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The Effect of Anionic Poisons on the Catalytic Oxidation of Formaldehyde on Platinum

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The coulometric method of measuring the relative catalytic activity of platinum black by determining its ability to adsorb hydrogen has been studied in the presence of several anions. The catalytic reaction studied was the catalytic oxidation of formaldehyde. It was found that the technique was suitable in the presence of several different anions but that it did not furnish a reliable measure of the catalytic activity in acid solutions in the presence of chloride ions. It was felt that the cause of this difficulty could be the adsorption of hydrogen on top of the adsorbed chloride ions.

INTRODUCTION

In our laboratories a series of studies are being made on the use of the coulometrically measured amount of hydrogen adsorbed on platinum (*1*) as a measure of the metal's catalytic activity for reactions occurring at metal solution interfaces (*2–4*). These studies have shown that the measured amount of adsorbed hydrogen is proportional to the catalytic activity in the absence of added catalytic inhibitors and in the presence of neutral organic additives. In fact the coulometric determination of the amount of adsorbed hydrogen was shown to be sensitive enough to determine the relative amount of different catalytic sites present on platinum.

A series of studies is now being made to determine whether this technique is widely applicable. The first of these studies was an investigation to determine whether the technique is useful for measuring catalytic activity in the presence of anionic poisons.

EXPERIMENTAL

Catalyst preparation. The electroplated wire catalysts were prepared using 2–5-cm lengths of 0.4-cm diameter platinum wire sealed in soft glass tubing. These wires were cleaned in aqua regia for 10–30 min, rinsed with distilled water, and transferred into a sulfuric acid or sodium hydroxide solution of the same concentration as that used in the experiment. There it was alternately charged cathodically and anodically. This process was continued until the surface was indicated to be clean by the uniform evolution of hydrogen and oxygen over the whole surface.

After cleaning, the catalyst was rinsed with distilled water and plated with platinum black in a 3% chloroplatinic acid solution containing 0.06% lead acetate (*5*) using different currents and different plating times to obtain different catalytic activities. After rinsing it was placed in the same sulfuric acid or sodium hydroxide solution as before and charged anodically and cathodically to remove adsorbed im-

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purities. It was then rinsed and placed in the electrolytic cell.

The coulometric measurement of the amount of adsorbed hydrogen. An "H" cell with a fritted glass disk separating the anode and cathode compartments was used to measure the amount of adsorbed hydrogen. The anode was the platinized platinum test catalyst electrode. The cathode was a large nonpolarizable platinized platinum gauze electrode.

The electrodes were saturated with hydrogen by bubbling hydrogen through the bath cell compartments until potential equilibrium was attained (0.00 V). The flow of hydrogen through the catalyst compartment was then stopped and the solution around the catalyst was bubbled with helium until the potential reached 0.05 V to remove the excess hydrogen. This lowered the residual current but did not appreciably change the amount of adsorbed hydrogen. The voltage was then swept linearly (at a voltage sweep rate of approximately 0.4 V/min) using a Heath polarograph to 1.45 V, oxidizing the adsorbed hydrogen. Current potential curves (they were also current time curves since the voltage sweep was linear with time) for the oxidation were recorded on a Mosely 2D-2A X-Y recorder and were measured three or four times for each experiment to check reproducibility. If the results varied by as much as 5% the system was changed and the whole experiment repeated. When the current potential curve was to be determined in the presence of an added anion the anion was added to the working electrode compartment in the form of the sodium salt. The procedure was then repeated. The measured number of coulombs was converted to the number of platinum sites by use of the reported values of 210 μC/cm^2 and 1.26×10^{15} atoms/cm^2 (*6*).

Catalytic studies. The catalytic reaction chosen for study was the catalytic oxidation of formaldehyde since the experimental parameters had been determined in previous experiments (3) and the reaction had been shown to be first order with respect to formaldehyde and first order with respect to active surface area. These facts were verified experimentally.

After the current voltage curves were obtained, hydrogen was bubbled through the solution until the potential reached 0.00 V and then the catalyst was transferred immediately to a reaction vessel (a 50-ml three-necked flask) containing 20 μg/ml of formaldehyde and 16 ml of the solution in which the area was determined (sodium hydroxide or sulfuric acid plus the anion). Oxygen was bubbled through the solution prior to the insertion of the catalyst and throughout the run. Zero reaction time was set as the time that the electrode was immersed in the reaction solution. One or one-half milliliter of the solution was withdrawn after each time interval for analysis. The sample was analyzed by a colorimetric method using chromotropic acid (*7*). The standardization curve was prepared from a stock formaldehyde solution which had been standardized by an iodometric method (*8, 9*).

During a kinetic run the solution was stirred and oxygen was bubbled through the solution at a rate of approximately 10 ml/min. Changes in the flow rate in this region did not affect the rate of the reaction. If one ran a blank (without catalyst) with a flow rate of 30 ml/min, the formaldehyde concentration decreased by volatilization by only 2.5% in 5 hr. The experiments were run at 25.0°C. The anionic poisons were added in the form of the sodium salt.

EXPERIMENTAL RESULTS

Current Voltage Curves in the Absence of Added Inhibitors

Figure 1 shows typical current voltage curves for the oxidation of hydrogen adsorbed on platinized platinum wire catalysts in 2 *N* sulfuric acid and in 2 *N* sodium hydroxide. Also drawn on the graphs are

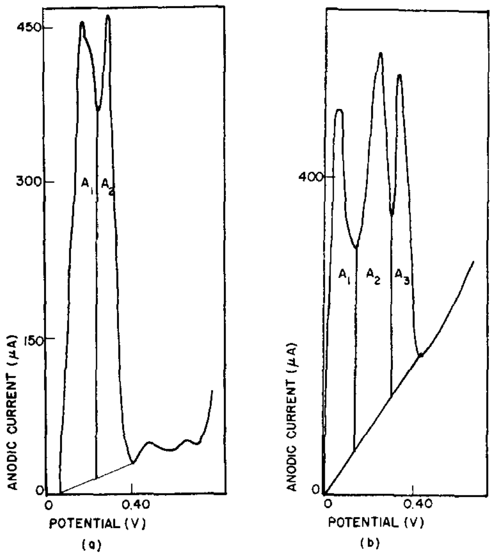

FIG. 1. Typical current potential curves for the oxidation of hydrogen adsorbed on platinum without added anions. (a), In 2 *N* sulfuric acid; (b), in 2 *N* sodium hydroxide.

lines dividing the area under the peaks into regions. As can be seen, the residual current line was drawn for convenience as a straight line from the origin of the curve to the minimum after the hydrogen oxidation peaks, and lines dividing this area into different regions were drawn from the minima to the residual line. The area within a region of the current-time curves is proportional to the number of coulombs used to oxidize hydrogen bonded to the platinum with a particular bonding energy and these different areas correspond to different catalytically active sites (*2*, *4*). In sulfuric acid the hydrogen region is split into two areas while in basic solutions it is split into three. This division is somewhat arbitrary since it is obvious that some of the major peaks contain a smaller peak; however, previous work (*2–4*) has shown that, for several reactions including the catalytic oxidation of formaldehyde, this simple division, within experimental error, furnishes a measurement of surface areas on the catalyst that have different catalytic properties.

The Effect of Chloride in Acid Solution

Figure 2 shows the effect of chloride ion on the current voltage curves in sulfuric acid solutions. In Fig. 3 is seen the effect of chloride ion on the measured areas under the two peaks in the hydrogen oxidation curve (the use of a logarithmic axis is done merely to collapse this axis).

From these two figures it can be seen that although the addition of chloride shifts the second peak, as has been previously noted, it does not appreciably change the areas of the two peaks (*10–12*). The small increase in A_1 is probably caused by a shift in the residual in the current voltage curve. The current voltage curve stays essentially the same until one reaches 3×10^{-5} *M* chloride. The shift in the second peak is such that at higher concentrations it merges with the first peak forming one peak. Thus at concentrations above 2×10^{-4} *M* the area of the separate peaks cannot be plotted in Fig. 3. The shift in the current voltage curve is reversible. Upon rinsing away the chloride, the curve returns to its former position.

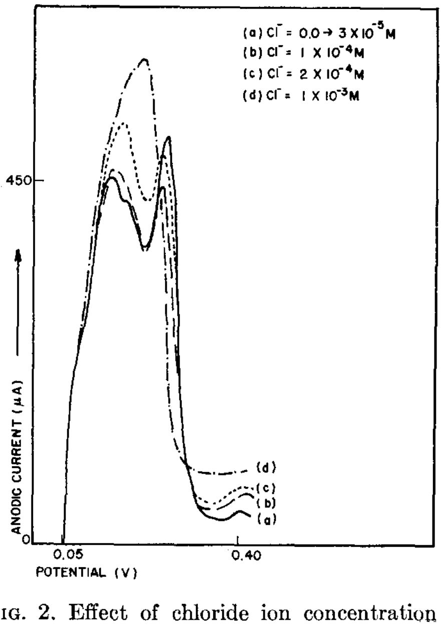

FIG. 2. Effect of chloride ion concentration on the current potential curve in sulfuric acid.

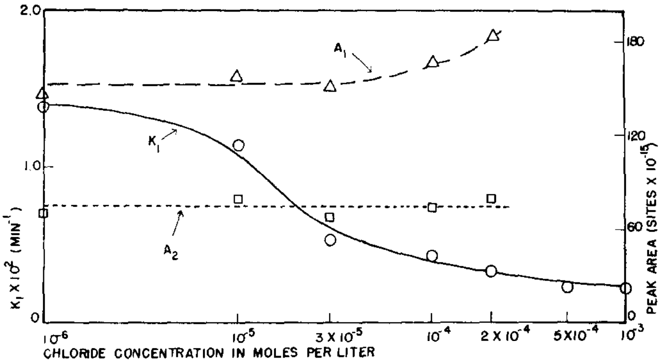

FIG. 3. A plot of k_1 vs log (Cl^-). A_1 = the area under the first peak in the current voltage curve; A_2 = the area under the second peak in the current voltage curve; k_1 = the reaction rate constant for the oxidation of formaldehyde.

Also shown in Fig. 3 is the effect of the addition of chloride ions on the rate constant for the oxidation of formaldehyde where k is obtained from the equation

$$\text{rate} = k[\text{formaldehyde}].$$

As can be seen there is a marked drop in the rate constant of the reaction. This drop starts at about the concentration that one begins to see a shift in the peak in the current voltage curve (3×10^{-5} M). Obviously the chloride acts as a poison for the catalytic oxidation of formaldehyde but does not correspondingly affect the area as measured by the coulometrically determined amount of adsorbed hydrogen.

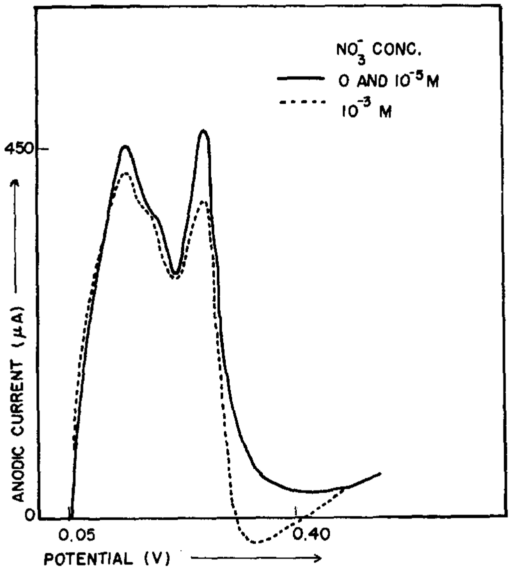

FIG. 4. Effect of nitrate ion concentration on the current potential curve in 2 N sulfuric acid solution.

The Effect of Nitrate

Figure 4 shows that the addition of nitrate ions to the solution has a little effect on the first peak and a somewhat larger effect on the second peak. The specific reaction rate constant did not decrease. In fact it increased slightly, from 1.98×10^{-2} to 2.20×10^{-2} min^{-1} upon the addition of nitrate (10^{-3} M). Very probably the nitrate caused a decrease in the amount of adsorbed hydrogen not by blocking the metal surface but by reacting with the adsorbed hydrogen. This reaction with the hydrogen is further indicated by the fact that a small cathodic current is observed immediately following the hydrogen oxidation reaction when nitrate is added. The slight increase in rate probably is caused by nitrate acting to oxidize small amounts of reducing impurities on the metal surface.

The Effect of Chloride and Sulfate Ions in Basic Solution

The addition of sodium chloride or sodium sulfate to a 2 or 0.01 M sodium hydroxide solution altered neither the rate

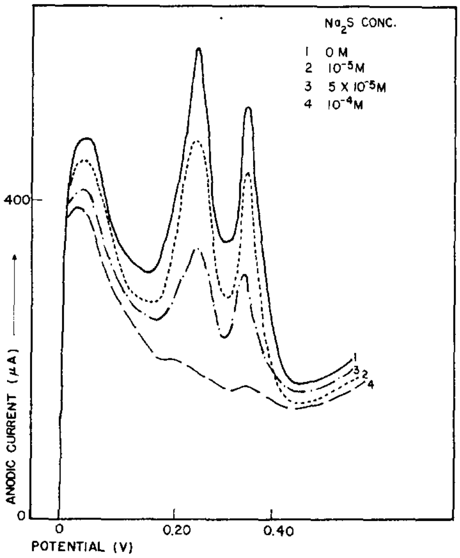

FIG. 5. Effect of added sodium sulfide on the current potential curves in 2 N sodium hydroxide solution.

constant nor the current voltage curves, indicating that neither of these ions is adsorbed on platinum in these basic solutions.

The Effect of Sulfide or Bisulfide Ions in Basic Solution

Figure 5 shows the effect of added sodium sulfide on the hydrogen oxidation curves in 2 M sodium hydroxide. Similar curves were obtained in 0.01 M sodium hydroxide. Figure 6 shows the effect of cyanide on the current voltage curve for the oxidation of hydrogen; similar curves were obtained in 2 N sodium hydroxide solutions.

Figure 7 shows the correlation that was obtained between the measured rate constant and the areas under the second and third peaks in the presence of cyanide and sulfide. (The lines are the best least-squares straight lines obtained for these points.) No good correlation was obtained between the area under Peak 1 or the total area and the rate constant.

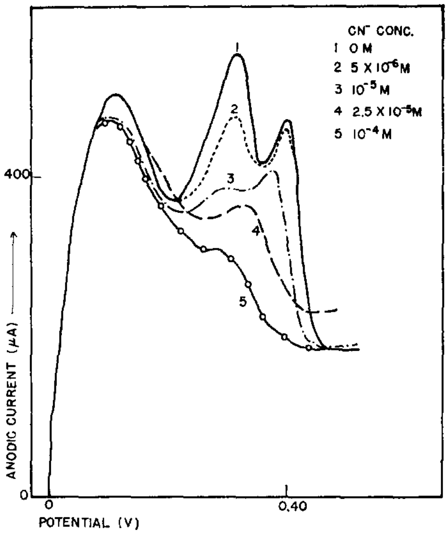

FIG. 6. Effect of cyanide ion concentration on the hydrogen peak areas in 0.01 N sodium hydroxide solution.

A possible explanation for the lack of correlation between the area under Peak 1 and the rate may be due to the fact that in basic solutions the first peak contains a contribution due to the oxidation of molecular hydrogen (*13*) rather than being caused entirely by the oxidation of adsorbed atomic hydrogen. Although there was a

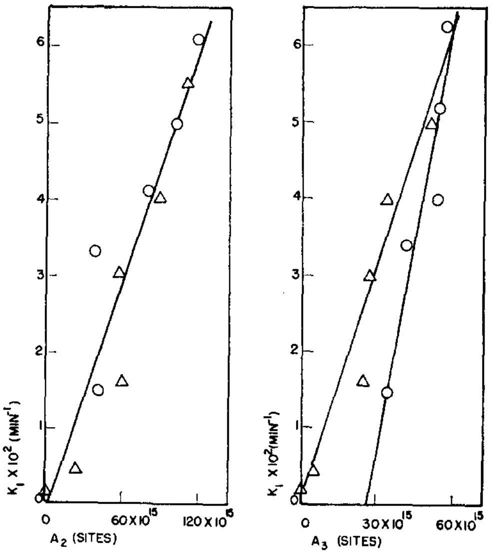

FIG. 7. Plots of k_1 vs A_2 and A_3 (2 N sodium hydroxide solution). (○), Cyanide used as a poison; (△), sulfide used as a poison.

linear plot between the rate and the area in Peak 3, the results obtained in sulfide and cyanide media did not agree with each other while the data obtained with the two types of additives were in agreement when the rate was correlated with the measured area in Peak 2. From this it was concluded that the reaction occurred primarily on the sites associated with Peak 2.

DISCUSSION OF RESULTS

Figure 7 as well as previous studies on unpoisoned catalysts (*2–4*) show that the coulometric technique is suitable for measuring the relative catalytic activity of platinized platinum for the oxidation of formaldehyde in the presence of a number of anions. This figure also indicates that the technique is suitable for differentiating between catalytically active sites (in this case sites corresponding to Peak 2) and noncatalytic sites (sites corresponding to Peak 1 and Peak 3).

However, in sulfuric acid solutions containing chloride, no correlation was obtained between the measured area and the catalytic activity. One explanation (10) that has been given for the effect of chloride on the current voltage curves is that chloride ions only start adsorbing at a potential in the hydrogen oxidation region. Thus if one visualizes that the catalytic oxidation occurs at a potential more anodic than the potential of the second peak one would get pronounced poisoning of the catalytic reaction but there would not necessarily be much change in the surface area. In fact the potential of the platinum during the catalytic oxidation is more anodic than the oxidation of hydrogen. The measured steady-state potential of the catalyst during the catalytic oxidation was 0.88 V while the potential of the last peak of the hydrogen oxidation was approximately 0.3 V.

There is another possible and somewhat more interesting explanation. The addition of chloride caused no decrease in the measured amount of adsorbed hydrogen in the concentration region studied here, indicating that chloride adsorbed in the hydrogen potential region did not block the adsorption of hydrogen at all. The shift in potential of the second peak could be explained by the adsorption of hydrogen atoms on top of chloride ions adsorbed on those sites, with the oxidation of the hydrogen atoms proceeding through the adsorbed chloride ion which would then be acting as an electron bridge. This would not decrease the measured amount of adsorbed hydrogen but it would shift the bonding energy between hydrogen and the electrode which is what was observed. The adsorbed chloride ion would also poison the catalytic oxidation which was also observed. The chloride ion has been already indicated to be an electron bridge in homogeneous reactions (*14*) and on bright platinum electrodes (*15*).

If this explanation is correct then the fact that the area did not decrease in the presence of chloride would indicate that one hydrogen atom is adsorbed on each chloride ion which in turn is adsorbed on a catalytic site.

SUMMARY

It has been shown that while the coulometric technique is suitable for measuring the relative catalytic activity of platinum black catalysts in some situations, difficulties are experienced in the presence of chloride ions in acid solutions. It is felt that the cause of these difficulties may well be the adsorption of hydrogen on adsorbed chloride and the action of these ions as electron transfer bridges in the oxidation of the adsorbed hydrogen.

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