close similarity in rate constants and activation parameters for the reduction products of both dichlororuthenium(III) isomers leaves the appropriate interpretation of these rates somewhat in doubt. It is possible that the rates of substitution for both *cis*- and *trans*-$RuCl_2$ isomers is the same. Alternatively isomerization may have occurred in the electrode reduction to give the same ruthenium(II) chloride complex. On the basis of the experimental data it is impossible to distinguish between these two alternatives.

There are two other rate studies which are related to the ruthenium(II) chloride complexes. Seewald, Sutin, and Watkins[13] observed the rate of decomposition of a chloride bridge intermediate in the chromium(II) reduction of $RuCl^{2+}$. An upper limit of $6.0 \times 10^{-2}$ sec$^{-1}$ was set by these authors for the rate of the reaction

$$[Ru\text{-}Cl\text{-}Cr]^{4+} \xrightarrow{k} Ru^{2+} + CrCl^{2+} \qquad (8)$$

This reaction would be expected to be somewhat faster than the hydrolysis of $RuCl^+$. Therefore, these results are not inconsistent with ours.

In a preliminary communication Kallen and Earley[14] reported the rate of addition of chloride to $Ru^{3+}$, catalyzed by $Ru^{2+}$. He showed that the rate of this reaction was limited by the substitution of chloride on ruthenium(II). At 25° he found the second-order rate constant for the reverse of reaction 2 was $8.5 \times 10^{-3}$ sec$^{-1}$. If this rate is combined with the forward rate we have measured for reaction 2, an equilibrium quotient of approximately 0.1 is obtained, if the small difference in temperature and the different ionic strengths are ignored. The reverse reaction did not contribute significantly to the measured reaction rate, under the experimental conditions which were used in this work (approximately zero free chloride concentration). This equilibrium constant is comparable in magnitude to other $M^{2+}$ systems.[15]

The rates of hydrolysis of the ruthenium(II) chloride complexes are much more rapid than those observed for the corresponding ruthenium(III) chlorides.[16] This large difference of rate upon reduction to ruthenium(II) was also noted by Endicott and Taube[17] for the chloropentaammine complexes. In both these systems the relative rates of the two oxidation states are estimated at a factor of approximately $10^4$.

In summary, we have shown that the ruthenium(II) chloride complexes exist as unstable intermediates when ruthenium(III) chloride species are reduced. A qualitative visible spectrum for the monochloro complex of this series was obtained. The rates of hydrolysis of these ruthenium(II) chloride complexes have been shown to be much more rapid than the corresponding ruthenium(III) complexes.

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# The Oxidation of Tin(II) by Hydrogen Peroxide

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In perchloric acid the oxidation of tin(II) by hydrogen peroxide is complicated and does not obey a simple rate law. During the course of the reaction the apparent extent of the reaction determined from spectrophotometric measurements differs markedly from the extent determined by direct chemical analysis. The reaction rate is inhibited by Cu(II) and obeys a second-order rate law in the presence of Cu(II). Isotope fractionation experiments give results intermediate between those expected for one- and two-electron mechanisms. All of the data appear to be consistent with a mechanism involving both one- and two-electron pathways.

## Introduction

The reduction of hydrogen peroxide may involve either a single 2-equiv step[1] or a sequence of 1-equiv steps.[2] Either of these mechanisms seems equally likely for the reduction of hydrogen peroxide by tin(II). In hydrochloric acid solutions, isotopic fractionation data[3] and lack of induced reduction[4] of $K_3Co(C_2O_4)_3$ have been taken as evidence for a single step 2-equiv mechanism. The reaction in perchloric acid solution has not been studied.

The stoichiometry and rate of the tin(II)–vanadium(V) reaction are vastly different in perchloric acid as compared to hydrochloric acid.[5] Therefore we decided to investigate the kinetics and mechanism of the tin(II)–hydrogen peroxide reaction in perchloric acid and compare the results with those obtained in hydrochloric acid solutions.

## Experimental Section

**Materials.**—Solutions of tin(II) perchlorate were prepared and analyzed as described previously.[5] Hydrogen peroxide solutions were prepared by dilution of Baker Analyzed 30% hydrogen peroxide and were standardized by conventional volumetric

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[1] J. H. Swinehart, *Inorg. Chem.*, **4**, 1069 (1965).

[2] C. F. Wells and M. A. Salam, *J. Chem. Soc. A*, 24, (1964).

[3] A. E. Cahill and H. Taube, *J. Amer. Chem. Soc.*, **74**, 2312 (1952).

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methods. Copper perchlorate was prepared by dissolving copper oxide in hot perchloric acid. Crystals of the copper salt were obtained by cooling the solution in an ice bath. Stock solutions were prepared by dissolving the recrystallized salt in dilute perchloric acid. Copper was determined spectrophotometrically as the ammine complex. Cobalt perchlorate was obtained from G. F. Smith Co. and was recrystallized from 9–10 *M* perchloric acid prior to use. Cobalt was determined spectrophotometrically.[6] Cerium(IV) perchlorate solutions were prepared from $(NH_4)_2Ce(NO_3)_6$. The starting material was reduced by hydrogen peroxide to cerium(III) which was precipitated as the oxalate salt. The cerium(III) oxalate was removed by filtration and ignited to cerium(IV) oxide. The oxide was dissolved in perchloric acid containing excess hydrogen peroxide. The excess hydrogen peroxide was destroyed by boiling the solution in the presence of a platinum gauze. The resulting cerium(III) solution was electrolytically oxidized to produce cerium(IV). The solution was standardized by titration with iron(II) sulfate. Stock solutions of perchloric acid and lithium perchlorate were prepared as before.[5]

**Rate Measurements.**—The apparatus and procedures used for rate measurements were essentially the same as described by Newton and Baker.[7] The progress of the reaction was monitored by measuring the absorbance at 250–270 nm, where tin(II) is the only reactant or product which absorbs strongly, as a function of time. All operations were carried out under an argon atmosphere.

**Extent of Reaction.**—A comparison of the extent of the reaction determined by spectrophotometry and direct chemical analysis was made by mixing the reactants in an absorption cell, allowing the reaction to proceed, and quenching the reaction by the addition of a known excess of cerium(IV). The amount of cerium(IV) remaining after quenching was determined by titration and allowed calculation of the extent of reaction. The absorbance at the time of quenching and $A_0$ and $A_\infty$ obtained from a replicate run which was not quenched were used to calculate the extent of reaction from the spectrophotometric data.

**Calculations.**—Apparent second-order rate constants were calculated from the absorbance *vs.* time data by use of a nonlinear least-squares computer program.[8]

**Oxygen Isotope Fractionation Experiments.**—Reaction mixtures were quenched by the addition of a known excess of cerium(IV). Samples of the oxygen liberated by reaction of cerium(IV) with unreacted hydrogen peroxide were collected by vacuum-line techniques and submitted[9] for isotopic analysis. The extent of reaction was determined by titration of the excess cerium(IV) with iron(II). Fractionation factors, as defined by Cahill and Taube,[3] were calculated from the data.

## Results

**Stoichiometry.**—Stoichiometry studies were carried out by mixing tin(II) and hydrogen peroxide in various mole ratios, allowing the reaction to go to completion, and determining the excess reagent left after reaction. For samples in which the Sn(II):$H_2O_2$ initial mole ratio varied over the range 20:1 to 1:20, the agreement between the amount of excess reagent found and the amount expected assuming 1 g-atom of Sn(II) reacts with 1 mol of $H_2O_2$ was usually ±0.5% or better. There was no evidence of metal ion catalyzed decomposition of $H_2O_2$.

**Rate Law.**—The absorbance *vs.* time curves obtained from rate runs show a rapid initial decrease in absorbance followed by a slower absorbance decrease. Second-order plots prepared from the absorbance *vs.* time data also exhibit curvature, particularly during the initial rapid portion of the reaction. Apparent second-order rate constants calculated from the data also indicate departure from second-order kinetics and are shown in Table I. The possibility was considered that the initial rapid portion of the reaction might be due to the rapid consumption of impurities in the reagents. Reagents which had been deliberately cross contaminated gave essentially the same results as uncontaminated reagents. Apparent initial rates calculated from the slopes of the absorbance *vs.* time curves had little or no correlation with reagent concentrations.

Somewhat similar behavior has been reported[10] for the analogous reaction between hydrogen peroxide and uranium(IV). Inhibition of the U(IV)–$H_2O_2$ reaction by Cu(II) and lack of reproducibility of the rate measurements were cited as evidence that the reaction proceeded by a chain mechanism involving free radicals. Because a similar mechanism is possible for the Sn(II)–$H_2O_2$ reaction, the effect of Cu(II) was investigated. The results are summarized in Table I. In the presence of Cu(II) the rate is decreased and obeys a second-order rate law. Increasing the Cu(II) concentration beyond that shown in Table I did not further inhibit the rate. Cobalt(II) ion was observed to have essentially no effect on the rate of the reaction.

TABLE I

APPARENT SECOND-ORDER RATE CONSTANTS[a]

| $10^3[Sn(II)]_0$, *M* | $10^3[H_2O_2]_0$, *M* | $10^3[Cu(II)]_0$, *M* | $k$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|---|
| 1.33 | 0.221 | 0.00 | 6.6 |
| 1.10 | 0.221 | 0.00 | 8.5 |
| 0.88 | 0.221 | 0.00 | 16.4 |
| 1.01 | 5.05 | 0.00 | 1.2 |
| 1.01 | 3.03 | 0.00 | 5.4 |
| 1.01 | 2.02 | 0.00 | 7.1 |
| 0.88 | 0.22 | 0.84 | 1.14 |
| 0.272 | 0.544 | 1.40 | 0.83 |
| 0.272 | 1.63 | 1.40 | 0.84 |
| 0.272 | 2.72 | 1.40 | 0.87 |
| 0.272 | 5.44 | 1.40 | 0.81 |
| 0.514 | 5.44 | 1.40 | 0.77 |
| 2.18 | 5.44 | 1.40 | 0.85 |
| 0.88 | 0.88 | 2.55 | 0.87 |

[a] Conditions: $[HClO_4] = 1.00\ M$, $\mu = 2.00\ (LiClO_4)$, 25°.

**Evidence for an Intermediate.**—A rationalization for the shape of the absorbance *vs.* time curves and for the effect of Cu(II) ion is that a non-steady-state intermediate which absorbs at 250–270 nm is produced during the course of the reaction. The observed absorbance curves would be a composite of the decay of Sn(II) and the grow-in of the intermediate. The effect of Cu(II) is to serve as a trap for the intermediate and to eliminate the reaction pathway which generates the intermediate.

If an intermediate which absorbs in the same region as Sn(II) is produced, it might be expected that the extent of reaction determined from spectrophotometric data and the extent of reaction determined by other means would not be in agreement. The results of experiments in which the extent of reaction was determined simultaneously by quenching the reaction with Ce(IV) and by spectrophotometry are summarized in Table II.

The data in Table II clearly demonstrate that there is a significant difference in the extent of the reaction as determined by the two methods. The observations are consistent with the hypothesis of a non-steady-state intermediate which absorbs in the 250–270-nm region.

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(6) J. S. Fritz and G. H. Schenk, Jr., "Quantitative Analytical Chemistry," 2nd ed, Allyn and Bacon, Boston, 1969, p 579.

(7) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(8) Supplied by Dr. T. W. Newton of the Los Alamos Scientific Laboratory.

(9) Isotopic ratio analyses were performed by the University of Utah Geology Department.

(10) F. B. Baker and T. W. Newton, *J. Phys. Chem.*, **65**, 1897 (1961).

Table II
Extent of Reaction: Quenching *vs.* Spectrophotometry[a]

| $10^3[Sn(II)]_0$, $M$ | $10^3[H_2O_2]_0$, $M$ | $10^2[Cu(II)]_0$, $M$ | % complete: Quenching | % complete: Spectrophotometry |
|---|---|---|---|---|
| 2.43 | 1.22 | 0.00 | 88 ± 3 | 38 ± 0.5 |
| 1.17 | 2.34 | 0.00 | 71 ± 3 | 56 ± 1 |
| 1.17 | 1.17 | 0.00 | 57 ± 3 | 46 ± 1 |
| 1.17 | 1.17 | 1.40 | 46 ± 3 | 50 ± 1 |

[a] Conditions: $[HClO_4] = 1.00\ M$, $\mu = 2.00$ ($LiClO_4$), 25°, λ 255 nm.

Cahill and Taube[5] have demonstrated that isotope fractionation studies of hydrogen peroxide reactions can be used to gain information about the mechanism. An initial 1-equiv step should yield a value of 1.00 for the fractionation factor, as defined by Cahill and Taube, and a value of 0.940 for an initial 2-equiv step. The value observed by Cahill and Taube for the Sn(II)–$H_2O_2$ reaction in hydrochloric acid was 0.943 indicative of a 2-equiv step.

The results of some fractionation experiments are shown in Table III. The values of the fractionation factors lie between those expected for a 1-equiv or a 2-equiv mechanism and suggest that both types of processes are operative. Our value obtained from HCl solutions does not agree with that reported by Cahill and Taube. A brief series of kinetic experiments indicates that marked deviation from second-order behavior occurs in HCl solutions. Adherence to a second-order rate law should have been observed if the mechanism was a single, 2-equiv step.

Table III
Results of Isotopic Fractionation Experiments

| $10^2[Sn(II)]_0$, $M$ | $10^2[H_2O_2]_0$, $M$ | $10^2[Cu(II)]_0$, $M$ | $[HClO_4]$, $M$ | [HCl], $M$ | Fractionation factor[a] |
|---|---|---|---|---|---|
| 2.1 | 3.0 | 0.0 | 1.24 | 0.0 | 0.972 |
| 1.9 | 3.0 | 6.0 | 1.29 | 0.0 | 0.965 |
| 1.5 | 3.0 | 0.0 | 0.00 | 0.96 | 0.957 |

[a] As defined in ref 3.

Higginson has used the induced reduction of $K_3Co(C_2O_4)_3$ as a test for the presence of Sn(III) as an intermediate in the oxidation of Sn(II). In experiments where the initial concentration of the cobalt complex was about equal to the Sn(II) and $H_2O_2$ concentrations, no induced reduction of $K_3Co(C_2O_4)_3$ could be detected.

## Conclusions and Summary

In perchlorate solutions the reaction between Sn(II) and $H_2O_2$ is complicated. Significant discrepancies in the apparent extent of reaction as determined by spectrophotometry compared to results obtained *via* quenching and titration techniques suggest the existence of a non-steady-state intermediate which absorbs in the wavlength region used to follow the disappearance of tin(II). The addition of Cu(II) ion appears to eliminate the reaction pathway giving rise to the intermediate, which probably is the result of a 1-equiv reduction of $H_2O_2$. However, even at high concentrations of Cu(II) ion the reaction still takes place and then obeys a second-order rate law which is consistent with a 2-equiv mechanism. It seems likely that the reaction takes place by parallel pathways involving 1- and 2-equivalent mechanisms. Isotope fractionation factors intermediate between those expected for the two mechanisms lend support to the dual nature of the mechanism.

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# Acidity Measurements at Elevated Temperatures. VI. Boric Acid Equilibria[1]

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Boric acid–borate equilibria have been studied by means of a hydrogen electrode concentration cell from 50 to 290°. The equilibrium in dilute boric acid solution, $B(OH)_3 + OH^- = B(OH)_4^-$, was studied as a function of KCl concentration from 0.13 to 1.0 *m*. A small ionic strength ($I$) dependence of the equilibrium quotient ($Q_{1,1}$) was observed which decreases slightly with temperature. The pressure dependence of the equilibrium quotient is very small up to 2000 psi. Values of $Q_{1,1}$ are given to better than 0.01 log unit by the expression

$$\log Q_{1,1} = \frac{1573.21}{T} + 28.6059 + 0.012078T - 13.2258 \log T + (0.3250 - 0.00033T)I - 0.0912I^{3/2}$$

for values of $I$ from 0 to 1 *m* and $T$ from 273 to 573°K. Results for more concentrated boric acid solutions (up to 0.6 *m*) in 1.0 *m* KCl have indicated the formation of the polynuclear species $B_2(OH)_7^-$ and $B_3(OH)_{10}^-$ and minor amounts of either $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$. The trimeric species is needed to fit the data at all temperatures studied (and previous data at 25°). The dimeric species, which has not been reported previously, is indicated quite strongly by the present results at 200° while the need for a fourth (tetrameric or pentameric) species is indicated by the results at 50°. The two alternative schemes—$B(OH)_4^-$, $B_2(OH)_7^-$, $B_3(OH)_{10}^-$, and $B_4(OH)_{14}^{2-}$ or $B_5(OH)_{18}^{3-}$—are both consistent with the data of Ingri at 25° and give as good a fit as the four-species scheme which he chose. Thermodynamic parameters have been derived for all the species in 1 *m* KCl and for $B(OH)_4^-$ at infinite dilution.

## Introduction

Boric acid–borate buffer mixtures serve as pH standards, occur in natural aqueous systems and in detergent solutions, and are used as burnable nuclear poisons in the coolants of pressurized water nuclear reactors. It is not surprising, therefore, that the equilibria which occur in various aqueous solutions of boric acid and borate have been extensively studied,

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