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EMIRS studies of formic acid electrooxidation on Pd, Au and Pd + Au alloys

Part 1. Investigation of the adsorbates derived from HCOOH and NaCOOH chemisorption at Pd in acid and alkaline solutions

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Abstract

An electromodulated IR reflectance spectroscopy (EMIRS) study of the adsorbed species resulting from HCOOH and NaCOOH chemisorption at a smooth Pd electrode is presented. In acid solution, large amounts of multibonded CO species are detected, in contrast with the absence of any type of CO adsorbate in alkaline solutions. For the latter, the appearance of adsorbed formate species can be concluded from the increase in the intensity of two bands at 1060 and 2960 cm^{-1} . These results suggest that the adsorbate is bound to Pd via two O atoms. In acid solution, however, the contribution of a formate species bound to the metal through a single O atom is discussed as the result of competitive adsorption with the multibonded CO species.

INTRODUCTION

Pd has been noted as a highly active catalyst for HCOOH electro-oxidation in acidic [1,2], neutral [3,4] and alkaline [5,6] solutions. A mechanism involving two parallel paths has been postulated, involving both a catalytic step, which produces CO_2 and H_2 , and an electro-adsorption step, which leads to different surface species, some of which are not too strongly bonded to the surface.

However, the nature of these adsorbed species is not yet well established, despite references to the numerous in situ reflectance spectroscopic investigations of CO [7–10], formaldehyde [11,12], methanol [10] and formate [12] adsorption.

In contrast, alloys of group VIII and group IB metals have attracted much interest in electrocatalysis. The Pd + Au alloys, for instance, which form a series of continuous solid solutions over the entire composition range, have been shown to present enhanced electrocatalytic activity (the so-called synergetic effect) compared with the pure component metals [4,13]. Similarly, substantial synergetic effects for the electro-oxidation of formic acid were obtained with Pd electrodes modified by foreign metal adatoms such as Au, Ag, Cu, Bi, Cd or Tl [14–16].

This paper is the first of a series which attempts to correlate the synergetic effect with changes in the nature of adsorbed intermediates, arising from the adsorption of formic acid and formate, that occur when the surface composition of the alloy is varied. Following the pioneering work by Nishimura et al. [12], this paper presents an electromodulated IR reflectance spectroscopy (EMIRS) study of the adsorbates produced during the electro-oxidation of formic acid and sodium formate at pure Pd in acid and alkaline solutions respectively. The influence of the mean modulation potential, the bulk concentration of electroreactive species, the adsorption time and pH on the adsorbed species is discussed as a first approach to understanding the mechanism of the electrocatalytic process. The next part of the series will be devoted to the study of adsorbates formed on Au + Pd alloys under similar experimental conditions.

EXPERIMENTAL

The experimental set-up and the corresponding procedure are essentially the same as described previously [17] and throughout the literature [18–20].

The IR spectrometer is an EMIRS III (Hi-Tek, UK) with a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector. A further improvement of the signal-to-noise ratio is achieved by averaging successive spectral scans, but in order to follow the adsorption process EMIR spectra recorded at the first scan are also given.

Studies were carried out in 0.5 M HClO₄ and 0.1 M NaOH solutions prepared using Millipore Milli-Q water and Merck Suprapure reagents. 10⁻¹ M and 10⁻³ M HCOOH or 10⁻² M NaCOOH solutions were prepared from Merck p.a. reagents.

The working electrode was a high purity (99.995%) palladium disc (Johnson Matthey, Specpure) of apparent area, 0.385 cm² carefully polished to a mirror finish with fine alumina down to 0.05 μm, and the counter-electrode was a gold wire. The reference was a Hg/HgSO₄/K₂SO_{4(sat)} electrode (MSE), to which the potentials are referred in the text. The purity of the entire system was checked (before adding HCOOH or NaCOOH) by recording the voltammogram of Pd in the supporting electrolyte alone in the spectro-electrochemical cell. All solutions were previously deaerated by bubbling nitrogen through.

The IR spectra of adsorbed species on Pd were examined in the spectral region between 900 and 3100 cm^{-1} as a function of electrode potential and concentration of electroreactive species. p-polarized light was used in all experiments. To avoid any artefact band, the spectral range was divided into sequences, depending on gratings and appropriate filters, following a procedure described in ref. 21. The amplitude δE of the modulation potential, was 0.4 V and the modulation frequency was 13.5 Hz . In most experiments, the mean pulse potential \bar{E} was varied between -0.4 and 0.2 V MSE .

RESULTS

A typical voltammogram of a Pd electrode in 0.5 M HClO_4 is shown in Fig. 1(a). The oxidation currents observed at potentials higher than 0.1 V MSE are due to the electro-oxidation of palladium, yielding surface palladium oxides as well as a

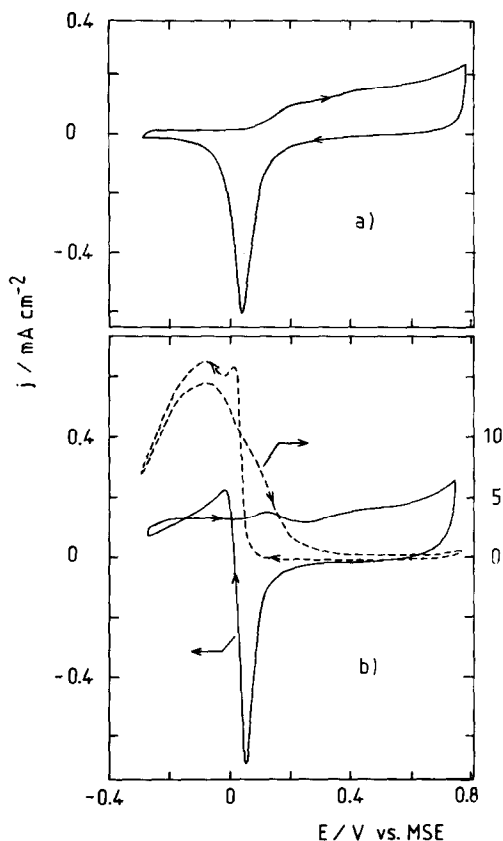


Fig. 1. Voltammograms of a Pd electrode in 0.5 M HClO_4 recorded using the spectroelectrochemical cell ($\nu = 70\text{ mV/s}$): (a) without HCOOH ; (b) with 10^{-3} M HCOOH and 10^{-1} M HCOOH (— —).

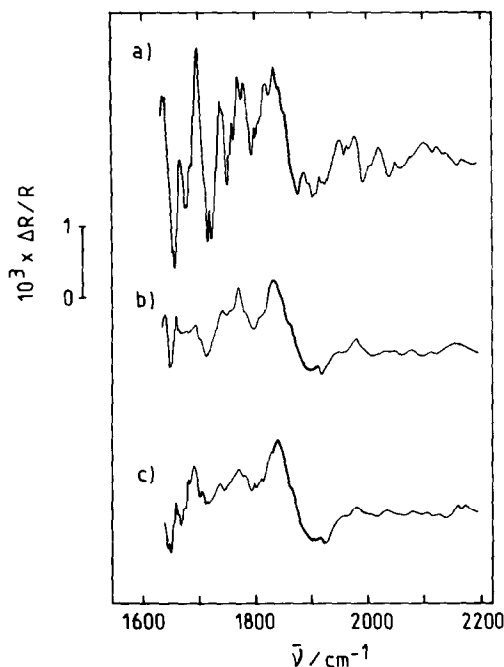


Fig. 2. EMIR spectra of the adsorbed species on a Pd electrode in 0.5 M $\text{HClO}_4 + 10^{-1}$ M HCOOH ($\delta E = 0.4$ V): (a) one scan, $\bar{E} = -0.4$ V/MSE; (b) five scans, $\bar{E} = -0.4$ V/MSE; (c) 10 scans, $\bar{E} = -0.2$ V/MSE.

small amount of soluble palladium species [22]. The reduction of all these species occurs from ca. 0.2 V downwards during the negative potential sweep. The full and broken curves in Fig. 1(b) show the j - E curves of the Pd electrode in the presence of 10^{-3} M and 10^{-1} M HCOOH respectively. In the latter case, it is particularly clear that the oxidation of HCOOH is inhibited at the threshold potential of oxide formation. During the reverse sweep, HCOOH oxidation starts again only after complete oxide reduction, in agreement with the previous work of Capon and Parsons [1,23]. We obtained very similar j - E curves with 10^{-3} M and 10^{-1} M NaCOOH in 0.1 M NaOH , apart from the expected potential shifts due to pH.

The EMIR spectra obtained in the range 1600 – 2250 cm^{-1} for the species formed at a Pd electrode in 0.5 M $\text{HClO}_4 + 10^{-1}$ M HCOOH solutions show numerous absorption bands in the first scan, and the resolution of some of them improves with averaging time (Fig. 2). However, as already shown in previous work [21], the attenuation of bands in that spectral region is due not only to signal averaging, but also results from changes in the superficial distribution of adsorbed species. The complex band between 1620 and 1730 cm^{-1} is partly ascribed to the bending mode $\delta(\text{HOH})$ of adsorbed water [24], at ca. 1625 cm^{-1} , followed by the peak associated with the stretching mode of the carbonyl groups of an acid at ca. 1700 cm^{-1} [17,25–27]. A rather strong bipolar band, with extrema at 1810 cm^{-1}

and 1900 cm^{-1} , is clearly visible in the first scan and remains unaltered in intensity after 10 scans (Fig. 2(b)), whereas the intensities of the bands between 1620 and 1730 cm^{-1} decrease considerably. The bipolar band can be assigned to CO species multibonded to the Pd surface [9], which were found at low coverage of CO adsorbed on Pd in HClO_4 solution [8] and predicted by Anderson and Awad [28] on the basis of molecular orbital calculations. No linear CO species (which would absorb at ca. 2070 [7,11]) were found under the experimental conditions employed, even when the mean potential of the pulse was increased (Fig. 2(c)). Only a small, if any, contribution of bridge-bonded CO can be detected at around 1925 cm^{-1} , see e.g. in Fig. 4(b), in agreement with Nishimura et al. [12]. Such a low formation of either linear or bridge CO species is consistent with the evidence that in contrast with other noble metals, almost no strongly bound intermediates are formed during HCOOH electro-oxidation on Pd, as formerly demonstrated [1,29].

The effect of the modulation potential is shown in Fig. 3, where it is clearly seen that, for sufficiently positive potential windows, complete electro-oxidation of adsorbed CO to CO_2 occurs. The wavenumber shift formerly observed in the bands of linear and bridge-bonded CO [7] at increasing potential pulse centres,

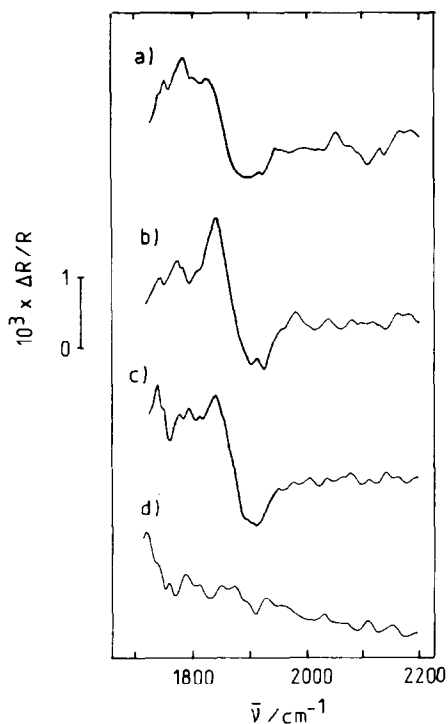


Fig. 3. EMIR spectra of the adsorbed species resulting from the chemisorption of 10^{-1} M HCOOH in 0.5 M HClO_4 at a Pd electrode after 10 scans ($\delta E = 0.4\text{ V}$): (a) $\bar{E} = -0.4\text{ V/MSE}$; (b) $\bar{E} = -0.3\text{ V/MSE}$; (c) $\bar{E} = -0.2\text{ V/MSE}$; (d) $\bar{E} = +0.2\text{ V/MSE}$.

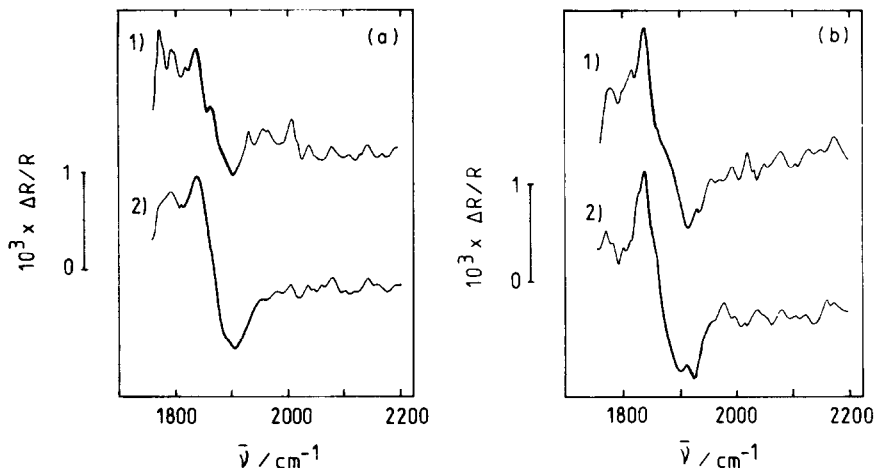


Fig. 4. EMIR spectra of the adsorbed species resulting from the chemisorption of HCOOH in 0.5 M HClO₄ at a Pd electrode after 10 scans ($\delta E = 0.4$ V) with (a) $\bar{E} = -0.2$ V/MSE and (b) $\bar{E} = -0.3$ V/MSE: curves 1, 10^{-3} M HCOOH; curves 2, 10^{-1} M HCOOH.

cannot be distinguished clearly in the case of multibonded CO species (Fig. 3). The decreasing π character of the C—O bond in going from linear to bridge-bonded and multibonded CO could certainly explain this behaviour.

The effect of the bulk concentration of HCOOH is shown in Figs. 4(a) and 4(b), for -0.2 V and -0.3 V respectively. Slightly less CO is formed with 10^{-3} M HCOOH (curves 1) than with 10^{-1} M HCOOH (curves 2). As the difference is more appreciable at -0.2 V than at -0.3 V, it can be concluded that the range of potentials over which CO adsorbed species are stable is much shorter at low HCOOH bulk concentrations. However, the intensity of the CO bands was found to be almost the same for the two solutions at $\bar{E} = -0.3$ V MSE, which, taking into account the 400 mV amplitude of the pulses, indicates that the maximum CO coverage is attained within the range -0.5 to -0.1 V.

Under similar experimental conditions to those used in the acid medium (Fig. 5(a)), the spectral response of 0.1 M NaCOOH in 0.1 M NaOH shows the absence of any type of adsorbed CO and the attenuation of the bands in the 1620–1720 cm^{-1} region, with the exception of the band at 1640 cm^{-1} (Fig. 5(b)). The absence of adsorbed CO species in the electro-oxidation of formate in K_2CO_3 solutions, was also confirmed by Nishimura et al. [12] in IR spectroscopy studies.

Although very interesting structural information is to be expected in the 900–1400 cm^{-1} range, the relatively low reflectivity R of the surface, as well as the lower response of detectors, affect the δR measurements in such a way that it becomes more difficult to extract signals from the noise. Unfortunately, in the present state of our equipment, it was not possible to improve the quality of spectra as longer spectral accumulation times always resulted in destruction of signals as a consequence of superficial changes (see above). Figure 6(a) shows

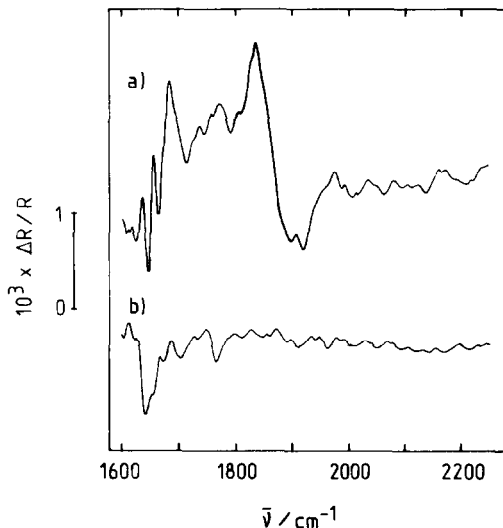


Fig. 5. EMIR spectra of the adsorbed species formed as follows: (a) 0.5 M $\text{HClO}_4 + 10^{-1}$ M HCOOH , $\delta E = 0.4$ V, $\bar{E} = -0.3$ V/MSE, 10 scans, (b) 0.1 M $\text{NaOH} + 10^{-1}$ M NaCOOH , $\delta E = 0.4$ V, $\bar{E} = -1$ V/MSE, 15 scans.

an EMIR spectrum obtained after averaging 10 scans for Pd in 0.5 M $\text{HClO}_4 + 10^{-1}$ M HCOOH . A complex band extends from 1000 to 1150 cm^{-1} , most probably as a result of two contributions. One, at ca. 1060 cm^{-1} , can be assigned to

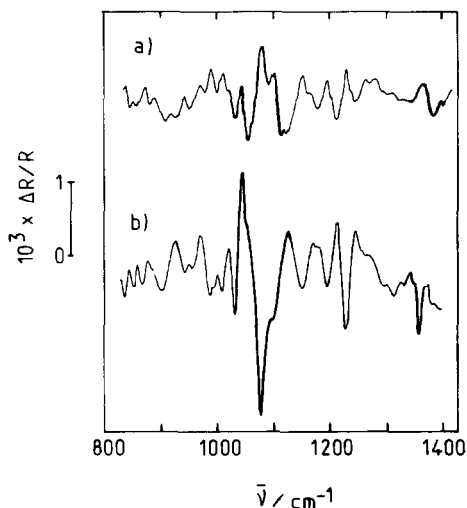


Fig. 6. EMIR spectra of the adsorbed species formed after 10 scans: (a) 0.5 M $\text{HClO}_4 + 10^{-1}$ M HCOOH , $\delta E = 0.4$ V, $\bar{E} = -0.4$ V/MSE; (b) 0.1 M $\text{NaOH} + 10^{-1}$ M NaCOOH , $\delta E = 0.4$ V, $\bar{E} = -1$ V/MSE.

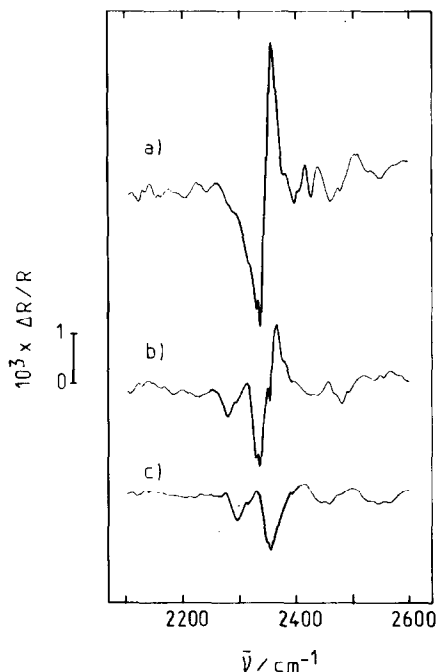


Fig. 7. EMIR spectra of the adsorbed species resulting from the chemisorption of 10^{-2} M NaCOOH in 0.1 M NaOH ($\delta E = 0.4$ V; $\bar{E} = -0.9$ V/MSE): (a) one scan; (b) five scans; (c) 10 scans.

the C—O stretch of an adsorbed formate species, while the second band or perturbation near 1100 cm^{-1} is certainly associated with perchlorate anions whose concentration is modulated near the surface [25,27]. This latter band is absent in NaOH (Fig. 6(b)), whereas the 1060 cm^{-1} band is very intense, as a consequence of the greater equilibrium concentration of formate ions at high pH values. This is also consistent with the fact that the peak at 1380 cm^{-1} , which can be assigned to the C—H bending mode of HCOO_{ads} species [30], is more clearly visible in alkaline solutions than at lower pH, where it is barely distinguishable from the noise.

In the $2200\text{--}2500\text{ cm}^{-1}$ wavenumber range, the EMIR spectra show a band near 2345 cm^{-1} due to the antisymmetric vibration of CO_2 (Fig. 7), even at potentials sufficiently negative for CO_2 not to be produced by electro-oxidation. The origin of this band has already been discussed [30], and its derivative shape can be taken as a proof that the corresponding species is adsorbed. Roughly, the complexity of the $\text{CO}_{2\text{ads}}$ band can be related to the profile of the true absorption band. Thus an EMIRS band could be modelled by subtracting two absorption bands, one of them being shifted by a few wavenumbers ($8\text{--}20\text{ cm}^{-1}$). The resulting band, which exhibits three features (labelled 1–3 in Fig. 8), can be compared with an experimental band obtained for a Pt electrode immersed in a

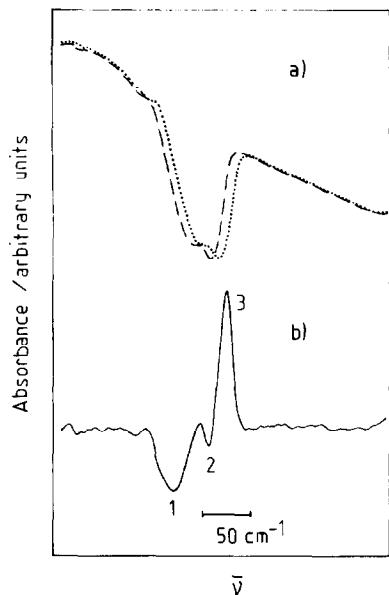


Fig. 8. Modelling of the CO₂ EMIRS band: (a) true absorption bands, one of which is intentionally shifted by 12 cm⁻¹; (b) model band resulting from the subtraction of the two bands above.

CO₂-saturated acidic solution (Fig. 9). It fits as well some of the spectra obtained in this work, particularly those of Fig. 7(b) and Fig. 10(a) (see below). However, it has to be emphasized that CO₂ is only weakly adsorbed and its reduction to CO_{ads} can easily take place, in agreement with our previous work [31].

The presence of CO₂ at these negative potentials, also recognized using on-line mass spectroscopy [32], could be understood in terms of a reaction mechanism involving two parallel paths, of which one is the catalytic decomposition of formic acid into CO₂ and H₂ [29,32], and the other is the electro-adsorption step yielding the various surface species. Thus molecular H₂ formed by the catalytic step was shown to be partially oxidized on a disc electrode and partially dissolved into the solution, as demonstrated by Gromyko et al. [33] using the ring-disc technique.

The pH dependence of the CO₂ band intensity can be observed by comparing the results shown in Figs. 7 and 10. In 0.1 M NaOH + 10⁻² M NaCOOH solutions, this band, which is clearly visible in the first scan, diminishes with the spectral accumulation time (Fig. 7), becoming single-sided with a companion band at ca. 2280 cm⁻¹, whose origin still remains unclear. Similarly, in 0.5 M HClO₄ + 0.1 M HCOOH solutions, the CO₂ band persists with time, although it changes from derivative to single shape after 10 scans (Fig. 10). Initially, the CO₂ signal is more intense in an alkaline medium than in an acid medium. Furthermore, it remains stable with time at potentials where no electro-oxidation takes place, which indicates that the catalytic decomposition of formate at higher pH values prevails over the electro-adsorption reaction. This conclusion is also consistent with the

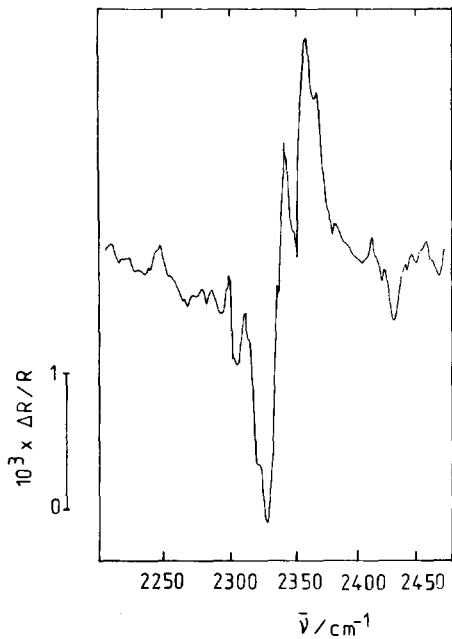


Fig. 9. EMIR spectra of CO_2 adsorbed on a Pt electrode immersed in a perchloric acid solution saturated with gaseous CO_2 . Usual conditions: $\delta E = 0.4 \text{ V}$; $\bar{E} = 0.2 \text{ V/RHE}$; $f = 13.6 \text{ Hz}$.

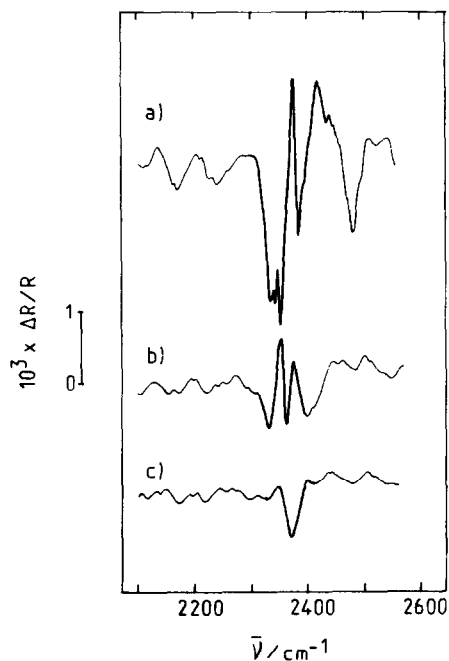


Fig. 10. EMIR spectra of the adsorbed species resulting from the chemisorption of 10^{-1} M HCOOH in 0.5 M HClO_4 ($\delta E = 0.4 \text{ V}$; $\bar{E} = -0.3 \text{ V/MSE}$): (a) one scan; (b) five scans; (c) 10 scans.

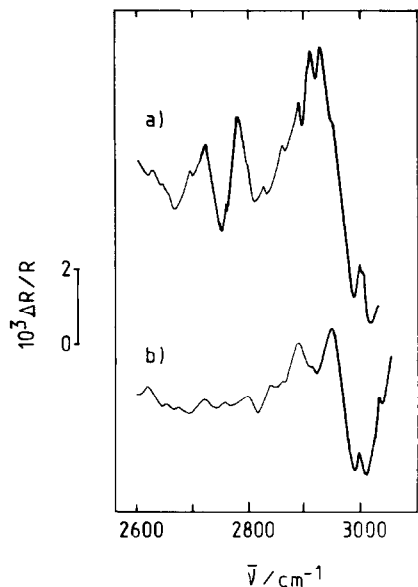


Fig. 11. EMIR spectra of the adsorbed species resulting from the chemisorption of 10^{-2} M NaCOOH in 0.1 M NaOH ($\delta E = 0.4$ V; $\bar{E} = -0.9$ V/MSE): (a) one scan; (b) 10 scans.

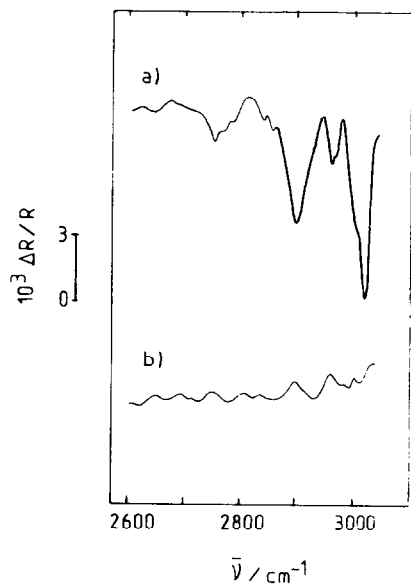


Fig. 12. EMIR spectra of the adsorbed species resulting from the chemisorption of 10^{-1} M HCOOH in 0.5 M HClO₄ ($\delta E = 0.4$ V; $\bar{E} = -0.3$ V/MSE): (a) one scan; (b) five scans.

absence of any CO_{ads} species formed in an alkaline medium, in contrast with an acid solution (Fig. 5).

At higher wavenumbers, i.e. above 2700 cm^{-1} , several signals probably due to C-H stretching modes are observed in 0.1 M NaOH (Fig. 11) and 0.5 M HClO_4 (Fig. 12). In the latter case, the first scan shows two clear and intense single-sided peaks at 2900 and 3000 cm^{-1} , while in the alkaline medium the strongest peak is double-sided with a band centred near 2950 cm^{-1} . Thus, in acid solutions, CO multibonded species predominate with time over formate species at one of the potential limits (probably the cathodic one), while the formate species remains the only fragment in alkaline solutions. It must also be emphasized that the fact that absorbances are changing with time, while the signal-to-noise ratio is not, fully supports the above interpretation.

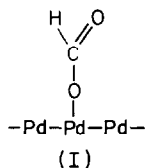
Furthermore, by comparing the spectra in the $800\text{--}1400\text{ cm}^{-1}$ range (Fig. 6) with those in the $2600\text{--}3000\text{ cm}^{-1}$ range (Figs. 11 and 12), we can conclude that there is a good correlation between the time and pH dependences of the bands at 1060 cm^{-1} and 2950 cm^{-1} , which are all attributed to IR active modes of adsorbed formate species.

CONCLUSIONS

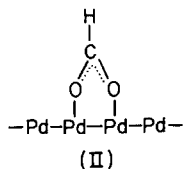
From the preceding results it emerges clearly that, depending on pH, potential and time, different intermediates are formed during the adsorption and electro-oxidation on Pd of either formic acid or sodium formate.

In acid solution, a rather strong band due to multibonded CO has been detected, which never appeared so intensely (nor in the linear or bridge-bonded form) in alkaline solution, a fact which is consistent with the experimental evidence that no strongly bound intermediates are formed during the electro-oxidation reaction in this medium.

The absence of any type of adsorbed CO in alkaline electrolytes can be correlated with the growth of the two bands at 1060 and 2950 cm^{-1} , indicating that a formate species is the main electroadsorption product of NaCOOH in alkaline solutions. This species is probably bound to the Pd surface through the two O atoms, i.e. in a configuration which gives rise to a large dipolar moment of the C-H bond perpendicular to the metal and consequently to an intense IR absorption band. In contrast, the formate species detected in HClO_4 solutions might be adsorbed through a single O atom because of the main occupancy of the adsorption sites by multibonded CO. Thus the structure of such an adsorbed formate, described as



would produce a dipolar moment for the C-H bond, whose projection on the normal to the surface would be lower than for the species in alkaline solution, which is represented as



This description is in agreement with the fact that the intensity of the band at ca. 2950 cm^{-1} decreased with the spectral accumulation time in an acid medium. Furthermore, a species such as I, would also have an antisymmetric stretching mode absorbing at ca. 1640 cm^{-1} , which almost coincides with the bending mode of adsorbed molecular water. Both these modes are responsible for the complex bands observed in this spectral region, as recently discussed [21].

Finally, it should be mentioned that adsorbed CO_2 can still be detected even at negative potentials where the electro-oxidation reaction is unlikely to occur. In alkaline solutions, the CO_2 band intensity remains almost unaltered with averaging, but in 0.5 M HClO_4 there is an attenuation of the band. This fact demonstrates that (i) the catalytic decomposition of the electro-active species is favoured at higher pH levels, (ii) and the poisoning of the Pd surface by CO species, even if low compared with other catalytic metals, is at a maximum in acid solutions and tends to disappear gradually on increasing the solution pH.

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