

Figure 7.—The reaction between  $\text{cis}-(\text{CH}_3\text{O})_4\text{WF}_2$  and  $(\text{CH}_3)_3\text{SiCl}$  observed by  $^1\text{H}$  nmr as a function of time. Assignments for reactant cis difluoride (I), intermediate cis chlorofluoride (IIb), and final product trans dichloride (III) are indicated.

step, which involves Si-Cl and W-F bonds,<sup>42</sup> but rather reorganization results from a second W-Cl bond forming. It should be noted that either another Si-Cl or another W-Cl can now interact. The latter prospect is favored since it was seen that upon consumption of  $(\text{CH}_3)_3\text{SiCl}$  in 1:1 reactions the cis WCIF spontaneously

(42) A four-center transition state has been discussed for this and the W-Cl + W-F cases as well, where presumably tungsten adopts a coordination number of 7. See ref 23b.

synproportionates stereospecifically to cis difluoride and trans dichloride, in addition to the fact that either dichloride isomer is unaffected by the presence of  $(\text{CH}_3)_3\text{SiF}$ . On the whole, the specificity seen for the Cl-F exchange reaction is entirely consistent with the essentially quantitative production of geometrically pure  $\text{cis}-(\text{CH}_3\text{O})_2\text{WF}_4$  by redistribution between  $(\text{CH}_3\text{O})\text{WF}_3$  and  $\text{cis}-(\text{CH}_3\text{O})_4\text{WF}_2$ .

Production of the trans dichloride isomer is in marked contrast to the stereochemistry found as a result of the reaction of  $\text{CH}_3\text{OSi}(\text{CH}_3)_3$  and  $\text{WCl}_6$ , where the cis isomer only is formed. The ability to prepare separately the two isomers is particularly noteworthy in that rather different methods of preparation of various other members of the series have produced identical isomer distributions; for example, in the preparation of  $(\text{CH}_3\text{O})_3\text{WF}_3$  the same isomer mixture is obtained whether the compound is prepared by fluorination of the chloride, by reaction of  $\text{CH}_3\text{OSi}(\text{CH}_3)_3$  with  $\text{WF}_6$ , or by the exchange reaction between  $(\text{CH}_3\text{O})_2\text{WF}_4$  and  $(\text{CH}_3\text{O})_4\text{WF}_2$ . Additionally, no partial or complete separation or selective reaction of the isomeric pairs was obtained in the series of mixed chloride-fluorides.<sup>23</sup> Thus the separate preparation of the two dichloro isomers is of considerable importance, as it may allow subtle differences in reactivity to be investigated as a function of stereochemical configuration alone. The trans form is, however, converted into the cis isomer in the process of crystallization, isolation, and redissolution, and further investigation of the stability relationship between the two isomers is required.

**Acknowledgments.**—The authors wish to express their indebtedness to Messrs. Richard A. Thompson and Kenneth L. Jewett for invaluable assistance in sample preparation and determination of many proton nmr spectra. It is a further pleasure to indicate the general help and advice of Dr. R. B. Johannesen in nmr matters but particularly to thank him for his aid in expediting computer solutions of complex spectra for  $^{19}\text{F}$  spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA 29208

## The Rates of Hydrolysis of the Monomeric Ruthenium(II) Chloride Complexes

By P. E. DUMAS<sup>1</sup> AND E. E. MERCER\*

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The electrochemical generation and identification of some monomeric ruthenium(II) chloride complexes and their rates of hydrolysis are reported. Cyclic voltammetry showed that these complexes undergo fairly rapid hydrolysis to ultimately form uncomplexed ruthenium(II). The rates of hydrolysis of the reduction products formed from  $\text{RuCl}_2^{2+}$  and  $\text{cis-}$  and  $\text{trans-RuCl}_2^+$  have been measured in 0.10 M *p*-toluenesulfonic acid.

Until recently the deep blue color of solutions formed by the action of strong reducing agents on ruthenium-(III) and -(IV) compounds in chloride solution had been attributed to ruthenium(II) chloride complexes. We have shown<sup>2</sup> that the blue complexes are dimeric ru-

thenium(II,III) species which probably involve chloride bridges. The reversible polarograms<sup>3</sup> of the monomeric ruthenium(III) chloride complexes<sup>4</sup> suggested that the ruthenium(II) chloride complexes existed as

(3) R. R. Buckley and E. E. Mercer, *J. Phys. Chem.*, **70**, 3103 (1966).

(1) Work carried out by P. E. Dumas in partial fulfillment of the Ph.D. degree, University of South Carolina, 1971.

(2) E. E. Mercer and P. E. Dumas, *Inorg. Chem.*, **10**, 2755 (1971).

(4) (a) H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **80**, 2646 (1958); (b) D. A. Fine and R. E. Connick, *ibid.*, **82**, 4187 (1960); (c) D. A. Fine and R. T. Connick, *ibid.*, **83**, 3414 (1961).

at least transient species in electrochemical reductions. Herein we report our observations on these intermediates.

### Experimental Section

The monomeric ruthenium(III) chlorides of the type  $\text{RuCl}_n^{(3-n)+}$  were prepared and isolated as described by Connick and coworkers.<sup>4</sup> Stock solutions containing the individual complexes were diluted with *p*-toluenesulfonic acid so that the final hydrogen ion concentration was 0.10 *M* and approximately  $4 \times 10^{-4}$  *M* in ruthenium.

**Equipment.**—Polarograms were recorded on either a Sargent Model XV polarograph or a multipurpose instrument designed by Propst.<sup>5</sup> A conventional three-electrode polarographic cell was used in this study, with a dme as the polarized electrode and a saturated sodium chloride calomel electrode as the reference electrode. Kalousek polarograms<sup>6</sup> were recorded in the multipurpose instrument. In the Kalousek technique a small-amplitude square wave is applied to the linear ramp potential and the current of the electrode reaction is observed only during the more positive half-cycle of the square wave. The temperature dependence on the ratio of the anodic peak to the normal diffusion current plateau can be used to distinguish between three fundamentally different types of electrode processes: reversible, irreversible, and reversible followed by a subsequent chemical reaction. In the latter case as the temperature is increased the rate of the chemical reaction will also increase, resulting in a smaller anodic current contribution to the Kalousek polarogram (more irreversible appearing). Cyclic voltammetric studies were conducted using the same cell with a hanging mercury drop electrode.<sup>7</sup> Reproducible mercury drops were collected under distilled water from a capillary with a constant head of mercury. The cell was thermostated to  $\pm 0.1^\circ$  in a constant-temperature bath. The cyclic voltammetry curves were recorded using the same multipurpose instrument mentioned above.<sup>5</sup> The signal was fed to both a time base recorder (Honeywell Model 16) and an X-Y recorder (Hewlett-Packard Model 7035 B). This permitted simultaneous recording of current-potential and current-time curves. Half-cycle times of 5, 10, 50, and 100 sec are available on this instrument. The voltage scan rate is determined by the setting of the initial and switching potentials. The relative voltages of the oxidation discharge, the reduction potentials, and the reduction discharge limited the scan rates which were available in our experiments.

The following procedure was used in a typical experiment. Twenty milliliters of solution containing the ruthenium(III) chloride complex was placed in the polarographic cell and purged with deoxygenated nitrogen, which had been presaturated with water vapor. The cell was thermostated at the desired temperature. After the solution reached constant temperature, the hanging mercury drop electrode was inserted and the first scan was recorded. The solution was removed from the cell and replaced with an identical solution, except the ruthenium complex was absent. Blanks were recorded with exactly the same instrument settings and temperature. The sample solution was analyzed for ruthenium<sup>8</sup> and its electronic spectrum was recorded. No significant decomposition of the samples were observed.

A Cary Model 14 recording spectrophotometer was used with quartz cells for all spectral studies. The rate of hydrolysis of  $\text{RuCl}^+$  was measured spectrophotometrically, as well as with cyclic voltammetry.

### Results

In the electrolytic reduction at  $0^\circ$  of dilute solutions which contained mixtures of monomeric ruthenium(III) chloride complexes, a sequence of color changes was observed. The initial yellow color gradually changed to gray as the reduction proceeded. When reduction was nearly complete, the solution changed to pink and the spectrum was that of  $\text{Ru}^{2+}$ .<sup>9</sup> This color was grad-

ually replaced by the blue color of the dimeric ruthenium(II,III) chlorides.<sup>2</sup> These changes take place in about 1.5–2 hr. The only color which was not accounted for by characterized species was the initial gray formed from the ruthenium(III) chloride complexes. Since the polarographic reduction waves for all of the ruthenium(III) chlorides<sup>3</sup> are characteristic of reversible one-electron reductions, it seemed reasonable to assume as a working hypothesis that this gray color was due to the monomeric ruthenium(II) chloride complexes.

Pure samples of  $\text{Ru}^{3+}$ ,  $\text{RuCl}^{2+}$ , *cis*- and *trans*- $\text{RuCl}_2^+$ , and *cis*- and *trans*- $\text{RuCl}_3$  were prepared by ion exchange as previously reported.<sup>4</sup> (Water to complete an octahedral coordination of the metal is omitted in these formulas for convenience.)

Each of these complexes was identified by its characteristic absorption spectrum. Conventional polarograms were recorded and the half-wave potentials (see Table I) were shown to be independent of chloride ion

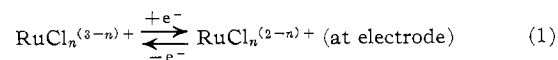
TABLE I  
HALF-WAVE POTENTIALS FOR THE REDUCTION  
OF Ru(III) COMPLEXES

Half-reaction	$E_{1/2}^a$ vs. sce, V
$\text{Ru}^{3+} + e^- \rightarrow \text{Ru}^{2+}$	-0.02
$\text{RuCl}^{2+} + e^- \rightarrow \text{RuCl}^+$	-0.16
<i>cis</i> - and <i>trans</i> - $\text{RuCl}_2^+ + e^- \rightarrow \text{RuCl}_2$	-0.26
<i>cis</i> - and <i>trans</i> - $\text{RuCl}_3 + e^- \rightarrow \text{RuCl}_3^-$	-0.35

<sup>a</sup> Estimated uncertainty in these potentials is  $\pm 0.02$  V.

in the concentration range from 0 to 0.1 *M*. Plots of  $E$  vs.  $\log(i/i_d - i)$  were linear with slopes between 55 and 62 mV. These plots were used to locate the  $E_{1/2}$  and were consistent with one-electron reversible reductions. The reversibility of these reduction waves was also confirmed by the shapes of the Kalousek<sup>10</sup> polarograms recorded over a temperature range from 0 to  $40^\circ$ . The Kalousek polarograms for the mono-, di-, and trichloride species all exhibited a smaller anodic to cathodic peak ratio at the higher temperature, whereas in the Kalousek polarograms recorded for  $\text{Ru}^{3+}$ , the anodic to cathodic peak ratio remained essentially constant over the same temperature range.

Cyclic voltammetry<sup>11</sup> curves were recorded for the chloride complexes of ruthenium(III). The curves for both isomers of  $\text{RuCl}_3$  indicated that the rate of the hydrolysis reaction was outside the accessible range of the instrument used in this study. When the voltage sweep rates for the mono- and dichloride complexes were decreased, the anodic sweep showed a decrease in peak current for the reoxidation to the parent species and a second peak growing in at a more positive potential. The location of the new peak in each case was approximately at the location expected for the next lower chloride complex. The two peaks were insufficiently resolved to locate their potentials accurately. The curves recorded on  $\text{Ru}^{3+}$ , were completely reversible in appearance even at the slowest scan rate. The results may be interpreted by the reaction sequence



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(7) L. Meites, "Polarographic Techniques," 2nd ed, Interscience, New York, N. Y., 1965, Chapter 8.

(8) F. P. Gortsema, Ph.D. Thesis, Purdue University, Lafayette, Ind., 1960.

(9) E. E. Mercer and R. R. Buckley, *Inorg. Chem.*, **4**, 1692 (1965).

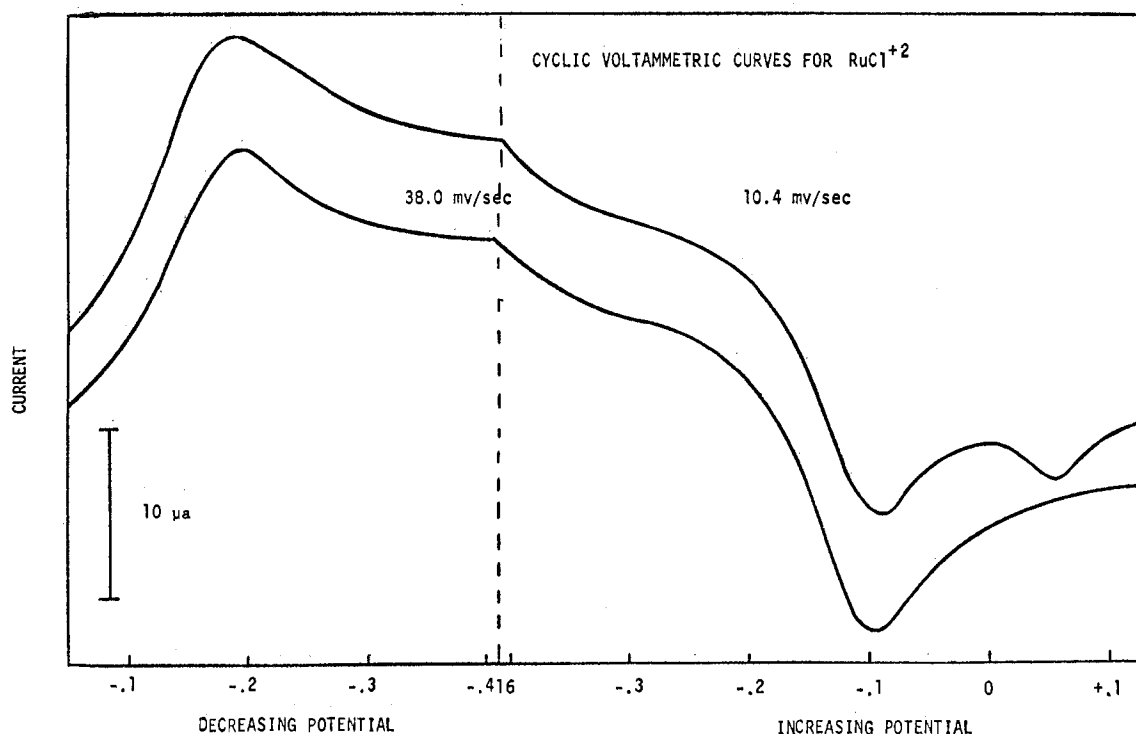
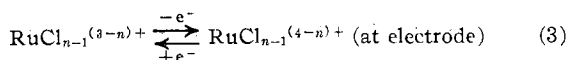
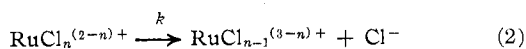


Figure 1.—Typical cyclic voltammetry curves for the reduction of  $\text{RuCl}^{2+}$  at two scan rates.



This reaction scheme can be studied by a variety of electrochemical methods. Chronoamperometry, chronopotentiometry,<sup>12</sup> and cyclic voltammetry are among the techniques which have been used in the past to study similar systems. Because rate constants are more easily found from chronoamperometry, the use of this method was considered. Unfortunately, the potentials of the two oxidations are too close to be resolved with this method. The same is true of chronopotentiometry. Cyclic voltammetry therefore was chosen to study the rates of these chemical reactions.

Figure 1 shows typical curves recorded on  $\text{RuCl}^{2+}$  at two different scan rates. The reoxidation of the two species is evident at the lower voltage scan rate. For each complex and temperature studied, a minimum of four scan rates on at least two independent samples was recorded. The scan rate was chosen in each case to show a significant change in the relative heights of the two peaks observed.

Correlations between experimental and theoretical current-potential curves have made it possible to develop various diagnostic criteria that can be used to measure the rates of postreduction chemical reactions. Some of these correlations are the ratio of anodic to cathodic peak currents, the variation of peak potential with the rate of voltage scan, variation of anodic or cathodic currents with sweep rate, and the variation of anodic peak potentials with the switching potential. Preliminary analysis of the experimental data obtained in this investigation indicated that the most reliable correlation would be a curve-fitting procedure between

the observed and theoretical anodic scans. This procedure was necessary because of considerable overlap of the two oxidation peaks.

The differential equations arising from Fick's laws, which describe this system, may be solved by a number of approximate methods for a planar electrode, using the boundary conditions imposed by this technique. Following the treatment used by Nicholson and Shain,<sup>11</sup> integral equations involving functions in generalized coordinates were obtained for the two redox couples involved in our reaction scheme. These are given by eq 4 and 5 where  $X_1$  and  $X_2$  are the current functions ex-

$$1 - \int_0^{at} \frac{X_1(z) dz}{\sqrt{at-z}} = \gamma_1 \theta_1 S \int_0^{at} \frac{e^{-\Psi(at-z)} X_1(z) dz}{\sqrt{at-z}} \quad (4)$$

$$\int_0^{at} \frac{X_2(z) dz}{\sqrt{at-z}} = \frac{\gamma_2 \theta_2 S}{1 + \gamma_2 \theta_2 S} \int_0^{at} \frac{(e^{-\Psi(at-z)} - 1) X_1(z) dz}{\sqrt{at-z}} \quad (5)$$

pressed in generalized coordinates, independent of both concentration and time,  $a = nFv/RT$ ,  $v =$  scan rate (mV/sec),  $at = nFvt/RT = (nF/RT)(E_i - E)$ ,  $t =$  time (sec),  $E_i =$  initial potential at  $t = 0$ ,  $E =$  potential at  $t \neq 0$ ,  $\Psi = k/a$ ,  $k =$  rate constant ( $\text{sec}^{-1}$ ),  $\theta S = C_{\text{ox}}/C_r = \exp[(nF/RT)(E - E^\circ)]$ ,  $\gamma =$  ratio of diffusion coefficients  $D_{\text{ox}}/D_r$ ,  $z = a\tau$ , and  $\tau =$  integration variable. Equations 4 and 5 were expanded into the following series solutions as described previously<sup>11</sup>

$$X_1(n) = \frac{1 - \sum_{i=1}^{n-1} (2\sqrt{\delta} a_{n-1} + \sqrt{\pi/\Psi} \gamma_1 \theta_1 S b_{n-1}) X_1(i)}{\sqrt{\delta} + \sqrt{\pi/\Psi} \gamma_1 \theta_1 S \text{erf} \sqrt{\delta \Psi}} \quad (6)$$

$$X_2(n) + \left[ \sum_{i=1}^{n-1} a_{n-1} X_2(i) \right] = \frac{\gamma_2 \theta_2 S}{2(1 + \gamma_2 \theta_2 S)} \left[ \sum_{i=1}^{n-1} C_{n-1} X_1(i) \right] \quad (7)$$

(12) C. N. Reilly in "Treatise on Analytical Chemistry," I. M. Kolthoff and P. J. Elving, Ed., Wiley, New York, N. Y., 1963, Chapter 42.

where

$$a_{n-1} = \sqrt{n-i+1} - \sqrt{n-1}$$

$$b_{n-1} = \operatorname{erf}\sqrt{\delta\Psi(n-i+1)} - \operatorname{erf}\sqrt{\delta\Psi(n-1)}$$

$$C_{n-1} = \frac{e^{-\delta\Psi(n-1)} - 1}{\sqrt{n-1}}$$

$$\delta = \frac{at}{n} = \frac{nFvt}{RTn} = \frac{nF E_i - E}{RTn}$$

A Fortran IV program for use on an IBM 7040 computer was written, to calculate the current functions,  $X_1$  and  $X_2$ . In the calculation  $E_i$  was always +170 mV or more relative to the reduction potential, and the current functions were calculated at 1-mV increments. The total current was assumed to be the sum of  $X_1$  and  $X_2$ . For each experimental scan several theoretical curves were generated duplicating the experimental conditions of potentials, scan rate, and temperature, assuming different values for the rate constant in reaction 2. These calculated curves were then compared to the experimental curves. The anodic current of each experimental curve was measured at 10–15-mV intervals along the potential axis, from which the current of the corresponding background was subtracted. The peak current for the first anodic wave was then normalized to the current for the same peak in the theoretical curve. The experimental curve and the theoretical curves were superimposed. The best fitting theoretical curve was assumed most closely to approximate the actual rate constant. This procedure was repeated with a narrower range of rate constants until the experimental and theoretical curves agreed to within 10% for all scan rates recorded at a given temperature. The best values obtained for the rate constants are summarized in Table II.

TABLE II

Complex	Temp, °C	Range of scan rates, mV/sec	Rate constant, <sup>a</sup> sec <sup>-1</sup>
RuCl <sup>+</sup>	23.8	4.10–5.47	$9.0 \times 10^{-4}$
<i>cis</i> -RuCl <sub>2</sub>	15.0	28.9–45.5	0.060
	20.0	28.9–45.5	0.090
	25.0	28.9–45.5	0.13
	30.0	28.9–45.5	0.17
<i>trans</i> -RuCl <sub>2</sub>	15.0	32.5–46.0	0.070
	25.0	32.5–46.0	0.14
	30.0	32.5–46.0	0.18

<sup>a</sup> The estimated limits of errors in the values of  $k$  reported are  $\pm 10\%$ .

At the scan rates used for the dichloro complexes, the correction for a spherical electrode was less than 2% of the total current and was ignored. For the RuCl<sup>2+</sup> scans the spherical correction was larger. In these scans, however, the voltage sweep rate was so slow that convection stirring probably produced some distortion of the wave shapes. For these reasons the rate constant reported for RuCl<sup>+</sup> hydrolysis is less reliable than the others.

The rate measured electrochemically for RuCl<sup>+</sup> suggested that this ion could be generated in sufficiently high concentrations to be observed spectrophotometrically.

A solution approximately  $5 \times 10^{-3} M$  in RuCl<sup>2+</sup> and 0.10  $M$  in *p*-toluenesulfonic acid was treated with zinc amalgam at 0° until the initial yellow color had changed

to gray. The solution was filtered under a nitrogen atmosphere and then transferred to a spectrophotometer cell. The visible spectrum showed a weak absorption maximum between 550 and 560 nm. Repeated scans of the visible spectrum showed that this absorption diminished with time and a peak at 530 nm appeared. The new band corresponds to a peak in the spectrum of Ru<sup>2+</sup>. The second peak in that spectrum was obscured by unreduced RuCl<sup>2+</sup>. Ion-exchange separation confirmed the presence of Ru<sup>2+</sup> in this solution. Since chloride produces a weaker ligand field than water, the presence of a weak band at longer wavelength (compared to Ru<sup>2+</sup>) in the gray complex tends to support our assignment of this species as RuCl<sup>+</sup>. In subsequent experiments where the rate of disappearance of the 550-nm band was followed, the RuCl<sup>+</sup> was generated in solution by electrolysis of RuCl<sub>2</sub><sup>+</sup> at  $-0.50 V$  vs. sce. The solution was electrolyzed for 15 min at 0°, then transferred to a quartz cell, and allowed to warm up to room temperature ( $23.8 \pm 0.5^\circ$ ). The rate of hydrolysis of the RuCl<sub>2</sub> is rapid enough that all the ruthenium(II) in solution was present as Ru<sup>2+</sup> and RuCl<sup>+</sup> before the initial absorbance measurements were made. The absorbance was recorded as a function of time until no further change was observed. Plots of  $\log(A - A_\infty)$  vs. time were linear (see Figure 2).

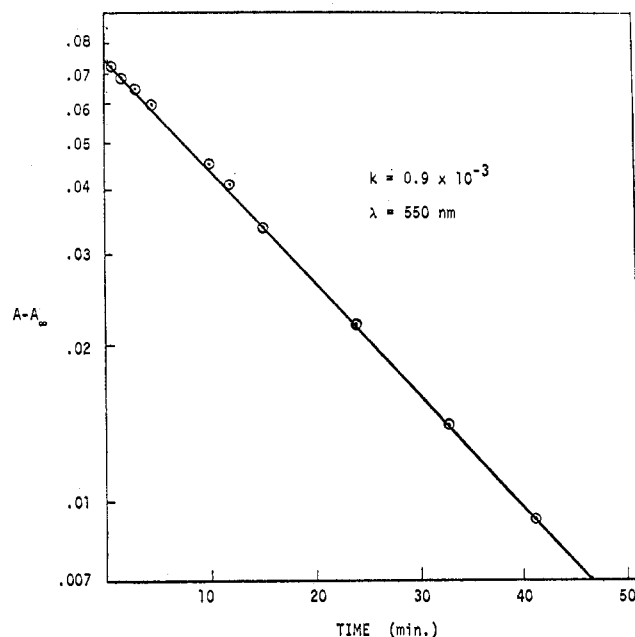


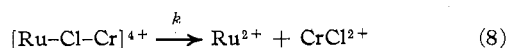
Figure 2.—First-order plot of the spectrophotometric data obtained for the hydrolysis of RuCl<sup>+</sup>.

Plots of the absorbance vs. time data in six separate runs consistently gave a first-order rate constant of  $0.9 \times 10^{-3} \text{ sec}^{-1}$ . The accuracy of this rate constant was limited by the small change in absorbance and the uncertainty in temperature. Nevertheless, the excellent agreement between this rate and that determined by cyclic voltammetry clearly shows that the same process was being followed in both experiments. It also confirms the validity of the data treatment used in the electrochemical studies.

The activation enthalpy and entropy for the reduction products of both *cis*- and *trans*-RuCl<sub>2</sub><sup>+</sup> were  $\Delta H^\ddagger = 11 \pm 1 \text{ kcal/mol}$  and  $\Delta S^\ddagger = 26 \pm 4 \text{ gibbs}$ . The

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<sub>2</sub> 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<sup>13</sup> observed the rate of decomposition of a chloride bridge intermediate in the chromium(II) reduction of RuCl<sub>2</sub><sup>+</sup>. An upper limit of  $6.0 \times 10^{-2} \text{ sec}^{-1}$  was set by these authors for the rate of the reaction



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

In a preliminary communication Kallen and Earley<sup>14</sup> reported the rate of addition of chloride to Ru<sup>3+</sup>, catalyzed by Ru<sup>2+</sup>. 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  $8.5 \times 10^{-3} \text{ sec}^{-1}$ . If this rate is combined with the forward rate we have measured for reaction 2, an equilibrium

(13) D. Seewald, N. Sutin, and K. O. Watkins, *J. Amer. Chem. Soc.*, **91**, 7307 (1969).

(14) T. W. Kallen and J. E. Earley, *Chem. Commun.*, 851 (1970).

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<sup>2+</sup> systems.<sup>15</sup>

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

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.

**Acknowledgments.**—This research was supported by the United States Atomic Energy Commission under Contract AT-(40-1)-3542. We also thank Professor Robert Philp for his helpful discussions and advice.

(15) L. G. Sillén, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

(16) R. E. Connick, "Advances in the Chemistry of Coordination Compounds," Macmillan Co., New York, N. Y., 1961, p 15.

(17) J. F. Endicott and N. Taube, *J. Amer. Chem. Soc.*, **84**, 4984 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
COLORADO STATE UNIVERSITY, FORT COLLINS, COLORADO 80521

## The Oxidation of Tin(II) by Hydrogen Peroxide

BY N. A. DAUGHERTY\* AND J. H. NIEWAHNER

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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<sup>1</sup> or a sequence of 1-equiv steps.<sup>2</sup> Either of these mechanisms seems equally likely for the reduction of hydrogen peroxide by tin(II). In hydrochloric acid solutions, isotopic fractionation data<sup>3</sup> and lack of induced reduction<sup>4</sup> of K<sub>3</sub>Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> have been taken as evidence for a single step 2-equiv mechanism. The reaction in perchloric acid solution has not been studied.

(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).

(4) E. A. M. Welton and W. C. E. Higginson, *J. Chem. Soc.*, 5890 (1965).

The stoichiometry and rate of the tin(II)–vanadium(V) reaction are vastly different in perchloric acid as compared to hydrochloric acid.<sup>5</sup> 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.<sup>5</sup> Hydrogen peroxide solutions were prepared by dilution of Baker Analyzed 30% hydrogen peroxide and were standardized by conventional volumetric

(5) B. Schiefelbein and N. A. Daugherty, *Inorg. Chem.*, **9**, 1716 (1970).