

Printed in India.

Electrochemistry

AD-LAYERS AND OXIDATION OF FORMIC ACID AT PLATINUM ELECTRODES

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(Communicated by H. V. K. Udupa, FNA)

(Received 16 November 1981)

Several foreign ad-atoms have been reported to enhance the rate of anodic oxidation of formic acid on platinum. This effect has been variously interpreted. Some authors believe that the catalytic effect is the consequence of the suppression of hydrogen adsorption which will otherwise participate in the formation of the strongly inhibitive 'O' type species. In as much as 'O' type species occupy two or three platinum sites, their formation may be retarded as a result of a 'third body' effect. However, in certain cases, it has been found that the sites unoccupied by the ad-atoms are almost completely blocked by the 'O' type species under conditions of steady state polarization. Therefore, an explanation of the catalytic effect must be sought in the rate-determining step for the oxidation process and how this step is influenced by the presence of foreign ad-atoms.

The literature on the subject is reviewed in the present article and an attempt made to provide a broader understanding of the role of foreign ad-atoms in the oxidation of formic acid at platinum electrodes.

Keywords : Ad-atoms; Oxidation; Formic Acid; Platinum; Electrodes; O-Type Species; Third Body Effect

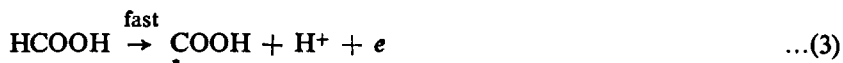
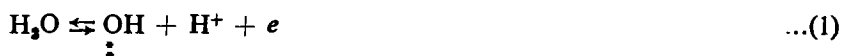
INTRODUCTION

IN recent years binary catalyst systems involving a platinum substrate and various metallic and non-metallic ad-atoms have attracted considerable attention for the oxidation of simple organic molecules such as methanol and formic acid. Enhanced catalytic activity has been reported for metallic ad-atoms such as Hg (Angerstein *et al.*, 1973) Pb, Tl, Bi and Cd (Adzic *et al.*, 1975a, 1977) Cu and Ag (Adzic *et al.*, 1975b; Breiter, 1969; and Taylor *et al.*, 1971) and Sn (Vassiliev *et al.*, 1979). The non-metallic ad-atoms which have been found to promote the oxidation of formic acid on platinum are iodide (Jayaram & Hira Lal, 1977) sulphur and selenium (Binder, *et al.*, 1968, 1969; Hiddleston, 1968; Loucka, 1972; and Jayaram *et al.*, 1978). Adsorbed acetonitrile has also been reported to act as a promoter (Angerstein *et al.*, 1973).

OXIDATION OF FORMIC ACID

The oxidation of formic acid on platinum occurs through two parallel pathways. One involves a strongly chemisorbed organic species which is mainly a species of

composition CHO. The other involves a more reactive surface intermediate COOH. The rate determining step in the oxidation of strongly chemisorbed organic species is a surface reaction with an adjacently adsorbed OH radical (Podlovchenko *et al.*, 1966; Breiter, 1968*a, b*; Khazova *et al.*, 1974; and Sidheswaran & Hira Lal, 1972).



The kinetic parameters conform to the following rate equation,

$$i = nFk \theta_M (1 - \theta_M) \exp(\alpha_{an} F \varphi_r / RT) \quad \dots(5)$$

where α_{an} is close to unity (Sidheswaran & Hira Lal, 1972).

The reactive intermediate pathway may be represented as follows (Murugkar & Hira Lal, 1976).



At potentials below 0.5V, the rate of oxidation of CHO is two orders of magnitude less than the rate of formic acid oxidation. Therefore, at such potentials, the bulk of the current may be said to obtain from oxidation *via* the reactive intermediate pathway. Murugkar *et al.* (1976) have obtained the following experimental rate equation for the steady-state oxidation of formic acid :

$$i = nFk C^{\alpha_1} \exp(-\alpha f \theta_M) \exp(\alpha_{an} F \varphi_r / RT) \quad \dots(10)$$

where $\alpha_1 = 0.72 \pm 0.05$, $\alpha f = 13$ and the overall anodic transfer coefficient $\alpha_{an} = 0.75 \pm 0.05$. The fractional coverage with strongly chemisorbed organic species, θ_M , appears as an exponential term and accounts for the severe inhibition of reaction in the steady-state as compared to the high initial rates.

The oxidation of methanol has also been suggested to involve similar parallel pathways (Breiter, 1968; Podlovchenko *et al.*, 1968; and Podlovchenko &

Petukhova, 1974) except that the rate of oxidation of methanol is only a few times larger than the rate of oxidation of strongly chemisorbed organic species. Hence, the strongly chemisorbed organic pathway may contribute significantly to the steady-state oxidation current under certain conditions.

The basic approach in studies with binary catalyst systems has been to prevent or inhibit the formation of strongly chemisorbed species by the presence of various preadsorbed layers. Whereas an exhaustive survey of the literature in this category is not intended in the present article, we shall consider examples where some definitive clues regarding the role of preadsorbed layers in modifying the reaction rate emerge.

Metallic Ad-atoms

Angerstein *et al.* (1973) have investigated the influence of mercury ad-atoms on the oxidation of formic acid. They report an increase in the rate of oxidation at low coverages with mercury, maximum activity being observed at $\theta_{\text{Hg}} = 0.25$ (Fig. 1). The catalytic effect has been attributed to the inhibition of formation of strongly chemisorbed species. These authors suggest that the strongly chemisorbed species is formed by a dimerization reaction resulting in an anhydride.

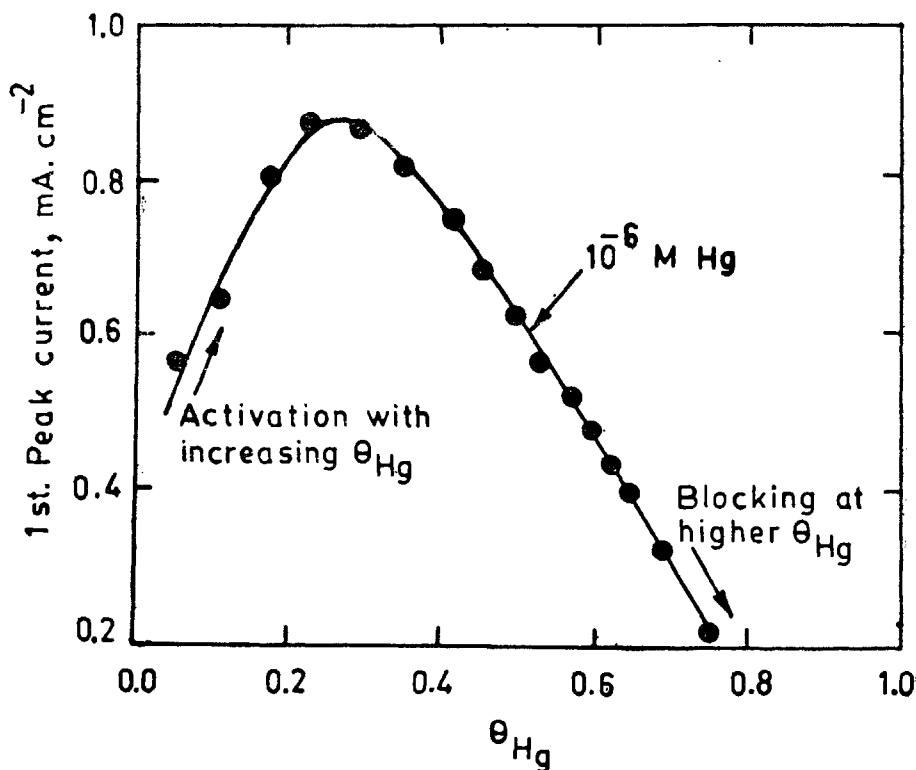
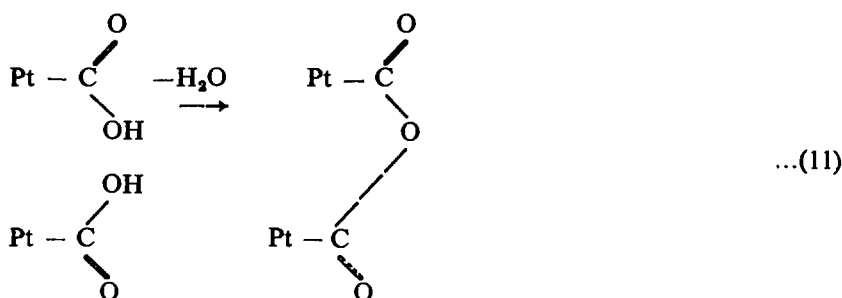


FIG. 1. Variation of the first peak current for formic acid oxidation with θ_{Hg} on Pt. (0.25 M HCOOH + 0.5 M H₂SO₄ at 25 °C, 100 mV. sec⁻¹) (after Angerstein *et al.*, 1973).



Such a reaction requires the availability of two adjacent COOH radicals. Adsorbed mercury atom acts as a 'third-body,' decreasing the probability of a reaction such as (11). As mentioned earlier, the generally accepted composition of the strongly chemisorbed species is CHO occupying three platinum sites. However, the concept of a 'third-body' effect seems useful even if reaction (11) is not valid. Deactivation at high coverages is thought to arise from simple blocking of platinum sites available for the reaction.

Adzic *et al.* (1975a, b, 1977) have investigated the effect of underpotential deposition of Pb^{2+} , Tl^+ , Bi^{3+} , Cd^{2+} , Cu^{2+} and Ag^+ . The oxidation of formic acid was found to be inhibited by Cu^{2+} and Ag^+ whereas previous workers (Breiter, 1969; and Taylor *et al.*, 1971) have reported a slight catalytic effect at low coverage. Varying degrees of catalytic effect are observed with the other ad-atoms. The most significant effect is observed with lead where the presence of 1×10^{-3} M Pb^{2+} in solution enhances the first anodic peak current ($\sim 0.5\text{V}$) 70 times (Adzic *et al.*, 1975). Effects occur as the highest in the potential region where platinum is free of oxide. An examination of the cyclic voltammograms reveals that the peak potentials are generally maintained in the presence of the ad-atoms.

The catalytic effect increases with concentration of adsorbing ions in solution, as shown in Fig. 2.

As would be expected, underpotential deposition of these cations suppresses the adsorption of hydrogen on platinum. Since adsorbed hydrogen is involved in the formation of CHO, it has been suggested that this is responsible for the catalytic effect of the ad-atoms. The above argument is only partially valid because the strongly chemisorbed species has also been shown to form by a disproportionation reaction outside the hydrogen adsorption region (Capon & Parsons, 1973). This is also borne out by experiments wherein the electrode is held at 0.5V in the presence of Pb^{2+} (Adzic *et al.*, 1975a, b). These results show that the poisoning species is indeed formed at potentials outside the hydrogen region even in the presence of lead. The other reason put forth to explain the catalytic effect is the 'third-body' effect advanced earlier by Angerstein *et al.* (1973). However, unlike mercury, this effect does not pass through a maximum in these cases (Fig. 2). (The maximum observed with Tl has been ascribed to other causes, since it appears after Tl ad-atoms at the surface have reached saturation coverage and hence, their concentration does not increase with further increase of Tl^+ concentration in solution). The absence of maxima could be understood if saturation coverage

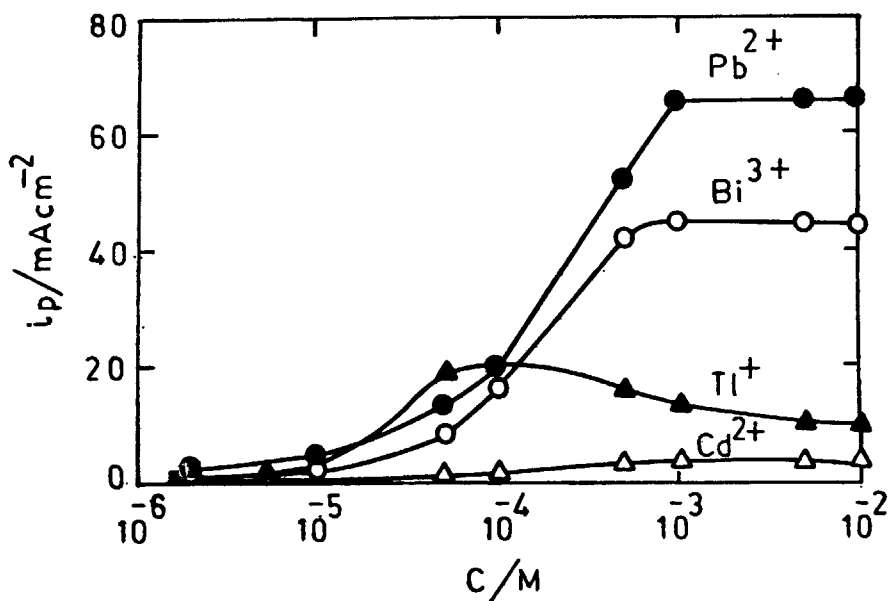


FIG. 2. Plots of the current of first anodic peak against concentration of cations in solution. The nature of cations is indicated on the curves (after Adzic *et al.*, 1975a, b).

with these metal ad-atoms is not sufficiently large to cause deactivation by simple blocking as witnessed with mercury. Adzic *et al.* (1977) have proposed recently that the first anodic peak observed during cyclic voltammetry in the presence of formic acid and Pb^{2+} in solution, corresponds to the maximum expected on the basis of the 'third-body' effect. However, in the absence of detailed information regarding the variation of θ_{Pb} with potential, the proposition is debatable because the peak occurs at the same potential in the presence of Pb^{2+} as in its absence.

In a recent communication, Vassiliev *et al.* (1979) have described the effect of tin ad-atoms on the oxidation of $HCOOH$, CH_3OH and other simple organic compounds. Tin ad-atoms were found to promote the oxidation of both $HCOOH$ and CH_3OH . The oxidation rate increased exponentially with θ_{Sn} (Fig. 3).

They have noted that the coverage with strongly chemisorbed organic species falls off linearly with the increase in coverage of the electrode surface with tin :

$$\theta_M = A - \gamma\theta_{Sn} \quad \dots(12)$$

where $\gamma \approx 1$ in most cases. They have further noted that the behaviour of the adsorption isotherm of organic species in the presence of a constant amount of tin on the surface remains similar to the adsorption isotherm on pure platinum surface. These observations show that tin ad-atoms physically block platinum sites for the formation of $\overset{\cdot}{C}\overset{\cdot}{H}\overset{\cdot}{O}$, but do not actively inhibit the formation of $\overset{\cdot}{C}\overset{\cdot}{H}\overset{\cdot}{O}$ on the rest of the platinum surface. This suggests that the 'third-body' effect may not play a major role in explaining the promoting action of tin ad-atoms.

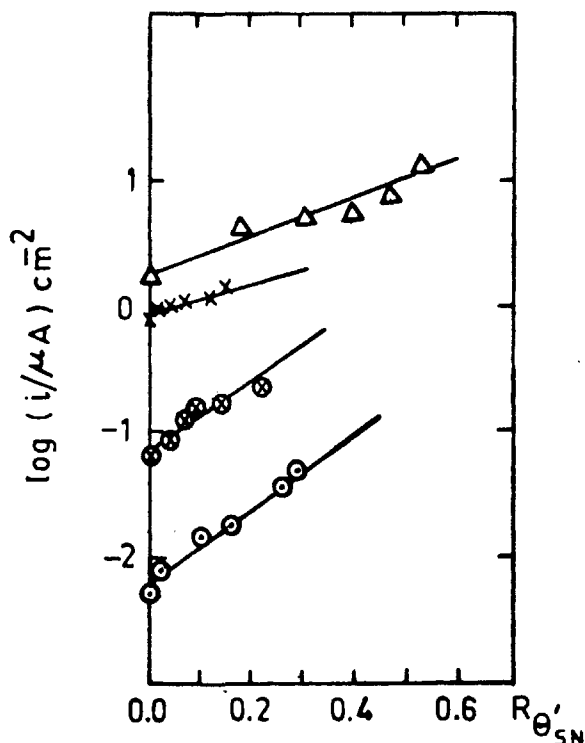


FIG. 3. Dependence of electro-oxidation rate on the surface coverage with tin ions for smooth platinum in 0.1M HCOOH + 0.5M H₂SO₄ solution, at $E = 0.4V$ (Δ); for platinumized platinum in 0.1M CH₃OH + 0.5M H₂SO₄ solution, at $E = 0.4V$ (\odot); 0.1M HCOOH + 0.5M H₂SO₄ at 0.3V (\otimes) and at 0.4V (\times) (after Vassiliev *et al.*, 1979).

The oxidation of strongly chemisorbed organic species was also found to be catalyzed by tin ad-atoms. As mentioned earlier, the oxidation of strongly chemisorbed organic species is controlled by a surface reaction with an adjacently adsorbed OH radical. On this basis, Vassiliev *et al.* (1979) have suggested that the promoting effect is due to the greater affinity of tin ad-atoms for OH (ads) as compared to platinum. However, they have assumed that the rate limiting step in oxidation of formic acid also is an interaction of a chemisorbed organic species with OH ads :



The currently accepted mechanism for the oxidation of HCOOH at low potentials ($\phi_r < 0.5V$) does not involve the above rate limiting step. To this extent, the reasoning put forth by these authors is open to criticism.

Non-metallic Ad-atoms

The influence of irreversibly adsorbed iodide has been reported by Jayaram and Hira Lal (1977). The dependence of oxidation rate on coverage θ_I is shown in Fig. 4.

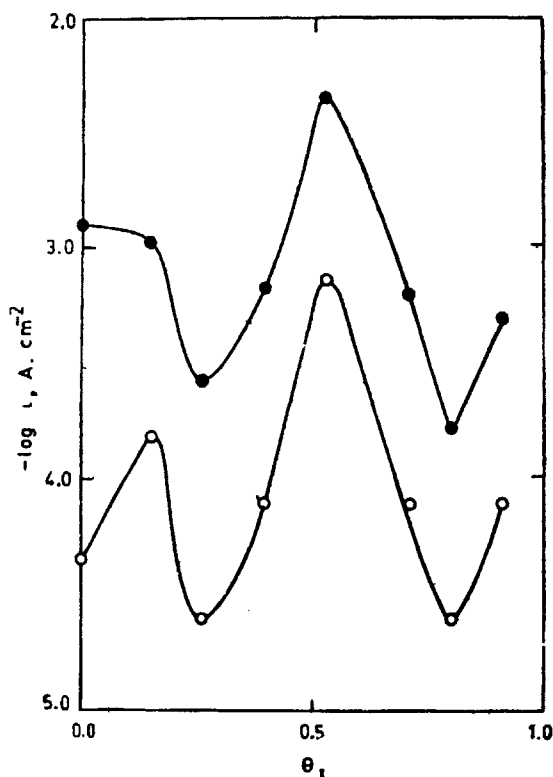


FIG. 4. $\log i$ vs. θ_I plots for oxidation of formic acid (0.5M) in 0.5M H_2SO_4 at 40°C . (1) 0.3V and (2) 0.4V (Jayaram & Hira Lal, 1977).

The catalytic effect is not easily comprehensible and does not correspond to any of the cases cited earlier. It was found that even in the presence of adsorbed iodide, the strongly chemisorbed organic species is found and the total coverage, $(\theta_M + \theta_I)$, is virtually unity. Therefore, the catalysis cannot be attributed to the 'third-body' effect. It has also been found that the number of electrons per site involved in the oxidation of the strongly chemisorbed organic species is not materially affected by adsorbed iodide (Jayaram, 1975). Nor in the oxidation of strongly chemisorbed organic matter catalyzed by adsorbed iodide (Kamath & Hira Lal, 1970). Thus, catalysis arises due to reasons other than those involved in the promoting effect of tin ad-atoms.

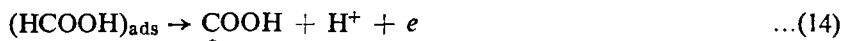
It has been suggested that the two maxima at $\theta_I = 0.15$ and 0.53 are associated with two forms of adsorbed iodide (Jayaram & Hira Lal, 1977). Though there is no direct evidence for two forms of adsorbed iodide, it was observed that both anodic and cathodic polarization is necessary for complete desorption of iodide from the electrode.

Adsorbed sulphur has probably presented the most intriguing picture of all the ad-atoms studied. Its influence on the oxidation of formic acid has been reported

by a number of workers (Binder *et al.*, 1968, 1969; Hiddleston, 1968; Loucka, 1972; and Jayaram *et al.*, 1978). The apparently contradictory results reported therein prompted a detailed investigation of the nature of adsorbed sulphur layer itself. It has been shown that a monolayer consists of two forms of adsorbed sulphur, $\overset{\cdot\cdot}{\text{S}}$ occupying 70 per cent of the sites and $\overset{\cdot}{\text{S}}$ occupying 30 per cent of the sites (Jayaram *et al.*, 1978; and Contractor & Hira Lal, 1978). At high θ_s , the presence of a bilayer is indicated.

Adsorbed sulphur catalyzed the oxidation of formic acid by about two orders of magnitude in certain cases; like adsorbed iodide, the enhancement cannot be explained by the 'third-body' effect because the total coverage ($\theta_s + \theta_M$) is virtually unity under conditions of steady-state oxidation (Jayaram *et al.*, 1978; and Contractor & Hira Lal — *in press*). Similarly, adsorbed sulphur has no catalytic effect on the oxidation of strongly chemisorbed organic species (Jayaram, 1975; and Contractor & Hira Lal — *in press*).

The catalytic effect depends upon the manner in which the adsorbed sulphur layer is obtained. The electrode can be completely covered initially and the desired θ_s can then be obtained by partial anodic stripping. A layer formed in this fashion exhibits the behaviour shown in Fig. 5. The logarithm of oxidation rate increases linearly with θ_s with a crossover at $\theta_s \approx 0.35$. The energy of activation is lowered in the presence of adsorbed sulphur, probably, due to a change in the mechanism of oxidation of formic acid. However, the energy of activation is independent of θ_s at $\theta_s > 0$ (Contractor & Hira Lal — *in press*). On this basis, it has been suggested that in the presence of adsorbed sulphur (and also iodide) the rate-limiting step (7) is replaced by the following reaction.



This is in conformity with the observation that $\theta_M + \theta_s$ (or θ_{-1}) is virtually unity and hardly any bare platinum sites are available for adsorption of hydrogen.

The exponential increase of the oxidation rate with θ_s has been explained by assuming Temkin conditions for the adsorption of HCOOH on a sulphur covered electrode. The oxidation rate thus formulated is given by (Contractor & Hira Lal — *in press*),

$$i = i_{\theta_T=0} \times \exp \sum a_j \theta_j \quad \dots(15)$$

where a_j is a coefficient representing the heterogeneity arising from the adsorption of species 'j', and θ_j is the fractional coverage with species 'j'. The two linear regions in Fig. 5 arise from the fact that the adsorbed sulphur layer consists of two types of species, $\overset{\cdot\cdot}{\text{S}}$ and $\overset{\cdot}{\text{S}}$ whose relative proportion varies with θ_s .

The desired θ_s can also be obtained by controlling the time of contact and concentration of the adsorbed. A layer obtained in this fashion exhibits a remarkably different behaviour as shown in Fig. 6. The catalytic effect passes through

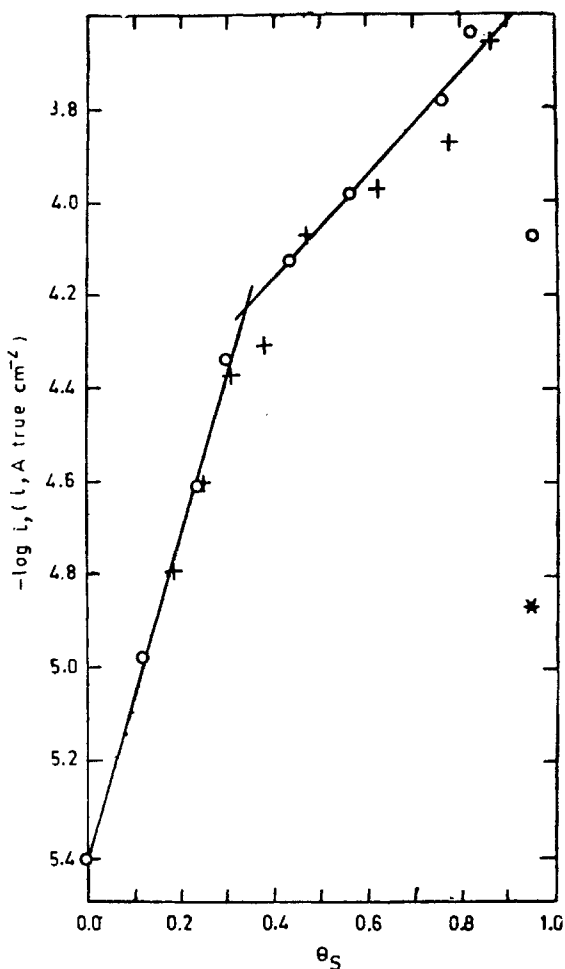


FIG. 5. $\log i$ vs. θ_S plot for oxidation of formic acid (0.5M) in 0.5M H_2SO_4 at 0.3V. Temperature 40 °C (O, +) layer adsorbed from SO_2 at $\phi_r^{\text{ads}} = 0.5\text{V}$ and stripped at 26 °C and 80 °C respectively. (*) layer adsorbed from SO_2 at $\phi_r^{\text{ad}} = 0\text{V}$ (Contractor & Hira Lal *in press*).

two maxima at $\theta_S = 0.30$ and 0.65 . With a layer obtained in the above manner and used without partial stripping, one must consider the presence of species such as S_2 and S_3 along with S and S^* even at low coverages. The coverage profile for the growth of such a layer may be constructed if one assumes that each inflexion in the $\log i$ - θ_S plot (Fig. 6) represents the coverage at which a new species makes its appearance on the surface, and that the order in which these species make their appearance is governed by their relative energies of adsorption. A profile was constructed on this basis and oxidation rate was calculated using eqn. (15) and substituting appropriate values for the coefficients a_j . Though agreement with experimental values is not very good, it shows qualitatively that eqn. (15) has a wider validity.

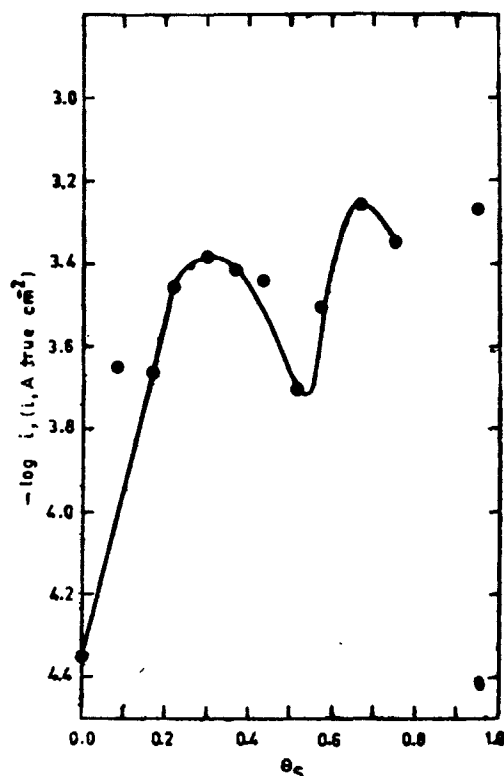


FIG. 6. $\log i$ vs. θ_S plot for the oxidation of formic acid (0.5M) in 0.5M H_2SO_4 at 0.3V. Temperature 80 °C. Desired θ_S obtained by adjusting the concentration of SO_2 ($\varphi_r^{\text{ad}} = 0.5\text{V}$).

The brief survey presented above shows that elements as diverse as mercury and sulphur promote the oxidation of formic acid when present as sub-monolayers. It is only to be expected that the factor responsible for the promoter action of one would be different from that of the other. It would be profitable to group the promoters on this basis. Such a classification must take into account the fact that oxidation of formic acid occurs *via* two parallel pathways. Therefore, enhancement of formic acid oxidation may result from promotion of either one of these pathways or both. Accordingly, the ad-atom promoters may be grouped into the following three classes.

1. *Promoter Action through 'Third-Body' Effect* : Such promoters may be expected to catalyze the oxidation by blocking some platinum sites and thus preventing the formation of strongly chemisorbed organic (which requires three adjacent sites) on at least a part of the surface. The platinum sites thus left bare would then act as additional centres for oxidation *via* the reactive intermediate pathway. The catalytic effect would increase with coverage until the deactivation due to blocking offsets what is gained by keeping some sites free of the strongly chemisorbed organic. The coverage at which maximum catalytic effect is observed must be

determined by the number of sites occupied by the ad-atom as compared to the number of sites required for the formation of strongly chemisorbed organic. Adsorbed mercury, acetonitrile, lead and probably silver and copper, act in this manner. Such promoters would not be effective if they are introduced after the strongly chemisorbed organic has been formed to the maximum extent. This has indeed been observed by Angerstein *et al.* (1973) with acetonitrile. Besides, such ad-atoms should be effective in the promotion of oxidation of both formic acid and methanol.

2. *Promoter Action through Catalysis of Strongly Chemisorbed Intermediate Pathway*: The promoter action of this class results primarily from catalysis of oxidation of the strongly chemisorbed organic species. This in turn is related to ease of formation of $(OH)_{ads}$ on these ad-atoms as compared to platinum. The catalytic effect in this case should increase exponentially with coverage by ad-atoms as the free energy of OH_{ads} is directly related to coverage. Adsorbed tin and ruthenium (Petry *et al.*, 1965; and Watanabe & Motoo, 1975) belong to this category of promoters. Mixed electro-deposits of Pt with antimony, arsenic and tin studied in relation to the oxidation of methanol (Koch *et al.*, 1976) also seem to fall in this group.

Since the promoter action results from a co-operative process where the platinum provides the adsorbed organic and the ad-atom provides $(OH)_{ads}$, one must expect deactivation at high coverage with the ad-atoms. Such a deactivation has indeed been observed in case of methanol oxidation on platinum-ruthenium alloys and co-deposits (Watanabe & Motoo, 1975). Vassiliev *et al.* (1979) have reported data only upto $\theta_{sn} = 0.5$; a deactivation may probably occur at higher coverage.

3. *Promoter Action through Catalysis of Reactive Intermediate Pathway*: The promoters in this category catalyze the oxidation of formic acid but do not catalyze the oxidation of the strongly chemisorbed organic species. The 'third-body' effect also does not play a major role here as the electrode is completely blocked even in the presence of ad-atoms. Adsorbed iodide and sulphur belong to this class as $\theta_M + \theta_S$ (or θ_I) is virtually unity at all coverages with the ad-atoms. These promoters affect the oxidation of formic acid in the same manner as the strongly chemisorbed organic species. Catalysis results from a favourable coefficient of heterogeneity as compared to the strongly chemisorbed organic species. The oxidation rate will change exponentially with coverage by the ad-atoms. Detailed features of $\log i$ as coverage plot will depend on the types of adsorbed species and the corresponding coefficients of heterogeneity. Since this class of promoters do not catalyze the oxidation of strongly chemisorbed organic species, they would have little effect on the steady-state oxidation of methanol. This is because the oxidation of methanol occurs to a significant extent *via* the strongly chemisorbed organic pathway. Adsorbed iodide and sulphur have been found to have little effect on the oxidation of methanol at low coverage and cause deactivation at intermediate coverages (Jayaram, 1975).

It is implicit in the above classification that promoters of classes two and three possess greater mobility in the adsorbed state as compared to those belonging to

class one. This permits a surface rearrangement and subsequent formation of strongly chemisorbed organic species, and hence a virtual absence of the 'third-body' effect. If the surface rearrangement is a slow process then a larger catalytic effect would be observed under potentiodynamic conditions (in the presence of adsorbing ions in solution) than in the steady-state.

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Discussion

V. S. BAGOTSKY (*The Institute of Electrochemistry of the Academy of Sciences of USSR, Moscow*) : Is the activity of Pt with S-adatoms lower than the activity of Pt at $\theta_r = 0$?

HIRA LAL : Yes, it is lower.