Necessity of Oxygenated Surface Species for the Electrooxidation of Methanol on Iridium

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The electrooxidation of methanol on an iridium disk in the pH range 0-14 was studied by Fourier transform infrared (FTIR) spectroscopy. The following solutions were used: 1 M H₂SO₄, 0.1 M HClO₄, 1 M H₃PO₄, and 1 M Na₂SO₄ whose pH had been adjusted to 2 with H₂SO₄, 0.5 M phosphate buffer of pH 7, 0.1 M borax buffer, and 1 M NaOH. Linear potential sweep (LPS) FTIR spectroscopy showed that the products of 0.1-1.0 M methanol electrooxidation on smooth Ir were CO₂ and formic acid in acidic media and bicarbonate/ carbonate and formate ions in alkaline media. Only at pH 7 and 9.2 neither formic acid nor formate ion was detected. The activity of Ir for methanol electrooxidation was very low. At all pH values dissociative chemisorption of methanol yielded chemisorbed CO, always in the linear form. At pH 14 this chemisorbed CO was completely electrooxidized by 0.6 V vs RHE, a value 0.4 V less positive than in perchloric and phosphoric acids of pH 1. This behavior is parallel to that of the appearance of formate/formic: at pH 14 formate is detected already at 0.4 V, while in perchloric and phosphoric acids of pH 1 formic acid is first detected at 0.9 V. This dependence on pH of the electrocatalytic activity of Ir both for the electrooxidation of chemisorbed CO and for that of methanol to formate/formic is in perfect agreement with the fact that the peak of the main Ir surface oxidation process occurs at 0.6 V vs RHE at pH 14, but at a rather more positive potential, 0.9-1.0 V vs RHE, in acidic media (super-Nernstian pH dependence). This agreement lends support to the hypothesis that the electrooxidation of organic compounds requires the presence of oxide, hydroxide, and/or oxyhydroxide groups on the Ir surface, which provide the O atoms necessary for the formation of CO_2 and formic/formate. However, in sulfuric acid, both at pH 0 and 2, formic acid was already observed at 0.7 V, possibly because in sulfuric acid a prepeak of Ir oxidation at 0.6 V that precedes the main peak at 1.0 V is better defined. The stretching frequency of linear CO increased by up to 60 cm^{-1} with increasing coverage and at the same coverage was higher in HClO₄ than in H₃PO₄ solutions. The Stark shift varied over the range 39-45 cm⁻¹ V⁻¹ with pH, CO coverage, and nature of the anion in the case of acids.

Introduction

Already in 1963 Breiter¹ concluded that Ir was less active than Rh, Pd, and Pt for the electrooxidation of methanol. Bagotzky et al.² found that the plot of the coverage of smooth Ir by residues of the dissociative chemisorption of methanol vs potential had the typical flat maximum, with a coverage of about 0.65. They also found that the pH greatly influenced the coverage by methanol residues, which showed a pronounced minimum of only 0.1 in the pH range 3-5. The steady-state electrocatalytic activity of Ir for methanol electrooxidation also showed a pronounced minimum, but at pH 7.

Podlovchenko et al.³ found in stationary measurements that the activity of their "surface skeleton" Ir (with a roughness factor, determined assuming a hydrogen monolayer charge of $220 \,\mu\text{C} \text{ cm}^{-2}$, of up to 5300) for methanol electrooxidation in 0.5 M H₂SO₄ was decreased by UPD Bi and Ag. This is in agreement with results of Ureta-Zañartu et al.,⁴ who found that eight UPD metals decreased the methanol electroactivity of an Ir wire in 1 M HClO₄ at sweep speeds lower than a few mV/s, i.e., those more related to industrial practice. It should be remarked that they found that the same UPD metals *increased* the Ir activity at higher sweep speeds, which shows how wrong conclusions on the electrocatalytic effect of electrode modifications can be reached if, as is usually the case, only CVs at sweep speeds higher than say 10 mV/s are carried out.

Aramata et al.⁵ studied by CV and IR spectroscopy the electrooxidation of methanol on Ir in acid medium and observed linearly chemisorbed CO. For a positive limit of 0.8 V an anodic peak appeared in the return negative sweep, obviously due to a more active surface produced by the reduction of a surface oxide. This anodic peak was much smaller for a positive limit of 1.2 V and disappeared completely for a 1.4 V limit, due to increasing irreducibility of the oxide, as is frequently the case.

As is well-known, the CV of Ir shows a reversible oxidation, whose peak lies at 1.0 V vs RHE in acid. Upon changing the pH the position of this peak does not remain the same with respect to the RHE. On the contrary, it shows a super-Nernstian pH dependence of about 30 mV vs RHE/pH unit (i.e., about 90 mV/pH unit when using a fixed reference electrode).⁶ A thick electrochromic oxide layer can be grown on Ir by potential cycling at pH <3.5, in spite of which the hydrogen area does not decrease, probably due to a very hydrated, permeable nature of the oxide.⁷

It is usually accepted in electrocatalysis that electrooxidation of organic compounds on metallic electrodes occurs first at potentials positive enough for electrooxidation of the metal to begin, the metal oxycompounds providing the required O atoms. This hypothesis has recently been confirmed by XANES⁸ (for CO electrooxidation on $Pt_{50}Ru_{50}$ nanoparticles) and by potential-

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modulated reflectance spectroscopy⁹ (for ethanol electrooxidation on polycrystalline Ni and Fe). Further confirmation has been provided by a XANES and EXAFS study of a carbonsupported Pt-Ru electrocatalyst, whose high activity for methanol electrooxidation was attributed to the formation of RuOH at low potentials.¹⁰ However, it was concluded that electronic effects should also be taken into account.

The super-Nernstian dependence of the electrooxidation of the Ir surface yields a good opportunity to check that electrooxidation of organics coincides with the start of iridium oxide formation. For this purpose we have studied by means of FTIR spectroscopy the electrooxidation of methanol on an Ir disc in acidic, neutral, and alkaline aqueous solutions.

Experimental Section

The Ir electrode was a 12 mm disc cut from Ir sheet, 99.9% pure and 0.25 mm thick, from Alfa Ventron. It was polished with successively finer grades of alumina down to 0.05 μ m, copiously rinsed with ultrapure water, and cleaned for 5 min in an ultrasonic bath just prior to use. Methanol (Riedel, 99.8%), with a nominal water content <0.01% confirmed by Karl Fischer test, and an ethanol content of <0.1% were used as received. The other reagents were of analytical grade.

The Ir electrode was glued with Araldit to the end of a 0.5 cm long, 12 mm o.d. Pyrex tube, and electric contact to a copper cable was made with Ag epoxy. This assembly was joined with heat-shrinkable polyolefin tubing with an inner adhesive lining to another Pyrex tube of 6 mm diameter, the flexible interconnecting tubing allowing to obtain uniform films of electrolyte solution by pressing the electrode against the fluorite window.

A conventional glass cell and a Teflon cell with a capacity of about 12 cm³ were employed for voltammetric and FTIR studies, respectively. The Teflon cell was positioned in a Spectra-Tech variable angle specular reflectance accessory so as to maximize the detected IR signal. The p-polarized light reached the CaF₂ window at an incidence angle of about 67°.

A P.A.R Model 362 scanning potentiostat was used. The reference electrode was SCE for the experiments in a conventional electrochemical cell and, due to space limitations, Ag/AgCl in saturated KCl for the FTIR experiments. However, the potentials are given versus the reversible hydrogen electrode (RHE).

Infrared reflectance spectra in the region $1000-3000 \text{ cm}^{-1}$ were collected with a Perkin-Elmer Model 1725-X FTIR spectrometer connected to a 486DX2P.C. A liquid nitrogencooled narrow-band MCT detector was used. The sample compartment was purged with dry, CO₂-free air from a Peak purge gas generator at a flow rate of 20 L min⁻¹. The spectral resolution was 8 cm⁻¹.

Differential FTIR spectra were obtained from interferometric scans continuously carried out during a linear potential sweep (LPS) at 1 mV/s, each 80 successive interferograms (taken in about 35 s) being separately collected (LPS-FTIRS). The reference spectrum was always taken at 0.1 V vs RHE, unless otherwise indicated.

Normalized differential reflectance is defined here as the difference between the reflectance at the sample potential, E_s , and that at the reference potential, E_r , divided by the reference reflectance, i.e., $\Delta R/R = R(E_s)/R(E_r) - 1$. With this definition upward and downward bands correspond to loss and gain of compounds, respectively, in the thin electrolyte layer and/or electrode surface. The bands originated by a Stark shift of a chemisorbed species are the so-called bipolar bands, with a positive and a negative lobe.



Figure 1. Dashed curves are the cyclic voltammograms (CVs) at 50 mV s⁻¹ of an Ir disk in 1 M H₂SO₄ (A), 1 M H₃PO₄ (B), 0.5 M, pH 7 phosphate buffer (C), and 1 M NaOH (D), recorded after potential cycling at 500 mV s⁻¹ until the CV was reproducible. Potentials are given versus the reversible hydrogen electrode (RHE), with which the super-Nernstian dependence of the main Ir oxidation process becomes clearly apparent. The CVs in the presence of 1 M methanol are shown as solid curves.

Results and Discussion

Cyclic Voltammetry. The dashed curves in Figure 1 are cyclic voltammograms at 50 mV s⁻¹ of Ir in 1 M H₂SO₄ (A), 1 M H₃PO₄ (B), pH 7 phosphate buffer (C), and 1 M NaOH (D) obtained after potential cycling at 500 mV s⁻¹ until a reproducible CV was obtained. In the RHE scale the main Ir oxidation process appears at a 0.3-0.4 V more negative potential at pH 14 than in acidic and neutral media, showing the super-Nernstian dependence mentioned in the Introduction.

In the presence of 1 M methanol, the CVs (solid lines) show a very slight increase in the anodic current over the potential range in which Ir electrooxidation occurs and a steep increase of the anodic current at about 1.4 V vs RHE, a potential only about 0.1 V less positive than in base electrolyte, showing the poor electrocatalytic activity of Ir for methanol oxidation. (The equilibrium potential for the electrooxidation of methanol to CO_2 and water is 0.01 V vs RHE¹¹). The hydrogen area decreased slightly, due to dissociative chemisorption of methanol, yielding linearly chemisorbed CO, as will be seen below.

The lack of electrocatalytic activity of Ir required the use of high methanol concentrations for its oxidation products to be detectable in FTIR experiments. Actually, the methanol concentration was of the order of, or even higher than, that of the buffers. Consequently, the electrooxidation of methanol produced large pH changes and these, in turn, large artifacts in the FTIR spectra, as will be seen below. Another consequence is that especially in neutral and alkaline media the potentials vs RHE shown against FTIR spectra should be viewed as maximum values.

FTIRS Results in Acidic Medium. In the differential spectrum obtained by positive polarization of Ir in $1 \text{ M H}_2\text{SO}_4$,



Figure 2. Differential LPS-FTIR spectra obtained during a positive linear potential sweep (LPS) at 1 mV s⁻¹ of an iridium disk in 1 M H₂SO₄, 1 M in methanol. During the LPS interferometric scans were continuously recorded, each 80 successive interferograms being separately collected in about 35 s. The reference spectrum was taken at the initial potential of 0.1 V vs RHE.

1 M in methanol linearly chemisorbed CO is evidenced by a bipolar band (due to the well-documented Stark shift) of linear (on top) CO at about 2045 cm⁻¹ (Figure 2). This bipolar band indicates that methanol already dissociates on Ir, yielding linear CO, at the potential of the reference spectrum, 0.1 V. The bipolar band becomes a monopolar upward band at 2045 cm⁻¹ at 0.7 V, indicating that at this potential the chemisorbed CO is completely electrooxidized, since the band intensity does not increase with further potential increase.

The maximum normalized reflectance change, $\Delta R/R$, of chemisorbed CO was 0.7%. The value for a (maximum) CO coverage of 0.60–0.65 on Ir(111) can be estimated as 1.9% from Figure 1 in ref 12. Therefore, a sizable fraction of the Ir surface is covered with chemisorbed CO, which is in apparent contrast with the CVs shown in Figure 1, in which the hydrogen area is about the same in the absence and presence of methanol. The reason for this apparent contradiction is that the CVs in Figure 1 are stabilized repetitive CVs at 50 mV/s, in which little methanol chemisorption can take place during the negative sweep, while the FTIR experimens were run at 1 mV/s from the negative limit, which allowed ample time for dissociative chemisorption of methanol to proceed.

Neither bridge-bonded nor multiply bonded CO was detected on the Ir surface in the presence of methanol over the pH range 0-14, in agreement with the results of Aramata et al.⁵ for methanol electrooxidation on polycrystalline Ir in acidic media and with those of Jiang et al.¹¹ for adsorption of CO on Ir(111) in 0.1 M HClO₄.

Dissolved CO₂ (downward peak at 2345 cm⁻¹) is first observed at 0.6 V. Formic acid (downward peak at 1720 cm⁻¹) first appears at 0.7 V, the same potential at which chemisorbed CO is completely electrooxidized, which indicates that both processes require the same surface iridium oxide or, alternatively, that chemisorbed CO completely poisons the electrooxidation of methanol to formic acid. This latter hypothesis is



Figure 3. Differential LPS-FTIR spectra obtained during a positive linear potential sweep (LPS) at 1 mV s^{-1} of an iridium disk in 0.1 M HClO₄, 1 M in methanol.

little tenable, since only a fraction of the Ir surface is covered by chemisorbed CO.

Although formic acid has two peaks at 1732 and 1216 cm⁻¹, as will be shown below, only the peak at 1720 cm⁻¹ appears in Figure 2, while the formic acid peak at 1216 cm⁻¹ is completely swamped by an artifact at 1208 cm⁻¹. As a matter of fact, both the downward peaks at 1208 and 1055 cm⁻¹ in Figure 2 are artifacts due to an increase of the HSO₄⁻ concentration in the thin layer, produced at the expense of SO₄²⁻ ions, whose loss originates an upward peak at 1100 cm⁻¹. These artifacts are originated by the acidification of the thin layer consequent to the electrooxidation of methanol, either to formic acid, which produces four H⁺ ions per methanol molecule, according to

$$CH_3OH + H_2O \Longrightarrow HCOOH + 4H^+ + 4e^-$$
(1)

or to CO₂, which frees six H⁺ ions per methanol molecule,

$$CH_{3}OH + H_{2}O \Longrightarrow CO_{2} + 6H^{+} + 6e^{-}$$
(2)

Even in base electrolyte, i.e., in the absence of organic compounds, the processes of hydrogen adsorption and desorption and of surface oxide formation and reduction can change the pH in the thin layer.^{13,14} Furthermore, even in the double layer region, i.e., in the absence of faradaic reactions, the change in the state of charge of the electrode can lead to the migration of ions into or out of the thin layer, a rapid process which can also originate artifacts.¹⁴

Water is consumed in the electrooxidation of methanol in acidic and neutral media, as seen in reactions 1 and 2. This loss of water originates an upward peak at about 1650 cm⁻¹ in all other acidic and neutral media (Figures 3-5 and 7). However, in 1 M H₂SO₄ it appears shifted to 1590 cm⁻¹ (Figure 2), probably because of the higher acidity of the medium, since this water band is very sensitive to pH, hydrogen bonding, and ionic strength.

The results in 0.1 M HClO₄ (Figure 3) and in 1 M H_3PO_4 (Figure 4) are essentially the same as those in 1 M H_2SO_4



Figure 4. Differential LPS-FTIR spectra obtained during a positive linear potential sweep (LPS) at 1 mV s⁻¹ of an iridium disk in 1 M H₃PO₄, 1 M in methanol.

(Figure 2). Dissolved CO₂ first appears at 0.4 and 0.7 V, respectively, and formic acid is first observed at a higher potential, 0.9 V in both cases. Chemisorbed CO is completely electrooxidized at a slightly higher potential, 1.0 V in both cases. It must be stressed that with these two acids the two bands of formic acid, at 1730 and 1214 cm⁻¹, appear simultaneously, which rules out the presence of formaldehyde, since aldehydes also show the carbonyl band at 1730 cm⁻¹, but not the C–O stretch at 1214 cm⁻¹. This is in contrast with the behavior of ethanol in 0.5 M HClO₄, in which case acetaldehyde is formed first, and acetic acid at higher potentials.¹⁵ No conclusions on the presence of formaldehyde can be drawn in the case of sulfuric acid, due to the large HSO₄⁻ peak at 1208 cm⁻¹, but it is reasonable to assume that also in this case no formaldehyde is produced.

The downward band at 1108 cm^{-1} in perchloric acid is due to migration of ClO_4^- ions into the thin layer to compensate for the increase in H⁺ concentration produced by methanol electrooxidation.

Also in 1 M Na₂SO₄ acidified with H₂SO₄ down to pH 2.0 (about the value of the second acidity constant of H₂SO₄, $pK_2 = 1.96^{16}$) the band of formic acid at 1730 cm⁻¹ appeared in the IR spectrum (Figure 5), but only after deconvolution (see inset in Figure 5) from the upward band at 1652 cm⁻¹ produced by the loss of water in the thin layer. Formic acid appeared at 0.7 V, a slightly lower potential than that of 0.9 V at which chemisorbed CO was completely electrooxidized.

Again, as in Figure 2 the downward bands at 1204 and 1050 cm⁻¹ are due to an increase in the HSO_4^- concentration in the thin layer, produced at the expense of SO_4^{2-} ions (upward band at 1115 cm⁻¹) by the acidification inherent to the electrooxidation of methanol.

Spectra of Formic Acid and Formate Ion. In order to obtain the IR spectrum of both formic acid and formate ion, we carried out the electroreductive deprotonation of 0.1 M formic acid in 0.1 M NaClO₄ aqueous solution, by means of an LPS-FTIRS experiment in which interferometric scans were continuously recorded during a negative linear potential sweep



Figure 5. Differential LPS-FTIR spectra obtained during a positive linear potential sweep (LPS) at 1 mV s⁻¹ of an iridium disk in a 1 M Na₂SO₄ solution whose pH had been adjusted to 2 with H₂SO₄, 0.5 M in methanol. In the inset a deconvoluted spectrum is shown in order to reveal the band at 1730 cm⁻¹ of formic acid which was swamped by the upward band of water loss at 1652 cm⁻¹. The band of formic acid at 1214 cm⁻¹ is completely hidden by the large downward band at 1204 cm⁻¹ produced by the increase of the amount of HSO₄- in the thin layer due to the acidification inherent to the electrooxidation of methanol.

at 2 mV/s. The electrochemical reaction is simply

$$2\text{HCOOH} + 2e^{-} \Rightarrow 2\text{HCOO}^{-} + \text{H}_2 \tag{3}$$

The reference potential was 0.1 V vs SCE, the first spectrum was recorded at a potential of -0.2 V and the last one at -0.4 V. Two upward peaks at 1216 and 1732 cm⁻¹ corresponding to the disappearance of HCOOH grow simultaneously with two downward peaks at 1352 and 1580 cm⁻¹ and a shoulder at 1382 cm⁻¹, due to the formation of HCOO⁻ ion at the expense of HCOOH (Figure 6). A small peak of water loss at 1657 cm⁻¹ is also present in the spectrum.

Neutral and Weakly Alkaline Media. In the electrooxidation of 0.5 M methanol on Ir in a pH 7 phosphate buffer (0.5 M K₂HPO₄ + 0.5 M KH₂PO₄), CO₂ (downward band at 2345 cm⁻¹) and bicarbonate ion (downward band at 1364 cm⁻¹) appear at 0.6 V, and chemisorbed linear CO (upward band at 2003 cm⁻¹) is completely electrooxidized at 0.7 V (Figure 7a). Contrary to the behavior in acidic medium neither HCOOH nor HCOO⁻ (actually at pH 7 formic acid, if present, should be ionized by more than 99.9%, since its acidity constant is $pK_a = 3.75^{16}$) was detected. Deconvolution of the upward peak of formate ion at 1580 cm⁻¹.

The presence in the spectrum of both CO_2 and bicarbonate ion was to be expected, since the first ionization constant of carbonic acid is 6.35.¹⁶ However, there is an acidification of the thin electrolyte layer, as evidenced by the large downward band at 1165 cm⁻¹ of H₂PO₄⁻ formed at the expense of HPO₄²⁻, whose disappearance originates a large upward band at 1095 cm⁻¹ (the second ionization constant of phosphoric acid is 6.86^{16}). As a matter of fact, the acidification was so strong



Figure 6. Differential LPS-FTIR spectra obtained in the electroreductive deprotonation of 0.1 M formic acid in 0.1 M NaClO₄ aqueous solution during a negative linear potential sweep (LPS) at 2 mV/s. The electrochemical reaction is 2HCOOH + 2e⁻ \Rightarrow 2HCOO⁻ + H₂. The two downward peaks at 1352 and 1580 cm⁻¹ and a shoulder at 1382 cm⁻¹ are due to the formation of HCOO⁻ ion at the expense of HCOOH, whose loss originates two upward peaks at 1216 and 1732 cm⁻¹.

that even H_3PO_4 (first ionization constant 2.14¹⁶) was formed in the thin layer, as revealed by the downward band at 1027 cm^{-1.17}

When the methanol concentration was increased from 0.5 to 1 M, CO_2 in solution, but no HCO_3^- , appeared in the FTIR spectra. (Linearly chemisorbed CO is also formed, although it is barely seen at the scale of Figure 7b.) Obviously, the absence of bicarbonate is due to exhaustion of the buffering power of the 0.5 M buffer by the electrooxidation of 1 M methanol. There is very little difference between two consecutive spectra at 1.4 V, showing that even at this potential the reaction rate is not high.

Borax. In the electrooxidation of 0.1 M methanol on Ir in 0.1 M borax, pH 9.2 chemisorbed linear CO (upward band at 1993 cm⁻¹) is completely electrooxidized at 0.5 V, and CO₂ (downward band at 2345 cm⁻¹) is first observed at a slightly higher potential, 0.7 V (Figure 8). As at pH 7, no bands assignable to formate ion or formic acid appear in the spectrum. The acidification of the thin layer inherent to the electrooxidation of methanol is stronger due to the use of a low buffer concentration, 0.1 M, mandated by the low solubility of borax, and consequently only CO₂, and no bicarbonate, is seen in the spectra. This acidification is also responsible for the downward peaks at 1413 and 1156 cm⁻¹, originated by an increase in the concentration of boric acid, H₃BO₃.¹⁷ There is, correspondingly, an upward band of $H_2BO_3^-$ ions at 1350 cm⁻¹. The downward peak at 1048 cm⁻¹ is probably an artifact, since there is a peak at this position in the energy spectrum with only air in the beam.

The upward and downward peaks that appear at 1694 and 1633 cm⁻¹, respectively, straddling the position of the water absorption at 1650 cm⁻¹, have not been assigned.

Sodium Hydroxide. The electrooxidation of 0.25 M methanol on Ir in 1 M NaOH produces chemisorbed linear CO (upward band at 1996 cm⁻¹), formate ion (downward bands at 1353 and 1582 cm⁻¹), and carbonate ion (downward band at 1384 cm⁻¹, which swamps the formate band at the same frequency) (Figure 9a). (The two small upward peaks of loss



Figure 7. Differential LPS-FTIR spectra obtained in a positive linear potential sweep (LPS) at 1 mV s⁻¹ of an iridium disk in a pH 7 phosphate buffer (0.5 M K₂HPO₄ + 0.5 M KH₂PO₄) in the presence of methanol at a concentration of 0.5 M (a, top) and 1 M (b, bottom). It can be seen that, in contrast to the results in acidic and strongly alkaline media, neither the peaks of formic acid at 1732, and 1216 cm⁻¹ nor those of formate ion at 1580, 1382 and 1352 cm⁻¹ appear in the LPS-FTIR spectra. The downward peaks at 2341 and 1364 cm⁻¹ in (a) indicate the formation of CO₂ and HCO₃⁻⁻ ion, respectively. At a twice higher methanol concentration the acidification of the electrolyte inherent to the electrooxidation of methanol is so high that only CO₂ (peak at 2341 cm⁻¹) and no HCO₃⁻⁻, is observed (b).

of gaseous CO_2 at about 2340 cm⁻¹ are due to an incomplete purging of the sample chamber before beginning the experiment.) It should be stressed that at this pH 14 an electrooxidation product of methanol, formate ion, could be detected already at 0.4 V, as compared with 0.8–0.9 V at pH 1, and that electrooxidation of chemisorbed CO was already completed at 0.6 V, as compared with 1.0 V at pH 1.



Figure 8. Differential LPS-FTIR spectra obtained in a positive linear potential sweep (LPS) at 1 mV s⁻¹ of an iridium disk in 0.1 M borax in the presence of 0.1 M methanol. The acidification inherent to the electrooxidation of methanol produces two downward peaks at 1413 and 1156 cm⁻¹ due to the increase of the concentration of boric acid at the expense of borate ions, whose loss originates an upward peak at 1350 cm⁻¹.

If the methanol concentration is increased to 2 M, the acidification brought about by its electrooxidation decreases the pH so much that CO₂ appears instead of carbonate or bicarbonate, which means that the pH must be lower than the pK_1 of carbonic acid, 6.35^{16} (Figure 9b). In this case there is no interference by the carbonate ion, and therefore the three formate bands clearly appear in the spectrum, which indicates that the pH must be higher than the pK_a of formic acid, $3.75.^{16}$ Consequently, the pH in the thin layer should be about 5.

Discussion

Products of Methanol Electrooxidation. We have found that besides CO_2 (or, obviously, bicarbonate or carbonate ions in neutral and alkaline media) the only product of methanol electrooxidation on Ir is formic acid and formate ions in acidic and alkaline media, respectively. It is interesting that, within the sensitivity of our FTIRS measurements, neither formic acid nor formate ion was produced in a pH 7 phosphate buffer or in a pH 9.2 borax buffer. This could perhaps be related to the above-mentioned pronounced minimum at pH 7 for the steady-state electrooxidation of methanol on smooth Ir.²

Necessity of Oxygenated Metal Surface Species for the Electrooxidation of Methanol on Iridium, As Deduced from Its pH Dependence. The FTIR spectra over the pH range 0-14 clearly show that in 1 M NaOH both complete electrooxidation of the linearly chemisorbed CO produced by the dissociative chemisorption of methanol and the electrooxidation of methanol to formic/formate occur already at 0.4-0.6 V vs RHE. Similarly, in sulfuric acid, both at pH 0 and 2, formic acid is already observed at 0.7 V, but in both perchloric and phosphoric acids at pH 1 a rather more positive potential, 0.9-1.0 V, is required.



Figure 9. Differential LPS-FTIR spectra obtained in a positive linear potential sweep (LPS) at 1 mV s^{-1} of an iridium disk in 1 M NaOH in the presence of methanol at a concentration of 0.25 M (a, top) and 2 M (b, bottom). At this high pH chemisorbed CO is completely electrooxidized at 0.6 V, at which potential the bipolar character of the CO peak is lost, only an upward peak of CO loss remaining. Also, formate begins to appear already at 0.4 V.

It is usually accepted that the electrooxidation of organic compounds on metals starts at those potentials at which oxidation of the metals begins, the metal oxycompounds providing the oxygen atoms necessary for the electrooxidation of the organic compounds.^{8,9} As mentioned above, the main surface process in the CV of Ir, involving the formation of a semimetallic Ir(IV) oxide and its reduction, probably to an iridium(III) oxide,¹⁸ has a super-Nernstian dependence on pH of about 30 mV vs RHE; *i.e.*, at pH 14 the main process appears

Electrooxidation of Methanol on Iridium

at a potential 0.4 V more negative (in the RHE scale, which corresponds to 1.2 V more negative if a fixed reference electrode is used) than at pH 0. This can be seen in Figure 1, where the main surface process appears at 0.6 V at pH 14, and at 0.9-1.0 V in acidic media.

The negative shift (in the RHE scale) with increasing pH of the potential of the main Ir surface oxidation process is exactly the same shift with pH observed in 1 M NaOH, in 0.1 M HClO₄, and in 1 M H₃PO₄ for the potential of electrooxidation of chemisorbed CO and of methanol to formic/formate on Ir. In other words, both Ir oxidation and complete electrooxidation of chemisorbed CO and start of methanol electrooxidation to formic/formate occur at 0.4–0.6 V vs RHE at pH 14 and at 0.9–1.0 V at pH 1 (in perchloric and phosphoric acids). This coincidence lends full support to the above assumption that electrooxidation of chemisorbed CO and organic compounds necessitates metal surface oxycompounds.

It can be objected that the results in sulfuric acid, at both pH 0 and pH 2, do not fall in line with the above model, since in both cases formic acid is already observed at 0.7 V, a potential 0.3 V lower than that of the peak of the main Ir oxidation process. However, this can be due to the fact that in sulfuric acid a prepeak at 0.6 V precedes the main oxidation peak of Ir, the oxide produced in this prepeak providing the oxygen atoms necessary for electrooxidation of the organics.

Over the pH range 0-2 formic acid is first observed at potentials only 0-0.2 lower than those at which chemisorbed CO is completely electrooxidized, probably because in both processes the same surface Ir oxycompound is involved. On the contrary, dissolved CO₂ appears already at 0.4-0.7 V, potentials about 0.5 V lower than those at which CO is completely electrooxidized. This small peak of CO₂ that appears at low potentials proceeds from the electrooxidation of chemisorbed CO, and it is only after electrooxidation of chemisorbed CO has been completed that a large peak of CO₂ is produced by the electrooxidation of methanol.

As far as we know, there is only one well documented case of electrooxidation of CO or organics on an oxide-free metal, and this is the electrooxidation of dissolved CO on oxide-free Pt (*i.e.*, at potentials in the double layer region of Pt) first reported by Kita et al.¹⁹ for polycrystalline Pt, later confirmed,²⁰ and finally extended to single crystal Pt(111).²¹ Diffusionlimited electrooxidation of dissolved CO occurs on only 10– 15% of the Pt atoms, namely, those which at the potentials concerned are free of chemisorbed CO, these free Pt atoms, either alone or in islands, probably acting as microelectrodes whose diffusion fields overlap, which would justify the experimental result that the stationary current is the same calculated for an electrode without blocked areas.^{20,21}

Dependence of the Frequency of the CO Stretching on the CO Coverage, the pH, and the Anion. In Figure 10 we show the dependence of the frequency of the stretching vibration of chemisorbed CO on the normalized differential reflectance change, for eight experiments at different pH values in the range 0-14, at the same pH 1 but with different acids (0.1 M HClO₄ and 1 M H₃PO₄), or at the same pH 1 and the same acid (1 M H₃PO₄) but at different coverages. The spectra were measured at 0.1 V vs RHE, using as reference the spectrum at 1.0 V, at which chemisorbed CO has been completely eliminated from the Ir surface by electrooxidation to CO₂.

From published IR spectra of CO chemisorbed on Ir(111) in 0.1 M HClO₄¹² it can be estimated that the *height* of the CO band is roughly proportional to the CO coverage up to saturation at 9.4×10^{14} CO molecules cm⁻². On the contrary, with polycrystalline Pt linearity of the integrated band intensity is



Figure 10. Plot of the frequency of the CO stretching vibration versus the differential reflectance (assumed to be approximately proportional to the coverage) for eight experiments of methanol electrooxidation on an iridium disk, conducted at different pH values, or at the same pH value obtained with different acids, or at the same acid and pH value but at different coverages. (a) 0.1 M borax, pH 9.2; (b) 1 M H₃PO₄, pH 1, low CO coverage; (c) 1 M Na₂SO₄ solution whose pH had been adjusted to 2 with H₂SO₄; (d) pH 7 phosphate buffer (0.5 M K₂HPO₄ + 0.5 M KH₂PO₄); (e) 1 M NaOH; (f) 0.1 M HCIO₄, pH 1; (g) 1 M H₂SO₄; (h) 1 M H₃PO₄, pH 1, high CO coverage.

observed only up to a coverage of 4.5×10^{14} CO molecules cm⁻², at which it reaches saturation.²² Also for CO chemisorbed on Ir(110) from the gas phase the integrated peak intensity increases linearly with CO coverage only up to 0.4 monolayer, after which it *decreases* slightly with increasing coverage.²³ Since the CO coverages reached in this work are only a fraction of a monolayer, it can be safely assumed that the CO band intensity is proportional to the coverage.

In Figure 10 it can be seen that the frequency of CO stretching in 1 M H₃PO₄, pH 1, increases by 60 cm⁻¹ when the differential reflectance (and therefore the coverage) increases 6-fold, from 0.1% (point b) to 0.6% (point h). This is in agreement with the reported increase in the frequency of CO chemisorbed on Ir(111) in 0.1 M HClO₄ by up to ca. 100 cm⁻¹ with increasing coverage.¹²

It can also be seen in Figure 10 that the pH would seem to influence the frequency of CO stretching, since at about the same differential reflectance, 0.1%, the CO frequency is about 30 cm⁻¹ higher in a pH 9.2 borax buffer (point a) than in 1 M H₃PO₄, pH 1 (point b). However, probably it is the nature of the anion rather than the pH that is the origin of this change in CO frequency, since for example at the same pH value of 1 the CO frequency is about the same for different values of the differential reflectance, but in different acids, 0.35% in 0.1 M HClO₄ (point f) and 0.61% in 1 M H₃PO₄ (point h), which means that the frequency increase produced by the higher CO coverage is compensated by the lower frequency (at the same coverage) in H₃PO₄ as compared with HClO₄. This influence of the anion on the CO frequency is not new, since it has been reported that at saturation coverage the frequency of CO stretching of CO chemisorbed on Pt was 9–15 cm⁻¹ higher in 1 M HClO₄ than in 1 M H₂SO₄. (The difference increased linearly with electrode potential because the Stark shift was higher in the former than in the latter acid.²⁴)



Figure 11. Dependence on the electrode potential of the frequency of the CO stretching vibration at four different pH values, shown against each curve. pH 0: 1 M H₂SO₄, $\Delta R/R = 0.54\%$, Stark shift 35 cm⁻¹ V⁻¹. pH 9.2: 0.1 M borax, $\Delta R/R = 0.08\%$, Stark shift 43 cm⁻¹ V⁻¹. pH 14: 1 M NaOH, $\Delta R/R = 0.26\%$, Stark shift 44 cm⁻¹ V⁻¹. pH 1: 1 M H₃PO₄, $\Delta R/R = 0.10\%$, Stark shift 40 cm⁻¹ V⁻¹.

Stark Shift. The value of the Stark shift of the frequency of the CO stretching of chemisorbed CO varied with pH and/ or coverage, as can be seen in Figure 11. It was 43.6 ± 2.3 and 44.6 ± 4.5 cm⁻¹ V⁻¹ at pH 9.2 and 14, with a differential reflectance of 0.08% and 0.26%, respectively. The Stark shift was 38.96 ± 0.03 cm⁻¹ V⁻¹ at pH 0 and for a differential reflectance of 0.54% and 40.0 ± 0.1 cm⁻¹ V⁻¹ in 1 M H₃PO₄ and for a differential reflectance of only 0.10%. Although these Stark shifts are lower than at alkaline pH, the observed difference is only two and one standard deviations lower than the Stark shift at pH 9.2 and 14, respectively. Assuming that this decrease of the Stark shift is true, it could be due either to a decrease of the Stark shift with increasing coverage¹² or to the dependence of the Stark shift on the nature of the anion.²⁴

Conclusions

Formic acid and CO_2 are formed in the electrooxidation of methanol on iridium in acid medium and formate ion and carbonate or bicarbonate ion in basic medium. Neither formic acid nor formate ion was detected at pH 7 or 9.2, at which only bicarbonate and CO_2 were produced.

On Ir both the electrooxidation of methanol to formic/formate and the complete electrooxidation of chemisorbed CO at pH 14 occur at 0.4-0.6 V, which is also the potential of the main surface process of Ir oxidation. On the contrary, in both perchloric and phosphoric acid at pH 1 both the electrooxidation of methanol and of chemisorbed CO occur at a more positive potential, 0.9-1.0 V, which is also the potential of the main surface process in acidic media (super-Nernstian dependence on pH). This coincidence of potentials lends support to the hypothesis that oxidation of the Ir surface is necessary for the electrooxidation of both chemisorbed CO and methanol to formic/formate. However, in sulfuric acid, at both pH 0 and 2, the electrooxidation of methanol to formic acid first occurred at 0.7 V, a potential lower than the main peak of Ir oxidation, perhaps because at this pH the main peak is preceded by a small peak at 0.6 V.

The frequency of CO stretching of CO chemisorbed on Ir increased by up to 60 cm⁻¹ with increasing coverage and at the same coverage was higher in HClO₄ than in H₃PO₄ solutions. The Stark tuning rate of CO chemisorbed on Ir varied from 39 to 45 cm⁻¹ V⁻¹ in the pH range 1–14, for a CO differential reflectance range of 0.08–0.54% and for different acids.

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