to be 0.91. This can be compared with the ratio k'_D/k_H, where k'_D is the rate constant for cyclobutane-d_8, as determined by Langrish and Pritchard.[10] Using their plot of k'_D/k_H (present notation) *vs.* 1/pressure at 449°, at 7 mm. pressure, the value for k'_D/k_H is 0.79. The change in the first-order rate constant caused by the replacement of hydrogen by deuterium appears to be almost linear.

In comparing the present values for A_D/A_H and $E_D - E_H$ with the corresponding quantities for cyclobutane-d_8 and cyclobutane as determined by Langrish and Pritchard,[10] it must be borne in mind that the temperature effect in the latter work was studied at an initial pressure of 1.25 mm., while in the present work a pressure of 7 mm. was used. At these pressures, the first-order rate constants for cyclobutane are known to fall off sharply.[4] Assuming that a comparison can be made, the ratio of the three pre-exponential factors are $A_H:A_D:A'_D::1:1.3:2.3$. The differences in the activation energies are $E'_D - E_H \sim 1400$ cal.; $E_D - E_H \sim 500$ cal. As Langrish and Pritchard have observed,[10] the trends in the A factor and the activation energy on substituting deuterium for hydrogen atoms in cyclobutane are qualitatively similar to the effects reported by Lindquist and Rollefson[14] and by Weston[15] on tritiated cyclopropane.

Acknowledgment.—The authors wish to thank Professor W. D. Walters for his helpful suggestions and encouragement during the course of this work.

[14] R. H. Lindquist and G. K. Rollefson, *J. Chem. Phys.*, **24**, 725 (1956).

[15] R. E. Weston, *ibid.*, **23**, 988 (1955); **26**, 975 (1957).

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE]

Ruthenium(III) Gluconate Complexes[1]

BY DONALD T. SAWYER, RAYMOND S. GEORGE AND JOHN B. BAGGER

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An investigation of polarographic methods for the determination of ruthenium has led to a systematic study of the complexes of ruthenium(III) with the gluconate ion. A reversible polarographic wave, which is independent of *p*H and gluconate ion concentration, is obtained above *p*H 13 for the reduction of ruthenium(III). In 0.2 *F* sodium gluconate at *p*H 14 the reduction wave has a half-wave potential of −0.67 v. *vs.* S.C.E. and a diffusion current constant of 1.17. When an excess of ruthenium(III) is added to a basic gluconate solution, soluble polymers are formed initially which have a molar ratio of metal to gluconate of approximately 6. The polymers hydrolyze slowly to give ruthenium oxide and a stable complex with a molar ratio of one ruthenium(III) per gluconate ion. Spectrophotometric studies of this stable complex indicate that there are two forms, one from *p*H 3.5 to *p*H 7.5 and a second above *p*H 8. The second form of the complex follows Beer's law when a ten-fold excess of gluconate ion is present and the *p*H is 14. The molar absorptivity is 4170 at 337 mμ. In basic gluconate solutions ruthenium(II) and ruthenium(III) exhibit a complex set of equilibria which have been studied polarographically. Reaction mechanisms are proposed for the equilibria on the basis of the polarographic studies.

The solution chemistry of ruthenium has not been studied extensively. Almost all of the older literature is concerned with the chloride and amine complexes, and with the properties of solid compounds.[2-4] Although there has been renewed interest recently in the aqueous solution chemistry of ruthenium,[5-9] chelate studies have been restricted to the terpyridyl[10] and bipyridine[11] complexes. Additional knowledge of the effect of chelation on ruthenium ions is desirable and has led to the consideration of several chelating agents, *e.g.*, citric acid, ethylenediamine, ethylenediaminetetraacetic acid, salicylic acid and gluconic acid. Because gluconic acid is known to form strong complexes with iron(III),[12] similar complex formation might be expected for ruthenium ions.

The present study is concerned with the results of a systematic study of the complexes formed between ruthenium(III) and gluconic acid. Polarographic and spectrophotometric techniques have been used to ascertain the nature and stability of the glucono-ruthenium(III) system. Because of the complex nature of the system and the slow rate of equilibration for many of the solutions, many of the data are approximate. However, by considering many pieces of data obtained by independent methods, a general understanding of the system can be obtained.

Previous polarographic studies of ruthenium with a dropping mercury electrode have been restricted to ruthenium(IV) in perchloric acid media[7] and to ruthenocene in alcoholic perchloric acid–perchlorate media.[13] Two additional polarographic studies of ruthenium, using solid microelectrodes, have been made; the cyanide complex of ruthenium(II)[6] and ruthenium(VI, VII, VIII) in basic solutions.[9]

Experimental

Equipment.—Polarographic data were obtained with a recording polarograph which has been described previously.[14] A modified cell was used to prevent attack by strongly basic solutions on the agar in the salt bridge.[15] All measurements

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[1] Presented before the Analytical Division of the American Chemical Society in Boston, Massachusetts, April, 1959.

[2] W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952, p. 228.

[3] "Gmelins Handbuch der anorganischen Chemie," Vol. 63, Verlag Chemie, G.m.b.H., Berlin, 1938.

[4] R. Charonnat, *Ann. chim.*, [10] **16**, 1 (1931).

[5] P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950).

[6] D. D. DeFord and A. W. Davidson, *ibid.*, **73**, 1469 (1951).

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

[8] R. E. Connick and C. R. Hurley, *ibid.*, **74**, 5012 (1952).

[9] M. D. Silverman and H. A. Levy, *ibid.*, **76**, 3319 (1954).

[10] F. P. Dwyer and E. C. Gyarfas, *ibid.*, **76**, 6320 (1954).

[11] R. R. Miller, W. W. Brandt and S. M. Puke, *ibid.*, **77**, 3178 (1955).

[12] R. L. Pecsok and J. Sandera, *ibid.*, **77**, 1489 (1955).

[13] J. A. Page and G. Wilkinson, *ibid.*, **74**, 6149 (1952).

[14] D. T. Sawyer, R. L. Pecsok and K. K. Jensen, *Anal. Chem.*, **30**, 481 (1958).

[15] R. L. Pecsok and R. S. Juvet, *ibid.*, **27**, 165 (1955).

were made at 25.0 ± 0.1°. Solutions were deaerated with purified nitrogen. Diffusion currents were measured using the tops of the oscillations (maximum current) and were corrected for residual current. All potentials were measured and reported *versus* the saturated calomel electrode. Half-wave potentials were measured to an accuracy of ±5 millivolts. The rate of flow of mercury was 2.04 mg./sec., and the drop time was 3.32 sec. at −0.68 volt applied potential.

Spectrophotometric data were obtained either with a Cary Model 14 recording spectrophotometer or a Beckman Model DU spectrophotometer. A Beckman Model G *p*H meter (with Type E-2 electrode for high *p*H) was used for *p*H measurements.

Electrolysis of ruthenium solutions was accomplished with a constant current coulometer constructed from the design of Reilley, Cooke and Furman.[16] This unit, with its continuously variable current, also served as the current source for manual controlled potential electrolysis; a gas coulometer was used to measure currents.[17]

Reagents.—Ruthenium solutions were prepared from ruthenium dioxide (Baker and Company, assay 59.6% RuO_2) or from ruthenium chloride (Fisher Scientific Company, purified). Commercial ruthenium chloride was found to contain approximately 85% of the ruthenium as ruthenium(IV) and 15% as ruthenium(III). Ruthenium dioxide was brought into solution by boiling with hydrochloric acid. Chloride ions were removed from ruthenium solutions by fuming with sulfuric acid.

Ruthenium(IV) solutions were prepared by adding sodium bismuthate to a chloride-free solution of ruthenium in sulfuric acid and distilling the resultant ruthenium tetraoxide into a chilled solution of hydrogen peroxide containing 1 *F* sulfuric acid.[6,7] After approximately 6 hr. the excess hydrogen peroxide was destroyed by boiling and the solution was filtered to remove any ruthenium dioxide. Solutions were analyzed for ruthenium(IV) by the iodometric method of Crowell and Yost.[18] Total ruthenium concentrations were determined spectrophotometrically by oxidizing the sample to ruthenium tetraoxide with potassium periodate.[7] Concentrations were determined at 385 mμ using 930 as the molar absorptivity.[8]

Solutions of ruthenium(III), which are brownish-green in color, were prepared by electrolytic reduction of ruthenium(IV) solutions (approximately 0.03 *F* in ruthenium and 1 *F* in sulfuric acid at a mercury-pool cathode). The anode consisted of a platinum wire which was shielded in a glass tube with a fritted disk. Electrolysis currents of 25–100 milliamperes were used and were continued until approximately five faradays per mole of ruthenium(IV) had been passed through the solution. Completeness of electrolysis was checked iodometrically and by polarography.

Sodium gluconate solutions were prepared determinately from D-glucono-δ-lactone (Matheson, Coleman and Bell) which had been recrystallized twice from ethylene glycol monomethyl ether. The purity of the lactone was determined by back-titrating, with standard acid, a sample to which excess standard base had been added. The lactone was found to be 99.7% pure. All other materials were reagent grade.

Results and Discussion

Polarographic Characteristics.—Ruthenium(III) gives an essentially reversible wave in the presence of sodium gluconate if the solution has a *p*H of 13 or greater. Below *p*H 12 the wave becomes an irreversible double wave. Reversibility was determined by subtracting the one-quarter wave potential from the three-quarter wave potential.[19] Waves were considered reversible if the difference was less than 85 millivolts, although 56 millivolts is the theoretical value. The effect of time on the ruthenium(III) stock solution is shown in Fig. 1. The freshly electrolyzed stock solution, upon adding gluconic acid and adjusting to *p*H 14, gives a reversible cathodic wave (a, Fig. 1). After the acidic stock solution has been prepared for 24 hr. or longer, immediate analysis of a freshly prepared basic ruthenium(III)–gluconate solution from the stock gives an anodic–cathodic wave (b, Fig. 1). If this basic solution is allowed to stand for a period of time, waves d-f result, with the last wave almost identical with wave a.

Consideration of the polarographic behavior of basic ruthenium(III)–gluconate solutions leads to several conclusions. Apparently the acidic stock solution of ruthenium(III) is unstable and gives the reaction

$$\mathrm{Ru(III)}\ \underset{\longleftarrow}{\overset{\longrightarrow}{1\ F\ \mathrm{H_2SO_4}}}\ \mathrm{Ru(II)_A} \qquad (1)$$

The course of this reaction is shown in Fig. 2, which illustrates the relative heights of the anodic and cathodic waves as a function of time after electrolytic preparation of a ruthenium(III) stock solution. The polarographic solutions are prepared from the acidic stock solution and run immediately. We have assumed that the equilibrium of reaction 1 is not significantly altered during the short period required to add gluconate ion, make a sample basic and run the polarogram. The acid stock solution comes to equilibrium in about 15 hr. at room temperature and contains approximately 56% ruthenium(III), assuming that the diffusion current constants are equal for the anodic and the cathodic waves. The existence of a ruthenium(II)$_A$ species is further confirmed by shaking a ruthenium(III) solution containing chloride ion with mercury metal. By adding gluconate ion and base an anodic wave is obtained which is identical to the anodic portion of wave b, in Fig. 1. Although the over-all equilibration for the acidic stock solution appears to be represented by equation 1, several intermediate reactions may take place. Ruthenium(III) in a sulfuric acid solution may oxidize water directly to give an equilibrium mixture of ruthenium(II)$_A$ and ruthenium(III). An alternative means for producing ruthenium(II)$_A$ spontaneously would be the disproportionation in a sulfuric acid solution of ruthenium(III) to ruthenium(II)$_A$ and ruthenium(IV). The ruthenium(IV) might then either oxidize water to oxygen in the sulfuric acid solution, or react with the gluconate ion in the basic solution to give ruthenium(III) and oxidation products. Efforts to determine the actual mechanism have not been successful, but the validity of reaction 1 is strongly supported by the polarographic data as well as by other data given below, *e.g.*, controlled potential coulometry.

The effect of the mercury column height was studied to determine if the polarographic currents for the anodic and cathodic waves were diffusion controlled. Table I summarizes the data and indi-

TABLE I

EFFECT OF MERCURY COLUMN HEIGHT

Hg height	Cathodic wave i, μamp.	Anodic wave i, μamp.	Total wave i, μamp.
h	5.05	3.46	8.51
$^1/_2h$	4.13	1.83	5.96
Theoretical,[19] for $^1/_2h$	3.57	2.44	6.01

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(16) C. N. Reilley, W. D. Cooke and N. H. Furman, *Anal. Chem.*, **23**, 1030 (1951).

(17) J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

(18) W. R. Crowell and D. M. Yost, *ibid.*, **50**, 374 (1928).

(19) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952.

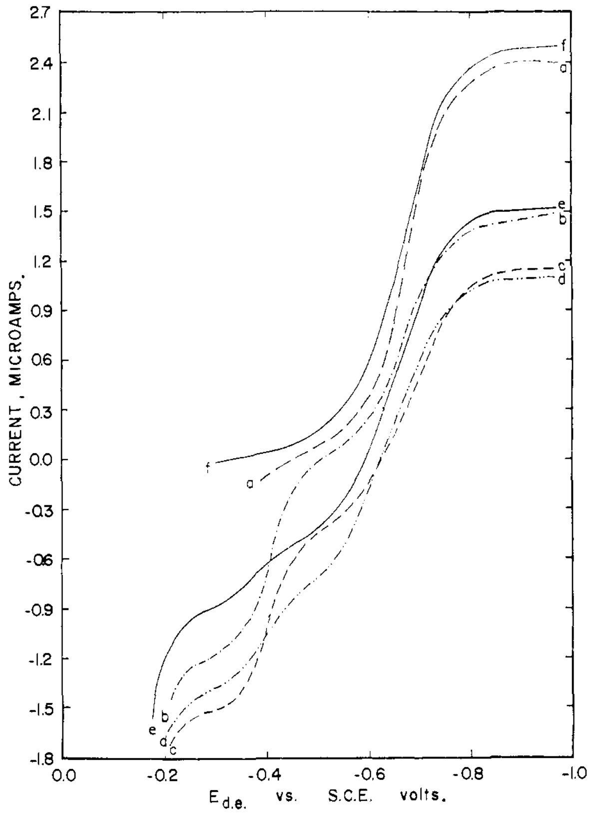

Fig. 1.—Polarograms of ruthenium in the presence of sodium gluconate: Ru(III), 1.0 × 10^{-3} *F*; $NaGH_4$, 0.2 *F*; *p*H 14. Curve (a) fresh Ru(III) stock solution; sample run immediately. (b) Solution b; 24 hour-old Ru(III) stock solution; sample run immediately. (c) Solution b, 45 minutes later. (d) Solution b, 6 hours later. (e) Solution b, 19.5 hours later. (f) Solution b, 37.5 hours later.

cates that although the individual waves do not follow the square-root law,[19] the combined total wave heights do. This behavior probably is due to a slow equilibrium reaction between the several ruthenium species.

Preparation of a ruthenium–gluconate solution, *p*H 14, from an equilibrated acidic stock solution and subsequent polarographic analysis over a period of time gives the data shown in Fig. 3. Considering this plus the polarographic waves in Fig. 1, a sequence of spontaneous reactions can be proposed.

$$\mathrm{Ru(II)_A} \xrightarrow[\mathrm{GH_4^-}]{\mathrm{OH^-}} \mathrm{Ru(II)_B} \tag{2}$$

$$\mathrm{Ru(II)_B} \xrightarrow[\mathrm{GH_4^-}]{\mathrm{OH^-}} \mathrm{Ru(III)} \tag{3}$$

where $\mathrm{Ru(II)_A}$ is the species present in the acidic stock solution. Using the convention of Pecsok and Juvet,[20] gluconate ion is represented as GH_4^- (H's refer to the secondary hydroxyl hydrogens). At *p*H 14 and 0.2 *F* gluconate ion, $\mathrm{Ru(II)_A}$ gives an anodic wave with a half-wave potential of −0.42 v. (b, Fig. 1)

$$\mathrm{Ru(II)_A} \xrightarrow[\mathrm{GH_4^-}]{\mathrm{OH^-}} \mathrm{Ru(III)} + e^- \tag{4}$$

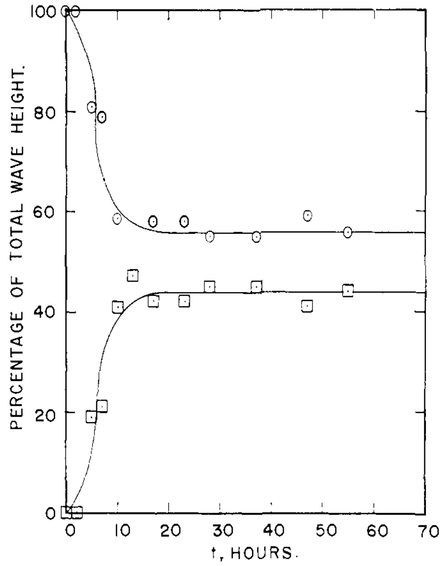

Fig. 2.—Effect of time on the polarographic waves for ruthenium(III) stock solution. All solutions were 1.0 × 10^{-3} *F* in Ru(III), 0.2 *F* in $NaGH_4$ and had a *p*H of 14. The polarograms were recorded immediately after preparation of the solution: ○, cathodic wave; □, anodic wave.

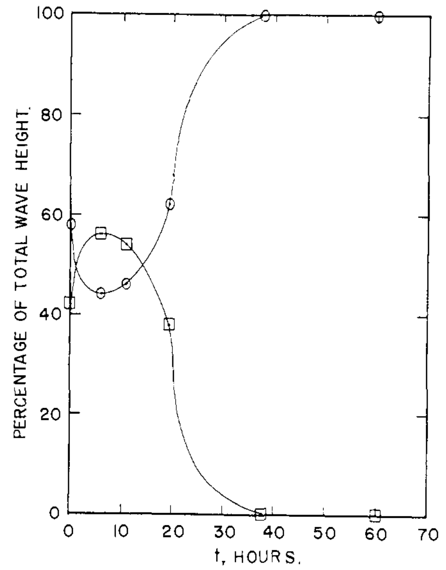

Fig. 3.—Effect of time on the polarographic waves of ruthenium-gluconate prepared from an equilibrated ruthenium(III) stock solution. All solutions were 1.0 × 10^{-3} *F* in Ru(III), 0.2 *F* in $NaGH_4$ and had a *p*H of 14: ○, cathodic wave; □, anodic wave.

The species, $\mathrm{Ru(II)_A}$, may be produced also by making an acidic solution of ruthenium 0.5 *F* in chloride ion and shaking it vigorously with mercury metal.

As the transition represented by reaction 2 takes place a second anodic wave appears which has the same half-wave potential as the cathodic wave for ruthenium (III)–gluconate (d, Fig. 1).

$$\mathrm{Ru(II)_B} \xrightleftharpoons[\mathrm{GH_4^-}]{\mathrm{OH^-}} \mathrm{Ru(III)} + e^- \tag{5}$$

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[20] R. L. Pecsok and R. S. Juvet, Jr., THIS JOURNAL, **77**, 202 (1955).

The reversibility of reaction 5 is illustrated by the waves in Fig. 1. As shown by Fig. 3, the spontaneous transitions represented by reactions 2 and 3 are completed in approximately 35 hr. to give a pure solution of ruthenium (III)–gluconate.

At *p*H 14 and 0.2 *F* gluconate ion, ruthenium(III) gives a cathodic wave with a half-wave potential of −0.67 v., which is essentially reversible (a and f, Fig. 1). The half-wave potential is independent of *p*H from *p*H 10 to *p*H 14.3, and of gluconate concentration from 5×10^{-3} *F* to 0.4 *F* gluconate. The wave height is proportional to the ruthenium(III) concentration over the region from 2×10^{-4} *F* to 1×10^{-2} *F* ruthenium. The diffusion current constant I is 1.17 ± 0.04 in 0.2 *F* gluconate ion at *p*H 14 (maximum rather than average current).

Although electrolytic reduction of an acidic ruthenium solution to ruthenium(III) is an effective method for preparing a sample for polarographic analysis, reduction of a hydrochloric acid solution of ruthenium with mercury metal is equally effective. The latter method reduces the ruthenium to ruthenium(II)$_A$

$$\left.\begin{matrix}\mathrm{Ru(IV)}\\ \mathrm{Ru(III)}\end{matrix}\right\} + 2\mathrm{Hg} + 2\mathrm{Cl}^- \longrightarrow \mathrm{Ru(II)_A} + \mathrm{Hg_2Cl_2} \qquad (6)$$

which can then be air oxidized to ruthenium(III) and analyzed. Alternatively, gluconate can be added to the ruthenium(II) solution which is then made basic and allowed to stand for several days. With time, the solution will be converted to pure ruthenium(III) by means of reactions 2 and 3. Actually, the total wave height (anodic plus cathodic) is roughly proportional to the ruthenium concentration (Fig. 1) and can be used as an approximate method of analysis.

An equilibrated basic ruthenium(III)–gluconate solution, when electrolyzed, gives almost pure Ru(II)$_B$ as expected. Controlled potential electrolysis at −0.9 v. required approximately one electron per ruthenium(III) ion for complete reduction to Ru(II)$_B$. This lends support to the postulated reactions 2 and 3. When pure Ru(II)$_A$ is formed by mercury–hydrochloric acid reduction, the anodic wave height for a given concentration is essentially equal to the cathodic wave height for ruthenium(III). This fact eliminates the possibility that Ru(II)$_A$ might be oxidized to some higher oxidation state other than ruthenium(III).

Attempts to study ruthenium(IV) in the presence of gluconate solutions were not successful. Polarographic studies of basic ruthenium(IV)–gluconate systems gave a drawn-out wave with the upper portion being identical with the ruthenium(III) wave. This behavior led to the postulate that ruthenium(IV) is reduced to ruthenium(III) in basic gluconate solutions. To confirm this supposition, ruthenium(IV) was added to an acidic as well as a basic 0.2 *F* gluconate solution. After 0.5 hr., both solutions were acidified with hydrochloric acid and analyzed iodometrically[18] for ruthenium(IV). For the acidic gluconate system, 50% of the ruthenium(IV) had been reduced; for the basic solution, 80% had been reduced. That a reduction of ruthenium actually occurs is further confirmed by these various color transitions. When ruthenium(IV) is added to an acidic gluconate solution a reddish-brown solution results. If the latter solution is made basic, it turns yellow green. Reacidifying the basic solution does not change its color and clearly indicates that the ruthenium(IV) ions have undergone a reaction. Ruthenium(IV) probably oxidizes the gluconate ion

$$\mathrm{Ru(IV)} + \mathrm{GH_4}^- \longrightarrow \mathrm{Ru(III)} + \text{Oxidation Products} \quad (7)$$

with the oxidation products causing the drawn-out portion of the polarographic wave. Actually, the polarographic waves for ruthenium(IV) in basic gluconate solutions exhibit a diffusion current plateau identical to ruthenium(III). The wave heights are directly porportional to be ruthenium concentration, indicating that ruthenium(IV) also can be analyzed polarographically. The diffusion current constant I is 1.11 in 0.2 *F* gluconate at *p*H 13 (maximum rather than average current), which is essentially the same as the value for ruthenium(III). The similarity in the wave shape, plus the closely similar diffusion current constants, support the conclusion that the ruthenium(IV) wave is actually due to the polarographic reduction of ruthenium(III).

Spectrophotometry of Ruthenium(III).—Absorption spectra for ruthenium(III) in gluconate solutions at various *p*H's are shown in Fig. 4. Because the solutions equilibrated slowly, the spectra were recorded five weeks after the solutions had been prepared. Below *p*H 3 the absorption maximum is at 289 mμ, between *p*H 3.5 and *p*H 7.5 the maximum is at 320 mμ, and above *p*H 8 the maximum is at 337 mμ. Ruthenium(III) also gives a maximum at 289 mμ in the absence of gluconate ion and hence ruthenium(III) apparently is not complexed by gluconate below *p*H 3.5. The spectra indicate that a gluconate complex is formed above *p*H 3.5 and that a second form of the complex, possibly involving the addition of a hydroxide ion, appears above *p*H 8. At *p*H 14 the complex follows Beer's law in the presence of a 10-fold excess of gluconate (2.5×10^{-3} *F*) and has a molar absorptivity of 4170 at 337 mμ.

The spectrum of the ruthenium(III)–gluconate complex at *p*H 13–14 was studied in an attempt to establish its formula. Solutions of varying composition were prepared, and the absorbance measured at 337 mμ after equilibrating for at least one day. Job's method of continuous variations[21] was applied and gave data indicating at least 6 Ru/$\mathrm{GH_4}^-$ for one day old solutions. After standing for several more days, the absorbances for these solutions had changed to give a ratio of 2–4 Ru/$\mathrm{GH_4}^-$. As the solutions equilibrated, precipitation occurred in those solutions with a high ratio of Ru/$\mathrm{GH_4}^-$ and caused additional ruthenium(III) to be coprecipitated.

In a further attempt to establish the ratio of Ru/$\mathrm{GH_4}^-$, a series of solutions were prepared with a constant gluconate concentration and increasing ruthenium(III) concentrations. The results of this study are shown in Fig. 5, with the time of equilibration indicated for each curve. The effect of co-precipitation is clearly shown for those solutions in which precipitates have formed. Although the first curve in Fig. 5 indicates a ratio of at

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[21] P. Job, *Ann. chim.*, [10] **9**, 113 (1928).

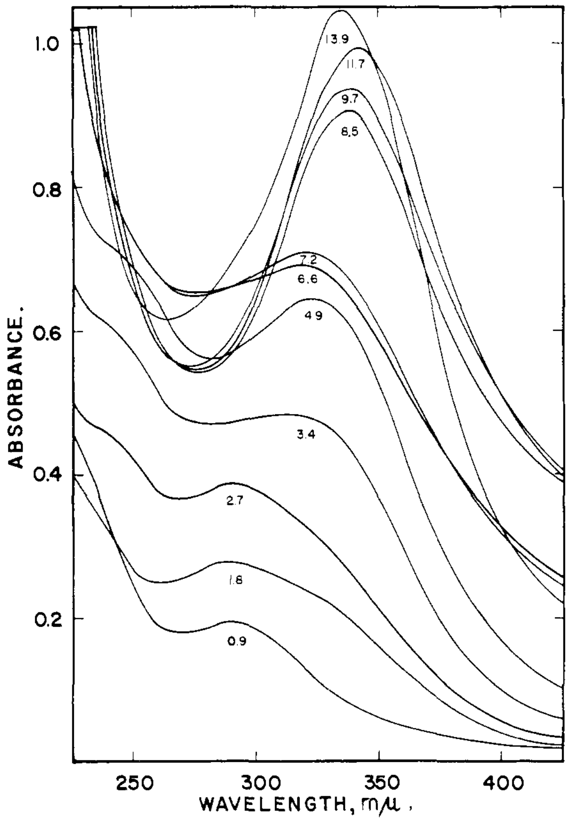

Fig. 4.—Absorption spectra of ruthenium(III)-gluconate solutions at various *p*H's. All solutions were 2.5×10^{-4} *F* in Ru(III) and 2.5×10^{-3} *F* in NaGH_4. The *p*H was adjusted with sulfuric acid or sodium hydroxide. The *p*H of the equilibrated solutions is indicated on the spectra.

least 6 Ru/GH_4^-, after 57 days the indicated ratio is 1 Ru/GH_4^- and precipitates have formed in all solutions with a greater ratio of ruthenium(III). Apparently a polymer involving six or more ruthenium ions per gluconate ion is formed initially, then the polymer slowly hydrolyzes with time to give the 1/1 complex

$$\text{Polymer} \longrightarrow x\,\text{Ru}_2\text{O}_3 + \text{Ru(III)-GH}_4 \qquad (8)$$

Finally, an attempt was made to prepare and isolate a ruthenium(III)-gluconate compound. A material was isolated from a basic solution of ruthenium(III) and sodium gluconate by adding ethanol and cooling. The isolated product, which was crystallized twice from water–ethanol, dissolves slowly in basic gluconate solution. Analysis of the recrystallized material for carbon and ruthenium gave a ratio of 3.4 Ru/GH_4^-. This lends support to the conclusion that a polymer is initially formed.

Conclusion

The data indicate that ruthenium(III) forms a stable complex with gluconate ion in basic solutions. The resulting complex is sufficiently strong to keep ruthenium(III) in solution in 2 *F* sodium hydroxide; the uncomplexed ion is soluble only in solutions below *p*H 4. The gluconate complex gives a reversible polarographic wave above *p*H 13 which is independent of *p*H or gluconate ion concentration. The reduction wave provides a convenient polarographic method of analysis for ruthenium. Previously the only satisfactory polarographic methods have been for perchloric acid solutions[7] or for ruthenium(VII) and (VIII) at a stationary platinum electrode.[9] Pure ruthenium(III) solutions are unstable in sulfuric acid and slowly decompose to give a mixture of ruthenium(II)$_\text{A}$ and ruthenium(III). Ruthenium(II)$_\text{A}$ is unstable in alkaline gluconate solutions and slowly hydrolyzes to ruthenium(II)$_\text{B}$ which is oxidized spontaneously to ruthenium(III).

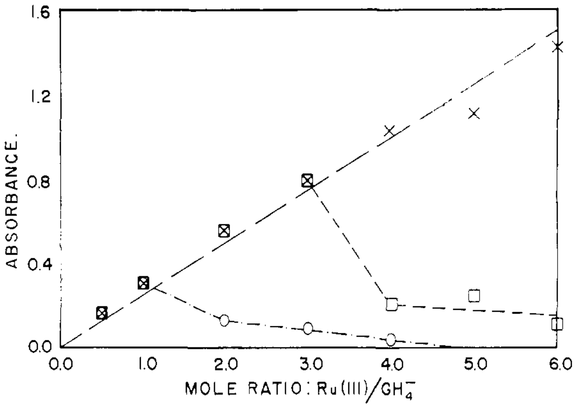

Fig. 5.—Effect of ruthenium(III) concentration and time on the absorbance of ruthenium(III) at 330 mμ. All the solutions were 1.0×10^{-3} *F* in NaGH_4 and had a *p*H of 13. The mole ratio of Ru(III) to GH_4 in the prepared solutions is given on the graph. The solutions were allowed to equilibrate for the indicated periods of time and then centrifuged. A portion of the centrifuged solution was diluted ten-fold and immediately analyzed on the spectrophotometer: X, 7 days after preparation of the solution; □, 19 days after preparation; O, 57 days after preparation.

Spectrophotometric studies confirm that the stable form of the glucono-ruthenium(III) chelate contains one gluconate per ruthenium. Although the exact formula and structure have not been determined for the complex, the similarity of ruthenium(III) and iron(III) leads the authors to suggest that the structure may be the same as the one proposed by Pecsok and Sandera for the ferric-gluconate system in strongly basic solutions.[12]

In addition to sodium gluconate, citric acid and ethylenediaminetetraacetic acid also have been tried as complexing agents. The resulting complexes are weak and decompose upon addition of base to give ruthenium oxide. Additional chelating agents are currently being investigated for complexing of ruthenium and will be reported in the future.

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