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THE POTENTIOMETRIC DETERMINATION OF OCTAVALENT OSMIUM

BY WILLIAM R. CROWELL AND H. DARWIN KIRSCHMAN

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Introduction

In order to facilitate the study of a number of problems concerning the chemistry of osmium, it became desirable to develop a method for the determination of octavalent osmium which would be more rapid and not less reliable than those usually employed. The generally accepted gravimetric methods are those involving the reduction of osmium compounds to the metal; and the most commonly mentioned volumetric method is the iodide method of Klobbie with its modifications. The former methods, while reliable if conducted under proper conditions, are tedious, and require rather elaborate precautions; the latter has a very difficult end-point and, even under the best conditions, it is hard to obtain reproducible results. In the light of the past experience of one of us with ruthenium[1] it was thought that a potentiometric method would prove most satisfactory. It has already been shown[2] that hydrazine compounds reduce octavalent osmium in an alkaline or alcoholic solution to the tetravalent state. It is shown in this paper that this reduction can be carried out in acid solution, and that the progress of the reaction can be followed potentiometrically. Conditions for obtaining reproducible results have been worked out and comparisons made with results obtained by the iodide and gravimetric methods. A study is being made of other reducing agents, such as titanous, chromous and ferrous salts, the results of which will be presented in a later paper.

Apparatus and Materials

The apparatus used consisted of (1) a motor-driven stirrer; (2) a 1 *N* potassium chloride-calomel reference half-cell; (3) an oxidation-reduction electrode, made by fusing a platinum wire 2 cm. long and 0.05 cm. in diameter into the end of a small glass tube; (4) a certified buret; (5) a Leeds and Northrup student potentiometer, using a Leeds and Northrup portable galvanometer of 2.84 megohms sensitivity; (6) a 125-cc. beaker as a titration vessel. Calibrated precision pipets were used throughout.

A stock solution of osmium tetroxide in potassium hydroxide was prepared as follows. Metallic osmium, either as purchased or as recovered from residues by reduction with zinc and subsequent ignition in a current of hydrogen, was fused with potassium hydroxide and potassium nitrate. The melt was treated with water and distilled with nitric acid into a solution of potassium hydroxide, whereby a solution of osmium tetroxide was obtained free from ruthenium tetroxide. After acidification the metal

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

[2] (a) Ruff and Borneman, *Z. anorg. Chem.*, **65**, 436 (1910); (b) *Ber.*, **50**, 484 (1917); (c) Paal and Amberger, *ibid.*, **40**, 1378 (1907).

was again precipitated with zinc from this solution and fused with potassium hydroxide and potassium permanganate. The fused material was again treated with water and distilled from sulfuric acid with a current of oxygen into a definite volume of potassium hydroxide solution of known strength (about 0.4 *N*), free from traces of organic matter. The solution of osmium tetroxide thus obtained was free from nitric acid, nitric oxide and other volatile impurities. The alkaline solutions of the tetroxide are much more stable than neutral solutions and behave identically on titration.

Hydrazine sulfate solutions were standardized with potassium iodate by the method of Bray and Cuy.[3] The thiosulfate solutions used were frequently compared with a potassium permanganate solution which had been standardized by means of sodium oxalate from the Bureau of Standards.

Pure hydrobromic acid was obtained by distillation of the 48% acid. The middle fraction was used. All reagents were of standard c. p. quality.

The Potentiometric Method

In order to determine the best conditions for the potentiometric titration of octavalent osmium with hydrazine sulfate, preliminary experiments were conducted at different temperatures using various concentrations of osmium tetroxide and of acid. The acids used were sulfuric, hydrochloric and hydrobromic. Since the last was found to give the most satisfactory end-point, the results with this acid will be described in detail.

In hydrobromic acid solutions below 2 *N* at room temperatures (20–25°) there is apparently no reaction between hydrazine sulfate and octavalent osmium. As the temperature is raised to 50–60° the occurrence of a reaction is shown by the formation of gas bubbles and by a color change of the solution, which depends upon the acid concentration. At acidities below 1 *N* an amber color of varying intensity or a black precipitate appears, probably due to hydrolyzed compounds of tetravalent osmium. At acidities above 1 *N* the color change is from light yellow to a deep red.

Under the conditions finally adopted a large drop in potential occurs when four equivalents of hydrazine sulfate have been added for every gram atom of octavalent osmium present. Further additions of the reducing agent produce no additional break, even when five or six equivalents are used. It is evident that the osmium is reduced from the octavalent to the tetravalent state, as is the case in an alkaline or alcoholic solution.[2a] The reaction is probably the following

$$N_2H_6SO_4 + H_2OsO_5 + 6HBr = N_2 + H_2SO_4 + H_2OsBr_6 + 5H_2O$$

Analyses conducted at various temperatures between 60 and 80° gave practically the same results. It is desirable, however, to keep the temperature constant to within 2° because of the rather large temperature coefficient of the cell.

Preliminary experiments showed that quantitative results could not be obtained by a titration of octavalent osmium solutions in open vessels, probably because of a loss of the tetroxide from the acidified solution at the temperature used for the titrations. The procedure finally adopted was as follows. By preliminary direct titration the

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[3] Bray and Cuy, This Journal, **46**, 858 (1924).

amount of hydrazine sulfate necessary was roughly determined, several per cent. less than the theoretical amount being required because of loss by vaporization. Sealed glass tubes were then prepared containing this amount of hydrazine sulfate, sufficient concentrated hydrobromic acid to make the final acidity 1.5 *N*, and the sample of the stock octavalent osmium solution, these being added in the order mentioned. The tubes were then heated in a boiling water-bath from half an hour to several hours. A tube was then cooled, broken and its contents washed into the titration vessel with from 10–20 cc. of a 1.5 *N* hydrobromic acid solution, the potentiometric titration being completed at 70°. A time of heating longer than half an hour was found to be unnecessary. The same results were obtained even if the quantity of hydrazine sulfate added to the tube before heating was as high as 99% of the total required for titration.

During the electrometric titration the equilibrium voltage is attained within two millivolts in less than three minutes, except in the immediate vicinity of the end-point. The volume of hydrazine sulfate used was determined from the point of inflection in the curve obtained by plotting voltage against volume of reagent added. The voltage drop at the end-point is from 30–60 millivolts for a 0.1-cc. change in volume of reagent added, depending upon the acid concentration and the condition of the platinum electrode. It was found necessary to replace the platinum electrode after 10–12 titrations, since the usual methods of reconditioning electrodes did not prove satisfactory. The inflection is sufficiently abrupt, as is shown by the curve in Fig. 1.

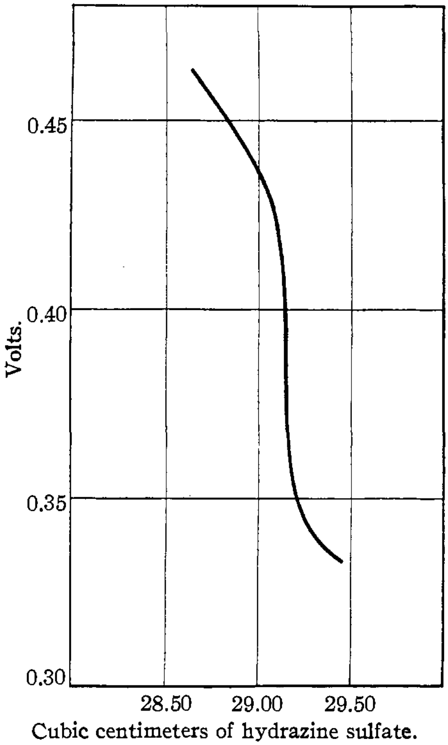

Fig. 1.

Determinations were made with solutions of osmium tetroxide of various concentrations. Corresponding concentrations of the reducing agent were used. The end-points in the most dilute solutions were not so sharp as in those of higher concentrations but the reproducibility was fairly satisfactory. Amounts of tetroxide as small as 10^{-5} mole may be determined by this method.

The Gravimetric and Iodometric Determinations

Comparative analyses by the gravimetric and iodometric methods were carried out at the same time as those by the potentiometric method, since it was found that the alkaline tetroxide solutions slowly decreased in concentration on standing, owing probably to loss of the osmium tetroxide formed by hydrolysis.

The procedure used in the gravimetric determinations was as follows. A measured portion of the stock osmium solution was pipetted into a glass-stoppered flask, several pieces of zinc sticks (Kahlbaum's) added and the solution made slightly acid with hydrochloric acid. The reaction was allowed to continue for several hours, acid being added from time to time. Too great an acid concentration, especially at the start, causes a too violent evolution of hydrogen and a consequent loss of the osmium tetroxide before reduction to a non-volatile compound has taken place. If the acid concentration is too low, there is a precipitation of basic salts of osmium, from which it is very difficult to reduce the osmium completely. To complete the reduction the solution was digested in the presence of an excess of zinc slightly below the boiling-point until no trace of color was observable. The acidity was then increased to dissolve the zinc completely and rapidly. The osmium metal was then filtered into a weighed Gooch crucible, ignited in a current of pure hydrogen and cooled in a stream of pure carbon dioxide. Duplicate results agreed within 0.2%.

The iodide method as described by Klobbie[4] and Krauss and Wilken[5] was modified as follows: 20 cc. of 2 *N* hydrochloric acid was heated to boiling, cooled in a current of carbon dioxide and to this was added one gram of potassium iodide dissolved in a few cc. of air-free water. To this solution was added a measured volume (2–10 cc.) of the stock tetroxide solution and the whole allowed to stand for three minutes. The solution was diluted to 200 cc. with air-free water and the liberated iodine titrated with standard thiosulfate solution. Unless these precautions are taken, the results are both high and variable due to the iodine liberated by the action of the oxygen of the air on the iodide. The addition of a few drops of a standard iodine solution enables the disappearance of the blue color of the starch to be determined several times with a given sample. Starch solution was added just before the end-point was reached. Usually from 4 to 6 end-points were determined on each of three samples. A strong light placed beneath the titration vessel aided materially in the determination of the end-point in the deeply colored solution.

The concentration of thiosulfate that seemed most satisfactory was approximately 0.025 *N* and the amounts of osmium solution taken were the equivalent of 8 to 15 cc. of the thiosulfate. The larger sample of tetroxide did not increase the precision of the titration because of the deeper color of the solution. The use of thiosulfate solutions as low in concentration as 0.01 *N* did not make it possible to obtain results of greater precision since the change in color with addition of thiosulfate was slow. The end-point correction for such solutions is comparatively large. Under the conditions described the average deviation of each end-point determination from the mean was about 0.25%.

Results of the Potentiometric, Gravimetric and Iodometric Determinations

Table I contains the results of the various determinations by the three methods. For the potentiometric process there was always used 2.005 cc.

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[4] Klobbie, *Chem. Centr.*, **11**, 65 (1898).

[5] Krauss and Wilken, *Z. anorg. Chem.*, **145**, 151 (1925).

of stock osmium solution, which varied from 0.005 to 0.05 mole per liter. The titration was made at 70° in a total volume of 35–45 cc.

Table I

Determinations of Octavalent Osmium by Potentiometric, Gravimetric and Iodometric Methods

Normality of acid	Hydrazine solution		Calcd. concn. of osmium soln., millimoles/liter		
	Millimoles per liter	Volume used, cc.	Potentiometric	Gravimetric	Iodometric
1.5	2.880	16.86, 16.88, 16.88, 16.93	24.32	...	24.26
1.5	2.880	16.76, 16.65, 16.73, 16.70	24.00	...	24.02
1.5	4.800	19.98, 20.15, 20.05	...	...	...
2.5	4.800	19.97, 19.98	47.94	....	47.82
1.5	2.880	16.48, 16.50	23.69	23.77	...
1.5	3.840	25.49, 25.43	...	...	...
2.5	3.840	25.41, 25.42	48.73	48.83	48.79
1.5	3.840[a]	12.41, 12.55, 12.57	23.96	...	23.80
1.5	0.960[b]	9.74, 9.76, 9.83	4.683	...	4.728
..	...	... ...	...	22.08	22.12

[a] The concentration of the hydrazine sulfate used to complete the titration was 0.960 millimole per liter.

[b] The concentration of the hydrazine sulfate used to complete the titration was 0.3840 millimole per liter.

From the above table it can be seen that the average difference between the results obtained by the potentiometric titration and those obtained by the gravimetric and iodometric methods is about 0.3%. The agreement of the hydrazine sulfate results among themselves is excellent, the average deviation of each volume required in titration from the mean volume being 0.04 cc.

Summary

A potentiometric method for the determination of octavalent osmium by reduction with hydrazine sulfate solution has been developed and a comparison of the results has been made with those obtained by modifications of the iodometric and gravimetric methods previously described. The accuracy of the method is estimated at 0.2–0.3%.

Pasadena, California