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Differences in Oscillations and Sequences of Dynamical States Caused by Anion Adsorption in the Electrochemical Oxidation of Formic Acid

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Effects of anions on the electrocatalyzed oxidation of formic acid at polycrystalline Pt under constant current conditions are studied by varying the electrolyte composition. A subcritical bifurcation and an apparently unique sequence of oscillatory states are observed when the supporting electrolyte is H_2SO_4. Different behaviors, including a different sequence of oscillatory states, are seen when $HClO_4$ is used as the supporting electrolyte. Effects of increasing the overall anion "adsorption strength" are also investigated by examining changes in the dynamical response when small amounts of HCl are added to the solution containing formic acid and $HClO_4$. When the concentration of HCl is increased beyond a small critical value, instabilities occur that are not observed when using either the HCl free $HClO_4$ solution or the H_2SO_4 solution. All the stated differences are in contrast to previously reported differences in potential control experiments that were caused by switching electrolytes. The differences in the latter experiments are quantitative. They were interpreted in terms of adsorption and blockage of surface reaction sites by anions. It is argued that the results of the current control experiments imply that anions are also directly involved in the oxidation process. They affect the formation and, consequently, the reactivity of surface water, surface bonded hydroxyl radicals, and Pt oxides.

1. Introduction

The electrochemical oxidations of methanol and formic acid have been extensively studied for several decades. See refs 1−3 for reviews. The two processes remain active research areas[4−18] because of applications in fuel cells[3] and because they provide models of electrochemical reactions involving both the existence of more than one reaction pathway and the adsorption of intermediates on the electrode surface.[2]

Anion adsorption affects the electrochemical oxidation of small organic molecules. In one investigation, effects of anions on the oxidation of methanol at polycrystalline Pt were studied by using different electrolytes and measuring current potential curves.[15] The peak methanol oxidation current obtained by using a sulfuric acid solution was 1.5 times that obtained with a phosphoric acid solution. The peak current measured when using a perchloric acid solution was greater than that obtained with the sulfuric acid solution by a factor of about 1.4. Methanol oxidation was severely inhibited in HCl solutions; at concentrations of $Cl^- \geq 2 \times 10^{-3}$M, methanol oxidation is completely blocked.[19] The results were attributed to competition between the adsorption of methanol and the adsorption of anions. The trend in peak currents was explained in terms of the "adsorption strengths" of anions, which are ordered as $ClO_4^- < HSO_4^- < H_2PO_4^- < Cl^-$.[15] A significant observation in the stated study is that the current−potential curves obtained from the phosphoric acid solution, the sulfuric acid solution, and the perchloric acid solution all have the same basic shape; i.e., the results are quantitative.

Markovic and Ross[16] obtained new information on the effects of adsorbed anions on methanol oxidation by studying the reaction on Pt(111) and Pt(100) electrodes. They deduced the potentials at which anions were adsorbed and correlated these results to the form of the current−potential curves for methanol oxidation. Their work changed part of the theory concerning methanol oxidation. It was believed that, as the potential is increased, oxides were the first species to severely inhibit the oxidation process. Instead, they showed that adsorbed anions strongly inhibit the process before oxides form.

In this paper, results are presented from experiments on the electrocatalyzed oxidation of formic acid at polycrystalline Pt conducted under conditions of constant current. The purpose of the study is to examine the effects of the adsorption of anions on instabilities that are known to occur in this process.[13,17,18,20,21] For reviews of electrochemical instabilities, see refs 22−24. It is found that nonlinear behaviors exhibited by the oxidation of formic acid, including sequences of oscillatory states, change drastically when perchloric acid, as the supporting electrolyte, is replaced by sulfuric acid. Except for different anions, all conditions in the experiments were approximately the same.

It seems unlikely that a greater adsorption strength and a greater blockage of reactions sites by the (hydrogen) sulfate ions are the only reasons for the great differences in observed behaviors. Therefore, experiments were conducted in which incremental amounts of HCl were added to the solution containing perchloric acid as the supporting electrolyte. Hydrochloric acid was used because Cl^- is strongly adsorbed.[19,25] There is also evidence that the effects of chloride ions on methanol oxidation are qualitatively similar to those of (hydrogen) sulfate ions.[16] Concentrations of HCl that are 3 orders of magnitude less than sulfuric acid concentrations achieve effects of the same magnitude.[16] If blockage of reaction sites was the only major effect of anions, adding incremental amounts of HCl to the perchloric acid solution would be expected to cause the observed behaviors to approach the behaviors observed with the sulfuric acid solution. Instead of such a result, behavior was observed with the perturbed perchloric acid solution that was not seen with the sulfuric acid solution nor the HCl free

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perchloric acid solution. The results of the experiments in which incremental amounts of HCl were added indicate a critical value exists for [HCl]. Increasing [HCl] past this value causes a radical change of behavior. Possible consequences of the existence of this critical value are discussed.

2. Experimental Section

High purity water, which was obtained from a Millipore system, was cycled and stored in an Easypure Watersystem (Barnstead, Dubuque, IA). Leading distributors of high purity $HClO_4$ do not provide an analysis of Cl^- impurities. Because Cl^- impurities can play a role in this type of study, three different brands of $HClO_4$ were used: Suprapur perchloric acid from EM Science (Merck), Gibbstown, NJ; redistilled perchloric acid, optima grade from Fisher Chemical, Fisher Scientific, Fair Lawn, NJ; and redistilled perchloric acid, 99.999%, from Aldrich Chemical Co., Inc., Milwaukee, WI. The results reported here can be obtained with all three brands. Sulfuric acid, double distilled, PPB/Teflon grade, was obtained from Aldrich.

Results in this paper are reported for solutions containing 0.10 M NaCOOH (Fisher Chemical, Fisher Scientific) and either 0.50 M $HClO_4$, referred to as the $HClO_4$ solution, or 0.49 M H_2SO_4, referred to as the H_2SO_4 solution. The activity of the sulfate ion on the electrode surface was reported to be greater than that in solution.[26] This report motivated experiments in which lower concentrations of H_2SO_4 were used. The lowest concentration used was 0.40 M. The potential response exhibited a distinctive characteristic when using lower [H_2SO_4] that was also observed with the 0.49 M H_2SO_4 solution but not seen with the $HClO_4$ solution. This characteristic occurs at the beginning of a sequence of states that will be discussed in section 4.

A disk, 7.65-mm diameter of polycrystalline Pt, was employed as the working electrode. The roughness factor for the Pt electrode was 1.63 and the actual "surface area" was 0.75 cm^2. The working electrode was embedded in Teflon and faced downward into the solution ($\approx$250 mL). A AgCl electrode, in which a Na_2SO_4 electrolyte surrounds the reference elements (Fisher Scientific), served as the reference electrode. All potential values are reported with respect to the reversible hydrogen electrode (RHE). Nitrogen flowed through each solution for one-half hour before the solution was used and it flowed through the top of the solution, well above the working electrode, during all experiments.

The Pt electrode was polished with fine alumina mixed with high purity water. The final particle size was 0.05 μm. The Pt electrode was washed with high-purity water and then placed in an electrochemical cell containing an electrolyte solution, a 0.50 M solution of $HClO_4$, or a 0.49 M solution of H_2SO_4. The potential was cycled between 30 and 1580 mV (RHE) at a rate of 100 mV/s until a limiting cyclic voltammogram corresponding to a clean polycrystalline Pt surface was obtained. The electrode was then transferred to a cell containing one of the two formic acid solutions. The temperature of the solution was maintained at 25.0 ± 0.2 °C.

Measurements were obtained on a model RDE4 potentiostat/galvanostat (Pine Instrument Co., Grove City, PA). Data were sent to both an $x-y$ recorder and a Hewlett-Packard (HP) model-9237 computer through an HP, model-3852A, data-acquisition unit equipped with a model-44702A, HP, 13-bit voltmeter. Collection rates ranged between 20 and 2400 points per min.

3. Results of Potential Controlled Experiments

Although the main results of this study are from current control experiments, results on the oxidation of formic acid under potential control conditions are presented first. Limiting current−potential curves (*I*/*E* curves) obtained by cycling the potential at a constant rate between two turning points (cyclic voltammetry) are shown in Figure 1. The solid *I*/*E* curve in Figure 1a was obtained by using the solution containing formic acid and perchloric acid (the $HClO_4$ solution), and the dashed *I*/*E* curve was obtained by using the solution containing formic acid and sulfuric acid (the H_2SO_4 solution). The mechanism for the oxidation of formic acid will be referred to in the description of the *I*/*E* curves. The mechanism consists of at least two reaction pathways. In one pathway, the direct route, all reactions are fast even at relatively low potentials. In the other pathway a strongly bonded surface intermediate forms, surface bonded CO (PtCO).[2] At low potentials PtCO reacts slowly. At sufficiently high potentials surface bonded OH (PtOH) forms. It is generally believed PtOH rapidly reacts with PtCO.

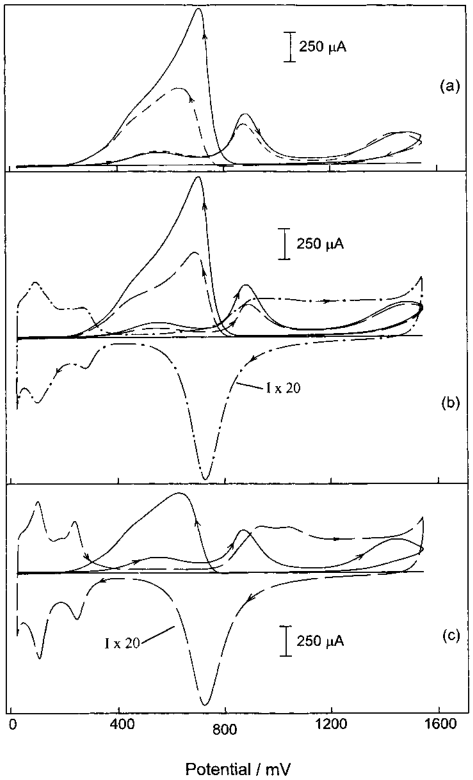

Figure 1. Limiting cyclic voltammograms. Current is plotted against potential (RHE). Scan rate = 100 mV/s. (a) Solid curve: [NaCOOH] = 0.10 M. [$HClO_4$] = 0.50 M. Dashed curve: [NaCOOH] = 0.10 M. [H_2SO_4] = 0.49 M. (b) Solid curve: [NaCOOH] = 0.10 M. [$HClO_4$] = 0.50 M. Dashed curve: same as solid curve but with 5.0×10^{-6} M HCl added. Dashed dot curve: The current is magnified by a factor of 20, $HClO_4$ (0.50 M) supporting electrolyte. (c) Solid curve: [NaCOOH] = 0.10 M. [H_2SO_4] = 0.49 M. Dashed curve: Current is magnified by a factor of 20, H_2SO_4 (0.49 M) supporting electrolyte.

In Figure 1a, it is seen that on the forward scan the *I*/*E* curves for the $HClO_4$ and H_2SO_4 solutions have the same general form over the potential range most studied (0−1200 mV). The greatest difference is that the curve for the $HClO_4$ solution passes through larger current values. The difference between the two curves is small at the first peak, which is generally associated with the reactions in the direct route.

The second peak on the forward scan occurs within potential values where PtCO is generally considered to react with PtOH. The ratio of the current peak obtained for the $HClO_4$ solution to that obtained for the H_2SO_4 solution is 1.24.

Toward the end of the forward scan there is a third peak in what is called the oxide region because platinum oxides form in this potential range. The peak current occurs at a potential for the H_2SO_4 solution that is 40 mV less than the potential at which the peak occurs for the $HClO_4$ solution.

During the reverse scan, *I*/*E* curves for both solutions exhibit a rapid increase in current to a relatively large value. The ratio of the peak current obtained from the $HClO_4$ solution to that obtained from the H_2SO_4 solution is 2.04. The increase in current on the reverse scan is initiated by the reduction of oxides. Consequently, details concerning the peak on the reverse scan are correlated to processes that occur at high potentials during the forward scan. For example, that the rise in current begins at a lower potential value for the H_2SO_4 solution implies that the system advanced to later stages of oxide formation.[27] However, evidence indicates that the difference between peak currents on the reverse scan is due to anion adsorption. The evidence is contained in Figure 1b where *I*/*E* curves are shown for the $HClO_4$ solution, solid curve, and for the same solution but with 5.0×10^{-6} M HCl added, dashed curve. Although the amplitude is smaller, the part of the *I*/*E* curve obtained during the forward scan for the solution containing HCl has a shape similar to the *I*/*E* curve for the HCl free $HClO_4$ solution. This similar shape extends into the oxide region. There is little difference between the two curves at the upper potential. Therefore, the fact that the peak on the reverse scan is smaller for the solution containing HCl is due to the presence of Cl^-. The ratio of the peak current on the reverse scan for the HCl free solution to that for the solution containing HCl is 1.96, which is close to the ratio involving the peak for the H_2SO_4 solution.

The *I*/*E* curve for the $HClO_4$ supporting electrolyte solution (without formic acid) is shown in Figure 1b (dashed−dot curve) and the curve for the H_2SO_4 supporting electrolyte solution is shown in Figure 1c, dashed curve. The rise in current around 800 mV for the supporting electrolyte curves is generally taken to be caused by the initiation of the formation of surface bonded OH.

The differences between the behavior exhibited by the oxidation of formic acid using the $HClO_4$ solution from that using the H_2SO_4 solution, Figure 1, at least for most of the forward scan, are similar to those obtained for methanol[15] in the sense that they are essentially quantitative. There are no drastic differences. The results can be explained in terms of adsorption and blockage of sites by anions.

4. Results of Current Controlled Experiments

In each current controlled experiment the system was left under open circuit conditions ($I = 0$) for 2 h. The current was then increased 0.50 μA every 15 min. When the steady-state potential response approached a value close to where the onset of oscillations occurred, the time increment for changing the current was set to at least 30 min, otherwise a severe overshoot would occur. In the region of oscillations, the current was held constant for considerably longer times.

Oscillatory Response of the Perchloric Acid Solution. When oscillatory behavior first appeared using the $HClO_4$ solution, it consisted of several small potential oscillations separated by a large oscillation. Despite the procedure of slowly approaching the oscillatory region, an overshoot occurred and considerable backtracking was required to stabilize and characterize oscillatory states. It was never clarified whether the reduction of current was required because of long time scales, whether drift played a role, or whether a subcritical bifurcation occurred.

After a low current oscillatory state was stabilized, increasing the current caused the traversal of a sequence of dynamical states in which the number of small oscillations per period decreased by one. Waveforms are displayed in Figures 2a−c for oscillatory states possessing one large oscillation and six, five, and four small oscillations per period. A continuation of this sequence is represented in Figure 3 where waveforms are shown for dynamical states with one large oscillation and three, two, and one small oscillation(s) per period. Increasing the current further caused the state in Figure 3c to deform. Eventually it was replaced through a reversed period doubling bifurcation by an oscillatory state possessing one large oscillation per period.

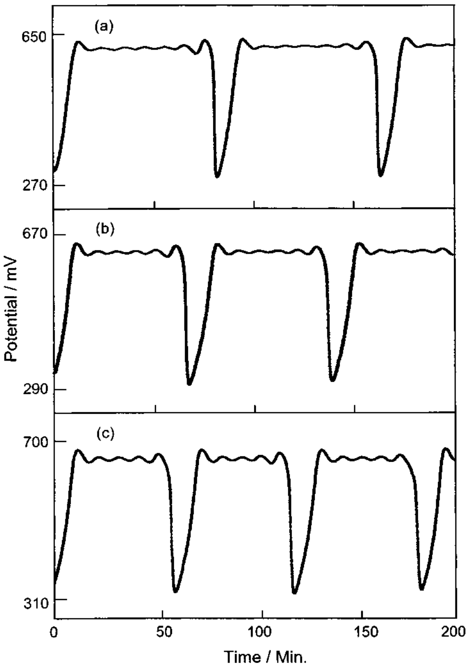

Figure 2. Mixed oscillations. Potential (RHE) is plotted against time. [NaCOOH] = 0.10 M. [$HClO_4$] = 0.50 M. (a) An oscillatory state with six small oscillation (S^6) and one large oscillation (L) for every period, $I = 5.0$ μA. (b) An S^5L state, $I = 6.0$ μA. (c) An S^4L state, $I = 6.5$ μA.

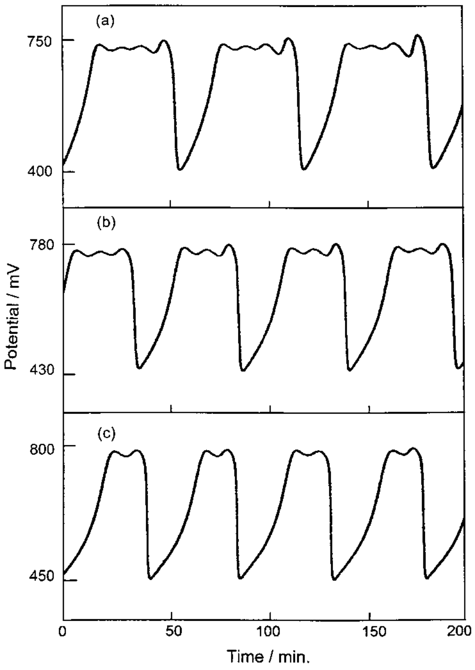

Figure 3. Continuation of the sequence in Figure 2. (a) An S^3L state, $I = 14.5$ μA. (b) An S^2L state, $I = 15.0$ μA. (c) An SL state, $I = 15.5$ μA.

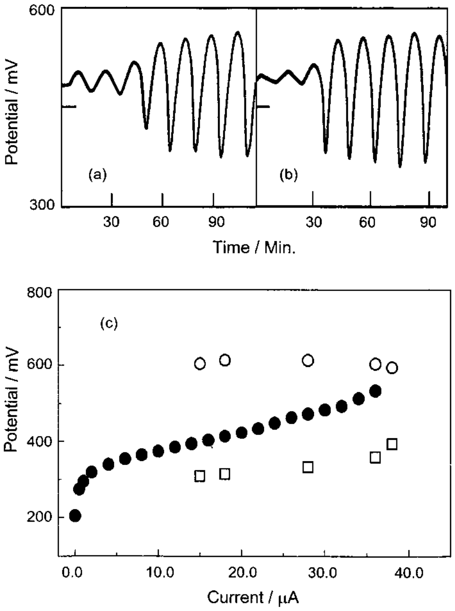

Figure 4. Transition to oscillations using the sulfuric acid solution. [NaCOOH] = 0.10 M. [H_2SO_4] = 0.49 M. (a) Potential is plotted against time. The current was increased by 0.5 μA to 39 μA at the point where the potential begins to increase. (b) A time series from another experiment which begins at the point where the current had been increased by 0.5 μA to 38 μA. (c) A plot of steady-state potential values vs current (solid circles), each of which was measured after a current increase. Also shown are maxima (open circles) and minima (open rectangles) of oscillations. Each oscillation was measured after a current decrease.

Oscillatory Response of the Sulfuric Acid Solution. In contrast to the $HClO_4$ solution, evidence was obtained for the H_2SO_4 solution regarding the type of bifurcation that causes a change from stationary behavior to oscillatory behavior. The evidence supports the idea that the transition is a subcritical one. Experiments that probed the transition were repeated several times. Large amplitude oscillations were always observed at the transition point and sustained small amplitude oscillations were never observed. Time series are shown in Figures 4a,b depicting transitions from stationary behavior to large amplitude oscillations. If the current was decreased after the transition, large amplitude oscillations remained stable for current values less than that at which oscillations first appeared on increasing the current. A plot of potential vs current is shown in Figure 4c. The closed circles represent steady-state potential values recorded after current increases. The open circles and open rectangles represent, respectively, maxima and minima of oscillations recorded after current decreases. The fact that evidence exists for a subcritical bifurcation is not as important as the observation of simple large-amplitude oscillations (one peak per period) at the point where stationary behavior became unstable. No small amplitude oscillations could be stabilized. This behavior is different from that observed near the transition point using the $HClO_4$ solution.

Simple large-amplitude oscillations were observed with the H_2SO_4 solution for a current range that followed the transition point. At sufficiently high values of the current, oscillations were discovered that exhibited additional characteristics. No bifurcation point could be identified when the first new characteristic appeared. This characteristic apparently occurs through a smooth transformation. Initially, a slight indentation was seen in the waveform as the potential decreased during an oscillation. Increasing the current caused this characteristic to develop further until a time series such as the one in Figure 5a was obtained. Similar responses are shown on an expanded time scale in Figure 5b,c. The response in Figure 5c is further developed than the one in Figure 5b.

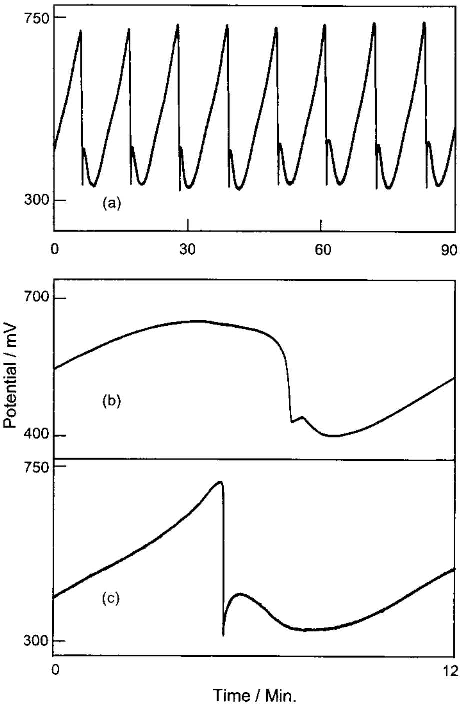

Figure 5. (a) Time series composed of sequences in which a small oscillation immediately follows a large sharp decrease in potential. $I = 55$ μA. (b) An expanded time scale from a time series recorded near a current value where characteristics of the small oscillation become visible. $I = 40$ μA. (c) An expanded time scale from a time series similar to that in (a). $I = 55$ μA.

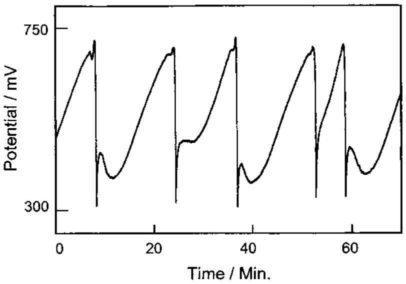

Figure 6. Transients. The behavior eventually became like that represented in Figure 7a. $I = 40$ μA.

Comparison of parts b and c in Figure 5 shows that as the current is increased the “small oscillation” increases in height and the approach to the largest potential value becomes sharper. Examination of transients indicates that, when the amplitude of the small oscillation reaches a sufficiently large value, a second small oscillation appears after the large oscillation that follows the original small oscillation. The second small oscillation appears to develop in the same way as did the original small oscillation. The original small oscillation is flattened and then squeezed out. The resultant waveform consists of two large oscillations followed by a small oscillation. The squeezing out of the original small oscillation is captured in the transient time series shown in Figure 6. A limiting state like the one that followed the transients in Figure 6 is shown in Figure 7a. One can imagine that developments similar to those that led to the time series in Figure 7a can continue which would lead to a time series in which three large oscillations were followed by one small oscillation, Figure 7b, and then one in which four

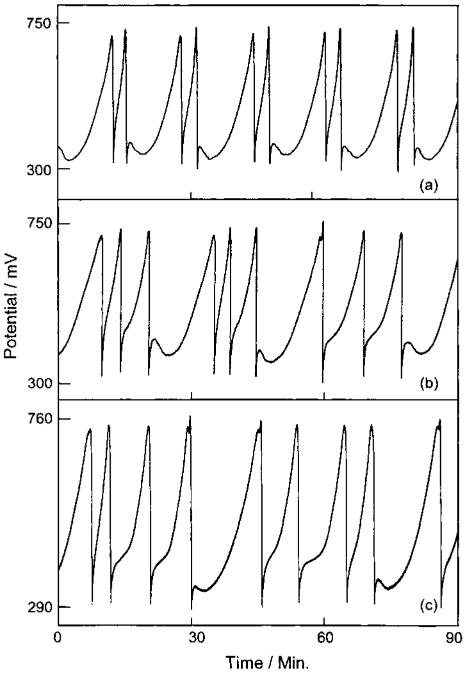

Figure 7. Sequence of oscillatory behaviors obtained by using the sulfuric acid solution. (a) Two large oscillations immediately precede a small oscillation. $I = 40$ μA. (b) Three large oscillations precede a small oscillation. $I = 40.5$ μA. (c) Four large oscillations precede a small oscillation. $I = 47.5$ μA.

large oscillations were followed by one small oscillation, Figure 7c.

Regardless of how the states in Figures 5a and 7 form, they are members of a sequence not observed during the oxidation of formic acid using $HClO_4$ as the supporting electrolyte. The sequence of dynamical states obtained by using the $HClO_4$ solution, Figures 2 and 3, is not observed when the H_2SO_4 solution is used. The two sequences differ drastically. In current control experiments, more than just quantitative differences arise in the oxidation of formic acid when $HClO_4$, as the supporting electrolyte, is replaced with H_2SO_4.

5. Oxidation of Formic Acid in Perturbed Perchloric Acid Solutions

Experiments were conducted in which small amounts of HCl were added to the $HClO_4$ solution. Current scans, at a rate of 5.6×10^{-4} μA s^{-1}, were first conducted. A scan was terminated when the system made a transition to a high potential stationary state. (Behavior obtained this way can be different from limiting behavior.). Results are shown in Figure 8 for a scan using an HCl free solution, Figure 8a, a scan using a solution containing 1.0×10^{-6} M HCl, Figure 8b, and a scan using a solution containing 5.0×10^{-6} M HCl, Figure 8c.

Comparison of parts a−c of Figure 8 reveals that a drastic change in behavior occurred on increasing the HCl concentration from 1.0×10^{-6} to 5.0×10^{-6} M. For the 5.0×10^{-6} M HCl solution, Figure 8c, it can be seen that potential oscillations appeared at approximately 25 μA and then, at a higher current, they look as if they were quenched. Following the quenching of oscillations, the potential appears to have moved along steady states. The system then began to oscillate again. Experiments were repeated several times and each time behavior like that represented in Figure 8c occurred when the 5.0×10^{-6} M HCl solution was used. This behavior was never observed with the HCl free solution nor solutions in which $[HCl] \leq 1.0 \times 10^{-6}$ M.

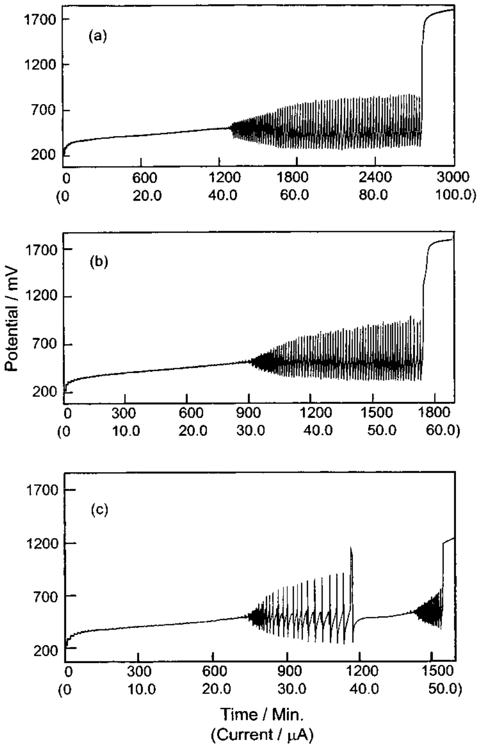

Figure 8. Results from experiments in which the current was increased 0.5 μA every 15 min. Potential is plotted against time and current. (a) $[NaCOOH] = 0.10$ M. $[HClO_4] = 0.50$ M. (b) The same as (a) but with 1.0×10^{-6} M HCl added. (c) The same as (a) but with 5.0×10^{-6} M HCl added.

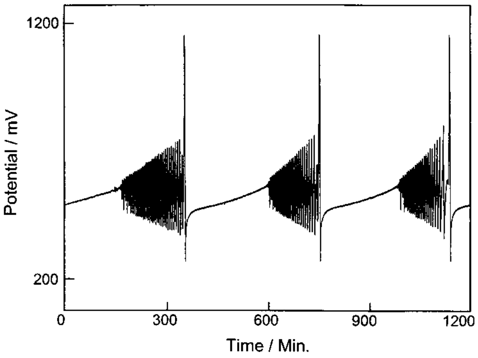

Figure 9. Time series that exhibits bursting. $[NaCOOH] = 0.10$ M. $[HClO_4] = 0.50$ M. $[HCl] = 5.0 \times 10^{-6}$ M. $I = 22$ μA.

Experiments that probed limiting behavior at a fixed current were conducted on solutions containing 1.0×10^{-6} and 5.0×10^{-6} M HCl. Oscillatory behaviors seen with the 1.0×10^{-6} M HCl solution had the same characteristics as those found with the HCl free solution. Experiments that used the 5.0×10^{-6} M HCl solution produced oscillatory behaviors that were not found with the HCl free $HClO_4$ solution nor the H_2SO_4 solution. Features of a response that only occurred with the solution containing 5.0×10^{-6} M HCl are captured in the time series in Figure 9. The response consists of sequences of sharp oscillations that are separated by long periods of time in which the potential appears to be relaxing in a monotone fashion toward a steady state. Instead of reaching a steady state the potential eventually begins to oscillate again. Within a sequence of oscillations, the amplitude of the oscillations increases with time (except for the second last one in a sequence). The amplitude of the last oscillation in a sequence is very large and after it is completed the system returns to behavior in which the potential appears to undergo a monotone relaxation toward a stationary state.

The drastic changes in behavior that take place on increasing [HCl] to 5.0×10^{-6} M are not due to increasing the concentration past the concentration of Cl^- present in the $HClO_4$ solution as impurities. Quantitative differences between results such as those in Figure 8a, using the HCl free solution, and results such as those in Figure 8b, using the solution containing 1.0×10^{-6} M HCl, imply that chloride ions as impurities have a concentration less than 1.0×10^{-6} M. In these experiments, the average value of the current at which oscillations were first observed was 45.1 μA [standard deviation (sd) = 7.7 μA] with the HCl free solution and 39.8 μA (sd = 5.1 μA) with the solution containing 1.0×10^{-6} M HCl. Cyclic voltammetry also provides evidence that the concentration of Cl^- present as impurities is less than 1.0×10^{-6} M. Although the I/E curves for the HCl free solution and the solution containing 1.0×10^{-6} M HCl are close together (on the scale of Figure 1) for most of the cycle, there is an easily measured difference at the second peak of the forward scan. The measured ratio of this peak current obtained when using the HCl free solution to that obtained with the solution containing 1.0×10^{-6} M HCl is 1.16. The ratio of peak currents on the reverse scan has the same value. These results provide strong evidence that the onset of behaviors such as those shown in Figure 8c and Figure 9 result from increasing the Cl^- concentration beyond a critical value.

6. Summary and Discussion

Nonlinear behaviors exhibited by the electrochemical oxidation of formic acid at polycrystalline Pt under constant current conditions undergo drastic changes when $HClO_4$, as the supporting electrolyte, is replaced by H_2SO_4. When $HClO_4$ is used as the supporting electrolyte, oscillatory states exist that consist of a number of small potential oscillations and one large potential oscillation within a period. With respect to an increasing current, the stabilized states are ordered in such a way that the number of small oscillations within a period decrease by one on passing from one state to the next. Near the beginning of the sequence, peak potentials are less than potentials where surface bonded hydroxyl radicals (PtOH) are generally considered to form.

When H_2SO_4 is used as the supporting electrolyte, a completely different sequence of potential oscillations occurs. For stabilized oscillatory states, a small oscillation was preceded by a number of large oscillations. Increasing the current causes the sequence to be traversed in such a way that the number of large oscillations increases by one. For each state, the peak potential of the small oscillation is substantially smaller than potentials where PtOH is considered to form.

The stated qualitative differences are more extreme than the differences obtained from potential control experiments conducted on methanol oxidation[15] and on the oxidation of formic acid, Figure 1. The results from the current control experiments appear singular in the sense that it seems doubtful that the results in the parameter space associated with one electrolyte solution could be mapped by a smooth transformation into the parameter space associated with the other electrolyte. However, the extent of anion adsorption, which is greater for the (hydrogen) sulfate ions, can be considered as a bifurcation parameter. Increasing ion adsorption may cause the dynamical behavior to change from that exhibited with the $HClO_4$ solution, Figures 2 and 3, to that exhibited with the H_2SO_4 solution, Figures 5 and 7. To test this idea, experiments were conducted in which small amounts of HCl were added to the $HClO_4$ solution. Hydrochloric acid was used for the following reasons: Coverage by ions on polycrystalline Pt in both HCl and H_2SO_4 electrolyte solutions (without solute) increases rapidly from zero within the hydrogen region and then begins to level out between 200 and 300 mV.[25,26] According to the measured isotherm for sulfuric acid, there is a second rapid increase in coverage at a potential greater than 1.0 V (RHE).[26] A second rapid increase in coverage occurs at a lower potential for HCl. However, this part of the isotherm levels out and more closely mimics the shape of the sulfuric acid isotherm ($E < 1.0$ V) as the concentration approaches the values used in the experiments reported here (See Figure 6, ref 25). Also, evidence was presented that indicates that HCl has an isotherm similar to that of sulfuric acid on Pt (111).[16] Furthermore, chloride ions appear to affect methanol oxidation qualitatively the same as (hydrogen) sulfate ions.[16] Finally, Cl^- is strongly adsorbed. In potential control experiments, a small concentration of Cl^- inhibits the oxidation of formic acid as well as much higher concentrations of (hydrogen) sulfate ions and in a similar way; see Figure 1.

Perturbing the $HClO_4$ solution by adding small amounts of HCl must increase anion adsorption and the blockage of reaction sites. Therefore, if anions only affect an oxidation process by blocking reactive sites, then perturbing the $HClO_4$ solution should cause the behavior exhibited by the oxidation of formic acid in the current control experiments to approach that observed with the H_2SO_4 solution. The approach to this behavior did not occur. Instead, behavior was found that occurred with neither the H_2SO_4 solution nor the HCl free $HClO_4$ solution.

One explanation for the results is that, besides simply blocking sites, anions play a more direct and involved role in the oxidation of formic acid. To see this as a viable possibility, first consider a brief overview of the oxidation process[2] and the accompanying oscillatory behavior.[20] The oxidation of formic acid possesses at least two reaction paths, the direct and indirect routes. Reactions occur at a rapid rate in the direct route even at relatively low potentials. In the indirect route, the intermediate surface bonded CO (PtCO) forms. This intermediate reacts slowly and blocks reaction sites at the low potentials where the reactions of the direct route can proceed at a rapid rate. Higher potentials are required for the rapid reaction and removal of CO. Although oversimplified, a description of oscillations in the oxidation of formic acid is as follows: In the oscillatory region, PtCO forms at a rate sufficiently rapid to cause the potential to increase so that, at the remaining vacant sites, the rate of reactions of the direct route can increase to values that satisfy the applied current. However, once the potential is driven to sufficiently high values, CO is rapidly removed through surface reactions. The reaction of PtCO produces a large increase in the number of vacant sites and this increase allows the reactions of the direct route to proceed at a slower rate and still satisfy the current. Consequently, the potential decreases. Surface bonded CO begins to form again and the process repeats.

Oxygen containing species must react with PtCO to produce CO_2. Surface bonded OH is most often proposed as a reactant.[2,17,18,28] A form of weakly surface bound water is also a plausible reactant.[6,8,21] Evidence that some form of water is a reactant is provided by some of the peak potentials in the oscillations, which have values less than the lowest value at which PtOH is generally considered to form. If the notion that PtCO can react with PtOH and/or water is accepted, then strong arguments exist in favor of the idea that anions have an involvement in the oxidation of formic acid that is greater than simply blocking surface reaction sites. The additional roles of the anions directly affect the reaction of PtCO and, consequently, affect oscillatory behavior.

Because an anion is hydrated in solution, it seems improbable that the adsorbed anion becomes essentially an identity onto itself, which, however, is how it is usually represented. Anion adsorption must involve adsorption of a complex consisting of water molecules bound to the anion. At low potentials the adsorption of the complex should be an electrostatic adsorption:[29]

$$s\mathrm{Pt} + \mathrm{A}^{-}{\cdot}t(\mathrm{H_2O}) + u\mathrm{H_2O} + v\mathrm{PtH_2O} = \mathrm{Pt}_{(n+x)}\mathrm{A}^{-}{\cdot}x\mathrm{H_2O} + y\mathrm{H_2O} + (s + v - x - n)\ \mathrm{Pt} \quad (1)$$

where s Pt represents s vacant surface sites, n is the number of surface sites shielded by the anion A^-, x is equal to $t + u + v - y$ and represents both the number of additional sites shielded by the anion−water complex and the "coordination number". It is assumed that each water molecule weakly bound to the Pt surface and each H_2O component of the adsorbed complex shield one surface site. Since the adsorption process does not involve electron transfer, the complex on the right-hand side (rhs) of eq 1 could exist up to a potential value of approximately 700 mV.

At higher potentials, anions can undergo full or partial discharge. The complex can undergo several other changes. An increase in surface coverage will cause the amount of water in a complex to decrease.[29] Increases in the potential will also initiate the discharge of water in the complex.[29] An overall reaction is used to represent these steps:

$$\mathrm{Pt}_{(n+x)}\ \mathrm{A}^{-1}{\cdot}x\mathrm{H_2O} \rightarrow \mathrm{Pt}_{(z+n)}\ \mathrm{A}^{-(1-\alpha)}{\cdot}(z-1)\ \mathrm{H_2O}{\cdot}\mathrm{OH}^{-(1-\beta)} + (x-z)\mathrm{H_2O} + (x-z)\mathrm{Pt} + \mathrm{H}^{+} + (\beta + \alpha)\ \mathrm{e}^{-} \quad (2)$$

In principle, the discharge of water will continue until all the water is affected:[29]

$$\mathrm{Pt}_{(z+n)}\ \mathrm{A}^{-(1-\alpha)}{\cdot}(z-1)\ \mathrm{H_2O}{\cdot}\mathrm{OH}^{-(1-\beta)} \rightarrow \mathrm{Pt}_{(z+n)}\ \mathrm{A}^{-(1-\alpha)}{\cdot}z\mathrm{OH}^{-(1-\beta)} + (z-1)\ \mathrm{H}^{+} + (z-1)\beta\mathrm{e}^{-} \quad (3)$$

At sufficiently high potentials, the discharge of the $OH^{-(1-\beta)}$ is completed, which can be accompanied with the desorption of the anion:

$$\mathrm{Pt}_{(v+n)}\mathrm{A}^{-(1-\alpha)}{\cdot}z\mathrm{OH}^{-(1-\beta)} \rightarrow z\mathrm{PtOH} + \mathrm{A}^{-} + [z(1-\beta) - \alpha]\mathrm{e}^{-} \quad (4)$$

At sufficiently large potential values and for a sufficient number of vacant sites, the discharge of water can occur at a rapid rate:

$$\mathrm{H_2O} + \mathrm{Pt} \rightarrow \mathrm{PtOH} + \mathrm{H}^{+} + \mathrm{e}^{-} \quad (5)$$

Assuming no electron transfer occurs in the double layer and that PtOH is prevalent where the initial appreciable amplitude occurs on the forward scan in the cyclic voltammogram for the electrolyte solution, then complexes such as those on the rhs of eqs 2 and 3 should exist between 650 and 800 mV (see Figure 1).

The above description, eqs 1−5, contains several assumptions and simplifications. Some are listed in the following: Variation of coverage will cause the coordination numbers, x and z, to vary. Anions may be capable of more than one orientation on the surface.[26] Not all anions desorb; e.g., the hydrogen sulfate ion continues to be adsorbed at high potentials.[26] Interactions through the metal between anion complexes are possible which can lead to the formation of sublattices.[29] The size of the complexes, the extent of their adsorption, and the extent of sublattice formation depend on the competition with the adsorption of formic acid. If sublattices form, spatial distributions on the electrode surface can be important.

Despite the shortcomings of eqs 1−5, the equations provide a picture that reveals the means by which anions can affect the oxidation of formic acid other than by blocking sites. From the overview of the oscillations presented above, it is clear that the reaction of PtCO plays an important role. In principle, PtCO can react with the oxygen-containing components in the surface complexes in eqs 1−3. The reactivity of these components varies with the particular anion. Reactivity of water in the complex on the rhs of eq 1 depends on the interactions between water and the ion. For ClO_4^- and HSO_4^-, these are ion−dipole and "dipole−dipole" ("hydrogen bonding"[29]) interactions. The strength of the interactions is different for the two ions. Ion−dipole interactions exist between water and Cl^-. The orientations of the oxygen-containing components affect reactivity. Orientations vary among different anions. The coordination numbers, x and z, eqs 1 and 3, which vary among anions, affect the orientation and the amount of reactive components available per adsorbed anion. Since all the stated quantities vary among anions, which causes the reactivity between PtCO and the oxygen-containing components to vary among anions, it follows that these variations cause differences in the nature of the oscillatory response.

The present understanding of the mechanism for the oxidation of formic acid[2] indicates that decreases in the potential during oscillations are directly correlated only to reactions that remove surface bonded CO ($E < 1.0$ V). The peak potentials of the small oscillations seen using the H_2SO_4 solution, Figure 7, are within a range of values where the reaction involving PtCO and the complex on the rhs of eq 1 could take place. Oscillations with such small peak potentials have not been previously observed during the oxidation of formic acid. The peak potentials belonging to the sequence of states that occur using the $HClO_4$ solution, Figures 2 and 3, are within a range of values where reactions involving PtCO and the complexes on the rhs of eqs 2 and 3, as well as intermediates between these two complexes, could take place. The amount of OH in these complexes increases with potential. The reactivity of the complexes with PtCO is expected to increase with the amount of OH, which is consistent with the nature of the sequence of states in Figures 2 and 3. Each sequential state exhibits a slightly higher peak potential and a shorter time at these high potentials; the time decreases because CO is removed at a faster rate by reacting with a more reactive complex. Finally, the complexes in eqs 1−3 may stabilize the system by serving as reactants and delaying the formation of PtOH. Using the $HClO_4$ solution, large amplitude oscillations, with large peak potential values, are stable for a large current range (see Figure 8a). However, once the potential reaches a value where PtOH is generally considered to be prevalent, >800 mV, the system makes a transition to a high potential steady state. The same result occurs using the H_2SO_4 solution. As described in a previous detailed analysis,[6] the formation of PtOH can occur at a rate greater than the rate of reaction between PtOH and PtCO. Consequently, a large number of sites begin to be blocked by hydroxyl radicals and the transition becomes necessary so that other types of reactions can take place at a rate that satisfies the current. The conjecture is consistent with the results in ref 16, where it was found that increasing the source of PtOH inhibits the oxidation of methanol.

Evidence was presented that supports the notion that, in formic acid solutions containing $HClO_4$ and small amounts of HCl, a critical value exists for [HCl] (for 0.10 M NaCOOH and 0.5 M $HClO_4$, $1.0 \times 10^{-6} < [\mathrm{HCl}]_{\mathrm{critical}} \leq 5.0 \times 10^{-6}$ M). If a concentration of HCl is used that is below the critical value, the potential response exhibited by the oxidation of formic acid under current controlled conditions is quite different from the response observed when a concentration of HCl is used that is greater than the critical concentration. No analogous critical concentration was detected in potential controlled experiments. (A one-to-one correspondence between the response in current controlled experiments and that of potential controlled experiments does not always exist because of different stability properties.[30]) The time series in Figure 9 suggests that, at the critical concentration, chloride ion complexes take on the ability to inhibit the entire reaction process for a finite time. The argument for this idea is as follows: The oscillation that terminates a sequence of oscillations in Figure 9 possesses a peak potential that has a value that is approximately equal to the value where oxide formation is initiated. Hence, the system passed through a large potential range where highly reactive PtOH is usually present. However, reaction between PtCO and PtOH did not cause the potential to decrease. This lack of reactivity can result from a large coverage of anion complexes. At very high potentials, a high-energy process can occur that couples with the desorption of anions. Following the desorption of anions, the potential undergoes a large drop.

The critical value for [HCl] will vary with the concentrations of formic acid and perchloric acid. The critical value reported here is below Cl^- concentrations that can arise in solutions prepared with ACS grade perchloric acid. Although effects from the presence of anions as impurities have been previously noted and studied (see for example, ref 16), this is the first time that they have been correlated to a sharp drastic change in dynamical behavior. Such a result may provide the foundation for the development of detectors.

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