Radiotracer and Electrochemical Study of the Adsorption and Electrocatalytic Oxidation of Glycerol at a Platinized Platinum Electrode

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Adsorption and electrocatalytic oxidation of glycerol at a platinized platinum electrode have been studied in acidic medium ($1 \text{ mol dm}^{-3} \text{ HClO}_4$). Adsorption phenomena were studied by a radiotracer method using ^{14}C -labelled glycerol. Competitive adsorption of glycerol with chloride ions was studied using ^{36}Cl -labelled HCl . Results of potentiostatic polarization studies were examined in the light of information obtained from radiotracer adsorption measurements. An attempt was made to explain the role of strongly chemisorbed organic species and chemisorbed oxygen in the polarization behaviour observed. It was assumed that the shape of the polarization curve is determined by two main factors: reactions on free metal sites and processes taking place on the top of the chemisorbed oxygen.

The electrocatalytic oxidation of aliphatic diols and some polyols at platinized and smooth platinum electrodes has been the subject of several studies. (See, for instance, Refs. 1–5 and references therein.) Despite the many-sided approach to the experimental material accumulated during the last decade, some controversy exists between the different authors concerning the mechanistic interpretation of the phenomena observed. Some authors are of the opinion that the oxidation process takes place exclusively *via* strongly chemisorbed species. Another group of authors assumes that weakly adsorbed species are involved in the main process and the formation and oxidation of the strongly chemisorbed species should be considered as side reactions. Unfortunately, it is very problematic to obtain

direct information on the adsorption processes by pure electrochemical methods. However, the radiotracer method offers a unique possibility of gaining direct information on the adsorption processes of organic species.⁶ In accordance with the considerations outlined above, the aim of this paper is to present some results obtained from a study of the adsorption and electrooxidation of glycerol by the simultaneous application of radiotracer and electrochemical methods.

EXPERIMENTAL

The radiotracer method used for the adsorption studies, preparation of the electrode and its pretreatment prior to the adsorption measurements are described elsewhere.⁷ Glycerol labelled with ^{14}C and HCl labelled with ^{36}Cl of $7.4 \times 10^6 \text{ Bq mmol}^{-1}$ specific activity were used. Some polarization measurements with non-labelled glycerol were carried out using the experimental technique and apparatus described in Ref. 8. All measurements were carried out in the presence of $1 \text{ mol dm}^{-3} \text{ HClO}_4$ supporting electrolyte. Potentials quoted in this paper refer to the hydrogen electrode immersed in this supporting electrolyte (rhe scale). The roughness factors of the platinized platinum electrodes used were about 300–400.

RESULTS

A typical polarization curve of glycerol obtained from a point-by-point potentiostatic measurement going in the direction of the higher

Fig. 1. Potentiostatic polarization curve of glycerol: $c=10^{-1}$ mol dm $^{-3}$.

potentials is shown in Fig. 1. Similar curves may be obtained in the case of smooth platinum electrode by potentiodynamic technique. In the potential range 500–1200 mV three distinct sections may be observed on the polarization curve. (Sections 1, 2 and 3 on the curve in Fig. 1.) It should be mentioned here that the polarization behaviour of glycerol was studied in the concentration range where the oxidation rate at a fixed potential did not change significantly with the concentration of glycerol. ($c > 1 \times 10^{-2}$ mol dm $^{-3}$). The attainment of a stationary or quasi-stationary state requires 10–20 min depending on the potential. The transient phenomena observed following the potential shifts to more positive values are different at the different sections of the polarization curve. These observations attest that the rate of the electrooxidation process is governed by some kind of secondary phenomena which are slower than the charge transfer processes involved in the overall transformation. According to the literature⁹ the main factors which should be taken into consideration for the explanation of the occurrence of the three sections on the polarization curve are as follows:

1. Inhibition of the oxidation process by strongly chemisorbed organic species. Oxidation of these species results in an increase of the oxidation rate as a result of formation of free metal sites (first section).

2. Inhibition of the oxidation process by oxygen adsorption (second section).

3. Oxidation of the organic species on the oxide layer formed on the surface of platinum (third section).

The occurrence of the reaction on the oxidized surface may be shown by means of separate experiments studying the oxidation on preoxidized electrodes. In this case the polarization curve shown in Fig. 2 is taken starting from high

Fig. 2. Polarization curve of glycerol at a preoxidized electrode (1400 mV, 15 min). $c_{\text{glycerol}} = 10^{-1}$ mol dm $^{-3}$.

Fig. 3. Current transients in the case of a preoxidized electrode. Potential: (1) 960; (2) 940; (3) 920; (4) 900; (5) 880; (6) 860; (7) 800 mV.

potentials. This curve may be conceived as if it were composed of two linear $\lg i-E$ plots. However, it is of interest to show how section 2 in Fig. 2 is obtained. This is demonstrated by Fig. 3.

It may be seen from the curve presented in Fig. 3 that the switching of the potential to a lower value is followed by the slow increase of the current (sections 1–6). It can be shown by blank experiments carried out in the absence of glycerol that these phenomena occur only at potentials where the reduction rate of the oxide layer is low and the amount of charge consumed during the reduction does not attain a significant value. However, switching the potential to a value where both the reduction rate and the extent of the reduction are considerable the initial increase of the current is followed by its rapid decrease (section 7).

Fig. 4. Potential dependence of the adsorption of glycerol at concentrations 2×10^{-3} (1) and 2×10^{-2} (2) mol dm^{-3} . Polarization curve at $c = 2 \times 10^{-2}$ mol dm^{-3} (3).

It may be assumed that the slow increase of the anodic current (oxidation rate) should be attributed to the slow formation of free metal sites by the slow reduction of the oxide layer. At each potential a steady (or equilibrium) state may be attained with respect to the number of free metal sites. The rapid decrease of the current at potentials $E < 800$ mV presumably may be explained by the increasing role of the inhibition caused by organic chemisorbed species formed on the free metal sites.

All these considerations outlined above may be confirmed by the radiotracer adsorption measurements.

Fig. 5. Potential dependence of the adsorption of chloride ions ($c_{\text{HCl}} = 4 \times 10^{-3}$ mol dm^{-3}) in the absence (1) and in the presence of glycerol (2) $c_{\text{glycerol}} = 10^{-1}$ mol dm^{-3} . Radiation intensity which is proportional to the amount adsorbed is expressed in counts/min (cpm).

Fig. 6. Potential dependence of the adsorption of glycerol on a preoxidized electrode ($E=1400$, $t=15$ min) $c=2 \times 10^{-2}$ mol dm $^{-3}$.

In Fig. 4 the potential dependence of the adsorption of glycerol is shown at two different concentrations and the polarization curve taken at the higher concentration is presented as well. Species adsorbed in the potential range 200–600 mV are strongly attached to the surface as no exchange of the adsorbed labelled species with non-labelled ones added to the solution phase was observed in a separate experiment. However, it should be emphasized that there is no possibility of distinguishing between the adsorption of glycerol and that of its oxidation products. At least some of the oxidation products remain labelled with ^{14}C and the experimental method used here detects all adsorbed particles present in labelled form. Thus the potential dependence presented in Fig. 4, strictly taken, cannot be considered as the potential dependence of the adsorption of glycerol, at least at the potentials where the oxidation of glycerol takes place. However, there is a possibility to show by an indirect tracer method described in Ref. 10 that with increasing potentials the strongly chemisorbed species are eliminated from the surface. Using ^{36}Cl -labelled chloride ions and non-labelled glycerol the effect of the latter on the adsorption of the former may be studied. Fig. 5 shows the potential dependence of the adsorption of chloride ions in the presence and absence of glycerol. Glycerol inhibits the adsorption of Cl^- -ions in a wide potential range (100–500 mV). This phenomenon can be ascribed to the strong chemisorption of glycerol. Increase of Cl^- adsorption may be observed only at potentials where the oxidation of glycerol starts. This means that the oxidation process is preceded by the

elimination of strongly chemisorbed species which can displace specifically adsorbed anions. This behaviour is similar to that observed in the case of other simple alcohols, and ethylene glycol.¹¹

The radiotracer method permits the study of adsorption phenomena also on a preoxidized electrode. Results of this study are shown by Fig. 6. Practically no adsorption of glycerol occurs on the oxidized surface. Increase of the adsorption may be observed only at the potentials where the increase of the oxidation current was found in the case of the experiments presented in Fig. 3. Fig. 7 shows that the increase of the oxidation current

Fig. 7. Simultaneous change of the adsorption of glycerol (1) and the oxidation rate (2) following a potential switch from 900 mV to 850 mV in the case of a preoxidized electrode, $c_{\text{glycerol}}=2 \times 10^{-2}$ mol dm $^{-3}$.

Fig. 8. Current – as a function of the charge passed through the system in the course of the exhaustive oxidation of 1 mmol glycerol at $E=700$ mV. Charge consumed in the oxidation is referred to 1 mol glycerol and expressed in F units.

at a given potential is connected with the simultaneous increase of the coverage with respect to glycerol. At potentials where the reduction rate of the oxide layer becomes significant the increase of the adsorption initially results in the increase of the oxidation rate but this stage is followed by the rapid decrease of current despite the continuous increase of the adsorption. Experiments carried out with preoxidized electrodes confirm our initial assumption that the increase of the oxidation rate in the potential range 800–900 mV should be attributed to the increase of free metal sites formed by the partial reduction of the oxide layer. Glycerol adsorbs on these sites and the oxidation rate is proportional to the coverage with respect to the adsorbed species. The observation made in the case of a considerable reduction of the oxide layer requires further explanations. This problem will be discussed later.

Experiments aiming at the exhaustive oxidation of a given amount of glycerol show that its complete transformation into CO_2 may be achieved even at low potentials. This is shown in Fig. 8. (For the complete oxidation of glycerol 14 F are required.)

However, there is no doubt that the oxidation process takes place in a stepwise manner. The first step in this reaction sequence is the formation of glyceraldehyde and to a lesser extent that of dioxacetone. At low potentials and high

glycerol concentrations the accumulation of these intermediates in the solution phase may be observed.^{12,13} (The presence of α -oxy-carbonyl compounds in the solution phase can be easily detected by the Fehling reaction.)

DISCUSSION

It may be concluded from the simultaneous application of radiotracer adsorption and electrochemical polarization measurements that, in accordance with previous views, in a wide potential range two different reactions occur with glycerol at a platinum electrode. The first reaction is the oxidation process on bare metal surface sites. This was clearly demonstrated by the observations made in the course of the reduction of the oxide layer. A significant oxidation current may be attained at very low glycerol coverages when the predominant part of the surface is covered by chemisorbed oxygen. On the other hand, following the elimination of the oxide layer there is a significant decrease of the oxidation rate despite the increase of the coverage with respect to glycerol. This phenomenon may be explained on the basis of information available from the literature concerning the behaviour of modified platinum electrodes.¹⁴ It has been shown that the catalytic activity of a platinum electrode may be increased by the

presence of strongly adsorbed species (for instance, metal adatoms).

It is assumed that the increase of catalytic activity is due to the prevention of the self inhibition of the oxidation process by the organic species. The inhibition is caused by side reactions leading to the strong chemisorption of the organic species studied. However, for the formation of these strongly chemisorbed species there is a need for several neighbouring surface sites. In the presence of preadsorbed species leaving only isolated free surface sites available for the reaction studied there will be insufficient neighbouring surface sites for the further formation of strongly chemisorbed species. It may be assumed that similar phenomena may play a role in the case of the stepwise reduction of the oxide layer. At the beginning of the reduction of the oxide layer the free metal sites are isolated from one another. Thus the formation of strongly chemisorbed species is inhibited. As the reduction of the oxide layer becomes more pronounced free surface sites will be formed around an adsorbed organic species. Thus more and more strongly chemisorbed species are formed and the reaction rate should decrease as the number of the strongly chemisorbed species increases.

The strong chemisorption of the organic species is accompanied by a significant change of the composition and structure of the molecule (dehydrogenation, rupture of C-C bonds *etc.*). These fragments cannot be involved in the main reaction sequence resulting in well-defined intermediates which can be detected in the solution phase. Presumably the oxidation of strongly chemisorbed species leads directly to CO₂ without the participation of any desorbable intermediate. On increasing the potential of the electrode the oxidation of strongly chemisorbed species occurs and free sites available for the main oxidation process are produced. At a given potential both processes, the formation of strongly chemisorbed species on the free sites and oxidation of these species, occur simultaneously. Finally, a steady state should be attained with respect to the number of sites freed from strongly chemisorbed species. Thus it may be expected that the rate of the main oxidation process will be proportional to the number of these sites.

It is known from the literature¹⁻⁵ that in the oxidation of alcohols the first step is a dehydrogenation reaction. Thus in the case at the

oxidation of glycerol the reactions leading to glyceraldehyde may be formulated as follows:

These processes are accompanied by the formation of strongly chemisorbed species which originate either from the weakly adsorbed species figuring in eqn. (1) or from the adsorbed radical figuring in eqn. (2). On the other hand, the oxidation of these strongly chemisorbed species should also be taken into consideration. The rate of reaction 2 presumably does not depend on the potential as this step is a chemical process without charge transfer. Only the coverage with respect to the weakly adsorbed species may be some function of the potential.

Similar argumentation may refer to the formation of strongly chemisorbed species as, according to our initial assumption, these species are formed from the weakly adsorbed molecules.

In contrast to this the oxidation of strongly chemisorbed species depends significantly on the potential. Thus the coverage with respect to strongly chemisorbed species; consequently, the number of sites available for the weak adsorption will depend on the potential. At the same time the rate of the main oxidation process depends on the coverage with respect to the weakly adsorbed species. The applicability of this model has been shown in the case of the interpretation of the phenomena observed in the course of the oxidation of ethylene glycol and its derivatives.¹⁵

The occurrence of the maximum on the polarization curve presented in Fig. 1 should be explained by the adsorption of oxygen. With increasing potentials the extent of the oxygen adsorption increases and the number of the sites available for the oxidation process decreases. As a result of this phenomenon, a maximum and thereafter the decrease of the oxidation rate should be observed. However, there is an additional phenomenon, the oxidation of the organic species on the oxide layer, which should be taken into consideration.

The nature of the reaction occurring at the oxide layer is not clear. According to the results obtained by means of tracer adsorption studies there is no significant adsorption of organic species on preoxidized electrodes. Thus there is no possibility of treating the problem in terms of heterogeneous kinetics involving reactions with adsorbed species. However, it is possible that the coverage with respect to the reacting species is so low that the adsorption cannot be followed by the method used in this work. On the other hand, the assumption of some direct reaction of the surface oxide or absorbed oxygen with organic molecules cannot be excluded completely. Disregarding the problems connected with the mechanism of this process, it is an experimental fact that the rate of the oxidation of the oxidized surface increases with increasing potentials.

Thus the initial inhibition caused by the formation of oxide layer should be followed by the increase of the oxidation rate as the potential is shifted to more positive values.

Summarizing our considerations it can be stated that the general tendencies observed in the electrocatalytic oxidation of glycerol are very similar to those reported in different alcohols, diols and their oxidative derivatives. Unfortunately, at present only a qualitative explanation of the phenomena observed could be given on the basis of the available experimental material.

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