THE STRUCTURE OF CHEMISORBED METHANOL

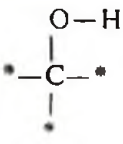
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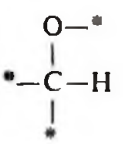
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The most probable structure of the chemisorbed methanol residue formed on platinized platinum electrode has been arrived at from kinetic and bond energy considerations.

Dissociative electrosorption of methanol on platinized-platinum electrode leads to the surface residue with a net stoichiometric composition of $\overset{*}{C}\overset{*}{H}\overset{*}{O}$[1]. This structure has been arrived at primarily from the open circuit adsorption studies[2]. These results were further confirmed by radio tracer studies[3] with labelled carbon. The following two probable structures have been proposed elsewhere[1]:



I



II

The elucidation of the exact structure of the residue by making a discrimination between these two probable structures has remained thus for incomplete. The present communication attempts to bridge this gap.

A) Kinetic Considerat on.

Galvanostatic anodic charging curves have been run with the chemisorbed organic residues and the following general mechanism for their electro-oxidation has been proposed[4,5].

$$H_2O \rightleftharpoons \overset{*}{OH} + H^+ + e^- \quad \ldots (1)$$

$$\overset{**}{R} + \overset{*}{OH} \rightarrow \overset{*}{ROH} \quad \ldots (2)$$

$$ROH + OH \rightarrow R(OH)_2 \rightarrow CO_2 + H_2O \quad \ldots (3)$$

where $\overset{**}{R}$ is the bidentate-type chemisorbed carbonaceous residue. For example, in the case of formaldehyde the chemisorbed residue has been identified as $\overset{**}{CO}$ and the oxidation mechanism proposed[2,6] is as follows:

$$\overset{*}{CO} + \overset{*}{OH} \rightarrow \overset{*}{C}(=O) - OH \quad \ldots (4)$$

$$\overset{*}{COOH} + \overset{*}{OH} \rightarrow HO-C(=O)-OH \rightleftharpoons H_2O + CO_2 \quad (5)$$

Similar mechanisms for the chemisorbed methanol structure I and II are :

For Structure I :

$$\overset{OH}{\overset{|}{*-C-*}} + OH \rightarrow \overset{OH}{\overset{|}{*-C-OH}} \rightleftharpoons \overset{O}{\overset{||}{*-C}} + H_2O \quad \ldots (6)$$

This step (6) is followed by step (4) and (5). Hence the oxidation of $\overset{*}{C}\overset{*}{O}H$ proceeds through $\overset{**}{CO}$ and $\overset{*}{C}OOH$ to the final product CO_2.

For Structure II

$$\overset{O-*}{\overset{|}{*-C-H}} + OH \rightarrow \overset{O-OH}{\overset{|}{*-C-H}} \quad \ldots (7)$$

III

The surface oxyhydroxide residue III will react twice further with OH as ;

$$\overset{O-OH}{\overset{|}{*-C-H}} + OH \rightarrow \overset{O-OH}{\overset{|}{*-C-H}} \quad \ldots (8)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$$

$$\overset{O-OH}{\overset{|}{*-C-H}} + OH \rightarrow OH-\overset{O-CH}{\overset{|}{C}}-H \rightleftharpoons \overset{O-OH}{\overset{|}{C}}-H + H_2O \quad (9)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad OH \qquad\quad \overset{||}{O}$$

IV

The oxyhydroxide intermediate IV can further undergo two types of reactions as described hereunder.

(i) **At the electrode :**

It could dissociatively chemisorb and react as follows:

$$O=\overset{O-OH}{\overset{|}{C}}-H \rightarrow O=C-O-OH + H^+ + e^- \quad \ldots (10)$$

$$O=C-O-OH + OH \rightarrow O=\overset{OH}{\overset{|}{C}}-O-OH \quad \ldots (11)$$

V

The intermediate V can dissociate into O_2 and CO_2. The O_2 thus liberated will chemically oxidise the residue present on the electrode and will raise the potential plateau of the reversible hydrogen electrode.

(ii) **At the bulk phase :**

The intermediate IV can get thrown into the bulk phase and can come back to the electrode partly and react as above. Otherwise the intermediate IV can release O_2 and CO_2 and this O_2 can either oxidize the chemisorbed residue present on the electrode or raise the potential plateau of the reversible hydrogen electrode.

Hence the O_2 gets generated and the potential plateau should be elevated if the structure II exists.

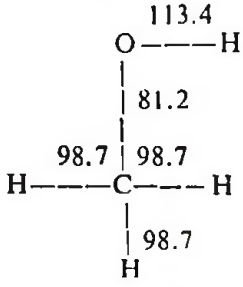
In other words, if the structure II exists, and if the oxidation of the residue occurs on an aged electrode, at the same current density, roughness factor, supporting electrolyte and temperature, the oxidation plateau for this structure II should be at a higher potential than that for the structure I and the length of the arrest of the oxidation of the organic res due should be decreased. Taking concrete examples, from the open circuit adsorption it is shown that the chemisorbed methanol is $\overset{*}{C}\overset{*}{O}H$ and the chemisorbed formaldehyde is $\overset{*}{C}\overset{*}{O}$. If Structure II exists in the case of methanol, then the potential arrest for its oxidation should be higher than that for chemisorbed formaldehyde at identical electrode and electrolyte conditions. However, we have noticed[2] identical potential arrests and this rules out the role of the structure II for the chemisorbed methanol.

Shape of the galvanostatic charging curves of chemisorbed methanol

If during the electrooxidation of the chemisorbed residue, any intermediate substance of the reaction gets formed at the electrode and consequently chemisorbs at the electrode further, the galvanostatic charging curve will have the peculiar shape at the low organic coverage region. This characteristic shape has been identified[7] to be caused by the existence of the CH-type residue. However, such a CH-type shape has not been identified with the chemisorbed methanol residue. If structure II existed on the electrode surface, we should have obtained the CH-type shape with chemisorbed methanol. The absence of the CH-type shape strongly suggests the absence of structure II and thereby shows that structure I is the most likely one. The residual current measured in the case of the CH type residues should be very much larger than for the O-type residue[7]. With chemisorbed methanol, we have noticed very insignificant residual current suggesting the absence of structure II.

B) **Bond Energy Consideration**

Bond energy concept also permits us to advance evidence favourably for structure II. The energies of the bonds present in methanol are depicted here :



The O—H bond energy is higher than the —C-H bond energy and hence the former will reluctantly dissociate in the presence of the latter. Therefore structure II will be unlikely or structure I is the most probable one.

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