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Registry No. $[Ru(bpm)_3]^{2+}$, 80263-32-7; $[Ru(bpm)_3]^+$, 109468-63-5; $Ru(bpm)_3$, 109468-64-6; $[Ru(bpm)_3]^-$, 109468-65-7; $[Ru(bpz)(bpy)_2]^{2+}$, 85335-53-1; $[Ru(bpz)(bpy)_2]^+$, 93462-10-3; $Ru(bpz)(bpy)_2$, 93462-18-1; $[Ru(bpz)(bpy)_2]^-$, 93461-91-7; $[Ru(bpz)_2(bpy)]^{2+}$, 85335-51-9; $[Ru(bpz)_2(bpy)]^+$, 93462-11-4; $Ru(bpz)_2(bpy)$, 93462-19-2; $[Ru(bpz)_2(bpy)]^-$, 93461-92-8; $[Ru(bpz)_3]^+$, 75523-97-6; $Ru(bpz)_3$, 75523-95-4; $[Ru(bpz)_3]^{2+}$, 75523-96-5; $[Ru(bpz)_3]^-$, 75523-94-3; $[Ru(bpm)_3]^{2-}$, 109468-66-8; $[Ru(bpy)_3]^{2+}$, 15158-62-0; $[Ru(bpy)_3]^+$, 56977-24-3; $Ru(bpy)_3$, 74391-32-5; $[Ru(bpy)_3]^-$, 56977-23-2.

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Surface Coordination Chemistry of Noble-Metal Electrodes. Hydrogen/Iodine Ligand (Adsorbate) Substitution at Smooth Polycrystalline Platinum

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Adsorbate (ligand) displacement/substitution has been found to occur between iodine and hydrogen at smooth polycrystalline platinum electrodes in aqueous acid, neutral, or base electrolyte; experimental measurements were based upon thin-layer electrochemical methods. The iodine/hydrogen substitution reaction is a two-electron redox-activated process, the mechanism of which appears to depend upon the pH of the solution. In the absence of an applied potential, iodine is the only species present on the Pt surface. When a negative potential is applied in the vicinity of the hydrogen evolution reaction, chemisorbed iodine is progressively desorbed as iodide ions accompanied by the immediate chemisorption of protons as hydrogen atoms; when the potential is subsequently made positive, the reverse displacement reaction occurs in which hydrogen is oxidatively desorbed as protons accompanied by the oxidative chemisorption of iodide as iodine. In acid media, iodine desorption occurs *after* evolution of molecular hydrogen; in basic solutions, iodine removal occurs *before* electrogeneration of hydrogen gas.

Introduction

Although the strong interaction of aqueous iodide at platinum electrodes had been reported in the past,[1] it has only recently been established that a spontaneous oxidation–reduction process occurs when a clean platinum surface is exposed to aqueous iodide or gaseous hydrogen iodide. In this process, (i) iodide ions are oxidized to form a chemisorbed monolayer of zerovalent iodine atoms, and (ii) protons or water molecules are reduced to produce hydrogen gas;[2,3] at single-crystal surfaces, the chemisorbed layer of iodine has been found to be highly ordered.[2] In acid solutions, the oxidative chemisorption of iodide may be represented by

$$I^-(aq) + H^+ \rightarrow I(ads) + {}^1/_2H_2(g) \qquad (1)$$

In neutral or basic media, the reaction may be written as

$$I^-(aq) + H_2O \rightarrow I(ads) + OH^- + {}^1/_2H_2(g) \qquad (2)$$

The heat of adsorption of iodine on Pt has been measured from thermal desorption experiments to be *at least* 30 kcal/mol;[2] this stability betrays the formation of strong metal–adsorbate bonds analogous to those in transition metal–halide complexes. The question as to whether iodine chemisorption on platinum can be represented as zerovalent iodine on zerovalent platinum [Pt–I(ads) or as a univalent platinum–iodide complex [Pt(I)–I^-] is largely unsettled although a recent study based on X-ray photoelectron spectroscopy supports the Pt–I(ads) representation.[4]

The spontaneous iodide-to-iodine oxidation upon contact with the Pt surface along with reactions 1 and 2 implies two important aspects of the surface chemistry of smooth polycrystalline platinum with iodine: (i) The standard potential for the Pt–I/Pt–I^- or I(ads)/I^-(ads) redox couple is shifted to negative values relative to that of the $I_2(aq)/I^-(aq)$ couple; that is, in the surface-bound state, iodine is more stable than iodide. (ii) Reactions 1 and 2 may be reversed by the presence of molecular hydrogen; that is, under certain electrochemical or catalytic conditions, ligand (adsorbate) substitution or displacement reactions between iodine and hydrogen may occur. The investigation of these fundamental surface processes was the purpose of this study.

The results obtained here demonstrate that adsorbate substitution or displacement can be made to transpire between iodine and hydrogen at smooth polycrystalline platinum electrodes in aqueous acid, neutral, or base electrolyte in the presence of ample amounts of hydrogen and/or by the application of sufficiently negative potentials. The displacement reaction is a two-electron redox-activated process, the mechanism of which appears to depend upon the pH of the solution. In the absence of an applied potential, iodine is more stable on the surface. When a negative (cathodic) potential is applied in the vicinity of the hydrogen evolution reaction, chemisorbed iodine is progressively desorbed as iodide ions accompanied by the immediate chemisorption of protons as hydrogen atoms; when the potential is subsequently made positive (anodic), the reverse displacement reaction occurs: hydrogen is oxidatively desorbed as protons accompanied by the oxidative chemisorption of iodide as iodine. In acidic media, iodine desorption occurs *after* evolution of molecular hydrogen; in basic solutions, iodine removal occurs *before* electrogeneration of hydrogen gas.

Experimental Section

Experimental measurements were based on thin-layer voltammetric and coulometric methods.[5] Thin-layer electrodes and their advantages in surface chemical studies have been discussed previously.[6] Smooth

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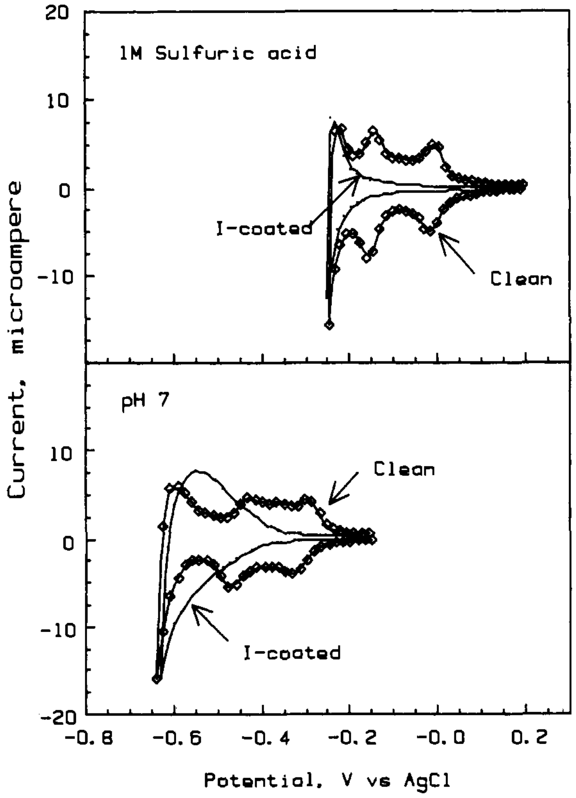

Figure 1. Thin-layer current–potential curves for clean and iodine-pretreated smooth polycrystalline Pt electrodes in molar sulfuric acid (top frame) and in 1 M $NaClO_4$ phosphate-buffered at pH 7 (bottom frame). The curves were initially scanned in the negative direction starting from the rest or equilibrium potentials (0.20 V in molar acid, −0.15 V at pH 7). Conditions: volume of the thin-layer cell, $V = 3.86$ μL; area of the electrode, $A = 1.04$ cm^2; sweep rate, $r = 3$ mV/s; temperature, $T = 298$ K.

polycrystalline platinum electrodes were utilized in this study; the preparation of these electrodes was as described earlier.[7] Electrochemical experiments with chemisorbed iodine were carried out in aqueous solutions containing 1 M H_2SO_4, 1 M $NaClO_4$ buffered at pH 7 (with NaOH and NaH_2PO_4[8]), 1 M $NaClO_4$ buffered at pH 10 (with NaOH and $NaHCO_3$[8]), or 1 M NaOH. Previous studies[9] have demonstrated that the anions derived from the supporting electrolytes employed are only weakly surface-active; hence, they are not expected to influence the chemisorptive properties of iodine and hydrogen significantly. Analytical reagent grade materials were utilized. The aqueous solutions were prepared by using pyrolytically triply distilled water.[10]

The electrode surface was cleaned electrochemically in 1 M H_2SO_4 by sequential oxidation at 1.2 V [Ag/AgCl (1 M Cl^-) reference] and reduction at −0.2 V.[5,6] At the positive potential, surface compounds and/or impurities are oxidatively desorbed and can be rinsed away from the thin-layer cell; removal of the surface impurities at this potential leads to chemisorption of oxygen (or formation of surface oxide); the active metal surface is regenerated by the application of the reducing potential. Surface cleanliness was verified by cyclic voltammetry.[5,6] The electrode surface was pretreated with a full monolayer of iodine by exposure of the clean electrode to aqueous 1 mM NaI[2,3] at the pH at which subsequent hydrogen substitution experiments were to be performed. Unless specified otherwise, electrochemical experiments with the iodine-coated surfaces were performed in the absence of iodide ions in the electrolyte solution.

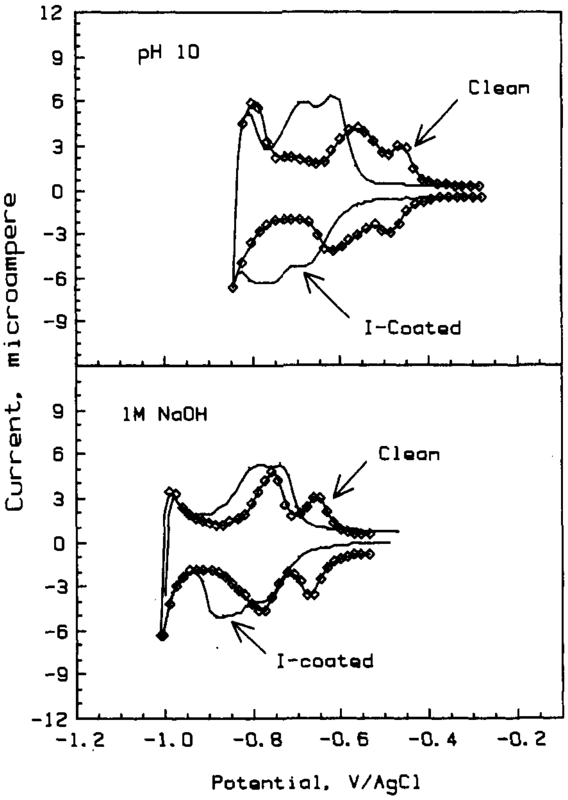

Figure 2. Thin-layer cyclic voltammetric curves for clean and iodine-pretreated smooth polycrystalline Pt electrodes in 1 M $NaClO_4$ carbonate-buffered at pH 10 (top frame) and in 1 M NaOH (bottom frame). The curves were initially scanned in the negative direction starting from the rest potential (−0.25 V at pH 10, −0.50 V in molar base). All other experimental conditions were as in Figure 1.

Measurements of the absolute surface coverage of chemisorbed iodine were done in 1 M H_2SO_4 by oxidation at 1.2 V for 60 s followed by coulometric reduction at 0.70 V.[2] The potential step at 1.2 V oxidizes surface iodine to aqueous iodate, while the second potential step at 0.7 V reduces the iodate to unadsorbed iodine[2,3] according to

$$IO_3^-(aq) + 5e^- + 6H^+ \rightarrow {}^1/_2I_2(aq) + 3H_2O \qquad (3)$$

At 0.70 V, the Pt electrode is still covered by surface oxide, which prevents the readsorption of iodine. In view of reaction 3, the surface coverage of iodine, Γ_I (mol cm^{-2}), can thus be calculated from the iodate reduction charge:

$$\Gamma_I = (Q - Q_b)_{IO_3^-}/5FA \qquad (4)$$

where F is Faraday's constant, Q_b the background charge measured in the absence of chemisorbed iodine,[2,3] and A the actual surface area determined by underpotential hydrogen deposition as described in detail elsewhere.[6,7]

Results and Discussion

Figure 1 shows thin-layer cyclic current–potential curves, initially scanned in the negative direction starting from the "rest" or equilibrium potential, in the hydrogen evolution region for clean and iodine-coated platinum in 1 M H_2SO_4 (top frame) and in 1 M $NaClO_4$ phosphate-buffered at pH 7 (bottom frame); the voltammograms for the I-pretreated surfaces were obtained in the absence of iodide in the supporting electrolyte, but no significant changes were observed in the presence of 1 mM NaI. The two reversible peaks for the clean surface, which appear positive of the hydrogen evolution reaction, are due to underpotential deposition of hydrogen atoms on the Pt surface; these surface processes are profoundly sensitive to the structure and composition of the electrode surface and are widely employed for verification of surface cleanliness and for the quantitative determination of the number of active Pt surface sites.[5]

It is clear that in molar acid, the formation of surface hydrogen is completely suppressed by chemisorbed iodine; that is, down to about −0.2 V, iodine is preferentially chemisorbed over hydrogen.

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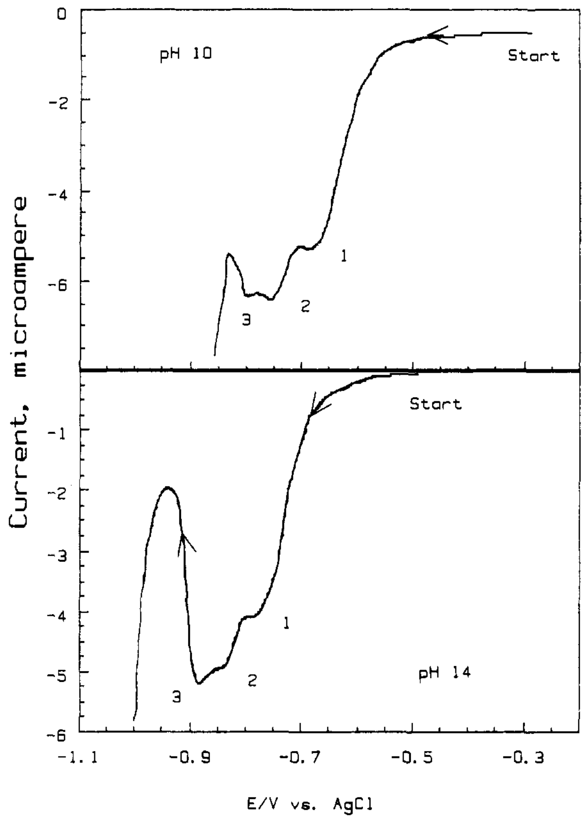

Figure 3. Thin-layer cathodic current–potential curves for an iodine-pretreated smooth polycrystalline Pt electrode at pH 10 (top frame) and in 1 M NaOH (bottom frame). The numbers identify the cathodic peaks discussed in the text. All other experimental conditions were as in Figure 1.

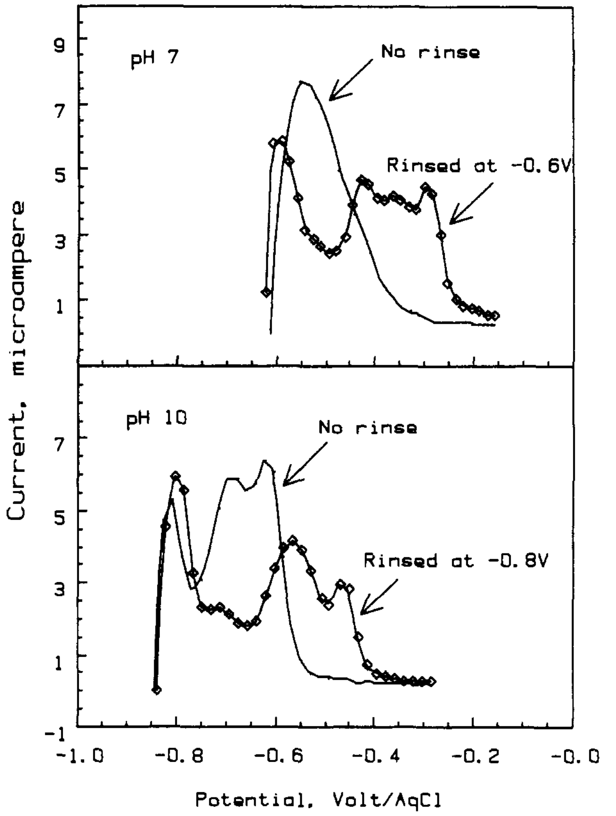

Figure 4. Thin-layer current–potential curves for an iodine-coated Pt electrode in 1 M $NaClO_4$ buffered at pH 7 (top frame) and pH 10 (bottom frame). The electrode was initially held at a preselected potential (−0.6 V at pH 7; −0.8 V at pH 10) for 60 s *and* rinsed in iodide-free supporting electrolyte at the selected potential prior to obtaining the voltammetric scans. All other experimental conditions were as in Figure 1.

However, the presence of iodine on the Pt electrode is unable to prevent the evolution of molecular hydrogen at potentials below −0.2 V. In general, the results obtained at pH 7 resemble those obtained in molar acid; in detail, the results differ in the sense that formation of chemisorbed hydrogen at pH 7 is no longer completely suppressed by surface iodine.

The upper half of Figure 2 shows thin-layer current–potential curves in the hydrogen region for clean and iodine-pretreated Pt in 1 M $NaClO_4$ carbonate-buffered at pH 10. The voltammograms, obtained in iodide-free solution, were initially scanned in the negative direction starting from −0.25 V, the rest potential; virtually identical current–potential curves were obtained when the electrolyte solution was added with 1 mM NaI. It is important to note that three barely resolved cathodic peaks appear for the iodine-coated surface just positive of the hydrogen evolution reaction; these peaks can be seen more clearly in Figure 3. The surface electrochemical processes that give rise to these reduction peaks can be considered reversible since (i) oxidation peaks are observed in the subsequent anodic scan and (ii) no changes in the current–potential curves were noted even after multiple cycling.

The lower half of Figure 2 shows thin-layer current–potential curves in the hydrogen region for clean and iodine-pretreated polycrystalline Pt in 1 M NaOH, initially scanned in the negative direction starting from the rest potential, −0.50 V. The voltammograms shown in this figure were obtained in iodide-free solution but no significant changes were observed when the experiments were performed in the presence of 1 mM NaI. Multiple cathodic peaks are also observed for the I-coated surface at this pH (Figure 3) although they are shifted by about 100 mV in the negative direction relative to those at pH 10.

It is reasonable to attribute the multiple cathodic peaks shown in Figure 3 to iodine/hydrogen substitution or displacement reactions, that is, concomitant cathodic stripping of iodine *and* cathodic deposition of hydrogen. (i) The standard potential for the *aqueous* $I_2(aq)/I^-(aq)$ couple is 0.39 V; consequently, any iodine desorbed from the surface into the solution at potentials well below 0.39 V will immediately undergo reduction to iodide. (ii) The cathodic peaks for the I-coated electrode appear at potentials below those for underpotential hydrogen deposition on the clean electrode (cf. Figure 2); hence, removal of iodine from the surface at the observed potentials should immediately result in the reductive chemisorption of hydrogen. The appearance of multiple peaks is not surprising since these are characteristic of coverage-dependent adsorption–desorption processes.[11]

Figure 4 shows the effect of rinsing the thin-layer cavity with *iodide-free* supporting electrolyte after application of (i) negative potentials and/or (ii) sufficient amounts of electrogenerated hydrogen; the purpose of these potential-controlled rinse experiments was to determine if iodine was quantitatively desorbed from the surface under the stated conditions. The top frame of Figure 4 was obtained at pH 7 with the rinse potential at −0.6 V, just *after* the onset of the hydrogen evolution reaction; the lower frame was at pH 10, with the rinse potential at −0.8 V, just *before* the hydrogen evolution reaction. The postrinse current–potential curves are virtually identical with those for clean (iodine-free) surfaces. These results demonstrate that chemisorbed iodine had indeed been completely desorbed from the surface; in the absence of the halogen, chemisorbed hydrogen was present on the surface. Results similar to those shown in Figure 4 were obtained when an I-coated Pt electrode was rinsed with pure supporting electrolyte at cathodic potentials in 1 M NaOH: The morphology of the current–potential curves approached that for a clean electrode when the thin-layer cell was rinsed at progressively negative potentials; in particular, rinsing the I-pretreated electrode at −1.0 V restored the electrode to its completely clean condition.

Experiments were performed in which the iodine coverage was measured after the thin-layer cell was rinsed with iodide-free

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Table I. Potential and pH Dependence of Iodine Coverage at Polycrystalline Pt[a]

soln	*E*, V	Γ_I, nmol/cm^2	soln	*E*, V	Γ_I, nmol/cm^2
1 M H_2SO_4	0.20	1.12	pH 10	0.04	1.15
	−0.15	1.11		−0.31	1.12
	−0.20	1.04		−0.46	0.99
	−0.25	0.92		−0.61	0.72
	−0.30	0.77		−0.69	0.43
	−0.35[b]	0.58		−0.78	0.05
pH 7	−0.15	1.13	1 M NaOH	−0.15	0.97
	−0.30	1.11		−0.35	0.96
	−0.40	0.94		−0.60	0.79
	−0.50	0.52		−0.72	0.54
	−0.60	0.24		−0.80	0.25
	−0.65	0.03		−0.86	0.04

[a] The average relative standard deviation of the measured coverages is ±6%. [b] Because of extensive hydrogen evolution inside the thin-layer cell, experiments below −0.35 V in molar acid were not performed.

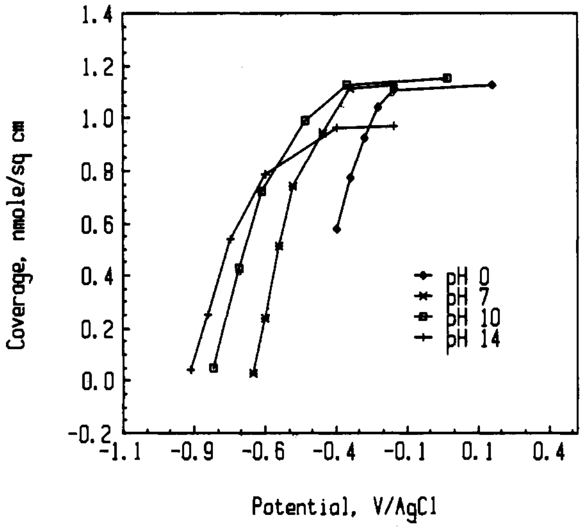

Figure 5. Absolute surface packing density of iodine on smooth polycrystalline Pt electrodes as a function of electrode potential in 1 M H_2SO_4 (pH 0), 1 M $NaClO_4$ buffered at pH 7, 1 M $NaClO_4$ buffered at pH 10, and 1 M NaOH (pH 14). The potential range available in molar acid was limited by hydrogen bubble formations and large ohmic drops, which occurred at potentials below −0.35 V. The solid lines interconnect the data points and do not represent any theoretical fit.

supporting electrolyte at *selected* potentials approaching the hydrogen evolution reaction; the results are tabulated in Table I and graphed in Figure 5. The results shown in this table *and* in Figures 1–5 provide compelling evidence for the following: (i) Regardless of pH, iodine is increasingly desorbed from the surface as the potential is made more negative. (ii) The surface binding sites vacated by iodine are occupied by hydrogen. (iii) When the potential scan is subsequently made anodic, hydrogen is desorbed and its vacated sites are reoccupied by iodine.

The following can be further noted from the present data: (i) In molar acid, chemisorbed iodine is not stripped from the surface unless ample amounts of electrogenerated hydrogen gas are present: appreciable removal of iodine does not commence until −0.25 V, about 30 mV *negative* of the onset of the hydrogen evolution reaction. Although about half of the iodine had already been desorbed in molar acid at −0.35 V, there is still no removal of iodine at *this same potential* at either pH 7 or pH 14; apparently, in molar acid, it is the participation of the electrogenerated molecular hydrogen, and not the application of cathodic potentials, that is the dominant factor in iodine desorption. (ii) In 1 M NaOH, complete removal of chemisorbed iodine was attained at −0.85 V, about 150 mV *positive* of the hydrogen evolution reaction. Evidently, above pH 7, it is the application of sufficiently negative potentials, and not the presence of molecular hydrogen, that accounts for iodine removal.

It is apparent from the present results that the mechanism for the hydrogenative displacement of iodine chemisorbed on the Pt surface is a function of pH. In molar acid, it is possible for the reaction sequence to be

$$H^+(aq) + e^- \rightarrow {}^1/_2H_2(g) \qquad (5)$$

$$H_2(g) + I(ads) \rightarrow H(ads) + H^+(aq) + I^-(aq) \qquad (6)$$

$$\text{net:}\quad H^+(aq) + I(ads) + 2e^- \rightarrow H(ads) + I^-(aq) \qquad (7)$$

In molar base, it is possible that the reaction takes place in the order

$$I(ads) + e^- \rightarrow I^-(ads) \qquad (8)$$

$$I^-(ads) + H_2O + e^- \rightarrow I^-(aq) + OH^- + H(ads) \qquad (9)$$

$$\text{net:}\quad I(ads) + H_2O + 2e^- \rightarrow H(ads) + OH^- + I^-(aq) \qquad (10)$$

It is important to point out the following: (i) As to be expected, the net reactions (7) and (10) are identical; for example, addition of OH^- to both sides of the equation in (7) yields reaction 10. (ii) Also as expected, the potential at which reaction 8 occurs is coverage-dependent; hence, three cathodic waves, rather than a single sharp peak, are seen in Figure 3.

It may be possible to test the plausibility of reaction 10 by measuring the *faradaic* charge under the cathodic peaks in Figure 3. For this analysis, the pH 14 data (bottom frame of Figure 3) in the region from −0.50 to −1.0 V were chosen since the cathodic peaks as well separated from the hydrogen evolution reaction, and extrapolation of the latter's exponential tail is more readily obtainable. Since at −1.0 V, iodine is completely desorbed and the surface becomes saturated with a full monolayer of chemisorbed hydrogen, Faraday's law for reaction 10 will be of the form

$$Q_{red} = FA(\Gamma_I + \Gamma_H) \qquad (11)$$

where Q_{red} is the reductive charge, Γ_I the *initial* coverage of iodine, and Γ_H the coverage of hydrogen *after complete removal of iodine* at −1.0 V. For the electrode used in these experiments, *A* was 1.04 ± 0.05 cm^2; Γ_I and Γ_H were found to be 0.97 ± 0.05 and 2.2 ± 0.1 nmol/cm^2, respectively. Hence, the expected total reductive charge should be close to 320 μC; in fact, the total reductive charge was measured to be 302 ± 15 μC, in agreement with the reaction postulated in eq 10.

The plausibility of reaction 10 can also be tested if it is approximated to be quasi-reversible; the current–potential curves in Figure 2 show that such an assumption is reasonable. In this approximation, the half-cell potential for reaction 10 can be shown to obey the following form of the Nernst equation:

$$E = E_1 - (1/2)0.0591 \log [OH^-] = E_2 - 0.0296\text{pH} \qquad (12)$$

where E_1 includes all pH-independent terms and E_2 incorporates the pK_w factor, K_w being the water dissociation constant. Equation 12 predicts that the peak potential for reaction 10 will be shifted *cathodically* by 30 mV/unit *increase* in pH. Comparison of the cathodic peaks obtained at pH 10 and pH 14 in Figure 3 reveals the following relevant features: (i) the overall morphologies of the reduction peaks are similar; (ii) the peak potentials for *each* of the three peaks are pH-dependent; and (iii) for each cathodic peak, a *negative* shift in potential of about 25 mV/unit *increase* in pH occurs. These observations are consistent with eq 10 or 12.

Acknowledgment is made to the Robert A. Welch Foundation for support of this research.