

into the cavity of the neutral macrocyclic polyethers owing to its smaller size and therefore the contact among the donor oxygen atoms of the macroring and  $Mg^{2+}$  is not so favoured as in the case of  $Ba^{2+}$  cation.  $Mg^{2+}$  has more difficulty to organize the available macroring donor atoms around itself after electrochemical reduction and thus inducing smaller binding increases,  $\Delta E^0_1$ . The binding of  $Ba^{2+}$  is larger when the ligands are reduced because its larger size fits better to the macroring cavity and induces a larger cation enhancements as is shown by the larger  $\Delta E^0_1$ .

The compound B with seven oxygen atoms in the macroring and a larger cavity shows similar voltammetric behaviour to compound A, meanwhile the binding affinities of the reduced compound B are different from the affinities of the reduced compound A. The order of binding increase of the cations is retained and the larger enhancements for the reduced compound B may reflect the influence of the larger number of binding sites in the crown ether macroring.

The results obtained suggest that the ligands A and B in the reduced form are more effective complexing agents towards the alkaline-earth metal ions  $Mg^{2+}$  and  $Ba^{2+}$  than their neutral forms. Moreover, the larger cation size favours the larger increase in its interaction with the reduced ligands.

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## THE ELECTROOXIDATION OF SMALL ORGANIC MOLECULES AND COMPARATION BETWEEN NOBLE AND NON-NOBLE ELECTRODE SURFACES

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### Summary

The electrooxidation of methanol and iso-propanol has been examined on Au(100) and compared with the electrooxidation on non-modified and modified glassy carbon electrodes. The studies with Au(100) have pointed out the role of the  $OH^-$  layer formation for the begining of the electrooxidation of alcohols in alkaline solution (1,2) on noble metals. The small differencies in the structure of alcohol ( $CH_3OH$  and iso-propanol) cause the big differencies in an electrochemical behaviour on noble electrochemical surfaces. The usually prepared GC electrode (3) is not active for the electrooxidation of alcohols at all and modified, Ag/GC electrode shows the different way of the adsorption-desorption processes of both alcohols connected with the electrochemical activity only deeply in the oxide region (5). The compárison with the electrooxidation of  $CH_2O$  on noble (4) and non-noble electrodes (5) indicates that the most simple molecule with the aldehyde group exhibits the unexpected electrocatalytic behaviour at Ag-GC surfaces in the region of the potential before the oxide formation. That means the general conclusion is not possible to make; each molecule requires a special explanation of the electrocatalytic phenomena.

The experimental part has been described in (2), (3) and (4).

In Fig. 1 is presented the electrooxidation of 0.01 M  $CH_3OH$  and 0.01 M iso-propanol on Au(100) at different values of the sweep rate.

It is obvious that sweep rate = 50 mV/sec is too fast for the exhibition of any electrocatalytical process in a case of both alcohols. With sweep rate = 5 mV/sec and 0.5 mV/sec the expected shape of the voltammograms are obtained in a case of iso-propanol, very similar to those, obtained with glycerol at Au(100)(2). The incipient potential of the reaction corresponds to the potential of AuOH formation on Au(100).

$CH_3OH$  remains unactive at sweep = 5 mV/sec and even at sweep rate = 0.5 mV/sec there is no signs of any significant oxidation processes. It can be said that only adsorption-desorption processes of  $CH_3OH$  occure at Au(100) under the experimental

conditions given in Fig. 1. This fact is very important for the explanation of the electrooxidation of  $\text{CH}_2\text{O}$  stabilized with  $\text{CH}_3\text{OH}$  at gold electrode surface. The influence of  $\text{CH}_3\text{OH}$  on that reaction should be studied separately (5).

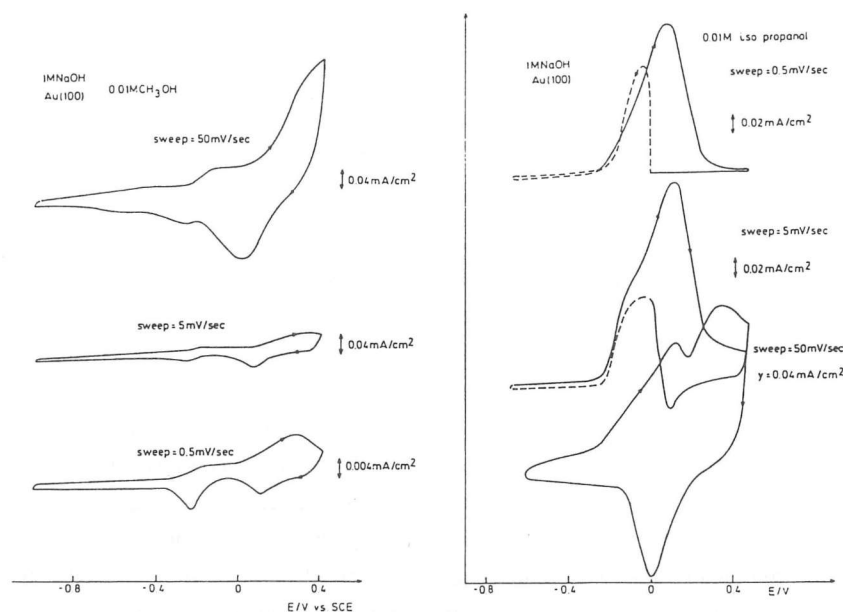


Fig. 1. Cyclic voltammograms of the 0.01 M  $\text{CH}_3\text{OH}$  and 0.01 M iso-propanol on Au(100) in 1 M NaOH, sweep rate = 0.5 mV/sec, 5 mV/sec and 50 mV/sec.

At Cg/GC surface 0.01 M  $\text{CH}_3\text{OH}$  and 0.01 M iso-propanol are not active.

In Fig. 2 is given the electrooxidation of 0.1 M  $\text{CH}_3\text{OH}$  on Au(100) under the same experimental conditions as in Fig. 1. It can be noticed that sweep = 0.5 mV/sec is necessary for the complete oxidation of  $\text{CH}_3\text{OH}$ . That indicates the slow adsorption and high concentration (0.1 M) of  $\text{CH}_3\text{OH}$  which is necessary for the beginning of the electrooxidation. The electrooxidation of 0.1 M isopropanol on Au(100) proceeds at 50, 5 and 0.5 mV/sec as is presented in Fig. 1 for sweep rate = 5 and 0.5 mV/sec. The

electrooxidation of  $\text{CH}_3\text{OH}$  on Au(hkl) at sweep = 0.5 mV/sec has been studied separately (6).

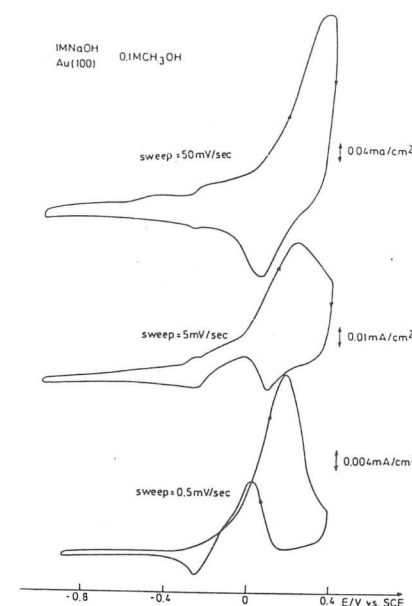


Fig. 2. Cyclic voltammograms of 0.1 M  $\text{CH}_3\text{OH}$  on Au(100) in 1 M NaOH, sweep rate = 0.5 mV/sec, 5 mV/sec and 50 mV/sec.

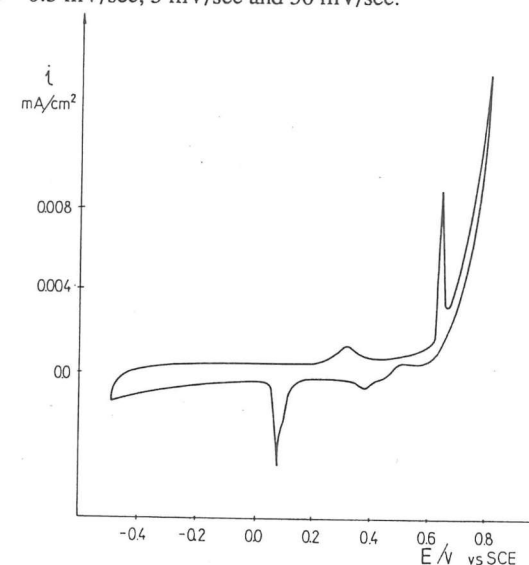


Fig. 3. The cyclic voltammogram of 0.1 M  $\text{CH}_3\text{OH}$  at Ag/GC electrode in 1 M NaOH, sweep rate = 5 mV/sec (5).

In Fig. 3 is given the methanol electrooxidation at Ag/GC which illustrates the quite different behaviour of alcohol on non-noble electrode surface. Methanol is active only very deeply in the oxide region at Ag/GC electrode. The similar behaviour exhibits isopropanol. That pointed out the advantage of the utilization of noble-metal electrodes in electrooxidation of mono-hydroxyl alcohols taking into account the area of the potential before the oxide formation. Another kind of the modification of GC probably can be more promising.

The electrooxidation of  $\text{CH}_2\text{O}$  is observed in the area before the oxide formation at Ag/GC electrode in 0.1 M NaOH (5). The advantage of that reaction on noble metal surfaces is appearance of much higher anodic currents at Au and Pt ( $\sim 20 \text{ mA/cm}^2$ ) (4).

The examination of the electrooxidation of polyhydroxyl alcohols at Ag/GC electrodes is in progress and comparative study with Pt(1) and Au(2) electrodes should be given separately. The preliminary results promise the different behaviour that has been obtained with mono-hydroxyl alcohol and  $\text{CH}_2\text{O}$ .

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#### REDOX PROPERTIES OF HYDRIDE COMPLEXES OF Pt(II) WITH A METAL-CARBON SINGLE BOND

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#### Abstract

The electrochemical investigation, by cyclic voltammetry and controlled potential electrolysis at Pt electrodes, is reported for complexes trans- or cis- $[\text{PtHRL}_2]$  [R = cyano- or trifluoro-alkyl, phenyl or cyano-phenyl; L = tertiary phosphine or 1/2 diphosphine] in acetonitrile, and they are shown to undergo Pt-H bond cleavage (with proton extrusion) upon anodic oxidation at ca. 0.8 ~ 1.7 V vs. SCE.

#### Introduction

We have been investigating [1-3] the activation of chemical bonds by electron transfer in palladium and platinum complexes with metal-carbon double bonds, in particular the monocarbenes cis- $[\text{MCl}_2\{\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{X}\}(\text{L})]$  (M = Pd or Pt; L = isocyanide or organophosphine, R = alkyl or aryl, X = NH or O), the dicarbenes cis- $[\text{MCl}_2\{\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{X}\}_2]$  and the dinuclear diaminocarbenes  $\{\text{MCl}[\mu\text{-CNCH}_2\text{CH}_2\text{Y}](\text{PPh}_3)_2\}$  (Y = NR or O). These species undergo anodic processes involving electroinduced proton extrusion upon heterolytic N-H or C-H bond cleavage [1,2].

In the present study, we have extended this type of investigation to various hydride complexes with Pt(II)-carbon single bonds and observed that proton loss results from metal-hydride bond cleavage induced by electron transfer.