± 4	0.10	2.2 ± 0.2
0.0070	24 ± 5		

[a] At 25°; $[SnCl_2] = 0.50$ M; $[HCl] = 1.00$ M.

The initial reaction rates, determined by least-squares fitting of a sixth-degree polynomial to the first minute of each run and taking its slope at zero time, show a direct first-order dependence upon the initial Cu(II) concentration.

A rate law consistent with these observations is

$$-d[Cu(II)]/dt = K_1[Cu(II)]^2/[Cu(II)]_0 \qquad (1)$$

where $[Cu(II)]_0$ represents the initial stoichiometric concentration of Cu(II).

(b) Cu(I) Dependence.—Additional copper(I) chloride decreased both the initial rate and the pseudo-second-order rate constant (K_2). A plot of log K_2 against log ($[Cu(II)]_0 + [Cu(I)]_0$) yields a straight

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[5] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 757.

[6] F. R. Duke and W. G. Courtney, *J. Phys. Chem.*, **56**, 19 (1952).

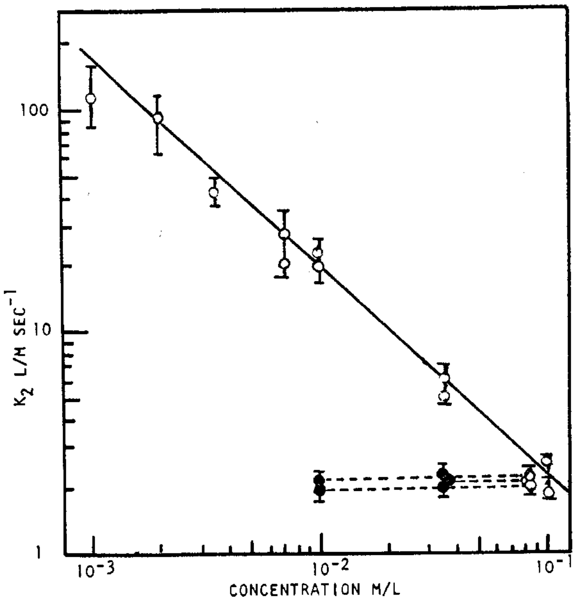

Figure 3.—Pseudo-second-order rate constants (K_2) *vs.* functions of initial Cu(II) and Cu(I) concentrations: open circles, K_2 *vs.* ($[Cu(II)]_0 + [Cu(I)]_0$); solid circles, K_2 *vs.* $[Cu(II)]_0$ for runs begun with excess Cu(I); ———, least-squares fit to open circles. The dotted lines connect two points for the same run for K_2 plotted against both concentration functions. Conditions: 25°, 0.50 M $SnCl_2$, 1.00 M HCl.

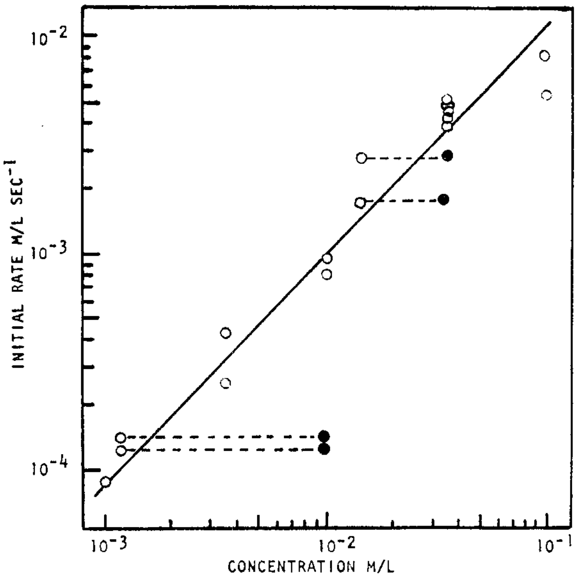

Figure 4.—Initial rate *vs.* functions of initial Cu(II) and Cu(I) concentrations: open circles, initial rate *vs.* $[Cu(II)]_0^2/([Cu(II)]_0 + [Cu(I)]_0)$; solid circles, initial rate *vs.* $[Cu(II)]_0$ for runs begun with excess Cu(I); ———, least-squares fit to open circles. The dotted lines connect two points for the same run for initial rates plotted against both concentration functions. Conditions: 25°, 0.50 M $SnCl_2$, 1.00 M HCl.

line with a least-squares slope of −0.95. Figure 3 contains such a plot. Log K_2 for runs begun with excess Cu(I) are also plotted against log [Cu(II)] on the same graph for comparison.

Figure 4 shows a plot of the logarithm of the initial rate against the logarithm of $[Cu(II)]_0^2/([Cu(II)]_0 + [Cu(I)]_0)$. Runs with initial excess Cu(I) are also shown plotted against the logarithm of $[Cu(II)]_0^2/[Cu(II)]_0$. A rate law consistent with observations cited up to this point is

$$-d[Cu(II)]/dt = K_3[Cu(II)]^2/[Cu(II)]_0 + [Cu(I)]_0) \qquad (2)$$

The value of K_3 determined from the pseudo-second-order rate constant of 15 different kinetic runs is 0.188 ± 0.015 sec^{-1}. The value of K_3 determined from the initial rates of 18 different kinetic runs was 0.116 ± 0.025 sec^{-1}. The error of the above values is twice the standard deviation of the mean. Runs from which these values were determined were made at the following stoichiometric concentrations: $[SnCl_2] = 0.50$ M and $[HCl] = 1.00$ M.

The two values of K_3 are quite close together. Lacking many data points very close to zero time (data points were taken every 10 sec during the first minute), it is necessary to view the K_3 value extracted from initial rates to be, at best, an estimate of the lower bound of the actual value. In spite of the fact that the two values reported differ by more than their error terms, it would be unrealistic to attach significance to this difference. Both techniques appear to be measuring the same number, the best value of which is determined from the pseudo-second-order rate constants.

(c) **Acid Dependence.**—Runs were made varying the hydrochloric acid concentration between 0.1 and 1.0 M. For all such runs, the total chloride concentration was held constant by adding potassium chloride such that the sum of the molar concentrations of KCl and HCl remained fixed at 1.00 M. No significant variation of rates was observed.

(d) **Sn(IV) Dependence.**—Initial concentrations of Sn(IV) as high as 0.025 M had no measurable affect on the reaction rates.

(e) **Sn(II) and Chloride Dependence.**—Runs were made with total Sn(II) concentrations of 2.01, 0.50, and 0.210 M. Hydrochloric acid concentration was adjusted to maintain an ionic strength of 1.02 ± 0.05. Table II lists the concentrations of the various species present in the solutions calculated from literature values of the stability constants of tin(II) chloride species.[7,8] along with the value of K_3 found for each solution.

Independent changes of total Sn(II) or total chloride

TABLE II

Sn(II) AND CHLORIDE DEPENDENCE

$[Sn(II)]^a$	2.01	0.05	0.210
[HCl]	0.50	1.00	1.05
$[Cl^-]$	0.60	0.92	1.00
$[Sn^{2+}]$	0.059	0.0061	0.0021
$[SnCl^+]$	0.41	0.065	0.024
$[SnCl_2]$	1.10	0.27	0.11
$[SnCl_3^-]$	0.42	0.16	0.072
K_3, sec^{-1}	0.344 ± 0.02	0.197 ± 0.02	0.079 ± 0.002

[a] The notation [Sn(II)] is used to designate the stoichiometric molar concentration of Sn(II).

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(7) G. P. Haight, J. Zoltewicz, and W. Evans, *Acta Chem. Scand.*, **16**, 311 (1962).

(8) L. G. Sillén, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

concentrations without varying the ionic strength would only have been possible by adding a nonreactive, noncomplexing salt. Potassium perchlorate or nitrate immediately comes to mind, but these compounds have been shown to be reducible by tin(II) chloride solutions in the presence of certain catalysts such as tungstate[9] and molybdate.[10] Rather than complicate matters by the possible inclusion of the kinetics of an additional reaction, it was felt best to report the available data and allow the reader to draw what conclusions he will.

A possible approach to the interpretation of this data would be to plot log K_3 against the logarithm of the concentrations of each of the tin(II) chloride species in hopes of finding a linear relationship with a slope of +1. As the reader may verify, log K_3 *vs.* log $[SnCl_3^-]$ yields a straight line with a slope very close to +1. While this relation is doubtless not unique, it does have the virtue of being simple and agreeing somewhat with one's chemical intuition.

Bearing in mind the questionable manner in which the Sn(II) and chloride dependences were obtained, the final rate law may be written as

$$-\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t = \frac{K_4[\mathrm{SnCl_3^-}][\mathrm{Cu(II)}]^2}{([\mathrm{Cu(II)}]_0 + [\mathrm{Cu(I)}]_0)} \qquad (3)$$

where, for an ionic strength of 1.02 ± 0.05 *M* and a temperature of 25°, $K_4 = 1.05 \pm 0.2\ M^{-1}\ \mathrm{sec}^{-1}$.

Rate Law in Sulfate–Chloride System.—Several runs were made in solutions which were 0.50 *M* in stannous chloride dihydrate and 1.00 *M* in sulfuric acid. Again, the initial rate showed a direct dependence upon the initial Cu(II) concentration. For the relationship

$$-(\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t)_{t=0} = K_5[\mathrm{Cu(II)}]_0 \qquad (4)$$

K_5 assumed the value of $0.0069 \pm 0.0015\ \mathrm{sec}^{-1}$ at 25°.

The data from a single run did not yield simple first- or second-order kinetics. An initial rapid reaction was followed by a portion in which a plot of 1/[Cu(II)] against time yielded a reasonable straight line, followed by a more rapid ending. The second-order portion lasted from 40 to 60% of the entire run, and showed an inverse dependence upon the initial Cu(II) concentration. Table III lists the pseudo-second-order rate constants extracted graphically from the linear portion of a 1/[Cu(II)] *vs.* time plot.

For the relationship

$$-\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t = K_6[\mathrm{Cu(II)}]^2/[\mathrm{Cu(II)}]_0 \qquad (5)$$

K_6 assumed the value of $0.0033 \pm 0.0003\ \mathrm{sec.}^{-1}$

Unlike the pure chloride system, the pseudo-first-order and pseudo-second-order rate constants derived from initial rates and complete runs, respectively, could not be reconciled as being two manifestations of the same constant (see K_3 above), the pseudo-second order rate constants being too low by a factor of 2.

Although investigation of tin(II) sulfate aqueous systems have been made,[11,12] the stability constants of tin(II) sulfate species were not known with sufficient accuracy to allow the preparation of other solutions with constant ionic strength. Consequently, the Sn(II) dependence was not determined.

Absence of Chloride.—Test tube experiments performed with tin(II) sulfate–sulfuric acid solutions prepared by ion exchange showed no perceptible reaction with Cu(II) over a 24-hr period at 25°.

Suggested Mechanism.—The dependence on Cu(II) and the retarding effect of Cu(I) may be described by the mechanism

TABLE III

INITIAL Cu(II) CONCENTRATION DEPENDENCE[a]

$[\mathrm{Cu(II)}]_0$, *M*	Pseudo-second-order rate const, $M^{-1}\ \mathrm{sec}^{-1}$	$[\mathrm{Cu(II)}]_0$, *M*	Pseudo-second-order rate const, $M^{-1}\ \mathrm{sec}^{-1}$
0.0010	4.1 ± 0.8	0.035	0.10 ± 0.02
0.0035	1.1 ± 0.1	0.10	0.024 ± 0.002
0.010	0.29 ± 0.05		

[a] At 25°; $[\mathrm{SnCl_2}] = 0.50\ M$; $[\mathrm{H_2SO_4}] = 1.00\ M$.

$$\mathrm{Cu(II)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Cu(I)} + \mathrm{X} \qquad (\mathrm{I})$$

$$\mathrm{Cu(II)} + \mathrm{X} \xrightarrow[k_2]{} \mathrm{Cu(I)} + \mathrm{Sn(IV)} \qquad (\mathrm{II})$$

where k_1 includes the $SnCl_3^-$ dependence and X represents a species containing Sn(III).

Assuming the steady-state condition for X and setting

$$[\mathrm{Cu(I)}] = [\mathrm{Cu(I)}]_0 + [\mathrm{Cu(II)}]_0 - [\mathrm{Cu(II)}] \qquad (6)$$

where the subscript "0" indicates initial concentration, the following rate law may be derived

$$-\mathrm{d}[\mathrm{Cu(II)}]/\mathrm{d}t = \frac{2k_1k_2[\mathrm{Cu(II)}]^2}{k_{-1}([\mathrm{Cu(I)}]_0 + [\mathrm{Cu(II)}]_0) + (k_2 - k_{-1})\,[\mathrm{Cu(II)}]} \qquad (7)$$

If the second term of the denominator is much smaller than the first during most of the run, the rate law reduces to the form of eq 2 where

$$K_3 = 2k_1k_2/k_{-1} \qquad (8)$$

To test the possibility that the reaction in sulfuric acid solution might be following the same mechanism under nonsteady-state conditions, the parameters k_1, k_{-1}, and k_2 were approximated by trial and error fitting of numerical solutions to the nonsteady-state equations. A Runge–Kutta integrating subroutine from the IBM Scientific Subroutine Package was used for generating trial functions. The results are presented in Table IV.

As may be seen, the values of k_1 are quite close to the value of the pseudo-first-order rate constant for the more rapid initial reaction (K_5). Unfortunately, the solutions of the differential equations were particularly insensitive to the values of k_{-1} and k_2, and at this stage it is doubtful whether or not the wide variations in k_{-1} and k_2 in Table IV can be considered significant.

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[9] G. P. Haight, *J. Am. Chem. Soc.*, **76**, 4718 (1954).

[10] (a) G. P. Haight, P. Mohilner, and A. Katz, *Acta Chem. Scand.*, **16**, 221 (1962); (b) G. P. Haight and A. Katz, *ibid.*, **16**, 659 (1962).

[11] C. A. Discher, *J. Electrochem. Soc.*, **100**, 480 (1953).

[12] C. A. Discher, *ibid.*, **100**, 45 (1953).

TABLE IV

APPROXIMATE k_1, k_{-1}, AND k_2 FROM CURVE FITTING[a]

$[Cu(II)]_0$, M	k_1, sec^{-1}	k_{-1} M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}
0.001	0.0075	15	8.8
0.0035	0.0093	6.0	4.3
0.010	0.0075	4.2	2.7
0.035	0.0062	3.5	1.2

[a] At 25°; $[SnCl_2] = 0.50\ M$; $[H_2SO_4] = 1.00\ M$.

The treatment given here does not demonstrate conclusively that the same mechanism is active in both hydrochloric acid and sulfuric acid solutions. A satisfactory treatment of the nonsteady-state reaction must await improved computing techniques.

Related Phenomena.—The suggested mechanism is similar to that reported by Wetton and Higginson[13] for the reduction of Fe(III) to Fe(II) by Sn(II) in hydrochloric acid solution. The same authors suggest the presence of Sn(III) as an intermediate in the reduction by Sn(II) of Ce(IV), Cr(VI), and Mn(VII).

The catalytic effect of Cu(I) to the reduction of Fe(III) noted by Reznik, *et al.*,[2] may have been caused, in part, by the injection of Sn(III) into the solution by the reduction of Cu(II), itself produced by oxidation of Cu(I) by Fe(III).

An explanation of the strong dependence upon free chloride concentration can only be speculative at this point. Two possibilities come to mind. First, one of the steps in the suggested mechanism may involve a chlorine atom transfer. Since both stable oxidation states of tin and copper are known to form labile coordination complexes with chloride ion, this is not unreasonable. The absence of chloride would prevent the reaction from following the above mechanism, and if another mechanism were not available, the reaction would not proceed (as was observed).

On the other hand, the ability of the $SnCl_3^-$ ion to act as a ligand to other metal ions suggests that the first step might be the formation of a Cu^{II}–$SnCl_3^-$ complex followed by the rapid disproportionation to Cu(I) and a Sn(III) species. The π-acceptor capabilities of $SnCl_3^-$ have been compared to that of the CN^- ion,[14] and it may be that the initial step of the proposed mechanism is analogous to the disproportionation of the $Cu(CN)_4^{2-}$ ion in the reduction of Cu(II) to Cu(I) by the CN^- ion.[6] Again, absence of chloride would make this mechanism impossible for the reaction to follow by removing the $SnCl_3^-$ ion from the reaction mixture.

If the second suggestion is correct, then the Cu(II)–$SnCl_3^-$ complex must be either a short-lived species or nonabsorbing in the wavelength region between 6400 and 10,000 Å. As most Cu(II) complexes do absorb in this region, the former is probably nearer the truth.

The present work cannot distinguish between the above two suggestions.

The absence of a colored intermediate would also support the suggestion that the mechanism does not involve reduction to Cu^0 and its subsequent oxidation to Cu(I) by Cu(II), which might seem probable as Sn(II) prefers two equivalent reactions. The Cu^0–Cu(II) species, containing two oxidation states of the same element, should be highly colored. Indeed, the preparation of Cu(I) by boiling copper(II) chloride and Cu^0 passes through a deeply colored stage, presumed to be due to the presence of this intermediate.

In any case, if the proposed skeletal mechanism is correct and if the computer fits to the nonsteady-state reaction are correct to an order of magnitude, then the nonsteady-state reaction may maintain a Sn(III) species at concentrations greater than 10^{-4} M for 10 min or more. Such solutions might serve as a useful source of trivalent tin.

Conclusions.—The reactive species in the copper-catalyzed reductions by tin(II) chloride solutions has not been identified. However, evidence has been cited supporting the existence of a long-lived reactive Sn(III) species. The existence of a very short-lived Cu(II)–$SnCl_3^-$ complex has also been suggested from quite tenuous kinetic evidence. A more detailed study of a catalyzed reaction may reveal that either or both moieties are kinetically important.

Acknowledgment.—This study was supported by a State University of New York Research Foundation Faculty Research Fellowship Award. The assistance of Mr. Roger Yetzer and the New Paltz Department of Mathematics in applying the IBM 1130 computer is gratefully acknowledged.

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[13] E. A. M. Wetton and W. C. E. Higginson, *J. Chem. Soc.*, 5890 (1965).

[14] R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).