

# The Potential Dependence of Intermediates in Methanol Oxidation Observed in the Steady State by FTIR Spectroscopy

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## ABSTRACT

The structure of electrochemical intermediates of methanol oxidation on platinum in aqueous sulfuric acid has been investigated under steady state conditions using polarization modulation Fourier transform infrared reflection absorption spectroscopy. Terminally bonded CO and bridge-bonded CO are observed in the cathodic to anodic sequence. However, only bridge-bonded CO is observed in the anodic to cathodic sequence. The conventionally assumed C—O—H group was not observed. The spectroscopic results are compared with similar information obtained by means of radiotracer and potentiodynamic techniques. A new mechanism is proposed which is intended to apply to the steady-state situation and may differ from that pertaining to potential sweep data.

The electrochemical oxidation of methanol is a well-known reaction which has been previously studied by classical electrochemical methods (1, 2). Electrochemical oxidation of methanol involves chemisorption. The chemisorption is associated with dehydrogenation on platinum surfaces (3). Subsequent reactions of the dehydrogenated species with water or hydroxide result in overall oxidation of methanol to carbon dioxide.

An adsorbed electrochemical intermediate has been proposed: C—O—H bonded to three platinum atoms (4). Adsorbed intermediates on electrodes can now be the subject of spectroscopic investigation (5, 6) and the results are discussed in this paper. The first *in situ* spectroscopic examination of a radical in this reaction was investigated by Beden *et al.* (7, 8) and later by Kunimatsu (9). They studied the adsorption of methanol on platinum using electrochemically modulated infrared spectroscopy (EMIRS), and found that the adsorbed species were linear and bridged CO, the former being the major surface species. The examination was carried out by means of a potential modulation technique, in which the electrode potential was allowed to oscillate between two different values at a rate of 8 Hz. Since multistep reactions involving organics take several minutes to attain steady state (10-12), the results of 8 Hz modulation studies may not allow a determination of the steady-state radical concentration as a function of potential. On the other hand, this can be attained by making observations at a series of constant potentials, using the polarization modulation approach<sup>1</sup> (14). Kunimatsu and Kita have utilized a variation of this approach in recent work (15, 16) which confirms that both linear and bridged CO are the adsorbed species in methanol oxidation on platinum.

## Experimental

**Electrode.**—An ohmic contact was made to a polycrystalline platinum foil of 1.0 cm diam which was then fixed on a polyethylene rod. The tip of the rod was melted and cooled to provide a leak proof seal. The electrode was polished with 0.05  $\mu\text{m}$  alumina paste, followed by rinsing with triply distilled water. The platinum electrode was immersed in concentrated nitric acid for 5 s to dissolve alumina, if any, left on the electrode and again washed with triply distilled water. The electrode was cycled (10 mV/s) between 0.05 to 1.4V NHE for 5 min to 0.5M aqueous sulfuric acid in a nitrogen atmosphere before addition of solute to the solution.

**Electrolyte.**—Triply distilled and pyrolyzed water was used to prepare the aqueous solutions. Sulfuric acid (Fisher Scientific) was used as received.

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<sup>1</sup> It is possible to use this technique for surface species if a fiducial measurement of a potential of zero adsorption is made (13). Correspondingly, the subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) is also a technique which may be used for examination of the steady-state condition at electrode surfaces.

**Cell.**—A Pyrex cell with an IR transparent ZnSe window was used for the FTIR studies. The prism window was mounted on a Teflon holder which was removed, polished, and cleaned periodically. A platinum wire coil was used as the counterelectrode. A saturated calomel electrode was used as reference. The cell compartment was flushed with nitrogen continuously during the experiments. The thickness of the electrolyte between the window and the electrode is 1  $\mu\text{m}$ .<sup>2</sup>

**Measurements.**—A Digilab FTS-20E spectrometer with a Nova 4 computer was used to record the IR spectra of adsorbed species. The optical arrangements and the Michelson interferometer are discussed elsewhere (18). A ZnSe photoelastic modulator was used to polarize the IR beam. Retardation of the photoelastic modulator was chosen so that the light is polarized at the expected adsorption maximum. The signal from the detector was fed into a lock-in amplifier through a high band-pass filter (50 kHz) with a reference signal from the photoelastic modulator at 74 kHz, where the difference between perpendicularly polarized light does not interact with the adsorbed species, the difference in light intensities of these two polarizations is due to adsorption of the surface adsorbed species. The intensities of the perpendicularly polarized and parallel polarized light are measured by bypassing the lock-in amplifier through a low bandpass filter (2 kHz). The difference in light intensity is normalized by dividing this by the total light intensity. The resultant contains the spectrum of the adsorbed species.

At a fixed bias potential, the difference light intensity  $I_p - I_s$  was recorded for 20 counts where  $I_p$  is the intensity of parallel polarized light and  $I_s$  is the intensity of perpendicularly polarized light. Then  $i_p + I_s$  was recorded for 20 counts. The difference intensity was recorded again. This alternating procedure was repeated until 500 counts were recorded for each. Then the potential of the working electrode was changed. The next set of data collection was started after a 5 min waiting period for the electrode to attain equilibrium conditions.

All experiments concerning potential dependence or concentration dependence for a given system were carried out on the same day without disturbing the cell arrangement.

## Results

**The IR difference spectrum.**—The spectra reported in this paper are obtained by subtracting the (polarization-modulation) solute spectrum recorded under identical conditions at a potential where adsorption is negligible. 0.0 V NHE was used as the reference potential, for there the concentration of the chemisorbed species is negligible (19).

<sup>2</sup> The thickness was determined by benzene absorption in the reflective layer, the effect of which has been treated by Chandrasekaran and Bockris (17).

**IR spectrum of the intermediate radicals.**—The differential IR spectrum of platinum in aqueous sulfuric acid containing 0.1M methanol is shown in Fig. 1 for the potential of 0.1V NHE. A broad absorbance maximum at  $2150\text{ cm}^{-1}$  (A) is present. It is very unlikely that this assignment of a peak here is due to background subtraction due to the regularity of the points which constitute the peak. The broadness is perhaps due to the fact that a 0.5M solution of  $\text{H}_2\text{SO}_4$  was used which could give rise to a substantial sulfate adsorption. The adsorption of sulfate ions would result in a shift in the bond frequency of CO due to interactions between these adsorbed species. Also it is to be noted that this type of CO does desorb as the potential becomes more anodic which correlates well to the increased adsorption of sulfate ions at increased anodic potentials. There are other absorbance maxima at  $1620\text{ cm}^{-1}$  (B),  $1185\text{ cm}^{-1}$  (C), and  $1050\text{ cm}^{-1}$  (D). (The peak at  $1520\text{ cm}^{-1}$  does not vary with potential and therefore is not further discussed.)

**The dependence of the intermediate radical concentrations on electrode potential.**—*Cathodic to anodic sequence.*—In this set of experiments the initial potential of the electrode was 0.0 V NHE and the electrode potential was shifted in steps. The absorbance maximum at  $2150\text{ cm}^{-1}$  (A) was observed at potentials less anodic than 0.4V NHE (Fig. 1, which refers to a potential of +0.1 on the NHE). The rather broad nature of the peak is presumed due to the fact that the material is adsorbed and in contact with solvent molecules which act to distort the peak. At potentials more positive than 0.4V NHE, peak A was no longer seen, but was replaced by a peak at  $1790\text{ cm}^{-1}$  (E) (Fig. 2, which refers to 0.54V NHE). The relative areas under the peaks A and E as a function of electrode potential are shown in Fig. 3. The data for E was calibrated using absolute coulombs from potentiodynamic and radiotracer results obtained in this laboratory (20). The calibration entailed setting the maximum coverage for peak E as determined by FTIR equal to the maximum coverage as determined by the potentiodynamic and radiotracer methods. The remainder of the points constituting this curve were normalized with respect to this known adsorption maximum. The calibration of peak A is based on the ratio found to exist in the FTIR spectra between peaks E and A for the maximum coverage conditions, 0.1V NHE for peak A and 0.7V NHE for peak E. An assumption made here is that the reaction of the radical resulting in peak A per unit area of occupancy of the surface is the same as that which results in peak E. It is seen that, qualitatively, the concentration of

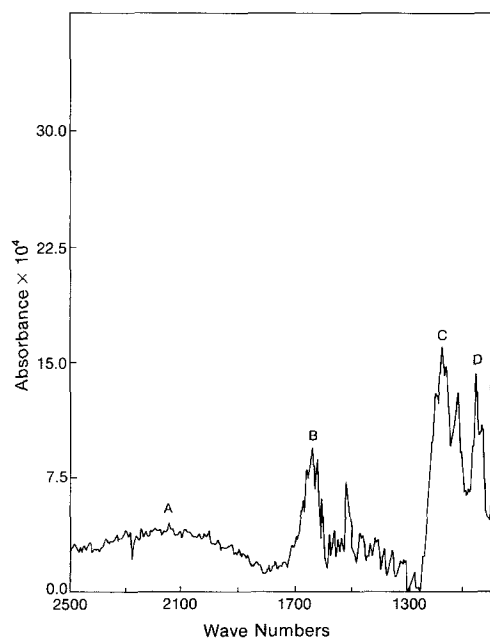


Fig. 1. Differential IR spectrum of platinum-aqueous sulfuric acid interface containing 0.1M methanol at 0.1V NHE in the sequence from 0.0 to 0.8V NHE.

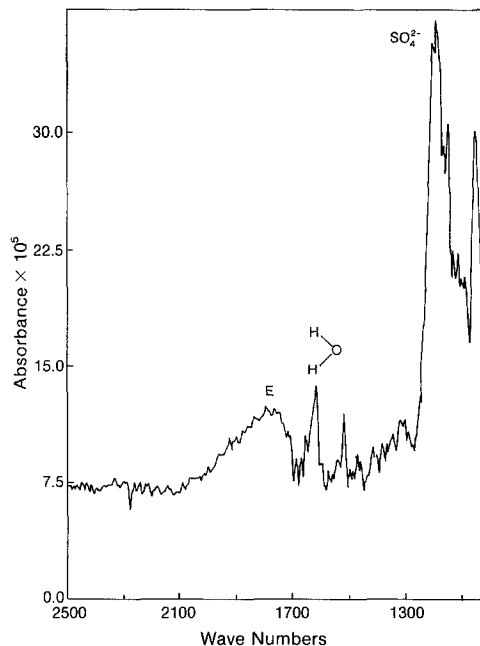


Fig. 2. Differential IR spectrum of platinum-aqueous sulfuric acid interface containing 0.1M methanol at 0.54V NHE in the sequence from 0.0 to 0.8V NHE.

species A increases in intensity from 0.0 V NHE, passes through a maximum at 0.1V, and decreases to 0 at potentials positive to 0.4V NHE. The intensity of peak E is more quantitative, having been related directly to other techniques to determine the coverage. The intensity of peak E commences to increase from 0.2V, passes through a maximum at about 0.7V and decreases sharply to zero at potentials positive to 0.8V.

The absorbance of peak B (Fig. 4) decreases with increase of potential. The absorbance intensities of peaks C and D increase with increase of potential.

*Anodic to cathodic sequence.*—The electrode was initially potentiostated at 0.8V and the potential was again shifted in a series of steps. The spectrum at 0.54V is shown in Fig. 5. The absorption has a maximum at  $1790\text{ cm}^{-1}$  and represent peak E. It is seen that a markedly different potential dependence of this peak (Fig. 6) is observed in this sequence, in comparison with that seen above. The absorbance intensity of the peak E increases with decreasing potential and becomes constant at potentials less positive than 0.4V.

The absorbance maxima at 1620, 1180, and  $1050\text{ cm}^{-1}$  were also observed in this set of experiments and the potential dependencies of absorbance intensities of these

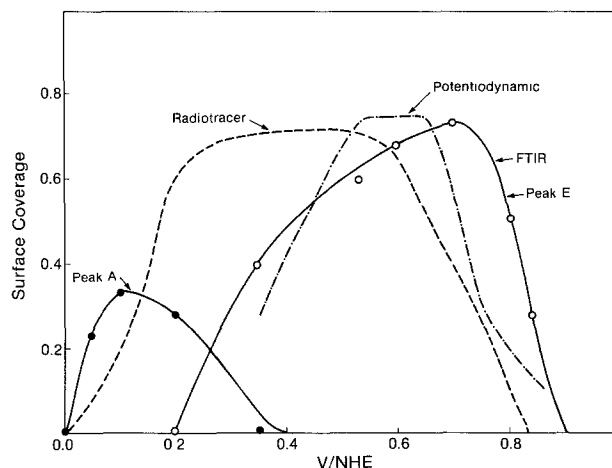


Fig. 3. Relative areas of peaks A and E as a function of electrode potential.

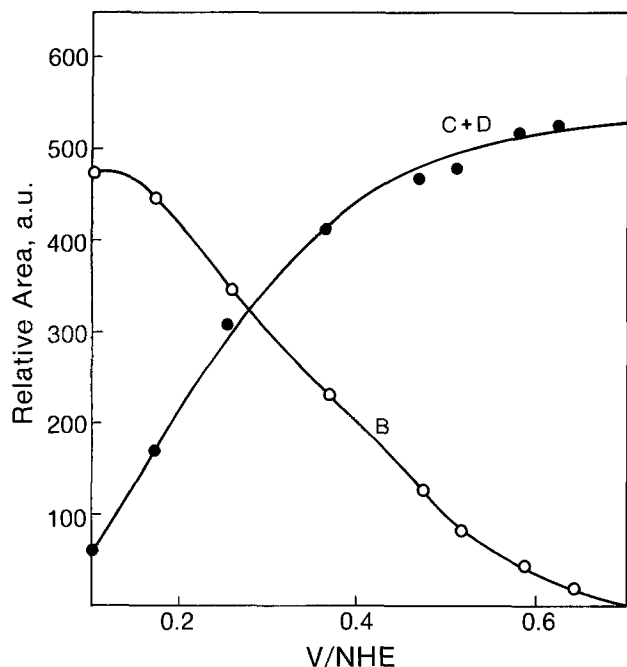


Fig. 4. Relative areas of peaks B, C, and D as a function of electrode potential.

peaks are very similar to those of the cathodic to anodic sequence.

*Adsorption of methanol on platinum in solutions containing HCl.*—Sulfate ions absorb in the region of  $1000\text{--}1300\text{ cm}^{-1}$ . C—O vibrations of methanol also may absorb in this region (21). In order to remove the interference of sulfate ion absorbance in this region, experiments were carried out in aqueous hydrochloric acid (0.1M) medium. The absorption spectrum at 0.54V is shown in Fig. 7. An absorbance maximum at  $1790\text{ cm}^{-1}$  is observed in the region of  $2500\text{--}1000\text{ cm}^{-1}$ . However, the peaks C and D are no longer present.

*Adsorption of CO<sub>2</sub> on platinum in aqueous sulfuric acid.*—The absorption spectrum of platinum in contact with aqueous sulfuric acid containing saturated carbon dioxide (and in the absence of methanol) was also studied

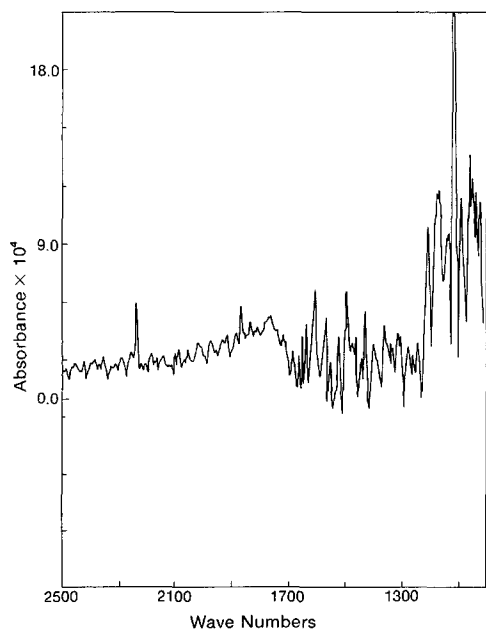


Fig. 5. Differential IR spectrum of platinum-aqueous sulfuric acid interface containing 0.1M methanol at 0.54V NHE in the sequence from 0.8 to 0.0 V NHE.

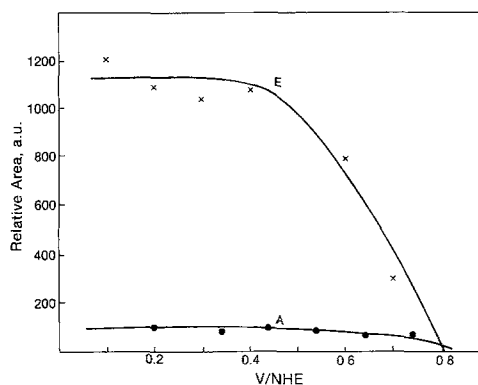


Fig. 6. Potential dependence of absorbance intensity as a function of electrode potential in the sequence from 0.8 to 0.0 V NHE.

and is shown in Fig. 8 for the potential of 0.5V NHE. A sharp absorption maximum at  $2370\text{ cm}^{-1}$  is seen. The area under the peak as a function of electrode potential is shown in Fig. 6. The surface concentration remains constant up to about 0.5V NHE and decreases with increased potential.

### Discussion

*Surface character of the species.*—The IR spectra reported in this paper were recorded using the Fourier transform polarization modulation approach. In this method, it is usually assumed (22) that the perpendicularly polarized light interacts with bulk solution species and not with the surface adsorbed species whereas parallel polarized light interacts with the bulk solution species as well as with the surface adsorbed species. Thus, when perpendicularly polarized light is used as the reference beam and parallel polarized light as analyzing, the spectra recorded are often taken to correspond to the surface species only. The concept of this method comes from a paper by Greenler (23, 24) in which the difference between the electric field vectors of perpendicular and parallel polarized light in the interfacial region are compared. This on-off concept has been assumed to be valid for adsorbed thin films (22).

The present authors have examined the validity of this approach for the solid-liquid interface (17). Absorbance of the surface film was calculated from complex refractive indexes, using Fresnel coefficients for adsorption of carbon dioxide on platinum. A three layer model (solution, film, and solid) was used in these calculations. They show that

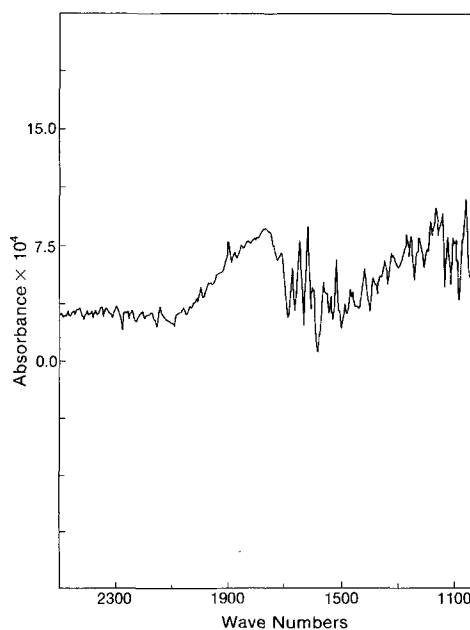


Fig. 7. Absorption spectrum of platinum aqueous hydrochloric acid interface containing 0.1M methanol at 0.54V NHE.

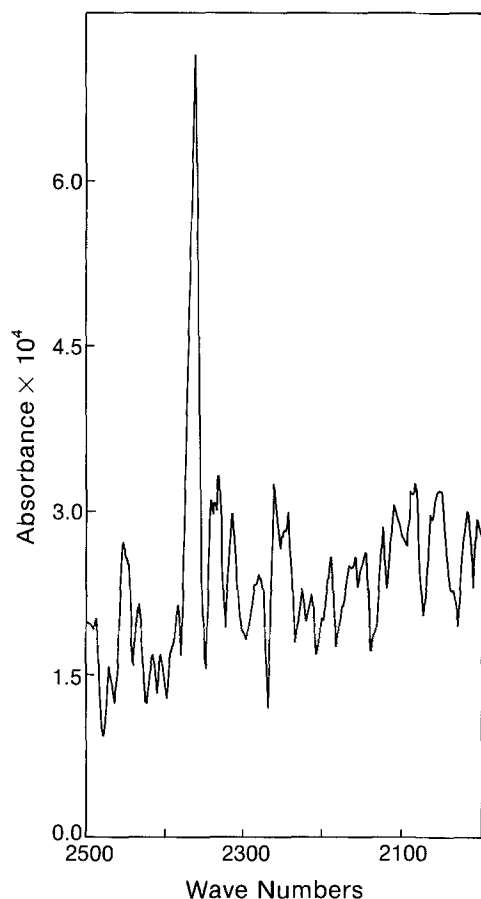


Fig. 8. Absorption spectrum of adsorbed carbon dioxide on platinum at 0.50V NHE.

the contribution of the solute in the solution near the surface of the electrode is negligible only when the surface coverage is more than 0.2. For small coverages, and for all coverages as a precaution, the solution contribution to the absorption spectrum was removed by subtracting the spectrum of the solution recorded under identical conditions at a potential where adsorption is negligible (thus removing contributions from the solute which are virtually potential independent).

Hence, the final equation used in determining adsorption is given by the following equation where  $p$  and  $s$  indicate the parallel and perpendicular components of the intensity, respectively

$$A = -2 \left( \frac{I_p - I_s}{I_p + I_s} \right)_V + 2 \left( \frac{I_p - I_s}{I_p + I_s} \right)_{Ref} \quad [1]$$

Under this situation, therefore (and insofar as the reference potential has been chosen correctly), no solution information at all is seen in the resultant spectra.

There are other qualitative evidences which support this. Spectral intensity of the adsorbed species varies with potential, while the solution concentration remains the same. The frequency of the absorbance maximum of the adsorbed species is often shifted to lower or higher frequencies compared to that of the same in homogeneous solution (5). Small but systematic shifts in frequencies of peaks with potential are seen (9, 25).

**Adsorption of sulfate and water.**—The absorbance maximum C (Fig. 1) at  $1130 \text{ cm}^{-1}$  and D (Fig. 1) at  $1050 \text{ cm}^{-1}$  correspond (21) to  $\text{HSO}_4^-$ . It has been observed in this laboratory that  $\text{SO}_4^{2-}$  is adsorbed from dilute aqueous sulfuric acid and  $\text{HSO}_4^-$  is adsorbed from concentrated sulfuric acid solutions (26). The present results (Fig. 4) confirm this observation. The surface concentration of adsorbed sulfate increases as the potential is increased from 0.0–0.8V NHE, as expected.

The adsorption of water on platinum electrodes has been studied using FTIR spectroscopy (27). Sodium fluoride, which does not adsorb appreciably on the electrode surface (28), was used as the electrolyte in these experiments. In these experiments, absorbance intensity for O—H stretching vibrations was found to increase at the more positive potentials. In the absence of adsorption of other species, orientation of water from a lying to a standing position was proposed for the increase in absorbance intensity. In contrast to this, a decrease in absorbance intensity for the O—H bending frequencies of water was observed with increasing potential. The anomalous decrease in OH absorbance may be due to displacement of adsorbed  $\text{H}_2\text{O}$  molecules by sulfate ions with increasing potential (Fig. 4).

**Steady-state nature of the results.**—The traditional account of the electrochemical oxidation of methanol regards C—OH as an intermediate, and the observed CO, not as an intermediate, but as a poison. This account comes up against the difficulty that, in spectroscopic work, the CO is easily visible, but no intermediate radical of COH can be seen. The nature of the results of the present paper obtained from steady-state values under potentiostatic conditions differs from the results obtained in other work in recent years. Thus, according to the work of the Beden *et al.* (7, 8, 29, 30) and Kunimatsu *et al.* (9, 15, 16), the method used was that of the potential sweep utilizing a scan rate of  $8.5 \text{ V s}^{-1}$ .

Such methods could be perfectly correct if they deal with simple redox reactions which do not involve intermediate adsorbates, but when the method itself involves intermediate adsorbates, then a certain time must be allowed for the steady state to be attained.

It has been shown by Bockris *et al.* (31) that, for the oxidation of ethylene, a potential sweep method does not attain a steady state, and that parameters such as Tafel constants obtained from these measurements did not correspond to the values characteristic of the steady state, so that it is difficult to make mechanistic studies by this method. There are numerous other works which show slow adsorption and readjustment of intermediates on Pt (10–12, 32).

In the work reported here, the concentration of CO has been allowed to go to the steady state, and CO is regarded not as a poison but as part of the intermediate radical formation, an assumption which corresponds both with the mechanism proposed and with the Tafel slopes observed.

The IR spectra reported were recorded and averaged over a 20 min period. The current density observed was between  $10\text{--}50 \text{ nA cm}^{-2}$ , thereby consuming only a very small percentage ( $\approx 5\%$ ) of methanol in the volume of the thin layer between the electrode and the zinc selenide window. The thin layer was reformed before each measurement by pulling the electrode back from the window and repositioning it before collecting the next spectra. Chandrasekaran and Bockris (17) have performed extensive calculations to ascertain the validity of Greenler's principle (23, 24) for thin films on electrodes. They have calculated that by not subtracting the spectrum at the reference potential the solution concentration varies from 3 to 55%, corresponding to an electrode coverage of 0.5–0.05 where the solution concentration is taken as 0.05 mol/liter and that at complete coverage as 40 mol/liter.

The steady-state measurements used would be expected to give different results from those which are measured in potential sweep measurements on Kunimatsu *et al.* (15, 16). The potentiodynamic sweep technique used by others results in measurement and consequently the collection of data before the steady-state situation has been achieved. It is very likely that a proposed mechanism for a reaction based on data taken before the steady-state condition is achieved will be substantially different, even contradictory, to a mechanism which might be proposed for the same reaction based on data that are collected after the steady state is reached.

**Identification of the nature of the radicals on the surface.**—The IR spectrum of methanol in homogeneous solution (14) has a strong absorbance maximum at

1030  $\text{cm}^{-1}$  due to C—O stretching vibrations. C—H stretching vibrations are seen in the region of 2800–3000  $\text{cm}^{-1}$ . The spectrum of the adsorbed species on platinum in contact with solutions containing methanol does not show absorption maxima corresponding to any one of these groups.

On the other hand, in the dissociative adsorption of methanol on platinum from the gas phase (33), a single absorption maximum is observed at 2150  $\text{cm}^{-1}$  which is assigned to the terminally bonded linear carbonyl group, Pt—C=O. Carbon monoxide has an absorption maximum at 2170  $\text{cm}^{-1}$  in the gas phase (34). The absorbance maximum observed in the present experiment at 2150  $\text{cm}^{-1}$  is thereby identified as terminally bonded carbon monoxide on platinum.

The absorbance maximum around 1600  $\text{cm}^{-1}$  (B) is due to O—H bending vibrations of adsorbed water molecule (21). Absorbance maxima at 1180 and 1050  $\text{cm}^{-1}$  are due to antisymmetric and symmetric stretching vibrations of the S—O group in the bisulfate ion (35).

Carbonyl groups of ketones and carboxylates absorb in the region of 1700–1800  $\text{cm}^{-1}$  (21), and hence the absorbance maximum at 1790  $\text{cm}^{-1}$  (peak E) is assigned to the bridge-bonded carbonyl group, (Pt)<sub>2</sub>CO. Due to the interaction of adsorbed species, it is very likely that the frequency can be shifted for lower frequencies. In the case of the adsorption of sulfate ions, previously discussed, which increases with potential, as expected, could easily be seen to cause large shifts in frequency corresponding to as much as 100 wave numbers. The observed band at 1790  $\text{cm}^{-1}$  assigned to bridge-bonded CO has been reported elsewhere at 1850  $\text{cm}^{-1}$ . The difference between these values (70  $\text{cm}^{-1}$ ) is proposed to be a result of the adsorbed species, sulfate ions.

Asymmetric stretching vibrations of carbon dioxide in the gas phase (36) are observed at 2349  $\text{cm}^{-1}$  and therefore the peak at 2370  $\text{cm}^{-1}$  must represent this vibration in adsorbed CO<sub>2</sub>.

Two possible structures of initially adsorbed methanol on platinum (before steady state) are shown in Fig. 9. Adsorption of methanol from an aqueous solution through oxygen would not lead to the dehydrogenation of methanol to give CO. The initial adsorption of methanol seems likely to occur through the face of the tetrahedron (Fig. 9A). Attempts to detect chemisorbed hydrogen at cathodic potentials were not successful [but see Ref. (33)]. It is possible that the absorbance of platinum hydride (37) at 2050  $\text{cm}^{-1}$  is buried under the 2150  $\text{cm}^{-1}$  peak for Pt—C=O. The dehydrated carbinol may be oxidized to give the terminally bonded carbonyl group. These successive dehydrogenations of methanol may be assumed to occur on a short time scale compared with the time of the experiment.

*The mechanism of methanol oxidation.*—The mechanism of electrochemical oxidation of methanol on platinum in aqueous sulfuric acid has been discussed by several authors (38, 39).

Bagotzky *et al.* (39) have recorded a Tafel slope of 55–60 mV/decade in the potential range of 0.42–0.55V and the Tafel slope changes to 110 mV/decade at higher anodic potentials indicating a change of reaction mechanism. These authors also have proposed C—OH as the primary intermediate which interacts in the rate-determining step with OH radicals discharged from water



Further oxidation of CO occurs through interaction with OH particles.

Sidheswaran and Lal (40) have correspondingly determined the Tafel slope in the narrow potential range of 0.45–0.55V NHE to be 72 mV/decade. They have proposed a mechanism similar to that of Bagotzky *et al.*

Leiva and Giordano (38) have studied the methanol adsorption and electrooxidation on platinum electrodes by means of potentiodynamic profiles. The current density maximum is shifted to more anodic potentials when the potential sweep rate is increased. In the absence of readorption of methanol, the number of electrons involved for the oxidation was calculated to be 1.2–1.5 electrons per site.

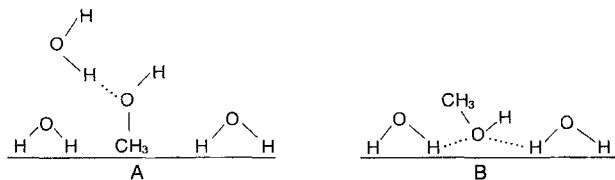


Fig. 9. Possible structures of adsorbed methanol on platinum aqueous sulfuric acid interface.

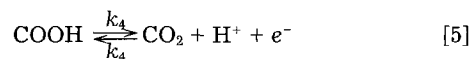
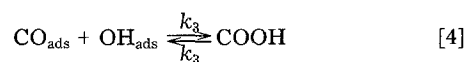
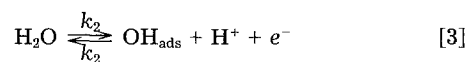
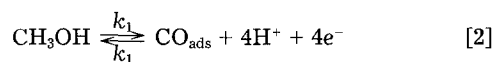
It was proposed that two different CO groups are adsorbed on the surface together, one requiring one electron per site and the other two electrons per site, which is consistent with CO as a possible intermediate in the oxidation of methanol.

Heitbaum *et al.* (41,42) have shown using differential electrochemical mass spectroscopy that one needs three electrons to oxidize the adsorbed species formed during the electrochemical oxidation of methanol to carbon dioxide. Since, electrochemical oxidation of CO involves only two electrons, these authors have proposed COH as the possible intermediate. This suggestion is difficult to bring into consistency with the observations reported here (Fig. 3) which can be interpreted only in terms of linearly bonded CO at low anodic potentials and bridge bonded CO at high anodic potentials.

Linearly bonded and bridge-bonded CO groups require two and one electron per site, respectively, for the formation of CO<sub>2</sub>. It is possible that both linearly bonded and bridge-bonded CO are present in mixtures (43, 44) which agrees with the spectroscopic results shown in Fig. 3 and the results of Leiva and Giordano (38). For the potential range 0.2–0.5V NHE, under the conditions that both linearly and bridge-bonded CO take part in the reaction, and utilizing the results of the measurement of the number of electrons involved, one can show that the expected amount for —C=O and C=O over the range in which both exist are between 20–50% and 80–50%, respectively.

Although the present surface spectroscopy clearly shows the presence of —C=O and —C=O as being present during methanol oxidation over the potential range 0–0.8 NHE, it might be argued that the radical O=C—H is present. This possibility may be eliminated, for: (i) C—H vibrations were not detected for the adsorbed species; (ii) aldehydic carbonyl groups absorb around 1700  $\text{cm}^{-1}$  whereas the absorbance maxima observed in the present experiment are 2150  $\text{cm}^{-1}$  and 1790  $\text{cm}^{-1}$ ; and (iii) three electrons per site are required for oxidation of this species to carbon dioxide whereas the experimentally observed value is 1.2–1.5.

Linearly bonded and bridge-bonded CO satisfy the experimental observations with regard to the number of electrons per site required for the oxidation of methanol [cf. particularly those of Leiva and Giordano (38)]. In view of the spectroscopic identification of chemisorbed species, the following mechanism and rate-determining step are proposed



The initial adsorption of methanol involves dehydrogenation followed by oxidation to give protons. The final product after the dehydrogenation process is adsorbed CO and four protons. The dehydrogenation and oxidation processes may occur in successive steps. At the equilibrium situation for H<sub>2</sub>O on platinum, pH 0, and 0.8V NHE, OH<sub>ads</sub> species will definitely be present on the electrode. The re-

action mechanism includes H<sub>2</sub>O discharge and the formation of intermediates (though at low concentrations) such as OH<sup>-</sup> or OH<sub>ads</sub> as stated here.<sup>3</sup> In the mechanism proposed here the adsorbed CO intermediate molecules react [4] with adsorbed OH molecules to form COOH. The reaction to form COOH acts to shift the equilibrium of Eq. [3] so as to shift the reaction towards the right, thus producing more OH<sub>ads</sub> for the overall reaction to continue. The adsorbed CO and OH interact in a rate-determining chemical reaction to give COOH.

The surface concentration of CO can be calculated for the reaction [2]

$$\theta_{\text{CO}} = \frac{k_1 C_{\text{CH}_3\text{OH}} e^{4VF/RT}}{1 + K_1 C_{\text{CH}_3\text{OH}} e^{4VF/RT}} \quad [6]$$

Thus, the sharp increase in adsorption coverage with potential (see Fig. 3) may be interpreted in terms of the  $4VF/RT$  term in the exponential part of the equation. When the term containing the potential is  $\ll 1$ ,  $\theta_{\text{CO}}$  will increase exponentially, with increase of anodic potential, but at sufficiently high  $V$ ,  $K_1 \exp(4VF/RT) \gg 1$  and  $\theta_{\text{CO}}$  becomes independent of electrode potential. (In the potential range of 0.3–0.7 V,  $\theta_{\text{CO}}$  remains constant.) In the present experiments (Fig. 3),  $-\text{C}=\text{O}$  is observed at low anodic potentials. The  $\theta(\text{C}=\text{O})$  increases rapidly with potential. However,  $\theta(\text{C}=\text{O})$  reaches a maximum value at 0.1 V and decrease thereafter with increase of anodic potentials, during which time it is replaced by  $-\text{C}=\text{O}$ . The apparent discrepancy in surface coverage in comparison with the radiotracer results may perhaps be interpreted in terms of relative absorption coefficients of  $\text{C}=\text{O}$  and  $\text{C}=\text{O}$ . If the coefficient for  $\text{C}=\text{O}$  is less than that of  $\text{C}=\text{O}$ , the  $\theta(\text{C}=\text{O})$  may be larger than what appears in Fig. 3, in comparison with  $\theta(\text{C}=\text{O})$ . The data for peak A should only be taken as qualitative in nature as no comparative data was available.

Similarly, for the water discharge reaction in equilibrium one has

$$\theta_{\text{OH}} = k_2 C_{\text{H}_2\text{O}} \exp(VF/RT) \quad [7]$$

It is reasonable to assume that  $\theta_{\text{OH}}$  follows Langmuir isotherm at low coverages and Temkin isotherm at high coverages.

The rate-determining step for the electrochemical oxidation of methanol is the chemical reaction involving adsorbed CO and adsorbed OH. Then

$$i = Fk_3\theta_{\text{CO}}\theta_{\text{OH}} \quad [8]$$

When  $\theta_{\text{CO}}$  is effectively constant with change of potential (see Fig. 3)

$$i = Fk_3\theta_{\text{CO}}k_2C_{\text{H}_2\text{O}} \exp(VF/RT) \quad [9]$$

which will give a Tafel slope of 60 mV/decade at low anodic potentials. At sufficiently anodic potentials [ $\theta_{\text{OH}}$  following a Temkin isotherm (45)]

$$i = Fk_3\theta_{\text{CO}} \exp(\tau\theta_{\text{OH}}/RT) \quad [10]$$

where the CO radical is  $\text{C}=\text{O}$ . The Temkin term  $r\theta_{\text{OH}}/RT$  can be calculated from the water discharge reaction under Temkin conditions to be

$$\frac{r\theta_{\text{OH}}}{RT} = -\ln k_2 \frac{C_{\text{H}^+}}{C_{\text{H}_2\text{O}}} + \frac{VF}{RT} \quad [11]$$

Substituting [11] in [10]

$$\ln i = \ln Fk_3\theta_{\text{CO}} - \tau \ln k_2 - \tau \ln \frac{C_{\text{H}^+}}{C_{\text{H}_2\text{O}}} + \frac{\tau VF}{RT} \quad [12]$$

If the value of  $\tau$  is taken as 0.5, the Tafel slope becomes 120 mV/decade [cf. the results of Bagotzky and Vassiliev (39)].

<sup>3</sup> The mechanism implies a finite concentration of intermediate OH radicals at pH = 0 and  $V = 0.2$  on the hydrogen scale. There is no evidence for such concentrations for ellipsometric or sweep data in the oxidation of Pt. However, this does not necessarily imply that OH radicals do not take part as low concentration intermediates.

The surface coverage-potential relation (Fig. 6) is the same for both sequences (0.0–0.8 V NHE and 0.8–0.0 V NHE) in the region of 0.3–0.9 V NHE. But, at potentials greater than 0.4 V the terminally bonded CO (peak A) is not observed in the sequence from 0.0 to 0.8 V NHE. The terminally bonded  $\text{C}=\text{O}$  is converted to bridge-bonded  $\text{C}=\text{O}$  (peak E in Fig. 6) at potentials greater than 0.4 V NHE which is consistent with the potentiodynamic and spectroscopic results (7–9, 15, 16, 29, 30, 38). However, the conversion of  $\text{C}=\text{O}$  to  $\text{C}=\text{O}$  is evidently not favored at potentials below 0.4 V NHE. The activation energy involved for the reverse process is more than that of the forward process, so that the bridge-bonded  $\text{C}=\text{O}$  is not electrochemically reduced in the experiment time in the region of 0 to +0.3 V and hence the surface coverage of  $\text{C}=\text{O}$  remains constant.

Thus, the present analysis, gives a consistent model for methanol oxidation in respect to the observed results of  $\theta_{\text{CO}}$  as a function of potential under steady-state conditions; and the two regions of the log  $i$ - $V$  relations. This has been done by assuming that CO is an active intermediate taking part in the reaction, and that the absence of any spectroscopic evidence for  $\text{C}-\text{OH}$  does mean it is not present.

This proposition, which contradicts the conclusions of other investigations (7–9, 15, 16, 29, 30) brings consistency to the interpretation of the spectroscopic observations reported in the steady state. When one looks at the conclusions, it is possible that the differences arise from a change of the rate-determining step which occurs in the steady state compared with the situation under potential sweep conditions (31).

*Adsorption of carbon dioxide on platinum.*—Carbon dioxide adsorbed on platinum shows a peak at 2370  $\text{cm}^{-1}$  which lies close to the absorption maximum of carbon dioxide in the gas phase at 2349  $\text{cm}^{-1}$  (24). This small shift in absorbance maximum is within the normal limits of change in frequency induced by adsorption (25). It is proposed that  $\text{CO}_2$  is adsorbed through one oxygen atom and the other oxygen is projecting towards the solution. Symmetric stretching vibrations of  $\text{CO}_2$  are not IR active as the change in dipole moment for this vibration is zero. Asymmetric stretching vibrations occur at 2349  $\text{cm}^{-1}$  and the bending vibrations of  $\text{CO}_2$  has an absorbance maximum at 667  $\text{cm}^{-1}$ , which is beyond the sensitivity of the instrument used. If  $\text{CO}_2$  were adsorbed parallel to the surface of the electrode, the dipole moment change normal to the surface for the asymmetric stretching vibrations is zero and is hence not seen by parallel polarized light.

At low anodic potentials ( $< 0.6$  V NHE) the surface concentration of  $\text{CO}_2$  remains. At sufficiently greater potentials, the concentration of  $\text{CO}_2$  decreases, due both to displacement, e.g., from  $\text{SO}_4^-$  and as a result of oxide formation.

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## Potentiodynamic and AC Impedance Investigation of Anodic Zirconium Oxide Films

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### ABSTRACT

Potentiodynamically grown thin oxide films of zirconium were investigated as a function of the electrode potential ( $0V \leq V \leq 9V$ ), the potential sweep rate ( $0.05 \text{ Vs}^{-1} \leq v \leq 4.00 \text{ Vs}^{-1}$ ) and the pH ( $1 \leq \text{pH} \leq 14$ ) in phosphate electrolytes. The oxides were characterized by coulometric and impedance measurements in the frequency range  $0.1 \text{ Hz} \leq f \leq 6.0 \times 10^4 \text{ Hz}$ . The rate of oxide growth changes with the sweep rate according to the high field law. The oxide growth kinetics depends on the pH of the forming electrolyte. The results are interpreted in terms of anion incorporation into the film. The system impedance is characterized by a low-frequency capacitive behavior associated with the oxide film and by a high-frequency resistive behavior corresponding to the electrolyte. The oxide capacity was found to be frequency dependent. The oxide impedance can be interpreted in terms of a dielectric relaxation model. A complex dielectric constant  $\epsilon = 31.5 - i 1.3$  was calculated at pH 14.

Zirconium, according to the nature of its oxide, can be included like Ta (1, 2), Ti (3-5), Nb (6, 7), Hf (8, 9), etc., in the so-called valve metals group, since  $\text{ZrO}_2$  blocks anodic but not cathodic electron transfer reactions (10-12). The metal is always covered by an oxide film of  $\text{ZrO}_2$ , as the potential for oxide formation is rather negative and the passivity extends over a wide pH range (13).

The behavior of zirconium, unlike other valve metals, is singular in several aspects. Thus, zirconium oxide incorporates anions from the electrolyte when anodically formed (14-19) and, on the other hand, during oxide growth; the current transport is due entirely to the  $\text{O}^{2-}$  ion migration (20, 21). Whereas the majority of valve metal oxides are amorphous, thick zirconium oxide films are crystalline

(22); particularly those obtained in  $\text{H}_3\text{PO}_4$  solutions are monoclinic  $\text{ZrO}_2$  (13).

As recently reported by photoelectrochemical measurements, the bandgap energy is ca. 5 eV (12, 23), and consequently, the oxide behaves as an electrical insulator. It has also been shown that at a given thickness, the capacity remains independent of the potential (12, 24). The oxide grows linearly with increasing potential, whereas the reciprocal capacity increases linearly with film thickness (12).

Capacity measurements have been used to detect failures in the protection character of the oxide films formed in steam water at high temperature and pressure (25, 26). Dielectric constant values in the 20-35 range have been reported from capacity measurements (12, 27, 28). Some authors have measured the oxide capacity at a frequency of

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