[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

THE POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTIONS

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Introduction

Among the problems engaging the attention of this Laboratory is that of a study of the rate of reaction between octavalent osmium and hydrobromic acid. Since the products of this reaction are quadrivalent osmium and bromine, it is apparent that its rate might be measured either by a determination at suitable time intervals of the remaining octavalent osmium, or of the bromine or quadrivalent osmium formed. Previous work on ruthenium[1] and octavalent osmium[2] and preliminary experiments on the potentiometric titration of hydrobromic acid solutions of bromine, octavalent and quadrivalent osmium indicated that trivalent titanium would be a satisfactory reducing agent for this purpose. In these last experiments the titration curve obtained by plotting voltage readings against cubic centimeters of reagent added showed three inflections. The first inflection corresponded to the reduction of the bromine to bromide ion, the second to the reduction of the octavalent osmium to the quadrivalent state and the third to the reduction of the quadrivalent osmium to the trivalent form.

The present paper deals with an investigation of the suitability of trivalent titanium as a reagent for determining one or more of these constituents with sufficient accuracy to warrant its use in the rate experiments. It describes the conditions employed and the results obtained in the potentiometric titration of hydrobromic acid solutions of (1) octavalent osmium, (2) bromine, (3) bromine in the presence of octavalent osmium, (4) bromine in the presence of quadrivalent osmium and (5) bromine, octavalent and quadrivalent osmium when present together.

Apparatus and Materials

The apparatus used was that employed in the potentiometric determination of octavalent osmium with hydrazine sulfate[2] except that provision was made for keeping the reducing agent as well as the titration vessel in an atmosphere of nitrogen.

Hydrobromic acid free of bromine was obtained by distilling the 42–48% acid and retaining the middle portion.

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[1] Crowell and Yost, THIS JOURNAL, **50**, 374 (1928).

[2] Crowell and Kirschman, *ibid.*, **51**, 175 (1929).

The bromine solution was prepared by distilling the C. P. reagent from potassium bromide and sulfuric acid into distilled water.

The stock solutions of osmium tetroxide were prepared as described in the above mentioned article,[2] and were about 0.5 *N* in potassium hydroxide.

The thiosulfate solution was frequently checked against a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

The titanium solutions were prepared from 1 *N* titanous chloride or sulfate. These were made 0.005–0.01 *N* in trivalent titanium and 0.3 *N* in hydrochloric, hydrobromic, or sulfuric acid. In order to remove traces of hydrogen sulfide, the undiluted acid and reagent were boiled together for one minute before making up to volume. The concentration of these solutions was determined by means of a solution of ferric sulfate which had been standardized against the permanganate solution. Standardizations were made before and after each set of three or four potentiometric titrations and the concentration was usually found constant within 0.1–0.2%. If the change was much greater than this the results obtained were rejected.

Titration of Octavalent Osmium with Titanous Chloride

Definite volumes of the standardized osmium tetroxide solution were titrated with a titanous solution in the presence of sulfuric, hydrochloric or hydrobromic acid. The procedure was as follows: the osmium solution was pipetted into the titration beaker containing about 50 cc. of the acid solution at room temperature, the cover of the beaker placed in position, a volume of titanous solution within 1–2 cc. of that required to reduce the osmium to the quadrivalent state added immediately and nitrogen then admitted slowly (one bubble every two seconds). This procedure was found necessary for accurate work on account of the volatility of the tetroxide. After the octavalent osmium had been reduced to quadrivalent, the nitrogen was bubbled through the solution more rapidly (1–2 bubbles per second). An amount of titanous solution was then added whose volume was within about 1 cc. of that necessary to effect reduction to the trivalent form and the titration continued until well past the inflection point.

The effect of different acids and of variations in the concentrations of these acids upon the color of the osmium solutions is an interesting feature of these titrations. The neutral or slightly acid solutions of octavalent osmium are colorless. When the reduction with titanous ion took place in a sulfuric acid solution, an amber color developed which persisted even after sufficient reagent had been added to reduce the osmium to the trivalent state. With this acid it was possible to obtain only one recognizable inflection in the titration curve, *viz.*, that corresponding to the reduction from the octavalent to the quadrivalent state. On addition of titanium reagent in the presence of hydrochloric acid the solution at first became light yellow, but when five equivalents of reducing agent per gram atom of osmium had been added, the solution became practically colorless. However, only one marked inflection in the titration curve was obtained, that corresponding to the octa–quadrivalent change. With hydrobromic acid (Curve B, Fig. 1) the solution became a deep orange-red as soon as reduction to the quadrivalent form was complete. Further addition of titanous solution produced a gradual change in color to a light yellow and when five equivalents of trivalent titanium per gram atom of osmium had been added, the solution became almost colorless. Two easily recognizable inflections were obtained: one when reduction to the quadrivalent state was complete; the other when reduction to the trivalent form had taken place. Since the most satisfactory drops in potential were obtained in solutions containing the hydrobromic acid, a more detailed study of the influence of the temperature and concentration changes was made with solutions containing this acid.

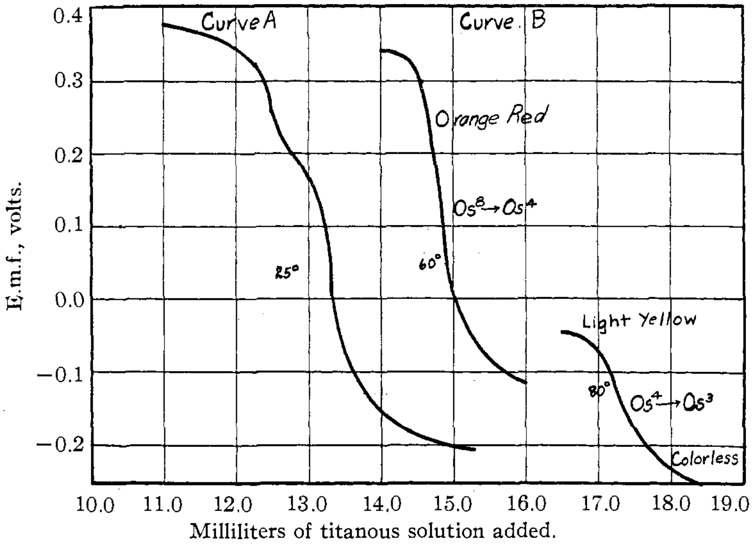

Fig. 1.—Potentiometric titration of hydrobromic acid solutions of octavalent osmium.

The concentration of hydrobromic acid which gave the largest drop in potential at the octa-quadrivalent end-point was found to be about 0.2–0.3 *N*. At acid concentrations below 0.1 *N* the solution became amber colored due probably to hydrolysis. At concentrations of acid higher than 0.3 *N* the drop in potential at this end-point was noticeably smaller and less abrupt. At room temperature a double inflection in the titration curve was obtained (Curve A, Fig. 1), while at 60° a single large drop in potential was obtained (Curve B, Fig. 1). Except in the immediate vicinity of the inflection point the voltage was considered constant when the rate of change was less than 3 millivolts per minute. In the reduction from the quadrivalent to the trivalent state the best inflections were obtained at a temperature of about 80° and at an acid concentration of about

1 N (Curve B, Fig. 1). A decided drift upward in the voltage readings was noticed at acidities below 1 N. The best results were obtained when the tetroxide solutions were first heated with strong hydrobromic acid in sealed tubes at the temperature of the steam-bath. On diluting these heated solutions to an acidity of about 1 N and titrating the quadrivalent osmium at 80°, sharper and greater drops of potential were obtained than when the titrations were carried out at the same temperature and acid concentration but without previous continued heating at 98°. Moreover, there was very little drift in the voltage readings. Results obtained in this manner will be described in more detail in the last section.

Table I contains the results of four typical titrations of a stock solution of octavalent osmium with titanous chloride. The end-points were determined from the inflection points of a curve obtained by plotting voltage against cubic centimeters of reagent added. The inflections could be determined to within 0.02–0.05 cc. The results are compared with those obtained by the modified iodimetric method.[2]

TABLE I

POTENTIOMETRIC TITRATION OF OCTAVALENT OSMIUM SOLUTIONS WITH TITANOUS CHLORIDE

Initial volume = 52–55 cc.

Normality of HBr	OsO_4 soln., cc.	Cc. of $TiCl_3$ used		OsO_4 found, millimoles/liter		
		$Os^8 \rightarrow Os^4$ infl.	$Os^4 \rightarrow Os^3$ infl.	$Os^8 \rightarrow Os^4$ infl.	$Os^4 \rightarrow Os^3$ infl.	Iodide method
0.2	4.96	18.30	23.70	6.33	6.56	6.35
.2	4.96	18.28	...	6.30	..	6.35
.3	2.005	9.80	12.25	6.26	6.26	6.35
.4	2.005	10.20	12.90	6.26	6.33	6.35

In the second experiment no satisfactory inflection corresponding to the reduction from quadrivalent to trivalent osmium was obtained. While the third and fourth experiments indicate that the quadri–trivalent break gives as good results as the octa–quadrivalent break, probably the data of the first experiment are more typical, since the general tendency is for the second inflection to give decidedly high results. The results determined from the first inflection point are usually lower than those obtained by the modified iodide method, due probably to loss of the volatile tetroxide during the titration and to the fact that the volatility of tetroxide even from an alkaline solution causes such a rapid decrease in concentration that it is important to make the potentiometric and iodimetric determinations simultaneously. In the later experiments improved technique made this difference much smaller as shown by the results given in Table III.

The Potentiometric Titration of Bromine with Titanous Sulfate

To determine the feasibility of estimating bromine in the presence of hydrobromic acid, octavalent and quadrivalent osmium, four series of experiments were conducted. Since Hendrixson[3] has shown that it is possible to determine bromine potentiometrically in its sulfuric acid solution by means of trivalent titanium, the first series was merely to confirm his results and consisted in the potentiometric titration of sulfuric acid solutions of bromine with the titanous sulfate. The second series was conducted in the presence of hydrobromic acid, the third series in the presence of this acid and 2 cc. of osmium tetroxide solution and the fourth series in the presence of this acid and 2 cc. of quadrivalent osmium solution.

In the first three series the samples of stock bromine solution were pipetted into 50–80 cc. of ice-cold distilled water containing the other constituents. A volume of titanous solution within 1 cc. of that required in a preliminary titration was added immediately and the titration rapidly completed below 5° while nitrogen was bubbled through the solution at the rate of one bubble every two to three seconds. Unless the bromine solution was run into a fairly large volume of cold solution the loss was incredibly high. It was found that if the contents of a 50-cc. pipet was allowed to drain into the empty titration vessel at room temperature and the titration conducted in this solution, the loss was over 10%.

The fourth series of experiments was carried out as follows: a 2-cc. sample of the stock tetroxide solution and 5 cc. of 8 *N* hydrobromic acid were heated for several hours at 98° in a closed tube. The tube was cooled in an ice-bath, opened under about 40 cc. of ice water, washed into the titration vessel with an additional 40 cc. of ice water and the liberated bromine titrated with the titanous solution. To this quadrivalent osmium solution, which now contained no free bromine, was added a known volume of the stock bromine solution and the titration carried out as before. In these solutions there was always present a small amount of octavalent osmium.[4] During a titration of the bromine the voltage readings became constant to within a millivolt in less than two minutes.

Results of the four series of titrations together with those obtained by the iodide method of bromine determination are recorded in Table II.

The results with sulfuric acid confirm those of Hendrixson. The results also show that bromine can be determined potentiometrically with trivalent titanium in the presence of hydrobromic acid. The average difference between the potentiometric and iodimetric methods in Series 1 and 2 where these acids were present is 0.3–0.4%. In Series 3 where osmium tetroxide was present the percentage difference between the titanous sulfate and iodide–thiosulfate methods varies from about 3% for the highest concentrations of osmium tetroxide and hydrobromic acid to about 0.5%

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[3] Hendrixson, THIS JOURNAL, **45**, 2013 (1923).

[4] This seems to indicate that the osmium is not completely reduced even on protracted heating in concentrated hydrobromic acid but that an equilibrium is reached in which the concentration of octavalent osmium is very small but measurable.

Table II

Potentiometric Titration of Bromine Solutions with Titanous Sulfate

Volume of bromine solution taken = 25.00 cc. Volume of osmium solution taken = 2.005 cc. Volume of solution before titration = 87–112 cc. Concentration of thiosulfate = 0.03124 *N*

Series	Acid and concn.	OsO_4 concn. millimoles/liter	Os^4 concn. millimoles/liter	$Ti(SO_4)_3$ Normality	$Ti(SO_4)_3$ Cc. used	Bromine found milliequivalents/liter Potentiometric	Bromine found milliequivalents/liter Iodide-thio.
1	1.4 *N* H_2SO_4			0.00845	14.55	4.918	4.910
	1.4 *N* H_2SO_4			.00845	14.55	4.918	4.910
	0.7 *N* H_2SO_4			.00845	14.53	4.911	4.910
	Neutral			.00845	15.05	4.935	4.910
2	0.5 *N* HBr			.01053	24.55	10.34	10.40
	0.5 *N* HBr			.01053	24.60	10.36	10.40
3	0.5 *N* HBr	0.1		.01053	25.20	10.61	10.40
	0.5 *N* HBr	.1		.01053	25.07	10.56	10.40
	0.5 *N* HBr	.5		.01053	25.45	10.72	10.40
	0.2 *N* HBr 1.0 *N* H_2SO_4	.1		.01029	23.54	9.69	9.62
	0.1 *N* HBr	.1		.01053	25.55	10.76	10.71
	0.1 *N* HBr 0.7 *N* H_2SO_4	.1		.01053	25.55	10.76	10.71
	0.1 *N* HBr	.5		.01048	25.74	10.80	10.71
4	0.27 *N* HBr		0.5	.00896	29.10	10.43	10.42
	0.27 *N* HBr		.5	.00896	28.95	10.38	10.39

for the lowest concentrations of these substances. In the latter case the concentration of the octavalent osmium is approximately 0.1 millimole per liter, while the concentration of the hydrobromic acid is 0.1 *N*. The experiments of Series 4 indicate that bromine can be determined without appreciable error in the presence of quadrivalent osmium as high in concentration as 0.5 millimole per liter when the hydrobromic acid is as high in concentration as 0.3 *N*.

Potentiometric Titration of Bromine, Octavalent and Quadrivalent Osmium in Hydrobromic Acid Solutions Containing All Three Constituents

The next step in the investigation was the determination of bromine, octavalent and quadrivalent osmium in hydrobromic acid solutions containing the three constituents in such proportions as to require on titration suitably large volumes of the reducing agent. These solutions were prepared as follows. Samples of 1.996 cc. of stock tetroxide solution which contained approximately 23 millimoles per liter and 5 cc. of 2.4 *N* hydrobromic acid were sealed into glass tubes of about 20-cc. capacity and heated at 98° for about three hours. The tubes were then cooled in an ice-bath, broken under about 40 cc. of the ice-cold water, rinsed into the titration vessel with an additional 40 cc. of the cold water and the titrations carried out immediately. As soon as the bromine–bromide ion inflection had been determined, an amount of titanous solution within 1–2 cc. of that necessary to reach the octa–quadrivalent end-point was added immediately. The temperature was then raised to 60° and the titration continued until the $Os^8 \longrightarrow Os^4$ break had been passed. Next, 2.5–8.0 cc. of 8 *N* hydrobromic acid was added, the temperature was raised to 80° and the quadrivalent–trivalent inflection point was determined. During the titration the nitrogen was bubbled through the solution in the same manner as in the titration of osmium tetroxide. A typical titration curve showing the three inflections is shown in Fig. 2.

The concentration of the stock osmium tetroxide was determined by the modified iodimetric method, care being taken to conduct the potentiometric and iodimetric determinations simultaneously.

The results obtained by the two methods are shown in Table III. For convenience the final results have been expressed in terms of milliequivalents of bromine. On this basis, if amounts of tetroxide are expressed as equivalent bromine, the titration of the 1.996 cc. of tetroxide solution before heating should be equal to the liberated bromine plus the undecomposed tetroxide after heating.

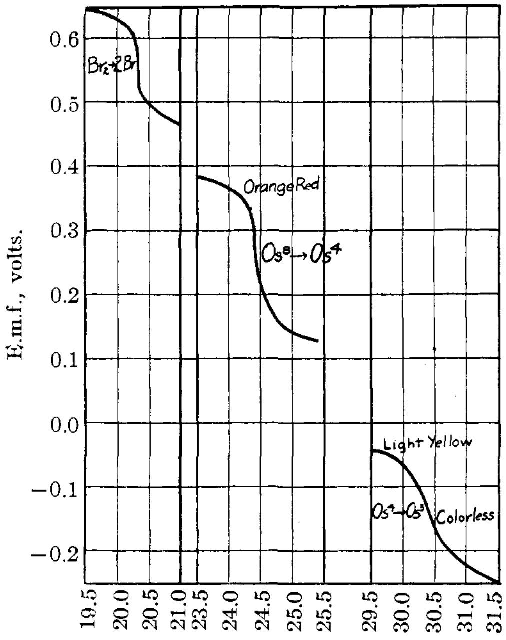

Fig. 2.—Potentiometric titration curve for solution containing bromine, hydrobromic acid, octa- and quadrivalent osmium.

TABLE III

POTENTIOMETRIC DETERMINATION OF BROMINE, OCTAVALENT AND QUADRIVALENT OSMIUM IN HYDROBROMIC ACID SOLUTIONS

Volume of OsO_4 solution used = 1.996 cc. Initial volume = 90–100 cc. Initial concentration of HBr in bromine titration = 0.17 *N*. Initial concentration of HBr in OsO_4 titration = 0.15 *N*. Initial concentration of HBr in Os^4 titration = 0.4–0.8 *N*

Titanous soln., *N*	Titanous solution used			Bromine found	Milliequivalents of total bromine calcd.		
	$Br_2 \longrightarrow Br^-$, cc.	$Os^8 \longrightarrow Os^4$, cc.	$Os^4 \longrightarrow Os^3$, cc.	$Br_2 \longrightarrow Br^-$ Infl., milliequivalents	$Os^8 \longrightarrow Os^4$ infl.	$Os^4 \longrightarrow Os^3$ infl.	Iodide method
0.00909	10.00	...	...	0.0909	....	....	0.1837
.00907	9.95	20.24	25.80	0.0903	0.1836	0.1872	.1837
.00906	10.15	20.40	25.95	.0919	.1849	.1882	.1837
.00906	...	20.12	...	....	.1822	....	.1837
.00905	10.20	20.40	...	.0923	.1845	....	.1837

An inspection of Table III shows that for the last four tubes the average deviation of the results of the bromine titrations from the mean is about 0.6%. The general tendency of this bromine value is to increase somewhat. However, the total bromine values (*i. e.*, the free bromine plus the undecomposed tetroxide) are of more significance and are in satisfactory agreement with those obtained by the iodimetric method, the average difference between the latter and the individual potentiometric values being about 0.5%.

It seems evident that it is possible by this method to conduct analyses of solutions in reaction tubes containing the four constituents and obtain results of determinations of bromine and of bromine plus octavalent osmium reliable to within 0.6%. In the rate experiments for which this method is primarily intended, this reliability is quite sufficient. The accuracy can be somewhat increased, if desired, by determining the concentration of the tetroxide solution added to the tubes before heating by potentiometric titration with hydrazine sulfate,[2] titrating only the liberated bromine with the titanous solution, and obtaining the undecomposed tetroxide by difference.

In the experiments where it was possible to obtain fairly good inflections in the curve corresponding to the reduction of the quadrivalent osmium to the trivalent, it will be seen that the values obtained are 2.0–2.5% higher than those obtained by the iodimetric method.

Summary

A method is described for the potentiometric determination of bromine and octavalent osmium in hydrobromic acid solutions containing bromine, octavalent and quadrivalent osmium by titration with solutions of titanous salts. The voltage–cubic centimeter curves obtained show three inflections—the first corresponding to the reduction of the bromine to bromine ion, the second to the reduction of the osmium from octavalent to quadrivalent and the third to the reduction of the quadrivalent osmium to trivalent.

Results reliable to 0.6% were obtained using the first two inflections. The third inflection was not found to be satisfactory for quantitative work.

The potentiometric titration of acid solutions of osmium tetroxide is described and some interesting color changes are noted.

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