Studies of Ruthenium(IV) and Its Reduction Products in Perchlorate Solutions

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Received December 23, 1968

Abstract: Ion exchange and membrane studies of Ru(IV) in perchloric acid indicate that the charge per atom is +1, the charge per species is +4, and Ru(IV) is tetrameric. Coulometric, cyclic voltammetric, and spectrophotometric studies indicate that tetrameric Ru(IV) can be reduced reversibly by two, one-electron processes to species with formal oxidation states of 3.75 and 3.5. Ru(3.5) is reduced reversibly to a transient species of Ru(III) which rapidly converts to a stable polymeric species of Ru(III) that can be reoxidized to Ru(IV) only irreversibly. Stable Ru(III) can be electrochemically reduced to Ru(II) which is immediately reoxidized by perchlorate to monomeric Ru^{3+}.

The chemistry of the lower oxidation states of ruthenium in noncomplexing media was first studied by Wehner and Hindman,[1] who prepared solutions of brown Ru(IV) by the controlled-potential reduction of RuO_4 in $HClO_4$, and yellow Ru(III) by the electrolytic reduction of Ru(IV) in $HClO_4$. Their work also indicated the existence of intermediate species with the formal oxidation states of 4.2 and 3.5 which they attribute to several hydrolytic species. Niedrach and Tevebaugh[2] as well as Atwood and DeVries[3,4] found three waves during the polarographic reduction of Ru(IV) to Ru(II); the Ru(IV) was prepared by the reduction of RuO_4 in $HClO_4$ with H_2O_2. The third wave was due to the Ru(III) → Ru(II) reduction; the first two were attributed to hydrolytic species[2] or to the existence of a definite species with a formal oxidation state of 3.5.[3,4] Cady[5] confirmed the existence of two intermediate oxidation states 4.2–4.3 and 3.5 by potentiometric and spectrophotometric titrations of RuO_4 in both perchloric and trifluoroacetic acids with various reducing agents; Atwood and DeVries[3,4] confirmed the existence of the 3.5 state by the potentiometric titration of Ru(IV) in perchlorate media with vanadous ion.

The most convenient explanation of Ru(3.5) is to assume the species to be dimeric as did Cady[5] and Atwood.[3] The existence of polymeric species of Ru(IV) in certain preparations was demonstrated by Gortsema and Cobble;[6-8] however, they also presented evidence[6,8] for the existence of a monomeric ruthenyl ion, RuO^{2+}, in perchloric acid. Atwood and DeVries found no difference in the polarographic behavior of both polymeric and "monomeric" Ru(IV), and assumed that Ru(3.5) is formed by reduction of dimeric Ru(IV). Although the ruthenyl structure is not necessarily inconsistent with the reported observations, the existence of nonintegral oxidation states in the vicinity of Ru(IV) and the low magnetic moment[6,9] (~0.9 BM) are more consistent with a polymeric species. This paper reports a reinvestigation of the nature of Ru(IV) in perchlorate media by measurement of its charge per atom and charge per species and by study of its reduction to lower oxidation states by coulometry and cyclic voltammetry.

Experimental Section

Preparation of Ru(IV). Ru(IV) perchlorate solutions were prepared as described by Niedrach and Tevebaugh[2] and by Gortsema and Cobble.[8] A solution of $\sim 5 \times 10^{-3}$ *M* RuO_4 in 1–2 *M* $HClO_4$ was prepared by distilling freshly prepared RuO_4 into the $HClO_4$ and stirring until dissolution was complete. The RuO_4 was reduced to Ru(IV) by the slow addition of unstabilized hydrogen peroxide to vigorously agitated ruthenium solution. The Ru(IV) solutions were allowed to stand for about 16 hr after preparation to allow the excess H_2O_2 to decompose before further processing.

Isolation and Concentration of Ru(IV). Ru(IV) was isolated and concentrated by a modification of the ion-exchange method used by Gortsema and Cobble to prepare "monomeric" Ru(IV). The Ru(IV) solution was diluted with water until the $HClO_4$ was about 0.5 *M*. Dowex 50W-X8, 200–400 mesh, cation-exchange resin in the hydrogen form was then added and the mixture agitated for about 1 hr. Most of the ruthenium was absorbed on the resin, but complete recovery was not attempted. The resin was recovered by decanting the supernatant solution, washing with water, and transferring to the top of a column of the same type of resin in the hydrogen form. The column was vibrated during loading to assure uniform packing. The ruthenium was then eluted or rather "pushed" at a very slow flow with a solution approximately 0.25 *M* $La(ClO_4)_3$ and 0.5 *M* $HClO_4$. Several hours was required for the elutriant to compress the ruthenium band before it began to move into the hydrogen-form resin. The band was easily followed by its intense brown color. The effluent from the column was collected in a series of 0.5-ml samples after the ruthenium began to come off. Each of these samples was tested for lanthanum by adding ~25 μl of sample to 5 ml of 0.1 *M* oxalic acid. Samples that showed a precipitate were rejected as was the first sample which was diluted by mixing in the outlet tip of the column. Recoveries of lanthanum-free ruthenium were 60–70%.

Visible absorption spectra of the Ru(IV) removed from the column were determined after dilution in 0.1 *M* $HClO_4$ These spectra agreed very closely with those reported by Gortsema and Cobble[6,8] for "monomeric" Ru(IV). Absorption maxima occurred at about 487 mμ with molar extinction coefficients of 710 to 722 compared with 709 ± 3 obtained by Gortsema and Cobble.

Determination of Charge per Atom. The charge per atom of Ru(IV) was determined by a modification of the method of Cady and Connick,[10] who showed that the charge per atom could be measured from a charge balance in ion-exchange equilibration.

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[1] P. Wehner and J. C. Hindman, *J. Am. Chem. Soc.*, **72**, 3911 (1950).

[2] L. W. Niedrach and A. D. Tevebaugh, *ibid.*, 73, 2835 (1951).

[3] D. K. Atwood, Ph.D. Thesis, Purdue University, 1960.

[4] D. K. Atwood and T. DeVries, *J. Am. Chem. Soc.*, **84**, 2659 (1962).

[5] H. H. Cady, USAEC Report UCRL 3757, 1957.

[6] F. P. Gortsema, Ph.D. Thesis, Purdue University, 1959.

[7] F. P. Gortsema and J. W. Cobble, *J. Am. Chem. Soc.*, **81**, 5516 (1959).

[8] F. P. Gortsema and J. W. Cobble, *ibid.*, **83**, 4317 (1961).

[9] J. M. Fletcher, *J. Inorg. Nucl. Chem.*, **8**, 277 (1958).

[10] H. H. Cady and R. C. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

Table I. Charge per Atom of Ru(IV) by Elution from Ion-Exchange Column

Elutriant concentration, mole/l. $[La^{3+}]$	$[H^+]$	Eluate concentration, g-atom/l. $[Ru(IV)]_f$	$[H^+]_f$	Charge/atom
0.256	0.552	0.606	0.683	1.05
0.264	0.499	0.622	0.634	1.06
0.264	0.499	0.671	0.587	1.05

The elutriant to and the eluate from the ion-exchange columns that were used to isolate Ru(IV) were analyzed for lanthanum and hydrogen ion. Assuming the lanthanum ion to be +3 and the hydrogen ion to be +1, the charge per ruthenium atom, a, can be calculated from the following equation

$$a = \frac{3[La^{3+}]_i + [H^+]_i - [H^+]_f}{[Ru(IV)]_f}$$

where i and f refer to the elutriant and eluate, respectively. The results of three measurements are shown in Table I.

Analyses. Ruthenium was determined spectrophotometrically as RuO_4 by the method used by Gortsema and Cobble.[6-8] The ruthenium solution was diluted with 0.1 M $HClO_4$ and oxidized to RuO_4 with periodic acid. The absorbance was measured at 385 mμ, and the concentration calculated using the molar extinction coefficient 930.[11]

Lanthanum was determined by titration with EDTA.[12]

Acid Analysis. Solutions that contained both lanthanum and hydrogen ions were passed through a cation-exchange column in the hydrogen form, and the effluent acid was determined by titration. Free acid of the original sample was determined by subtracting three times the lanthanum content in moles of the original sample from the acid eluted from the column.

When the ruthenium was present, a sample of the solution was diluted with water to a known volume and the pH of the resulting solution was measured. The same volume of water was adjusted to the same pH with pure perchloric acid and then titrated. The free acid content of the ruthenium solution was taken as that of the pure perchloric acid solution.

Absorption Spectra. A Beckman DU spectrophotometer with 1-cm quartz cells was used for routine analytical work. When complete spectra were desired, a Cary Model 14 recording spectrophotometer with either 1-cm or 2-cm quartz cells was employed.

Electrochemical Studies. All coulometric studies were carried out in a special cell.[13] This cell contained a 19-cm² gold electrode, an isolated counter electrode, and a mercury-mercurous sulfate (1 M sulfuric acid) reference electrode (mse). The cell also contained a magnetic stirring bar and a helium sparge tube. The isolated counter electrode consisted of a spiral of platinum wire immersed in a tube of 1 M sulfuric acid; a layer of sodium silicate resting on a frit at the bottom of the tube served as a bridge to the solution in the cell. The junction of the reference electrode consisted of an asbestos fiber back with a sodium silicate solution.

The potential of the mercury-mercurous sulfate electrode (1 M sulfuric acid) was 0.660 ± 0.003 V *vs.* the standard hydrogen electrode (including junction potentials). This electrode has been used in the measurement of the potentials of a variety of couples and in every instance the results agreed with the literature values to within ±0.005 V.

In the cyclic voltammetric studies, the large cylindrical gold electrode was replaced by a small gold electrode. This electrode was made by sealing 60-mil gold wire in a glass tube with Apiezon W wax. The wax masked all of the wire except the exposed end which was polished to a mirror finish by standard metallurgical techniques.

The operating procedure in all electrochemical studies was to place 10 ml of a solution containing the desired concentrations of $HClO_4$, $NaClO_4$, and Ru(IV) into the cell. The solution was then flushed for 5 min with helium (presaturated with water) to remove dissolved gases. The appropriate electroanalytical instrument was then started. Four different electroanalytical techniques were employed: scanning coulometry, step coulometry, controlled-potential coulometry, and cyclic voltammetry.

The instruments used were based on operational amplifiers, and the potentiostat circuits[14] were incorporated in a conventional three-electrode design. A multipurpose instrument[15] was used for step coulometry and cyclic voltammetry.

The scanning coulometer[13] was designed to scan potential of the gold working electrode (*vs.* the reference electrode) at a rate inversely proportional to the electrolysis current and to record the integrated current as a function of the potential of the working electrode. It thus records the number of coulombs of electricity involved in the reduction or oxidation as a function of the applied potential under nearly equilibrium conditions.

The stepping coulometer was designed to switch the control circuit between open-circuit and controlled-potential modes by means of a low-frequency (0.001 to 0.05 Hz) square wave. Electrolysis occurred on alternate half-cycles, and during these periods the working electrode was displaced from the previous open circuit potential by 10 mV. For the remaining part of each cycle the working electrode was permitted to drift to a new equilibrium potential. In this manner, coulograms of the integrated current *vs.* open-circuit potential were recorded under essentially equilibrium conditions.

The attachment for cyclic voltammetry was designed to function in the conventional manner.[16,17]

The controlled-potential coulometer which was used to prepare solutions for spectrophotometric studies has been described.[18] This instrument was used because it accommodated larger currents than the general purpose instrument and was necessary for the preparation of solutions of sufficient concentration for spectrophotometric studies.

Results and Discussion

Charge per Atom and Charge per Species. We determined the charge per atom of Ru(IV) to be +1. The charge per species, determined by the membrane equilibrium method and reported previously,[19] was found to be +4. These results indicate that Ru(IV) in dilute perchloric acid is a tetramer rather than a monomer as proposed by Gortsema and Cobble[6,8] based on their values of +2 for both charges.

Scanning Coulometry. The general aspects of the reduction of Ru(IV) were studied by scanning coulometry. Figure 1 is a typical example of all such coulograms after the corrections for double-layer background. This particular example was obtained in 1 M perchloric acid containing 3.15×10^{-5} M Ru(IV). The cathodic wave (curve 1) shows two processes to be involved in the reduction of Ru(IV) to Ru(III), each involving 0.5 faraday/g-atom of ruthenium. The slight excess of charge necessary to reduce Ru(IV) to Ru(III) over that calculated theoretically was probably caused by an electrode process that was not accounted for in the background correction.

When the Ru(III) freshly prepared by the reduction of Ru(IV) was reoxidized, the coulogram shown in curve 2 was obtained; this indicates that Ru(III) is reoxidized to Ru(IV) irreversibly. Reduction of the Ru(IV) species produced by the reoxidation of Ru(III), however, gave a curve nearly identical with curve 1; this indicates that this species was the same as the original Ru(IV).

If Ru(IV) is reduced to the extent of only 0.5 faraday/g-atom and then reoxidized, coulograms similar to these shown in Figure 2 are obtained. Curve 1 is the reduction scan and curve 2 is the reoxidation scan.

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(11) R. E. Connick and C. R. Hurley, *J. Am. Chem. Soc.*, 74, 5012 (1952).

(12) J. S. Fritz, R. T. Oliver, and D. J. Pietrzyk, *Anal. Chem.*, 30, 1111 (1958).

(13) R. C. Propst, *ibid.*, 35, 958 (1963).

(14) W. L. Underkofler and I. Shain, *ibid.*, 35, 1778 (1963).

(15) R. C. Propst, USAEC Report DP-903, 1964.

(16) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, New York, N. Y., 1954, Chapter 6.

(17) L. Meites, "Polarographic Techniques," 2nd ed, Interscience Publishers, New York, N. Y., 1965, p 577.

(18) R. C. Propst, USAEC Report DP-798, 1963.

(19) R. M. Wallace, *J. Phys. Chem.*, 68, 2418 (1964).

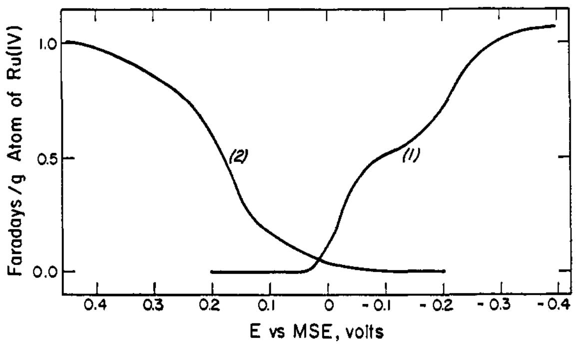

Figure 1. Scanning coulogram of reduction of Ru(IV) to Ru(III) and reoxidation of Ru(III) at 3.45 × 10^{-5} *M* Ru in 1 *M* $HClO_4$.

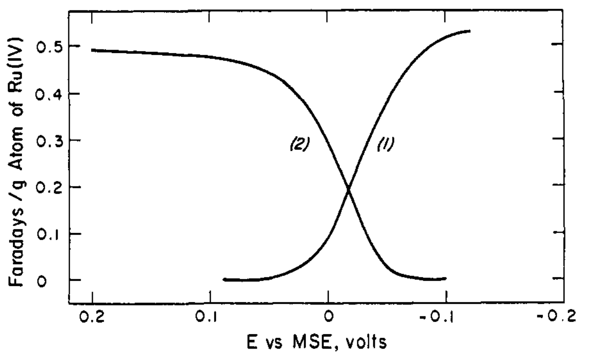

Figure 2. Scanning coulogram of reduction of Ru(IV) to Ru(3.5) and reoxidation of Ru(3.5) in 1 *M* $HClO_4$.

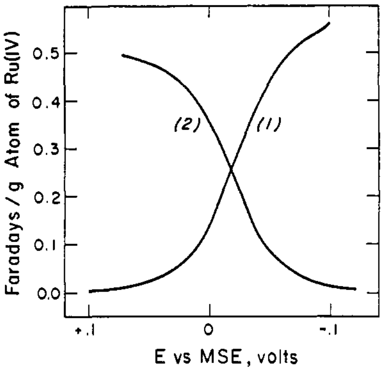

Figure 3. Step coulogram of reduction of Ru(IV) to Ru(3.5) and reoxidation of Ru(3.5) in 1 *M* $HClO_4$.

These indicate that the first process is very nearly reversible. Scanning coulograms were obtained at perchloric acid concentrations of 1.0, 0.1, and 0.01 *M* to which sufficient sodium perchlorate had been added to maintain the ionic strength constant at 1 *M*. The general behavior at each acid concentration was that just described. The half-wave potentials of each of the reduction waves, however, decreased with increasing acid concentrations (Table II); this indicated that hydrogen ions were consumed during the reduction.

Table II. Summary of Half-Wave Potentials from Scanning Coulograms

H^+, *M*	$E_{1/2}$, reduction wave, V First wave	Second wave	$E_{1/2}$, oxidation wave, V
1.0	−0.030	−0.24	−0.22
0.1	−0.110	−0.38	+0.20
0.01	−0.210	−0.42	+0.20

A series of coulograms was run at 1 *M* perchloric acid in which the concentration of ruthenium was varied between 3.45 × 10^{-6} and 3.45 × 10^{-5} *M*. The height of each wave was proportional to the total amount of ruthenium in the cell. The curves at the lower concentration were more poorly defined than those at higher concentrations, and the half-wave potentials varied slightly but systematically with concentration. The half-wave potentials decreased with increasing concentration in the reduction waves and increased with increasing concentration in the oxidation wave; this suggests that the shift is caused by lack of complete equilibrium in the scans.

The species of ruthenium formed in each reduction wave were stable several hours at room temperature, but on long standing in perchlorate solutions, both were oxidized spontaneously back to the original Ru(IV). For example, when Ru(IV) was reduced in 1 *M* perchloric acid to the end of the first reduction wave and reoxidized immediately, the theoretical quantity of electricity was required; however, when reduced and allowed to stand for 16 hr, only 70% of the theoretical quantity was required to reoxidize it. Subsequent reduction of the oxidized species gives the same reduction waves as the original Ru(IV).

The results of studies with scanning coulometry are consistent with the existence of the Ru(3.5) species proposed by Cady[5] and by Atwood and DeVries,[3,4] and further showed that the reduction of Ru(IV) to Ru(3.5) can probably be carried out reversibly but that the reduction of Ru(3.5) to Ru(III) cannot be. The apparent reversibility of this first process suggested that if it could be studied under completely reversible conditions, application of the Nernst equation would give the number of electrons involved in the reduction and enable testing of the conclusion that Ru(IV) is tetrameric. Step coulometry was chosen for these studies because potentials can be measured under essentially equilibrium conditions more readily than with scanning coulometry.

Step Coulometry. Figure 3 contains typical step coulograms of the reduction of Ru(IV) to Ru(3.5) (curve 1) and of the reoxidation of Ru(3.5) (curve 2). The two curves cross at a point close to that at which 0.25 faraday/g-atom of Ru is consumed. The slopes at that point are nearly identical, numerically. The oxidation wave is symmetric over the entire range, while the reduction wave is a mirror image of the oxidation wave until about 80% of the Ru(IV) is converted to Ru(3.5). These results demonstrate that step coulometry yields reversible titration curves over 80% of the reduction and that the Nernst equation can be reliably applied. Deviations from reversible behavior in the reduction wave, when more than 80% of the Ru(IV) was converted to Ru(3.5), were caused by the spontaneous oxidation of Ru(3.5) by perchlorate ion. Although this spontaneous oxidation is slow, the rate of reduction also becomes slow near the end of the reduction so that some of the accumulated charge was expended in reducing ruthenium that had been oxidized by perchlorate.

The results of a series of step coulograms run at constant ionic strength (1 *M*) but at several different perchloric acid concentrations and different total ruthenium concentrations are shown in Table III.

Table III. Summary of Step Coulometric Measurements

$HClO_4$ concn, mole/l.	Ruthenium concn, g-atom/l.	$E_{1/2}$ *vs.* mse, V	n	$K^{1/2}{}_{obsd}$
1.0	5.74×10^{-6}	−0.002	1.46	0.74
	2.87×10^{-5}	−0.014	1.36	0.94
	5.74×10^{-5}	−0.016	1.38	0.90
	1.43×10^{-4}	−0.013	1.35	0.96
0.10	5.74×10^{-6}	−0.088	1.52	0.64
	2.87×10^{-5}	−0.082	1.64	0.44
	5.74×10^{-5}	−0.078	1.62	0.48
	1.43×10^{-4}	−0.078	1.59	0.52
0.010	7.38×10^{-6}	−0.148	1.63	0.46
	1.85×10^{-5}	−0.148	1.62	0.48
	3.69×10^{-5}	−0.146	1.62	0.48
	7.38×10^{-5}	−0.145	1.63	0.46
	1.85×10^{-4}	−0.148	1.67	0.40

Although the half-wave potentials vary greatly with acidity, they are virtually independent of ruthenium concentration at constant acidity which indicates the absence of polymerization or dipolymerization during the reduction.

The number of electrons, n, involved in the process was calculated from the Nernst equation

$$E = E_{1/2} - \frac{RT}{nF} \ln \frac{[\mathrm{Ru(3.5)}]}{[\mathrm{Ru(IV)}]} \qquad (1)$$

where it was assumed the ratio of the two forms is given by

$$\frac{[\mathrm{Ru(3.5)}]}{[\mathrm{Ru(IV)}]} = \frac{2S}{1 - 2S} \qquad (2)$$

where

$$S \equiv \frac{Q}{VF[\mathrm{Ru}]_t} = \text{(number of faradays per gram atom)} \qquad (3)$$

and where Q is the instantaneous accumulated charge, in coulombs, V is the volume of the solution in liters, F is the faraday constant, and $[\mathrm{Ru}]_t$ is the total ruthenium concentration in gram atoms per milliliter.

All values of n are considerably greater than unity; this indicates that the reduction of Ru(IV) to Ru(3.5) is not a simple one-electron reduction. Because n varies with acidity and because its values are nonintegral and less then 2, the reduction cannot be explained on the basis of the simple two-electron process one might expect for the reduction of tetrameric Ru(IV) to tetrameric Ru(3.5).

The apparently nonintegral values of n, its variation with acidity, and the independence of the half-wave potential on ruthenium concentration can best be explained by assuming tetrameric Ru(IV) to be reduced to tetrameric Ru(3.5) by two one-electron processes involving a rather unstable tetrameric Ru(3.75) as an intermediate. Thus

$$\mathrm{Ru(IV)} + e^- \longrightarrow \mathrm{Ru(3.75)}$$

$$E = E_{1/2}{}^{(1)} - \frac{RT}{F} \ln \frac{[\mathrm{Ru(3.75)}]}{[\mathrm{Ru(IV)}]} \qquad (4)$$

$$\mathrm{Ru(3.75)} + e^- \longrightarrow \mathrm{Ru(3.5)}$$

$$E = E_{1/2}{}^{(2)} - \frac{RT}{T} \ln \frac{[\mathrm{Ru(3.5)}]}{[\mathrm{Ru(3.75)}]} \qquad (5)$$

Addition of eq 4 and 5 yields

$$E = \frac{E_{1/2}{}^{(2)} + E_{1/2}{}^{(2)}}{2} - \frac{RT}{2F} \ln \frac{[\mathrm{Ru(3.5)}]}{[\mathrm{Ru(IV)}]} \qquad (6)$$

which is equivalent to eq 1 except that the mole ratio of the two species is no longer given by eq 2.

Subtracting of eq 4 and 5 and rearranging yields

$$\frac{[\mathrm{Ru(3.75)}]}{[\mathrm{Ru(IV)}][\mathrm{Ru(3.5)}]} = \exp\left[\frac{F}{RT}(E_{1/2}{}^{(1)} - E_{1/2}{}^{(2)})\right] \equiv K \qquad (7)$$

Equation 7 is an expression for the equilibrium constant for the reaction

$$\mathrm{Ru(IV)} + \mathrm{Ru(3.5)} \rightleftharpoons 2\mathrm{Ru(3.75)}$$

The total ruthenium concentration $[\mathrm{Ru}]_t$ is the sum of all the species present

$$[\mathrm{Ru}]_t = [\mathrm{Ru(IV)}] + [\mathrm{Ru(3.75)}] + [\mathrm{Ru(C.5)}] \qquad (8)$$

while the accumulated charge is related to the concentrations of the reduced species and the volume of the solution in the cell as follows.

$$\frac{Q}{VF} = \frac{1}{4}[\mathrm{Ru(3.75)}] + \frac{1}{2}[\mathrm{Ru(3.5)}] \qquad (9)$$

If eq 7, 8, and 9 are combined, the ratio of Ru(3.5) to Ru(IV) concentration can be expressed in terms of Q and K. It is convenient to make the following substitution. Let

$$\gamma^2 \equiv [\mathrm{Ru(3.5)}]/[\mathrm{Ru(IV)}] \qquad (10)$$

and

$$P \equiv 2S/(1 - 2S) \qquad (11)$$

where S is defined by eq 3; then

$$\gamma^2 + \frac{K^{1/2}}{2}\gamma(1 - P) - P = 0 \qquad (12)$$

and from eq 6

$$E = \frac{E_{1/2}{}^{(1)} + E_{1/2}{}^{(2)}}{2} - \frac{RT}{F} \ln \gamma \qquad (13)$$

Equations 12 and 13 can be solved explicitly for E in terms of P, but it is more convenient to consider them as parametric equations. The range of S is $0 \leq S \leq {}^1/_2$; thus the range of P is $0 \leq P \leq \infty$. When $P = 1$ ($S = {}^1/_4$) in eq 12, $\gamma = 1$ irrespective of the value of K; substitution into eq 13 thus shows that E evaluated at $S = {}^1/_4$, the midpoint of its range, is a constant, and independent of K; hence, the half-wave potential retains its usual significance. If K is large, the coulogram would contain two distinct waves, but if it is small, only a single wave will result whose slope at the midpoint depend upon the value of K. (It can be shown that if $K > 16$, there will exist three inflection points in a graph of S *vs.* E, and hence two waves; if $K < 16$ only one inflection point is possible, and hence a single wave.)

The equilibrium constant K is most conveniently evaluated directly from the experimental data by determining the slope of the plot of Q *vs.* E at the half-wave potential. Differentiation of eq 13 subject to eq 12, 11, and 10 yields

$$\left(1 + \frac{K^{1/2}}{2}\right) = \frac{1}{2}\frac{F}{RT}\, Q_t \bigg/ \left(\frac{\mathrm{d}Q}{\mathrm{d}E}\right)_{E_{1/2}} \qquad (14)$$

where Q_t is the number of coulombs necessary to reduce all of the Ru(IV) to Ru(3.5) and $(\mathrm{d}Q/\mathrm{d}E)E_{1/2}$ is the slope of the curve evaluated at the half-wave potential (*i.e.*. $S = {}^1/_4$).

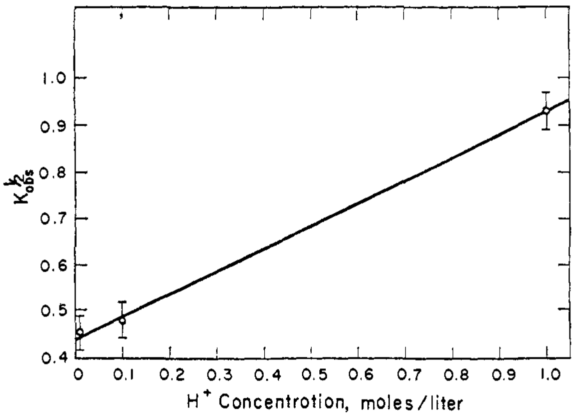

Figure 4. $K^{1/2}_{obsd}$ *vs.* H^+ concentration at ionic strength 1.0 *M*.

Since the apparent numbers of electrons, n, were determined from the slopes of the same coulograms using eq 1, 2, and 3, rather than those described above, K and n are directly related to each other. This relation is

$$n = \frac{4}{2 + K^{1/2}} \tag{15}$$

Since K can vary between 0 and 16 without showing any evidence of two reduction waves, the apparent number of electrons involved could vary between 2 and $^2/_3$ in such a system.

Table III contains values of the half-wave potentials for the over-all process together with those of $K^{1/2}$ calculated as described above. Both $E_{1/2}$ and K are independent of ruthenium concentration but vary with hydrogen ion concentration. The ~60-mV increase in $E_{1/2}$ for each decade increase in hydrogen ion concentration indicates that approximately one hydrogen ion is consumed for each electron transferred. The reduction reactions can then be formulated as follows.

$$\text{Ru(IV)} + H^+ + e^- \longrightarrow \text{H Ru(3.75)} \tag{16}$$

$$\text{HRu(3.75)} + H^+ + e^- \longrightarrow \text{H}_2\text{Ru(3.5)} \tag{17}$$

$$E = \frac{E_{1/2}^{(1)} + E_{1/2}^{(2)}}{2} - \frac{RT}{2F}\ln\frac{[\text{H}_2\text{Ru(3.5)}]}{[\text{Ru(IV)}]} + \frac{RT}{F}\ln(\text{H}^+) \tag{18}$$

$$K = \frac{[\text{HRu(3.75)}]^2}{[\text{Ru(IV)}][\text{H}_2\text{Ru(3.5)}]} \tag{19}$$

These reactions are therefore consistent with the variation of $E_{1/2}$ with H^+ concentration but imply that K should be independent of H^+ concentration. The observed variation of K with H^+ concentration can be explained by assuming a second protonated species of Ru(3.75) to be involved in the reduction according to the equilibrium.

$$\text{HRu(3.75)} + H^+ \rightleftharpoons \text{H}_2\text{Ru(3.75)} \tag{20}$$

K in eq 19 can then be represented in terms of the total concentration of Ru(3.75) species, $[\text{Ru(3.75)}]_t$, the equilibrium constant K_a for eq 20 and the hydrogen ion concentration.

$$K = \frac{[\text{Ru(3.75)}]_t^2}{[\text{Ru(IV)}][\text{H}_2\text{Ru(3.5)}]}\,\frac{1}{[1 + K_a(\text{H})^+]^2} \tag{21}$$

The term on the right of (21) involving the quotient of concentrations of ruthenium species is the observed equilibrium constant defined by eq 7 which will now be called K_{obsd}. Substitution of the symbol in eq 21 and rearranging yields

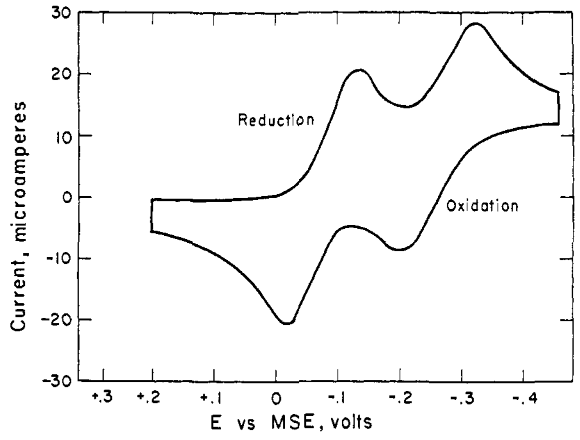

Figure 5. Cyclic voltammetric scan of Ru(IV).

$$K^{1/2}_{obsd} = K^{1/2} + K_aK^{1/2}(\text{H}^+) \tag{22}$$

Figure 4 contains a plot of $K^{1/2}_{obsd}$ *vs.* the hydrogen ion concentration that shows that the data in Table III obey eq 22 within experimental error. The values of $K^{1/2}_{obsd}$ obtained at the lowest ruthenium concentration were ignored because they were less reliable. The values of $K^{1/2}$ and K_a determined from the data were 0.44 and 1.11, respectively.

A more complete description of this system will probably require the assumption of more than one protonated species of Ru(IV) and Ru(3.5) to explain why the shift in $E_{1/2}$ is slightly greater than the 60 mV/decade change in acidity. The present data, however, are not sufficiently extensive to warrant such a treatment.

Cyclic Voltammetry. Studies with scanning and step coulometry showed that Ru(IV) can be reversibly reduced to Ru(3.5) but that the reduction of Ru(3.5) to Ru(III) yields a product which cannot be reversibly reoxidized to Ru(IV). Both coulometric techniques are rather slow; titrations require at least 30 min. This suggested that Ru(3.5) might be reduced reversibly to a transient species of Ru(III) which spontaneously converts to the stable form, and that the transient species might be detected by a more rapid electrochemical technique such as cyclic voltammetry.

Cyclic voltammetric studies were run in 0.1 *M* perchloric acid at ionic strength 1.0 *M* and Ru(IV) concentrations varying between 6.9×10^{-5} and 1.4×10^{-3} *M*. Figure 5 is a typical cyclic voltammogram after background correction. The upper part of the curve shows the current at a gold microelectrode as the impressed voltage is rapidly increased in the cathodic direction; the lower part is the current when the direction of the voltage scan is reversed immediately afterward. The upper curve therefore represents the reduction of Ru(IV) and the lower one represents the reoxidation of the reduction products very shortly after they were formed. The particular result shown in Figure 5 was for a 1.4×10^{-3} *M* Ru(IV) solution run with a scanning period of 10 sec each for the reduction and oxidation waves.

The results with lower Ru(IV) concentrations were qualitatively the same as that shown in Figure 5. The heights of the peaks were of course smaller but their

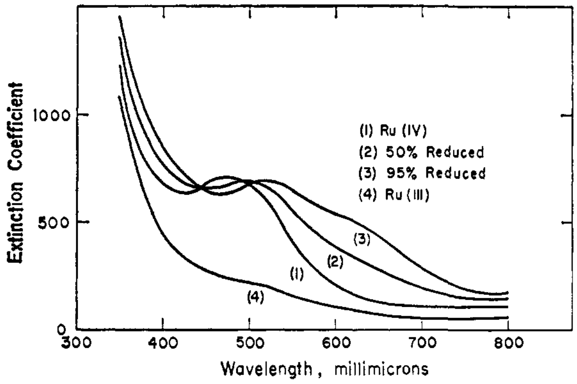

Figure 6. Spectra of solutions during reduction of Ru(IV) to Ru(3.5) in 0.1 M $HClO_4$ and 0.9 M $NaClO_4$.

positions were virtually independent of ruthenium concentration. Results were qualitatively the same when the scanning period was decreased to 0.01 sec.

The two maxima in the reduction wave are at approximately the potentials expected for the reduction of Ru(IV) to Ru(3.5) and of Ru(3.5) to Ru(III) based on the results of scanning and step coulometry. The existence of two minima in the reoxidation wave indicates that both species formed in the reduction are rapidly reoxidized by the same route followed in the reduction.

In voltammetry, the current maxima are always at potentials more cathodic than $E_{1/2}$ during reduction and more positive than $E_{1/2}$ during oxidation.[20] Values of $E_{1/2}$ for the two processes were therefore estimated by taking the average of the peaks potentials for each process in reduction and reoxidation waves. This procedure while not rigorous should be sufficiently accurate to help identify the processes involved. The value of $E_{1/2}$ for the reduction of Ru(IV) to Ru(3.5) determined in this manner was −0.080 V *vs.* mse—in excellent agreement with the value obtained by step coulometry at the same acid concentration. $E_{1/2}$ for the second process [presumably the reduction of Ru(3.5) to the transient form of Ru(III)] was −0.26 V *vs.* mse as opposed to −0.38 V obtained with scanning coulometry for the reduction of Ru(3.5) to the stable form of Ru(III). Direct comparison of the values may not be very meaningful because the latter process is irreversible, but they do show that the second peak in cyclic voltammetry is due to the conversion of Ru(3.5) to some form of Ru(III) since $E_{1/2}$ is less cathodic for that process than for scanning coulometry, which was demonstrated to produce a form of Ru(III).

In a further study, a solution of Ru(IV) was reduced by scanning coulometry to the stable form of Ru(III) in a cell which also contained a gold microelectrode. The resultant Ru(III) solution was then studied by cyclic voltammetry. The current voltage scans with this solution were the same as the background scans—confirming that the stable form of Ru(III) cannot rapidly be reoxidized at a gold electrode. It also proves conclusively that the species responsible for the second peak in cyclic voltammetry of Ru(IV) is not the stable Ru(III).

Further Observations. A number of studies were carried out on solutions of the various ruthenium species prepared by the controlled-potential coulometric reduction of Ru(IV). A series of six solutions was prepared in which a 6.0×10^{-4} M solution of Ru(IV) in 0.1 M $HClO_4$–0.9 M $NaClO_4$ was reduced at −0.18 V *vs.* mse to varying extents between Ru(IV) and Ru(3.5). The visible absorption spectra of these solutions were measured, three of which are shown in Figure 6, together with that of Ru(III) prepared by reduction of the Ru(IV) solution at −0.40 V *vs.* mse. Care was taken in the reduction of these six solutions that the accumulated charge did not exceed that required to produce Ru(3.5) so that no species other than these occurring between Ru(IV) and Ru(3.5) were present. These spectra were analyzed by the matrix rank method[21,22] which indicated three species to be present which contributed to the spectra.

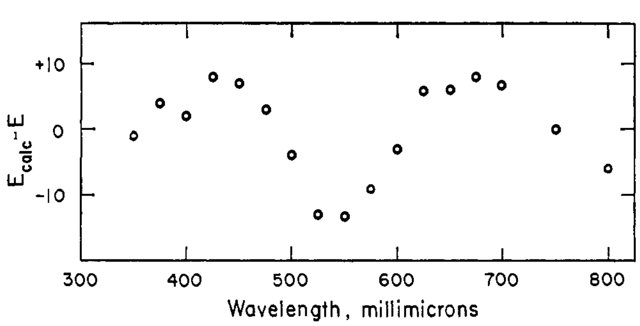

Figure 7. Calculated and observed spectrum of solution 2.

Further indications of the presence of a third species are the absence of an isosbestic point near 500 mμ and our inability to express, accurately, the intermediate spectra as linear combinations of those of Ru(IV) and the solution which was predominantly Ru(3.5). For example, the best least-squares fit of spectrum 2 in Figure 6 as a linear combination of spectra 1 and 3 gave a synthetic spectrum which was then compared with the actual spectrum. Figure 7 is a plot of the difference between the extinction coefficients of the calculated spectrum, E_{calcd}, and those of actual spectrum, E, as a function of wavelength. If only two species existed in these three solutions, the points in Figure 7 would be expected to scatter randomly about zero with a standard deviation of about 3 based on an assumed standard derivation of ±0.003 for each absorbance measurement. Although the actual values of $E_{calcd} - E$ are small, they are considerably larger than the estimated error in several instances (largest value, −13); in addition, they vary systematically with wavelengths indicating very strongly that a third absorbing component is present. The spectral data therefore tend to confirm the existence of Ru(3.75).

The general characteristics of our ultraviolet spectra of ruthenium species agree with Atwood's observations.[14] The original Ru(IV) spectrum had a peak at 480 mμ and a shoulder at 300 mμ. Upon reduction to Ru(3.5) the peak shifted to 520 mμ and the shoulder at 300 mμ disappeared. The spectrum of Ru(III) contained a single peak at 290 mμ.

The spectrum of Ru(III) produced by the reduction of Ru(IV) at −0.4 V *vs.* mse showed no trace of a peak at 225 mμ corresponding to the monomeric Ru^{3+} of Cady.[5] However, when Ru(III) so produced was reduced at −0.6 V, such a peak did appear which grew in height at the expense of the one at 290 mμ, as the reduction was continued. Absorption of this mixture on a cation-exchange column and subsequent elution

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(20) Reference 16, p 120.

(21) R. M. Wallace, *J. Phys. Chem.*, **64**, 899 (1960).

(22) R. M. Wallace and S. M. Katz, *ibid.*, **68**, 3889 (1964).

with 0.3 *M* lanthanum perchlorate resulted in the separation of the two species. The species with the absorption maximum at 225 mμ was eluted as a discrete band in front of the lanthanum just as the Ru^{3+} described by Cady. The species with the peak at 290 mμ eluted only as a diffuse band with lanthanum and resisted all attempts to "push" it.

The most plausible explanation of the above results was suggested to us by E. E. Mercer. The Ru(III) produced by the reduction of Ru(IV) at −0.4 V is a polymeric species. Reduction of that species at −0.6 V results in the formation of monomeric Ru(II) which is rapidly oxidized to monomeric Ru^{3+} by perchloric acid.

Summary

Ru(IV) in perchloric acid media is a tetrameric species with a charge of +4 which can be reduced reversibly at a gold electrode by two, one-electron processes to tetrameric species with formal oxidation states of 3.75 and 3.5. Because approximately one hydrogen ion is involved as a reactant in each of these reactions, the reduced species can be formulated as $[\mathrm{H\ Ru(3.75)}]^{4+}$ and $[\mathrm{H_2Ru(3.5)}]^{4+}$. A more complete description requires the assumption of the species $[\mathrm{H_2Ru(3.75)}]^{5+}$ as well.

Tetrameric $[\mathrm{H_2Ru(3.5)}]^{4+}$ is then reduced by a two-electron process, the details of which are not known, to a transient species of Ru(III) (presumably also tetrameric). The transient form of Ru(III) undergoes a spontaneous conversion to a stable polymeric form of Ru(III). The lifetime of the transient Ru(III) is greater than 10 sec but less than 30 min. Stable Ru(III) can be reoxidized irreversibly back to the original tetrameric Ru(IV), but there do not appear to be any well-defined reversible steps in this process. Stable Ru(III) can also be reduced to Ru(II) which is spontaneously oxidized by perchloric acid to monomeric Ru^{3+}.

The potential diagram for the processes involved in the reduction of Ru(IV) to $H_2Ru(3.5)$ at ionic strength 1 *M*, referred to the normal hydrogen electrode, is shown below. The signs follow the IUPAC conventions. The potential for the reduction of $H_2Ru(3.5)$ to the transient form of Ru(III) determined by cyclic voltammetry in 0.1 *M* H^+ and ionic strength 1 *M* was 0.40 V *vs.* the normal hydrogen electrode. No study of the acid dependence of this process has been made so the number of hydrogen ions involved is not known.

$$\begin{tikzcd}
 & \mathrm{H_2Ru(3.75)} \arrow[dr, dash, "0.657\ \mathrm{V}"] & \\
{[\mathrm{Ru(IV)}]} \arrow[ur, dash, "0.621\ \mathrm{V}"] \arrow[dr, dash, "0.618\ \mathrm{V}"'] \arrow[rr, dash, bend right=70, "0.639\ \mathrm{V}"'] & & \mathrm{H_2Ru(3.5)} \\
 & \mathrm{H\ Ru(3.75)} \arrow[ur, dash, "0.660\ \mathrm{V}"'] &
\end{tikzcd}$$

Acknowledgments. We wish to acknowledge the assistance of F. G. McNatt and J. W. Crooks with the experimental work. The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

Liquid Ammonia Solutions. VII. Solutions of Carbon Acids

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Received December 30, 1968

Abstract: The reaction of a series of hydrocarbon acids with potassium amide in liquid ammonia has been investigated using spectrophotometric techniques reported previously. The acidity and spectroscopic characteristics of di(*p*-tolyl)methane and 4,4′-dimethoxydiphenylmethane permit the ionization constants of these substances to be determined; at −34.5°, the ionization constants of di(*p*-tolyl)methane and di(4-methoxyphenyl)methane are 7.33×10^{-28} and 2.53×10^{-29}, respectively.

Weakly acidic carbon and nitrogen acids such as diphenylmethane and aniline can be deprotonated in liquid ammonia solutions containing amide ions, the strongest base that can exist in this solvent. In the case of carbon acids, *i.e.*, compounds that donate a proton by fission of a carbon–hydrogen bond, the equilibrium described by eq 1 is established when the conjugate base formed by deprotonation with amide ion is of comparable strength to the latter. The relative strengths of hydrocarbon acids should be related to the equilibrium constants defined in the usual manner (eq 2). Since many of the conjugate bases (R^-) are highly colored in liquid ammonia solution, it should be possible to monitor the position of equilibrium 1 using the absorption band(s) characteristic of the conjugate base, the band characteristic of the amide ion,[1] or both. We present here the results of a spectrophotometric investigation of the equilibria established between a series of carbon acids and potassium amide in anhydrous liquid ammonia.

$$\mathrm{RH} + \mathrm{NH_2^-} \rightleftharpoons \mathrm{R^-} + \mathrm{NH_3} \tag{1}$$

$$K = (a_{\mathrm{R^-}})(a_{\mathrm{NH_3}})/(a_{\mathrm{RH}})(a_{\mathrm{NH_2^-}}) \tag{2}$$

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[1] R. E. Cuthrell and J. J. Lagowski, *J. Phys. Chem.*, 71, 1298 (1967).