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THE OXIDATION STATES OF RUTHENIUM IN ITS HALIDE COMPOUNDS

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Introduction

In order to interpret the results of an investigation on the catalytic reduction of perchloric acid by hydrobromic acid,[1] and to make more complete the tables of reactions given in "Qualitative Analysis for the Rare Elements" by A. A. Noyes and W. C. Bray,[2] accurate information was needed as to the chemistry of ruthenium in its lower states of oxidation; for the literature on the nature and properties of the quadri-, tri- and bivalent compounds is not consistent. The experiments described in this paper were therefore carried out with the view of helping to remove the uncertainty as to the states of oxidation of ruthenium in its halide compounds.

We wish to express here our appreciation of the helpful suggestions made by Professor A. A. Noyes. Financial assistance was received through a grant made to him by the Carnegie Institution of Washington.

A review of the previous work has recently been published by J. L. Howe.[3] It will suffice therefore to mention here only those researches directly related to our investigation.

A series of experiments carried out by Ruff and Vidic[4] shows that ruthenium tetroxide is reduced completely by potassium iodide in normal acid to the trivalent state and no further; and that, when 2 *N* hydrobromic acid is used as the reducing agent, the reduction products consist of ruthenium in both the tri- and quadrivalent states, the proportions of each depending on the experimental conditions. Their results show, however, that even with hot concentrated hydrochloric acid trivalent ruthenium is produced only very slowly.

Under the belief that solutions of trivalent ruthenium chloride resulted from the action of hydrochloric acid, Remy and Wagner[5] obtained with sodium amalgam results which they interpreted as indicating that the deep blue compounds of ruthenium contain the metal in the univalent state, contrary to the prevailing idea that they are bivalent. Zintl and Zaimis[6] arrived at the same conclusion when they found that a small

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[1] These results are to be published in the near future.

[2] A. A. Noyes and W. C. Bray, "Qualitative Analysis for the Rare Elements," Macmillan Co., New York, **1927**, p. 492.

[3] Howe, THIS JOURNAL, **49**, 2381 (1927).

[4] Ruff and Vidic, *Z. anorg. allgem. Chem.*, **136**, 49 (1924).

[5] Remy and Wagner, *Ber.*, **60**, 493 (1927).

[6] Zintl and Zaimis, *Ber.*, **60**, 842 (1927).

excess over one equivalent of titanous sulfate or chromous sulfate produced a deep blue color in solutions which they believed to contain the ruthenium as a trivalent chloride. By reducing a ruthenium chloride and bromide dissolved in absolute alcohol with hydrogen in contact with platinum black, Gall and Lehmann[7] obtained deep blue solutions, from which on evaporation solid compounds resulted whose composition was found to correspond to the formulas $RuCl_2$ and $RuBr_2$. Zintl and Zaimis accounted for these compounds by assuming them to be $HRuCl_2$ and $HRuBr_2$; but the fact[8] that such compounds of other univalent metals are very unstable makes this assumption improbable.

Another source of confusion has arisen from the fact that until recently two distinct types of pentachloro salts of trivalent ruthenium were believed to exist and were given the formulas $M_2RuCl_5.H_2O$ and $M_2Ru(H_2O)Cl_5$. Howe, however, as a result of the work of Charonnat[9] and recent experiments of his own, now considers that the formulas of these salts are $M_2RuCl_5.H_2O$ and M_2RuCl_5OH; that is to say, that the ruthenium in those compounds exists in the trivalent and quadrivalent states, respectively. It should be mentioned that S. G. C. Briggs[10] is not in aggreement with these conclusions.

Plan of the Investigation

The general plan of the investigation was as follows:

(1) To confirm the results of Ruff and Vidic that ruthenium is reduced by iodide in an acid solution to the trivalent state. This was done by determining the number of equivalents of iodine liberated in an acid solution of potassium iodide by the ruthenium tetroxide obtained by distilling with potassium permanganate a known volume of a stock solution of ruthenium chloride which had been evaporated with sulfuric acid to dense white fumes.

(2) To study the states of oxidation of ruthenium in the solution of its chloride obtained by dissolving in hydrochloric acid an hydroxide prepared by the reduction of potassium ruthenate with ethyl alcohol by the method of Krauss and Kükenthal. This was done by determining the number of equivalents of iodine liberated in a hydrochloric acid solution of potassium iodide by known volumes of the ruthenium chloride solution before and after chlorination.

(3) To determine the states of oxidation of ruthenium produced by reduction of unchlorinated and chlorinated chloride solutions with titanous sulfate, especially its state in the yellow and deep blue solutions obtained successively with this reagent. This was done by making a potentiometric

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[7] Gall and Lehmann, *Ber.*, **59**, 2856 (1926).

[8] Engel, *Ann. chim. phys.*, [6] **17**, 378 (1889).

[9] Charonnat, *Compt. rend.*, **181**, 866 (1925).

[10] Briggs, THIS JOURNAL, **48**, 2127 (1926); *J. Chem. Soc.*, **127**, 1042 (1925).

titration of a known volume of the chloride solution with titanous sulfate, noting the number of equivalents of titanium required to produce a marked inflection in the titration curve and also the number of equivalents required to produce the yellow and blue colors in the solution.

(4) To study in ways similar to those described in (2) and (3) a salt of ruthenium bromide prepared by digesting the chloride with bromine and hydrobromic acid and evaporating the solution with potassium bromide.

Preparation of Standard Ruthenium Solutions

Stock solutions of ruthenium chloride were made by heating for five minutes just below the boiling point with concentrated hydrochloric acid an hydroxide which had been prepared by the reduction of potassium ruthenate with ethyl alcohol as described by Krauss and Kükenthal.[11] It was found that the hydroxide would not dissolve completely even on continued heating, but left a small black residue, which was filtered off. The concentration of the ruthenium was determined by evaporating definite volumes of the stock solution to dryness and igniting the residue in a stream of hydrogen, whereby the ruthenium is converted to the metallic state.

Reduction of Ruthenium Tetroxide by Iodide to the Trivalent State

Since the conclusion that ruthenium is reduced by iodide to the trivalent state is the basis of the following work, it seemed desirable to confirm the results of Ruff and Vidic to this effect. For this purpose a definite volume (5.00 cc.) of the stock solution of ruthenium chloride was evaporated with sulfuric acid till dense white fumes appeared; 10 cc. of water was added, followed by 20 cc. of a solution containing 1 g. of potassium permanganate, and the resulting mixtures were distilled in a current of carbon dioxide.[12] The distillate containing the ruthenium as tetroxide was absorbed in a 2 *N* hydrochloric acid solution containing potassium iodide. The liberated iodine was determined with standard thiosulfate. The results are given in Table I.

TABLE I

RESULTS OF THE DISTILLATION EXPERIMENTS

Cc. of Ru solution (0.01475 atomic)	Cc. of 0.0509 *N* thiosulfate Required	Calcd. for five equivalents	Atoms of iodine liberated per atom of Ru
5.00	7.10	7.25	4.90
5.00	7.24	7.25	4.99
5.00	7.17	7.25	4.95

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[11] Krauss and Kükenthal, *Z. anorg. allgem. Chem.*, **132**, 316 (1924).

[12] This distillation process may also be used for the preparation of ruthenium tetroxide and is far more satisfactory for this purpose than any of the other known methods (see Ruff and Vidic, Ref. 4).

Reduction of Ruthenium by Iodide in Solutions of its Chloride

A definite volume (5.00 cc.) of a stock solution of ruthenium chloride 0.0295 atomic in ruthenium was diluted with enough water and hydrochloric acid to make the final acid concentration 2 *N* and the volume 100 cc.; 1 g. of potassium iodide was added and the liberated iodine was titrated with 0.0487 *N* thiosulfate, using starch as the indicator. Of the thiosulfate 0.76 cc. was used, while 3.03 cc. would have been required if the ruthenium had all been in the quadrivalent state. This shows that the ruthenium hydroxide prepared according to Krauss and Kükenthal contains a considerable proportion of quadrivalent ruthenium.

Chlorine was bubbled slowly for five minutes through two other 5.00-cc. portions of the stock solution in 100 cc. of 2 *N* hydrochloric acid, the excess of chlorine was expelled by boiling, 1 g of potassium iodide was added and the liberated iodine was determined as before.[13] Typical results are given in Table II.

TABLE II

IODIMETRIC TITRATION OF RUTHENIUM CHLORIDE SOLUTIONS

Expt.	Cc. of Ru soln. (0.0295 atomic)	Cc. 0.0487 *N* $Na_2S_2O_3$ Unchlorinated soln.	Chlorinated soln.	Calcd. for one equivalent
1	5.00	0.76	..	3.03
2	5.00	..	3.02	3.03
3	5.00	..	3.10	3.03

The color of the unchlorinated solutions was light orange-red; that of the chlorinated solutions, dark orange-red.

These results show that in the chlorinated solution the ruthenium is all in the quadrivalent state, and that the acid solution of the hydroxide contains both trivalent and quadrivalent ruthenium.

Titration of Ruthenium Solutions with Titanous Sulfate

Measured volumes (5.00 cc.) of a stock solution 0.0148 atomic in ruthenium were diluted with enough water and hydrochloric acid to make the volume 50 cc. and the acid concentration 2 *N;* these solutions were titrated electrometrically in an atmosphere of carbon dioxide with a 0.0222 *N* titanous sulfate solution. The points where a rapid change in potential occurred are shown in Table III.

TABLE III

ELECTROMETRIC TITRATIONS OF RUTHENIUM SOLUTIONS WITH TITANOUS SULFATE

Expt.	Temp., °C.	Cc. of Ru soln., 0.0148 atomic	Cc. of Ti^{III} soln., 0.0222 atomic Unchlorinated soln.	Chlorinated soln.	Calcd. for one equivalent
1	25	5.00	1.10	..	3.33
2	25	5.00	..	3.30	3.33
3	80	5.00	..	3.22	3.33

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[13] The possibility that RuO_4 might be present in the chlorinated mixtures is precluded by the concentration of the hydrochloric acid and the treatment by heating.

The electrometric titration curves corresponding to the experiments given in the table are shown in Fig. 1. A sharp break in the curves occurs when one equivalent of titanous salt is added to the chlorinated solution. In the case of the unchlorinated solution the break occurs when about one-third of an equivalent is added. No further breaks of a reproducible nature were observed in the curves, although several equivalents of titanous sulfate were always added.

The curves resulting from the titration of the cold mixtures are similar to that shown by Zintl and Zaimis. The color changes observed during the titration with titanous sulfate were practically the same as those described by them. At first the solutions are dark orange-red (if previously chlorinated). When nearly one equivalent of the reducing agent has been added the color becomes bright yellow. After passing the end-point the color changes rapidly through olive green to dark blue; and this blue color persists even after several equivalents have been added. In the solutions heated to 80° a small dark precipitate formed.

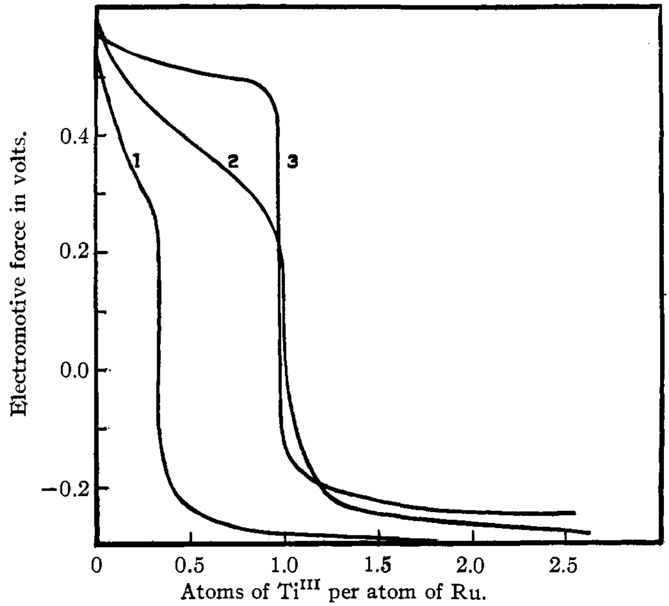

Fig. 1.—Electrometric titrations. Curve 1, unchlorinated solution at 25°; Curve 2, chlorinated solution at 25°; Curve 3, chlorinated solution at 80°.

These results clearly show that the sudden change in potential occurs when all of the quadrivalent ruthenium has been reduced, that is, at the transition from the trivalent to the bivalent state, and not at the transition from bivalent to univalent as concluded by Zintl and Zaimis, and that, therefore, in all probability, the blue color is characteristic of bivalent, not univalent, ruthenium as had been considered to be the case previous to the work of these investigators. In the case of the unchlorinated solution, the break in the curve confirms our conclusion, drawn from the iodimetric titrations, that quadrivalent ruthenium is present.

Preparation and Behavior of a Bromide Salt of Quadrivalent Ruthenium

It was found that when ruthenium chloride solutions containing moderate amounts of hydrobromic acid are heated with bromine a crimson solution results after the excess of bromine has been expelled. On treating these solutions with a small excess of potassium bromide and evaporating in a vacuum desiccator containing sulfuric acid and solid sodium hydroxide a black crystalline residue results. This residue was washed with water and alcohol and dried in the desiccator again. The product thus obtained was analyzed for bromine, potassium bromide and ruthenium as follows. A weighed amount was ignited in a stream of hydrogen, the hydrobromic acid liberated was absorbed in acidified silver nitrate solution and the resulting silver bromide dried and weighed. The potassium bromide remaining in the residue after ignition was extracted with water and the bromide in the extract was determined as silver bromide. Finally, the residue of ruthenium remaining after the extraction was ignited in a stream of hydrogen and then weighed as the metal. The salt was found to have the following percentage composition.

	Ru	KBr	Br (liberated as HBr)
Found, %	17.03	38.29	40.25
Calcd. for K_2RuBr_5OH, %	17.05	39.91	40.20

This is probably the same salt that Howe described originally[14] as $K_2RuBr_5 \cdot H_2O$, but which he now considers[3] to be K_2RuBr_5OH. The results given here are in accord with this conclusion but care must be exercised in drawing conclusions from the results of the analysis alone, for the calculated composition of the salt $K_2RuBr_5H_2O$ would also be in good agreement with the analytical results.

To determine to which of these formulas the behavior of the salt corresponds, its power of oxidizing iodide was studied. A solution of the salt was made up by dissolving a weighed amount in 2 *N* hydrochloric acid and diluting to a definite volume with more acid of the same concentration. Measured volumes of this solution were diluted to 100 cc. with 2 *N* hydrochloric acid, potassium iodide was added and the liberated iodine was titrated with standard thiosulfate. The results are presented in Table IV. They clearly show that in the bromide the ruthenium is in the quadrivalent state, thus eliminating the possibility that the salt is $K_2RuBr_5.H_2O$.

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[14] Howe, This Journal, **26**, 944 (1904).

TABLE IV

IODIMETRIC TITRATIONS OF THE BROMIDE SALT

Expt.	Cc. of Ru soln., 0.00742 atomic	Cc. of 0.0500 N thiosulfate Used	Calcd. for one equivalent
1	10.00	1.40	1.48
2	20.00	2.95	2.96
3	25.00	3.65	3.70

Known volumes of the same stock solution were also titrated electrometrically with standard titanous sulfate solution, both before and after treating with chlorine. The excess of chlorine and liberated bromine was expelled by boiling. The color changes were the same as those observed in the experiments with the ruthenium chloride solutions. The results are recorded in Table V. They again show that in the bromide salt the ruthenium is quadrivalent.

TABLE V

ELECTROMETRIC TITRATIONS OF THE BROMIDE SALT

Expt.	Cc. of Ru soln., 0.00742, atomic	Cc. of Ti^{III} soln., 0.0280 atomic Unchlorinated soln.	Chlorinated soln.	Calcd.
1	10.00	2.65	..	2.65
2	10.00	2.62	..	2.65
3	10.00	..	2.70	2.65
4	10.00	..	2.70	2.65

Summary

The conclusion of Ruff and Vidic that ruthenium compounds in hydrochloric acid solution are reduced by iodide to the trivalent state and no further was confirmed by titrating with thiosulfate the iodine liberated in a solution of the tetroxide obtained by distilling with sulfuric acid and permanganate a known volume of a stock solution of ruthenium chloride which had been evaporated with sulfuric acid to dense white fumes (see Table I).

A hydrochloric acid solution of the ruthenium hydroxide prepared by reducing potassium ruthenate with ethyl alcohol by the method of Krauss and Kükenthal was found to liberate about one-fourth of an atom of iodine per atom of ruthenium, showing that the hydroxide is a mixture of trivalent and quadrivalent compounds. When this solution was saturated with chlorine and the excess expelled by boiling, one atom of iodine was liberated for each atom of ruthenium (see Table II).

Electrometric titrations with titanous sulfate were made with the hydrochloric acid solution of ruthenium hydroxide and with the solution of it that had been treated with chlorine. In both cases an end-point was reached when all of the quadrivalent ruthenium had been reduced to the trivalent form, not as concluded by Zintl and Zaimis when the

ruthenium was reduced to the bivalent state (see Table III and Fig. 1). It may therefore be concluded that the dark blue compounds which form after a small excess of titanous sulfate has been added are compounds of bivalent ruthenium, not of univalent ruthenium as supposed by these authors and by Remy and Wagner.

A bromide salt of ruthenium was prepared by digesting the chloride with bromine and hydrobromic acid and evaporating the solution with potassium bromide. An analysis of this salt showed that it conforms to the formula $K_2RuBr_5(H_2O)$ or K_2RuBr_5OH. Titrations of hydrochloric acid solutions of this salt with thiosulfate after treating it with potassium iodide, and with titanous sulfate by the electrometric method, showed that the ruthenium in the salt was in the quadrivalent state (see Tables IV and V). These results indicate that the true formula of the salt is K_2RuBr_5OH, thus confirming the recent views of Howe.

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[CONTRIBUTION FROM THE METALLURGICAL LABORATORIES OF HARVARD UNIVERSITY]

THE CRYSTAL STRUCTURE OF THE SYSTEM CADMIUM-MERCURY

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The system cadmium-mercury is interesting for a number of reasons. Its composition-temperature diagram (Fig. 1) is the only known example of Roozeboom's Type IV.[2] Various compositions among the mercury-rich alloys have been used in the construction of standard cells. Numerous measurements on electrode potential, and on vapor pressure, of the liquid and partly liquid alloys have led a number of investigators to postulate the existence of intermetallic compounds.[3] These, however, do not appear on the constitution diagram proposed by Bijl[4] (Fig. 1) and repeatedly confirmed.[5] Recently T. W. Richards and C. E. Teeter, Jr.,[6] measured the heats of dilution of these alloys in mercury at room temperature and found no critical points suggestive of a compound.

A few measurements of the crystal structure of the system have been

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[1] National Research Fellow.

[2] Roozeboom, *Z. physik. Chem.*, **30**, 385 (1899).

[3] (a) Hildebrand, Foster and Beebe, THIS JOURNAL, **42**, 545 (1920); (b) Richards and Forbes, *Carnegie Institution Publication*, No. **56** (1906); (c) *Z. physik. Chem.*, **58**, 738 (1906); (d) Hildebrand, *Trans. Am. Electrochem. Soc.*, **22**, 319, 335 (1913).

[4] Bijl, *Z. physik. Chem.*, **41**, 641 (1902).

[5] (a) Puschin, *Z. anorg. Chem.*, **36**, 201 (1903); (b) Jänecke, *Z. physik. Chem.*, **60**, 409 (1907); (c) Schulze, *ibid.*, **105**, 177 (1923); (d) Tammann and Mansuri, *Z. anorg. Chem.*, **132**, 69 (1923).

[6] Unpublished research.