predominate. The difference between the frequency factors B measured in isocomposition media and those in isodielectric media was calculated by the equation of Amis and Cook.[2]

The r values used in the calculations of the difference between the critical increments and the difference between the frequency factors in the two kinds of media were identical. The r value obtained from the slope of the line log $k_{\kappa=0}$ *versus* $1/D$ was almost twice that used in the above calculations.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE INSTITUTE OF PHYSICAL CHEMISTRY AT CHARLES UNIVERSITY, PRAGUE, CZECHOSLOVAKIA]

The Polarographic Reduction of Osmium Tetroxide

BY W. R. CROWELL, J. HEYROVSKY[1] AND D. W. ENGELKEMEIR

The high valence state of osmium in osmium tetroxide and therefore the possibility of obtaining a comparatively large number of forms in its reduction renders a study of its polarographic reduction of particular interest. The purpose of the present paper was to conduct a study of the reduction of osmium tetroxide by use of the dropping mercury electrode with a view to determining how many steps are possible in this reduction, the identification of these steps, the conditions under which the compounds formed may be prepared, the approximate reduction potentials of the osmium couples involved and the analytical possibilities of such a process. The identification of the valence states of the various steps was accomplished by comparing the polarogram made with osmium tetroxide with that made with potassium osmate.

Preliminary experiments showed that it was not possible to conduct a polarographic reduction of osmium tetroxide or of quadrivalent osmium compounds in an acid solution because of the reduction of these compounds by mercury. Polarograms obtained in solutions of sodium, potassium, lithium and tetramethylammonium hydroxides did not show consistent and well-defined waves.[2] The best results were obtained with solutions of barium and calcium hydroxides. The curves shown in Figs. 2 and 3 were made by using saturated solutions of calcium hydroxide.

Experimental

Reagents.—A potassium hydroxide solution of osmium tetroxide and crystals of potassium osmate, $K_2OsO_4{\cdot}2H_2O$, were prepared according to the methods recently described by one of the authors.[3] The calcium hydroxide solution of osmium tetroxide was prepared by acidifying the potassium hydroxide solution of the tetroxide with sulfuric acid and distilling the tetroxide into a saturated solution of lime water. The osmate solution consisted of potassium osmate dissolved in saturated lime water in an amount not sufficient to cause appreciable precipitation of calcium osmate. The solutions were filtered through a sintered glass filter to free them from calcium carbonate and were stored in glass stoppered bottles. The nitrogen used in freeing the solutions from air was first passed through a hydrochloric acid solution of chromous chloride. The mercury was purified by passing through a nitric acid washing tower, drying and distilling *in vacuo*. All chemicals were of reagent grade.

Procedure.—The apparatus in the early stages of the work consisted of a standard model of the Heyrovsky polarograph, while that used in the last stages was essentially of the same type with some modification in its mechanical details. With the latter apparatus was used a standard Leeds and Northrop galvanometer with a figure of merit of 4.9×10^{-9} amp./mm./meter. The mercury capillary tube had a drop time of approximately three seconds. Nitrogen was bubbled through all solutions for thirty minutes before each run. Since it was found that even in the alkali solutions there was a small tendency for the mercury to react with the tetroxide, an apparatus of the type shown in Fig. 1 was used in which the anode and cathode compartments were separated by a short arm having a heavy 2-mm.-bore stopcock. The dropping mercury in the cathode compartment fell into a capillary tube, and was withdrawn from time to time in order to prevent overflowing from the capillary into the main body of the solutions. The stopcock between the two compartments was kept closed except during a run. The tetroxide solution previously freed from dissolved air was added to a saturated lime water solution by means of a Heyrovsky buret. The osmate solution, because of its instability, had to be prepared fresh for each run and was used in undiluted form. The anode consisted of mercury covered with a thin layer of mercuric oxide in contact with lime water saturated both with calcium hydroxide and mercuric oxide. The potential of this half cell at 25° has been shown by Samuelson and

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(1) War conditions within recent months have rendered communications with Dr. Heyrovsky impracticable, and therefore it has been necessary to carry out the final stages of this work and to write this article without the benefit of his collaboration.

(2) A portion of this part of the work was conducted by Mr. Frank J. Dolezal, a research student in chemistry at the University of California at Los Angeles.

(3) Wm. R. Crowell, Don M. Yost and John D. Roberts, THIS JOURNAL, **62**, 2176 (1940).

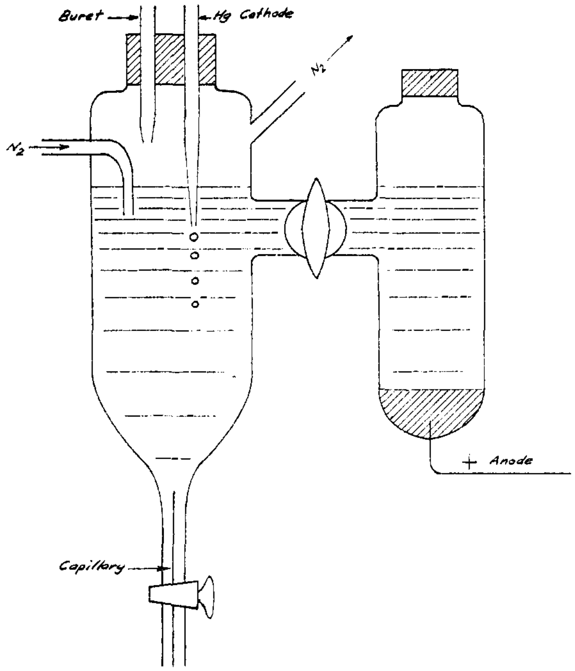


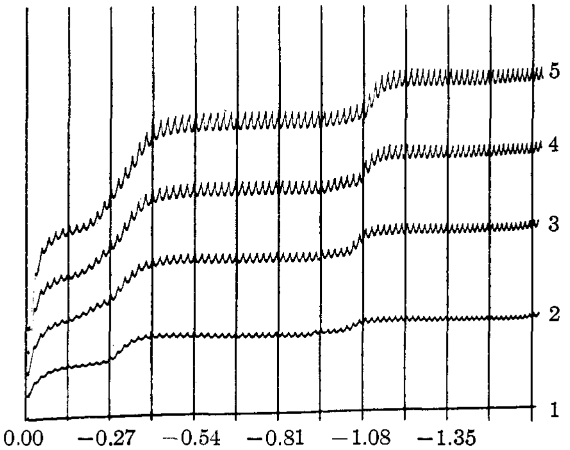
Fig. 1.—Apparatus for polarographic decomposition of osmium tetroxide.

Brown[4] to be −0.091 volt against the normal calomel electrode. The potential applied across the turns of the polarographic drum was measured by means of a Student Type Leeds and Northrop potentiometer before each run. The current was allowed to flow through the windings for thirty minutes before starting the first run in order to ensure its reaching a steady value. The potential drop per turn was kept at about 0.14 to 0.16 volt.

Results

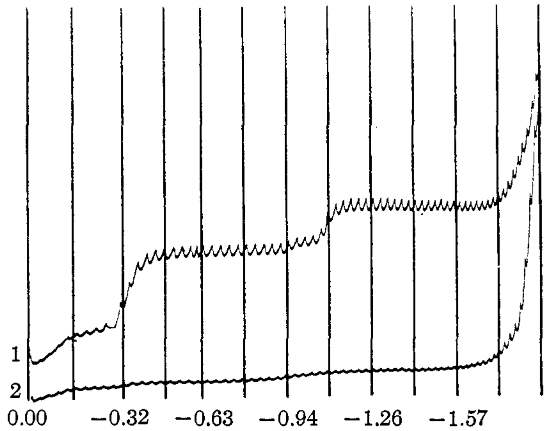
Figure 2 shows a series of polarograms obtained by use of a saturated lime water solution 0.0050 M in osmium tetroxide dropped in 0.70-ml. portions into 18 ml. of saturated lime water at 25°. In Fig. 3 is shown a polarogram made with a saturated lime water solution 6.1×10^{-4} M in potassium osmate at the same temperature. It will be noted in each figure that the galvanometer zero is shifted upward as each successive curve is recorded and therefore in comparing wave heights one should measure from the zero ordinates indicated.

Referring to Fig. 2, it will be noted that there are three clearly defined steps in the curves, that the first two steps are practically the same height and that the third step is one-half the height of the other two. In Fig. 3, on the other hand, there are two distinct steps which correspond both in potentials and in relative heights to steps two and three in Fig. 2. It is evident, then, that the state of oxidation of osmium at the beginning of step two in Fig. 2 is hexavalent, and that the first step is a reduction from the octavalent to the hexavalent form. Since the height of the second wave in Fig. 2 is the same as that of the first, the second step must be a reduction from the hexavalent to the quadrivalent state. Since the valence change in the last step must be one-half that of the other two, it follows that the reduction is from quadrivalent to trivalent. The couples involved in the three steps are probably the following



E, volts (potential of dropping electrode against mercuric oxide electrode).

Fig. 2.—Curves for saturated lime water solutions of osmium tetroxide: (1) lime water alone; (2) 1.9×10^{-4} M OsO_4; (3) 3.7×10^{-4} M OsO_4; (4) 5.4×10^{-4} M OsO_4; (5) 7.1×10^{-4} M OsO_4; sensitivity 1/30.



E, volts (potential of dropping electrode against mercuric oxide electrode).

Fig. 3.—Curves for saturated lime water solutions of potassium osmate: (1) lime water alone; (2) lime water 6.1×10^{-4} M in K_2OsO_4; sensitivity 1/30.

(1) $HOsO_5^- + 2\epsilon \longrightarrow OsO_4^{=} + OH^-$
(2) $OsO_4^{=} + 2H_2O + 2\epsilon \longrightarrow OsO_2 + 4OH^-$
(3) $2OsO_2 + H_2O + 2\epsilon \longrightarrow Os_2O_3 + 2OH^-$

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[4] Samuelson and Brown, THIS JOURNAL, **57**, 2711 (1935).

Heyrovsky and Ilkovic[5] have shown that the potential at the midpoint of the current–voltage wave, or the half-wave potential, is characteristic for the reaction involved and is usually independent of the concentration of the constituent reduced, the size of capillary, rate of dropping and sensitiveness of the galvanometer. Half-wave potentials were determined for reactions (2) and (3) from measurements made on several diagrams. Since the first waves in Fig. 2 start immediately from zero applied e. m. f., it is probable that the tetroxide oxidizes the mercury slightly to mercuric oxide in these solutions and therefore any measurements of the first half-wave in Fig. 2 would have little value. A noticeable irregularity in the first wave if the concentration of tetroxide is 0.01 *M* or above is evidence of this reaction. The slight negative current at the start of the run in the case of the osmate curve is probably due to the polarization of the mercury drop by traces of tetroxide which were so small that there was no appreciable reduction due to reaction with the mercury. The following values are averages of three measurements of half-wave potentials which agreed within 0.01 volt and are expressed against the normal calomel electrode according to the convention followed by Heyrovsky.[5]

	Reaction (2)	Reaction (3)
$HOsO_4^{=}$	−0.446 v.	−1.198 v.
K_2OsO_4	− .434 v.	−1.192 v.

A comparison of tetroxide and osmate concentration ratios with measured wave height ratios obtained from corresponding waves in polarograms such as those shown in Figs. 2 and 3 shows that it is practicable to determine osmium polarographically with an error of approximately 5%. By comparing the waves obtained with an unknown osmium solution with those obtained from known solutions of approximately the same osmium and calcium hydroxide concentrations, greater accuracy than this probably can be secured.

The data may be used for determining the conditions necessary in the preparation of calcium osmate, osmium dioxide and osmium trioxide. If a solution of the tetroxide is reduced, platinum electrodes probably should be used, but if the reduction is carried out with a solution of the osmate, the electrodes may be of mercury.

The authors wish to thank Mr. John Herman for his kindness in allowing them the use of his polarograph during the preliminary stages of the work.

Summary

A study of the polarographic reduction of osmium tetroxide in a saturated solution of calcium hydroxide at 25° shows that the c. v. curve consists of three distinct waves and that the three steps in the reduction probably correspond, respectively, to

$$HOsO_5^{-} \longrightarrow OsO_4^{=} + OH^{-}$$
$$OsO_4^{=} + 2H_2O \longrightarrow OsO_2 + 4OH^{-}$$
$$2OsO_2 + H_2O \longrightarrow Os_2O_3 + 2OH^{-}$$

The half-wave potentials of steps two and three are found to be −0.44 v. and −1.20 v., *vs.* the N. C. E. The half wave potential of step one is not included since this value is of little significance due to slight oxidation of the mercury by osmium tetroxide. A curve obtained with a saturated lime water solution of potassium osmate showed two waves corresponding to the last two found with the solutions of the tetroxide.

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PRAGUE, CZECHOSLOVAKIA
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[5] Heyrovsky and Ilkovic, *Collection Czechoslav. Chem. Communications*, **7**, 198–214 (1935).