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

The Mechanism of the Anomalous Reduction of Certain Anions at the Dropping Mercury Electrode

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RECEIVED APRIL 21, 1955

The polarographic reduction of tetrachloroplatinum(II) ion and certain other oxidizing compounds that give a minimum at the diffusion current plateau has been investigated. Based on the results of the experiments the following mechanism for the minimum is proposed. At potentials more positive than the value where the true electroreduction of the compound starts, it will oxidize chemically the mercury at the electrode surface. The chemical oxidation proceeds in two steps: a comparatively slow step to give Hg_2^{++} ions and a rapid step resulting in Hg^{++} ions. However, the mercuric ions react with the mercury at the surface producing mercurous ions which again are oxidized by the compound and the catalytic cycle goes on until all of the compound which reaches the electrode has been reduced. The current flowing through the cell is then the result of the electroreduction of the mercurous ions. Due to the fact that the catalytic cycle is much faster than the diffusion of the compound, the process is diffusion controlled. At increasingly negative potentials, the rate of electroreduction of mercurous ions becomes progressively faster, and finally competes with the chemical oxidation. The catalytic cycle gradually drops off leaving part of the compound unreacted and the current decreases. At still higher negative potentials the electroreduction of the mercurous ions, produced in the first step of the chemical oxidation, will occur instantaneously leaving no time for them to be further oxidized. The bottom of the minimum has been reached and the current is now governed by the slow rate of the chemical reaction producing the mercurous ions. The current rises again at a potential where the true electroreduction of the compound commences.

In recent years several investigators have found a pronounced minimum in the diffusion plateau of a number of compounds.[2–14] In these cases the reduction usually starts at early potentials (*versus* the saturated calomel electrode, S.C.E.) and gives a smooth diffusion current. At more negative potentials, a peculiar drop in the current is observed. After a flat minimum, where the current in some cases almost falls to zero, it rises again and under certain conditions levels off to the original height before the supporting electrolyte is reduced.

To explain this phenomenon, Laitinen and Onstott[7] developed a repulsion theory according to which the current decreases at higher negative potentials as a result of electrostatic repulsion of the negatively charged ions ($PtCl_4^=$) to be reduced. Krjukova[5] independently offered a similar explanation. The theory of Laitinen and Onstott has been quoted by a number of authors,[10,12,13] whereas Frumkin and Florianovich[9] advanced an explanation based upon a Boltzmann distribution factor which causes an exponential decrease in surface anion concentration which more than compensates, in a certain potential range, the increasing rate of electroreduction with increasing negative potential. They were unable to account satisfactorily for the steep dip in the reduction curves of tetrachloroplatinate(II) ion in the presence of excess chloride.

In a recent paper,[14] the oxidation of mercury by noble metal salts is mentioned. In the present investigation, evidence is presented that the previous explanations given for the dips are inadequate, and that a mechanism involving attack of the mercury surface can be used to explain minima in several types of polarographic waves.

Experimental

The polarographic and oscillographic apparatus as well as the rotating platinum electrode (RPE) assembly employed in this investigation have been described elsewhere.[15–17]

The chemicals used as supporting electrolytes and as buffers were of reagent grade and were used without further purification. The compounds investigated were in most cases obtained from Dr. John C. Bailar, Jr., University of Illinois, and were recrystallized and dried before use.[18] Potassium tetrachloroplatinum(II) was made from reagent grade hexachloroplatinum(IV) acid according to Keller.[19] The recrystallization of the product did not, however, succeed according to the description. Four and a half grams of the tetrachloroplatinum(II) salt was dissolved in 80 ml. of water and eight drops of concentrated hydrochloric acid were added, but no precipitation occurred. The solubility of this salt was given to be 0.93 g. per 100 ml. of water at 16° and 5.3 g. at 100°. These same values are reported in the "Handbook of Chemistry and Physics."[20] However, the "Handbook of Chemistry" (Lange)[21] reports an entirely different value for the solubility (16.6 g. in 100 ml. of cold water) which is in accordance with the findings in this investigation. The recrystallization was finally done as Klason[22] suggested and the product was dried at 90° for an hour.

Results

Testing the Theory of Frumkin and Florianovich.—According to this theory, it would not be expected that the reduction of a second anion, starting within a few hundred millivolts more positive than the potential range where the mini-

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[1] A preliminary report on the subject appeared in the Doctoral Thesis of P. Kivalo, Åbo Akademi, Åbo, Finland, 1954.

[2] I. M. Kolthoff, L. S. Guss, D. R. May and A. I. Medalia, *J. Polymer Sci.*, **1**, 340 (1946).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography II," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, p. 519.

[4] J. J. Lingane and L. Meites, Jr., THIS JOURNAL, **69**, 1021 (1947).

[5] T. A. Krjukova, *Doklady Akad. Nauk S.S.S.R.*, **65**, 517 (1949).

[6] F. L. English, *Anal. Chem.*, **22**, 1501 (1950).

[7] H. A. Laitinen and E. I. Onstott, THIS JOURNAL, **72**, 4565 (1950).

[8] R. W. Becker, Master's thesis, University of Illinois, 1949.

[9] A. N. Frumkin and G. M. Florianovich, *Doklady Akad. Nauk S.S.S.R.*, **80**, 907 (1951).

[10] N. Konopik and E. Berger, *Mn. Chem.*, **84**, 666 (1953).

[11] R. L. Pecsok and R. S. Juvet, Jr., THIS JOURNAL, **75**, 1202 (1953).

[12] I. Filipovic, Z. Hahl, Z. Gasparac and V. Klemmcic, *ibid.*, **76**, 2074 (1954).

[13] E. P. Parry and M. G. Yakubik, *Anal. Chem.*, **26**, 1294 (1954).

[14] R. P. Simpson, R. L. Evans and H. A. Saroff, THIS JOURNAL, **77**, 1438 (1955).

[15] H. A. Laitinen and P. Kivalo, *ibid.*, **75**, 2198 (1953).

[16] P. Kivalo, K. B. Oldham and H. A. Laitinen, *ibid.*, **75**, 4148 (1953).

[17] P. Kivalo, *ibid.*, **77**, 2678 (1955).

[18] The authors are grateful to Dr. Bailar for his kind coöperation.

[19] R. N. Keller, "Inorganic Syntheses," II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 247.

[20] C. D. Hodgman, "Handbook of Chemistry and Physics," 33rd Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1951–1952, p. 544.

[21] N. A. Lange, "Handbook of Chemistry," 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 254.

[22] P. Klason, *Ber.*, **37**, 1360 (1904).

mum in the curve of the first anion occurs, could yield an additive current at all potentials, because both anions must be subjected to a similar Boltzmann distribution behavior. To test this, two substances, one of which gives a minimum, were simultaneously reduced. Figure 1 illustrates the results of these experiments. The upper curve is the ordinary polarogram of $K_3Fe(CN)_6$, whereas the polarogram of $K_2S_2O_8$ exhibits the typical minimum. When both are present simultaneously, the third curve is obtained. Clearly, the reduction processes are additive at each potential in the vicinity of the dip.

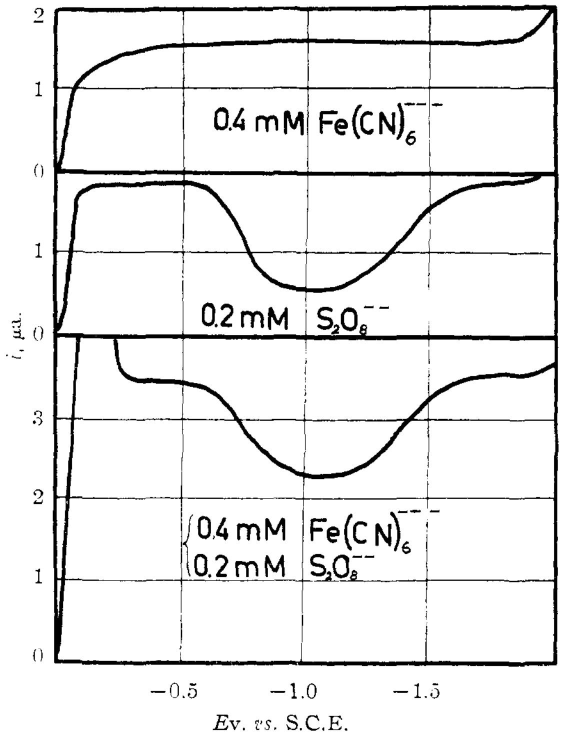

Fig. 1.—Polarograms obtained in 0.01 *M* NaOH supporting electrolyte.

This theory is also inadequate to account for a region of potential-independent current at the bottom of a dip or the behavior of electrically neutral oxidants, which are cited below.

Testing the Repulsion Theory.—It was thought that a complex ion with zero charge would not, if reducible, give a minimum because no electrostatically repulsive forces could act upon it. Figure 2 shows a family of polarograms obtained with *cis*-diamminodichloroplatinum(II) which is a complex of zero charge. On the basis of this finding which clearly indicates that the charge of the reducible species has nothing to do with the electrode reaction producing the anomalous minimum, it may be concluded that electrical repulsion fails to give a satisfactory explanation for the cause of the phenomenon.

Experiments with K_2PtCl_4.—Inasmuch as the tetrachloroplatinum(II) anion exhibits a very pronounced minimum in its diffusion plateau, its polarographic behavior was studied more in detail in order to gain further insight into the problem.

(a) **Reduction in a Non-complexing Medium.**—Figure 3 shows a family of polarograms in which $NaClO_4$ has been used as the supporting electrolyte. There are three characteristic features about the polarograms that should be particularly noted. Firstly, the reduction starts at about +0.25 v. against S.C.E. The current rises steeply from an anodic wave which is probably caused by the chloride ions set free during the reduction of the platinum complex. Because the platinum complex at least at positive potentials oxidizes mercury chemically, the early part of the reduction wave actually is due to the reduction of mercurous ions. (The interference in the beginning of the wave between +0.25 and +0.10 v. is thought to be due to a film formation of the slightly soluble Hg_2PtCl_4.) Secondly, in addition to the ordinary maximum at the beginning of the waves, there appears a second maximum in the diffusion plateau at around −0.40 v. It is hardly noticeable at low concentrations but very pronounced already at 0.6 m*M* concentration

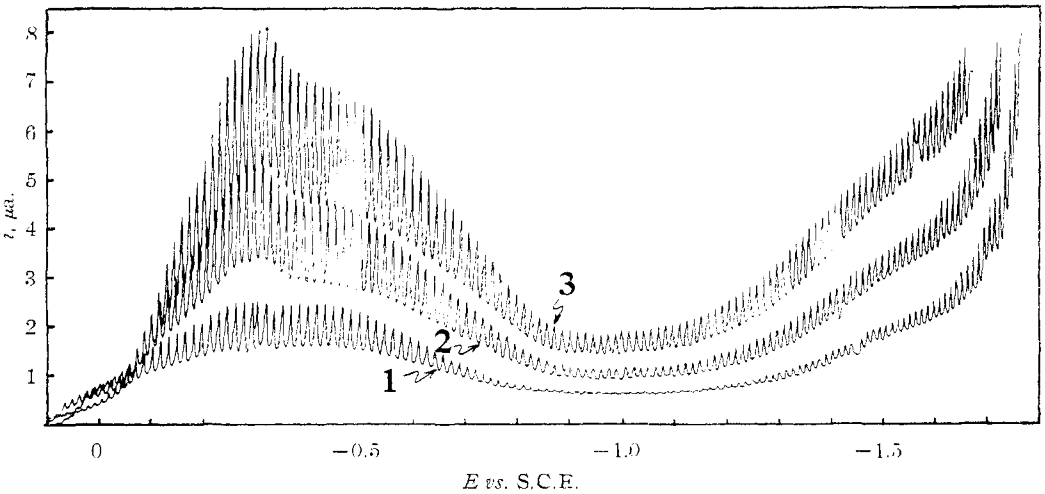

Fig. 2.—Polarograms of *cis*-diamminodichloroplatinum(II) obtained in 1 *M* NaCl supporting electrolyte: curve 1, 0.2 m*M*; curve 2, 0.4 m*M*; curve 3, 0.6 m*M* concentration of the complex.

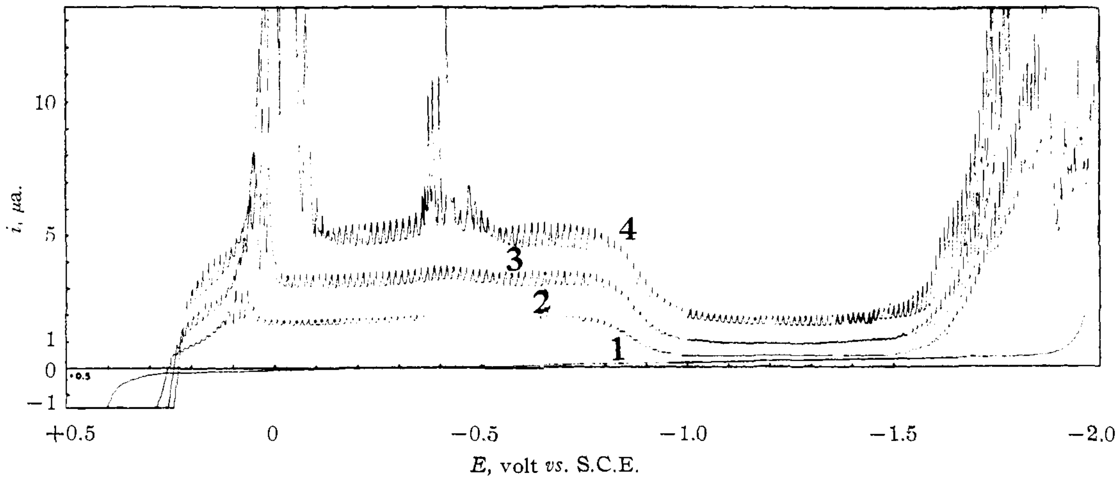

Fig. 3.—Polarograms of K_2PtCl_4 obtained in an 0.1 *M* $NaClO_4$ supporting electrolyte: curve 1, 0 m*M*; curve 2, 0.2 m*M*; curve 3, 0.4 m*M*; curve 4, 0.6 m*M* concentration of the complex.

of the complex. In searching for an explanation for this unusual phenomenon[23] it was discovered that the same maximum is observed also in the reduction plateau of $HgCl_2$. This is shown in Fig. 4. It can be safely concluded that the appearance of the maximum in the diffusion current of tetrachloroplatinum(II) ion that mercury ions are involved in its reduction process even at that negative potential. The cause of this maximum is probably found in the fact that it occurs at a potential in the vicinity of the electrocapillary maximum, and that the product of the reduction is mercury. The uncharged electrode–solution interphase might be especially sensitive to stirring.

And thirdly, it is seen that the current at the bottom of the minimum is proportional to the concentration of the reducible compound and that the current also is independent of the potential.

(b) **The Hydrolysis of K_2PtCl_4.**—It was soon discovered that tetrachloroplatinum(II) underwent hydrolysis which somewhat affected its polarographic reduction. The product of the hydrolysis according to Taube,[24] is $PtCl_3H_2O^-$ and/or $PtCl_3OH^=$. A measurement revealed that the *p*H of a water solution of an 0.8 m*M* concentration of the complex falls from 6.90 to 5.15 within 5 hours indicating thus considerable hydrolysis. The presence of chloride ions inhibits the hydrolysis while nitrate and perchlorate ions seem to increase its rate. The polarogram of an aged solution of K_2PtCl_4 (prepared the day before in water exhibits the same general features as a freshly prepared one except for the fact that the two maxima are somewhat more pronounced and the depth of the minimum has decreased to about 50%. By boiling a solution of the complex for three hours the minimum almost disappeared. Because the hydrolysis results in an ion which apparently is reduced through another mechanism (without the minimum) than the $PtCl_4^=$ ion, the experiments to be described below were always carried out using freshly prepared solutions of the tetrachloro complex.

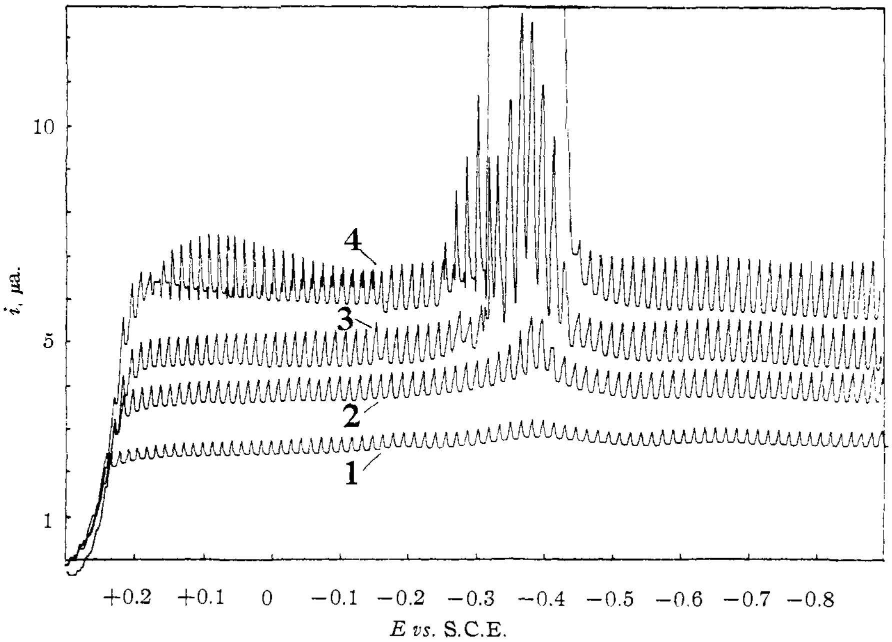

Fig. 4.—Polarograms of $HgCl_2$ obtained in an 0.1 *M* KNO_3 supporting electrolyte: curve 1, 0.3 m*M*; curve 2, 0.45 m*M*; curve 3, 0.60 m*M*; curve 4, 0.75 m*M* concentration of the mercury salt.

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(23) A similar maximum, occurring in the middle of a reduction plateau, has been reported by Lingane and Niedrach (THIS JOURNAL **71**, 196 (1949)). They found it in the reduction of Te(IV) and explained it to be due to the beginning of the reduction of Te to $Te^=$ which stops for some unknown reason.

(24) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

(c) **The Effect of *p*H.**—Figure 5 illustrates the effect of variation of hydrogen ion concentration. The polarograms were obtained using an 0.4 m*N* solution of K_2PtCl_4 containing 1 *M* NaCl per liter. At high hydroxyl ion concentration the fairly well developed wave seen after the minimum is most likely due to the irreversible reduction of the platinum complex as was pointed out by Laitinen and Onstott.[7] The fact that its height is dependent on the *p*H, suggests that some catalytic hydrogen evolution might occur already at this potential. The steep rise of the current which follows the wave certainly is due to the hydrogen evolution which is shown by the appearance of the wave with the maximum in the most alkaline solution used. When the hydrogen ion concentration is increased, the height of this wave increases tremendously and it will start at more and more positive potentials masking completely the irreversible $PtCl_4^=$ wave. Beginning from a hydrogen ion concentration of 0.005 *M* a peculiar hump is developing at -1.05 v. (curve 6 in Fig. 5). At 0.25 *M* HCl the hump has grown to a large maximum (curve 12 in Fig. 5). One can also notice that starting from 0.1 *M* concentration of HCl a new small wave is developing at about 0.75 v. (curve 10 in Fig. 5). Evidently the catalytic hydrogen evolution occurs in three steps. This phenomenon was noticed by Slendyk and Herasymenko[25,26] in the reduction of certain other platinum metals and they postulate that the finely divided metal set free in the course of the reduction gives three different types of crystallite each having unlike catalytic properties.

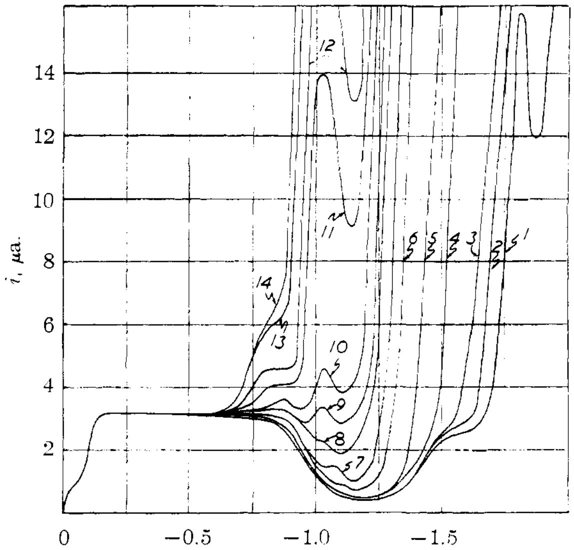

Fig. 5.—Polarograms of 0.4 m*M* K_2PtCl_4 obtained in an 1.0 *M* NaCl supporting electrolyte at various hydrogen ion concentrations.

Curve	Addition	Curve	Addition
1	0.5 *M* NaOH	9	0.075 *M* HCl
2	0.03 *M* NaOH	10	0.1 *M* HCl
3	Borate buffer *p*H 9.25	11	0.25 *M* HCl
4	Borate buffer *p*H 7.75	12	0.5 *M* HCl
5	Acetate buffer *p*H 4.15	13[a]	1.0 *M* HCl
6	0.005 *M* HCl	14[a]	1.6 *M* HCl
7	0.01 *M* HCl		
8	0.05 *M* HCl		

[a] No NaCl added.

The early part of the polarograms was found to be independent of *p*H, save for the maxima (see Fig. 2) which were pronounced in acid solutions but disappeared in alkaline medium. For the sake of simplicity the maxima were not drawn in the figure.

(d) **The Kinetic Control of the Current at the Minimum.**—Laitinen and Onstott discovered that the current in the plateau before the minimum is diffusion controlled.[7] The present investigation revealed, when the dependence of the current from the mercury head was measured at various potentials along the descending portion of the wave, that the current becomes more and more kinetically controlled when the bottom of the minimum was approached. When the current levelled off, it was completely independent of the height of the mercury column.

Table I lists the results of the experiments.

Table I

Variation of Mercury Head in the Reduction of 0.5 m*M* K_2PtCl_4. A solution of 1 *M* NaCl per liter was used as supporting electrolyte. The back-pressure correction employed here is 1.5 cm.[27] and the average currents were corrected for the residual value.

E, v. *vs.* S.C.E.	−0.750	−0.875	−0.950	−1.050	−1.200
i/i_d	1.0	0.84	0.49	0.16	0.05
h, cm.	*i*, μa.	*i*, μa.	*i*, μa.	*i*, μa.	*i*, μa.
28.5	2.64	2.40	1.63	0.57	0.18
38.5	3.07	2.66	1.76	.57	.18
48.5	3.36	2.86	1.83	.60	.19
58.5	3.78	3.18	1.85	.60	.18
73.5	4.48	3.78	1.87	.60	.20

The kinetic control could have two causes: either is the electron transfer reaction slow or there is a chemical reaction which produces the electrochemically active substance at a slow rate. From Fig. 2 one can easily draw the conclusion that the present case involves the latter mechanism since the current is seen to be independent of the potential over a wide range. It will be discussed in detail below.

(e) **Current–Time Relationship and Oscillographic Polarography.**—On the plateau before the minimum the current was found to be approximately proportional to $t^{1/6}$ whereas at the bottom of the minimum the current has nearly the kinetic dependence, *i.e.*, $i \sim$ const. $t^{2/3}$ (due to the small absolute value of the current in the latter case, a correction must be made for the residual value, where $i_r \sim$ const. $t^{-1/3}$). This result was the expected one in light of the previous experiment.

Figure 6 shows a tracing of an oscillographic polarogram of the platinum complex. The characteristic "mercury maximum" is seen as well as the minimum. The process can be considered completely irreversible as is evidenced by the absence of any oxidation current.

(f) **Reduction at a Rotating Platinum Electrode.**—As expected, the reduction of the tetrachloro

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(25) I. Slendyk, *Coll. Czech. Chem. Communs.*, **4**, 335 (1932).

(26) P. Herasymenko and I. Slendyk, *ibid.*, **5**, 479 (1933).

(27) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 78-80.

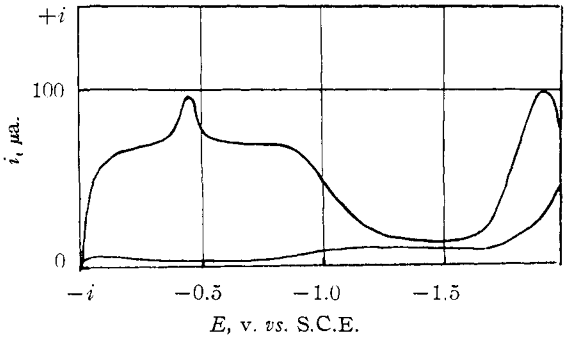


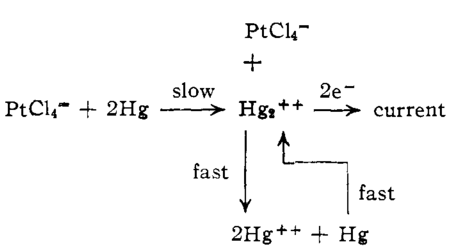
Fig. 6.—Tracing of an oscillographic polarogram of 0.05 mM K_2PtCl_4 obtained in an 1.0 M KNO_3 supporting electrolyte.

complex at the RPE was quite different from that at the DME. When the chloro complex is dissolved in a neutral chloride supporting electrolyte, the reduction produced maximum-like "humps" (see Fig. 7) whose height is roughly proportional to the concentration of the complex ion. The waves were nearly reproducible also with decreasing negative polarization. If, on the other hand, the solution was immediately made alkaline (pH 7.4–10.3) *no waves were found* before the discharge of the hydrogen ion, which starts at around −1 volt.

In one set of experiments the platinum complex was dissolved in water to be used as the stock solution from which various amounts were pipetted into a supporting electrolyte consisting of 1 M NaCl and the buffer. The waves obtained are shown in Fig. 7. The apparent minimum in the curves, seen just before the final rise of the current, is a very surprising effect and was at first thought to be due to a similar mechanism causing the minimum encountered at the DME. However, the fact that pH affects the position of the "humps" very strongly and furthermore that they disappear in 1 M NaOH (the waves were suppressed with less alkali when the tetrachloro salt was directly dissolved in NaCl), suggests that the hydrolysis product of the tetrachloro complex might be involved in this phenomenon. In any event, this "minimum" cannot be of the same origin as the minimum observed at the DME, since the latter is independent of pH.

The very important conclusion which can be drawn from these experiments is that the early reduction of the tetrachloro compound at the DME, as compared to that at the RPE, evidently is catalyzed by the presence of mercury.

The Proposed Mechanism of the Minimum.—Based on the results of the experiments described in the previous paragraphs, the following mechanism was found capable of explaining the cause of the minimum in the reduction plateau of K_2PtCl_4 at the DME. Consider the scheme



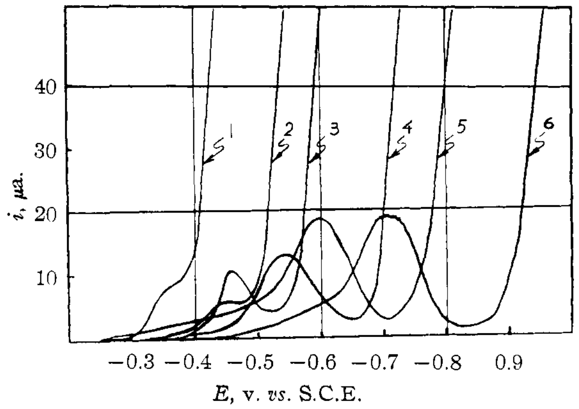


Fig. 7.—Polarograms of 0.4 mM K_2PtCl_4 obtained with the rotating platinum electrode using 1.0 M NaCl as the supporting electrolyte and varying the hydrogen ion concentration.

Curve	Addition	pH
1	Acetic acid	2.70
2	Acetate buffer	4.50
3	Acetate buffer	5.40
4	Borate buffer	7.40
5	Borate buffer	8.70
6	Sodium hydroxide	10.3

The underlying principle in the scheme is that mercury is chemically oxidized by the chloro complex in the potential range more positive than −1.4 volt where the electroreduction of the complex commences. However, the chemical oxidation proceeds in two steps: first the comparatively slow step forming Hg_2^{++} ions followed by the second rapid step resulting in Hg^{++} ions. It is a well known fact that mercuric ions react with mercury to form mercurous ions and that the equilibrium of the reaction is established very quickly. In a medium like the present one, the mercuric ions are quantitatively transformed into mercurous ions.[28] Taking this into account it is seen that the concentration of the mercurous ions is kept fairly high allowing all of the platinum which reaches the electrode surface to be reduced. The current flowing through the cell is then the result of the electroreduction of the mercurous ions. Due to the fact that the catalytic cycle is much faster[29] than the diffusion of the platinum complex, the current is controlled by diffusion.

When the potential is made more negative, the rate at which the mercurous ions are electroreduced is getting proportionally faster, and finally this reaction will compete with the chemical oxidation. The catalytic cycle will gradually drop off leaving part of the platinum complex unreacted and the result is a decrease in the current. At still higher negative potential, the straight reduction of the mercurous ions will occur instantaneously as soon as they are produced by the chemical reaction leaving no time for them to be oxidized by the rest of the platinum salt. The bottom of the minimum has been reached and the current is now governed by the slow rate of the first step in the chemical oxida-

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(28) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 2732 (1941).

(29) It was shown experimentally that the $PtCl_4^=$ ion oxidizes a suspension of calomel almost instantaneously.

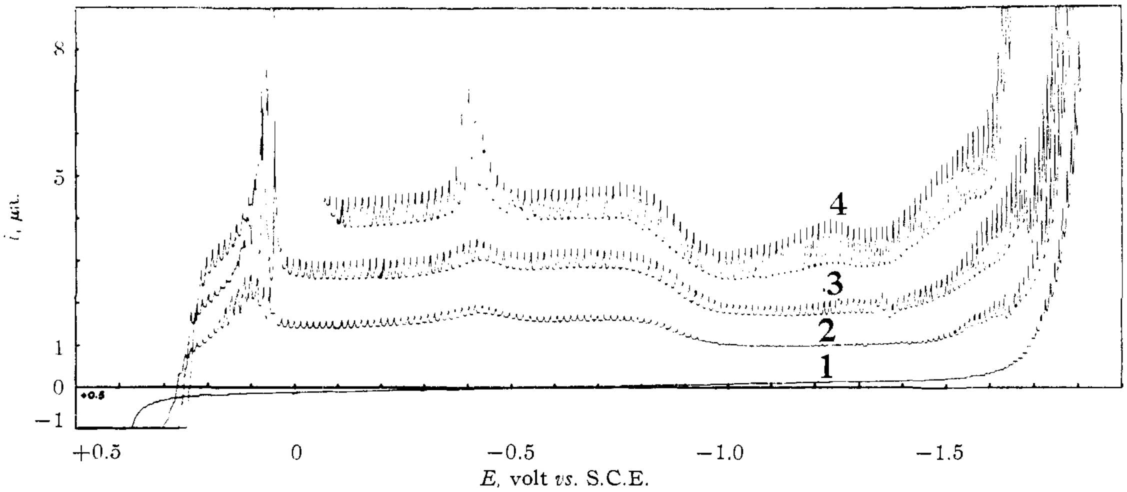

Fig. 8.—Polarograms of $(NH_4)_2PtCl_6$ obtained in an 0.1 *M* KNO_3 supporting electrolyte: curve 1, 0 m*M*; curve 2, 0.1 m*M*; curve 3, 0.2 m*M*; curve 4, 0.3 m*M* concentration of the complex.

tion. The current should be kinetically controlled, independent of the potential and proportional to the concentration of the chloro complex, all of which have been experimentally verified. Similarly, the result of the oscillographic experiment is in accordance with the new theory.

The interference of an adsorbed film of camphor[7] is now explained on the basis of its interference with the oxidation of the mercury surface.

Experiments with Other Compounds Producing a Minimum.—The **hexachloroplatinum(IV)** ion produces a minimum similar to that of the tetrachloro complex.[8,9,14] In Fig. 8 three polarograms of the former are shown, obtained in a nitrate supporting electrolyte. Compared with Fig. 3 it is seen that the form of the polarograms is identical. The tetravalent platinum gives, however, twice as much current as the divalent compound using the same concentration and the current at the minimum does not drop more than to half of the value at the diffusion plateau. Using an 0.2 m*M* concentration of the hexachloro compound the dependence of the current at the minimum (−1.1 v.) from the mercury head was studied and it was found that diffusion control existed at the bottom.

The mechanism suggested for the divalent platinum complex is valid also in this case. A slight modification is, however, necessary. The tetravalent platinum is electroreduced to the divalent state in a normal way and the product, the tetrachloro complex, is then reduced according to the above mechanism.

That the hexachloro complex is electroreduced first to the divalent state is supported by some experiments with the RPE. It was discovered that the complex in a chloride medium is reduced at the platinum electrode in two steps of equal height: the first a long drawn out wave with $E_{1/2} \sim +0.05$ v. and a second with $E_{1/2} \sim -0.35$ v. (the latter splits further into two waves, when the concentration is increased; $E_{1/2} \sim -0.52$ v.). The first wave is undoubtedly the two-electron reduction to the divalent state and because it starts at early potentials at a surface it is very likely that the same happens at the mercury surface.

Contrary to the tetrachloro compound, in this case no maximum-like waves were found with the RPE. When the hexachloro complex was dissolved in 0.1 *M* NaOH, only one suppressed wave was observed at −0.25 v.

A family of polarograms of *cis*-**diamminodichloroplatinum(II)** obtained with the DME has been shown in Fig. 2.

The reduction of this compound at the RPE produces one wave with $E_{1/2} \sim -0.35$ v. in 0.1 *M* KNO_3 medium. In this case a slight drop in the current was observed just before the hydrogen ion discharge starts.

The **persulfate** ion exhibits a pronounced minimum in a very dilute supporting electrolyte only[6,9] (see Fig. 1). Why the minimum disappears when neutral electrolyte is added, as was discovered by Frumkin and Florianovich,[9] cannot be explained by means of the present theory, but the interpretation offered by these authors involving ion-pair formation which aids the reduction is the best available at present.

At the bottom of the minimum the current was found to be kinetically controlled and also in this case the reduction at the RPE starts at much more negative potential than at the DME.

In all the above three cases studied, the peculiar "mercury maximum" has been found indicating that mercury is being oxidized by the compounds. Similarly, the reduction of these compounds at the RPE in high alkali concentration was almost completely suppressed contrary to the behavior at the DME, again indicating the interaction of mercury. It is therefore believed that the proposed theory clarifies the cause of the minimum in the reduction of these species.

Frumkin and Florianovich reported that ferricyanide also exhibits a minimum,[9] but the present authors were unable to verify his finding. As a matter of fact, it was discovered that ferricyanide reduces both at the DME and the RPE with $E_{1/2} \sim +0.15$ v. This result would indicate that this ion is electroreduced at all potentials more negative than the above value, and consequently no minimum could even be expected.

Discussion

Although the authors believe that the proposed theory is a general one capable of explaining the cause of minima in the diffusion plateaus of polarographic waves of highly oxidizing compounds, there are certain other "minima" that do not fall into this category and consequently must have some other mechanism.

A case very similar to the present one, although not involving oxidation of mercury, was reported by Laitinen and Ziegler.[30] The polarographic reduction of tungsten (VI) in the presence of perchloric acid produces a very large catalytic current at potentials corresponding to the reduction of W(VI) to W(V). The catalytic current is due to the perchloric acid which oxidizes W(V) back to the hexavalent state which again is electroreduced to W(V) and so forth. At somewhat more negative potential the current falls off producing a "minimum." Here the electroreduction of W(V) to W(III) starts to interfere with the chemical oxidation of the pentavalent form and the catalytic cycle drops off. The principle is thus identical with the one presented in this paper.

Other cases of polarographic minima do not necessarily fall into a similar category. For example, a minimum in the reduction of hexamminecobalt(III) ion has been attributed to the formation of a film of cobalt(II) hydroxide.[31] The examples given by Pecsok and Juvet,[11] Kolthoff and Lingane,[3] Konopik and Berger,[10] Filipovic, *et al.*,[12] and Parry and Yakubik[13] merit further investigation.

Acknowledgment.—The authors are grateful to Dr. K. B. Oldham for valuable discussions in connection with this research.

This investigation was carried out under the sponsorship of the Office of Naval Research, contract N6-ori-07136-NR 052-282.

URBANA, ILLINOIS

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The Anodic Waves of Cysteine at the Convection and Dropping Mercury Electrodes

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RECEIVED JUNE 13, 1955

Current–voltage curves of cysteine at the convection mercury electrode (C.M.E.) were studied over the *p*H range between 1 and 13 at cysteine concentrations from 10^{-4} to 10^{-3} *M* and compared with polarograms observed at the dropping mercury electrode (D.M.E.). Polarograms run from negative to positive potentials at the C.M.E. in cysteine solutions more acid and more alkaline than *p*H 9 exhibit a prewave which is attributed to the formation of a film of mercurous cysteinate on the electrode. The film breaks down at more positive potentials when the "normal" wave corresponding to the formation of mercurous cysteinate at the electrode appears. From the area of cathodic dissolution patterns in polarograms recorded from positive to negative potentials the thickness of the film is calculated to correspond to that of a monomolecular layer of mercurous cysteinate. The film formed at the D.M.E. in solutions of *p*H 5 and of cysteine concentrations larger than 0.00025 *M* was also found to be of monomolecular dimension. Film formation at both electrodes is eliminated at 80° and also at 25° in the presence of sufficient surface active disulfides like dithiodiglycolic acid.

Under proper conditions[2] cysteine gives an anodic wave at the dropping mercury electrode (D.M.E.) which corresponds to a reversible reaction

$$\mathrm{RSH + Hg \rightleftharpoons HgRS + H^+ + e^-} \qquad (1)$$

In solutions with *p*H between 2 and 9 a prewave is observed at cysteine concentrations greater than 0.00025 *M*, the false diffusion current being almost independent of the cysteine concentration. Grubner[3] reports normal waves without a prewave at a temperature of 90°. The false diffusion current at room temperature has been attributed[2,3] to the formation of a film of mercurous cysteinate (HgRS) on the surface of the drop which prevents further electrode reaction with mercury until the potential is made positive enough to cause a breakdown of the film.

In a recent communication[4] the convection mercury electrode(C.M.E.) was found well suited for a study of electro-active films on mercury surfaces.

In order to obtain more insight into the properties and formation of the mercurous cysteinate film the anodic waves of cysteine at the convection mercury electrode were studied in detail. Current–voltage curves observed at the convection mercury electrode in cysteine solutions of *p*H lower than 9 and also in 0.1 *M* sodium hydroxide exhibit similar characteristics as those found at the dropping mercury electrode as indicator electrode. Current–voltage curves were recorded from positive to negative potentials and *vice versa*. The polarograms indicate that the resistance exhibited by the film is greater when the potential is varied from negative to positive values than *vice versa*.

From the area of the cathodic dissolution patterns observed in polarograms recorded from positive to negative potentials the thickness of the film was found to be independent of the cysteine concentration, length of time of anodic polarization and to have the dimensions of a monomolecular layer. A film of monomolecular thickness was also postulated to be formed at the dropping mercury electrode.

Experimental

The experimental setup of the convection electrode was the same as described previously.[5] The effective area of

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