Lifetime of Activated Platinum Surface

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The electrochemical reduction of preoxidized platinum electrodes produced a surface state that exhibited decreased "activity" toward the prewave of adsorbed hydrogen with time. The half-life of this activated surface state was of the order of 46 min. The ratio of coulombs for platinum oxidation compared to the hydrogen prewave gave for m in $\text{Pt}^* \cdots (\text{H}_2)_m$ (adsorbed) a value of 0.3, where Pt* designates the activated platinum.

Introduction

Various pretreatment methods have been employed to "activate" a platinum surface where the activation supposedly produced an enhancement in the reversibility of the electrode reaction. Attempts have been made to explain this phenomenon of activation in terms of the chemical and physical nature of the platinum surface. Lingane[1] and Sawyer and Interrante[2] for example have observed the necessity of preoxidizing the electrode prior to the reduction of oxygen and have proposed a mechanism which involved platinum oxide. Others, notably Anson,[3,4] Anson and King,[5] and Davis[6] have studied the effect of oxide on the reversibility of electrode reactions at platinum. An oxide bridge-type mechanism has been invoked[6-8] to explain the increased activity associated with a preoxidized platinum electrode, but Anson and King's results do not support this contention.

The activity of platinum electrodes in relation to surface structural changes has been studied by Shibata.[9-11] On the basis of visible "coarsening" of the surface by alternating current electrolysis[9,10] and of decreased rates of activity in terms of hydrogen overpotential associated with varying pretreatment times,[11] Shibata had concluded that when an electrode was oxidized and then reduced, a thin layer of unstable atoms was formed. The high activity was due to the presence of these unstable surface platinum atoms whose rate of crystallization was apparently slow.[11,12] Anson[4,8] and Anson and King[5] on the basis of the similarity in behavior between a preoxidized and reduced electrode and a chemically platinized electrode concluded that the electrochemical reduction of oxide formed a thin platinized surface which accounted for the enhanced activity. The platinized surface would be the same surface as described by Shibata[11] and Bonnemay,[12] and henceforth will be designated as Pt*.

The overpotential for the reduction of proton or water to form hydrogen[13] or the oxidation of hydrogen[11,14] decreased when a preoxidized and subsequently either electrochemically or chemically reduced electrode was used. On the reduction a small prewave occurred immediately before the hydrogen evolution. This prewave has been interpreted as being due to adsorbed hydrogen on the platinized surface.[4,14,15] The possibility of more than one form of adsorbed hydrogen to produce fine structure on the prewave has been investigated by Franklin and Cooke.[16]

There has been presented evidence that oxygen at

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(1) J. J. Lingane, *J. Electroanal. Chem.*, **2**, 296 (1961).

(2) D. T. Sawyer and L. V. Interrante, *ibid.*, **2**, 310 (1961).

(3) F. C. Anson and J. J. Lingane, *J. Am. Chem. Soc.*, **79**, 4901 (1957).

(4) F. C. Anson, *Anal. Chem.*, **33**, 934 (1961).

(5) F. C. Anson and D. M. King, *ibid.*, **34**, 362 (1962).

(6) D. G. Davis, Jr., *Talanta*, **3**, 335 (1960).

(7) I. M. Kolthoff and E. R. Nightingale, *Anal. Chim. Acta*, **17**, 329 (1957).

(8) F. C. Anson, *J. Am. Chem. Soc.*, **81**, 1554 (1959).

(9) S. Shibata, *J. Chem. Soc. Japan, Pure Chem. Sect.*, **79**, 239 (1958).

(10) S. Shibata, *ibid.*, **80**, 453 (1959).

(11) S. Shibata, *Bull. Chem. Soc. Japan*, **36**, 525 (1963).

(12) M. Bonnemay, *Z. Elektrochem.*, **59**, 798 (1955).

(13) L. P. Hammett, *J. Am. Chem. Soc.*, **46**, 7 (1924).

(14) D. T. Sawyer and E. T. Seo, *J. Electroanal. Chem.*, **5**, 23 (1963) (and pertinent references therein).

(15) R. P. Buck and L. R. Griffith, *J. Electrochem. Soc.*, **109**, 1005 (1962).

(16) T. C. Franklin and S. L. Cooke, Jr., *ibid.*, **107**, 556 (1960).

platinum exists as a oxide film, while at the same time, the evidence does not preclude the possibility that oxygen is an absorbed film.[17] Feldberg, Enke, and Bricker[18] have studied the anodic and cathodic polarization of a platinum electrode and concluded that the active electrode was the "half-reduced" state.

In this paper the dependence of the number of coulombs consumed in the cathodic and anodic hydrogen prewave will be investigated with respect to the number of coulombs involved in the oxidation and reduction of the platinum oxide, and the variation with the time following activation. The data are consistent with reduction of oxide surface producing Pt*.

Experimental

The experimental arrangement for the chronopotentiometric measurements were conventional in all respects. The triangular wave generator and potentiostat used for cyclic voltammetry were built following the circuit design of Alden, Chambers, and Adams.[19] A Leeds and Northrup Model H Azar strip chart recorder or Electro-Instruments Model 100TB X-Y recorder were used for the current–voltage (CV) traces.

The following additions or changes were made to a previously described[20] special quartz cell: A Leeds and Northrup No. 117136 bridge containing the same solution as in the cell made connection to a commercial Leeds and Northrup calomel electrode which served as the reference electrode; and either platinum wire or planar foil sealed in soft glass tubing were used for the working electrodes. Platinum was obtained from two different sources: Wildberg Bros. Smelting Co., San Francisco, Calif., 99.98% Pt; and Engelhard Industries, Inc., Newark, N. J., 99.989% Pt, (main impurities: Fe 34 p.p.m. and Pd 25 p.p.m.). The bridge and electrodes were sealed to an O-ring top which fitted the cell tightly. All seals were air tight against leakage. The degassing procedure and equipment was previously described.[21]

The areas of the electrodes were evaluated through ferrocyanide oxidation using the diffusion coefficient value[22] of 0.67 × 10^{-5} cm. sec.$^{-1}$. They compared favorably to the measured geometric areas. The electrodes were stored in 1 *F* H_2SO_4.

Reagent grade sulfuric acid and sodium or potassium carbonate were used without further purification. Water was redistilled from alkaline permanganate.

Results and Discussion

A platinum foil or wire electrode stored for several hours in a 1 *F* H_2SO_4 solution exhibits the cyclic CV patterns shown in Fig. 1 and 2 for polarization in

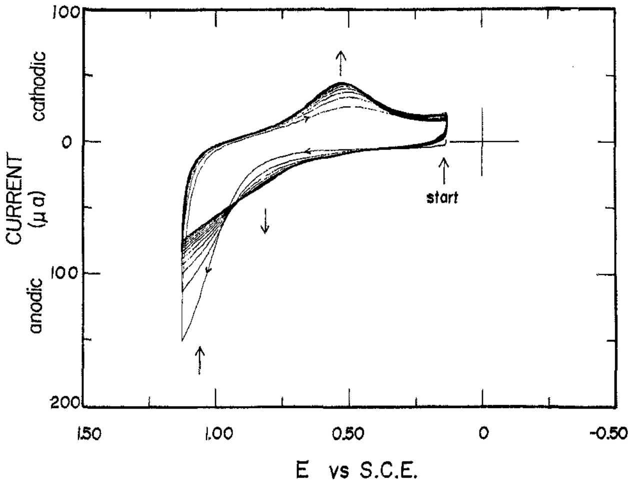

Figure 1. Cyclic scan of platinum electrode in 1 *F* H_2SO_4. Electrode stored for 24 hr. in 1 *F* H_2SO_4 prior to scan. Steady-state CV reached after about 10 cycles. (Arrows indicate direction of current change with each scan.) Scan rate is 0.13 v. sec.$^{-1}$.

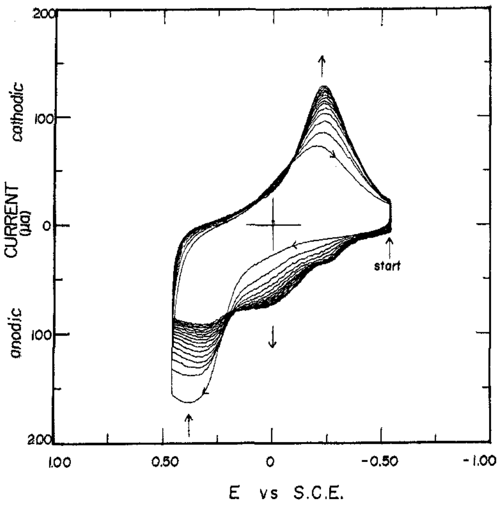

Figure 2. Cyclic scan of platinum electrode in 1 *F* Na_2CO_3. Electrode stored for 12 hr. in 1 *F* H_2SO_4 prior to scan. Steady state reached after about 15 cycles. (Arrows indicate direction of current change with each scan.) Scan rate is 0.13 v. sec.$^{-1}$.

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(17) M. W. Breiter and J. L. Weininger, *J. Electrochem. Soc.*, **109**, 1135 (1962).

(18) S. W. Feldberg, C. G. Enke, and C. E. Bricker, *ibid.*, **110**, 826 (1963).

(19) J. R. Alden, J. Q. Chambers, and R. N. Adams, *J. Electroanal. Chem.*, **5**, 152 (1963).

(20) J. N. Pitts, Jr., H. W. Johnson, and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(21) T. Kuwana, *Anal. Chem.*, **35**, 1398 (1963).

(22) M. von Stackelberg, M. Pilgram, and V. Toome, *Z. Elektrochem.*, **57**, 342 (1953).

Table I: Coulombs for Oxidation and Reduction at Platinum[a]

Electrode area, cm.^{2}	Solution, 1 F	Q_a	Q_c	Q'_c	Q'_a	$T_{0.5}$, min.	$\frac{Q'_a}{Q_a}$	$\frac{Q_c}{Q_a}$	$\frac{Q'_a}{Q'_c}$	$\frac{Q_c + Q'_c}{Q_a + Q'_a}$
5.44	Na_2CO_3	860	718	184	136	52.0	0.158[b]	0.835	0.740	0.906
5.44	H_2SO_4	410	398	147	133	41.5	0.325	0.970	0.905	1.00
5.44	Na_2CO_3	925	758	310	271		0.293	0.820	0.875	0.892
0.81	Na_2CO_3	612	503	205	179		0.342	0.820	0.873	0.894
0.60	Na_2CO_3	1105	987	386	326		0.295	0.895	0.845	0.960
0.60	H_2SO_4	765	666	422	227		0.297	0.870	0.538[b]	1.09
0.10	Na_2CO_3	330	310	925	90	40.0	0.272	0.940	0.973	0.961
0.10	H_2SO_4	570	570	390	338	51.3	0.593[b]	1.00	0.867	1.06
					Av.:	46.2 ± 5.4	0.304 ± 0.20	0.894 ± 0.051	0.868 ± 0.037	0.970 ± 0.050

[a] Scan rate: 0.13 v. sec.$^{-1}$; all values of Q in μcoulombs/cm.^{2}. [b] Scan limits: 1 F H_2SO_4: Q_a and Q_c, 1.125 to 0.125 v. *vs.* s.c.e.; Q'_a and Q'_c, 0.125 to −0.190. 1 F Na_2CO_3: Q_a and Q_c, 0.50 to −0.50 v. *vs.* s.c.e.; Q'_a and Q'_c, −0.50 to −0.85. Omit these values in average.

degassed solutions of 1 F H_2SO_4 and 1 F Na_2CO_3, respectively. The shape of the polarization curves changes with each cycle until a steady-state pattern is attained. In the basic carbonate solution the steady-state CV patterns are more reproducible from day to day than the sulfuric acid solution. In both cases, however, the number of coulombs consumed in the anodic wave, Q_a, is *ca.* 10% greater than the coulombs, Q_c, consumed in the cathodic portion (see Table I, columns 3 and 4). The values of Q_a and Q_c for a given scan limit of potential appears to be independent of the scan rate between 0.13 and 0.0195 v.-sec.$^{-1}$. Data for basic carbonate solution are summarized in Table II.

If a platinum electrode is cycled as above and then allowed to polarize cathodically, a wave is observed to precede the larger current for the hydrogen evolution. The prewave only appears if the electrode is preoxidized and then reduced and undoubtedly corresponds to the chronopotentiometric prewave previously observed by Anson.[4] The cyclic CV curves for activated electrode in 1 F Na_2CO_3 and 1 F H_2SO_4 are shown in Fig. 3A and 3B, respectively. The CV curve in acid is closely similar to one shown previously by Buck and Griffith.[15] In carbonate, the potential of the cyclic pattern shifts by *ca.* 0.06 v./pH from the acid and appears similar with the exception of some loss in the fine structure of the prewave. If the direction of the polarization is reversed at the foot of the current for the evolution of hydrogen into solution, an anodic wave, which is essentially a mirror image of the cathodic prewave, is obtained. The number of coulombs for the cathodic prewave, Q'_c, and the anodic wave, Q'_a, are summarized in columns 5 and 6 of Table I. The values of Q'_c and Q'_a appear to be independent of the scan rate (see Table II). The average ratio of Q'_a:Q'_c is 0.868 ± 0.037 for the data in Table I. The inequality between the values of Q_a and Q_c, and Q'_c and Q'_a indicates that all of the oxide is not reduced

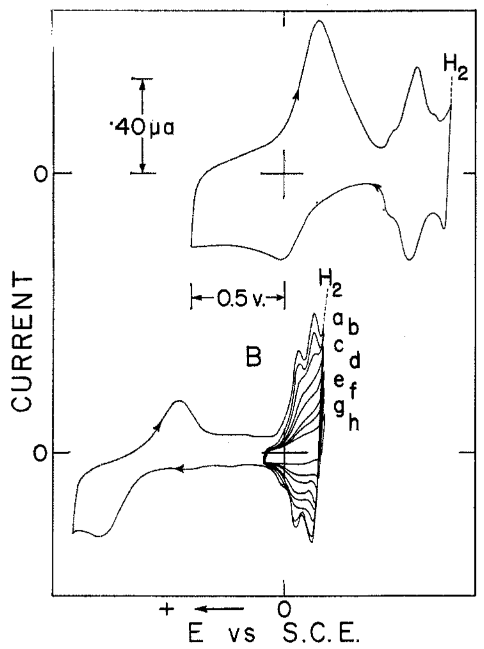

Figure 3. Trace A: Cyclic scan of activated platinum electrode in 1 F Na_2CO_3 between the potential limits of +1.125 to −0.190 v. *vs.* s.c.e. Trace B: Cyclic scan of activated platinum electrode in 1 F H_2SO_4 between the potential limits of +1.125 to −0.190 v. *vs.* s.c.e. Traces a–g between the potential limits of 0.125 and −0.190 v. *vs.* s.c.e. were taken after intervals of time: 0, 10, 25, 40, 70, 100 and 130 min., respectively. Scan rate: 0.13 v. sec.$^{-1}$.

Table II: Effect of Scan Rate

Scan rate, v. sec.$^{-1}$	Q_a[a]	Q_c	Q'_c	Q'_a	Q'_c, recycle[b]	Q'_a, recycle	$\frac{Q_c + Q'_c}{Q_a + Q'_a}$
0.13	1060	920	386	317	342	334	0.950
0.0625	1140	1000	343	334	342	317	0.912
0.0325	1110	990	402	308	350	325	0.985
0.0195	1130	1050	410	342	360	334	0.990
Av.	1110 ± 30	990 ± 35	385 ± 21	325 ± 13	349 ± 6	328 ± 6	0.960 ± 0.030

[a] Scan of Pt electrode in 1 *F* Na_2CO_3. All values of Q in μcoulombs/cm.^{2}. [b] Q'_a and Q'_c recycle is coulombs consumed when electrode is cycled once around (scan limits: −0.50 to −0.87 v. *vs.* s.c.e.) the hydrogen prewave after a complete cycle was made around both the oxide and hydrogen prewave (scan limits: +0.50 to −0.87 v. *vs.* s.c.e.).

in the potential region of the main oxide reduction wave but continues into the potential region of the hydrogen prewave. If this is the case, the value of $(Q_c + Q'_c)/(Q_a + Q'_a)$ should approach unity. Experimentally, the average values are 0.97 ± 0.05 and 0.96 ± 0.03 for the data presented in Tables I and II, respectively. If the above reasoning is correct, the value of $Q'_a:Q'_c$ should also approach unity upon each successive cycle if the electrode is cycled only in the potential region of the prewave. Columns 6 and 7 of Table II shows the values of Q'_c and Q'_a for the recycle in the prewave region. The average ratio of $Q'_a:Q'_c$ is 0.94 as compared to 0.85 for the ratio of the first cycle (data: column 4 and 5 of Table II). If the potential is allowed to continued cycling around the prewave region, the values of Q'_a and Q'_c become equal.

Both the oxide and prewave CV curves are independent of solution stirring. When both the oxide and hydrogen prewave CV's are affected by stirring, the solution contains some dissolved oxygen. If only the values of Q'_a to Q'_c are changed by stirring, the potential range being scanned is sufficiently cathodic to evolve hydrogen into the solution. When the value of Q'_a remains constant irrespective of whether or not the solution is stirred and whether hydrogen is evolved in the cathodic portion during stirring, it is an indication that the Pt* is saturated or at a maximum coverage with adsorbed hydrogen. Thus, the reactions involved at the platinum surface consistent with the above results and the conclusions of other workers[4,5,11,14] are

$$PtO + 2H^+ + 2e^- = Pt^* + H_2O \qquad (1)$$

$$Pt^* + 2mH^+ + 2me^- = Pt^* \ldots (H_2)_m \text{ adsorbed} \qquad (2)$$

or, if an oxidized electrode is immersed in dissolved hydrogen

$$PtO + H_2 = Pt^* + H_2O \qquad (3)$$

and

$$Pt^* + mH_2 = Pt^* \ldots (H_2)_m \text{ adsorbed} \qquad (4)$$

where PtO represents platinum oxide (not distinguished from possibility of $Pt(OH)_2$ in basic solutions, but differentiated from molecular oxygen held on platinum surface through weak electrostatic forces) and m may be any positive integer or noninteger value. If the Pt* is a real physical state, the formation and subsequent reduction of oxide seems to necessitate the formation and rupture of bonds between platinum and oxygen atoms.

The values of Q_a and Q_c depend on the anodic and cathodic potential limits as well as somewhat on the prior history of the electrode. In particular, care must be taken to prevent oxygen evolution on the anodic limit. (There is indication from previous work that the potential for oxygen evolution can be differentiated during oxide formation at least in basic solutions.[23]) It is interesting to note that the value of Q'_c or Q'_a is directly related to the amount of oxide formed. In Table I the average ratio of $Q'_a:Q_a$ is 0.304 ± 0.020. A similar result is found in Table II. If one assumes that platinum oxide formation and reduction is a two electron per atom process and that adsorbed hydrogen is molecular, the value of m is 0.3.

The values of Q'_a and Q'_c are time dependent. That is, if the activated electrode is allowed to stand for periods of time (no electrical connections) in a thoroughly degassed solution and then cycled around the hydrogen prewave, both Q'_a and Q'_c decrease (see Fig. 3B, traces a–h). In Fig. 4, curve B, a typical plot of the logarithm of the values of Q'_a as a function of time for carbonate solution is shown. The curve is

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[23] T. Kuwana, *J. Electroanal. Chem.*, **6**, 164 (1963).

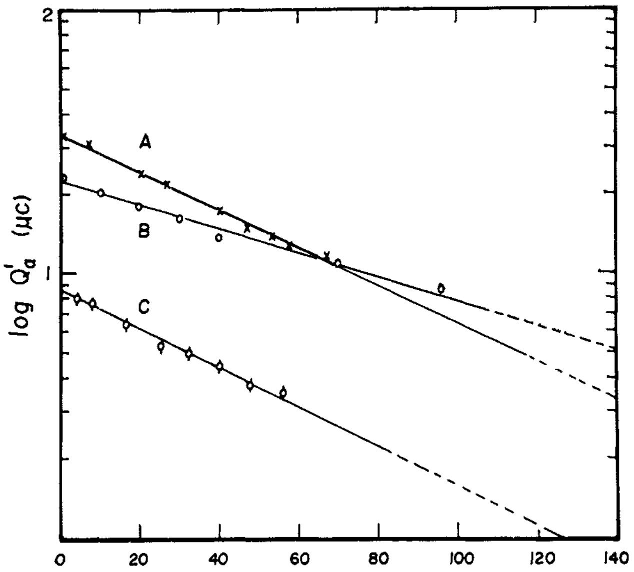

Figure 4. Logarithm of Q'_a plotted as a function of time. Curves A and C evaluated from continuously cycling the electrode in 1 *F* Na_2CO_3 and 1 *F* H_2SO_4, respectively. Potential limits of scan: −0.50 to −0.85 and +0.125 to −0.190 v. *vs.* s.c.e.; 1 *F* Na_2CO_3 and 1 *F* H_2SO_4, respectively. Curve B: Q'_a evaluated from intermittently cycling a platinum electrode in 1 *F* Na_2CO_3.

linear. The slope of the curve is similar to those found in 1 *F* H_2SO_4. Several values of the decay of Q'_a in terms of half-life, $T_{0.5}$, are given in Table I.

If Pt* is truly a dislocated, either atomic or small crystalline platinum, the more stable thermodynamic state should be the larger, crystalline platinum, Pt_c. The rate of the conversion of the reaction

$$\mathrm{Pt}^* \xrightarrow{k_1} \mathrm{Pt_c} \qquad (5)$$

where k_1 is the rate constant and is expected to depend only on the rate of surface migration and reorientation of Pt* as it "fits" into the larger crystalline lattice structure. If the hydrogen prewave is $\mathrm{Pt}^* \ldots (H_2)$ (adsorbed), then the decrease of Q'_a and Q'_c with time is perhaps a measure of k_1.

If Pt* conversion is purely random and statistical, the rate will be first order with respect to the surface concentration of Pt*. Furthermore, the validity of measuring the apparent rate of Pt* conversion by the hydrogen prewave will depend on the constancy of *m* and on the following reactions

$$\mathrm{Pt}^* \ldots (\mathrm{H_2})_m \text{ (adsorbed)} \xrightarrow{k_2} \mathrm{Pt}^* + m\mathrm{H_2} \text{ (soln.)} \qquad (6)$$

$$\mathrm{Pt}^* \ldots (\mathrm{H_2})_m \text{ (adsorbed)} \xrightarrow{k_3} \mathrm{Pt_c} + m\mathrm{H_2} \text{ (soln.)} \qquad (7)$$

$$\mathrm{Pt}^* \ldots (\mathrm{H_2})_m \text{ (adsorbed)} \xrightarrow{k_4} \mathrm{Pt_c} \ldots (\mathrm{H_2})_m \text{ (adsorbed)} \qquad (8)$$

$$\mathrm{Pt} + 2\mathrm{H}^+ + 2\mathrm{e}^- \longrightarrow \mathrm{Pt} \ldots (\mathrm{H_2}) \text{ (adsorbed)} \qquad (9)$$

The constancy of the values of Q'_a to Q'_c with scan rate (see Table II) in the basic solution indicates, at least, that the rate of reaction 6 is slow if it occurs at all to any extent. A completely deactivated electrode (allowed to stand in degassed solution 12 hr. or more) shows no prewave and only the normal, large current due to hydrogen formation into solution. On cycling, the anodic prewave is also absent for a deactivated electrode and there is no evidence for contributions from reaction 9 in the potential region of the prewave. If reaction 8 occurs, it is only an additional path by which Pt* is removed from the system. Just by studying the prewave, reaction 8 cannot be distinguished from reaction 7. Conversion of Pt* by these two reactions should have a different rate than by reaction 5.

Rather than allowing the electrode to stand for various periods and then evaluating the prewave, the electrode was continuously cycled around the prewave at a scan rate of 0.13 v. sec.$^{-1}$. The values of Q'_a evaluated in this manner are plotted as a function of time for 1 *F* Na_2CO_3 and 1 *F* H_2SO_4 in Fig. 4, curves A and C, respectively. The curves are both linear with similar slopes. If both the values of Q'_a and Q'_c for the same run are plotted as a function of time as above, two linear curves, which intersect due to a slight difference of slopes, are obtained. The reason for this is believed to be attributable to the slow absorption of hydrogen into the platinum metal which makes the value of Q'_c slightly larger than Q'_a during the early part of the run. At longer times, however, the amount of absorbed hydrogen becomes appreciable and contributes to Q'_a. During these latter stages, if the potential is allowed to scan in the region between the oxide and hydrogen prewave, an anodic wave attributed to absorbed hydrogen[16] is observed.

The first-order decay in quantity of reaction 2 is an indirect measure of the rate of reaction 5. The value of Q'_a can, thus, be expressed at any time, *t*, as follows

$$(Q'_a)_t = (Q'_a)_{t=0} e^{-k_1 t} \qquad (10)$$

where

$$(Q'_a)_{t=0} = mQ_a \qquad (11)$$

and the value of k_1 calculated is 0.015 min.$^{-1}$.

A relationship of similar form as (10) has been set forth by Bonnemay[24,25] for poisoning of "active" sites on platinized platinum by bromine. Poisoning by other halogens was also investigated. It cannot be disputed that "active" sites of Pt* may be deactivated by adsorption of certain anions or organic molecules or through chemical reaction to form a platinum compound on the surface. Presence of oxygen in alkaline solution to form oxide would be an example of the latter. It seems unlikely, however, that any of the above reasons accounts satisfactorily for the present experimentally observed results, particularly to explain the similarity of the half-lives irrespective of whether the solution was 1 *F* H_2SO_4 or 1 *F* Na_2CO_3 or whether the electrode was continuously or intermittently cycled to obtain the decay data.[26]

An interesting question arises with regard to the mechanism of hydrogen evolution or hydrogen oxidation. Does electron transfer occur through the adsorbed hydrogen without any appreciable exchange of the adsorbed with the solution hydrogen? Recent tracer experiments by Osteryoung and Anson[27] has indicated that adsorbed iodide on platinum does not exchange and is inactive electrochemically as far as the oxidation of solution iodide or iodine is concerned. A similar situation, perhaps to a lesser extent, may exist with the hydrogen system.

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(24) M. Bonnemay, *J. Chim. Phys.*, **50**, 142 (1952).

(25) M. Bonnemay, *Compt. rend.*, **239**, 642 (1954).

(26) NOTE ADDED IN PROOF.—Polarization characteristics of absorbed hydrogen have been recently examined in the presence of chloride, cyanide, and perchlorate ions. The half-life of decay was essentially independent of these ions. Closer examination of decays at short times revealed a fast decay with half-life the order of 3–5 min. It has been brought to our attention that Breiter and Kennel (*Z. Elektrochem.*, **64**, 1180 (1960)) had examined similar short decays over a period of 20 min. Our short decay data are in fair agreement with theirs.

(27) R. Osteryoung and F. C. Anson, private communication.