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AN INVESTIGATION OF THE SOLUTION
CHEMISTRY OF RUTHENIUM IN ITS LOWER VALENCE STATES

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Final report describing the results of work
carried out under Contract No. AT (11-1)-
89-Project No. 1 between the Atomic Energy
Commission and Northwestern University.

By

Donald D. DeFord, William G. Hime,
Claude A. Lucchesi, and Hans Horn.

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I. INTRODUCTION

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This report describes the results of work carried out at Northwestern University during the period 1 September 1950 to 31 August 1952 under Contract No. AT (11-1)-89-Project No. 1 with the Atomic Energy Commission.

The primary purpose of the work reported was the elucidation of the nature of the ionic species present in solutions of ruthenium in its lower valence states. Most of the effort was concentrated on solutions of ruthenium(IV) in chloride media. Unfortunately many of the data were accumulated before it was realized that equilibrium is reached only very slowly in these solutions. Consequently many of the data are without quantitative significance, although they are subject to qualitative interpretation. For this reason, only a small portion of the data has been included in this report. Those which have been reported have been carefully selected and are believed to be reliable.

II. PREPARATION OF RUTHENIUM CHLORIDES

Since pure compounds of ruthenium in its lower valence states were required for this investigation, various methods for synthesizing such compounds were investigated. Most of the effort was concentrated on the preparation of the chlorides.

Dry Chlorination of Ruthenium Metal. Hill and Beamish (1) have reported that ruthenium metal may be converted to the trichloride, RuCl_3 , by dry chlorination at 700°C . for a period of 48 hours. Variations of the procedure of these authors were attempted in an effort to prepare the trichloride in a single crystalline form in a reasonable period of time. None of these variations were successful. This method offers little promise as a convenient preparative method.

Wet Chlorination of Ruthenium Metal. Under suitable conditions ruthenium metal is attacked by aqueous chlorine solutions to yield ruthenium

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tetroxide. Preliminary experiments indicated that the formation of the tetroxide occurred most rapidly in the pH range 8.0-9.5. Since the introduction of chlorine into an aqueous solution causes a rapid decrease in the pH of the solution, various buffers to maintain the pH in or near the desired range were tried. The experimental procedure involved passing a stream of chlorine into a suspension of ruthenium metal in the buffer solution in a distilling flask; the evolved tetroxide was then trapped in a series of receivers containing hydrochloric acid. Buffer solutions tried included sodium phosphate, borax, and solid calcium carbonate. Various temperatures between room temperature and the boiling point of the buffer solution were tried; the rate of introduction of chlorine was varied between wide limits; in some experiments inert sweep gases such as air or nitrogen were employed. In no case was more than a small quantity of the metal which was introduced converted to the tetroxide before the pH fell to values too low for the oxidation reaction to proceed.

Thiers, Graydon and Beamish (2) have reported that 10 mg. quantities of ruthenium can be quantitatively distilled by passing chlorine through a suspension of the metal in sodium hydroxide solution. Apparently their method is limited to small quantities of ruthenium, or the metal which they used was more finely divided and more reactive than that employed in this investigation.

Preparation of $K_2Ru(OH)Cl_5$. The method finally selected for the preparation of ruthenium salts involves fusion of the ruthenium metal with a mixture of sodium hydroxide and sodium peroxide to convert the ruthenium to the ruthenate. This fusion mixture was then dissolved and this solution was used for the preparation of the desired ruthenium salts. The procedure finally employed for the preparation of the salt known as potassium hydroxypentachlororuthenate(IV), $K_2Ru(OH)Cl_5$, is described below.

Five grams of powdered ruthenium metal were mixed with 15 g. of sodium

hydroxide and 15 g. of sodium peroxide in a silver or a nickel crucible. The crucible was then heated, slowly at first and finally to a dull red heat for 20-30 minutes. The fused melt was stirred occasionally with a small nickel spatula. This treatment converts the ruthenium essentially quantitatively to the ruthenate. The crucible was then cooled and the contents were dissolved in warm water to give a solution of the ruthenate.

(Some hydrous dioxide also separates during the dissolution process.)

The aqueous solution was then treated with a few milliliters of alcohol (to reduce the ruthenium to the dioxide) and was digested on the steam bath for about 1/2 hour. The precipitate of the hydrous dioxide was then removed by centrifugation. (The precipitate clogs all filters so badly that filtration is impossible.) The precipitate was then washed three times with hot dilute potassium hydroxide solution and was then dissolved in 250 ml. of 6-8 M hydrochloric acid. The acid solution was then digested on the steam bath for 1/2 hour to effect complete solution of the hydrous dioxide. During the digestion process, chlorine gas was bubbled through the solution constantly to insure that all the ruthenium remained in the tetrapositive state. The solution was filtered hot through sintered glass to remove any insoluble residue. The solution was then heated almost to boiling and 8 grams of potassium chloride, dissolved in a minimum quantity of water, was added dropwise and with constant stirring. The solution and precipitate were then digested on the steam bath for a least one hour with chlorine bubbling through the solution, and the product was then removed from the hot solution by filtration through a sintered glass crucible. The product was washed repeatedly with hot 8 M hydrochloric acid and was then dried at 110°. Yields of 80-90%, based on the initial weight of ruthenium taken, are realized. The corresponding ammonium salt has been prepared in an analogous manner.

In some cases dioxide was subjected to distillation (3) in order to separate the ruthenium from possible contaminants. The evolved tetroxide

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was absorbed in 6-8 M hydrochloric acid. The hydrochloric acid solution was then treated as described above. Preparations involving the more lengthy distillation procedure did not appear to be significantly superior to those obtained by the simpler method.

III. ANALYSIS OF $K_2Ru(OH)Cl_5$

Preliminary studies on the properties of the $K_2Ru(OH)Cl_5$ preparations described above indicated that different preparations had somewhat different properties even though the method of synthesis remained the same. For this reason a method of analysis was developed to determine the composition of these preparations. This salt, as well as possible contaminants such as $K_2Ru(OH)_2Cl_4$ and K_2RuCl_6 , are easily reduced in hydrogen to yield ruthenium metal, potassium chloride, hydrogen chloride, and water. A method of analysis based upon this reaction was devised.

Apparatus. The apparatus employed for the reduction is shown in Fig. 1. By proper adjustment of stopcock S either nitrogen or hydrogen could be passed into the apparatus. These gases were obtained from commercial cylinders through pressure reduction valves. The entering gases were purified by passage through drying tubes containing Ascarite and Anhydrene. The sample was contained in a Selas MFC-1.2 micro filter crucible which was supported in the central portion of the furnace by a short length of glass tubing, T, resting on the rubber stopper at the bottom of the furnace tube. A small homemade furnace, 5 1/4-inches long and operated at 500° C., was employed. The exit gases passed through a Schwartz tube containing Anhydrene (to absorb water), thence to a second Schwartz tube containing Ascarite and Anhydrene (to absorb hydrogen chloride), and then through a sulfuric acid trap and bubble counter.

Procedure. Dry the crucible at 500° C. for 1/2 hour and weigh. Weigh 0.5-1.0 g. of sample into the crucible, place the crucible in the furnace,

Fig. 1 Hydrogen Reduction Apparatus

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and assemble the apparatus. Pass a stream of hydrogen through the apparatus for 10 minutes to remove all oxygen from the system. Turn the furnace on and operate for 1/2 hour after the temperature reaches 500° C. During the reduction process continue to pass hydrogen through the system at a rate of approximately one bubble (sulfuric acid trap) per second. Turn the furnace off and pass nitrogen through the system until the crucible cools almost to room temperature. (In the apparatus employed it was possible to raise the furnace to permit faster cooling of the crucible.) Allow the Schwartz tubes to stand for 1/2 hour to reach equilibrium and then weigh against similar tubes used as tares. Remove and weigh the crucible and its contents. Leach the contents of the crucible thoroughly with hot water to remove the potassium chloride, dry, and again reduce the residue of ruthenium as described above. After the second reduction is completed, weigh the crucible and its ruthenium metal contents.

Since the ruthenium metal formed in the reduction process is very finely divided, it will adsorb hydrogen if allowed to cool in a hydrogen atmosphere. When the crucible is exposed to the air under these conditions, the ruthenium catalyzes the oxidation of both adsorbed hydrogen and any hydrogen gas remaining in the crucible. This reaction is sometimes extremely vigorous, and frequently the ruthenium reaches a red heat and is itself partially oxidized. For this reason it is necessary to displace the hydrogen before exposure to the atmosphere.

The finely divided ruthenium metal is partially oxidized when leached with water and then dried at 110° C. For this reason a second reduction of the ruthenium residue after the leaching is completed is required for precision analyses. Alternatively, the chloride in the leaching water may be titrated with silver to obtain a direct measure of the potassium chloride present. The ruthenium may then be determined by difference.

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When a determination of oxygen in the sample is not required, the Schwartz tubes and trap may be replaced by a gas-washing flask containing water to absorb the hydrogen chloride. The resulting solution may then be analyzed by titration with sodium hydroxide or with silver nitrate. This procedure yields more precise determinations of the hydrogen chloride than the method employing absorption in Ascarite. However, a direct determination of oxygen is usually desirable since a determination of this element by difference includes all of the errors in the determination of the other elements.

The increase in weight of the Schwartz tube containing Anhydron permits a calculation of the percentage of oxygen in the sample but does not indicate whether this oxygen exists as oxide, hydroxide, or water. It appears that most of the oxygen exists as hydroxide and the results presented below are calculated on that basis.

Experimental Results. Analytical results on several preparations of $K_2Ru(OH)Cl_5$, obtained by the method outlined above, are presented in Table I. In general the results of replicate determinations on the same sample agree very well; the maximum deviation between replicate determinations is 0.3% absolute and the average deviation of individual results from the mean is less than 0.1% absolute. Unfortunately, however, the sum of all constituents is not as close to 100% as would be desirable. With the exception of the first series of analyses, which were made before the final technique had been developed, the sum is always above 100% and averages 101.0%. It is believed that this error is probably due to high results in the determination of oxygen (or hydroxyl). Although blanks were run frequently and were found to be negligably small, traces of oxygen in the hydrogen gas would undoubtedly be converted to water in the presence of metallic ruthenium which acts as a catalyst.

Although replicate analyses on a single preparation agree very well, it is quite apparent that the composition of different preparations differ

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Table I. Composition of $K_2Ru(OH)Cl_5$ Preparations.

No.	%Ru	%KCl ^a	%Cl ^a	%OH	Total %
1 ^a	27.7	42.7	26.3	2.3	99.0
	27.8	42.6	26.0	2.5	98.9
	27.5	42.6	25.9	2.6	98.6
2 ^b	27.2	42.2	28.9	3.2	101.5
	27.3	42.1	28.8	3.3	101.5
	27.0	42.2	29.1	3.2	101.5
3 ^c	27.3	41.8	26.5	5.2	100.8
	27.1	41.8	26.3	5.3	100.5
	27.1	41.6	26.6	5.4	100.7
4 ^d	27.3	40.2	29.0	4.4	100.9
	27.2	40.4	29.1	4.3	101.0
5 ^e	27.75	40.77	28.87 ^h	j	j
		40.80 ^g	28.86 ⁱ		
	27.78	40.54	28.78 ^h	j	j
		40.86 ^g	28.76 ⁱ		
Theory					
$K_2Ru(OH)Cl_5$	27.06	39.91	28.47	4.56	100.00
$K_4(Cl_5RuORuCl_5)$	27.73	40.89	29.18	2.19 (0)	100.00

- a. Salt prepared in 6 M hydrochloric acid and recrystallized from 6 M hydrochloric acid.
- b. Salt prepared in 8 M hydrochloric acid and recrystallized from 8 M hydrochloric acid.
- c. Salt prepared in 6 M hydrochloric acid, dissolved in water, treated with an equal volume of 12 M hydrochloric acid, and recrystallized from this solution (6 M hydrochloric acid).
- d. Salt prepared in 6 M hydrochloric acid to which less than the stoichiometric amount of potassium chloride was added. Not recrystallized.
- e. Salt prepared in 6 M hydrochloric acid to which a 40% excess over the stoichiometric amount of potassium chloride was added. After the initial heating the crystallization was performed at 0° C. Not recrystallized.
- f. The percentage of KCl is based either upon the weight of the potassium chloride residue remaining in the crucible after reduction or upon titration of the chloride in this residue with silver nitrate. The % Cl is the volatile chlorine, which is evolved as HCl during the reduction. Except as otherwise indicated the % KCl was determined from the weight of the KCl residue and % Cl from the gain in weight of a Schwartz tube containing Ascarite.

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- g. Based upon titration of the leached potassium chloride with silver nitrate using dichlorofluorescein indicator.
- h. Based upon titration of the evolved hydrogen chloride with sodium hydroxide.
- i. Based upon titration of the chloride in the solution after alkalimetric titration (see Note h) with silver nitrate using dichlorofluorescein indicator.
- j. Not determined.

very appreciably from each other and from the theoretical composition of both $K_2Ru(OH)Cl_5$ and $K_4(Cl_5RuORuCl_5)$. When the analyses shown in Table I are converted to molar ratios, the data shown in Table II are obtained.

Table II. Molar Composition of $K_2Ru(OH)Cl_5$ Preparations

<u>No.</u>	<u>Ru</u>	<u>KCl</u>	<u>Cl</u>	<u>O</u>
1	1.00	2.09	2.69	0.55
2	1.00	2.10	3.03	0.70
3	1.00	2.08	2.78	1.16
4	1.00	2.01	3.04	0.95
5	1.00	2.00	2.97	-----
Theory $K_2Ru(OH)Cl_5$	1.00	2.00	3.00	1.00
$K_4(Cl_5RuORuCl_5)$	1.00	2.00	3.00	0.50
$K_2Ru(OH)_2Cl_4$	1.00	2.00	2.00	2.00

The values for potassium chloride in the first three preparations are all high; no explanation can be offered for these anomalous values. It should be noted, however, that these three preparations were all recrystallized; the last two preparations, which were not recrystallized, analyzed correctly

for Ru/KCl ratio. Comparison of the Ru/Cl and Ru/O ratios would indicate that preparation No. 4 is mostly $K_2Ru(OH)Cl_5$ and preparation No. 5 mostly $K_4(Cl_5RuORuCl_5)$. Preparation No. 2 appears to be a mixture of these two, and preparation No. 3 appears to contain some more highly hydrolyzed species such as $K_2Ru(OH)_2Cl_4$.

Recent work of Mathieson, Mellor, and Stephenson (4) indicates that the compound usually formulated as $K_2Ru(OH)Cl_5$ actually contains $(Cl_5RuORuCl_5)^{-4}$ ions in the crystal lattice and should be more properly formulated as $K_4(Cl_5RuORuCl_5) \cdot H_2O$. Apparently the water of crystallization can be removed by long heating to yield $K_4(Cl_5RuORuCl_5)$ (see analysis of preparation No. 5 above, which was dried for several days at $110^\circ C.$). Preparations dried for short periods of time are probably largely the hydrate, $K_4(Cl_5RuORuCl_5) \cdot H_2O$.

It is quite apparent that the analytical method must be refined to the point of giving a precision of the order of $\pm 0.01\%$ if unequivocal conclusions are to be drawn regarding the composition of $K_2Ru(OH)Cl_5$ preparations.

Unfortunately X-ray diffraction studies of the various preparations were not made. Studies of this type in conjunction with precise elemental analysis should prove most useful in identifying the products present in the preparations. Infra-red spectra taken in potassium bromide wafers or in Nujol mulls should also be useful in future work.

IV. SPECTRAL STUDIES OF THE CHLORO COMPLEXES OF RUTHENIUM(IV)

Wehner and Hindman (5) have made a comprehensive study of the chloro complexes of ruthenium(IV) which are formed when solutions of ruthenium(IV) perchlorate are treated with chloride. In order to supplement and to confirm the data of Wehner and Hindman, a study has been made of the spectra of solutions of $K_2Ru(OH)Cl_5$ at various hydrogen ion and chloride ion concentrations.

By a combination of kinetic and equilibrium studies, Wehner and Hindman

have identified a series of several complexes which are formed successively when ruthenium perchlorate solutions are treated with chloride. Among the complexes which appear to have been identified with reasonable certainty are the violet complex, $[\text{Ru}(\text{H}_2\text{O})_2(\text{OH})_2\text{Cl}_2]$, the yellow(II) complex (designated Y(II)), $[\text{Ru}(\text{H}_2\text{O}(\text{OH})_2\text{Cl}_3)]^-$, and the yellow(III) complex (designated Y(III)), $[\text{Ru}(\text{OH})_2\text{Cl}_4]^{2-}$. A series of yellow complexes, which form rapidly when chloride is added to ruthenium(IV) solutions, could not be positively identified, but all of these complexes apparently contain less than two chloride ions per ruthenium atom. Wehner and Hindman's data also indicated the existence of two species more highly chlorinated than Y(III), but their data gave no conclusive information on these species. These species were believed to be $[\text{Ru}(\text{OH})\text{Cl}_5]^-$ (designated Y(IV)) and $[\text{RuCl}_6]^{2-}$ (designated Y(V)).

In this study salts such as $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ and $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$, containing five chloride ions per ruthenium atom, were employed as starting materials. The hydrolysis of these compounds have been studied to ascertain whether or not the intermediate species formed by reaction of chloride ion with ruthenium can also be formed by hydrolysis of the more highly chlorinated species.

Kinetic Study of the Hydrolysis of $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ Solutions. A series of spectra of a solution of $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ in 1.0 M hydrochloric acid, taken at various times after dissolution, are shown in Fig. 2. These spectra were recorded in a 1.0 cm. cell on a Cary Model XIV recording spectrophotometer at a scan rate of 1 mμ per second. In all cases the spectra were recorded starting from 500 mμ. The times shown are those at which the recordings were begun and were measured from the instant of adding the hydrochloric acid to the solid sample. Spectrum No. 1 for zero time was obtained by extrapolating a plot of $\log A_s$ versus time to zero time. The sample solution was at room temperature (but not thermostated). The exact concentration of the ruthenium salt was not measured precisely but was of the order of 3×10^{-4} M.

Fig. 2. Spectra of $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ Solutions as a Function of Time:
 1, Zero time (calculated); 2, 3.5 min.; 3, 15 min.; 4, 35 min.;
 5, 60 min.; 6, 115 min.; 7, 180 min.

Because of the volatility of ammonium chloride, it was not possible to analyze $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ preparations in the same manner as described previously for $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$. The ammonium salt was analyzed for ruthenium by the method described, however, and was found to contain $30.88 \pm 0.06\%$ ruthenium. Theoretical percentages for $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ and $(\text{NH}_4)_4\text{Ru}_2\text{OCl}_{10}$ are 30.51 and 31.36%, respectively. It would appear, therefore, that the salt used was largely $(\text{NH}_4)_4(\text{Cl}_5\text{RuORuCl}_5) \cdot \text{H}_2\text{O}$, with perhaps some anhydrous compound present also.

Unfortunately it was extremely difficult to obtain curves analogous to those shown in Fig. 2 when starting with the potassium salt. The potassium salt dissolves quite slowly in cold 1.0 M hydrochloric acid, and it was not possible to effect quantitative dissolution quickly enough to study the early changes in the spectrum. The ammonium salt dissolves almost instantly. Such spectra as were obtained on the potassium salt showed the same type of spectral changes as the ammonium salt.

The spectrum of freshly dissolved $(\text{NH}_4)_2\text{Ru}(\text{OH})\text{Cl}_5$ is characterized by a strong absorption band with a maximum at about $370 m\mu$ and a less intense band with a maximum at $485 m\mu$. The intensity of the $370 m\mu$ band decreases rapidly upon standing, and the wavelength of maximum absorption shifts to $390 m\mu$. The change in the $485 m\mu$ band is less spectacular, but the intensity of this band decreases slightly and the position of maximum absorption shifts steadily to shorter wavelengths.

While it is not possible to interpret these data with certainty, they are not inconsistent with the data of Wehner and Hindman. The spectra obtained after the solution had stood 30-60 minutes are very similar to those calculated by Wehner and Hindman for the Y(III) complex, $[\text{Ru}(\text{OH})_2\text{Cl}_4]^-$, characterized by absorption peaks at $385 m\mu$ and $476 m\mu$. If one assumes that the $[\text{Cl}_5\text{RuORuCl}_5]^{4-}$ ions in the crystal lattice are very rapidly converted to $[\text{Ru}(\text{OH})\text{Cl}_5]^-$ ions upon dissolution and that these ions then undergo further slower hydrolysis

to $[\text{Ru}(\text{OH})_2\text{Cl}_4]^-$ both sets of data are consistent.

The steady movement of the longer wavelength absorption band from an initial maximum at $485\text{ m}\mu$ to $475\text{ m}\mu$ after standing about 1 hour and then to $465\text{ m}\mu$ after standing 3 hours indicates that further hydrolysis of the Y(III) complex to the Y(II) complex, $[\text{Ru}(\text{H}_2\text{O}(\text{OH})_2\text{Cl}_3)]^-$, is taking place. According to Wehner and Hindman, the latter complex is characterized by a maximum at $454\text{ m}\mu$, and mixtures of Y(II) and Y(III) exhibit an absorption peak somewhere between 454 and $476\text{ m}\mu$.

The Yellow(II)-Yellow(III) Equilibrium. Since Wehner and Hindman had made a study of the Y(II)-Y(III) equilibrium, starting from ruthenium(IV) perchlorate and chloride, this equilibrium was rechecked starting from $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$. A series of solutions, each $0.99 \times 10^{-4}\text{ M}$ in $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$ and 1.0 M in hydrogen ion but with chloride ion concentrations varied from 0.1 to 1.0 M , were prepared. All solutions had an ionic strength of 1.0 , and were prepared by mixing appropriate quantities of a stock solution, which was $0.99 \times 10^{-3}\text{ M}$ in $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$ and 1.0 M in hydrochloric acid, with the necessary quantities of 1.0 M perchloric acid and/or 1.0 M hydrochloric acid. After preparation all solutions were heated in a bath of boiling water for 1 hour and then allowed to stand at room temperature for seven days to reach final equilibrium. (The initial heating in boiling water greatly decreased the time required for the solutions to reach equilibrium.)

The spectrum of each solution was then obtained with the Cary Model XIV spectrophotometer using a 1.0 cm. cell. The concentration of the Y(II) and Y(III) complexes were then determined by a two-color analysis at the wavelengths $454\text{ m}\mu$ and $385\text{ m}\mu$; using Wehner and Hindman's values of the extinction coefficients (2750 at $385\text{ m}\mu$ and 6100 at $454\text{ m}\mu$ for the Y(II) complex; 8140 at $385\text{ m}\mu$ and 3270 at $454\text{ m}\mu$ for the Y(III) complex). The results are tabulated in Table III.

Table III. The Yellow(II)-Yellow(III) Equilibrium.

(1) [Cl ⁻] m./l.	(2) A _s (454)	(3) A _s (385)	(4) [Y(II)] m./l. X 10 ⁴	(5) [Y(III)] m./l. X 10 ⁴	(6) Total Ru m./l. X 10 ⁴	(7) [Y(III)] [Y(II)]EC ₁ ⁻² (m./l.) ⁻¹
0.1	0.540	0.285	0.85	0.06	0.91	0.82
0.2	0.555	0.300	0.87	0.08	0.95	0.45
0.5	0.550	0.325	0.84	0.11	0.95	0.26
1.0	0.520	0.350	0.75	0.20	0.95	0.27

The general shape of the absorption curves were very similar to those obtained by Wehner and Hindman. The calculated value (Column 6) for the total concentration of ruthenium, $0.95 \times 10^{-4} \text{ M}$ is in excellent agreement with the actual concentration, $0.99 \times 10^{-4} \text{ M}$. These facts leave no doubt that the absorbing species obtained upon hydrolysis of $\text{K}_2\text{Ru}(\text{OH})\text{Cl}_5$ under these conditions are identical with those formed by reaction of ruthenium(IV) perchlorate with chloride.

It is of interest to note that the equilibrium constant (Column 7) for the Y(II)-Y(III) equilibrium is much less than the value of 2.28 reported by Wehner and Hindman. This difference is undoubtedly due to the fact that the latter study was made at an ionic strength of 6.2, while the present study was at an ionic strength of 1.0. The shift in the apparent equilibrium constant with changing ionic strength is in the expected direction if the Y(II) ion is singly charged and the Y(III) doubly charged. In fact, this shift lends further support to Wehner and Hindman's formulae for these ions.

Although the values for the equilibrium constant shown in Column 7 are not truly constant, the deviation of the two values at low chloride ion concentrations is not surprising. In both of these solutions the concentration of the Y(III) complex is very low, and thus slight experimental errors may

lead to large errors in the calculated constant. Furthermore, although the spectral curves cross in the region 450-480 $m\mu$, there is no isosbestic point. Therefore, the solutions must contain more than two species. The absorption at 454 $m\mu$ (Column 2) increases as the chloride ion concentration is reduced from 1.0 to 0.2 M and then decreases as the chloride ion concentration is further decreased. This behavior shows conclusively that the Y(II) complex is converted to some other specie, presumably one still more highly hydrolyzed, as the chloride ion concentration decreases.

The effect of varying hydrogen ion concentration in the range 0.10 M to 1.0 M was also studied. In the range from 0.2 to 1.0 M , the spectra were essentially independent of hydrogen ion concentration, in agreement with the findings of Wehner and Hindman. The spectra taken in 0.10 M acid showed slightly, but significantly, lower absorption at all wavelengths from 350 to 500 $m\mu$, particularly in the 454 $m\mu$ region. This behavior would indicate that the Y(II) complex is further hydrolyzed at low hydrogen ion concentrations, as well at low chloride ion concentrations as mentioned previously.

Studies at Low Hydrogen Ion and Chloride Ion Concentrations. It has already been pointed out that species other than Y(II) and Y(III) appear when the hydrogen or chloride ion concentrations are decreased to the order of 0.10 M . As the concentration of either or both of these ions is decreased still further, the absorption maxima in the 350-500 $m\mu$ region which are characteristic of the Y(II) and Y(III) species gradually disappear completely. The absorption throughout this region decreases, but increases slightly at longer wavelengths. The spectra show no well-defined maxima, but are characterized by ill-defined, broad maxima or inflection points in the 400-500 $m\mu$ region. A few typical spectra are shown in Fig. 3. All spectra shown were obtained on solutions $0.99 \times 10^{-4} M$ in ruthenium, using 10 cm. cells.

In general the spectra obtained at low hydrogen ion and chloride ion concentrations were poorly reproducible and were not suitable for quantitative

Fig. 3. Spectra of Ruthenium(IV) Solutions at Low Hydrogen Ion or Chloride Ion Concentrations: 1, 0.010 M H^+ , 0.010 M Cl^- ; 2, 0.12 M H^+ , 0.010 M Cl^- ; 3, 0.91 M H^+ , 0.010 M Cl^- ; 4, 0.010 M H^+ , 0.10 M Cl^- ; 5, 0.10 M H^+ , 0.10 M Cl^- .

interpretation of any kind. Some qualitative conclusions can be drawn, however. Spectrum No. 2, for a solution $0.99 \times 10^{-4} \text{ M}$ in ruthenium, 0.010 M in chloride and 0.12 M in hydrogen ion, is almost identical with the absorption curve reported by Wehner and Hindman for ruthenium in perchloric acid solution. Spectrum No. 3, for a solution identical with that employed for spectrum No. 2 except for a hydrogen concentration of 0.91 M , is very similar to spectrum No. 2. It would appear that the major absorbing specie in both of these solutions is the same as that encountered in perchloric acid solutions, and therefore, that the complex contains no chloride. Spectrum No. 5, for a solution $0.99 \times 10^{-4} \text{ M}$ in ruthenium, 0.10 M in hydrogen ion and 0.10 M in chloride, shows an inflection point in the vicinity of $430 \text{ m}\mu$ indicating the possible existence of the Y(1B) and/or the Y(1C) complex postulated by Wehner and Hindman. According to the latter authors the Y(1B) complex, characterized by an absorption maximum at $443 \text{ m}\mu$, may possibly be $[(\text{HO})_2\text{ClRu}-\text{OH}-\text{Ru}(\text{OH})_2\text{Cl}]^+$ and the Y(1C) complex, characterized by an absorption maximum at $420 \text{ m}\mu$, may possibly be $[\text{Ru}(\text{OH})\text{Cl}_2]^+$. However, if either of these complexes is present in the solution employed for spectrum No. 5, it must be present in relatively small amounts. The molar extinction coefficient for spectrum No. 5 is approximately 1000 at $430 \text{ m}\mu$, while the complexes reported by Wehner and Hindman have extinction coefficients of the order of 4000 at this wavelength.

Spectra obtained on solutions which were $0.99 \times 10^{-3} \text{ M}$ in ruthenium using 1.0 cm cells, were slightly but significantly different from those obtained on solutions $0.99 \times 10^{-4} \text{ M}$ in ruthenium, using 10 cm. cells. It would appear, therefore, that at least some of the absorbing species in these solutions are polymeric.

It is significant that there is absolutely no evidence for the existence of the violet complex, characterized by an intense absorption peak at $562 \text{ m}\mu$ and postulated to be $[\text{Ru}(\text{H}_2\text{O})_2(\text{OH})_2\text{Cl}_2]$ by Wehner and Hindman. Apparent-

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ly this complex cannot be formed by hydrolysis of more highly chlorinated species.

Studies on the 700 $m\mu$ Absorption Band. Ruthenium solutions which are 0.1 M or greater in chloride ion concentration and 0.1 M or greater in hydrogen ion concentration show a weak absorption maximum in the vicinity of 700 $m\mu$. A few typical spectra are shown in Fig. 4.

It is immediately apparent that the absorption in the vicinity of 700 $m\mu$ increases as the chloride ion concentration decreases and that the position of the maximum moves from about 688 $m\mu$ at 0.10 M chloride ion concentration to about 710 at 5.0 M chloride ion concentration. This behavior suggests that the observed absorption band is a combination of two different bands, one with an absorption maximum in the vicinity of 680-690 $m\mu$ and the other with a maximum in the vicinity of 710-720 $m\mu$. The former is the more intense band and must be associated with a less highly chlorinated species than the latter. It is probable that these bands are due to the Y(II) and Y(III) complexes, respectively, but evidence for this postulation is not conclusive.

Spectra taken at hydrogen ion concentrations of 0.5 M are not significantly different from those taken at hydrogen ion concentrations of 1.0 M, indicating that the equilibrium involved is independent of hydrogen ion concentration. Spectra taken on solutions which were 0.99×10^{-2} M in ruthenium, using 1.0 cm. cells were not significantly different from those taken on solutions 0.99×10^{-3} M in ruthenium, using 10 cm. cells, indicating that the degree of polymerization of both species is the same and probably that both are monomeric. These observations are consistent with the postulation that the absorbing species are the Y(II) and Y(III) complexes.

The broadening of the absorption band and the increase in the general level of absorption at low concentrations of chloride ion indicate that

Fig. 4. Spectra of Ruthenium(IV) Solutions: 1, 0.99×10^{-3} M Ru, 0.10 M Cl^- , 1.0 M H^+ , 10 cm. cell; 2, 0.99×10^{-3} M Ru, 0.20 M Cl^- , 1.0 M H^+ , 10 cm. cell; 3, 0.99×10^{-3} M Ru, 0.50 M Cl^- , 1.0 M H^+ , 10 cm. cell; 4, 0.99×10^{-3} M Ru, 1.0 M Cl^- , 1.0 M H^+ , 10 cm. cell; 5, 4.95×10^{-2} M Ru, 5.0 M Cl^- , 5.0 M H^+ , 1.0 cm. cell.

an additional specie or species is being formed in significant amounts under these conditions.

Summary and Conclusions. The absorption spectra of freshly prepared solutions of $K_2Ru(OH)Cl_5$ and $(NH_4)_2Ru(OH)Cl_5$ have been obtained. These solutions are believed to contain $[Ru(OH)Cl_5]^-$ ions and are characterized by absorption maxima at $370\text{ m}\mu$ and $485\text{ m}\mu$. These solutions undergo rapid hydrolysis to form the Y(III) complex previously described by Wehner and Hindman. Further hydrolysis to the Y(II) complex preceeds more slowly. Both kinetic and equilibrium experiments on solutions prepared from $(NH_4)_2Ru(OH)Cl_5$ and $K_2Ru(OH)Cl_5$ are consistent with Wehner and Hindman's formulas $[Ru(OH)_2Cl_4]^{2-}$ and $[Ru(H_2O)(OH)_2Cl_3]^-$ for the Y(III) and Y(II) complexes, respectively.

The violet complex previously reported by Wehner and Hindman cannot be formed by hydrolysis of $[Ru(OH)Cl_5]^-$. At very low chloride ion concentrations, the major absorbing specie formed by hydrolysis of $[Ru(OH)Cl_5]^-$ is apparently the same specie as exists in perchloric acid solutions of ruthenium(IV). It is possible that some of the Y(1A), Y(1B) and Y(1C) complexes previously described by Wehner and Hindman may form by hydrolysis of $[Ru(OH)Cl_5]^-$ in 0.10 M HCl , but evidence for the formation of these complexes is not conclusive.

V. POLAROGRAPHIC STUDIES.

A large number of polarograms in a variety of supporting electrolytes were obtained with dropping mercury, stationary platinum, and rotated platinum microelectrodes. Unfortunately, all of this work was carried out before the spectrophotometric studies described in the previous section, and before it was realized that the solutions came to equilibrium only very slowly. Consequently most of the data obtained are almost worthless. The results of only a few series of experiments which are believed to be

reliable and significant are described below.

Several papers describing polarographic studies of ruthenium have been reported in the literature. Niedrach and Tevebaugh (6) have studied the reduction of ruthenium(IV) at the dropping mercury electrode in perchloric acid solutions. Three reduction waves, with half-wave potentials in the vicinity of $+0.6$, $+0.4$ and -0.1 volt versus the normal hydrogen electrode, were observed. The first two waves correspond to reduction of two different hydrolytic species of ruthenium(IV) to ruthenium(III) and the third to reduction of ruthenium(III) to ruthenium(II). The half-wave potentials and the diffusion currents of all three waves are dependent upon the hydrogen ion concentration. Silverman (7) has studied the polarographic behavior of ruthenate and perruthenate solutions. Turk (8) has reported the results of polarographic studies of ruthenium(IV) solutions at a graphite electrode, and Alkire (9) studied the polarography of ruthenium(IV) at the dropping mercury electrode in nitric acid and in acetate media. Willis (10) was unable to observe any reduction waves at the dropping mercury electrode when solutions of ruthenium(III) and ruthenium(IV) chloro complexes were studied. Likewise Herasymenko and Slendyk (11) observed no reduction of ruthenium at the dropping mercury electrode, but reported a catalytic hydrogen wave. The results of the latter investigators (10, 11) do not agree with the results of the present work described below.

Polarographic Studies of Ruthenium(III) and Ruthenium(IV) in Hydrochloric Acid Solutions, Using the Dropping Mercury Electrode. Typical polarograms of ruthenium(III) and ruthenium(IV) in an acid chloride supporting electrolyte are shown in Fig. 5. These polarograms were recorded with a Sargent Model XXI polarograph at a temperature of 25° C. The capillary employed had a drop time of 5.07 sec. at -0.5 volts versus the S.C.E.; the capillary constant, $m^{2/3}t^{1/6}$, was 1.74. Both solutions contained 0.05% gelatin as a maximum suppressor. Both solutions were degassed in the conventional manner

Fig. 5. Typical Polarograms of Ruthenium Solutions in Chloride Supporting Electrolytes: 1, 3.1×10^{-4} M Ru(IV), 0.030 M HCl, 1.0 M KCl; 2, 3.1×10^{-4} M Ru(III), 0.12 M HCl, 1.0 M KCl.

by sweeping with nitrogen. Mercury was not allowed to come into contact with either solution until the actual recording of the polarograms was begun. Both curves have been corrected for the residual current. The ruthenium(IV) solution was prepared from a stock solution of $K_2Ru(OH)Cl_5$ which was 0.15 M in hydrochloric acid and which had stood at room temperature for twelve days before preparation of the sample. The ruthenium(III) solution was prepared by heating a portion of the stock solution of $K_2Ru(OH)Cl_5$ described above with ethyl alcohol for two days. The temperature was maintained just below the boiling point. This solution was then evaporated to dryness and dissolved in dilute hydrochloric acid. The solution stood at room temperature for two days before preparation of the final sample.

The polarogram of the ruthenium(IV) solution shows one reduction wave which appears at a potential more positive than the anodic dissolution wave of mercury. The polarogram also shows a second reduction wave, the height of which is identical with that of the first wave, with a half-wave potential of -0.29 volts versus the S.C.E. The polarogram of the ruthenium(III) solution shows a single reduction wave with a half-wave potential of -0.28 volts versus the S.C.E.

There is no doubt that the first wave for the ruthenium(IV) solution is due to a reduction of the ruthenium to the tripositive state and that the second is due to a reduction to the dipositive state. The wave for the ruthenium(III) solution is due to a reduction to the dipositive state. The diffusion coefficient of ruthenium(IV), as calculated from the Ilkovic equation, is $0.75 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ and that of ruthenium(III), $0.85 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

The wave corresponding to the reduction of ruthenium(III) to ruthenium(II) is irreversible for solutions of both ruthenium(III) and ruthenium(IV). The irreversibility is much more pronounced for solutions of ruthenium(IV), probably because the reduction of the two different species (See Section

IV) of ruthenium(IV) yields two different species of ruthenium(III) which do not reach equilibrium in a time which is short in comparison with the drop time. It is significant, however, that the half-wave potential for the (III)-(II) wave is essentially the same in solutions of both ruthenium(III) and ruthenium(IV).

Although polarograms of many different solutions, having hydrogen ion concentrations between 0.030 and 1.0 M and chloride ion concentrations between 0.10 and 1.0 M , have been obtained, the half-wave potential for the (III)-(II) wave has always been found to lie between -0.26 and -0.30 volts. The small variations of potential that have been observed seem to be random, and are probably not outside the limits of experimental error. It must be concluded, therefore, that this potential is independent of both hydrogen and chloride ion concentrations.

If one assumes a value of ± 0.25 volt for the potential of the saturated calomel electrode and if one assumes that the diffusion coefficients of ruthenium(II) and ruthenium(III) are approximately equal, the potential of the ruthenium(II)-ruthenium(III) couple may be calculated from the observed halfwave potential, -0.28 volt. This calculation leads to a value of -0.03 volt on the hydrogen scale. (The sign convention employed here is the one in common use in polarography; the sign of the potentials would be reversed in the Latimer (12) convention.) The potential for this couple has also been determined by Backhouse and Dwyer (13), who reported a value of +0.08 volts. Since the polarographic reduction wave is irreversible, it would be expected that the standard potential calculated from the measured half-wave potential would be somewhat more negative than the true value. For this reason, the value calculated above is not inconsistent with the value of Backhouse and Dwyer. These authors found also that the potential of the ruthenium(II)-ruthenium(III) couple was independent of hydrochloric acid concentration over the range studied, 1.5-6.8 M .

The diffusion currents for solutions of both ruthenium(IV) and ruthenium(III) have been found to be proportional to ruthenium concentrations provided all solutions are prepared in exactly the same manner. Different methods of preparation result in changes in diffusion currents, particularly for ruthenium(IV) solutions. This behavior is not surprising since different methods of preparation yield different species of ruthenium(IV). The different species of ruthenium(IV) undoubtedly have different diffusion coefficients which cause the diffusion current to vary depending upon the particular species present.

Solutions of ruthenium(III) prepared by reduction of ruthenium(IV) in a Walden silver reductor or by electrolysis yielded polarograms essentially identical with that shown in Fig. 5 for reduction with ethanol.

A rounded maximum appears at the top of the (III)-(II) reduction wave unless a large concentration of maximum suppressor is present. Gelatin in a concentration of 0.05% suppresses this maximum completely.

A third reduction wave, not shown in the polarograms of Fig. 5 was observed in many of the solutions studied. This wave occurs at about -0.6 volts and is followed closely by the hydrogen discharge wave. The height of this third wave is usually much too great to be due to a reduction of ruthenium(II) to the metal. It is very probably a catalytic hydrogen wave superimposed on the ruthenium reduction wave. The half-wave potential and the height of the wave vary as the concentration of hydrochloric acid in the supporting electrolyte is varied.

Polarographic Studies with Platinum Microelectrodes in Chloride Media.

Results obtained with both stationary and with rotating platinum microelectrodes were generally erratic and not reproducible. Most of the difficulties encountered are now believed to have been due to the use of solutions which had not yet come to equilibrium. It is possible also that metallic ruthenium may have been plated onto the electrode after it had been used for some time, and that this deposit led to results which varied

from those obtained at a clean platinum surface. These studies should be repeated on equilibrated solutions, since the technique seems to offer considerable promise in elucidating the nature of the ruthenium(III) and ruthenium(IV) species in chloride media.

In general, solutions of ruthenium(IV) in acid chloride supporting electrolytes showed two reduction waves at both stationary and rotated platinum microelectrodes. The first of these waves occurred at potentials around +0.5 to +0.6 volts and the second at potentials around 0.0 to +0.2 volts. These waves are believed to be due to reduction of the Y(III) and Y(II) complexes (See section IV) of ruthenium(IV), respectively. The half-wave potentials and the diffusion currents for both waves appear to be dependent of hydrogen ion and chloride ion concentrations. The diffusion plateau of the second wave is frequently masked by the hydrogen discharge wave. Both waves appeared to be irreversible.

A typical polarogram, showing only the first reduction wave, is illustrated in Fig. 6. The second wave was in this case masked by hydrogen discharge. The polarogram illustrated was obtained at a stationary electrode, using a solution which was 3.1×10^{-4} M in $K_2Ru(OH)Cl_5$, 0.13 M in hydrochloric acid and 0.10 M in potassium chloride. The stock solution of $K_2Ru(OH)Cl_5$ from which the final solution was prepared was 0.15 M in hydrochloric acid and had stood at room temperature for one week. The final solution stood at room temperature overnight.

The half-wave potential of the polarogram shown in Fig. 5 is +0.62 volt versus the S.C.E. This value corresponds to +0.87 volt on the hydrogen scale for this particular ruthenium(III)-ruthenium(IV) couple. Backhouse and Dwyer (14) have reported a value of +0.96 volts for the ruthenium(III)-ruthenium(IV) couple in hydrochloric acid, extrapolated to zero acid concentration. They reported also that the potential of the couple is depressed markedly by chloride ion and to a lesser extent by hydrogen ion. The value calculated above is thus not inconsistent with their data.

Fig. 6. Polarogram of $K_2Ru(OH)Cl_5$ in Chloride Supporting Electrolyte with Stationary Platinum Electrode.

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