

Improvements in the Efficiency of the Oxidation of Formic Acid Obtained by Increasing the Overall Anion Adsorption Strength

B. E. Kumara Swamy, Jamala Maye, Charles Vannoy, and Mark Schell*

The Department of Chemistry, Southern Methodist University, Dallas, Texas 75275

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Measurements are reported on changes in the efficiency of the electrochemical oxidation of formic acid that were caused by varying the overall “anion adsorption strength”. The adsorption strength was varied by changing the fractions of sulfuric acid and perchloric acid in the electrolyte. It was found within certain conditions that, given two solutions, formic acid oxidation is more efficient in the solution with the larger overall expected anion adsorption strength. The result was found within two very different concentration ranges for sulfuric acid and perchloric acid, and it was obtained in both current- and potential-control experiments. From past experimental results and theoretical considerations, a larger anion adsorption strength would be predicted to cause the oxidation reaction to be less efficient.

Introduction

The effect of the electrolyte’s anion composition on electrochemical processes at metal electrodes is a large research area.^{1–37} Early studies of anion adsorption^{1,2} provided important information, such as isotherms, which represent anion surface concentrations as a function of potential. Later studies provided more detailed, specific information about anion adsorption, much of which was obtained using modern and/or improved methods. Examples of methods used in studies of anion adsorption are different forms of infrared spectroscopy,^{3–7} surface-enhanced Raman spectroscopy,⁸ scanning tunneling microscopy,⁹ employment of the electrochemical quartz crystal microbalance,¹⁰ improved radioactive labeling techniques,^{11,12} auger electron spectroscopy,¹³ and in situ X-ray reflectivity.¹⁴

Examples of specific details concerning anions are taken from Lachenwitzer et al.,⁶ where 47 references are listed about the adsorption at Pt of the hydrogen sulfate and sulfate anions. The study in Lachenwitzer et al.⁶ applied subtractive normalized interfacial Fourier transform spectroscopy. The S–(OH) stretch and the SO stretches of the hydrogen sulfate ion, and the SO stretches of the sulfate anion, were used to determine that the hydrogen sulfate anion is the predominately adsorbed species at Pt(111) from solutions containing NaF, HF, and K₂SO₄, for pH < 3.3. The sulfate anion is the predominately adsorbed species for pH > 4.7.

In a study that used an electrolyte consisting of a mixture of acids, similar to that used in the study presented here, a radioactive labeling technique was employed to examine surface species.¹¹ The charge of the anion adsorbed onto a Pt(111) surface from an aqueous perchloric acid/sulfuric acid media changed with potential. The change is consistent with a progression in the dissociation of the hydrogen sulfate anion to the sulfate anion. At relatively high potentials, the surface anion had a charge of –1.7. It was concluded that the species was a partially discharged sulfate anion. It was suggested that the difference between the –1.7 charge and a –2 charge (the latter characterizes a sulfate anion in solution) was due to electron donation from the sulfate ion to Pt. This research helped resolve

discrepancies in the understanding of the adsorption of anions from solutions containing sulfuric acid. The paper also contains a brief review of anion adsorption.

When metals of different atoms are used as electrodes, anion adsorption behavior is different. See, for example, Marinkovic et al.⁵ The accumulated work on anion adsorption suggests a generalization: defects, differences in electrode geometries, different crystallographic structures, and other differences in morphology can cause great differences in the behavior of the same anion.^{5,7,14,16–21}

Besides achieving information about the double layer and a greater understanding of the fundamentals of the process, the study of anion adsorption is important because of the effects of anions on electrochemical processes.^{10,14,22–34} A simple theory of the effects of anion adsorption on electrochemical processes is formulated in terms of the competition between anions and reactants for surface sites and in terms of the “adsorption strengths” of anions.²³ An anion, in general, is adsorbed to a greater or lesser extent than other species. The following anions are ordered according to their anion adsorption strength:



An anion with a large adsorption strength, such as the chloride ion, Cl[–], is expected to inhibit an electrochemical process more than an anion with smaller adsorption strength, such as the perchlorate ion, ClO₄[–].

The simple theory on the effects of anion adsorption applies to several observations. The effects of anions on the oxidation of methanol at polycrystalline Pt were studied using different electrolytes and measuring current–potential curves.²³ The peak methanol oxidation current decreased following the trend given by anion adsorption strengths given in eq 1. The highest peak current was obtained using a perchloric acid solution and the lowest peak current was obtained using a solution that contained chloride ions.

Other results can be interpreted in terms of anion adsorption strength and competition for surface sites. A study¹⁰ using voltammetry and an electrochemical quartz crystal microbalance deduced that the upper limit of the potential range for water adsorption was different in the presence of different anions.

* To whom correspondence should be sent. E-mail: mschell@smu.edu. Fax: (214) 768-4089.

Decreases in the upper limit for water adsorption followed the trend given by anion adsorption strengths; the largest limit was obtained when the perchlorate ion was the major anion in solution, and the smallest limit was obtained when the chloride ion was the predominant anion in solution. The rate constants for a redox reaction were found to decrease in the presence of halide anions.²⁸ The decrease follows the increase in adsorption strength of halide anions, $F^- < Cl^- < Br^-$. Research was conducted on the effects of the chloride ion at different metals [Pt(111), Pt(100), Pt(111)–Pd: layers of palladium on Pt(111)] during the oxygen reduction reaction and hydrogen oxidation and reduction reactions.^{19,33} In this work, it was shown¹⁹ that a perchloric acid solution inhibited the oxygen reduction reaction less than a solution containing sulfuric acid. Solutions with chloride ions inhibited the reaction the most.

Previous studies have provided evidence that anions affect electrochemical processes in at least one way different from the inhibiting effect caused by blocking surface sites.^{35–37} In the study presented here, it is shown that the efficiency of a process can improve even though the expected overall anion adsorption strength increases. The process examined is the electrochemical oxidation of formic acid.^{33–39} The overall anion adsorption strength is varied by varying the fractions of sulfuric acid and perchloric acid in the electrolyte. The results cannot be explained in terms of anion adsorption strengths.

Experimental Section

All solutions were prepared using high purity water that was first obtained from a Millipore system and then was cycled and stored in an Easypure Watersystem (Barnstead, Dubuque, IA). High purity water was used in all cleaning procedures and electrode treatment. Sulfuric acid, double distilled, PPB/Teflon grade, was purchased from Aldrich Chemical Co., Inc., Milwaukee, WI. Perchloric acid was obtained from Aldrich (redistilled $HClO_4$, 99.999%). Sodium formate, $NaCOOH$, was obtained from Fisher Chemical, Fisher Scientific, Fair Lawn, NJ.

Experiments were conducted in a three-compartment electrochemical cell located in a water bath possessing a temperature of 25.0 ± 0.2 °C. The main compartment of the electrochemical cell consisted of a three-neck flask and contained the solution under investigation. A second compartment, separated from the main compartment by a glass membrane, contained the counter electrode. A platinum foil was employed as the counter electrode. A third compartment contained the reference electrode and a solution with the same composition as that of the main compartment. Contact was made with the main compartment through a stopcock. The reference electrode was $Ag/AgCl/1.0$ M sodium sulfate. However, all potential values reported are with respect to the reversible hydrogen electrode (RHE). Cyclic voltammograms were measured using a Pt working electrode in perchloric acid to check the potential of the reference electrode. The lowest potential cathodic hydrogen peak in the voltammogram is at 100 mV.

The working electrode was a polycrystalline Pd disk, 7.65 mm diameter (Pine Instrument Co., Grove City, PA). The disk was embedded in Teflon. The disk was at the end of a 20.5 cm long rod, mostly Teflon covered, with a stainless steel core.

The Pd disk was polished with alumina (Buehler, Lake Bluff, IL) mixed with high purity water. The polishing was done on Microcloths (Buehler) glued to flat mirrors. A different Microcloth was used for each size of alumina. The final particle size was $0.05 \mu m$. After the initial cleaning of the electrode, it was only necessary to polish with the $0.05 \mu m$ particle size during

the time the experiments described were conducted. Before transferring the electrode to a solution or between solutions the disk was washed with high purity water and then it was covered with a layer of high purity water or with a layer of formic acid solution. A Teflon cap was placed loosely over the disk in such a way that it did not touch the liquid layer on the electrode surface.

After polishing, the electrode was transferred to an electrochemical cell that contained either 0.49 M sulfuric acid or 0.50 M perchloric acid. The potential was cycled between 300 and 1500 mV. If a limiting cyclic voltammogram corresponding to a clean surface was obtained, see the ones in Figure 3a in Chen and Schell,³⁵ the electrode was transferred to a formic acid solution; otherwise, it was polished again.

The working electrode passed through the neck that was above the center of the main compartment of the electrochemical cell. The final location of the disk was about 1.5 cm below the surface of the solution with the disk facing down into the solution. Nitrogen flowed through each solution for one half-hour before the solution was used, and it flowed through the top of the solution, above the level of the Pd disk, during all experiments. All openings of the cell were sealed with plastic, but with an allowance for the outward flow of nitrogen.

No electrode surface is perfectly smooth. Asperities exist that protrude beyond the visible solid liquid phase boundary.⁴⁰ These protrusions add to the amount of electrode material that is active. The total amount of electrode material that is active is called the area.⁴⁰ Calculating the area allows the normalization of results by the use of current density. The ratio between the measured area and the geometric area is called the roughness factor.⁴⁰ The roughness factor itself is important. Varying the roughness factor can change electrochemical behavior that does not scale with current densities.⁴⁰ Changes in the roughness factor changed the rate of dissolution of copper.⁴¹ They were also shown to affect the frequency dispersion in impedance behavior.⁴² An increase in roughness factor increased an electrode's catalytic response to a reduction reaction.⁴³

One method for measuring the area for many noble metal electrodes takes advantage of the adsorption and desorption of hydrogen. The area can be calculated if a complete monolayer of hydrogen atoms is achieved on the electrode. The charge under the current peaks can be measured for hydrogen desorption.⁴⁰ It is not possible to use this method for palladium, as no hydrogen peaks form and hydrogen enters the metal.⁴⁰

Several other methods for measuring area exist.⁴⁰ It has been suggested to choose a method for measuring the area that approaches the experimental situation in which the electrode will be used.⁴⁰ A large portion of the results presented is from experiments in which cyclic voltammetry was applied, and so a method involving voltammetry was used to measure the area. The method is based on the Randle–Sevcik equation for the peak current from a cyclic voltammogram arising from the electrochemical reduction or oxidation without adsorption of an electroactive species.⁴⁴ The equation is given by

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} S^{1/2} c \quad (2)$$

where the constant, 2.69×10^5 , has units of coulombs per mole times volt to the $1/2$ power, $C/(mol V^{1/2})$. The other symbols in the Randle–Sevcik equation are defined as follows: I_p is the peak current in a voltammogram with units C/s , n is equal to the number of electrons transferred when the electroactive species reacts, A is the electrode area in units of cm^2 , D is the diffusion coefficient of the electroactive species and has units

of cm^2/s , S is the scan rate and has units of V/s , and c is the concentration of the electroactive species and has the units mol/cm^3 .

Cyclic voltammetry was applied to an aqueous solution of 0.10 M KNO_3 and 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$. With an upper potential limit of 1500 mV (RHE) and a lower potential limit of 300 mV, the current was measured during a potential cycle beginning and ending at the upper limit. A cathodic peak occurs during the potential decrease at which the electroactive species, $\text{Fe}(\text{CN})_6^{3-}$, is reduced. The current–potential curve was measured for 6 scan rates: 0.218, 0.170, 0.140, 0.100, 0.075, and 0.050 V/s . Preceding the application of a potential cycle, the electrode was treated electrochemically by holding the potential at 1.90 V for 10 s, 0.375 V for 14 s, and -0.025 V for 1.5 s. This procedure, without any time gaps, was repeated 30 times. The potential was preset to go to the value of 375 mV after the last sequence finished. The electrochemical treatment was to ensure film formation would have no effects.⁴⁴

A slope was obtained from a linear regression analysis of a plot of the measured current cathodic peak against the square root of the sweep rate. To calculate the area of the electrode, the slope was divided by $n^{3/2}$ (which equals one for the electroactive species $\text{Fe}(\text{CN})_6^{3-}$), the concentration $1.00 \times 10^{-5} \text{ mol}/\text{cm}^3$, $2.69 \times 10^5 \text{ C}/(\text{mol V}^{1/2})$, and the square root of the diffusion coefficient of the electroactive species D . The diffusion coefficient was measured by the same procedure for measuring the area of the Pd electrode, except that a Pt electrode with known area was used. The average of two measurements gave $D = 7.10 \times 10^6 \text{ cm}^2/\text{s}$, which is about 1.5% different from the average value obtained in Konopka and McDuffie⁴⁵ for 0.10 M KCl solutions, and also about 1.5% different from the value given in Petrovic,⁴⁴ which was measured in a 0.10 M KNO_3 solution. The value for the area obtained by dividing the slopes with all of the stated quantities is 1.45 cm^2 , which gives a roughness factor of 3.15. The area is an average of three measurements. The standard deviation for the three measurements is 0.06 cm^2 . The average standard deviation of the slopes obtained in the linear regression analyses, divided by the quantities that divided the slope to yield an area, gives a value that is 1/3 the magnitude of the standard deviation for the measured values.

A Model RDE4 potentiostat/galvanostat (Pine Instrument) was used to apply a current and measure the potential in current-control experiments. The same instrument was used to apply a triangular wave and measure the current in potential-control experiments. Measurements with a voltmeter served as an additional check on current and potential readings. Measurements were sent to an x–y recorder (The Recorder Co., San Marcos, TX) and to a Hewlett-Packard (HP), model-9237 computer through a HP, model-3852A, data acquisition unit.

Results and Discussion

Current-Control Experiments. Experiments were conducted in which a large constant current ($8.07 \mu\text{A}/\text{cm}^2$) was applied to the oxidation of formic acid. The rate of reaction becomes too slow at low potentials to satisfy the applied current at long times. However, the rate of reactions can satisfy the current at low potentials for short times. The experiments reveal the temporal evolution of the potential from low to high values.

In the experiments, the time it took the potential to reach the value 1361 mV [the reversible hydrogen electrode scale (RHE)] was measured. The same trends were obtained using a lower potential, 1060 mV. The initial time for the potential evolution was taken to be the instant the large constant current was

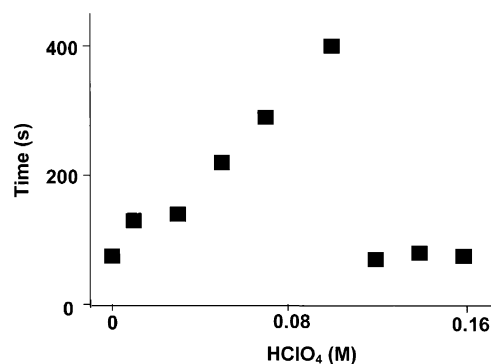


Figure 1. Time that the potential took to reach the value 1361 mV (RHE) plotted against the concentration of perchloric acid. The concentration of sulfuric acid equaled 0.49 M minus the concentration of perchloric acid. $[\text{HCOOH}] = 0.20 \text{ M}$.

applied. Preceding the application of the large constant current, the potential was brought to a value equal to 400 mV (RHE) in each experiment by decreasing the current from zero. This value belongs to the interval in which the “double layer” exists for the solution without formic acid.

In one set of experiments, the time to reach a high potential was first measured for a solution in which 0.20 M formic acid and 0.49 M sulfuric acid were mixed. In subsequent experiments, perchloric acid was mixed into the solution. The smallest amount of perchloric acid added was 0.01 M. The results for these experiments are shown in Figure 1. The time it took to reach high potentials is plotted against the concentration of perchloric acid. The concentration ranges from 0 to 0.16 M.

The time that the system takes to reach a high potential, Figure 1, appears to increase linearly with respect to the perchloric acid concentration within the concentration range from 0.00 to 0.10 M. A linear regression analysis was applied to the first six data points in Figure 1 using the equation

$$t = m[\text{HClO}_4] + t_0 \quad (3)$$

where t is equal to the time the potential takes to reach 1361 mV, m is a constant that multiplies the perchloric acid concentration, and t_0 is the time that the potential takes to reach 1361 mV when the solution contained no perchloric acid. The analysis revealed that eq 3 has a slope (m) equal to $3.14 \times 10^3 \text{ s}/\text{M}$ with a standard deviation of 120 s (Recall that the calculation of the standard deviation in a linear regression analysis only uses the variable in the vertical direction.), an intercept, t_0 , of 73.0 s, and a correlation coefficient equal to 0.988.

The increase in the time to reach a high potential with respect to increases in the perchloric acid concentration is consistent with previous experimental results and theory on how anions affect electrochemical process. The (hydrogen) sulfate anion (Both the hydrogen sulfate anion and the sulfate anion are in solution and we represent this by writing hydrogen in parentheses.) has a larger adsorption strength than the perchlorate anion. Therefore, beginning with a solution that has sulfuric acid and no perchloric acid and then mixing in small amounts of perchloric acid, the overall anion adsorption strength is expected to decrease. A decrease in anion adsorption is expected to increase the reaction sites at which formic acid reacts. An increase in reaction sites will allow a larger rate of reaction at lower potentials. Thus, the current can be satisfied with a slower increasing potential.

The linear regression analysis does not prove a linear relation exists between the time it took the potential to reach a high

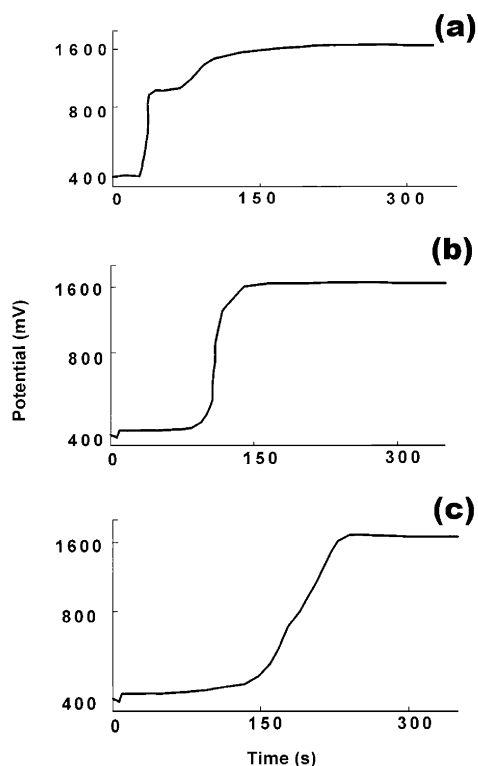


Figure 2. Temporal evolution of the potential. Potential is plotted against time. $[\text{HCOOH}] = 0.20 \text{ M}$ (a) $[\text{H}_2\text{SO}_4] = 0.49 \text{ M}$. $[\text{HClO}_4] = 0.00 \text{ M}$. (b) $[\text{H}_2\text{SO}_4] = 0.44 \text{ M}$. $[\text{HClO}_4] = 0.05 \text{ M}$ (c) $[\text{H}_2\text{SO}_4] = 0.35 \text{ M}$. $[\text{HClO}_4] = 0.14 \text{ M}$.

value and the concentration of perchloric acid. It shows that a linear relation is a good approximation for the perchloric acid concentration range of 0.00 to 0.10 M. The linear approximation ceases to be a good approximation at concentrations of perchloric acid greater than 0.10 M. The limited range of a linear approximation is not surprising given the nonlinear behaviors exhibited by the electrochemical oxidation of formic acid.^{35–37,39} What is surprising is that the break in the linear approximation corresponds to a drastic decrease in the time the system takes to reach a higher potential. See the drop in the value of the time at a concentration greater than 0.10 M in Figure 1. Given the understanding of anion adsorption strengths, it would be expected that any deviation in a linear relation would correspond to a nonlinear increase in the time to reach a higher potential. Although the deviation from linearity occurs at a rather large concentration, it is considerably lower than that used in experiments where perchloric acid was considered as a non-interacting background electrolyte.^{2,3}

The temporal evolution from three different experiments is shown in Figure 2. The potential is plotted against time. Figure 2a depicts the temporal evolution of the potential for the case of sulfuric acid in the solution and no perchloric acid. The case in which the solution contains 0.05 M perchloric acid is shown in Figure 2b. The time that the potential took to reach 1361 mV is greater than what it was in Figure 2a. Figure 2c contains the temporal evolution for the case in which 0.14 M perchloric acid is in the solution. The time the potential took to reach the value of 1361 mV was shorter than it was in Figure 2b.

A second set of experiments was conducted, beginning with one in which the solution contained perchloric acid but no sulfuric acid. Small amounts of sulfuric acid were mixed into solutions used in subsequent experiments. The smallest amount of sulfuric acid added was 0.01 M. The amount of perchloric acid was adjusted to maintain a constant pH. Results from this

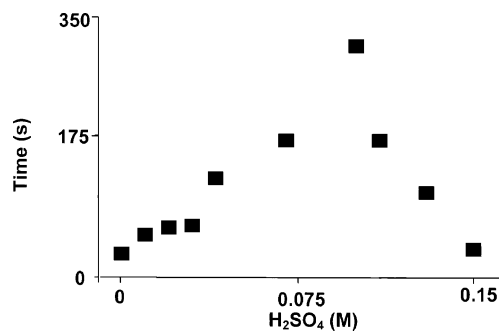


Figure 3. Time that the potential took to reach the value 1361 mV plotted against the concentration of sulfuric acid. The concentration of perchloric acid and sulfuric acid summed were approximately equal to 0.50 M. $[\text{HCOOH}] = 0.20 \text{ M}$.

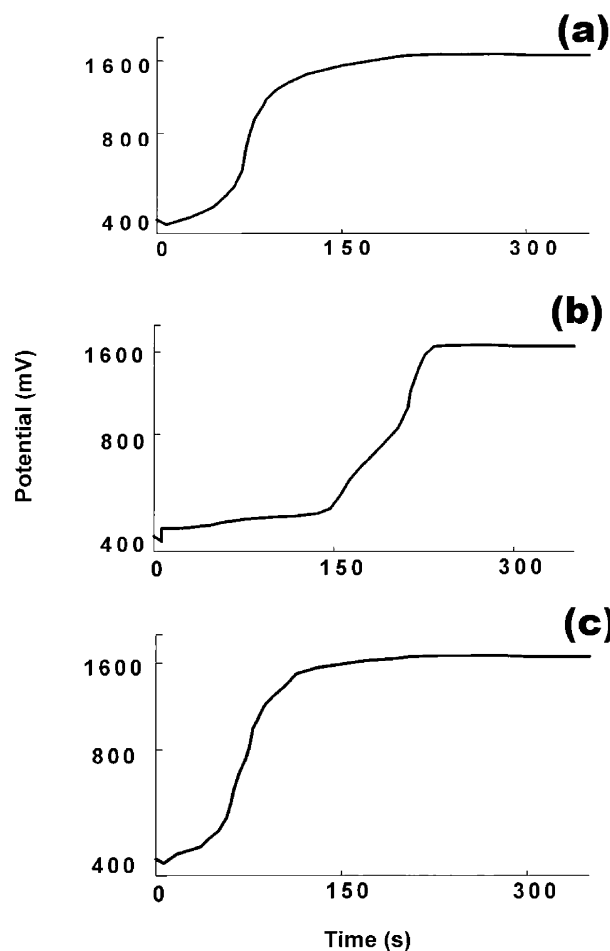


Figure 4. Temporal evolution of the potential. Potential is plotted against time. $[\text{HCOOH}] = 0.20 \text{ M}$ (a) $[\text{H}_2\text{SO}_4] = 0.00 \text{ M}$. $[\text{HClO}_4] = 0.50 \text{ M}$. (b) $[\text{H}_2\text{SO}_4] = 0.01 \text{ M}$. $[\text{HClO}_4] = 0.49 \text{ M}$ (c) $[\text{H}_2\text{SO}_4] = 0.07 \text{ M}$. $[\text{HClO}_4] = 0.43 \text{ M}$.

second set of experiments are shown in Figure 3, where the time the potential took to reach 1361 mV is plotted against the concentration of sulfuric acid.

The relation between the time that the system takes to reach a large potential and the concentration of sulfuric acid appears to be linear for the concentration range of 0.00 to 0.10 M. A linear regression analysis was conducted on the first seven data points from Figure 4. The results are given in terms of the following equation:

$$t = m[\text{H}_2\text{SO}_4] + t_0 \quad (4)$$

where the terms in the equation have the same meanings as those in eq 3, except that the concentration of perchloric acid has been replaced with the concentration of sulfuric acid. The analysis yields the slope (m) 2.14×10^3 s/M with a standard deviation of 77.3 s, an intercept of 88.4 s, and a correlation coefficient equal to 0.980.

The results are surprising because the slope is positive. Assuming that only the characteristics of anion adsorption are responsible for the differences in the results among the different solutions, and using the present understanding of anion adsorption strengths, a negative slope would be predicted.

Additions of small amounts of sulfuric acid to the perchloric acid–formic acid solution would be expected to increase the overall anion adsorption strength. It would then follow that increases would occur in the amount of anions adsorbed onto the electrode surface. An increase in anions adsorbed would cause fewer vacant sites to be available for reactions to take place. Fewer reaction sites would cause the potential to rise more quickly so that the reactions that could take place would occur at a rate large enough to satisfy the applied current. The results in Figure 3 are inconsistent with the stated scenario. Note however that, as in the case of adding perchloric acid to the sulfuric acid–formic acid solution, the time to reach high values decreases at a concentration of sulfuric acid just above 0.10 M.

Three examples of the temporal evolution of the potential, which were used in the construction of Figure 3, are shown in Figure 4. The plot of the potential as a function of time in Figure 4a is from an experiment in which a solution was used that contained perchloric acid and no sulfuric acid. The case in which the solution contained 0.01 M sulfuric acid is shown in Figure 4b. Figure 4c depicts the case in which a solution was used that contained 0.07 M sulfuric acid.

An explanation of the results, Figures 1–4, only in terms of anion adsorption strengths seems out of the question. By invoking these properties it would follow that a solution containing formic acid, perchloric acid, and sulfuric acid would lead to a more efficient oxidation process when the fraction of perchloric acid is increased. A theory based solely on anion adsorption strengths can explain why the time for the potential to reach high values becomes longer when small amounts of perchloric acid are added to the solution that contains formic acid and sulfuric acid. However, continued additions of perchloric acid eventually caused a decrease in the time the potential takes to reach a high value. Furthermore, the time the potential takes to reach high values increases when small amounts of sulfuric acid are added to a solution in which the bulk of the electrolyte consisted of perchloric acid. It would be an incredible result if anion adsorption properties decreased when strongly adsorbed anions are added to a solution containing anions that are adsorbed weakly.

Previous results provided evidence that anions affect electrochemical reactions in ways other than that of blocking reaction sites at noble metals.^{35–37} The plots in Figures 1 and 3 are consistent with the idea that anions, besides blocking sites, play another role in the reaction process. All the evidence that supports the idea that anions play a role in the reaction of oxygenated organics different from simply blocking surface sites has been obtained in current-control experiments. No such evidence has been captured in a tremendous number of potential-control experiments.²² Results from potential-control experiments consistent with the results from the current-control experiments are presented next.

Potential-Control Experiments. Cyclic voltammetry was applied to solutions of the same compositions as those studied

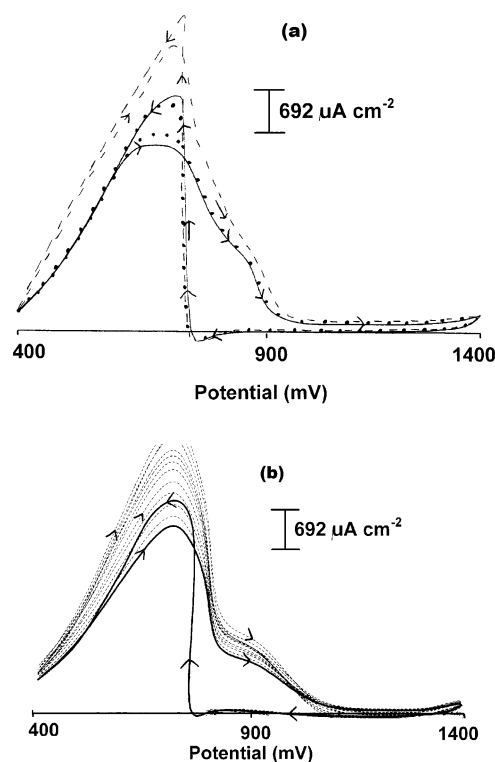


Figure 5. (a) Limiting cyclic voltammograms. Current is plotted against potential. $[\text{HCOOH}] = 0.20$ M. Lower potential limit = 400 mV. Upper potential limit = 1400 mV. Sweep rate = 0.10 V/s. Zero current is at the baseline (bottom of the figure). The largest current peak in a CV occurs on the reverse scan. Solid curve: $[\text{H}_2\text{SO}_4] = 0.49$ M. $[\text{HClO}_4] = 0.00$ M. Dashed curve: $[\text{H}_2\text{SO}_4] = 0.42$ M. $[\text{HClO}_4] = 0.07$ M. Dotted curve: $[\text{H}_2\text{SO}_4] = 0.33$ M. $[\text{HClO}_4] = 0.16$ M. (b) Transients from the decay to the limiting cyclic voltammogram represented by the dotted curve in (a). Only the forward part of the transient scans is shown.

in the current-control experiments. Three measured cyclic voltammograms (CVs) are shown in Figure 5a. In the experiments, the lower potential limit was set at 400 mV and the switching potential or upper potential limit was set at 1400 mV. (Upper and lower potential limits for all other experiments are stated in the figure captions.) In all experiments in which cyclic voltammetry was applied, the scan rate was 100 mV/s. In each experiment, the potential was cycled between the lower and upper limit until a limiting CV was obtained, that is, the current–potential curve that is reached after transients decay and that is retraced on each cycle. The lower potential limit was often used as the initial potential. However, except for Figure 5b, all current–potential curves presented are limiting CVs. The same limiting CVs in Figure 5a were reached by choosing a number of values between the lower and upper potential limit as the initial potential. The last potential value of the cycling process was arbitrary and its value will have no effect on limiting CVs.

The CV represented by the solid curve in Figure 5a was measured in an experiment using a solution that contained 0.20 M formic acid, 0.49 M sulfuric acid, and no perchloric acid. The peak current of the forward part of the cycle (I_{pf}) is 2.85 mA/cm², and the corresponding peak potential (E_{pf}) is 690 mV. The peak current for the reverse part of the cycle (I_{pr}) is 3.63 mA/cm², which occurs at the potential (E_{pr}) = 735 mV. The CV represented by the dashed curve is for a modified solution that contained 0.07 M perchloric acid (As in the current-control experiments, the total amount of sulfuric acid and perchloric acid was adjusted to maintain the same pH for all solutions.); The peak currents and peak potentials are $I_{pf} = 4.46$ mA/cm²,

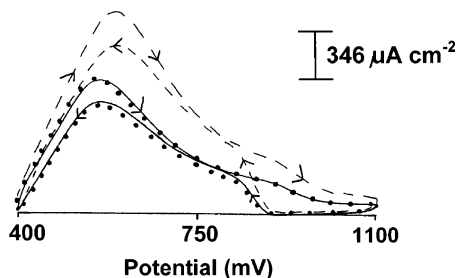


Figure 6. Limiting cyclic voltammograms. The conditions are the same as in Figure 5a, except the upper potential limit = 1100 mV. The largest current peak in a CV occurs on the forward scan.

$E_{pf} = 795$ mV, $I_{pr} = 4.87$ mA/cm², and $E_{pr} = 730$ mV. It is seen that the modification led to a substantial increase in peak current. This result can be explained in terms of the present understanding of anion adsorption. The perchlorate anion has an adsorption strength smaller than that of the (hydrogen) sulfate anions. Mixing perchloric acid into the solution decreases the overall anion adsorption strength. A lower anion adsorption strength will free up reaction sites that, in turn, cause a larger peak current. The CV in Figure 5a represented by the dotted curve was measured in an experiment that used a solution containing 0.16 M perchloric acid. The peak currents and peak potentials are $I_{pf} = 3.00$ mA/cm², $E_{pf} = 655$ mV, $I_{pr} = 3.45$ mA/cm², and $E_{pr} = 645$ mV. It is seen from the latter CV that the additional amount of perchloric acid caused the current to decrease. This result cannot be explained in terms of adsorption strengths.

The results shown in Figure 5a are consistent with those of the current-control experiments. The curves shown in 5b are transient curves obtained for the solution containing 0.16 M perchloric acid. The initial transients were far off the scale of Figure 5b. The transients for the other two cases did not have peak currents near as high as those in Figure 5b. The decay from large peak current illustrates that changes are slowly occurring on the electrode surface, and, also, the type of decay is evidence that our results are related to those changes.

The current–potential curves in Figure 5a make large excursions into the oxide region. In the direction of increasing potential, the oxide region is the region at high potentials that follows the large current peak. The amplitude of the CVs is small, without much variation on the reverse scan in this region. An oxide layer forms on the electrode surface because, as the potential increases, the rate of formation of surface OH eventually outpaces the rates of reactions associated with the oxidation of formic acid. Surface OH is the precursor of oxides.⁴⁶ On the reverse sweep the oxides and any OH are reduced. Because oxides dominate at high potential, their reduction can have a substantial effect on the nature of the surface. A measure of the effect of oxide reduction can be gained by using a smaller upper potential limit.

In Figure 6, CVs are shown that were obtained in experiments in which the upper potential limit was reduced 300 mV from that used in Figure 5. The experiments used solutions containing 0.2 M formic acid. In one case, the solid curve, the solution contained 0.49 M sulfuric acid and no perchloric acid. For this case, the peak current of the forward part of the cycle (I_{pf}) is equal to 0.917 mA/cm² and the corresponding peak potential (E_{pf}) is 549 mV; the peak current for the reverse part of the cycle (I_{pr}) is 0.769 mA/cm² and the corresponding potential (E_{pr}) is equal to 528 mV. The dashed curve in Figure 6 corresponds to a CV from an experiment that used a solution containing 0.42 M sulfuric acid and 0.07 M perchloric acid. The peak

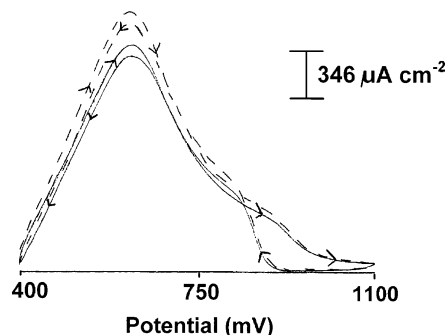


Figure 7. Limiting cyclic voltammograms. Current is plotted against potential. [HCOOH] = 0.20 M. Solid curves. Lower potential limit = 400 mV. Upper potential limit = 1100 mV. Sweep rate = 0.10 V/s. Zero current is at the baseline. The largest current peak in a CV occurs on the forward scan. Solid curve: [H₂SO₄] = 0.00 M. [HClO₄] = 0.50 M. Dashed curve: [H₂SO₄] = 0.07 M. [HClO₄] = 0.43 M.

currents and peak potentials are $I_{pf} = 1.37$ mA/cm², $E_{pf} = 538$ mV, $I_{pr} = 1.13$ mA/cm², and $E_{pr} = 525$ mV. The third CV in Figure 6, the dotted curve, was from an experiment that used a solution containing 0.33 M sulfuric acid and 0.16 M perchloric acid. The peak currents and peak potentials are $I_{pf} = 0.899$ mA/cm², $E_{pf} = 545$ mV, $I_{pr} = 0.744$ mA/cm², and $E_{pr} = 532$ mV. By examining the results in Figure 6, it is seen that the solution containing 0.07 M perchloric acid yielded the highest current and the solution containing 0.16 M perchloric acid did not. These results are consistent with the results of the current-control experiments.

Besides the smaller amplitudes in Figure 6, there are other differences in the way the system responded using an upper potential limit different from that in Figure 5. As stated, the initial transients for the solution containing 0.07 M perchloric acid and a large upper potential limit were very high in current, more than twice the amplitude of the limiting CV, Figure 5. This was not the case for using the smaller upper potential limit, Figure 6. Also, the relaxation was longer to the limiting CV in Figure 5. For the solution containing 0.07 M perchloric acid, the relaxation to the limiting CV in Figure 5 took about 5/3 times the number of cycles required to relax to the limiting CV in Figure 6. Another difference is that the largest amplitudes of the CVs in Figure 5 were obtained on the reverse scan whereas the largest amplitudes of the CVs in Figure 6 occurred on the forward scan.

Two CVs are depicted in Figure 7 that were measured in experiments that used solutions containing 0.20 M formic acid. The solid curve is a CV from an experiment in which the solution contained 0.50 M perchloric acid and no sulfuric acid. The peak currents and peak potentials are $I_{pf} = 1.57$ mA/cm², $E_{pf} = 549$ mV, $I_{pr} = 1.48$ mA/cm², and $E_{pr} = 538$ mV. The other CV, the dashed curve, is from an experiment that used a solution containing 0.43 M perchloric acid and 0.07 M sulfuric acid. The peak currents and peak potentials are $I_{pf} = 1.81$ mA/cm², $E_{pf} = 537$ mV, $I_{pr} = 1.70$ mA/cm², and $E_{pr} = 535$ mV. It is the solution containing 0.07 M sulfuric acid that yields the largest current. Experiments using solutions containing 0.15 M sulfuric acid yielded a peak current much less than that of the latter solution. The result obtained using a small amount of sulfuric acid is consistent with the results from the current-control experiments.

Conclusions

A large amount of evidence indicates that anions affect the electrochemical oxidation of formic acid in ways that cannot

be explained in terms of anion adsorption strengths and the blocking of reaction sites on the surface of the electrode. The evidence was obtained in both current- and potential-control experiments. In the experiments, the overall anion adsorption strength was varied by changing the fractions of sulfuric acid and perchloric acid in solution.

Current-control experiments revealed that for some solutions, the potential, in response to a large, applied, constant current, reaches high values over a time interval that is longer than that observed for the potential response obtained using solutions possessing a smaller overall anion adsorption strength. In potential-control experiments, the current measured using some solutions was lower than that obtained for solutions that possessed a larger overall anion adsorption strength. The results from both the current- and potential-control experiments were obtained in two very different ranges of concentrations of sulfuric acid and perchloric acid.

One consequence of the results is that care is indicated in making assumptions about any noninteracting properties of perchloric acid. The result should also have useful applications in fuel cells.

Although it seems clear that anions play a role in the reaction process, besides blocking surface sites, it is not easy to deduce that role. Some results are suggestive. Applying cyclic voltammetry to a solution containing 0.16 M perchloric acid, 0.33 M sulfuric acid, and 0.20 M formic acid led to transients with large amplitudes, Figure 5. However, the current of the limiting CV was less than that of the limiting CV for a solution containing less than half the amount of perchloric acid. The initial large current of the former solution could be in response to the larger amount of perchloric acid. The large current cannot be sustained. It seems safe to assume that the decay to the limiting CV is accompanied by the relaxation to a particular arrangement of anions on the electrode surface.

Hydrated anions adsorbed on the electrode surface will interact with other species, including reactive intermediates^{35–37} and other anion complexes.⁴⁷ Whether it is a random array of anions or a structured two-dimensional lattice, it can severely inhibit reaction when it is sufficiently dense in occupation and highly connected, that is, each anion can interact with several anion complexes.

Adding small amounts of sulfuric acid to a formic acid + perchloric acid solution, and adding small amounts of perchloric acid to a formic acid + sulfuric acid solution, yielded increases in the efficiency of the oxidation of formic acid. In both cases, instead of improved efficiencies, decreased efficiencies occurred when the added acid reached concentrations just over 0.10 M. Adsorption of the anion of smaller concentration provides impurities that perturb the connected structure of the other anion. Because of differences in the symmetry of the charge distribution around ClO_4^- , HSO_4^- , and SO_4^{2-} , the perturbation provides locations where the anion of larger concentration cannot interact with as many other anion complexes. Vacant sites are freed up at these locations and the efficiency of the reaction increases. At sufficiently large concentrations of both anions, a different but connected mixed anion structure is formed, and the efficiency of the oxidation reaction decreases. The explanation is simplified relative to all possible interactions of the anion complexes; for example, anion complexes can partake in reaction.^{35–37}

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References and Notes

- (1) Horanyi, G.; Solt, J.; Nagy, F. *J. Electroanal. Chem.* **1971**, *31*, 87.
- (2) Horanyi, G.; Solt, J.; Nagy, F. *J. Electroanal. Chem.* **1971**, *31*, 95.
- (3) Kunimatsu, K.; Samant, M. G.; Seki, H. *J. Electroanal. Chem.* **1989**, *258*, 163.
- (4) da Cunha, M. C. P. M.; Weber, M.; Nart, F. C. *J. Electroanal. Chem.* **1996**, *414*, 163.
- (5) Marinkovic, N. S.; Marinkovic, J. S.; Adzic, R. R. *J. Electroanal. Chem.* **1999**, *467*, 291.
- (6) Lachenwitzer A.; Li, N.; Lipkowski, J. *J. Electroanal. Chem.* **2002**, *532*, 85.
- (7) Hoshi, N.; Kuroda, M.; Ogawa, T.; Koga, O.; Hori, Y. *Langmuir* **2004**, *20*, 5066.
- (8) Zawada, K.; Bukowska, J. *Electrochim. Acta* **2004**, *49*, 469.
- (9) Funtikov, A. M.; Stimming, U.; Vogel, R. *J. Electroanal. Chem.* **1997**, *428*, 147.
- (10) Santos, M. C.; Miwa, D. W.; Machado, S. A. S. *Electrochem. Commun.* **2000**, *2*, 692.
- (11) Kolics, A.; Wieckowski, A. *J. Phys. Chem. B* **2001**, *105*, 2588.
- (12) Horanyi, G. *Corros. Sci.* **2004**, *46*, 1741.
- (13) Thomas, S.; Sung, Y.-E.; Kim, H. S.; Wieckowski, A. *J. Phys. Chem.* **1996**, *100*, 11726.
- (14) Wang, J. X.; Marinkovic, N. S.; Zajonz, H.; Ocko, B. M.; Adzic, R. R. *J. Phys. Chem. B* **2001**, *105*, 2809.
- (15) Kerner, Z.; Pajkossy, T. *Electrochim. Acta* **2002**, *47*, 2055.
- (16) Marinkovic, N. S.; Wang, J. X.; Zajonz, H.; Adzic, R. R. *J. Electroanal. Chem.* **2001**, *500*, 388.
- (17) Kuroda, M.; Hori, Y.; Hoshi, N. *J. Electroanal. Chem.* **2002**, *521*, 155.
- (18) Lust, K.; Lust, E. *J. Electroanal. Chem.* **2003**, *552*, 129.
- (19) Stamenkovic, V.; Markovic, N. M.; Ross, Jr., P. N. *J. Electroanal. Chem.* **2001**, *500*, 44.
- (20) Macia, M. D.; Campiña, J. M.; Herrero, E.; Feliu, J. M. *J. Electroanal. Chem.* **2004**, *564*, 141.
- (21) Rodes, A.; Orts, J. M.; Pérez, J. M.; Feliu, J. M.; Aldaz, A. *Electrochem. Commun.* **2003**, *5*, 56.
- (22) Parsons, R.; VanderNoot T. *J. Electroanal. Chem.* **1988**, *257*, 9.
- (23) Sobkowski, J.; Franaszczuk, K.; Dobrowolska, K. *J. Electroanal. Chem.* **1992**, *330*, 529.
- (24) Markovic, N.; Ross, Jr. P. N. *J. Electroanal. Chem.* **1992**, *330*, 499.
- (25) Markovic N. M.; Ross, P. N., Jr. *J. Phys. Chem.* **1993**, *97*, 9771.
- (26) Lu, G.-Q.; Crown, A.; Wieckowski, A. *J. Phys. Chem. B* **1999**, *103*, 9700.
- (27) Attard, G. A.; Harris, C.; Herrero, E.; Feliu, J. *Faraday Discuss.* **2002**, *121*, 253.
- (28) Wakabayashi, N.; Kitamura, F.; Ohsaka, T.; Tokuda, K. *Electrochem.* **1999**, *67*, 1181.
- (29) Ikezawa, Y.; Terashima, H. *Electrochim. Acta* **2002**, *47*, 4407.
- (30) Da Silva, L. M.; De Faria, L. A.; Boodts, J. F. C. *Electrochim. Acta* **2003**, *48*, 699.
- (31) Tripkovic, A. V.; Popovic, K. D.; Grgur, B. N.; Blizanac, B.; Ross, P. N.; Markovic, N. M. *Electrochim. Acta* **2002**, *47*, 3707.
- (32) Muñoz, A. G.; Bessone, J. B. *Electrochim. Acta* **1998**, *43*, 1067.
- (33) Arenz, M.; Schmidt, T. J.; Wandelt, K.; Ross, P. N.; Markovic, N. M. *J. Phys. Chem. B* **2003**, *107*, 9813.
- (34) Lamy-Pitara, E.; El Moulahid, S.; Kerkeni, S.; Barbier, J. *Electrochim. Acta* **2003**, *48*, 4311.
- (35) Chen, S.; Schell, M. *J. Electroanal. Chem.* **2001**, *504*, 78.
- (36) Chen, S.; Noles, T.; Schell, M. *Electrochem. Commun.* **2000**, *2*, 171.
- (37) Chen, S.; Noles T.; Schell, M. *J. Phys. Chem. A* **2000**, *104*, 6791.
- (38) Wang, X.; Hu, J.-M.; Hsing, I.-M. *J. Electroanal. Chem.* **2004**, *562*, 73.
- (39) Okamoto, H.; Kon, W.; Mukouyama, Y. *J. Phys. Chem. B* **2004**, *108*, 4432.
- (40) Trasatti, S.; Petrii, O. A. *Pure Appl. Chem.* **1991**, *63*, 711.
- (41) Vaskelis, A.; Norkus, E.; Stalnionienė, I.; Stalnionis, G. *Electrochim. Acta* **2004**, *49*, 1613.
- (42) Bidóia, E. D.; Bulhões, L. O. S.; Rocha-Filho, R. C. *Electrochim. Acta* **1994**, *39*, 763.
- (43) Casella, I. G.; Gatta, M. J. *Electroanal. Chem.* **2004**, *568*, 183.
- (44) Petrovic, S. *Chem. Educ.* **2000**, *5*, 231.
- (45) Konopka, S. J.; McDuffie, B. *Anal. Chem.* **1970**, *42*, 1741.
- (46) Conway, B. E.; Barnett, B.; Angerstein-Kozłowska, H.; Tilak, B. V. *J. Chem. Phys.* **1990**, *93*, 8361.
- (47) Angerstein-Kozłowska, H.; Conway, B. E.; Hamelin, A.; Stoicoviciu, L. J. *Electroanal. Chem.* **1987**, *228*, 429.