vent, particularly in water solutions where the basic oxygen of the ether[24] would be hydrogen bonded to water molecules and (c) photolysis at −196° gave the same products as the vapor phase photolyses, whereas at low temperatures a biradical might be expected to undergo reactions other than a thermal decomposition into C_2H_4 and CH_2O.

Processes VI, VII and VIII are all analogous to the type of photodecomposition that Gomer and Noyes[3] postulated for ethylene oxide, equation 1. These reactions are postulated as very minor primary processes, which could account for the formation of CH_4, C_2H_6 and traces of other hydrocarbons. Analyses did not identify propionaldehyde as a photolysis product, but it would be expected to undergo secondary photolysis that would lead to the formation of H_2, CO, CH_2O and C_2H_4 as well as C_2H_6 and CH_4,[25] although in different ratios than were found for these products in the oxetane photolyses. Another source of ethane could be from ethyl radicals resulting from the reaction of ethylene with hydrogen atoms produced by the secondary photolysis of CH_2O.

These studies have indicated that intramolecular primary process I accounts, directly or indirectly, for about 98% of the products of oxetane photolysis. The high energy of the absorbed radiation in the 2000 Å. region suggests that the quantum yield of this decomposition into C_2H_4 and CH_2O might be near unity, in which case oxetane would be valuable as a sensitive and convenient chemical actinometer.

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[24] H. S. Gutowsky, R. L. Rutledge, M. Tamres and S. Searles, THIS JOURNAL, **76**, 4242 (1954).

[25] F. E. Blacet and J. N. Pitts, Jr., *ibid.*, **74**, 3382 (1952).

NATICK, MASS.

[CONTRIBUTION NO. 2385 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Effect of Surface Oxidation on the Voltammetric Behavior of Platinum Electrodes. The Electroreduction of Iodate

BY FRED C. ANSON

RECEIVED AUGUST 4, 1958

Chronopotentiograms of iodate ion reduction at platinum electrodes show that the iodate reduction proceeds much more reversibly at oxidized than at reduced electrodes. The reduction of the platinum oxides on the surface of an oxidized platinum electrode appears to catalyze the reduction of iodate ion. In solutions of *p*H 1 and below the cathodic reduction of iodate to iodide at unoxidized electrodes proceeds by means of iodine as an intermediate.

A platinum electrode which has been oxidized has a coating of PtO and PtO_2 on its surface[1] and displays quite different voltammetric behavior than for an unoxidized electrode.[2] This study delineates the way in which the oxidation of a platinum electrode influences the reduction of iodate ion at its surface.

The polarographic behavior of iodate ion at mercury electrodes is well known[3] but the only previous report of iodate ion reduction at platinum electrodes was made by Shain[4] who observed a reduction wave at a (presumably unoxidized) rotating platinum electrode in $5F$ H_2SO_4.

In the present study the reduction of iodate ion at reduced and oxidized platinum electrodes was investigated with the chronopotentiometric technique.[5] The experiments show that the reduction of iodate ion occurs very close to the potential where hydrogen ions are reduced at *unoxidized* electrodes in neutral or moderately acid solutions. However, at *oxidized* electrodes the reduction of iodate occurs at potentials from 200 to 600 millivolts more positive (oxidizing). This decrease in overvoltage apparently is due to a catalysis of iodate reduction when it is accompanied by the reduction of the oxide film on an oxidized platinum electrode.

Experimental

The experimental arrangement for the chronopotentiometric measurements was identical to the one previously described.[2c] A Varian model G-10 recorder with a 10 millivolt intrinsic range and a 1 second full scale deflection time was used.

The bright platinum electrode employed had an area of 7.3 cm.^{2} per side.

The auxiliary electrode was a platinum wire immersed in a sample of the test solution in a glass tube terminating in a sintered glass disc. The extent of electrode oxidation was determined as previously[1,2c] by stirring the electrode free of the oxygen formed during oxidation, allowing the solution to become quiescent, passing a constant cathodic current through the electrode and measuring the cathodic transition time for the reduction of the platinum oxides.

Oxidation of the platinum electrode while in the test solution was accomplished by passing an anodic current of *ca.* 25 milliamperes through the electrode for 5 seconds. Earlier experiments[1] have shown that the surface of a platinum electrode can be oxidized to a rather reproducible maximum extent after which all of the current goes toward oxidizing water. The completely oxidized electrode contained 1.3×10^{-3} microequivalent of platinum oxides per cm.^{2}.

The area of the gold electrode which was used was 6.5 cm.^{2} per side. In contrast to platinum there appeared to be no well-defined upper limit for the extent to which the gold electrode could be anodically oxidized in 0.1 *M* sulfuric acid.

The current-voltage curves were obtained with an "Autograph" X-Y recorder model G-3 (F. L. Mosely Co., Pasadena, Calif.). The polarizing voltage was obtained from a 1000 ohm Helipot potentiometer driven by a synchronous motor.

All measurements were made in oxygen-free solutions.

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[1] F. C. Anson and J. J. Lingane, THIS JOURNAL, **79**, 4901 (1957).

[2] See, for instance: (a) S. S. Lord and L. B. Rogers, *Anal. Chem.*, **26**, 284 (1954); (b) I. M. Kolthoff and N. Tanaka, *ibid.*, **26**, 632 (1954); (c) F. C. Anson and J. J. Lingane, THIS JOURNAL, **79**, 1015 (1957); (d) I. M. Kolthoff and E. R. Nightingale, *Anal. Chim. Acta*, **17**, 329 (1957).

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Pub., Inc., New York, N. Y., 1952, p. 574–575.

[4] I. Shain, *Anal. Chem.*, **26**, 281 (1954).

[5] P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Pub., Inc., New York, N. Y., 1954, Chapt. 8.

Results and Discussion

Figure 1 contains chronopotentiograms of the reduction of iodate ion at reduced and oxidized platinum electrodes in a solution buffered at *p*H 3. Cathodic chronopotentiograms of the reduction of molecular iodine and of the oxidized electrode itself in the absence of iodate are also included to aid in interpretation.

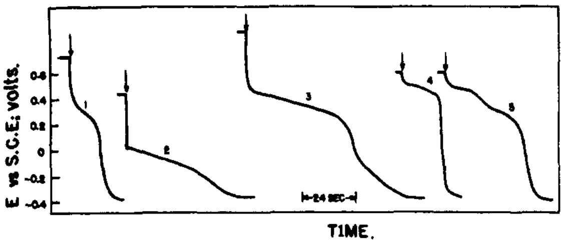

Fig. 1.—Cathodic chronopotentiograms for the reduction of iodate, iodine and the oxidized electrode in a phosphate buffer solution of *p*H 3: (1) reduction of the oxide film on the oxidized platinum electrode in iodate-free solution; (2) reduction of iodate in 0.8 millimolar iodate solution at the unoxidized electrode; (3) reduction of iodate at the oxidized electrode; (4) reduction of iodine in 1.2 millimolar iodine solution at the unoxidized electrode; (5) reduction of iodine at the oxidized electrode. All chronopotentiograms were obtained with a current density of 0.3 milliamp./cm.^{2}. The beginning of each chronopotentiogram is marked with an arrow.

Curve 2 in Fig. 1 is the chronopotentiogram of the reduction of iodate obtained with a reduced electrode. The potential pause is followed by a poorly defined inflection to hydrogen evolution. The potential at which the pause occurs is much more reducing than the potential at which iodine is reduced to iodide ion (compare with curve 4); it corresponds to the direct irreversible reduction of iodate to iodide ion.

Curve 3 in Fig. 1 shows the striking effect that oxidation of the electrode has on the subsequent iodate chronopotentiogram. The poorly defined potential inflection in curve 2 is changed to the sharp potential break in curve 3 when the electrode is oxidized by anodizing at 25 ma. for 5 seconds before the iodate chronopotentiogram is measured.

Curve 1 in Fig. 1 is the cathodic chronopotentiogram obtained with an oxidized electrode in a solution buffered at *p*H 3 but containing no iodate. The potential pause corresponds to the reduction of the platinum oxide film on the surface of the electrode.[1] It is significant that the potential, +0.4 volt *vs.* S.C.E., at which the reduction of the oxide film first begins contributing to the current is just the point where the potential pause begins in the chronopotentiogram for the reduction of iodate in curve 3. Furthermore, the potential inflections in the chronopotentiograms for platinum oxide reduction and iodate ion reduction both occur just after the electrode has reached a potential of *ca.* + 0.2 volt *vs.* S.C.E. These two facts strongly suggest that the reason that iodate ion is reduced at much more oxidizing potentials at oxidized platinum electrodes is because the electroreduction of the platinum oxides provides a means for an accompanying reduction of iodate ion. That is, the reduction of the platinum oxide itself must have commenced before the reduction of iodate ion can begin. This concomitance is responsible for both potential pauses commencing at the same potential.

Thorough oxidation of a platinum electrode produces on its surface a rather reproducible amount of PtO and PtO_2 which is not significantly increased by further oxidation.[1] Consequently with solutions of higher iodate ion concentrations for which the current is increased in order to keep the transition time constant, the transition time for the reduction of the fixed amount of oxide film becomes quite small. However, in spite of the relatively small number of equivalents represented by the oxide film, it can be responsible for the reduction of a much larger number of equivalents of iodate ion. In one experiment the reduction of 0.2 microequivalent of platinum oxide was accompanied by the reduction of 200 microequivalents of iodate ion.

That the oxide film on the electrode does not affect the reduction of iodine to iodide is shown in curve 5 of Fig. 1. The two inflections in this curve correspond to the reduction of iodine to iodide at the oxidized electrode followed by the reduction of the oxide itself.

Effect of *p*H.—Cathodic chronopotentiograms of the reduction of iodate are generally similar to those in Fig. 1 for *p*H values between 1 and 6. At *p*H values greater than 6 oxidation of the electrode has no effect on the chronopotentiograms. At *p*H values less than 1 the chronopotentiograms have a distinctly different form which is not influenced by oxidation of the electrode. The potential pause occurs at the potential corresponding to the reduction of iodine to iodide. This indicates that the reduction of iodate proceeds by means of the electroreduction of iodine at these *p*H values. Recent evidence by Laitinen and Subcasky[6] has shown that iodine also acts as an intermediate in the reduction of iodate at mercury electrodes in acidic solution.

The effect on a cathodic iodate chronopotentiogram of the reduction proceeding by means of iodine is shown in Fig. 2. Figure 2 is a cathodic chronopotentiogram for a 0.8 millimolar iodate solution in 0.3 *F* sulfuric acid. The unusual potential behavior in this chronopotentiogram results

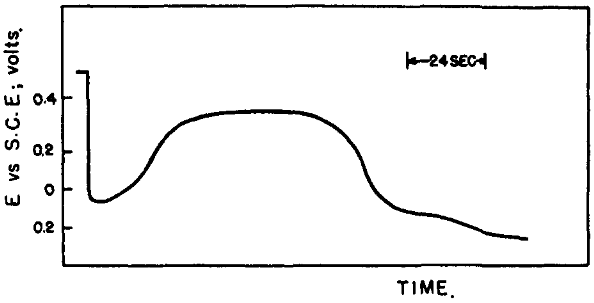

Fig. 2.—Cathodic chronopotentiogram for 0.8 millimolar iodate solution in 0.3 *F* sulfuric acid at a current density of 0.52 milliamp./cm.^{2}.

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(6) H. A. Laitinen and W. J. Subcasky, THIS JOURNAL, **80**, 2623 (1958).

because the predominant reaction occurring at the electrode changes during the course of the chronopotentiogram. For the first few seconds iodate ion is reduced to iodide ion at the electrode. The iodide reacts with the iodate present at the electrode surface to form iodine. Subsequently, as the concentration of iodine at the electrode builds up, the predominant electrode reaction becomes the reduction of iodine to iodide. The latter reduction takes place at a much less reducing (negative) potential than the former so the electrode potential rises to an *anodic* maximum even though a constant *cathodic* current continues to flow through the electrode. Finally when the concentration of iodate at the electrode decreases to the point where the rate of its reaction with the iodide is too slow to provide iodine as fast as it is being consumed the potential inflects and the predominant reaction at the electrode changes again.

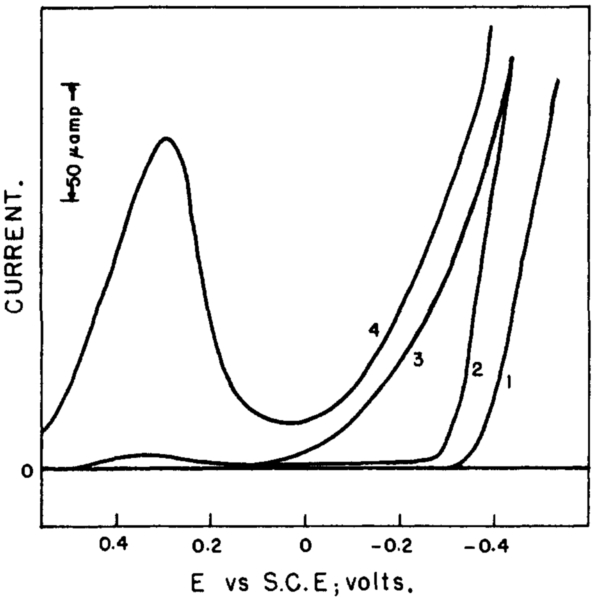

Fig. 3.—Cathodic current voltage curves for 1.0 millimolar iodate in 0.7 *F* sulfuric acid: (1) residual current with reduced electrode; (2) residual current with oxidized electrode; (3) iodate reduction with reduced electrode; (4) iodate reduction with oxidized electrode.

Mechanism of the Effect of the Oxide Film.—The possibility that the effect of the platinum oxide film is to catalyze the reaction between iodide and iodate ions at the electrode surface, and thus to allow the reaction to proceed through iodine reduction, can be discarded on the basis of chronopotentiograms obtained in solutions of varying *p*H. If the effect of the film were simply to catalyze the iodate–iodide reaction then the reduction of iodate at oxidized electrodes should occur near the potential where iodine is reduced. In fact, the reduction of iodate at oxidized electrodes begins at the potential where reduction of the platinum oxide begins at each *p*H and not at the potential where iodine is reduced to iodide.

A mechanism involving a specific electronic interaction between iodate ion and the platinum oxides on the electrode surface, which is analogous to mechanisms proposed by Marcus[7] for electron exchange at electrodes, appears to be more compatible with the experimental results. The first step in the reduction of iodate ion at an oxidized electrode can be imagined to consist of the transfer of an electron to iodate from the electrode by means of a platinum oxide bridge which can only serve as an electron-carrying bridge at electrode potentials where the platinum oxide itself begins to be reduced. Such a mechanism is compatible with the experimental observation that changes in the *p*H of the test solutions alter the potential at which iodate reduction occurs only insofar as the *p*H affects the potential at which the platinum oxides are reduced.

Once the reduction of iodate begins the current divides between iodate ion reduction and platinum oxide reduction. The time that passes before the potential inflects, *i.e.*, the transition time, is the time required to reduce completely the platinum oxide film, *not* the time required for the iodate ion concentration to fall to zero at the electrode. The time required for the reduction of the film is determined by the diffusion of iodate ion because the fraction of the total current which results in the film reduction depends on the concentration of iodate at the electrode. However the Sand equation[5] is not applicable to this kind of dual reduction process and the product of current and the square-root of the transition time is not a constant.

Evidence from Current–Voltage Curves.—Further evidence showing that the platinum oxide film catalyzes the iodate reduction by being co-reduced is contained in the current–voltage curves in Fig. 3. Curve 1 is the residual current curve obtained with a reduced stationary platinum microelectrode for the sulfuric acid supporting electrolyte of *p*H 0.7. Curve 3 resulted when the solution was made 1.0 millimolar in iodate and the current–voltage curve recorded with the reduced electrode. Curve 4 was obtained after the electrode was oxidized and the cathodic current–voltage curve again recorded. The sharp rise of the current to a maximum results from the platinum oxide-induced reduction of iodate. The current decreases following the maximum results from the decline in the iodate reduction current as the catalyzing oxide film is removed from the electrode surface by reduction. Curve 2 is the residual current curve for the oxidized electrode. The small bump commencing at about +0.55 volt *vs.* S.C.E. is due to the reduction of the oxide film. One can see from curve 2 that an oxidized electrode maintained at a potential of +0.5 volt or less will lose its oxide film and the rate of film reduction will increase as the potential is held at more reducing potentials. In three experiments with a millimolar iodate solution of *p*H 0.7 an oxidized microelectrode was maintained at a potential of 0.5, 0.4 and 0.3 volt *vs.* S.C.E. in the stirred solution. In all three experiments the current decayed with time but at very different rates. The time required for the current to fall to less than 10 microamperes was 7.5 minutes with the potential at 0.5 volt, 2.1 minutes with the potential at 0.4 volt, and 1.0 minute with the potential at 0.3 volt *vs.* S.C.E. No decrease in

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(7) R. A. Marcus, *Trans. N. Y. Acad. Sci.*, **19**, 452 (1957).

current with time occurs when species such as ferric iron or iodine are reduced in identical experiments and the results with iodate clearly show that the oxide film is indispensable for the reduction to proceed at these potentials. As soon as the oxide is removed from the electrode the iodate ion reduction current stops flowing.

Experiments with Analogous Anions.—Additional chronopotentiometric experiments have shown that the platinum oxide film produces effects entirely similar to those described above for iodate ion reduction when periodate ion is reduced, the only difference being that periodate ion in acidic solutions chemically oxidizes the platinum electrode. No effect of the oxide was detectable for the reduction of bromate or chlorate at oxidized platinum electrodes. Experiments with gold electrodes showed that the reduction of iodate ion is not noticeably different at oxidized or reduced electrodes even though oxide films are known to exist on oxidized gold electrodes.[8]

Conclusions

In a previous study[2c] it was shown that the oxidation of iodine to iodate at platinum electrodes proceeds prior to oxygen evolution at reduced electrodes but not at oxidized electrodes. Further, the potential at which the iodine is oxidized is very close to the potential at which the platinum electrode itself is oxidized. This fact and the results of the present study suggest that the kinetics of both the oxidation of iodine to iodate and the reduction of iodate to iodine at platinum electrodes involve concomitant oxidation and reduction of the platinum.

The general tendency for platinum oxide films to increase the reversibility of electrochemical couples has been cited by Kolthoff and Nightingale.[2d] However there are exceptions to this rule (*e.g.*, the oxidation of iodine to iodate)[2c], and the immediate relationship between the reduction of the oxide film and the (more reversible) reduction of the electroactive ion is not found in the other reported cases where electrode oxidation increases reversibility (*e.g.*, the ferric–ferrous couple).[2d] It seems unlikely that a single interpretation will be able to account for all of the effects on electrode reactions which the oxide films on oxidized platinum electrode have been observed to cause.

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[8] A. Hickling, *Trans. Faraday Soc.*, **42**, 518 (1946).

[CONTRIBUTION NO. 1521 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Calibration of Conductance Cells at 25° with Aqueous Solutions of Potassium Chloride[1]

BY JOHN E. LIND, JR.,[2] JAMES J. ZWOLENIK[3] AND RAYMOND M. FUOSS

RECEIVED NOVEMBER 7, 1958

All available precision data on the conductance of aqueous solutions of potassium chloride at 25° up to concentrations of about 0.01 N were analyzed by means of the linear conductance equation $\Lambda' = \Lambda_0 + Jc$, where $\Lambda' = \Lambda + Sc^{1/2} - Ec \log c$, and $S = 94.65$ and $E = 58.74$ are theoretically predictable constants. The weighted average of the results gives $\Lambda_0 = 149.93$ and $J = 198.4$. The equation gives $\Lambda' = 151.909$ for a 0.01 *demal* solution, which agrees with the Jones and Bradshaw standard within 0.003. The equation may be used to calibrate conductance cells with potassium chloride at several concentrations up to about 0.012 N, instead of at a single fixed point.

For many years, conductance cells were calibrated according to the specifications of Kohlrausch and Holborn.[4] Kraus and Parker[5] in 1922 discovered some discrepancies in these standards, and Parker and Parker[6] shortly thereafter redetermined the absolute conductance of several potassium chloride solutions. Later, Jones and Bradshaw[7] in 1933 repeated the absolute determinations and again found discrepancies in the work of their predecessors. A repeated check by Jones and Prendergast[8] was consistent with the 1933 values to about 0.02%, but Benson and Gordon[9] summarize reasons for preferring the Jones and Bradshaw standards.

All of the recommended standards have one feature in common: absolute specific conductances are given for one fixed concentration (approximately 1.0, 0.1 and 0.01 N) for use in the nearby ranges of cell resistance. Aside from the tedium of preparing a solution precisely to a predetermined value, use of a fixed point means that a given cell must be calibrated at only one value of cell resistance. It would be preferable to determine the cell constant over a range of cell resistances, in order to be certain that no stray shunts were present. It is a matter of sad experience that a cell may behave properly at low resistances (where it is calibrated) but give increasingly unreliable results as the resistance increases. At present, no direct method is available for calibrating cells at resistances greater than that of 0.01 demal potassium chloride, but from the point of view of recent theoretical work[10] it is the range below 0.04 N in water for 1-1 salts which is most interesting. Thanks to the theory, however, it is possible to devise a method of calibrating cells at higher resistances, because it fur-

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[1] Project NR 051-002 of the Office of Naval Research, Report No. 58. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

[2] National Science Foundation Research Fellow.

[3] Office of Naval Research, Research Assistant.

[4] F. Kohlrausch, L. Holborn and H. Diesselhorst, *Wied. Ann.*, **64**, 417 (1898); F. Kohlrausch and L. Holborn, "Leitvermögen der Elektrolyte," Teubner, Leipzig, 1898.

[5] C. A. Kraus and H. C. Parker, THIS JOURNAL, **44**, 2422 (1922).

[6] H. C. Parker and E. W. Parker, *ibid.*, **46**, 312 (1924).

[7] G. Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933).

[8] G. Jones and M. J. Prendergast, *ibid.*, **59**, 731 (1937).

[9] G. C. Benson and A. R. Gordon, *J. Chem. Phys.*, **13**, 473 (1945).

[10] R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1957); R. M. Fuoss, THIS JOURNAL, **80**, 3163 (1958).