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The Preparation and Analysis of Solutions of a Trivalent Osmium Bromide

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The methods described for the preparation of trivalent osmium halide compounds usually involve the production of a mixture of trivalent and quadrivalent forms which are difficult to separate. This statement applies to the chlorides in such methods as those of Moraht and Wischin,[1] Ruff and Bornemann,[2] and Claus and Jacoby[3] as well as to the bromides in the method of Moraht and Wischin.[1] Since any solutions prepared from these compounds would be contaminated with the quadrivalent form and possibly other impurities, it was the purpose of the authors to develop a simple and reliable method for the preparation of solutions of a pure trivalent compound. The present paper describes a procedure for the preparation of solutions of osmium tribromide by electrolytic reduction of potassium bromoösmate in a hydrobromic acid solution, presents three methods of analysis of the reduced osmium solutions and in so doing demonstrates that the reduced osmium is in the pure trivalent state; finally it offers evidence as to the constitution of the potassium salt of the trivalent bromide complex.

Experimental

Materials.—The potassium bromoösmate was obtained by the method of Crowell and Baumbach.[4] The hydrobromic acid was prepared from red phosphorus and bromine by the well-known method. Commercial carbon dioxide was purified by passing it through a saturated solution of potassium permanganate in 6 *N* sulfuric acid and then through a solution 0.3 *M* in chromous sulfate and 1 *N* in sulfuric acid.

Preparation of Trivalent Osmium Solutions.—The apparatus used for carrying out the electrolytic reduction is shown in Fig. 1. B is a 100-cc. electrolytic beaker, E a platinum cathode of 52-mesh wire gauze two inches (5 cm.) high and one and three-eighths inches (3.4 cm.) in diameter, F a carbon rod anode about one-fourth inch (6.4 mm.) in diameter, G a porous porcelain cup four inches (10 cm.) high, one inch (2.5 cm.) in diameter and three-sixteenths inch (4.8 mm.) thick to separate the anode and cathode compartments. A is a source of purified carbon dioxide, C and D is a stopcock system which allows carbon dioxide to bubble through the solution in the cell or to force the solution out through the two way stopcock D. H is a glass tube out of which either the carbon dioxide may escape or the cell solution can be forced into a pipet.

The solution reduced consisted of 0.15 g. of potassium bromoösmate in 50.0 cc. of 3.2 *N* hydrobromic acid. In the anode compartment was a solution of 3.2 *N* hydrobromic acid. A calomel electrode 1.000 *N* in potassium chloride was connected with the cathode compartment in order to control the electrolysis. The potentiometer reading during the reduction varied from about 0.40 to 0.50 v. and the current remained at about 50 m. a. for approximately two hours or until the deep red of the bromoösmate had been replaced by a light yellowish brown. It was found that more concentrated solutions could be used and a careful control of the voltage was unnecessary. The current could be two or three times that stated and could continue until there was considerable evolution of hydrogen without any reduction of osmium to a valence state lower than three.

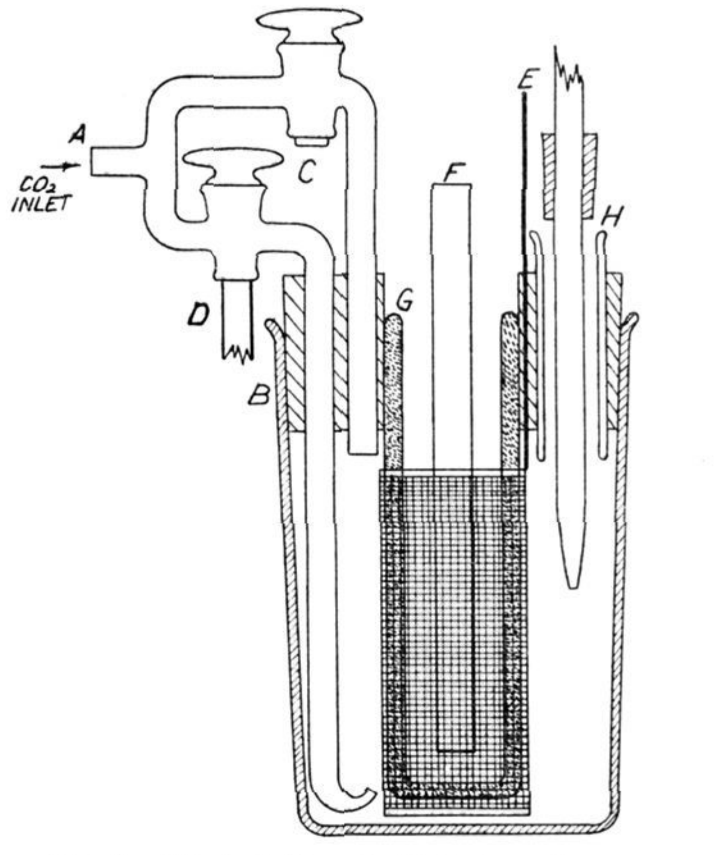

Fig. 1.—Electrolytic reduction apparatus.

Establishment of the Valence State of the Reduced Osmium.—That the osmium in the reduced solutions was in the trivalent state was proved by analyzing portions of the solutions by three independent methods.

In Method I the reduced osmium solution was brominated in a concentrated hydrobromic acid solution and, after the removal of the excess bromine, titrated potentiometrically with chromous sulfate by the method of Crowell and Baumbach.[4] In this procedure it was assumed that the osmium was oxidized to the quadrivalent form by the bromine, since it is known[5] that only the quadrivalent form results when osmium tetroxide or quadriva-

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[1] Moraht and Wischin, *Z. anorg. Chem.*, **3**, 153 (1893).

[2] Ruff and Bornemann, *ibid.*, **65**, 429 (1910).

[3] Claus and Jacoby, *Bull. Acad. St. Petersburg*, **6**, 145 (1863).

[4] Crowell and Baumbach, THIS JOURNAL, **57**, 2607 (1935).

[5] W. R. Crowell, *ibid.*, **54**, 1324 (1932).

Table I

Analysis of Reduced Osmium Solutions

Concn. of chromous sulfate soln. = 0.01014 *N*. Concn. of bromine soln. = 0.1972 *N* (1 *N* in HBr). Concn. of hydrazine sulfate soln. = 0.00978 *N*

Method	Run	Red. Os soln., cc.	Br_2 soln. added, cc.	$N_2H_6SO_4$ soln. equiv. to excess Br_2, cc.	$N_2H_6SO_4$ soln. equiv. to Br_2 used, cc.	$CrSO_4$ soln., cc.	Equiv. of Br_2 per g. atom of Os	Concn. of Os soln. assuming red. Os is Os_3 g. atom/l.
I	1	9.98				17.83		0.01813
	2	9.98				17.83		.01813
II	3	9.98	0.997	1.45	18.66		1.001	.01815
	4	9.98	.997	1.46	18.65		1.001	.01814
	5	9.98	.997	1.42	18.69		1.003	.01818
III	6	2.001	.997	1.43	18.67		5.000	.01813
	7	2.001	.997	1.41	18.69		5.006	.01815
	8	2.001	.997	1.43	18.67		5.000	.01813

lent osmium is heated in concentrated hydrobromic acid solutions or mixtures of concentrated hydrobromic acid and bromine. In the titration of the brominated solution, therefore, the number of equivalents of chromous sulfate required should be equal to the number of gram atoms of trivalent osmium originally present.

In Method II the reduced osmium solution was treated with a known excess of bromine in a concentrated hydrobromic acid solution and the unreduced bromine titrated potentiometrically with hydrazine sulfate solution by the method of one of the authors.[5] In this case the number of equivalents of bromine reduced should be equal to the number of gram atoms of trivalent osmium originally present.

In Method III the reduced osmium solution was treated with a known excess of bromine in a dilute hydrobromic acid solution and the amount of bromine remaining determined as in Method II. By this procedure the osmium is oxidized to the octavalent state and, therefore, the number of equivalents of bromine reduced per gram atom of reduced osmium should be five. One of the authors has shown that when quadrivalent osmium is treated with bromine in a dilute hydrobromic acid solution (0.1 *N* or below), the product is pure octavalent osmium.[5] Any osmium present in a valence state lower than four will, of course, be oxidized in the same manner.

Analysis of Reduced Osmium Solutions.—Results of the analyses of the osmium solutions are shown in Table I. Column 1 gives the method of analysis and in Column 9 are the osmium concentrations calculated on the basis that the original form was trivalent.

In Runs 1 and 2 Method I was followed. The volume of reduced osmium solution indicated in Column 3 was pipetted into about 10 cc. of concentrated hydrobromic acid containing excess bromine, the mixture boiled in the flask attached to the titration apparatus used by Crowell and Baumbach,[4] cooled in carbon dioxide, rinsed into the titration beaker, and the oxidized osmium titrated with chromous sulfate. The number of gram atoms of reduced osmium should be equal to the number of equivalents of chromous sulfate required per liter of solution calculated from the data in Columns 3 and 7. Convincing evidence regarding the state of oxidation of the osmium in the solutions before and after bromination was obtained by observing the potentials of the solutions in the potentiometric apparatus. That the osmium in the brominated solution was quadrivalent was indicated by the fact that the potential of the solution was the same within a few millivolts as that of the quadrivalent osmium solution used in the electrolytic reduction. That the osmium in the reduced solution was trivalent was indicated by the fact that the potential of the solution was the same within a few millivolts as that obtained at the equivalence point in the chromous sulfate titration of the quadrivalent osmium solution.

In Runs 3, 4 and 5 Method II was used. The volume of bromine solution stated in Column 4, and 10 cc. of oxygen-free, concentrated hydrobromic acid were sealed with the osmium solution in a glass tube and heated in the hot water-bath at 100° for about thirty minutes. The tube was cooled, broken under about 200 cc. of ice-cold distilled water, and the excess bromine was titrated with hydrazine sulfate solution. The values in Column 8 should be 1.000 and those in Column 9 should be equal to the equivalents of bromine reduced per liter of osmium solution calculated from the data in Columns 3 and 6.

In Runs 6, 7 and 8 Method III was used. The bromine solution and 45 cc. of oxygen-free, distilled water were sealed with the osmium solution in a glass tube, the tube was heated as before and the bromine remaining determined as in Method II. The values in Column 8 in this case should be 5.000 and those in Column 9 should be equal to the number of equivalents of bromine reduced per liter of osmium solution divided by five.

The results prove beyond a reasonable doubt that the reduced osmium is trivalent, (1) because the values of the concentration of the reduced osmium solution obtained by the three methods agree so well with each other, (2) because the amounts of bromine reduced per gram atom of osmium agree so closely with the assumed values and (3) because the potential of the reduced osmium solution is so nearly the same as that of the trivalent osmium solution obtained at the equivalence point in the reduction of the quadrivalent bromide with chromous sulfate.

The results also show that any one of the three methods may be used for the determination of trivalent osmium and that the probable error is less than 0.2%.

Analysis of Solutions Containing Trivalent and Quadrivalent Osmium.—The data in Table II show how trivalent and quadrivalent osmium may be determined in solutions containing both forms. The quadrivalent osmium is determined first by direct titration of a portion of the solution with chromous sulfate. A second portion is then brominated in a concentrated hydrobromic acid solution and a

TABLE II

ANALYSIS OF SOLUTIONS CONTAINING TRIVALENT AND QUADRIVALENT OSMIUM

Concn. of Os_4 soln. before mixing = 0.01906 *M*. Concn. of Os_3 soln. before mixing = 0.01900 *M*. Concn. of chromous sulfate soln. = 0.01014 *N*.

Run	Os_4 soln. in mixture, cc.	Os_3 soln. in mixture, cc.	$CrSO_4$ soln. before bromination, cc.	$CrSO_4$ soln. after bromination, cc.	Concn. of Os in mixture, g. atom/l.			
					Os_4		Os_3	
					Present	Found	Present	Found
1	5.010	5.000	9.42	18.76	0.00954	0.00954	0.00949	0.00946
2	5.010	5.000	9.43	18.79		.00955		.00948
3	5.010	5.000	9.42	18.77		.00954		.00947

second chromous sulfate titration made for total osmium. It will be seen that the difference between the experimental values and the concentrations of osmium present is not greater than 0.3%.

The Constitution of the Trivalent Bromide.—In order to determine the constitution of the trivalent compound a portion of the reduced solution was evaporated with potassium bromide in the presence of carbon dioxide, the excess potassium bromide removed, and the product analyzed. Since the sample was partially oxidized by the air during this process, it was necessary to determine both the quadrivalent and the trivalent osmium. In order to do this, one portion of the sample was analyzed by Method II and another portion by Method III as previously described, the former portion being oxidized by bromine to the quadrivalent state and the latter to the octavalent state. From a hydrazine sulfate titration of the bromine the amount reduced in each case was found and the number of gram atoms of each form of osmium in 100 g. of sample was determined. Since the quadrivalent form crystallizes out as K_2OsBr_6, the amount of it could be calculated and an allowance for its presence made in the composition of the mixture.

Following are the data for the preparation and analysis of one of the samples. About 25 cc. of the reduced osmium solution to which was added a small excess of potassium bromide was evaporated in a small closed tube in a stream of carbon dioxide while the tube was kept at about 80° in a hot water-bath. After washing out the excess potassium bromide with oxygen-free ethyl alcohol solution and drying, a sample was weighed from the tube into 25.01 cc. of oxygen-free hydrobromic acid solution kept under an atmosphere of carbon dioxide. The concentration of the solution was 0.01557 g. of sample per cc.; 15.00 cc. of this solution together with 2.001 cc. of 0.2001 *N* bromine solution and sufficient concentrated hydrobromic acid to make its normality in the mixture about 6 were sealed in a Pyrex tube and heated. A titration of the unreduced bromine required 16.10 cc. of 0.00983 *N* hydrazine sulfate solution. A second portion of the osmium solution consisting of 5.015 cc. together with 2.995 cc. of bromine solution and enough water to make the hydrobromic acid in the mixture about 0.05 *N* was sealed in another tube, heated and the excess bromine titrated as before. The volume of hydrazine sulfate solution required was 11.54 cc. From the data of the two titrations the number of moles of trivalent and of quadrivalent salt in 100.0 g. of sample were calculated and found to be 0.1037 and 0.0259, respectively. The percentage of K_2OsBr_6 was, therefore, 19.4, which meant that the percentage of trivalent salt was 80.6. The last value divided by 0.1037 gave a molecular weight of 777.

By another determination made in a similar manner a value of 780 for the molecular weight was obtained. Since the molecular weight of K_3OsBr_6 is 788, the experimental values, while not highly accurate, agree closely enough with this value to indicate that the osmium in the reduced solution was probably in the form of bromoperosmite. This conclusion is consistent with the work of Claus and Jacoby,[3] who reported the formula of their chloride to be $K_3OsCl_6 \cdot 3H_2O$.

Upon examination under the magnifying glass, the trivalent salt showed itself to be in the form of dark brown regular octahedral crystals.

Summary

A method of preparing solutions of a trivalent osmium bromide by electrolytic reduction of a hydrobromic acid solution of potassium bromoosmate is described. Three methods of analysis of the solutions are presented together with evidence that the valence state of the reduced osmium is three. The formula of the potassium salt of the trivalent bromide complex is shown to be K_3OsBr_6.

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