THE MECHANISM OF ELECTROCATALYTIC OXIDATION OF FORMIC ACID ON Pt (100) AND Pt (111) IN SULPHURIC ACID SOLUTION: AN EMIRS STUDY

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(Received 31st August 1987)

ABSTRACT

The oxidation of formic acid at single crystal Pt (111) and Pt (100) electrodes in aqueous sulphuric acid was investigated using in-situ IR spectroscopy. The strongly adsorbed poisoning species, CO\textsubscript{ads}, was formed more slowly and to a lesser extent on the (111) surface. Correlation between the voltammetry and the spectra led to the assignment of broad bands near 1750 cm\textsuperscript{-1} to absorption by reactive intermediates, probably (COOH\textsubscript{ads}). A detailed reaction scheme consistent with the electrochemical and spectroelectrochemical data and featuring linked, parallel pathways involving adsorbed poison and adsorbed reactive intermediate, is presented.

INTRODUCTION

The oxidation of formic acid on a platinum electrode has received considerable attention in electrocatalysis research during the past thirty years [1–10]. It requires fewer oxidation steps than hydrocarbons and is often considered as a model from which to elucidate the oxidation mechanism of other small organic molecules. A dual path mechanism for formic acid oxidation at platinum has been proposed [11] and developed especially by Capon and Parsons [12,13], i.e.

\[
\begin{align*}
HCOOH & \rightarrow \text{reactive surface intermediate} \rightarrow \text{CO}_2 \\
& \rightarrow \text{chemisorbed intermediate ("poison")} \rightarrow \text{CO}_2
\end{align*}
\]

This scheme is now generally accepted, but the nature and the surface dependence of the intermediates are still a point of discussion. Recent efforts in the fundamental research of this type of reaction have developed mainly in two directions. The first
uses platinum single crystal planes as electrocatalysts to explore the dependence of the reaction on the surface structure and the electrocatalytic activity of each surface structure [14–18]. The second direction is an attempt to identify the intermediates in order to reach a detailed knowledge of the reaction [16,17,19–23]. The EMIRS [20,23] and electrochemical studies [21,22] have converged recently in agreement that the strongly chemisorbed, poisoning intermediate in formic acid oxidation is an adsorbed carbon monoxide species which can be bonded in more than one configuration to the platinum surface. The electrochemical investigations show that this poison could be formed at platinum from a spontaneous dissociative adsorption process and that the formation and the oxidation of the poison depend on the platinum surface structure. For the reactive intermediate the species $x$COOH has generally been proposed [13,16,24].

In this paper, the identification of the reactive intermediate and the observation of the different stages of formic acid oxidation at platinum single crystal planes were attempted mainly using EMIRS experiments. The results are analysed in parallel with the results of electrochemical studies for the overall formic acid oxidation as well as for the electrochemical behaviour of the poison after isolation from its generating species.

EXPERIMENTAL

The electrochemical studies were carried out in the Laboratoire d'Electrochimie Interfaciale (L.E.I.) du CNRS de Bellevue. The platinum single crystal planes used and the experimental conditions were described in ref. 22 and applied without modification to the crystals of bigger size required for spectroscopic experiments. The voltammograms were recorded at a scan rate of 50 mV s$^{-1}$ and the potential was measured against the reversible hydrogen electrode (RHE).

The EMIRS experiments were carried out in the Department of Chemistry of the University of Southampton. The EMIRS technique has been described in detail elsewhere [25]. For the present measurements, the EMIRS cell was fitted with a 2 mm thick silicon window and the working electrode was placed within a few micrometers of the window in order to minimize absorption of the IR radiation by the aqueous electrolyte. The platinum single crystal planes Pt (100) and Pt (111) used for the EMIRS experiments were disks with a diameter of 7 mm. They were first polished with alumina from 5 μm down to 0.05 μm before being mounted in the glass holders. The solutions were prepared using Aristar grade sulphuric acid and spectroscopy reagent HCOOH with triply distilled water. All IR scans were performed with a modulation frequency at 8.5 Hz and a sweep rate at 1.9 cm$^{-1}$ s$^{-1}$ covering the wavenumber range from 1750 to 2150 cm$^{-1}$. The spectra obtained were generally averaged over 2 or 3 scans and, exceptionally, up to 10 scans depending on the noise level. The modulation potentials were recorded against a saturated calomel electrode, but for convenience are quoted in this paper on the RHE scale.

For both types of experiment, the platinum single crystal electrodes were treated before each measurement in a gas oxygen flame and transferred to the experimental
cells with a drop of ultra-pure water to prevent surface contamination from the atmosphere [26]. All measurements were carried out at room temperature.

The general EMIRS experimental procedure was programmed so that the lower limit of the modulation potential was fixed at 0.13 V, where the hydrogen adsorption and the dissociative adsorption of formic acid may take place at free platinum surface sites, and the upper limit of the modulation potential was stepped at intervals of +0.1 V starting at 0.33 V. Since the resulting spectrum is the difference between the two spectra defined by the two modulation limits, the information obtained from the spectrum concerns the differences in the species adsorbed on the platinum surface at the two limits.

RESULTS

Electrochemical results

The voltammogram for the overall oxidation of formic acid in 0.25 M HCOOH + 0.5 M H₂SO₄ and also that for the oxidation of the poisoning intermediate (P.I.) alone in 0.5 M H₂SO₄ on Pt (100) are shown in Fig. 1.

It is evident by comparing the two voltammograms that the surface activity of Pt (100) is inhibited by the P.I. during the positive sweep, and the maximum activity is obtained in the negative sweep only when the P.I. is removed from this surface by the oxidation at relatively high potential. As may be seen from the curve of the P.I. oxidation alone, the beginning of this oxidation occurs at about 0.5 V and the P.I. formed below this potential (by spontaneous dissociative adsorption or by some other process) is accumulated at the surface of the Pt (100). This is why the surface of Pt (100) is almost completely blocked by the P.I. during the positive sweep.

The overall oxidation of HCOOH and the oxidation of the P.I. alone on Pt (111) are presented in Fig. 2.

On both the (111) and the (100) planes the oxidation current of HCOOH on the negative sweep approaches zero below 0.23 V; this value may be taken as the threshold oxidation potential of HCOOH on the two planes.

Comparison of the overall oxidation curves for HCOOH on Pt (100) and on Pt (111) allows two conclusions to be drawn:

1. The differing activities on the positive and the negative sweeps give an indication that the formation of the P.I. is slower on Pt (111) than on Pt (100); this may also be seen from the difference in current density between the first positive sweep after the electrode was held at 0.2 V for a defined time, and the subsequent positive sweep immediately following the first.

2. The difference in current density during the first positive sweep for the two cases shows that the maximum blocking of the surface by the P.I. is smaller for Pt (111) than for Pt (100); this has been also mentioncd in ref. 27.

Consequently the surface sites of Pt (111) are less blocked by the P.I. than those of Pt (100), and when the potential is higher than the threshold oxidation potential for HCOOH, more reactive intermediates may be supposed to be present on the
Fig. 1. (-----) Voltammogram of HCOOH oxidation at Pt (100) in 0.25 M HCOOH + 0.5 M H₂SO₄ solution. The current peak on the negative sweep is distinguished by arrows for the first and second cycles; the positive sweeps are essentially coincident. (-------) Voltammogram in 0.5 M H₂SO₄ for the oxidation of the poisoning intermediate formed by placing the Pt (100) electrode in contact with HCOOH at open circuit.

Fig. 2. (-----) Voltammogram of HCOOH oxidation at Pt (111) in 0.25 M HCOOH + 0.5 M H₂SO₄ solution for the first and second cycles. (-------) Voltammogram in 0.5 M H₂SO₄ for the oxidation of the poisoning intermediate formed by placing the Pt (111) electrode in contact with HCOOH at open circuit.

surface of Pt (111). It is evident that these characteristic differences between formic oxidation on Pt (111) and on Pt (100) would be expected to show up in the IR absorption bands of the reactive intermediate and the poisoning intermediate in the EMIRS spectra.

EMIRS results

Pt (100)

The EMIRS spectra obtained with Pt (100) in 0.25 M HCOOH + 0.5 M H₂SO₄ are shown in Fig. 3.

When the modulation limits are 0.13 and 0.33 V, three IR absorption bands may be distinguished from the spectrum: the biggest one is a bipolar band with the positive peak at 2035 cm⁻¹ and the negative peak at 2060 cm⁻¹ (the zero crossing point of this band is at 2045 cm⁻¹), the second band is at around 1875 cm⁻¹ and the third one, which spreads in the range 1800 to 1750 cm⁻¹ (or lower wavenumbers, but limited here by the present experimental conditions), is the smallest band existing in this spectrum.
Fig. 3. EMIRS spectra obtained with Pt (100) in 0.25 M HCOOH + 0.5 M H₂SO₄ solution. The modulation potentials are marked for each spectrum.

From previous studies [20,23,28], it is known that the bipolar band and the band in the range 1875 cm⁻¹ are due respectively to IR absorption by the C–O stretch of linearly and bridge bonded CO on the platinum surface. The third, lower frequency band, is probably due to a chemically distinct species adsorbed on the surface. Considering the electrochemical results which indicate that the maximum occupation of Pt (100) surface sites by the P.I. is less than 100% [29], it can be conjectured that this species may be formed from an electrochemical oxidation process of HCOOH at the free Pt (100) surface sites available for this modulation condition, i.e. with an upper potential limit at 0.33 V.

An increase of the electromodulation upper potential limit causes the various bands in the spectra to undergo variations as follows:

(1) When the upper potential limit is increased up to 0.53 V, the wavenumber of the bipolar band zero crossing point increases from 2045 to 2050 cm⁻¹ and there is an increase in the peak-to-peak intensity which reaches a maximum value when the upper potential limit is at 0.53 V. The band near 1875 cm⁻¹ is shifted slightly to lower wavenumbers and its intensity becomes smaller.

(2) A further increase of the upper potential limit causes the peak-to-peak intensity of the bipolar band to decrease. At the same time a maximum intensity of the band in the range 1875 cm⁻¹ is found to occur with the upper potential limit at 0.63 V and the band position at 1845 cm⁻¹, i.e. a negative shift of 30 cm⁻¹ relative to the modulation limits 0.13 to 0.33 V. At potential limits beyond 0.73 V the two bands disappear completely.

(3) Absorbance in the range 1750 to 1800 cm⁻¹ persists throughout all the modulation conditions. The intensity of the band in this region increases with an increase of the upper potential limit, but its sign changes, and its maximum
### TABLE 1
EMIRS data obtained with Pt (100) in 0.1 M HCOOH + 0.5 M H$_2$SO$_4$ solution

<table>
<thead>
<tr>
<th>Modulation potential/V</th>
<th>Band near 1780 cm$^{-1}$</th>
<th>Band near 1870 cm$^{-1}$</th>
<th>Bipolar band</th>
<th>Relative amplitude $R = (I_1/I_3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Position /cm$^{-1}$</td>
<td>Amplitude $I_1$</td>
<td>Position /cm$^{-1}$</td>
<td>Amplitude $I_2$</td>
</tr>
<tr>
<td>Lower pot.</td>
<td>Upper pot.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td>0.33</td>
<td>1764</td>
<td>1.7</td>
<td>1875</td>
</tr>
<tr>
<td>0.13</td>
<td>0.43</td>
<td>1769</td>
<td>1.3</td>
<td>1870</td>
</tr>
<tr>
<td>0.13</td>
<td>0.53</td>
<td>1785</td>
<td>1.9</td>
<td>1870</td>
</tr>
<tr>
<td>0.13</td>
<td>0.63</td>
<td>1774</td>
<td>-10.8</td>
<td>1845</td>
</tr>
<tr>
<td>0.13</td>
<td>0.73</td>
<td>1780</td>
<td>2.9</td>
<td>1850</td>
</tr>
<tr>
<td>0.13</td>
<td>0.83</td>
<td>1789</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td>0.93</td>
<td>1780</td>
<td>1.6</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 2
EMIRS data obtained with Pt (111) in 0.1 M HCOOH + 0.5 M H$_2$SO$_4$ solution

<table>
<thead>
<tr>
<th>Modulation potential/V</th>
<th>Band near 1780 cm$^{-1}$</th>
<th>Band near 1870 cm$^{-1}$</th>
<th>Bipolar band</th>
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<tr>
<td>Lower pot.</td>
<td>Upper pot.</td>
<td></td>
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</tr>
<tr>
<td>0.13</td>
<td>0.33</td>
<td>1780</td>
<td>1.5</td>
<td>-</td>
</tr>
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<td>0.13</td>
<td>0.43</td>
<td>1770</td>
<td>2.1</td>
<td>-</td>
</tr>
<tr>
<td>0.13</td>
<td>0.53</td>
<td>1785</td>
<td>3.4</td>
<td>-</td>
</tr>
<tr>
<td>0.13</td>
<td>0.63</td>
<td>1780</td>
<td>2.4</td>
<td>-</td>
</tr>
<tr>
<td>0.13</td>
<td>0.73</td>
<td>1770</td>
<td>2.2</td>
<td>-</td>
</tr>
<tr>
<td>0.13</td>
<td>0.83</td>
<td>1774</td>
<td>1.7</td>
<td>-</td>
</tr>
</tbody>
</table>
amplitude occurs for the modulation limits 0.13 to 0.63 V where the peak is negative. At more positive potentials the band is positive in sign and of lower amplitude, although it becomes the dominant feature on the spectrum due to the disappearance of the bipolar band and the band in the range 1840 to 1880 cm$^{-1}$.

The relative intensities of the bands and their positions are reported in Table 1. The parameter $R$ in this table is defined as

$$R = \frac{I_1}{I_3}$$

where $I_1$ is the relative peak intensity of the band between 1750 and 1800 cm$^{-1}$ and $I_3$ is the peak-to-peak relative intensity of the bipolar band. $R$ is significant in assessing the importance of the band in the range 1750 to 1800 cm$^{-1}$ in each spectrum. $R$ increases especially when the modulation upper potential limit is higher than 0.53 V, i.e. when the poisoning intermediate can be oxidized.

It should be noted that a similar variation of the bipolar band and the band near 1875 cm$^{-1}$ with increase of the upper potential limit has been observed with polycrystalline platinum [20].

*Pt (111)*

On the EMIRS spectra in Fig. 4 a band in the range 1750 to 1800 cm$^{-1}$ is clearly observed with a relatively large amplitude compared to the bipolar CO band; it is present even in the spectrum with the modulation limits 0.13 to 0.33 V. The electrocatalytic activity indicated by the electrochemical results, Fig. 2, suggests that this band may be ascribed to IR absorption by a reactive intermediate. On increasing the upper potential limit, the relative intensity of this band increases and reaches its maximum value at a modulation from 0.13 to 0.53 V. The band becomes

![Fig. 4. EMIRS spectra obtained with Pt (111) in 0.25 M HCOOH + 0.5 M H$_2$SO$_4$ solution. The modulation potentials are marked for each spectrum.](image-url)
more and more dominant in the spectrum when the upper potential limit is increased above 0.53 V and the bands from the poisoning species decline.

The bipolar band, corresponding to IR absorption by linearly bound CO, is visible as in the case of Pt (100) and in the same potential domain for the upper potential limits. The maximum peak-to-peak intensity for this band is found with the modulation limits from 0.13 to 0.43 V and the zero crossing point is then at 2054 cm$^{-1}$. When the modulation upper potential limit is increased above 0.43 V, the peak-to-peak intensity is decreased. At higher modulation upper potential limits, i.e. above 0.73 V, this band disappears completely from the spectra.

The relative intensities of the bands and their positions in the spectra obtained with Pt (111) are reported in Table 2. In this case no band is visible in the range 1840 to 1880 cm$^{-1}$ where a bridge bonded CO species would be absorbing. The parameter $R$ for this case shows the same evolution as in the case of Pt (100), but the $R$ values for Pt (111) are higher which confirms the conclusion drawn from the electrochemical results, i.e. in the case of Pt (111) the surface sites are less blocked by the P.I. and more surface sites are accessible for the main oxidation of HCOOH via the reactive intermediate.

From a comparison of the evolution of the IR absorption bands in the spectra with the oxidation behaviour of HCOOH and that of the P.I. alone, it is evident that when the upper potential limit of the modulation is below the threshold of oxidation of the P.I. (0.5 V) two types of intermediate exist on the surface and the oxidation of HCOOH takes place through the reactive intermediate produced on the free surface sites. When the modulation upper potential limit is above the threshold potential for the oxidation of the P.I., it is progressively removed to leave an increasing number of free sites at the surface; thus the major adsorbed surface species observed in these conditions is the reactive intermediate. This explains the evolution with the upper potential limit of the relative intensities of the two bands in the spectra obtained with Pt (111).

DISCUSSION

A comparison of the electrochemical data for the overall oxidation of formic acid and its poisoning intermediate isolated on Pt (100) or on Pt (111) with the corresponding EMIRS spectra, confirms the earlier conclusion that the bipolar band and the band in the vicinity of 1975 cm$^{-1}$ are due to the IR absorption of linearly and bridge bonded CO species respectively, i.e. the poisoning intermediate, and that the band in the range 1750 to 1800 cm$^{-1}$ may be due to IR absorption by another chemical species. This is suggested by the evidence that the latter band becomes more important in the IR spectrum when the upper potential limit is above 0.53 V, i.e. when the oxidation of the poisoning intermediate takes place and its surface concentration decreases. This means that more surface sites are free from blocking by the P.I. and become accessible for the oxidation of formic acid via the reactive intermediate. For electrodes of both orientations, the maximum relative intensity of the band in the range 1750 to 1800 cm$^{-1}$ is obtained at the upper potential limit
where the peak-to-peak intensity of the bipolar band decreases (see Tables 1 and 2). The adsorbed species producing this band is probably the reactive intermediate in the formic acid oxidation which may be identified, referring to refs. 30 and 31, as a COOH species. Compared to the absorption band for a simple carbonyl stretch, the observed band is very broad and extends to quite high wavenumbers, indicating that the species can exist in more than one adsorption site and that there might be considerable interaction between neighbouring species.

For complex irreversible reactions, the EMIRS difference spectra do not give a simple relation between the band intensity and the surface concentration of the adsorbed species [20,32,33]. However, the appearance of the bands and their evolution with the modulation conditions which are reported in tables 1 and 2 give some indication of the adsorbed species produced from formic acid at different stages of its oxidation. This may be summarized as follows:

(a) Under the modulation conditions where the P.I. is stable on the platinum surface, i.e. when the upper potential limit is below 0.53 V, a high proportion of surface hydrogen sites, but different for the two electrodes, are blocked by the P.I. Only a small number of the surface hydrogen sites are free for the main oxidation of formic acid via the reactive intermediate; consequently the corresponding IR spectra indicate that the main IR absorption bands are due to linearly or bridge bonded CO.

Under these modulation conditions, the maximum extent of blocking by the P.I. may be reached for each electrode, but the surface of the Pt (111) is less blocked than that of Pt (100) [22,27]. Thus more reactive intermediates may be produced on the surface of Pt (111) than on the Pt (100) surface and indeed the IR spectra show then that in the case of Pt (111) the absorption in the range 1750 to 1800 cm⁻¹ is more pronounced and the parameter $R$ in Table 2 is bigger than that in Table 1. This result suggests that the broad band observed in this range is due to IR absorption by the reactive intermediate.

(b) When the upper limit is above 0.53 V, oxidation of the P.I. occurs, thus freeing more surface sites for the main oxidation via the reactive intermediate. For both orientations the IR bands corresponding to the P.I. decrease their intensity and disappear completely at higher potentials, while the band corresponding to the reactive intermediate remains in all the spectra. Although the actual intensity of the band in the range 1750 to 1800 cm⁻¹ decreases with an increase in the upper potential limit of modulation, it becomes relatively more important due to the disappearance of the P.I. bands in the spectra. This situation is seen as an increase of $R$ with upper potential limit in the two tables.

In a recent paper, Kunimatsu and Kita [34] reported the same evolution with electrode potential of the IR absorption band intensity for linearly bound CO produced from HCOOH or CH₂OH at polycrystalline platinum surfaces. These results confirm that the decrease of the peak-to-peak intensity of the bipolar band corresponds to the decrease of the surface concentration of the P.I. due to its oxidation at potentials above 0.5 V.

It should be noticed that, although the surface is free from poison when the
potential is above 0.5 V on the negative sweep, the current for oxidation of HCOOH on the negative sweep starts off at a low value and increases with decreasing potential for both the (111) and (100) surfaces. Moreover, the maximum relative intensity of the band corresponding to the reactive intermediate is obtained at an upper potential limit of 0.53 V for Pt (111) and 0.63 V for Pt (100). These two factors indicate that the oxidation of HCOOH via the reactive intermediate is controlled by the adsorption isotherm for HCOOH on the surface.

On the basis of the experimental results and the discussion given above, a general mechanism for formic acid oxidation on a platinum surface may be detailed and described in the following way:

1. HCOOH molecules are adsorbed on the platinum surface in an amount determined by the adsorption isotherm for the crystallographic orientation chosen,

\[ \text{HCOOH} + z [\text{Pt}] \rightleftharpoons [\text{Pt}]_z \text{HCOOH} \]  

where [Pt] is a platinum surface site and \( z \) is the number of appropriate adsorption sites. The reaction then may occur through two pathways according to the surface conditions at the electrode potential.

2. In all of the potential range used in this experiment, i.e. from 0.05 up to 1.0 V, the spontaneous dissociative adsorption of formic acid may take place on the free surface hydrogen sites and this leads to the production of CO adsorbed on the surface

\[ [\text{Pt}]_x \text{HCOOH} \rightarrow [\text{Pt}]_x \text{CO} + (z - x) [\text{Pt}] + \text{H}_2\text{O} \]  

where \( x \) is the number of hydrogen sites blocked per CO: \( x = 1 \) for linearly bound CO and 2 or 3 for bridge bonded CO.

3. In the range of potential \((E < 0.5 \text{ V})\) where the P.I. is stable, the CO species formed according to reaction (2) is accumulated at the surface.

4. When the potential is above the threshold potential for formic acid oxidation, which is nearly 0.23 V as may be observed from the overall oxidation current of HCOOH on the negative sweep, the main oxidation of formic acid via the reactive intermediate may occur by forming electrochemically the reactive intermediate on the free surface sites;

\[ [\text{Pt}]_z \text{HCOOH} \rightarrow [\text{Pt}]_y \text{COOH} + (z - y) [\text{Pt}] + \text{H}^+ + e^- \]  

\[ [\text{Pt}]_y \text{COOH} \rightarrow \text{CO}_2 + y [\text{Pt}] + \text{H}^+ + e^- \]  

where \( y \) is the number of sites occupied per COOH adsorbed species. Reactions (3) and (4) are fast electrochemical reactions; the whole reaction may be considered to be a direct charge transfer at unblocked surface sites, i.e.

\[ \text{HCOOH} \rightleftharpoons (\text{HCOOH})_{\text{ads}} \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 e^- \]  

5. In the potential range where the hydrogen adsorption equilibrium occurs,

\[ [\text{Pt}]_H \rightarrow [\text{Pt}] + \text{H}^+ + e^- \]  

the species \([\text{Pt}]_{x}\text{COOH}\) formed through reaction (3) may combine with adsorbed hydrogen

\[
[\text{Pt}]_{x}\text{COOH} + [\text{Pt}]\text{H} \rightarrow (1 + y - x) [\text{Pt}] + [\text{Pt}]_{x}\text{CO} + \text{H}_2\text{O}
\]

and lead to the formation of the poisoning intermediate and to an enhancement of surface blocking.

(6) When the potential is sufficiently high, OH species are formed on the free surface sites,

\[
\text{H}_2\text{O} + [\text{Pt}] \Rightarrow [\text{Pt}]\text{OH} + \text{H}^+ + e^- 
\]

The poisoning intermediate is oxidized rapidly by combining with OH, the promoter of its oxidation [29], according to

\[
[\text{Pt}]_{x}\text{CO} + [\text{Pt}]\text{OH} \rightarrow (1 + x) [\text{Pt}] + \text{CO}_2 + \text{H}^+ + e^- 
\]

(1 + x) free sites are restored by this reaction at which HCOOH molecules may adsorb as in reaction (1). Thus the reactions (3) and (4) may occur in competition with the reactions (2), (8) and (9). This means that under these conditions the oxidation of HCOOH may occur via two parallel pathways: one through the reactive intermediate and the other through the poisoning intermediate. But in this potential range the electrochemical formation of the reactive intermediate (reaction 3) is faster than the chemical formation of the poisoning intermediate (reaction 2); the overall oxidation of HCOOH passes principally through the reactive intermediate and is limited by the adsorption rate of HCOOH on each plane.

(7) At high potentials the species \([\text{Pt}]\text{OH}\) may be oxidized further, i.e. to \([\text{Pt}]\text{O}\)

\[
[\text{Pt}]\text{OH} \rightarrow [\text{Pt}]\text{O} + \text{H}^+ + e^- 
\]

Both the formation of the reactive intermediate and the formation of the poisoning intermediate may be inhibited by the production of \([\text{Pt}]\text{O}\) at the surface.

The description above gives the stage by stage oxidation of formic acid on platinum in acid medium with successive increases of potential, i.e. in the positive sweep. On a negative potential sweep, when the potential is above 0.5 V, the HCOOH oxidation occurs in two parallel pathways, but mainly through the reactive intermediate. When the potential is below 0.5 V the poisoning intermediate formed is accumulated at the surface; thus the HCOOH oxidation may occur only via the reactive intermediate at the unblocked surface sites until the threshold for this oxidation is reached. The rate of formic acid oxidation both on the positive and the negative sweep depends on the blocking of surface sites and the HCOOH adsorption rate.

The complete mechanism of HCOOH oxidation at a platinum surface discussed above may be written as shown in Scheme 1. In addition, it should be noted that another route for the formation of the adsorbed CO poison has been observed [35]; the reduction of \(\text{CO}_2\) by adsorbed hydrogen:

\[
\text{CO}_2 + 2 [\text{Pt}]\text{H} + (x - 2) [\text{Pt}] \rightarrow [\text{Pt}]_x\text{CO} + \text{H}_2\text{O}
\]
The mechanism described above is a general picture of formic acid oxidation on a platinum surface in which the surface structure effects of platinum may be emphasized in the following three aspects.

(1) Anisotropy in intrinsic properties. The different atomic surface structures correspond to different electronic surface structures [36,37] which lead to different energy barriers for the electrical charge transfer process and to different equilibrium adsorption properties for the organics. This may be the origin of the difference in the activity between Pt (100) and Pt (111) for the main oxidation of HCOOH via the reactive intermediate.

(2) Anisotropy for the interaction between formic acid and the platinum surface in the irreversible adsorption process with the organics. The rate of the dissociative adsorption and the proportion of the linearly or bridge bonded P.I. produced from the dissociative adsorption at each plane are different. Furthermore the efficiency of each surface structure for this dissociative adsorption is different [27]. The proportion of the reactive intermediate with different modes of bonding is also likely to be different for different surface structures.

(3) Anisotropy in OH species formation. The adsorbed OH species is the promoter of the P.I. oxidation. Thus the different behaviour of the various orientations for OH adsorption may influence the overall oxidation behaviour of HCOOH.

ACKNOWLEDGEMENTS

Support for this work from the U.K. Science and Engineering Research Council, the UGC (Special Equipment Grant) and from the Office of Naval Research, Washington, is gratefully acknowledged. S.G.S. wishes to thank Prof. Roger Parsons for arranging his stay in Meudon and Southampton.
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