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

The Formal Potential of the Bromoperosmite-Bromoösmate Electrode in Hydrobromic Acid Solutions

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The present paper reports results of measurements at 25° of the formal potential of the bromoperosmite--bromoösmate half cell in solutions of hydrobromic acid, using types of cell

$$\mathrm{Pt}\left\{\begin{matrix}\mathrm{K_3OSBr_6}(C_1f)\\ \mathrm{K_2OSBr_6}(C_2f)\\ \mathrm{HBr}(C_3f)\end{matrix}\right\}, \mathrm{HBr}(C_3f), \mathrm{H_2}(p\ \mathrm{atm}) + \mathrm{Pt}\quad \text{(Type II)}$$

$$\mathrm{Pt}\left\{\begin{matrix}\mathrm{K_3OSBr_6}(C_1f)\\ \mathrm{K_2OsBr_6}(C_2f)\\ \mathrm{HBr}(C_3f)\end{matrix}\right\}, \mathrm{HBr}(C_3f), \mathrm{Hg_2Br_2}(s), \mathrm{Hg}(l)\quad \text{(Type I)}$$

The solutions were approximately 1 to 4 weight formal in hydrobromic acid and 0.02 to 0.002 weight formal in total osmium concentration. Measurements in solutions less than 1 *f* in hydrobromic acid were not attempted because even at this acid concentration it was not found practicable to obtain satisfactorily reproducible results. Measurements in acid solutions more concentrated than 4 *f* were not made because of the uncertainty in the hydrobromic acid activity coefficient data obtained by graphical methods in the region from 3 to 6 *f*.

Experimental

Reagents.—The potassium bromoösmate was obtained by repeated treatments of pure potassium osmate ($K_2OsO_4 \cdot 2H_2O$) crystals with 48% hydrobromic acid and evaporation of the excess acid. The potassium osmate was prepared from osmium metal as described by Crowell, Yost and Roberts.[1]

The potassium bromoperosmite was prepared from the bromoösmate by electrolytic reduction of its hydrobromic acid solution by the method of Crowell, Brinton and Evenson.[2]

The hydrobromic acid was prepared from three times recrystallized potassium bromide by distillation with 95% sulfuric acid, redistillation of the product and retention of the middle fraction.

The chromous chloride was prepared from a 0.3 *M* solution of chromic chloride 1 *N* in hydrochloric acid by reduction with amalgamated zinc in a Jones reductor.

The carbon dioxide whose source was commercial Dry Ice was purified by passing the gas successively through a solution of chromic acid, a glass wool filter, a hydrochloric acid solution of chromous chloride and finally through a hydrobromic acid trap containing the same concentration of acid as that in the cell.

The hydrogen was obtained from a tank of electrolytic hydrogen and was washed by successive passage through the hydrochloric acid solution of chromous chloride, and through a bubbler containing hydrobromic acid of the same concentration as that in the cell.

Experimental Procedures.—Figure 1 shows a diagrammatic sketch of the all glass cell and electrolytic reduction apparatus including the hydrogen half cell. Four and 5 represent the cathode and anode compartments of the electrolytic cell with a platinum gauze cathode in 4 and a carbon anode in 5. Air is removed and the solution mixed by a current of carbon dioxide entering through 7. A hydrobromic acid solution of the bromoösmate of known concentration is introduced into the cell and a current of about 17 milliamperes allowed to flow. For this current about 12 volts are required. After the desired proportion of trivalent and quadrivalent osmium is obtained, the solution is made to flow into the osmium couple electrode compartment A which in turn makes connection with the hydrogen electrode by means of the stopcock B. Voltage measurements are made by means of a Leeds and Northrup Type K potentiometer which was standardized by use of a Weston cell previously checked by the Bureau of Standards. A portion of the osmium solution is removed by means of a 10-ml. pipet 6 and by use of the glass joint at 8 it is added to the potentiometric titration beaker where the solution is titrated for quadrivalent osmium with chromous chloride solution. Since the total osmium concentration of the solution before reduction is known, the concentration of the trivalent form may then be calculated.

Figure 2 shows a diagrammatic sketch of the potentiometric titration apparatus. The titration beaker 6 is kept free from air by a continuous current of carbon dioxide which may enter at either of the two points indicated. The boiling flask 2 can be used to introduce and deaerate standard solutions or after removal of the glass stopper it can serve as a water bubbler in the titration of the electrode solutions. The osmium solution enters the titration beaker by means of the glass joint already mentioned and which is located at 5. The buret 1 contains a hydrochloric acid solution of approximately 0.02 *N* chromous chloride prepared by dilution of the 0.3 *M* solution. Sealed to the top of the buret is a glass bulb filled with nitrogen at a pressure slightly greater than one atmosphere. The chromous chloride is stored in a five-liter flask under nitrogen at about 10 pounds gage pressure and is introduced into the buret through the side arm shown. Air free wash water may be added at the point indicated H_2O to rinse out either the boiling flask or the left-hand capillary tube. A normal calomel electrode is located at 4. At 3 is a mercury-sealed glass stirrer, at 7 is a mercury seal, and at the left of the stirrer is a platinum electrode.

In the earlier work, the couple potentials were determined by use of a mercurous bromide electrode. The electrolytic reduction cell and the osmium couple cell were separate units independent of each other and maintained air free by the passage of carbon dioxide. A known volume of the hydrobromic acid solution of the bromoosmate was added to the osmium couple compartment by means of a glass tube which formed a part of the apparatus. After deaeration a known volume of the hydrobromic acid solution of the bromoperosmite was pipetted into the bromoösmate solution, the two solutions mixed and the tube sealed off. When the cell measurements were completed the seal was broken and two samples of the osmium solution removed. The first sample was titrated immediately with chromous chloride in order to determine the bromoösmate. After addition of concentrated hydrobromic acid and oxidation of the trivalent osmium with bromine, the second sample was titrated for total osmium. The mercurous bromide electrode was prepared and its potentials determined as described by Mertes, Crowell and Burke.[3]

All cell measurements were made in a water thermostat at 25 ± 0.02°. The chromous chloride is standardized with recrystallized potassium ferricyanide as follows. About 10 ml. of an approximately 0.05 *M* solution of the ferricyanide is pipetted into the boiler of the potentiometric titration apparatus and 2 ml. of a saturated solution of sodium bicarbonate added. While a current of carbon dioxide is passed through the mixture it is boiled for about three minutes. The cooled solution is then transferred

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(1) Crowell, Yost and Roberts, THIS JOURNAL, **62**, 2176 (1940).

(2) Crowell, Brinton and Evenson, *ibid.*, **60**, 1105 (1938).

(3) Mertes, Crowell and Burke, *ibid.*, **64**, 3021 (1942).

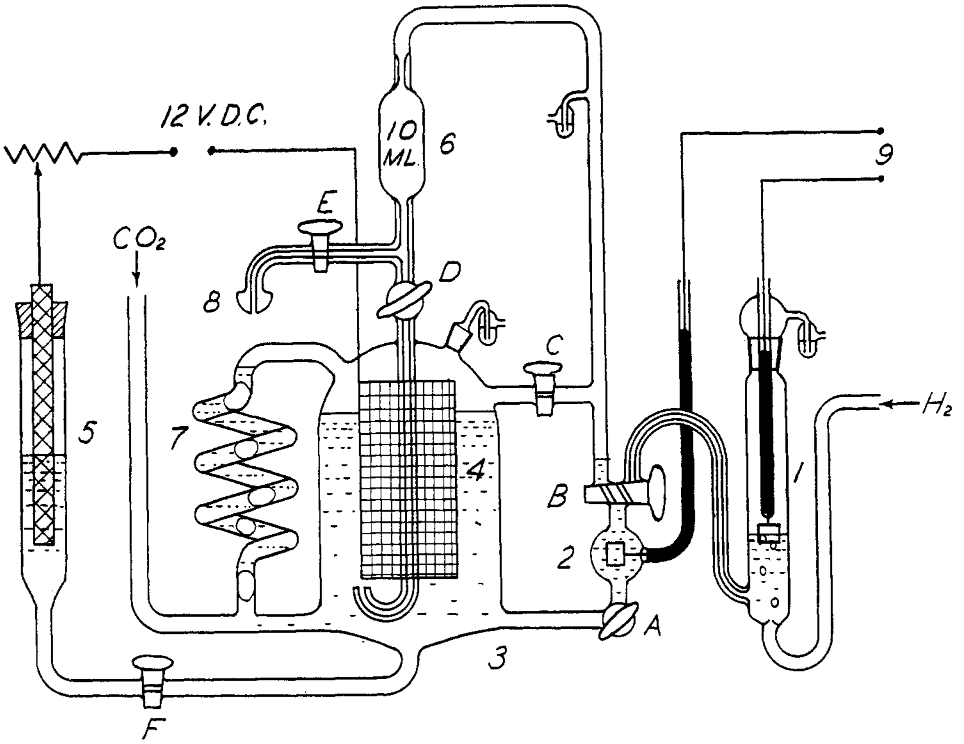

Fig. 1.—Apparatus for electrolytic reduction and cell voltage measurement.

to the titration beaker and 7 ml. of 2 *N* hydrobromic acid are added to the boiler and deaerated. The acid is transferred to the beaker and the potentiometric titration carried out in an air free atmosphere. The sodium bicarbonate is added to prevent hydrolysis of the ferricyanide and the hydrobromic acid serves to speed up the reaction. It is not necessary to add more zinc salt since the chromous chloride solution carries a sufficient amount furnished by the amalgamated zinc used in its preparation.

Results and Discussion

Potential Measurements and Calculation of Results.—In reporting results, the convention adopted assumes that the formal potentials of all couples which show a greater tendency than hydrogen to go from the reduced to the oxidized state are positive, and that those showing a less tendency are negative. In any depicted cell the flow of electrons in the external circuit is considered to be from the electrode with the more positive couple potential to that with the less positive potential, and the cell e.m.f. is considered to be positive if the reduced form in the couple with the more positive potential appears on the left hand side of the cell reaction equation.

In the case of the hydrogen half cell, the cell reaction was assumed to be

$$1/2H_2 + OsBr_6^- = OsBr_6^= + H^+$$

If we let E represent the cell potential, E_0' the formal potential of the bromoperosmite–bromoosmate couple, Os_{III} and Os_{IV} the formal concentrations of the osmium compounds, HBr the formal concentration of hydrboromic acid, H_2 the pressure of hydrogen in atmospheres, and $\gamma_\pm$ the

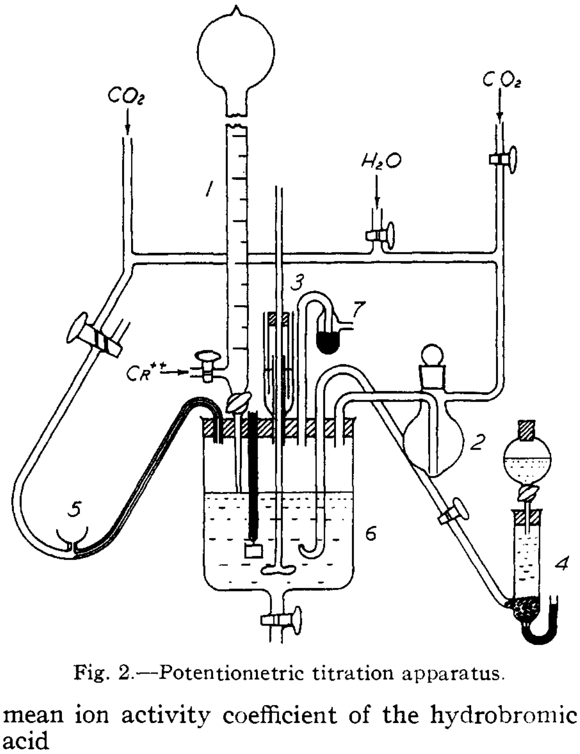

Fig. 2.—Potentiometric titration apparatus.

mean ion activity coefficient of the hydrobromic acid

$$-E^{0\prime} = E + 0.05913 \log \frac{(Os_{III})(HBr)(\gamma_\pm)}{(Os_{IV})[H_2]^{1/2}} \text{ at } 25°$$

If we let $E^{0''}$ represent the potential of the cell for equal formal concentrations of the two osmium

TABLE I

FORMAL POTENTIAL OF THE BROMOPEROSMITE–BROMOÖSMATE ELECTRODE

HBr concn., wt. f.	Total Os (wt. *f*)	$\mathrm{Os_{III}/Os_{IV}}$	$p\mathrm{H_2}$, mm.	E	$\gamma_\pm$	$E^{0''}$		$E^{0'}$	
						$\mathrm{Hg_2Br_2}$	$\mathrm{H_2}$	$\mathrm{Hg_2Br_2}$	$\mathrm{H_2}$
1.029	0.02986	1.213		0.2466	0.880	0.2516		0.3929	
1.029	.02921	0.2220		.2920	.880	.2533		.3946	
1.029	.02767	6.04		.2073	.880	.2535		.3948	
1.029	.02239	4.35		.2300	.880	.2678		.4091	
1.029	.02200	0.930		.2706	.880	.2688		.4101	
							Av.	.4003 ± 7.5 mv.	
2.115	.03000	0.3321		.2602	1.217	.2318		.3467	
2.115	.03010	0.7811		.2398	1.217	.2335		.3484	
2.115	.02967	2.081		.2143	1.217	.2331		.3480	
2.115	.03000	3.323		.2019	1.217	.3227		.3476	
							Av.	.3477 ± 0.7 mv.	
2.115	.002195	0.1821	723.9	.3664	1.217		0.3226		0.3476
2.115	.002195	1.051	726.4	.3233	1.217		.3246		.3494
2.115	.002195	1.303	724.2	.3175	1.217		.3243		.3492
								Av.	.3487 ± 0.8 mv.
3.245	.03071	1.870		.2117	1.806[a]	.2278		0.3214	
3.245	.03071	0.4937		.2459	1.806	.2277		.3213	
3.245	.03030	0.938		.2295	1.806	.2279		.3215	
3.245	.03028	3.054		.1995	1.806	.2281		.3217	
							Av.	.3215 ± 0.1 mv.	
3.245	.02376	0.2858	727.8	.3058	1.816		0.2737		0.3196
3.245	.02376	1.552	725.2	.2635	1.816		.2748		.3209
3.245	.002186	0.5659	729.0	.2896	1.816		.2750		.3210
3.245	.002186	3.252	730.0	.2449	1.816		.2752		.3212
								Av.	.3207 ± 0.5 mv.
3.996	.02379	0.4089	729.0	.2742	2.38		.2512		.310
3.996	.02379	0.8955	725.6	.2555	2.38		.2527		.311
3.996	.02379	1.356	723.9	.2456	2.38		.2534		.312
3.996	.002189	0.7277	729.0	.2587	2.38		.2505		.309
3.996	.002189	1.261	728.1	.2448	2.38		.2508		.309
								Av.	.310 ± 1 mv.

[a] Determined from mercurous bromide half cell data.

compounds

$$E^{0''} = E + 0.05913 \log (\mathrm{Os_{III}})/(\mathrm{Os_{IV}})$$

In the case of the mercurous bromide half cell the assumed reaction was

$$2\mathrm{Hg} + 2\mathrm{Br}^- + 2\mathrm{OsBr_6}^{=} = 2\mathrm{OsBr_6}^{\equiv} + \mathrm{Hg_2Br_2}$$

In this case

$$-E^{0'} = E + 0.1391 + 0.05913 \log \frac{(\mathrm{Os_{III}})}{(\mathrm{Os_{IV}})(\mathrm{HBr})(\gamma_\pm)}$$

It should be pointed out that in the preceding expressions it is realized that the assumption that the activity coefficients of the hydrogen and bromide ions are equal to each other and to $\gamma_\pm$, and that the $\mathrm{Os_{III}/Os_{IV}}$ formal concentration ratio can be used interchangeably with the activity ratio are not rigorously correct, but in the absence of a knowledge of the values of the individual ion activity coefficients these are probably the most useful and acceptable assumptions that can be made.

Results are shown in Table I. The values for $\gamma_\pm$ in column 6 were obtained from a curve plotted from data furnished by James[4] and Bates and Kirschman.[5] Because of the gap between data at 3 and 6 *f*, the $\gamma_\pm$ at 3.996 *f* is considerably less accurate than those at the other concentrations and therefore only three significant figures are used to express its value. The hydrogen pressures in column 4 were obtained from the corrected barometer readings after deduction of the activity of the water calculated on the assumption that at these acid concentrations the amount of hydrobromic acid in the vapor phase could be disregarded. In columns 7 and 9 are the data obtained when the mercurous bromide half cell was used, and in columns 8 and 10 that obtained with the hydrogen half cell.

In all runs it was noted that at each acid concentration cell potentials usually increased with passage of time which meant that the formal potential became more negative. The potential

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[4] G. M. James in Taylor's "Treatise of Physical Chemistry," Vol. I, p. 772 (1931).

[5] Bates and Kirschman, THIS JOURNAL, 41, 1991 (1919).

readings in the 1.029 *f* acid solution drifted slowly for several days and it was doubtful that a true equilibrium was ever reached. The inconsistency of the values of $E^{0''}$ and $E^{0'}$ and their large deviations from the average value are characteristic of these runs. Even in 2.115 *f* acid solutions constant voltage readings were attained very slowly. It usually required from three to five days to reach values which remained constant within 0.2 to 0.5 millivolt. In the 3.245 and 3.996 *f* acid solutions constant voltage was obtained after six to eight hours, remaining constant for as long as twenty-four hours and in all cases for at least six hours.

Discussion.—A study of the results in Table I shows that the higher the acid concentration the smaller is the negative value of the formal potential and the effect of increase in acid concentration is considerably greater at the lower concentrations than at the higher values. These effects together with the tendency of the cell potentials at each acid concentration to increase with passage of time led to the belief that this behavior was due to hydrolysis of the bromoperosmite. It was thought that the main reactions involved are

I $OsBr_6^{=} = OsBr_6^{-} + e$

II $OsBr_6^{=} + H_2O = OsBr_5OH^{=} + H^+ + Br^-$

If we let E' represent the potential of the half cell for reaction I, E^0 its molal reduction potential, and $\gamma_{Os_{III}}$ and $\gamma_{Os_{IV}}$ the unknown activity coefficients of the two osmium ions

$$E' = E^0 - 0.0591\left(\log\frac{(Os_{IV})}{(Os_{III})} + \log\frac{\gamma Os_{IV}}{\gamma Os_{III}}\right)$$

In concentrated acid only reaction I need be considered, but in the more dilute acid solutions slow hydrolysis might take place as shown in reaction II, thus increasing the $(Os_{IV})/(Os_{III})$ ratio. It is quite possible that in this region the $\gamma_{(Os_{IV})}/\gamma_{Os_{III}}$ ratio decreases with increase in acid concentration which would also cause the formal potentials to become less negative with increased acid concentration. Even so, the fact that the equilibria are so slow at the lower acid concentrations, and the fact that osmium salts tend to hydrolyze in fairly strong acid solutions lead one to suspect that hydrolysis is a factor here. The increase in cell potentials with passage of time would indicate a predominance of hydrolysis of the trivalent rather than the tetravalent form.

The dependence of the formal potentials on the $(Os_{III})/(Os_{IV})$ ratio and on a tenfold change in total osmium concentration was considered but it will be seen from the data that the trends in both cases are not sufficient to warrant drawing any general conclusions.

It was aimed to keep the solution contact potentials a negligible factor as far as practicable by having the total osmium salt concentrations low compared to the acid concentrations in the two half cells. The worst case is the 1.029 *f* solution but even here other factors are much more serious. The slight, if any, effect of a ten-fold change in the total osmium concentration on the value of the calculated $E^{0'}$ at the other acid concentrations would indicate that the error due to contact potentials was largely eliminated.

Dwyer, McKenzie and Nyholm have reported results of determinations of the trivalent–quadrivalent osmium couples in various concentrations of hydrobromic[6] and hydrochloric[7] acid. They carried their measurements down to and including 0.1 *f* acid and for the "redox potential" extrapolated to zero acid strength they showed a value of 0.452 volt for both cases. The authors of the present paper did not attempt to obtain values of couple potentials extrapolated to zero acid concentration for the following reasons: first they did not regard results obtained in solutions much more dilute than 2 *f* to be of great value due to the erratic hydrolysis equilibria in the more dilute acid solutions; second, even if equilibria were attainable, they did not regard the extrapolated values to be of much significance since it seemed evident that several reaction couples were involved. In comparing the technique followed in the present work with that of the workers mentioned it seems probable that the likelihood of the presence of appreciable liquid junction potentials should be considerably less in the former than in the latter case.

Summary

Determinations of the weight formal potential of the bromoperosmite–bromoösmate electrode at 25° in different concentrations of hydrobromic acid were made, using a mercurous bromide half cell in one series of measurements and a hydrogen half cell in another series. It was not found practicable to obtain satisfactorily reproducible results in acid solutions much more dilute than 2 formal, probably due to the fact that the $OsBr_6^{=} = OsBr_6^{-} + e$ main reaction is accompanied by a slow hydrolysis reaction such as $OsBr_6^{=} + H_2O = OsBr_5OH^{=} + H^+ + Br^-$. Following are the approximate, average values of the formal potentials obtained, referred to the standard molal hydrogen electrode

In 2.115 f HBr	−0.349 volt
In 3.245 f HBr	−0.321 volt
In 3.996 f HBr	−0.310 volt

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[6] Dwyer, McKenzie and Nyholm, *J. Proc. Roy. Soc. N. S. Wales*, **80**, 183 (1947).

[7] *Ibid.*, **80**, 242 (1947).