were purely ionic in character, the expected distance between these atoms would be the sum of the ionic radii, 1.94 Å., using the value of 1.40 Å. given by Pauling.[18] The observed distance 1.79 Å. is

appreciably shorter, possibly being indicative of a covalent link, as suggested by the electronegativity of ruthenium. Double bond character may also contribute to a short interatomic distance.

(18) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1940, p. 346.

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Polarographic Studies of Ruthenium in Oxidation States IV, VI, VII and VIII[1,2]

BY MEYER D. SILVERMAN AND HENRI A. LEVY

Standard potentials of −0.59 and −1.00 volt have been obtained polarographically for the ruthenate–perruthenate and perruthenate–ruthenium tetroxide couples, respectively, using a stationary platinum electrode.

With the exception of the work of Connick and Hurley,[3] very little new information on the aqueous solution chemistry of ruthenium in the VI, VII and VIII oxidation states has been accumulated during the past 25 years. The older literature is well summarized in Gmelin[4] and also by Charonnat.[5]

Concurrent with this work, Connick and Hurley[3] measured potentials of cells containing ruthenium-(VI) and -(VII) in alkaline solution and obtained a standard potential for the couple in excellent agreement with the polarographic result here reported. They also measured an approximate equilibrium constant for the disproportionation of ruthenate into perruthenate and ruthenium dioxide and from these data calculated a potential for the (IV)–(VI) couple. These investigators, and also the present authors,[6] have previously established by spectrophotometric studies the pH ranges in which the various oxidation states are experimentally accessible.

Polarographic studies involving ruthenium have previously been limited to the lower oxidation states.[7-9] In the present work, two oxidation–reduction couples were successfully investigated, the ruthenium(VI)–(VII) couple and the (VII)–(VIII) couple. Each was studied in oxidation and reduc-

tion over a range of total ruthenium concentration and pH, and at two concentrations of supporting electrolyte ($NaClO_4$).

Attempts to obtain the ruthenium(VI)–(IV) potential polarographically were unsuccessful. Half-wave potentials from reduction waves showed proper dependence on pH, (corresponding to four hydroxyl ions liberated per RuO_4^- reduced), but not on ruthenate concentration; furthermore, the shape of the wave (plot of E_i vs. $\log i/(i_d - i)$) was not indicative of a reversible couple. Oxidation waves could not be obtained.

Experimental

The starting materials for preparation of the solutions were solid potassium perruthenate, a stock solution of potassium ruthenate ($ca.$ 0.02 M) in $ca.$ 0.1 M KOH, and an aqueous solution of ruthenium tetroxide. From a solution of spectrographically pure ruthenium chloride, freed of chloride by repeated fuming with sulfuric acid, ruthenium tetroxide was distilled using potassium permanganate as an oxidizing agent. The tetroxide was kept for periods up to several weeks as a solution in ice-cold distilled water, or as crystalline solid in the ice-box. Potassium perruthenate was prepared[10] by absorbing the tetroxide in dilute potassium hydroxide. Small black crystals which were deposited after standing overnight in the ice-box were filtered and washed with ice-cold distilled water. Chemical analysis of the crystals after drying *in vacuo* confirmed their identity as potassium perruthenate. Potassium ruthenate stock solution was prepared by dissolving crystals of the perruthenate, or by absorbing distilled ruthenium tetroxide, in 1 M potassium hydroxide. All other chemicals employed were of reagent grade.

The solid platinum electrodes used throughout this investigation were prepared in a manner described by Rogers and co-workers.[11] Whenever deposition of RuO_2 on the Pt electrode was noted a fresh electrode was used. A Sargent automatic polarograph, model XX, was used. The resistance of the cell was measured before each run with a conductivity bridge (model RC-1B, Industrial Instruments, Inc.). The pH was measured with a Beckman model G pH meter, using the high pH type E glass electrode. All experiments were carried out at 24.5 ± 0.5°.

In a given experiment, a dilute solution of the appropriate ruthenium species, ruthenate, perruthenate or ruthenium tetroxide, in sodium perchlorate as supporting electrolyte, was placed in the polarographic cell. A double bridge the arms of which contained sodium perchlorate of the same concentration, and saturated ammonium chloride, respectively, connected this cell to a saturated calomel half-cell.

(1) From the doctorate thesis of M. D. Silverman, August, 1950. This document is based on work sponsored by the Atomic Energy Commission under the resident graduate program of the Oak Ridge National Laboratory, the Oak Ridge Institute of Nuclear Studies, and the University of Tennessee.

(2) Presented before the Division of Physical and Inorganic Chemistry, 115th National Meeting, American Chemical Society, San Francisco, Calif., March, 1949.

(3) R. E. Connick and C. R. Hurley, THIS JOURNAL, **74**, 5012 (1952).

(4) "Gmelin's Handbuch der anorganischen Chemie," 8 Auflage, Verlag Chemie, Berlin, 1938.

(5) R. Charonnat, "Traité de Chimie Minerale," Vol. XI, Masson and Cie, Paris, 1932.

(6) M. D. Silverman and J. A. Swartout, Quarterly Reports of the Chemistry Division, Oak Ridge National Laboratory, CNL-37 (April, 1948) and ORNL-286 (September, 1949); also unclassified report ORNL-746 (August, 1950).

(7) D. D. DeFord and A. W. Davidson, THIS JOURNAL, **73**, 1469 (1951).

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

(9) E. Turk, Quarterly Reports of the Chemical Engineering Division, Argonne National Laboratory, ANL-4292 (March, 1949), 4329 (June, 1949), and 4372 (September, 1949).

(10) H. Debray and A. Joly, *Compt. rend.*, **106**, 1994 (1888).

(11) L. B. Rogers, H. H. Miller, R. B. Goodrich and A. F. Stehney, *Anal. Chem.*, **21**, 777 (1949).

Sodium perchlorate was adopted as the supporting electrolyte after is was found that chloride ion catalyzed the decomposition of ruthenium solutions; the double-bridged system served to avoid contact between ruthenium solutions and chloride ion. Junction potentials were kept very small (< 1 mv.) by using the same concentration of sodium perchlorate in both beakers and the first bridge, and saturated ammonium chloride in the second bridge; the specific advantages of the latter material have been demonstrated by Murray and Acree.[12]

Results and Discussion

The polarographic data are summarized in Table I. Under the column headed "Solution" are listed the ruthenium compounds which served as starting materials. The $E_{1/2}$ values listed are the observed half-wave potentials (vs. hydrogen) corrected for instrumental errors and IR drop. Unless considerable decomposition of the solution had already occurred, oxidation and reduction waves were run on the same solution with the same electrode.

TABLE I

POLAROGRAPHIC POTENTIALS FOR THE $RuO_4^{=}$–RuO_4^- AND RuO_4^-–RuO_4 COUPLES AT 25°

Solution	pH	Half wave potential, volts (VI)-(VII) couple Oxidn.	Redn.	(VII)-(VIII) couple Oxidn.	Redn.
		$\mu = 0.10$			
KRuO₄	10.6	0.598	0.606	0.998	0.998
	10.6	.603	.617	1.024	1.012
	10.6	.601	.620	1.007	1.005
	10.7	.592	.615	1.005	1.000
	10.8	.592	...	...	...
	10.8	.574	.602	...	1.025
	11.2	.607	.623	...	...
	11.9	...	.619	...	1.011
	12.0	...	...	1.016	...
	12.0	...	...	0.966	...
	12.1	.607	..	0.973	...
KRuO₄ + RuO₄	9.0	...	.620	1.003	0.986
	11.0	.590	.602	...	1.015
	11.6	.629	.575	1.006	...
K₂RuO₄ + RuO₄	9.5	...	.593	1.016	0.998
	10.5	.601	.619	1.002	1.005
	10.6	.610	.636	1.002	1.008
	10.8	.603	.583	0.989	1.034
	11.0	.620	.558	1.009	1.008
	11.0	.594	.592	1.000	0.997
Average		0.604	0.607	1.001	1.005
		$\mu = 0.04$			
KRuO₄	10.3	0.581	0.609	1.006	1.008
	10.6	.599	.609	0.998	...
	10.8	.592	.583	1.000	1.025
KRuO₄ + RuO₄	9.0	.596	.608	1.007	1.018
	10.7	.598	.619	1.002	1.003
Average		0.594	0.605	1.003	1.010

The reproducibility of the data is in accord with that reported by Rogers and co-workers[11] for other studies involving the solid platinum electrode. Although the instrumental limits of accuracy were less than ±0.01 volt, the limits of reproducibility of the experimental measurements were somewhat wider; therefore the potentials are reported as being accurate to +0.02 v.

(12) C. N. Murray and S. F. Acree, J. Research Natl. Bur. Standards, 7, 713 (1931).

Polarographic maxima were observed intermittently, frequently when oxidation waves were run with solutions of high pH (near 12) containing mainly ruthenate. Suppressing agents could not be employed because higher oxidation states of ruthenium are easily reduced. Maxima occurred very infrequently during reduction.

Reversibility of the couples was indicated in many measurements by the observation that $E_{1/2}$ values obtained from cathodic waves are within experimental error the same as those obtained from anodic waves. Another criterion, that the plot of $\log i/(i_d - i)$ vs. E_1 give a straight line whose reciprocal slope is $0.059/n$, was fairly well satisfied by about ten waves analyzed. The slopes obtained (0.048–0.055) differ somewhat from the theoretical slope of 0.059 v., but are in accord with the measurements of other workers who have studied the solid platinum electrode.[13]

It should be noted that the values obtained for the half-wave potentials for both the ruthenate–perruthenate and perruthenate–ruthenium tetroxide couples are independent of the pH of the cell solution, indicating that hydroxide ion is not involved in the cell reaction. This is consistent with the usual formulation of the VI and VII species as $RuO_4^=$ and RuO_4^-, and on the basis of this formulation it indicates that ruthenium tetroxide is largely present in solution as a neutral species.

Standard thermodynamic potentials were estimated from the half-wave potentials in the usual manner.[14] The ratio of diffusion current constants was taken to be unity, as has been found in other cases where the oxidized and reduced species are structurally similar.[15,16] The activity coefficient ratio was estimated by means of a modified Debye–Hückel expression.[17] The values obtained are -0.59 v. for the (VI)-(VII) couple and -1.00 v. for (VII)-(VIII) (Latimer[18] sign convention).

The value for the (VI)-(VII) couple is exactly that reported by Connick and Hurley[3] and is in excellent agreement with the predicted potential of -0.60 given by Latimer.[19] For the (VII)-(VIII) couple, Latimer predicted values of -1.0^{20} and -0.9^{19}; our value is in good agreement with the former.

On the basis of the above potentials and the equilibrium data of Connick and Hurley,[3] the potential scheme for Ru(IV) to -(VIII) in alkaline solution may be formulated as

$$RuO_2 \xrightarrow{-0.35} RuO_4^= \xrightarrow{-0.59} RuO_4^- \xrightarrow{-1.00} RuO_4$$
$$\overline{\,-0.79\,}$$
$$\underline{\,-0.57\,}$$
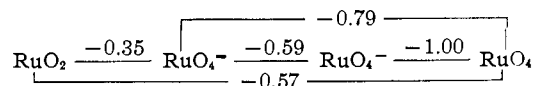
The potentials here reported imply that both

(13) L. B. Rogers, private communication.

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1952, Second Edition, Vol. I, p. 206.

(15) K. A. Kraus and F. Nelson, THIS JOURNAL, 71, 2515 (1949).

(16) I. M. Kolthoff and J. J. Lingane, ref. 14, p. 52.

(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., Second Edition, 1949, New York, N. Y., p. 120.

(18) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice–Hall, Inc., Second Edition, 1952, New York, N. Y.

(19) W. M. Latimer, ref. 18, p. 230.

(20) W. M. Latimer, ref. 18, 1st Edition, p. 216.

Ru(VII) and -(VIII) oxidize water irreversibly in alkaline solution. Furthermore, the disproportionation of Ru(VII) to -(VIII) and -(VI) does not proceed to an appreciable extent; this in accord with spectrophotometric data[3,6] and is in contrast to previous information in the literature.[21]

(21) R. Charonnat, ref. 5, p. 399.

Reaction between Iron(II) Complexes of Polyethylenepolyamines and p-t-Butylcumene Hydroperoxide[1]

BY R. J. ORR AND H. LEVERNE WILLIAMS

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The reaction between p-t-butylcumene hydroperoxide and iron(II)–polyethylenepolyamine complexes was investigated. The primary reaction was first order with respect to hydroperoxide for compounds containing secondary amine groups. When primary amines only were used the reaction became more complex. Bimolecular rate constants were measured under various conditions of pH and temperature. Apparent values of the Arrhenius constants were calculated from these. When solvated coördination spaces for the hydroperoxide were available on the iron(II) the results could be explained by considering the reaction to follow association of the hydroperoxide and the iron(II) complex. When the coördination shell of the iron(II) tended to be filled with complexing groups other than solvent the mechanism of the electron-transfer was uncertain. Deductions were made on factors affecting the reactivity of the iron(II) complexes and were supported by polarographic evidence of the existence of different complexes. Cathodic and anodic waves have been measured on alkaline solutions of iron(II)–diethylenetriamine and iron(II)–triethylenetetramine complexes. The change in the half-wave potentials with pH suggests that the series of hydroxy substitutions involved in the diethylenetriamine complex differs from those in the triethylenetetramine complexes.

Introduction

The quality of butadiene–styrene elastomers increases as the temperature of the polymerization decreases. The basis for these low temperature processes are oxidation–reduction systems which yield free radicals suitable for initiation of the polymerizations. To understand more fully the factors governing these reactions, a study, the earlier results of which have been reported in a series of publications,[2–7] has been continued. Studies were made when iron(II) was complexed with polyethylenepolyamine and the complex reacted with cumene hydroperoxide. The general reaction characteristics were determined, and the effect of the structure of the polyethylenepolyamine was discussed.[7] It was desirable to find the effect of variation in the structure of the substituent on the hydroperoxide on the rate when iron(II) complex with polyethylenepolyamines was the reducer. The hydroperoxide chosen was p-t-butyl cumene hydroperoxide and the kinetics of the reaction with the iron(II) complexes of five polyethylenepolyamines of the general formula $H_2N-C_2H_4(NH-C_2H_4)_xNH_2$ for values of x from 0 to 4 was studied.

The structure in alkaline solution of the iron(II) complexes of the polyethylenepolyamines of the general formula $H_2N(C_2H_4)_xC_2H_4NH_2$ was of interest together with some measure of determining the

(1) Presented before the Division of Physical and Inorganic Chemistry, 124th Meeting, American Chemical Society, Chicago, Ill., September 6–11, 1953.

(2) J. W. L. Fordham and H. L. Williams, *Can. J. Res.*, **B27**, 943 (1949).

(3) (a) J. W. L. Fordham and H. L. Williams, THIS JOURNAL, **72**, 4465 (1950); (b) **73**, 1634 (1951).

(4) J. W. L. Fordham and H. L. Williams, *ibid.*, **73**, 4855 (1951).

(5) R. J. Orr and H. L. Williams, *Can. J. Chem.*, **30**, 985 (1952).

(6) R. J. Orr and H. L. Williams, *J. Phys. Chem.*, **57**, 925 (1953).

(7) R. J. Orr and H. L. Williams, *Disc. Faraday Soc.*, **14**, 170 (1953).

purity of the mixtures of these polyethylenepolyamines. The polarographic behavior of iron(II) and its complexes has been made the subject of a number of investigations.[8–11] The results suggested that similar studies of the iron(II)–polyethylenepolyamine complexes might be of value.

Experimental

The experimental methods used in the study of the reaction of cumene hydroperoxide with iron(II) complexes of polyethylenepolyamines[7] were found to be almost universally applicable with the exception of certain purification details of the reagents. The cumene hydroperoxide was received as a 68% solution. The sodium salt was precipitated and dried. The stock solution of hydroperoxide was made by dissolving this salt in a methanol–water solution. The p-t-butylcumene hydroperoxide was received as a slurry of hydroperoxide analyzing about 50% hydroperoxide. Cooling to 0° and separating the solid from the liquid yielded a solid product about 80% hydroperoxide. The purity could be raised above 98% by one fractional reprecipitation from benzene. Analyses were made by an iodimetric procedure.[12]

All polyethylenepolyamines were purified by precipitation as the hydrochlorides. All of the polyamines except the pentaethylenehexamine were found to be free of amine contaminants. The pentaethylenehexamine was contaminated with other complex-forming amines, probably lower polyethylenepolyamines.

Technical grade methyl methacrylate was distilled, discarding initial and final fractions. Once distilled water was redistilled from an alkaline permanganate solution. Iron(II) sulfate, sodium hydroxide, potassium dihydrogen phosphate, α,α'-bipyridine, sodium acetate, acetic acid and methanol were reagent grade. Oxygen was removed from nitrogen gas by passage through three scrubbers containing alkaline pyrogallol solution, over copper filings at 300–400°,

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd ed., 1952, p. 475.

(9) J. Prajzler, *Collection Czechoslov. Chem. Communs.*, **3**, 406 (1931).

(10) B. Schrager, *ibid.*, **1**, 275 (1929).

(11) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

(12) Hercules Powder Company, private communication.