ROLE OF ADSORBED MATERIAL IN THE ANODIC OXIDATION OF PRIMARY ALCOHOLS

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From the relationship between the surface coverage and the reaction rate it was concluded that the adsorbed material is an inhibitor of the alcohol oxidation. Thus the investigation of adsorbate cannot be applied for the study of alcohol oxidation.

Introduction

In the investigation of the anodic oxidation of primary alcohols, either the adsorption and the role of adsorbed material in the reaction was not properly considered [1] or the adsorbed material was only investigated and the properties of its behaviour were supposed to be those of the oxidation [2, 3].

The relationship between the adsorption phenomena and the oxidation of primary alcohols has been less investigated [4] and the results do not support the view that the adsorbate is the reaction intermediate of alcohol oxidation [2].

In order to obtain further data, experiments were carried out by the potential impulse method [5] in connection with the relationship between the change in rate of the reaction and the surface coverage.

Experimental

The measurements were carried out on Pt electrode in $1 N$ H_2SO_4 solution which contained n-propanol in $0.1 M/l$ concentration. The electrode was rotated with 1000 r.p.m. Its real surface was $1.6 cm^2$ and the roughness factor 2.65. The equipment and the procedure have been described earlier [5]. The potential is given against the hydrogen electrode in the same solution.

Results

The measurements have shown, that the rate of the oxidation depends both on the potential and the time of the electrolysis. The current increases with the potential and at higher potential values the decrease with increasing electrolysis

time is less (Fig. 1). BAGOTZKY has interpreted the decrease in current by assuming that the reaction proceeds in two steps. The first is a dissociative adsorption which produces organic radicals and rapidly oxidizing H atoms, the second step is the oxidation of organic adsorbate to CO_2 [2]. Since this latter is a slow process, the formation of the adsorption intermediate produces the current until the surface coverage does not reach the value at which the rates of formation and oxidation of organic intermediate will become equal.
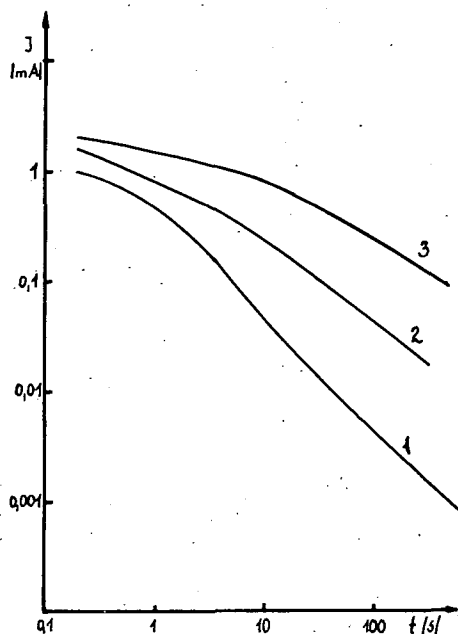
RIGHTMIRE has found [1] that the primary product of ethanol oxidation is acetaldehyde and the end-product is acetic acid. Our analytical results showed the same. The main product of n-propanol oxidation was propionaldehyde. Therefore, the assumption that the current producing process is the CO_2 formation does not seem to be justified, and the aldehyde formation has to be accepted as the main current producing process.

According to the other interpretation of the current decay in organic oxidation (6—8), the decrease in current is not due to the decrease of adsorption rate, but to the accumulation of the species which are not involved in the reaction. These species inhibit the reaction by decreasing the active surface area. It is obvious that the decrease or increase in coverage will cause an increase or decrease in current.

In the case of the primary alcohols it is possible to change the coverage by changing the potential. In Fig. 2 the coverage values are indicated at different potential values for 0.1 M/l n-propanol solution

Fig. 1. Change in current with the time of electrolysis in 0.1 M/l n-propanol solution at 400 mV (1), 600 mV (2), and 800 mV (3).

at t_{ads}: 600 s. The coverage is $\Theta = 0.6$ at 400 mV, and decreases approximately with $\Delta\Theta = 0.1$ from 400 mV to 500 mV; between 500—600 mV it changes only slightly and, from 600 mV, it decreases linearly with the potential. According to this change, it can be expected that the coverage measured at 400 mV will decrease after switching over to 780 mV until it does not reach the proper steady-state value. Simultaneously, the current will also change and, if the adsorbate is an intermediate, the current decreases, while the adsorbate is an inhibitor, the current increases.

After ten min. electrolysis carried out at 400 mV, the potential was switched over to 780 mV and both the coverage and the current values were measured at different times (Fig. 3).

After chainging the potential, the coverage was found to decrease and the current to increase in the same time, thus we have to accept the inhibition effect.

This might also be concluded from another relationship between the decrease of coverage and the experimentally measured current. If the change in coverage involves charge transfer and Q_0 is the charge necessary to cover the surface, assum-

ing one electron transfer for one Pt atom, the value of current which corresponds to decrease in the coverage can be given as

$$i = Q_0 \frac{d\Theta}{dt}.$$

In these experiments Q_0 is 0.35 mC, therefore the value of current is $i=2\,\mu A$. Since the experimentally measured change in the same time was about 20—30 μA, it cannot be the current of the coverage change, but it is to be attributed to the change of the rate of inhibited reaction.
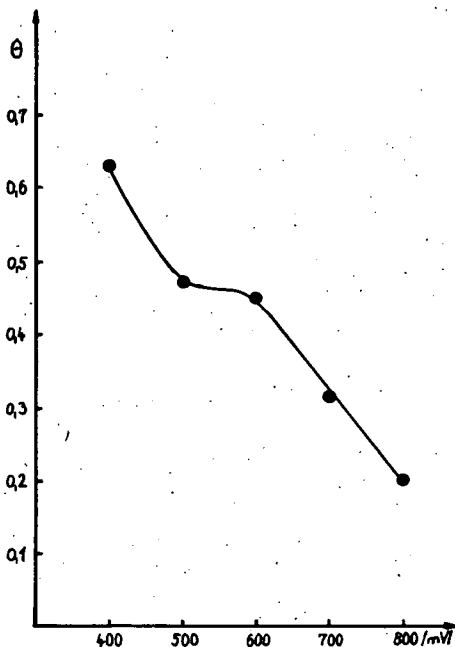

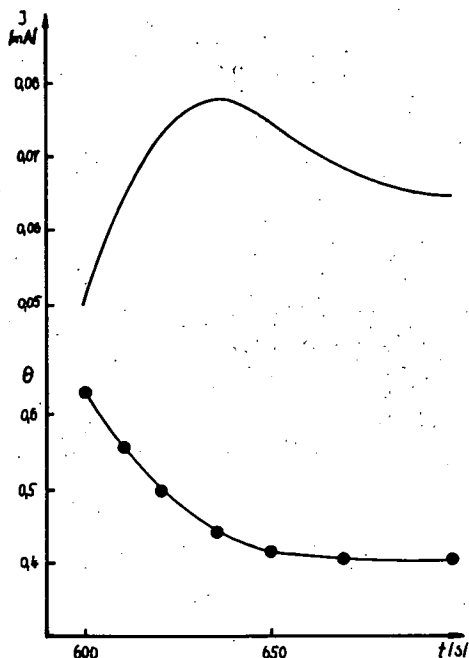Fig. 2. Relationship between coverage and potential in 0.1 M/l n-propanol solution.

Fig. 3. Change of coverage and current with time after switching from 400 mV to 780 mV.

The phenomena observed with n-propanol are in agreement with the results obtained with sec-propanol [8] and formic acid [7], therefore it might be assumed that the inhibition is generally valid for the processes of dehydrogenation. Thus, in this type of reactions the adsorbate which can be measured on the surface is not the intermediate of the main process and its investigation is not equivalent with the study of the main reaction.

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РОЛЬ АДСОРБИРОВАННОГО ВЕЩЕСТВА ПРИ АНОДНОМ ОКИСЛЕНИИ ПЕРВИЧНЫХ СПИРТОВ

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На основании изучения зависимости скорости реакции от степени покрытия поверхности электрода показано, что адсорбированное вещество ингибирует процесс окисления спиртов. Из этого положения следует, что изучение адсорбата не является изучением окисления спирта.