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Polarography of Tungsten(VI). Catalytic Reduction of Perchlorate

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In the voltage region corresponding to the reduction of tungsten(VI) to tungsten(V), a catalytic current of the order of 100 times the diffusion controlled value is observed in 12 M perchloric acid containing small concentrations of hydrochloric acid. The current is strongly dependent on perchloric and hydrochloric acid concentration, and is proportional to tungsten (VI) concentration. It is shown that the catalytic current is due to the reoxidation of tungsten(V) to tungsten(VI) by perchloric acid. The pseudo-unimolecular rate constant at 25° is 1630 sec.$^{-1}$, and the activation energy is estimated to be 13.4 kcal. mole^{-1}.

It has been found by Kolthoff and Parry[2] that tungstate in dilute perchloric acid yields catalytic polarographic currents in the presence of hydrogen peroxide, caused by the formation of peroxytungstate. In the present investigation it was found that tungsten(VI) in concentrated perchloric acid containing a small amount of hydrochloric acid gives another type of catalytic current due to the reduction of perchlorate. This phenomenon is analogous to the catalytic reduction of perchlorate by molybdenum,[3] but is due to the formation of tungsten(V), whereas the molybdenum catalysis has been attributed to molybdenum(IV).[4]

Experimental

Polarograms were recorded with a Sargent Model XXI Polarograph. A Rubicon or a Leeds and Northrup Student potentiometer was used to check potentials at several points along the voltage axis. An H-cell[5] was used in all experiments.

The characteristics of the capillary in 5 M hydrochloric–7 M perchloric acids were as follows: m = 1.340 mg./sec.; t = 5.75 sec. at h = 60.0 cm. In all experiments, the temperature was thermostatically controlled at 25.0 ± 0.1°, except in the determination of temperature coefficient when the temperature was regulated to within 0.3°.

All data on wave heights in the tables are time-average currents obtained with damping. In the figures, which are presented to give the general shapes of the curves, the peak currents without damping are plotted.

A solution of tungsten(VI) was prepared according to the following method: Tungsten(VI) oxide 1-hydrate was prepared by dissolving 106 g. of sodium tungstate dihydrate in 100 ml. of hot water, and adding 100 ml. of concentrated nitric acid. The precipitate was washed thoroughly with water and dried at 170°. Eight grams of the dry product and 7 g. of potassium carbonate were dissolved in 20 ml. water and added slowly with stirring to one liter of concentrated hydrochloric acid. A small amount of potassium chloride precipitated, leaving a clear, colorless solution. Gravimetric analysis by the cinchonine method[6] showed the tungsten(VI) concentration to be 0.02894 ± 0.00007 M. This solution served as a stock solution from which all experimental solutions were prepared.

Results

A series of polarograms was recorded for 0.144 mM tungsten(VI) in hydrochloric acid–perchloric acid mixtures of total molarity equal to 12, but containing the following ratios of hydrochloric to perchloric acid: 12/0, 10/2, 8/4, 5/7, 1/11, 0.5/11.5, 0.2/11.8, 0.04/12. In concentrated hydrochloric acid, the normal diffusion-controlled, two-step reduction of tungsten(VI) to tungsten(V) and to tungsten(III) was observed, in agreement with Lingane and Small.[7] When perchloric acid was added, the solubility of tungsten(VI) passed through a minimum at 10 M hydrochloric and 2 M perchloric acids, in which 0.144 mM tungsten(VI) did not remain completely dissolved. In spite of this, the current of the first wave, when corrected for residual current, had increased somewhat as compared to 12 M hydrochloric acid. A slight increase in the height of the first wave, and a steeper slope of the plateau of the second wave occurred as the perchloric acid concentration was increased to 7 M. In this curve, a slight dip in the second wave occurred just before hydrogen evolution be-

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[1] Abstracted from Ph.D. thesis of W. A. Ziegler, 1952. Now at the Mallinckrodt Chemical Co., St. Louis, Mo.

[2] I. M. Kolthoff and E. P. Parry, THIS JOURNAL, **73**, 5315 (1951).

[3] R. Holtje and R. Geyer, *Z. anorg. Chem.*, **246**, 265 (1941).

[4] G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

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

[6] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," 9th Ed., Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1942.

[7] J. J. Lingane and L. A. Small, THIS JOURNAL, **71**, 973 (1949).

gan. This dip became more pronounced with increasing perchloric acid concentration, and the first wave increased enormously in height as the hydrochloric acid concentration was decreased below 1 *M* (Fig. 1). In 0.04 *M* hydrochloric–12 *M* perchloric acids, a slight maximum (not suppressed by 0.01% gelatin or tropeolin 00) appeared on the first wave. At a potential corresponding to the appearance of the second wave (beginning at −0.50 v.), a dip occurred instead. Tendency for direct interaction between tungsten(VI) and mercury, as evidenced by a film of calomel on the mercury pool collecting at the bottom of the cell, increased as the concentration of hydrochloric acid was decreased.

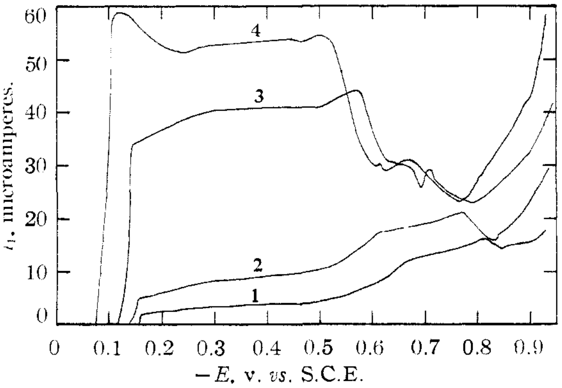

Fig. 1.—Polarograms of 0.144 m*M* tungsten(VI): curve 1, 1 *M* HCl, 11 *M* $HClO_4$; curve 2, 0.5 *M* HCl, 11.5 *M* $HClO_4$; curve 3, 0.2 *M* HCl, 11.8 *M* $HClO_4$; curve 4, 0.04 *M* HCl, 12 *M* $HClO_4$. Peak currents with no damping are plotted.

Effect of Hydrochloric Acid Concentration.—In order to run a curve in the absence of chloride, 100 ml. of 12.1 *M* perchloric acid was added to 10 ml. of 1 *M* sodium tungstate. The precipitate of tungstic acid was filtered off on a sintered glass funnel and a polarogram was run on the filtrate. The curve had a first wave height of 1.4 microamperes, with a slight indication of a second wave levelling off at 3.1 microamperes, and a gradual rise to 5.6 microamperes before a pronounced dip just before hydrogen evolution began. Evidently a small concentration of tungsten(VI), giving some indication of the catalytic effect as evidenced by the dip, can exist in 11 *M* perchloric acid. No current due to tungsten was observed in 8.7 *M* sodium perchlorate or 0.1 *M* sodium perchlorate with 0.1 *M* sodium tungstate.

A series of polarograms on solutions containing 0.144 m*M* tungsten(VI) in 11.5 *M* perchloric acid and varying hydrochloric acid gave the results listed in Table I. The solutions containing less than 0.10 *M* hydrochloric acid were bubbled with nitrogen that had been passed through concentrated hydrochloric acid. The solutions of higher concentrations were not bubbled because the escaping hydrogen chloride appeared to flush out the oxygen. Samples of each solution were withdrawn immediately after the completion of a polarogram and titrated for chloride by the Volhard method.

TABLE I

WAVE HEIGHT AT −0.35 V. IN 11.5 *M* $HClO_4$, 0.144 *M* TUNGSTEN(VI)

C_{HCl}, *M*	*i*, μamp.
0.0137	28.6
.0158	27.7
.0704	17.5
.202	9.25
.307	5.55
.34	5.35

Effect of Perchloric Acid Concentration.—The pronounced effect of perchloric acid concentration is shown in Fig. 2. At 6 *M* perchloric acid, the tungsten was not completely in solution. A horizontal limiting current was not reached before the dip at perchloric acid concentrations less than 9 *M*, and no maximum was observed below 12 *M* perchloric acid.

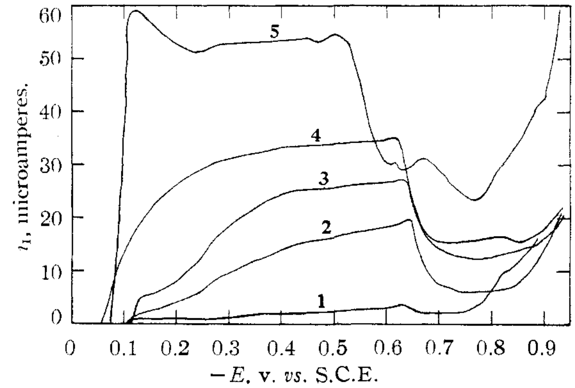

Fig. 2.—Polarograms of 0.144 m*M* tungsten(VI) in 0.04 *M* HCl and various concentrations of $HClO_4$: curve 1, 8 *M*; curve 2, 9 *M*; curve 3, 10 *M*; curve 4, 11 *M*; curve 5, 12 *M* $HClO_4$. Curves 1–4 full damping; curve 5, no damping, peak currents plotted.

Effect of Tungsten(VI) Concentration.—The limiting current at −0.35 v. *vs.* S.C.E. (corrected for residual current) was determined for various concentrations of tungsten (VI) in 0.04 *M* hydrochloric acid–12 *M* perchloric acid. The data (Table II), although showing considerably more scatter than for normal polarographic diffusion currents, indicate a proportionality between current and concentration. The magnitude is of the order of a hundredfold greater than would be expected for a diffusion-controlled process.

TABLE II

LIMITING CURRENT AT −0.35 V. AT VARIOUS CONCENTRATIONS OF TUNGSTEN(VI)

C, m*M*	*i*, μamp. (cor.)	*i/C*
0.144	34.8	242
.0862	22.7	263
.0287	7.84	273
.0144	3.52	244
.00862	2.25	261
.00287	0.735	256

Effect of Height of Mercury Column.—A series of polarograms of a solution of 0.144 m*M* tungsten (VI) in 0.04 *M* hydrochloric acid–12 *M* perchloric acid were run with the height of mercury column varied from 99.0 to 20.0 cm. Eleven experiments gave a current of 33.9 ± 0.7 microamperes (corrected for residual current). Due to minor irregularities of the wave immediately following the maximum, it was not always possible to measure the current at −0.35 v., but at some nearby horizontal region.

Effect of Temperature.—The effect of temperature on the limiting current at −0.35 v., corrected for residual current, of a solution of 0.0862 mM tungsten(VI) in 0.04 M hydrochloric acid–12 M perchloric acid is given in Table III.

TABLE III

COMPARISON OF LIMITING CURRENT OF TUNGSTEN(VI) WITH DIFFUSION CURRENT CONSTANT OF $PtCl_4^{=}$ AT VARIOUS TEMPERATURES

t, °C.	i, μamp.	I^a	log i/I
5.0	5.88	...	...
10.0	8.24	(3.03)	0.435
15.0	11.40	3.40	.525
20.0	15.26	(3.78)	.607
25.0	20.30	4.10	.695
30.0	25.54	(4.32)	.772
35.0	31.56	4.48	.848
40.0	40.14	(4.65)	.937
45.0	...	4.79	...

[a] Values in parentheses interpolated from plot of log I *vs.* $1/T$.

For comparison, the diffusion current constant, $i_d/cm^{2/3}t^{1/6}$, of tetrachloroplatinate(II) ion in 0.1 M potassium chloride[8] is given. From the increasing value of log i/I with increasing temperature, it is obvious that the temperature coefficient of the limiting current of tungsten(VI) is much greater than that of a diffusion-controlled current.

Controlled Potential Electroreduction.—An attempted electroreduction of 0.144 mM tungsten(VI) in 0.14 M hydrochloric acid–12 M perchloric acid at a controlled cathode potential of −0.35 v. failed because of the copious formation of a film of mercurious chloride due to direct interaction between tungsten(VI) and mercury. The film prevented the passage of appreciable current even with good stirring and eventually all the chloride was removed from the solution, so that the tungsten precipitated out.

A micro scale experiment was performed, using 2.00 ml. of the same solution, with a dropping mercury cathode adjusted to −0.35 v. with respect to an external saturated calomel electrode by means of a polarograph. The mercury was removed from the solution by use of a J-shaped cell with provision for mercury overflow. The mercury surface was protected from contact with the solution by means of a few drops of 1,2-dibromoethane. After the dissolved oxygen had been removed, the electrolysis current was recorded polarographically, and the total current was evaluated by graphical integration. The initial current was 28.3 microamperes, the final current 20.4 microamperes after 166 minutes of electrolysis during which 0.428 coulomb of electricity had passed. This represents fifteen times the theoretical quantity of electricity required to reduce all the tungsten(VI) to tungsten(V); yet 72% of the original tungsten(VI) was still present, as indicated by the final current. The mercury pool was coated with calomel even though it was protected from the solution. Removal of the tungsten probably resulted from precipitation due to the decrease of chloride concentration.

Discussion

The abnormal wave height, the constancy of wave height with varying height of mercury column, the abnormal temperature coefficient, and the results of the controlled potential electroreduction experiment all clearly indicate the catalytic nature of the wave. Its strong dependence on perchloric acid concentration suggests that perchloric acid is the oxidant.

The intermediate in the catalytic wave is clearly indicated to be tungsten(V) by the region of potentials in which the current is observed and by the dip in current at the potential corresponding to the reduction of tungsten(V) to tungsten(III). In the region of the dip, the diffusing species is tungsten(VI), which is partly reduced directly to tungsten(III) and partly reoxdized from tungsten(V) back to tungsten(VI). Direct chemical evidence for the reaction between 12 M perchloric acid and tungsten(V) was provided by reducing tungsten(VI) to tungsten(V) by means of bismuth amalgam. Rapid addition of a large quantity of perchloric acid caused a momentary color change to yellow (probably colloidal tungstic acid) and then to colorless. Slow addition of perchloric acid resulted in precipitation of hydrated tungstic acid.

The reaction scheme

$$\mathrm{W(VI)} + e^- \longrightarrow \mathrm{W(V)} \qquad (1)$$

$$\mathrm{W(V)} + \mathrm{HClO_4} \longrightarrow \mathrm{W(VI)} \qquad (2)$$

appears to be an excellent example of the type of catalytic process discussed recently by Delahay and Stiehl.[9] However, in view of the peculiar variation of the wave height with changes in perchloric acid concentration in the range 10 to 12 M, it is valid only to calculate a pseudo-unimolecular rate constant for the disappearance of tungsten(V) in 0.04 M hydrochloric acid–12 M perchloric acid solution. This constant is given by kC_z in the notation of Delahay and Stiehl. Because of the large magnitude of this constant, the simplified equation for the time average catalytic current in microamperes becomes

$$i_C = 0.753 \times 10^6\, nm^{2/3}t^{2/3}D_A{}^{1/2}C_Ak_u{}^{1/2} \qquad (3)$$

where n is the number of electrons involved in the electrode reaction (here $n = 1$), m is the rate of flow of mercury in mg. sec.$^{-1}$, t is the drop time in sec., D_A is the diffusion coefficient of tungsten(VI) in cm.^{2} sec.$^{-1}$, C_A is the bulk concentration of tungsten(VI) in moles per liter and k_u is the pseudo-unimolecular rate constant in sec.$^{-1}$.

From the diffusion current constant of tungsten(VI) in 12 N hydrochloric acid, we estimate $D = 4.6 \times 10^{-6}$ cm.^{2} sec.$^{-1}$. Taking the average value of 256 microamperes per millimole per liter (Table II) for the time-average catalytic current at 25°, $m = 1.340$ mg. sec.$^{-1}$, $t = 5.78$ sec., we calculate $k_u = 1630$ sec.$^{-1}$. This large value of k_u justifies the use of the approximate equation (3).[9]

To calculate the activation energy from the tem-

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(8) E. I. Onstott, Ph.D. Thesis, University of Illinois, 1950.

(9) Paul Delahay and G. L. Stiehl, THIS JOURNAL, **74**, 3500 (1952).

perature dependence of i_C requires a knowledge of the temperature dependence of D_A, which unfortunately cannot be directly determined for tungsten(VI) in 12 M perchloric acid. Therefore, the data of Onstott[8] for the diffusion current of tetrachloroplatinate(II) ion in 0.1 M potassium chloride were used. A plot of log i/I, given in the last column of Table III, *versus* the reciprocal of absolute temperature, turned out to be linear. From the slope of the line, an activation energy of 13.4 kcal. per mole is calculated.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography of Tungsten(VI) in Hydrochloric Acid. Mechanism of the Tungsten(V)-Tungsten(III) Wave

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The reduction wave of tungsten(V) to tungsten(III) in hydrochloric acid or mixtures of hydrochloric acid and lithium chloride is shown to be unsymmetrical in shape. The plot of log $(i_d - i)/i$ *versus* potential shows two linear regions intersecting usually near the half-wave point. By applying the steady state treatment of Evans and Hush to the electrode process, and assuming that tungsten(V) is reduced directly to tungsten(III) but tungsten(III) returns *via* tungsten(IV) to tungsten(V) it is possible to account for the unsymmetrical wave form. From the observed slopes of the linear regions of the logarithmic plots, reasonable values of transfer coefficients are calculated.

Souchay[2] has studied the polarography of tungsten(VI) in weakly acidic solutions and in the heteropoly acids and Stackelberg, *et al.*,[3] reported a single reduction wave of tungsten(VI) in concentrated hydrochloric acid. The first thorough polarographic study of the various oxidation states obtainable in hydrochloric acid was made by Lingane and Small.[4] For tungsten(VI) they found two polarographic waves, the first of which began at a potential more positive than that of the oxidation of mercury, and corresponded to a reduction to tungsten(V). The second wave corresponded to the further reduction to tungsten(III) and was identical with the wave of tungsten(V) being reduced to tungsten(III).

It was remarkable, however, that although the reduction of tungsten(V) to tungsten(III) gave a wave of "reversible slope," the anodic curve of red tungsten(III) corresponded only to oxidation to tungsten(IV). Collenberg and Backer,[5] who studied the electrolytic reduction of alkali metal tungstates in concentrated hydrochloric acid, observed that as soon as the tungsten(V) state was passed, tungsten(IV) and tungsten(III) were produced simultaneously. At temperatures of 0 to 9°, appreciable quantities of tungsten(IV) were formed; at a temperature of 16–18°, red $Rb_2WCl_5 \cdot H_2O$ was formed and could be isolated, and at higher temperatures, the red tungsten(III) compound was transformed to the yellow-green $Rb_3W_2Cl_9$.

Lingane and Small[4] also observed the transformation of the red form to the yellow-green form, and presented evidence for a third intermediate colorless form of tungsten(III). From measurements of the cathode potential with interrupted current in coulometric reduction of tungsten(V) and from observations of the color of intermediate solutions, it was concluded that "either tungsten(IV) or a compound of tungsten(V) and tungsten(III) is produced transiently" especially at higher initial concentrations of tungsten(V).

Collenberg and Backer[5] also electrolyzed 12-tungstosilicic acid and found that trivalent tungsten is formed before reduction to the +4 state was complete. They concluded that either the reductions W(V) → W(IV) and W(V) → W(III) occur simultaneously or that an effective +4 oxidation state is reached by reaction between tungsten(V) and tungsten(III).

In the present investigation, the shape of the rising portion of the tungsten(V) → tungsten(III) wave is interpreted by means of a kinetic treatment, in which the role of tungsten(IV) is clearly indicated.

Experimental

Preliminary experiments confirmed the observation by Lingane and Small[4] that the reduction wave of tungsten(V) is identical with the second wave of tungsten(VI). Therefore, for convenience, the same tungsten(VI) stock solution as previously described[6] was investigated in various media.

A Sargent Model III Manual Polarograph was used. Its "current multiplier," or sensitivity selector, had been calibrated potentiometrically against the voltage drop across a standard resistor. The potential setting was checked at every third or fourth reading against a Leeds and Northrup Student potentiometer. Corrections were made for iR drop by measuring the a.c. resistance in the conventional manner. The cell resistance was found to be quite appreciable, and to increase with increasing hydrochloric acid concentration (resistance values of 1730, 2180 and 2540 ohms, respectively, were observed for 8, 10 and 12 M hydrochloric acid in the conventional H-cell).

The rate of flow of mercury was determined by the procedure of Lingane and Kolthoff.[7] Values of m and t were determined in each of the media used and at each voltage at which diffusion currents were measured. The values of $m^{2/3}t^{1/6}$ were 1.680 ± 0.001 mg.$^{2/3}$sec.$^{-1/2}$ at −0.4 v. (*vs.* S.C.E.) and 1.697 ± 0.002 at potentials of −0.69 to −0.74 v., where the first and second wave heights were measured and did not vary appreciably with hydrochloric acid concentration. The mercury column height was 60.0 cm. and the temperature was 25.0 ± 0.1° in all experiments.

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[1] Experimental work from Ph.D. Thesis of W. A. Ziegler, 1952.

[2] (a) P. Souchay, *Ann. chim.*, **18**, 61, 73, 169 (1943); **19**, 102 (1944); **20**, 73, 96 (1945); (b) A. Tchakirian and P. Souchay, *Ann. Chim.*, **1**, 232 (1946); (c) P. Souchay, Proceedings of the I. International Polarographic Congress, Prague, 1951, p. 327.

[3] M. von Stackelberg, P. Klinger, W. Koch and E. Krath, *Forschungsberichte Tech. Mitt. Krupp, Essen*, **2**, 59 (1939).

[4] J. J. Lingane and L. A. Small, THIS JOURNAL, **71**, 973 (1949).

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[7] J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 825 (1939).