MECHANISM OF ANODIC OXIDATION OF PRIMARY ALCOHOLS

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Previous investigations [1—3] have shown that the rate of oxidation of primary alcohols is controlled by a non-electrochemical step. Results of further study support the view that the rate-determining step is an adsorption process of non-electrochemical type.

Introduction

Earlier investigations concerning oxidation of primary alcohols on Pt electrode in acidic solution resulted in contradictory opinions regarding the kinetic charac-teristics of the reaction. Regarding the chemistry and the stoichiometry of oxidation, it was assumed [4] that the process goes to the formation of CO_2, whereas other results [5] and our gas-chromatographic analysis showed definitely that the alcohol—aldehyde transformation is the main current producing reaction in the overall process. Thus the experimentaly measured current corresponds to this reaction. The data concerning the change in rate of the reaction with the potential are in variance too. In the literature, attemps to characterize the rate by Tafel-slope [6], and the experience that the rate is not or only slightly changing with the potential can be found [7]. On the other side, experimental results regarding the role of adsorbed material in the current generating process were scarcely found in literature [8, 9]. During the course of our investigations of the mechanism of oxidation it was con-cluded that the adsorbed material cannot be considered to be the intermediate product of aldehyde formation [14, 2]. The material adsorbed on the surface gives rise to an inhibition effect and the decrease in the rate of the process with time is due to the increase in the amount of adsorbed material. Since the intermediate product of the alcohol—aldehyde reaction could not be detected, its amount must be very small ($\theta < 0.1$) and negligible in comparison with the amount of adsorbate causing the inhibition (similarly to the results of PODLOVCHENKO [10]). Therefore, in describing the characteristics of the process, the inhibition effect has to be taken into account with every kinetic parameter. In this way, the value of the rate of the process is proved to be independent of the potential, i.e. the rate-determining step is not an electrochemical process [3].

In the interpretation of the characteristics of the oxidation which considers the adsorbed material as an intermediate [4], the experimentally measured current at 400 mV is in direct connection with the adsorption. This is due to the premise that at this potential value only adsorption takes place and the current results

from the charge transfer which occurs during the adsorption. On this basis, the rate of change of the coverage and the experimentally detectable current are in close relationship. Assuming one electron transfer on each adsorption centre during the adsorption, the two rates were found to be equal [4, 11] in the case of methanol and higher primary alcohols. Although other relations were also obtained for methanol [12], it was accepted as a proof that the process of oxidation goes only to the first step *i.e.* to the adsorption at this potential.

Since in the oxidation of primary alcohols the adsorbed material shows an inhibiting effect, experiments have been carried out to obtain further data on the above relationship.

Experimental

The equipment and the method applied in the investigation have been described elsewhere [1]. The measurements were carried out at 25 °C in $1N$ H_2SO_4 solution prepared from triple distilled water, finally distilled in a closed system from charcoal. Sulphuric acid was Merck p.a. product. A hydrogen electrode in the same solution served as reference electrode, and special care was taken for its preparation, *i.e.* its potential value. During the measurements, the disc type working electrode was rotated with 1000 r.p.m.; its real surface area was 1.6 cm². Highly purified N_2 gas was used to deoxygenate the solution.

Results and discussion

Measurements were carried out in the case of ethanol, *n*-propanol, *n*-butanol and propionaldehyde. The progress of adsorption as well as the simultaneous current were measured, too. Each adsorption value was obtained with freshly cleaned surface and simultaneously the current passed during the adsorption was recorded each time to ensure reproducibility.
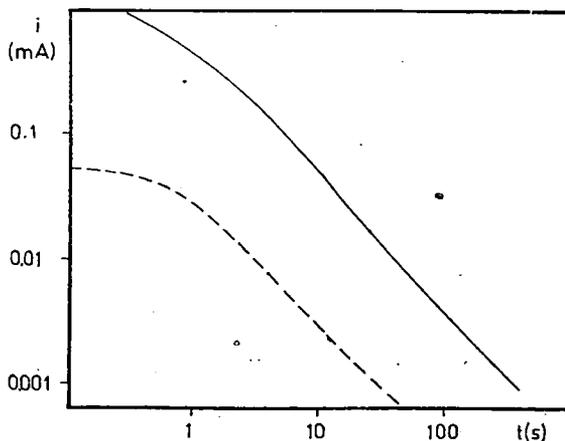

Fig. 1. Experimentally measured (—) and calculated (— — —) current for 0.1 mole·dm⁻³ *n*-propanol solution

With the assumption that one electron transfer occurs at each adsorption centre during the adsorption, the current corresponding to the rate of increase in coverage was calculated. This and the experimentally measured current are given in Figs. 1—3.
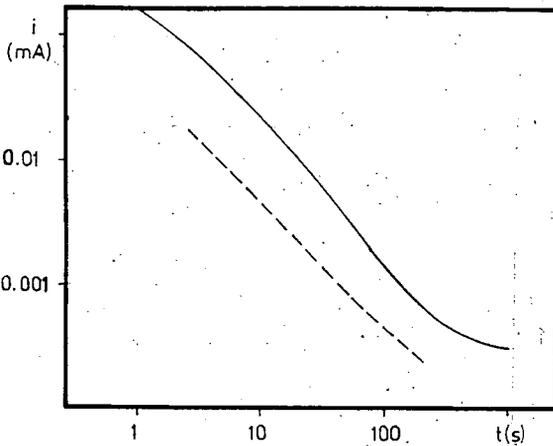

Fig. 2. Experimentally measured (—) and calculated (— — —) current for 0.1 mole·dm^{-3} n-butanol solution

for the alcohols. As can be seen, the experimentally measured current is higher with all materials. This deviation is contrary to the assumption that the adsorbed material is an intermediate product and supports the view that two processes are taking place on the surface. One is the alcohol—aldehyde reaction, and the other the adsorption process which results in strongly bounded species and inhibits the alcohol—aldehyde transfer.
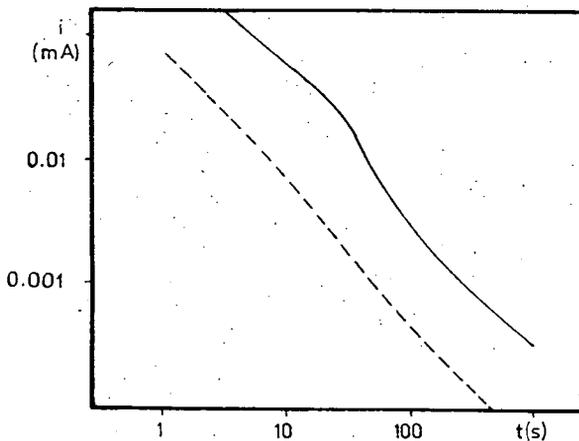

Fig. 3. Experimentally measured (—) and calculated (— — —) current for 0.1 mole·dm^{-3} ethanol solution

Since the investigations carried out on the oxidation of propionaldehyde have shown [15] that the organic material adsorbed at 400 mV is an intermediate of the aldehyde oxidation, it was expected, that in this case the two currents should be equal. The experimental results shown on Fig. 4 are in agreement with this assumption and the above conclusions.

As the rate of the oxidation of primary alcohols does not change with the potential if the currents belonging to the same coverage are compared [3], it may
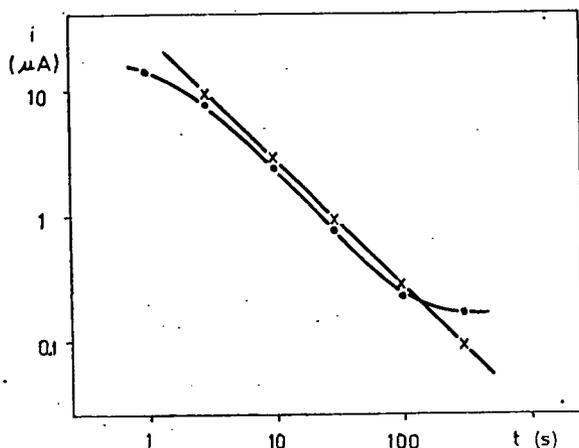

Fig. 4. Experimentally measured (·) and calculated (×)
current for 0.1 mole·dm⁻³ propionaldehyde solution

be assumed that the non-electrochemical rate-determining step is connected with the adsorption of the reacting alcohol molecule or with some other chemical change of the adsorbed intermediate. The second possibility should give rise to an appreciable amount of intermediate product on the surface. This could not be detected, therefore the first assumption is to be considered as valid.

Further data might be obtained by investigating members of the homologue series of alcohols. It could be expected that the reaction rate would not change within the homologue series in the case of equal inhibition effect, *i.e.* coverage, because of the same reactivity of the functional group in each member. The experimentally observed currents given in Fig. 3 of [3] show that the reaction rate decreases in order of ethanol, *n*-propanol, *n*-butanol, which is apparently at variance with the equal reactivity of the functional groups. In order to explain the change in current, it seems to be obvious that it is connected with the change in molecular size. On this basis it can be assumed that the rate-determining step in the reaction depends on the size of the molecule. In this respect the diffusion of the organic reagent has to be disregarded, since its effect was eliminated by the experimental arrangement; furthermore the kinetical behaviour of the reaction excludes this possibility. Similarly, the desorption might be excluded, too, because of the inhibiting effect of the adsorbed material.

In order to explain the effect of the molecular size, one possibility remains, namely that the rate-determining step is the adsorption of the reagent molecule. Several cases might be taken into account:
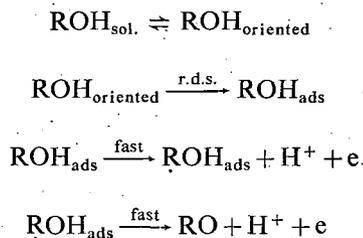
(i) The alcohol molecule has to be oriented properly for the reaction, which is in favour of smaller molecule.

(ii) The larger molecule has to remove possibly more water molecules from the surface before the reaction [13].

(iii) The larger molecule which is already strongly attached to the surface, and therefore acts as an inhibitor, interferes to a larger extent with the incoming molecule than the smaller one.

Although we have to consider all these possibilities, it seems that with increasing coverage the second and third effect should be more important than the first one.

On the basis of the experimental results, the following processes might be suggested for the alcohol—aldehyde transformation:

$$ROH_{sol.} \rightleftharpoons ROH_{oriented}$$

$$ROH_{oriented} \xrightarrow{\text{r.d.s.}} ROH_{ads}$$

$$ROH_{ads} \xrightarrow{\text{fast}} ROH_{ads} + H^+ + e$$

$$ROH_{ads} \xrightarrow{\text{fast}} RO + H^+ + e$$

With the suggested steps we do not exclude the possibility that the adsorption step in the process might take place with dissociation followed by fast charge transfer and desorption. However, it seems unlikely that, in such cases, only the ionisation of the forming H atoms should be fast and the reaction of the forming organic radicals should be slow. This would be in contradiction with the inhibiting effect of the adsorbed material, since under such circumstances the intermediate product of aldehyde formation should accumulate.

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МЕХАНИЗМ АНОДНОГО ОКИСЛЕНИЯ ПЕРВИЧНЫХ СПИРТОВ

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На основании предыдущих исследований [1—3] пришли к выводу, что скорость окисления определяется стадией не электрохимического характера. Полученные экспериментальные данные подтверждают представление, что процесс, определяющий скорость окисления не электрохимической природы, носит адсорбционный характер.