PHYSICAL AND INORGANIC CHEMISTRY

The Electrode Potential of Ruthenium(IV) and Its Lower Oxidation States[1]

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RECEIVED MARCH 2, 1962

From titration data obtained for the reduction of ruthenium(IV) perchlorate with vanadium(II) sulfate, the electrode potentials of Ru(IV) and Ru(III) were calculated. The existence of a state with oxidation number 3.5 was confirmed. In the polarographic reduction of Ru(IV) in perchloric acid solutions three waves were observed and the dependence of the half-wave potentials on pH was determined. Both monomeric and polymeric Ru(IV) species were studied.

Both potentiometric and polarographic techniques were used in a study of Ru(IV) and its lower oxidation states in perchloric acid solutions for which information is meager. Wehner and Hindman[3] reported values for the electrode potential of Ru(IV) ranging from +0.55 to +1.17, depending on reactions involving electrolytic reduction of Ru(IV) or oxidation of Ru(III). More definitive work by Cady and Connick[4] estimated the potential as +1.00 v. They also report the possibility of the existence of a (3.5) state. In the study of ruthenium(IV) perchlorate by Niedrach and Tevebaugh,[5] and by Turk,[6] two waves were observed for the reduction of Ru(IV) to Ru(III) and half-wave potentials were reported. In our investigation two breaks were observed in the titration curve of the reduction of Ru(IV) to Ru(III) with vanadium(II) sulfate, and the potentials were determined for the half-cell reactions of Ru(IV) to Ru(3.5) and Ru(3.5) to Ru(III). From polarographic data the potential of Ru(III) was determined.

Experimental

Materials.—Monomeric Ru(ClO₄)₄ solutions for the potentiometric titrations were prepared according to the method of Gortsema and Cobble[7] in which a quantity of low cross-linked Dowex 50 WX4 exchange resin (2 to 4%) was equilibrated with Ru(IV) solution and then eluted with 0.1 M cerium(III) perchlorate or 1 M perchloric acid. It has been shown that a transformation of the polymer to the monomer occurs during the passage through the ion exchange resin.[8] The Ru(IV) concentrations used were 0.00122 to 0.00148 M, and the pH values were 1.12 to 1.17.

Vanadium(II) sulfate solutions (0.0154 M) were prepared by dissolving a weighed amount of vanadium pentoxide in 500 ml. of 1 M H₂SO₄. The solution was evaporated to 150 ml. in the presence of granulated zinc. While still hot, oxygen-free nitrogen was bubbled through the solution for a short time in a closed system. The resulting deep purple solution was diluted with degassed conductivity water and stored over lightly amalgamated zinc in the reservoir of a Karl Fisher buret under positive pressure of pure nitrogen.

For the polarographic studies the solutions were prepared from RuO₄ dissolved in HClO₄ and reduced by the slow addition of hydrogen peroxide at low pH with rapid stirring to favor the formation of Ru(IV) in the monomeric state. The solutions were standardized by placing aliquots in the spectrophotometric cell, adding a crystal of periodic acid to oxidize the Ru to RuO₄. The molar absorptivity (1 cm., mole per liter) for RuO₄ in perchloric acid is 930 at 385 mμ. The solutions were 0.001 M Ru(ClO₄)₄ with 0.1 M NaClO₄ as supporting electrolyte. The pH was varied from −0.40 to 2.35 by controlling the HClO₄ concentration.

Apparatus.—The polarograms were obtained with a Sargent model XV polarograph. A conventional H-type cell was used with an agar plug separating the two compartments. The reference electrode was prepared from Hg and Hg₂Cl₂(s) and a saturated solution of NaCl in place of KCl which caused the precipitation of KClO₄ with the perchloric acid in the Ru(IV) solutions. By comparison with a calomel cell prepared with KCl ($E = +0.2415$ v.) the electrode potential of the NaCl–calomel cell was determined to be +0.2360 v. at 25°.

(1) This research was supported by E. I. du Pont de Nemours and Company and the Atomic Energy Commission under Subcontract AX-2271 of AT(07-2)-1.

(2) (a) From the Ph.D. thesis of D. K. A., Purdue University, 1960; (b) presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962.

(3) P. Wehner and J. C. Hindman, J. Am. Chem. Soc., 72, 3911 (1950).

(4) H. H. Cady and R. E. Connick, ibid., 80, 2646 (1958).

(5) L. W. Niedrach and A. D. Tevebaugh, ibid., 73, 2835 (1951).

(6) E. Turk, Argonne National Laboratory, Reports ANL-4292 (March 1949), 4329 (June 1949), 4372 (September 1949).

(7) F. P. Gortsema, Doctoral thesis, Purdue University, January 1960; Dissert. Abstracts, 21, 48 (1960), L. C. Card No. Mic 60-2206.

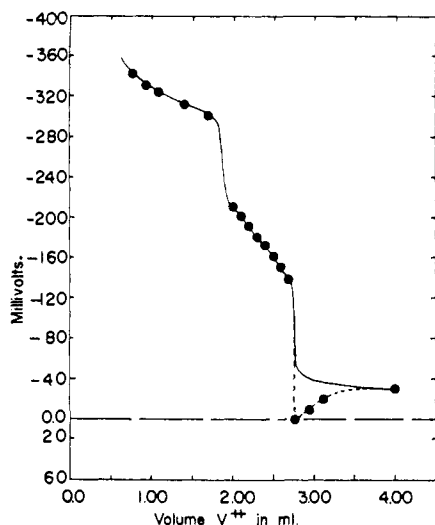(8) D. K. Atwood and Thos. De Vries, J. Am. Chem. Soc., 83, 1509 (1961).

Fig. 1.—Typical curve for the titration of ruthenium(IV) perchlorate with vanadium(II) sulfate.

The rotating platinum microelectrode (RPME) was made by having a small platinum bead on the side of a glass tube, 6 mm. o.d., and rotating at 1660 r.p.m. The motor was a capacitance-type synchronous motor such as is used for the chopper assembly of a Perkin–Elmer infrared spectrometer.

Oxygen-free nitrogen was used at all times to displace oxygen from the solutions, but it was not necessary to use a maximum suppressor. The resistance of the various solutions in the cells never exceeded 350 ohms. All measurements were made at 25°.

For analytical purposes the absorbancies of solutions were measured with a Beckman model DU spectrophotometer. To study the spectra of the materials and reduction products a Cary model 14 recording spectrophotometer was used.

Potentiometric Titration.—For the titrations the electrodes were bright platinum foil and a Beckman saturated calomel electrode, and the potentials were measured with a Beckman model G pH meter. The titrations were carried out at room temperature in a closed system under positive nitrogen pressure. The potentials reached equilibrium very slowly, and attempts to use a catalyst in order to form a "bridge" for the electron transfer were unsuccessful. Materials tried for this purpose were bromide, iodide, cupric, ferrocyanide and uranyl ions. Throughout the entire titration anywhere from three minutes to a two-hour wait was necessary before a constant potential reading could be obtained for any one point on the curve. In the region following the second break (see Fig. 1) the potential often dropped rapidly to a value below the final value and then gradually rose to one which was plotted. This slow drift in potential may be due to a change in the nature of the ionic species of Ru(III) because Wehner and Hindman[3] had observed (their Fig. 7) a slow change in the absorption spectrum of Ru(III) in the 300 mμ region, requiring 24 hr. and 6 hr. in 1 M and 6 M HClO₄, respectively.

Two breaks were observed in the titration curve, and the equivalents used were such that the first break occurs when Ru(IV) has been reduced to a 3.5 oxidation state and the second break when it has all been reduced to Ru(III).

Electrode potentials were calculated from the cell potentials measured when 25 and 75% of the Ru(IV) was reduced. Four determinations gave the values 0.305, 0.312, 0.320, 0.323, average 0.315 v. Using 0.242 as the electrode potential of the s.c.e., the electrode potential for the half-cell reaction 2Ru(IV) + e = Ru₂(3.5) is +0.56 v. Results for the second part of the titration curve gave the values 0.168, 0.171, 0.191, average 0.177 v., and +0.42 as the electrode potential for the half-cell reaction Ru₂(3.5) + e = 2Ru(III). Both of these potentials are for solutions in which the pH was 1.12–1.17.

Polarography.—When ruthenium(IV) perchlorate solutions were polarographically reduced, three waves were obtained whose half-wave potentials shifted to more positive values when the
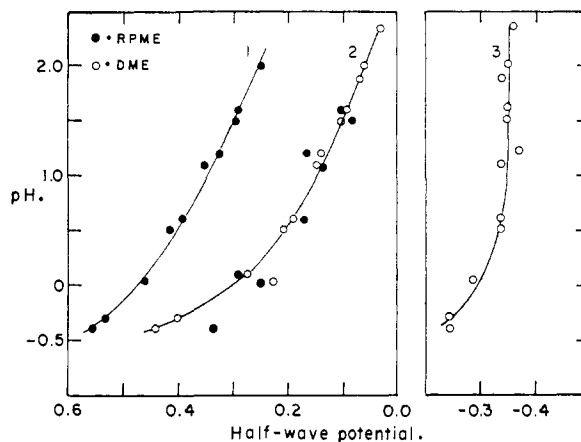

Fig. 2.—Dependence of half-wave potentials on hydrogen ion concentration for 0.001 M Ru(ClO₄)₄ in 0.1 M NaClO₄, for waves 1, 2 and 3, using a dropping mercury electrode (DME) and a rotating platinum microelectrode (RPME).

perchloric acid concentration was increased (see Fig. 2). In 1 M HClO₄ the first wave shifted to a potential more positive than the mercury oxidation wave, and it was necessary to use the RPME. In 0.1 M HClO₄, using a d.m.e., the $E_{1/2}$ values on the hydrogen scale were 0.59, 0.39 and −0.11 v. for 0.001 M Ru(IV) solutions which results compare favorably with the values 0.56, 0.40 and −0.14 reported by Niedrach and Tevebaugh.[5] In the potentiometric titration an intermediate with an oxidation number of 3.5 was shown to exist. The three waves may thus be ascribed to the three reduction steps Ru(IV) → Ru(3.5) → Ru(III) → Ru(II). Furthermore the wave heights were in the ratio 1 : 0.95 : 2.4, but it was difficult to establish the plateau of the third wave.

That the third wave was due to the reduction of Ru(III) to Ru(II) was established by polarographic reduction of Ru(III) solutions prepared by two different methods. An excess of hydrazine was added to a Ru(IV) solution, and the mixture was stirred for several hours.[9] The solutions were amber yellow in color, and stable over a period of months if an excess of hydrazine was maintained. The polarograms obtained showed a wave for the reduction of hydrazine at −0.02 v. vs. the NaCl–calomel reference electrode and the third wave at about −0.4 v. as in the above-mentioned experiments.

Electrolytic reduction of Ru(IV) was accomplished by using a cell similar to the polarographic cell but with a platinum foil cathode and the Na-Cl–calomel reference electrode. The potential across the cell was set at a value corresponding to the plateau of the second Ru(IV) reduction wave. Nitrogen was bubbled through the cell during the electrolysis. At the completion of the reduction, the solution was amber yellow in color and gave a spectrum of Ru(III) with the expected peak at 290 mμ. As in the case of the above Ru(III) solution, the first two Ru(IV) reduction waves were absent, and a *single* oxidation wave appeared in their place while the third wave remained un-

(9) Suggested by R. M. Wallace, Savannah River Laboratory, E. I. du Pont de Nemours and Co., Inc., Aiken, S. C.

changed. The wave which was ascribed to hydrazine was also absent.

It has been shown[7] that Ru(IV) can exist as an RuO^{++} monomer and a polymer of varying length. It was not possible to prepare polymeric Ru(IV) solutions with absolute certainly of excluding all monomer. However, by a single ion exchange technique pure RuO^{++} solutions which contained virtually no polymer were prepared and their polarograms compared with those of Ru(IV) solutions of varying degree of polymerization. No dependence of shape, number of waves or values of half-wave potentials on degree of polymerization could be found. Half-wave potentials, shape and diffusion current seemed to depend only on the pH of the solution.

Half-wave Potentials.—Half-wave potentials were determined at different pH values for 0.001 M Ru(ClO$_4$)$_4$ in 0.1 M NaClO$_4$ as supporting electrolyte, using both a d.m.e. and a RPME. The potentials shifted to more positive values with an increase in the hydrogen ion concentration, and when pH was plotted versus $E_{1/2}$, the failure to obtain straight lines indicated the presence of various species of Ru(IV) and Ru(III) requiring from one to three protons in the reduction step for each electron used, the number increasing with a decrease of the pH. Only for the reduction of Ru(III) to Ru(II) was there no dependence of the potential on pH except at smaller pH values (see Table I and Fig. 2).

It has been reported that Ru(IV) solutions are extensively polymerized, that the ions are hydrated to varying degrees and that appreciable amounts of RuO^{++} are present.[7,10] The absorption spectrum of a RuO^{++} monomer solution has a very pronounced shoulder at 300 mμ, which can also be seen in Fig. 4 of the paper by Wehner and Hindman.[3] This shoulder diminishes in intensity as the solution becomes more polymeric and disappears when solutions containing the Ru(3.5) species are reduced to Ru(III). It seems reasonable to assume that the RuO^{++} end is reduced for hydrated polymeric species such as (RuO$_2$(OH$_2$)$_2$)$_x$-RuO^{++} or (Ru(OH)$_4$)$_x$RuO^{++}.
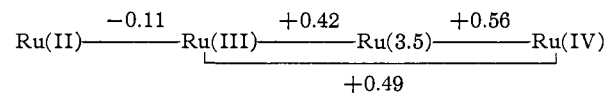
During the course of the investigation the dependence of the diffusion current on the height of the mercury column was observed. Polarograms were obtained for only the second and third waves since no study was possible of the first wave which

(10) F. P. Gortsema and J. W. Cobble, J. Am. Chem. Soc., **83**, 4317 (1961).

would have been representative of that reaction. The mercury height was varied from 17.5 to 67.5 cm. in 10 cm. steps and a correction was made for the back pressure for the capillary. At the foot of the wave the diffusion current did not vary with the square root of the mercury height, thus providing evidence that the reactions were rate controlled. As the plateau of the wave is reached there was a gradual change from a rate controlled to a diffusion controlled reaction with i_d proportional to $(h - c)^{1/2}$. The results were obtained for Ru(IV) solutions at a pH of 0.1 ± 0.02. The studies were done with both monomeric ($\epsilon_{480} = 731$) and polymeric ($\epsilon_{480} = 994$) solutions.

TABLE I

HALF-WAVE POTENTIALS FOR Ru(IV) REDUCTION WAVES AT VARIOUS pH's

Concn., $M \times 10^4$	pH	$E_{1/2}$ versus calomel electrode			
		1 RPME	2 RPME	2 DME	3 DME
Series no. 1					
9.52	2.35	...	...	+0.030	−0.360
9.74	1.99	+0.251	...	.060	.350
9.78	1.59	.290	+0.100	.090	.353
9.78	1.19	.325	.159	.143	.371
9.68	0.58	.380	.165	.189	.340
10.04	0.10	.411	.238	.268	.328
10.04	−0.30	.531	.358	.40	.243
Series no. 2					
10.41	1.88	+0.189	...	+0.067	−0.342
9.84	1.49	.294	+0.102	.082	.348
9.71	1.09	.349	.136	.145	.339
9.60	0.49	.414	...	.204	.339
9.84	0.03	.461	.246	.223	.285
9.96	−0.40	.556	.331	.440	.246

Potential Diagram.—The electrode potentials determined from the titration data can be compared with the half-wave potentials for the three waves and the following potential diagram for the lower oxidation states of ruthenium can be given

$$\text{Ru(II)} \overset{-0.11}{\rule{1.5cm}{0.4pt}} \text{Ru(III)} \overset{+0.42}{\rule{1.5cm}{0.4pt}} \text{Ru(3.5)} \overset{+0.56}{\rule{1.5cm}{0.4pt}} \text{Ru(IV)}$$
$$\underset{+0.49}{\underbrace{\rule{5cm}{0pt}}}$$

These values are for solutions at pH 1. For other acidities corrections must be made using data shown in Fig. 2. It must also be mentioned that when the reactions are rate controlled, small variations in $E_{1/2}$ occur with changes in drop time and the values are not simply related to free energy changes.