made at a heating rate of 300° per hour. The tungstic acid first loses water to form tungsten trioxide. This reaction overlaps the stepwise reduction to metallic tungsten. The details of the reduction have been reported recently by Hegedus and co-workers.[8] The metallic tungsten is then relatively inert in the temperature range 780 to 920° after which it carburizes slowly to tungsten carbide over a period of 4.5 hours at 1025°. The slower reaction in the thermobalance crucible compared to the combustion boat is probably due to the deeper vessel and greater bed-depth in the former. This run was made with a sample of tungstic acid that gave a residue weight of 73.35% when fired in hydrogen. The following data were derived from the thermobalance curve: sample weight = 0.9000 g.; minimum weight = 0.6619 g., theory for W = 0.6602 g.; final weight = 0.7032 g., theory for WC = 0.7005 g. The product contained 6.21% C by analysis, and gave an X-ray diffraction pattern showing only WC.

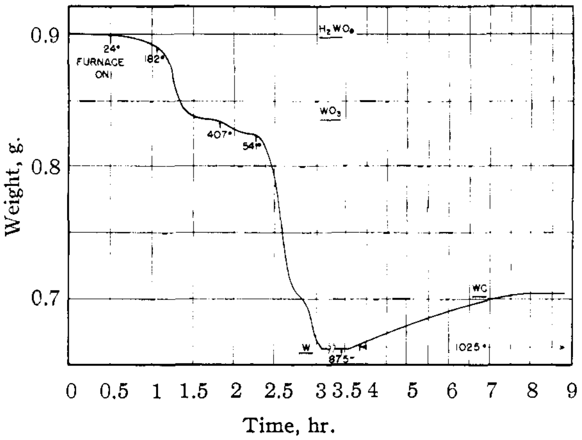

Fig. 1.—Thermobalance curve from heating H_2WO_4 in $H_2 + CH_4$.

Acknowledgment.—We wish to thank Drs. E. H. Winslow and E. L. Brady for helpful advice.

SCHENECTADY, N. Y.

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[8] A. J. Hegedus, T. Millner, J. Neugebauer and K. Sasvari, *Z. anorg. allgem. Chem.*, **281**, 64 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Polarographic Characteristics of Osmium. I. The +8 State

BY LOUIS MEITES

RECEIVED APRIL 6, 1957

Information is presented concerning the reduction of +8 osmium from a number of common supporting electrolytes at both dropping mercury electrodes and large stirred mercury electrodes.

Introduction

Osmium tetroxide is widely used both as a catalyst for oxidation–reduction titrations and as a powerful oxidizing agent in its own right for various purposes of organic chemistry. Though the elucidation and further development of such procedures would doubtless be greatly aided by a detailed understanding of the oxidation–reduction chemistry of osmium, and in spite of the growing interest in the analytical chemistry of the platinum metals, our present fund of information relating to the electrochemistry of the numerous oxidation states of osmium is exceedingly meagre. The present series will describe the results of a systematic effort to elucidate the oxidation–reduction equilibria which interrelate the oxidation states of this element in aqueous solutions, beginning in this paper with those processes which are involved in the reduction of +8 osmium.

The available information concerning the electrochemistry of osmium has been briefly summarized by Latimer.[1] Crowell, Heyrovsky and Engelkemeir[2] were the first to investigate the polarographic characteristics of osmium(VIII). They found it impossible to obtain polarograms in acid media because of the reduction of the osmium by their mercury pool "reference" electrode. Nor could they secure "consistent and well-defined" waves in solutions of lithium, sodium, potassium or tetramethylammonium hydroxide. In saturated (*ca.* 0.02 *M*) calcium hydroxide, however, they observed a well-defined triple wave which they attributed to stepwise reduction to the +6, +4 and +3 states on the basis of the relative heights of the waves.

Zuman[3] reported that osmium(VIII) in neutral or acidic media gives a wave which rises from zero applied e.m.f. and represents reduction to the +6 state. Kolthoff and Parry[4] found a double wave in an 0.5 *M* acetate buffer of *p*H 4.7 and attributed it to stepwise reduction to the +6 and +2 states. Breda, Meites, Reddy and West[5] secured no wave for osmium(VIII) in an 0.5 *M* malonate buffer, which doubtless merely reflects a rapid chemical reduction of osmium(VIII) by excess malonate.

Experimental

All polarograms were secured with an automatically recording polarograph designed and constructed by the author. The cell used was of the modified H-type[6] equipped with a sintered-Pyrex gas-dispersion cylinder to permit rapid de-

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[1] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., Second Edition, 1952, pp. 230–233.

[2] W. R. Crowell, J. Heyrovsky and D. W. Engelkemeir, THIS JOURNAL, **63**, 2888 (1941).

[3] P. Zuman, *Collection Czechoslov. Chem. Communs.*, **15**, 1107 (1950).

[4] I. M. Kolthoff and E. P. Parry, *Anal. Chem.*, **25**, 188 (1953).

[5] E. J. Breda, L. Meites, T. B. Reddy and P. W. West, *Anal. Chim. Acta*, **14**, 390 (1956).

[6] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

aeration.[7] Prepurified nitrogen was used for deaeration. All measurements were made at 25.0 ± 0.1°.

The potentiostat and current integrator were secured from Analytical Instruments, Inc., Bristol, Conn.; the operating characteristics of both have been described elsewhere.[8] The controlled potential electrolyses were carried out in a double-diaphragm cell with a conical working electrode compartment.[8]

Stock solutions of osmium(VIII) were prepared by dissolving weighed amounts of the reagent grade tetroxide in cold water and diluting to known volume. All other chemicals were ordinary reagent grade. Weights and volumetric apparatus were calibrated by standard techniques.

Data and Discussion

Strongly Alkaline Media.—Figure 1 shows tracings of typical polarograms of osmium(VIII) in sodium hydroxide solutions of various concentrations between 0.3 and 10 M. (Entirely similar phenomena are observed in solutions of potassium or lithium hydroxide.) If the sodium hydroxide concentration is either below about 0.5 M or above about 4 M the polarogram consists of three well-defined diffusion-controlled waves. The first of these always rises from zero applied e.m.f., showing that osmium(VIII) is spontaneously reduced by metallic mercury in these media. The half-wave potentials of the second and third waves are −0.61 ± 0.01 v. and −1.51 ± 0.02 v., respectively (all potentials are referred to the saturated calomel electrode) at any sodium hydroxide concentration above 1 M; but in 0.3 M sodium hydroxide they are slightly more negative (−0.74 v. and −1.57 v.). Both the second and third waves are irreversible, the third more so than the second, at all sodium hydroxide concentrations.

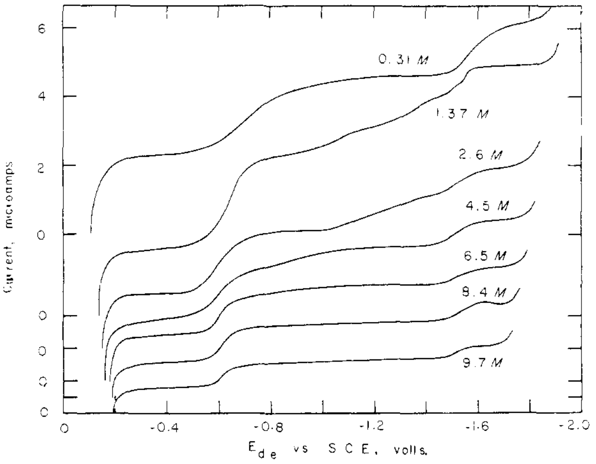

Fig. 1.—Polarograms of 0.43 mM osmium(VIII) in solutions containing various concentrations of sodium hydroxide. The zero-current line for each curve is indicated by the short line on the left-hand scale, and the corresponding concentration of sodium hydroxide is shown at the right.

The "1.37 M" curve in Fig. 1, which is typical of the polarograms secured at intermediate concentrations of alkali metal hydroxide in the absence of a maximum suppressor, evidently represents the difficulty encountered by Crowell, Heyrovsky and Engelkemeir[2] in their work with these media. The abnormal increase in current starting at about −0.8 v. is simply the "anomalous wave" discovered by Orlemann and Kolthoff.[9] This does not occur in dilute supporting electrolytes[9] (which is the reason why Crowell, Heyrovsky and Engelkemeir obtained better waves in saturated calcium hydroxide solutions), nor, apparently, at very high ionic strengths.[10] It is also eliminated by the addition of a maximum suppressor,[9] and in fact the addition of 0.005% Triton X-100 to a solution of osmium(VIII) in 1.4 M sodium hydroxide gave a polarogram essentially identical with the "0.31 M" curve in Fig. 1.

The heights of the successive waves in both dilute and concentrated sodium hydroxide media are in the ratio of 2:2:1, which appears to confirm the VIII → VI → IV → III scheme proposed by Crowell, Heyrovsky and Englekemeir.[2] Further support for this scheme is provided by the data of Table I, which demonstrate conclusively that two electrons are consumed in the reduction of each atom of osmium(VIII) on the plateau of the first wave, and that a reduction of osmium(VIII) on the plateau of the second wave consumes exactly four electrons. The final solutions of osmium(VI) and osmium(IV) were perfectly clear; the former were light pink, while the latter were a pure and fairly deep purple.

TABLE I

CONTROLLED POTENTIAL ELECTROLYSES OF OSMIUM(VIII) IN SODIUM HYDROXIDE MEDIA

5.052 ml. of 13.40 mM osmium(VIII) (= 0.0677 mmole) was added to 60–70 ml. of sodium hydroxide of the specified concentration

$E_{w.e.}$ vs. S.C.E., v.	[NaOH], M	Millifaradays consumed	Millifaradays/mmole (= n)
−0.35	0.10	0.1344	1.985
	0.30	.1360	2.009
	1.0	.1355	2.001
	3.7	.1351	1.996
	9.9	.1357	2.004
		Mean	1.999 ± 0.007
−1.00	0.10	0.2685	3.966
	0.30	.2708	4.000
	1.0	.2708	4.000
	3.7	.2717	4.013
	9.9	.2715	4.010
		Mean	3.998 ± 0.013

An especially interesting phenomenon was observed when a 1 mM solution of osmium(VI) in 1 M sodium hydroxide, which had been prepared by the reduction of osmium(VIII) at −0.35 v. *vs.* S.C.E., was re-electrolyzed at −1.00 v. *vs.* S.C.E. The initial pink color of the osmium(VI) changed rapidly toward purple; when about one faraday had been consumed per mole of osmium(VI), the solution was of an extremely intense bluish purple. As the electrolysis continued, this color faded and its bluish cast disappeared, and the flow of current finally ceased after the passage of the quantity of electricity expected for a two-electron reduction of

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[7] L. Meites and T. Meites, *Anal. Chem.*, **23**, 1194 (1951).

[8] L. Meites, *ibid.*, **27**, 1116 (1955).

[9] E. F. Orlemann and I. M. Kolthoff, THIS JOURNAL, **64**, 833 (1942).

[10] L. Meites, *ibid.*, **75**, 3809 (1953).

the osmium(VI) to osmium(IV). The formation and subsequent disappearance of the intermediate color may reflect nothing more than an "optical interaction"[11] between osmium(IV) and osmium(VI), or it may point to the transitory formation of osmium(V).

Conclusive evidence that the third wave corresponds to reduction to osmium(III) could not be obtained coulometrically, though the fact that the relative wave heights are independent of sodium hydroxide concentration leaves little doubt that this is the case. The reduction of osmium(VIII) at a large mercury electrode gives a relatively high residual current even when the electrode potential is as low as −1.50 v. *vs.* S.C.E. Following Page[12] and MacNevin and McIver,[13] an attempt was made to apply a correction for the residual current by assuming that it remained constant throughout the electrolysis. Actually, however, the current continued to decrease until long after the osmium must have been completely reduced, and consequently the calculated value of n increased steadily to a value well above 8. Probably the reduction of water at the large electrode is induced by the reduction of osmium to the +3 state.

The reduction of osmium(VIII) in sodium hydroxide solutions at potentials on the third wave yields a grayish solid which probably consists of hydrous osmium(III) oxide, for it dissolves readily in 4 M hydrochloric acid without visible evolution of hydrogen, and the color of the resulting solution is the characteristic light straw of the chloro-osmium(III) complex prepared by the direct electrolytic reduction of osmium(VIII) in 4 M hydrochloric acid.

The diffusion current constant ($I = i_d/Cm^{2/3}t^{1/6}$) of the first wave of osmium(VIII) is substantially independent of the sodium hydroxide concentration between about 1 and 5 M, and is equal to $3.1_9 \pm 0.2_1$. In 0.3 M sodium hydroxide it is 4.08 ± 0.13, and in concentrated media it decreases steadily to 1.32 ± 0.07 in 9.7 M sodium hydroxide. These changes reflect the changing viscosities of the solutions.

Mineral Acid Media.—As is shown in Fig. 2, a polarogram of osmium(VIII) in 7.3 M (43%) phosphoric acid consists of a single wave which rises from zero applied e.m.f. This is quite well-defined with very dilute osmium solutions, but its plateau becomes more and more irregular as the concentration of osmium is increased above about 0.1 mM. The diffusion current constant is 6.4 ± 0.2, which is considerably lower than the values secured in other mineral acid media because of the relatively high viscosity of the phosphoric acid. The final current rise begins at a considerably more positive potential in the presence of osmium than in its absence.

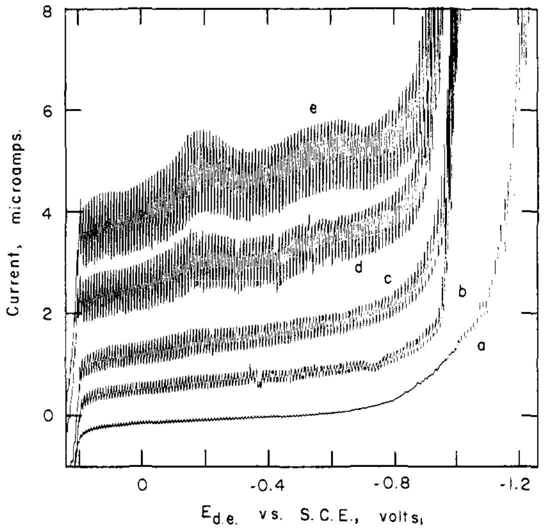

Fig. 2.—Polarograms of (a) 0, (b) 0.0425, (c) 0.0823, (d) 0.1554 and (e) 0.220 mM osmium(VIII) in 7.3 M phosphoric acid.

Polarograms of very dilute solutions of osmium(VIII) in 0.5 M sulfuric acid are virtually identical with curves a and b of Fig. 2, but the distortion of the plateau at osmium concentrations above 0.1 mM is much more severe in sulfuric than in phosphoric acid. The diffusion current constant, measured at 0 v. *vs.* S.C.E., is 8.5 ± 0.4. In the presence of 0.002% Triton X-100, a polarogram of osmium(VIII) in 0.5 M sulfuric acid consists of two waves. The first rises from zero applied e.m.f., is fairly well-defined, and has a diffusion current constant of 8.0 ± 0.2, virtually the same as that of the single wave secured in the absence of the maximum suppressor. The second wave is very irreversible and has a small rounded maximum. Its half-wave potential is −0.39 ± 0.02 v., and its height is very nearly half that of the first wave. Controlled-potential electrolyses of solutions of osmium(VIII) in 0.5 M sulfuric acid give the same product over the entire accessible range of potentials, and it is therefore doubtful that this second wave has any genuine chemical significance.

Figure 3 shows some typical polarograms of osmium(VIII) in 1 M hydrochloric acid. The height of the first wave is proportional to both $m^{2/3}t^{1/6}$ and the concentration of osmium, and its diffusion current constant is 9.59 ± 0.04 in 1 M, 9.47 ± 0.11 in 4 M, and 11.8 ± 0.5 in 12 M hydrochloric acid. In 12 M hydrochloric acid osmium(VIII) is rather rapidly reduced by chloride ion, so that the higher diffusion current constant in this medium may simply reflect a difference between the diffusion coefficients of osmium tetroxide and chlorine.

The height of the plateau at −0.55 v., on the other hand, increases rapidly with increasing osmium(VIII) concentration and is proportional not to $m^{2/3}t^{1/6}$ but to the height of the column of mercury above the capillary tip (*i.e.*, to $1/t$). These are the accepted criteria for an adsorption wave. Saturating the solution with ammonium chloride results in a slight improvement in the shape of the first wave but causes an enormous increase in the height of the maximum at −0.7 v. The adsorption wave in 1 M hydrochloric acid is eliminated by adding 0.002% Triton X-100 and increasing the

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(11) J. E. Whitney and N. Davidson, THIS JOURNAL, **71**, 3809 (1949).

(12) J. A. Page, Ph.D. Thesis, Harvard University, 1954.

(13) W. M. MacNevin and R. D. McIver, *Anal. Chem.*, **27**, 1994 (1955).

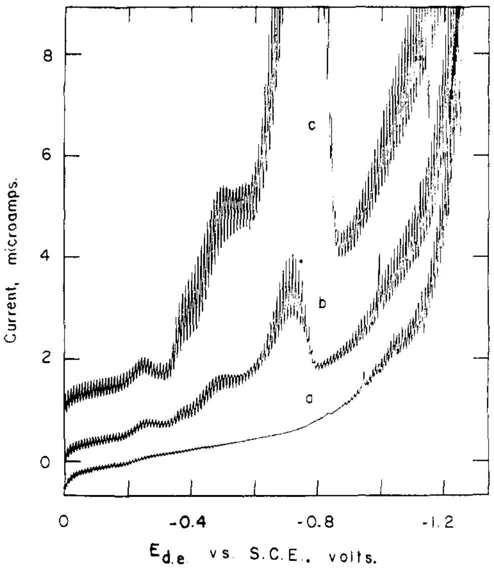

Fig. 3.—Polarograms of (a) 0, (b) 0.0216 and (c) 0.0630 m*M* osmium(VIII) in 1 *M* hydrochloric acid.

drop time to 5 sec.: under these conditions the first wave is very well-defined, but the maximum which follows it is unaffected. In 4–12 *M* hydrochloric acid this maximum merges with the final current rise due to the reduction of hydrogen ion.

In 1 *M* perchloric acid the polarogram of osmium(VIII) is nearly the same as in 1 *M* hydrochloric acid. The first wave is again diffusion-controlled and is very well-defined even in the absence of a maximum suppressor. Its diffusion current is 10.0 ± 0.2. In this medium the half-wave potential of the second (adsorption) wave changes from -0.43 to -0.47 v. as the osmium concentration is increased from 0.07 to 0.2 m*M*.

In all of these media the reduction of osmium(VIII) at a large mercury cathode whose potential is kept constant at a value on the plateau of the first wave consumes 5 faradays per mole, and therefore proceeds directly to the +3 state. The product of such a reduction in phosphoric, sulfuric or perchloric acid is brown colloidal hydrous osmium(III) oxide, but in 4 or 12 *M* hydrochloric acid the reduced solutions are perfectly clear and light straw in color, evidently because of the formation of a chloro-complex ion such as $OsCl_6^{=}$. This ion is also the principal product of a similar reduction in 1 *M* hydrochloric acid, but in that case the appearance of a small brownish turbidity shows that some of the hydrous oxide is formed as well. When suspensions of the hydrous osmium(III) oxide in phosphoric, sulfuric or perchloric acid media were further electrolyzed at more negative potentials, visible evolution of hydrogen generally began at about -0.5 v. *vs.* S.C.E. Prolonged electrolyses at potentials more negative than this resulted in the slow conversion of the brown hydrous oxide into a light gray material which is believed to be the same compound of osmium(II) obtained in pyridine solutions.

None of these media is well suited to the coulometric determination of osmium by controlled-potential electrolysis at a mercury cathode. In the phosphoric, sulfuric and perchloric acid media metallic mercury reacts rapidly with osmium(VIII) to give a black solid which is very difficult to reduce electrolytically; in dilute hydrochloric acid calomel is formed by a similar reaction; and in strong hydrochloric acid it is impossible to prevent loss of chlorine into the stream of nitrogen used for deaeration.

Solutions of Organic Acids.—Polarograms of osmium(VIII) in saturated tartaric acid (Fig. 4) consist of three waves, the third of which begins at -0.7 v. and is due to the catalytic evolution of hydrogen. The first rises from zero applied e.m.f. and has a diffusion current constant of 4.41 ± 0.14, which cannot be directly compared with values secured in other media because of the high viscosity of this supporting electrolyte. The half-wave potential of the second wave, which is quite poorly defined, is -0.408 ± 0.006 v. and its diffusion current constant is 5.5 ± 0.2, which is exactly $^{5}/_{4}$ of that for the first wave. The ratio of these wave heights indicates that the reduction scheme involves the stepwise formation of the +4 and +3 states, and this is confirmed by coulometric experiments. The reduction product at potentials on the plateau of the first wave is a greenish precipitate, probably hydrous osmium(IV) oxide.

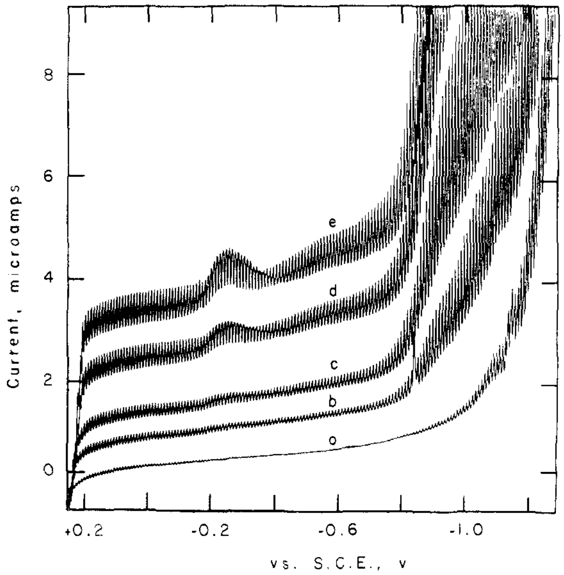

Fig. 4.—Polarograms of (a) 0, (b) 0.0515, (c) 0.0987, (d) 0.185 and (e) 0.260 m*M* osmium(VIII) in saturated tartaric acid.

Osmium(VIII) is reduced slowly by citric acid, and consequently detailed information concerning the polarography of osmium(VIII) in saturated citric acid cannot be secured. Only a single wave is obtained; in view of the relative acidities of tartaric and citric acids, it no doubt represents the same direct reduction to osmium(III) observed in mineral acid media.

Weakly Acidic Buffers.—Figure 5 shows some typical polarograms of osmium(VIII) in a buffer containing 0.1 *M* pyridine and 0.1 *M* pyridinium ion, and having a *p*H of about 5.4. They consist of four waves. The first rises from zero applied e.m.f., has a diffusion current constant of 3.94 ± 0.04 (virtually the same as that for the first two-electron wave in 0.3 *M* sodium hydroxide), and represents a reduction to osmium(VI). This is very nearly the lowest *p*H at which osmium(VI) can be formed by the reduction of osmium(VIII) at a mercury cathode. The half-wave potential of the second wave is −0.078 ± 0.001 v., its diffusion current constant is 6.79 ± 0.07, and it represents reduction to osmium(IV). The third wave, which, like the second, is irreversible, has a half-wave potential of −0.619 ± 0.005 v. and a diffusion current constant of 7.94 ± 0.06, and it corresponds to a five-electron reduction to osmium(III). The fourth wave is distorted by an enormous maximum, especially at higher osmium concentrations, which is unaffected by maximum suppressors, and consequently its plateau is very short. However, measurements with very dilute (0.005–0.03 m*M*) solutions of osmium(VIII) show that the total height of this wave is just 1.5 ± 0.2 times that of the total second wave, indicating that this fourth wave represents a six-electron reduction to the +2 state. Controlled-potential electrolyses at potentials on this wave gave a light grey precipitate which was probably hydrous osmium(II) oxide.

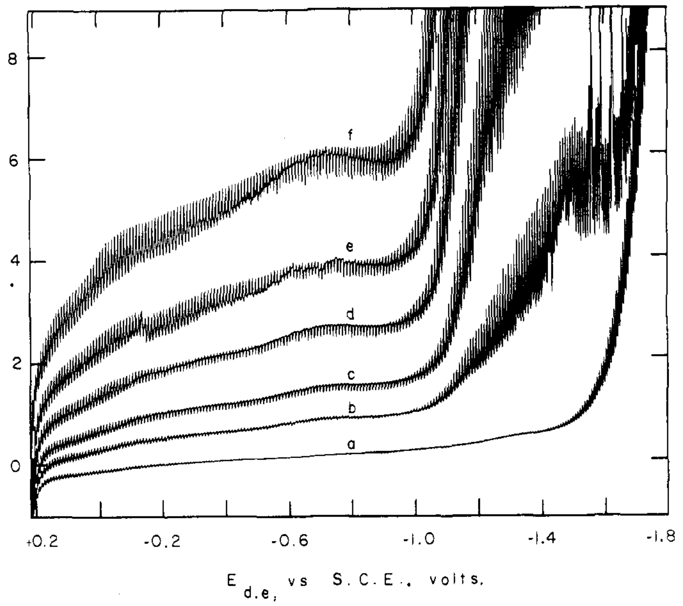

Fig. 6.—Polarograms of (a) 0, (b) 0.0259, (c) 0.0506, (d) 0.0979, (e) 0.163 and (f) 0.257 m*M* osmium(VIII) in 1 *M* acetic acid–1 *M* sodium acetate.

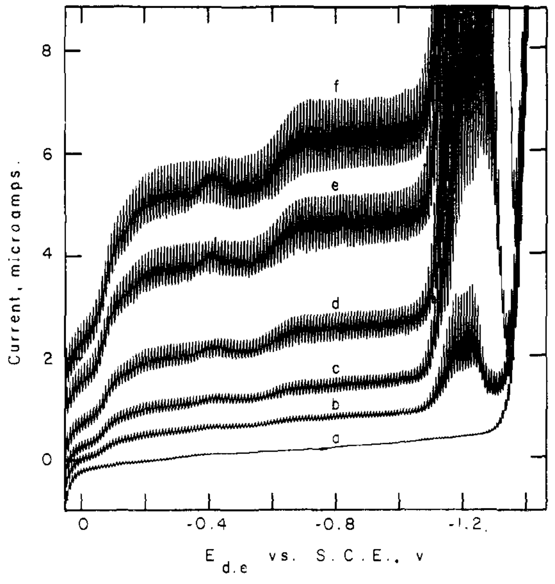

Fig. 5.—Polarograms of (a) 0, (b) 0.0259, (c) 0.0506, (d) 0.0979, (e) 0.184 and (f) 0.258 m*M* osmium(VIII) in 0.1 *M* pyridine–0.1 *M* pyridinium chloride.

Kolthoff and Parry[4] reported that a polarogram of osmium(VIII) in an acetate buffer of *p*H 4.7 consisted of two waves, the first of which rose from zero applied e.m.f. and represented reduction to osmium(VI), while the second, at $E_{1/2}$ = + 0.1 v., represented reduction to osmium(II). This has not been possible to confirm. A typical polarogram of osmium(VIII) in an acetate buffer of this *p*H, shown in Fig. 6, actually consists of four waves. The first rises from zero applied e.m.f. and represents reduction to osmium(VI), while the second, at $E_{1/2}$ = ± 0.0 v. represents reduction to osmium(IV). The third, at $E_{1/2}$ = −0.45 v., is better defined than either of these. Its diffusion current constant is 8.6 ± 0.3, virtually equal to the mean of the values obtained for five-electron waves in other media, and so it must represent reduction to osmium(III). This was confirmed coulometrically. The fourth wave, $E_{1/2}$ = −1.3 v., is primarily due to the catalytic evolution of hydrogen.

Ammoniacal Ammonium Chloride Media.—Figure 7 shows some typical polarograms of osmium(VIII) in 1 *M* ammonia–0.1 *M* ammonium chloride. These consist of three well-defined waves.

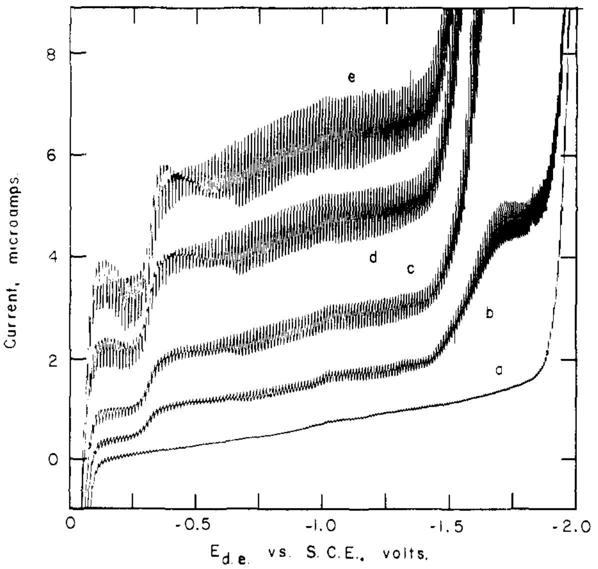

Fig. 7.—Polarograms of (a) 0, (b) 0.0506, (c) 0.0980, (d) 0.183 and (e) 0.274 m*M* osmium(VIII) in 1 *M* ammonia–0.1 *M* ammonium chloride.

The first rises from zero applied e.m.f.; the half-wave potentials of the second and third are −0.318 ± 0.002 and −1.58 ± 0.01 v., respectively. The third wave is much too high to correspond even to an eight-electron reduction of the osmium, and its height increases abnormally rapidly with increasing osmium concentration. It is therefore believed to be a catalytic hydrogen wave.

In 1 *M* ammonia–0.1 *M* ammonium chloride the diffusion current constant of the total second wave is 8.17 ± 0.15; in 1 *M* ammonia–1 *M* ammonium chloride it is 7.81 ± 0.26. Both of these values are definitely lower than the average value (9.4 ± 0.4) found for the five-electron reductions which occur in dilute mineral acid media. By coulometry at controlled potential it was found that in 1 *M* ammonia–0.1 *M* ammonium chloride 4.82 ± 0.03 faradays are required for the reduction of each mole of osmium(VIII); the corresponding figure for 1 *M* ammonia–1 *M* ammonium chloride is 4.59 ± 0.02 faradays/mole. These values are almost exactly proportional to the corresponding values of *I*. The reduction product is a yellowish-brown precipitate in 1 *M* ammonia–0.1 *M* ammonium chloride, but a brownish-yellow colloidal suspension in 1 *M* ammonia–1 ammonium chloride.

The half-wave potential of the second wave is −0.241 ± 0.001 v. in 1 *M* ammonia–1 *M* ammonium chloride, −0.272 ± 0.003 v. in 0.1 *M* ammonia –0.1 *M* ammonium chloride, and −0.220 ± 0.004 v. in 0.1 *M* ammonia–1 *M* ammonium chloride. Consequently $\Delta E_{1/2}/\Delta p\mathrm{H} = -65 \pm 13$ mv., and $\Delta E_{1/2}/\Delta \log[\mathrm{NH_3}] = +31$ mv. The interpretation of these data is complicated by both the irreversibility of the wave and the slow chemical reaction of osmium(VIII) with ammonia[14] which involves the formation of osmiamates and also, at least on warming, some reduction of the osmium. This is probably the cause of the non-integral values of *n* obtained in the coulometric experiments.

Cyanide Media.—The addition of osmium(VIII) to 0.1 or 1 *M* solutions of potassium cyanide results in an almost immediate reduction of the osmium to the +6 state, probably as $K_2(OsO_2)(CN)_4$.[15] Polarograms of the resulting solutions in 0.1 *M* cyanide consist of two well-defined diffusion-controlled waves. The diffusion current constant of the first, which rises from zero applied e.m.f., is 5.3 ± 0.1; that of the second, for which $E_{1/2} = -0.81 \pm 0.01$ v., is 7.0 ± 0.2. The latter value is very nearly $^4/_5$ of the average diffusion current constant for a five-electron reduction in dilute mineral acid media, and it is exactly $^4/_3$ of the diffusion current constant of the first wave. These observations suggest that the first wave corresponds to a three-electron reduction, and the second to a four-electron reduction, of the osmium(VI). This is confirmed by the data shown in Table II.

TABLE II

CONTROLLED-POTENTIAL ELECTROLYSES OF OSMIUM(VI) IN POTASSIUM CYANIDE MEDIA

[KCN], *M*	$E_{\text{w.e.}}$, v. *vs.* S.C.E.	Mmoles Os taken	Millifaradays consumed	Millifaradays/ mmole (= *n*)
0.1	−0.62	0.0664	0.1989	2.995
		.0801	.2413	3.013
			Mean:	3.004 ± 0.009
	−1.00	.0664	.2660	4.006
			.2654	3.997
1.0		.01336	.0535	4.005
		.0401	.1599	3.987
		.0664	.2660	4.006
			.2655	3.999
		.0801	.3205	4.001
			Mean:	4.000 ± 0.005

The solutions of the osmium(II) cyanide complex prepared by controlled-potential electrolyses at potentials on the plateau of the second wave were bright yellow, as was the solid $K_4Os(CN)_6 \cdot 3H_2O$ prepared by Martius,[16] and in either 0.1 or 1 *M* potassium cyanide were perfectly clear up to at least 5 m*M*. Though apparently stable indefinitely under nitrogen, they underwent rapid oxidation when exposed to the air. From this air-oxidation, as from either the electrolytic oxidation of osmium(II) or the electrolytic reduction of osmium(VI) in 0.1 *M* cyanide solutions at electrode potentials near −0.6 v., there resulted an intensely blue solution which was stable toward further oxidation by air. These solutions contain a cyanide complex of osmium(III), whose formation is apparently facilitated by the presence of excess cyanide, for Martius[16] was unable to oxidize solutions of pure potassium osmium(II) cyanide with any of a number of chemical oxidizing agents.

Solutions of the osmium(III) cyanide complex in 0.1 *M* potassium cyanide prepared by the controlled-potential reduction of osmium(VI) give a single cathodic wave which is identical with the second wave of osmium(VI), and which represents reduction to the +2 state. This wave is nearly but not quite reversible, for $E_{3/4} - E_{1/4} = -69 \pm 5$ mv., regardless of whether the osmium is originally present in the +6 or the +3 state. Solutions of the osmium(II) complex in 0.1 *M* cyanide give an anodic wave ($E_{1/2} = -0.74 \pm 0.02$ v. *vs.* S.C.E., $I = -1.6 \pm 0.1$) which corresponds to re-oxidation to the +3 state. The wave is not well-defined, for it merges with the anodic cyanide wave. Willis' failure to observe an anodic wave for the oxidation of osmium(II) (as $Os(CN)_6^{-4}$) in cyanide media[17] is due to the fact that in the 1 *M* cyanide medium he employed the wave is still more irreversible and even less well-defined. In 1 *M* cyanide the cathodic wave of osmium(III) and the second wave of osmium(VI) have half-wave potentials of −0.98 ± 0.02v.

Other Media.—Both saturated hydrazine dihydrochloride and potassium thiocyanate slowly reduce osmium(VIII). Solutions prepared by adding osmium(VIII) to either of these supporting electrolytes give waves rising from zero applied e.m.f., but the actual oxidation state of the osmium is unknown and dependent on the age of the mixture, so that the data obtained are certainly irrelevant to the electrochemistry of osmium(VIII).

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[14] (a) C. Claus and Jacoby, *J. prakt. Chem.*, **90**, 93 (1863); (b) J. Fritsche and H. Struve, *ibid.*, **41**, 107 (1847).

[15] F. Krauss and G. Schrader, *ibid.*, [2] **120**, 36 (1929).

[16] C. A. Martius, *Lieb. Ann.*, **117**, 362 (1861).

[17] J. B. Willis, THIS JOURNAL, **67**, 547 (1945).

Summary.—Strongly acidic solutions of osmium(VIII) are reduced directly to the +3 state at dropping mercury electrodes. Less strongly acidic solutions give an additional wave, corresponding to the intermediate formation of osmium(IV). At *p*H values above about 5, there is also a third wave representing the formation of osmium(VI). Data are given for the half-wave potentials and diffusion current constants of these waves under a wide variety of conditions.

In cyanide media osmium is chemically reduced to the +6 state, and polarograms of the resulting solutions show two waves attributed to the reduction scheme VI → III → II. The polarographic characteristics of osmium(II) and (III) in cyanide media are briefly discussed. Cyanide media are better suited than any others yet investigated for the determination of osmium by polarography or coulometry at controlled potential.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Mechanism of Chemisorption: Benzene and Cyclohexane on Nickel, and the Catalytic Hydrogenation of Benzene

BY P. W. SELWOOD

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Magnetization–volume adsorption isotherms have been obtained for benzene and for cyclohexane on nickel–silica catalysts up to 150°. Results also have been obtained for hydrogen admitted over pre-adsorbed benzene or cyclohexane, and *vice versa*. Benzene and cyclohexane are chemisorbed on nickel by a minimum six and eight site attachment, respectively. Chemisorbed benzene must be desorbed before hydrogenation. Hydrogenation from the vapor phase or van der Waals phase may be observed down to about −25°. Hydrogen chemisorbed with a heat of adsorption of less than about 12 kcal. per mole is removable by benzene at room temperature. The participation of d-electrons in a functioning catalyst has been demonstrated by direct observation of magnetization changes attendant on the removal of chemisorbed hydrogen from a nickel surface by benzene molecules from the van der Waals phase.

Introduction

The purpose of this work was to extend our studies of surface reactions through use of the changes of magnetization which occur when gases are chemisorbed on finely divided nickel.[1] The systems studied were benzene, cyclohexane, and several combinations of benzene or cyclohexane with hydrogen. The adsorbent was nickel–silica catalyst.

Experimental

Magnetization–volume isotherms, and magnetizations as a function of time, were obtained on the volumetric adsorption apparatus and low frequency a.c. permeameter previously described.[2] Considerable improvement in convenience and precision was gained by placing the secondaries coaxial along the axis of the primary solenoid which was enlarged to 5100 turns. This arrangement made it possible to reduce the samples and to make measurements at any desired temperature without disturbing the relation between sample and secondaries. Convenience also was improved by placing an automatic Toepler pump in the gas handling system and a Varian G-10 (10 mv.) recorder after the Hewlett–Packard 400-D millivoltmeter in the electrical circuit. The primary was operated at 0.76 amp. stabilized 60 cycle a.c. at about 200 v. The secondary e.m.f. for a typical reduced sample at room temperature averaged about 5 to 10 mv. The zero reading in the absence of any sample was less than 0.1 mv. and was highly reproducible. The sensitivity of this device is such that the chemisorption of 0.01 cc. of hydrogen per g. of nickel in about 5 g. of catalyst produces a perceptible change of secondary e.m.f. Additional precision, if needed, could be obtained by improvement of temperature control in the sample, and by increased stabilization of primary current, and of back e.m.f. used to extend the zero in the recorder circuit.

Catalyst samples were either a Universal Oil Products Co. nickel–kieselguhr containing 52.8% Ni, or a coprecipitated nickel–silica containing 37.5% Ni. Details concerning these catalysts, which are referred to below as "U.O.P." or as "coppt.," respectively, were given in earlier papers.[2,3] Reductions were performed *in situ* for 12 hr. at 360° in flowing hydrogen, followed by evacuation at 10^{-6} mm. for 2 hr., and cooling *in vacuo* to the temperature of measurement. All isotherms were run in about 0.05 mm. of helium, to promote heat transfer. Measurements were made on 6 to 8-g. samples, in a dead space as determined with helium of about 10 cc. (S.C.).

Electrolytic hydrogen was purified by a Deoxo unit, followed by silica gel at −196°. Helium was passed over copper–asbestos at 600° and then over silica gel at −196°. Cyclohexane was Fisher Reagent Grade. Benzene was a specially purified sample obtained through the courtesy of Dr. W. Keith Hall of the Mellon Institute. Benzene and cyclohexane were introduced to the catalyst as required from a 500-cc. reservoir at a maximum pressure of 60 mm. The pressure of these two vapors over the catalyst samples was always a small fraction of a mm. except for those measurements made at 150°.

Some further details of procedure are given below.

Results

All gas volumes taken up are given as cc. (S.C.) of gas or vapor per g. of nickel. It will be understood that for benzene and cyclohexane considerable quantities are physically adsorbed by the silica support.

Figure 1 shows magnetization–volume isotherms at 25° on U.O.P. catalyst. Three situations are represented: (1) hydrogen on the bare surface; (2) benzene on the bare surface (after re-evacuation at 360°); and (3) hydrogen on the surface which is already covered, in part, to the extent of 5.3 cc. (S.C.) of benzene vapor per g. of nickel. Results with a sample of copptd. catalyst were strictly comparable with those shown except that the volume of hydrogen adsorbed on the bare surface to 1 atm. pressure is somewhat greater.

In our first work with the Faraday balance[1] we failed to observe any effect of benzene on the magnetization of nickel. This failure is seen now to

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(1) P. W. Selwood, T. R. Phillips and S. Adler, THIS JOURNAL, **76**, 2281 (1954).

(2) P. W. Selwood, *ibid.*, **78**, 3893 (1956).

(3) P. W. Selwood, *ibid.*, **79**, 3346 (1957).