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Study of the electrooxidation of 1,3-propanediol on a gold electrode in basic medium

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A study of the mechanism of electrooxidation of 1,3-propanediol on a gold electrode in basic medium has been made. The kinetic parameters measured, together with other experimental data, allow the formulation of a mechanism in which both 1,3-propanediol and OH^- ions adsorb on the gold surface and the rate determining step is an interaction between both coverages with the result of the formation of an adsorbed radical, whose oxidation leads to the formation of 3-hydroxypropanoic acid which has been identified by nuclear magnetic resonance (NMR).

1. Introduction

The direct oxidation, in a fuel cell, of organic compounds derived from biomass, such as alcohols, is a very attractive way of converting chemical energy into electrical energy. The fuels mainly used have been methanol and ethylene-glycol. The latter has been specially studied, not only for its possible use in a fuel cell [1], but also because it is the simplest among the aliphatic diols [2, 3].

This work was carried out to investigate the influence of several factors, such as concentration, pH or temperature, on the oxidation mechanism of a diol of low molecular weight such as 1,3-propanediol.

In comparison with ethylene-glycol, there are few studies of the electrochemical oxidation of propanediols. Sokolova [4] carried out studies on platinum in acid medium. Also Huser *et al.* [5] studied the oxidation of 1,2-propanediol and 1,3-propanediol. They found, in perfect agreement with Sokolova, that the behavior of 1,2-propanediol towards oxidation is not that of a secondary alcohol, such as 2-propanal [6]; on the contrary, a great similarity exists with ethylene-glycol. On the other hand, 1,3-propanediol oxidizes in a very similar way to that of primary alcohols [4, 6] and only the oxidation of one of the two alcohol functions takes place.

Raicheva *et al.* [7] and Iotov *et al.* [8] studied the oxidation of propanediols on gold, platinum and Au/Pt alloys in alkaline solution. They found that, in the case of 1,3-propanediol, current densities were 28 times higher on a 40/60 Pt/Au alloy that on pure platinum.

2. Experimental details

Cyclic voltammetry was employed as the experimental method. Plots were obtained from a conventional electronic device consisting of a Brucker Mod.310 potentiostat, a PAR Mod.175 Generator and a Hewlett-Packard Mod.7047A X–Y Recorder.

The experiments were carried out in a double walled Pyrex glass electrochemical cell. The working electrode was a gold plate (99.999% pure) of $1\,cm^2$ geometrical area. A gold counter electrode and a mercurous sulphate reference electrode (MSE) were used.

All experiments were carried out at 25° C except when measuring activation enthalpy. Accuracy was always $\pm 0.2°$ C.

Electrolyte solutions were prepared from bidistilled water which was previously purified by means of a Millipore Mod. Milli-Q system, and from P.A. Merck K_2SO_4 and KOH reagents. 1,3-propanediol was Merck 'zur synthese' reagent.

Prior to each measurement, solutions were deoxygenated with N_2, and an N_2 atmosphere was maintained above the electrolyte solution during the experiment.

3. Results

Voltammetric i/E curves show that the oxidation of 1,3-propanediol in alkaline medium starts in a potential range corresponding to the electrode surface coverage by the OH^- ions. Oxidation rate increases at more anodic potential, reaching its maximum value when the formation of gold oxides begins. For 1,3-propanediol concentrations higher than 5×10^{-3} M and potentials more anodic than the peak potential, E_p, oxidation is inhibited. Nevertheless, for lower concentrations, the appearance of a second peak is observed at potentials close to the peak potential corresponding to the formation of gold oxides in the absence of electroactive substance.

Figure 1b shows the effect of changes in the lower potential limit, E_c, on the oxidation peak in the anodic sweep. The maximum current density decreases as OH^- ion adsorption decreases, confirming that the reaction is catalysed by the hydroxyl ions.

The cathodic sweep only shows gold oxide reduction peaks when the diol concentration is $C_{1,3} < 5 \times 10^{-2}$ M. However, a peak corresponding to 1,3-propanediol oxidation appears over the whole concen-

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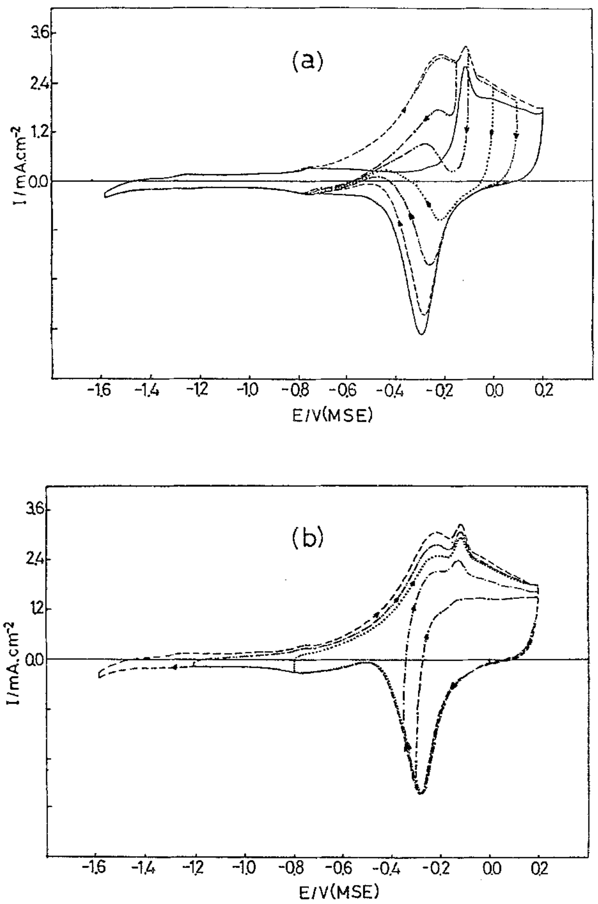


Fig. 1. Influence of upper E_a (a) and lower E_c (b) potential limits on the cyclic voltammograms for the oxidation of 1,3-propanediol on an Au electrode (0.1 M KOH, $C_{1,3} = 5 \times 10^{-3}$ M, $T = 25°$C, $v = 50\,\mathrm{mV\,s^{-1}}$).

tration range, taking place at similar potentials to those in the anodic sweep. This oxidation peak is clearer if the anodic potential limit corresponds to the beginning of the formation of surface gold oxides (Fig. 1a). An increase in the potential limit, E_a, makes the gold oxide reduction process more irreversible and the oxidation of 1,3-propanediol takes place at more cathodic potentials with a corresponding decrease in current density.

3.1. *Determination of kinetic parameters*

Curves $i = f(E)$ were recorded at a sweep rate of $v = 5\,\mathrm{mV\,s^{-1}}$ in KOH (pH = 13), 1,3-propanediol solutions. Diol concentration ranged from 10^{-3}–10^{-1} M and temperature was 25°C.

The plot of the log of current density against potential shows two Tafel zones (Fig. 2). The first Tafel zone, which corresponds to the start of the curve, shows an average value for the slope of 110 ± 3 mV. The value of the product of the transference coefficient by the number of electrons transfered (αn) is 0.54 in a concentration. In fact, the plot of log i as a function of those potentials the current density is proportional to concentration. In fact, the plot of log i is a function of the log of concentration shows straight lines whose slope is 1 in a potential range from -0.88 to -0.79 V (Fig. 3).

At more anodic potentials there is a second Tafel zone, whose slope implies a very low value for the product αn (Table 1). When concentration is $C_{1,3} < 10^{-2}$ M the order is still 1, but it decreases at higher concentrations until it reaches a zero value at $C_{1,3} = 10^{-1}$ M and at a potential corresponding to the maximum current (Fig. 4).

On superposing the potentiodynamic curves there is a slight shift in the peak potential towards more anodic values when the concentration of 1,3-propanediol increases. This fact could indicate the adsorption of diol on the electrode surface, so decreasing the

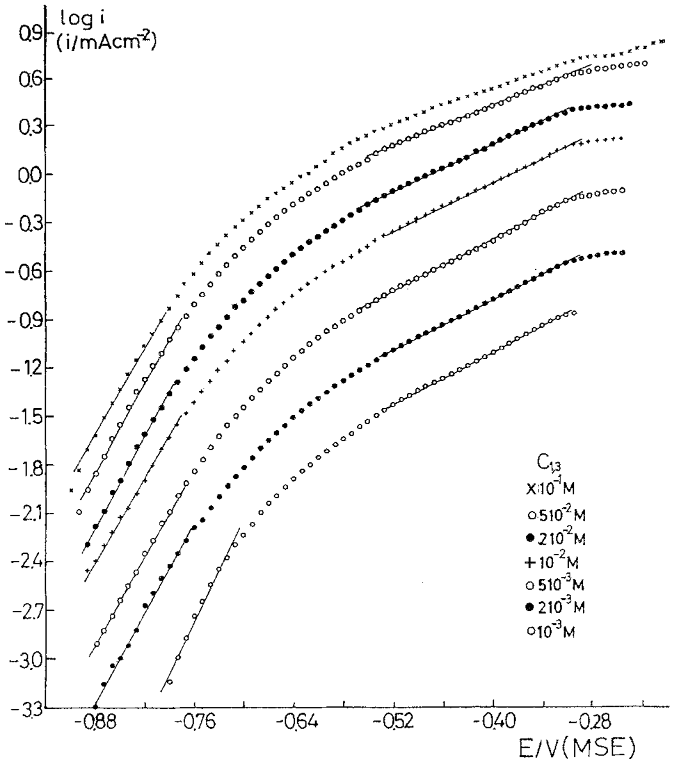


Fig. 2. Tafel slopes at different 1,3-propanediol concentrations in KOH + K_2SO_4 (pH = 13), $v = 5\,\mathrm{mV\,s^{-1}}$, $T = 25°$C.

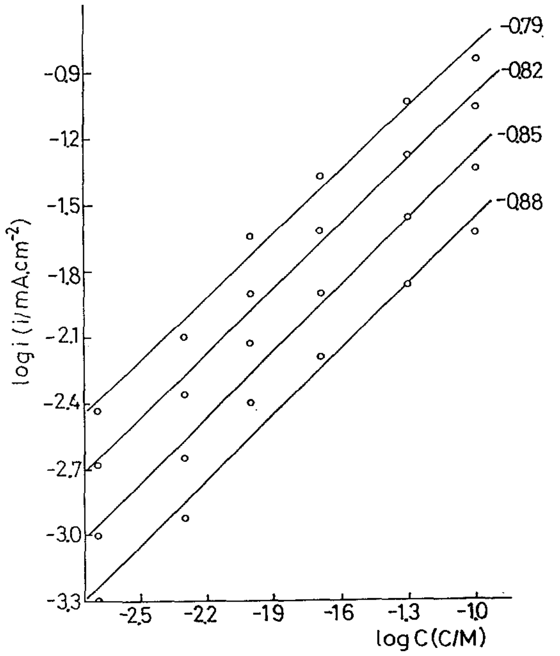


Fig. 3. Dependence of log i on $C_{1,3}$, at constant potential, in KOH + K_2SO_4 (pH = 13), T = 25°C.

coverage of adsorbed OH^- and it being necessary to apply a more anodic potential in order to attain the maximum current density.

Also, a study was carried out in the pH range 11.68–13.80, at a 1,3-propanediol concentration of 2×10^{-2}M. An increase in the OH^- ion concentration makes oxidation easier, so that it commences at more cathodic potentials. From the analysis of the curves recorded at quasi-stationary conditions (v = 5 mV s^{-1}) two Tafel zones were obtained (Fig. 5). The first Tafel zone, at more cathodic potentials, shows a constant slope of 106 ± 3 mV and a value for αn of 0.55. This value can be compared to the one calculated from the Tafel lines at different concentrations.

Due to the cathodic shift at the beginning of oxidation on increasing pH, it is only possible to calculate the order with respect to the OH^- ion concentration in a potential range from −0.83 to −0.81 V, obtaining a value of 0.6 in a pH range 11.68–13.10. This value is maintained at more anodic potentials, but over a smaller pH range (Fig. 6).

At more anodic potentials (from −0.55 to −0.35 V) there is a second Tafel zone. The αn value calculated from the Tafel slope is shown in Table 2. At these potentials the current density increases on increasing the OH^- concentration, showing a positive reaction order.

However, the current density at the peak potential increases with pH only up to 12.56. At higher pH, a limiting current is reached, but at progressively more cathodic potentials, because the OH^- coverage (θ_{OH}) necessary to attain the maximum intensity (at a constant diol concentration) is obtained at progressively more cathodic potentials on increasing pH. A further increase in θ_{OH}, either by increasing the pH at a constant potential, or by applying a potential more anodic than the peak potential (E_P) at a constant pH value, implies a decrease in the coverage by electroactive substances and, consequently, inhibition of the oxidation. The order with respect to OH^- concentration will be negative.

Table 2.

pH	13.80	13.10	12.79	12.56	12.11	11.68
α	0.15	0.14	0.14	0.14	0.14	0.11

3.2. *Determination of the activation energy*

Figure 7 shows the effect of temperature on the oxidation of 1,3-propanediol at a concentration of 2×10^{-2}M and pH = 13. On increasing the temperature from 3 to 39° C, the current density increases over the whole potential range and the beginning of oxidation takes place at more cathodic potentials.

From the slopes of the straight lines log i/T vs $1/T$ (Fig. 8), a constant value of the apparent activation enthalpy, $\Delta H^{\neq}$, of 10.5 kcal mol^{-1} ≈ 44 kJ mol^{-1} is obtained at different potentials within the Tafel region (Fig. 9).

Considering that the rate equation for 1,3-propanediol oxidation ($C_{1,3} = 2 \times 10^{-2}$M) at pH = 12.79 in a potential range within the first Tafel region is:

$$i = nFK(k_B T/h)C_{1,3}^{1}C_{OH}^{0.6}\exp(-\Delta H^{\neq}/RT) \times \exp(\Delta S^{\neq}/R)\exp(\alpha nFE/RT)$$

then

$$\ln i/T = \ln[nFK(k_B/h)C_{1,3}^{1}C_{OH}^{0.6}] + \Delta S^{\neq}/R - \Delta H^{\neq}/RT + \alpha nFE/RT$$

The apparent activation entropy, $\Delta S^{\neq}$, can be calculated by extrapolation at $1/T = 0$. The value varies from −43 to −39 cal mol^{-1} K^{-1} over a potential range of −0.84 to −0.76 V (Fig. 9).

Once $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are known, Gibb's free activation energy $\Delta G^{\neq}$ at 25° C can be obtained. Its variation with potential is shown in Fig. 9.

3.3. *Determination of final products*

In order to propose an oxidation mechanism for 1,3-propanediol, it is fundamental to know the intermediates and the reaction products. To this purpose, elec-

Table 1.

$C_{1,3}$	10^{-1}	5×10^{-2}	2×10^{-2}	10^{-2}	5×10^{-3}	2×10^{-3}	10^{-3}
α	0.10	0.12	0.14	0.14	0.15	0.15	0.15

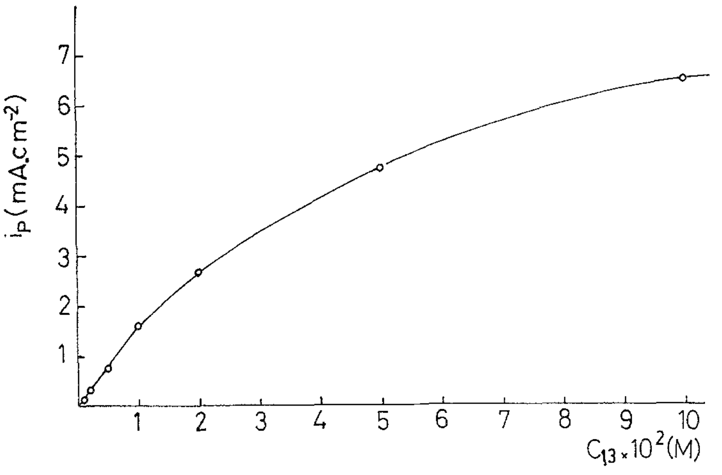


Fig. 4. Change of i_P with 1,3-propanediol concentration in KOH + K_2SO_4 (pH = 13), v = 5 mV s^{-1}, T = 25° C.

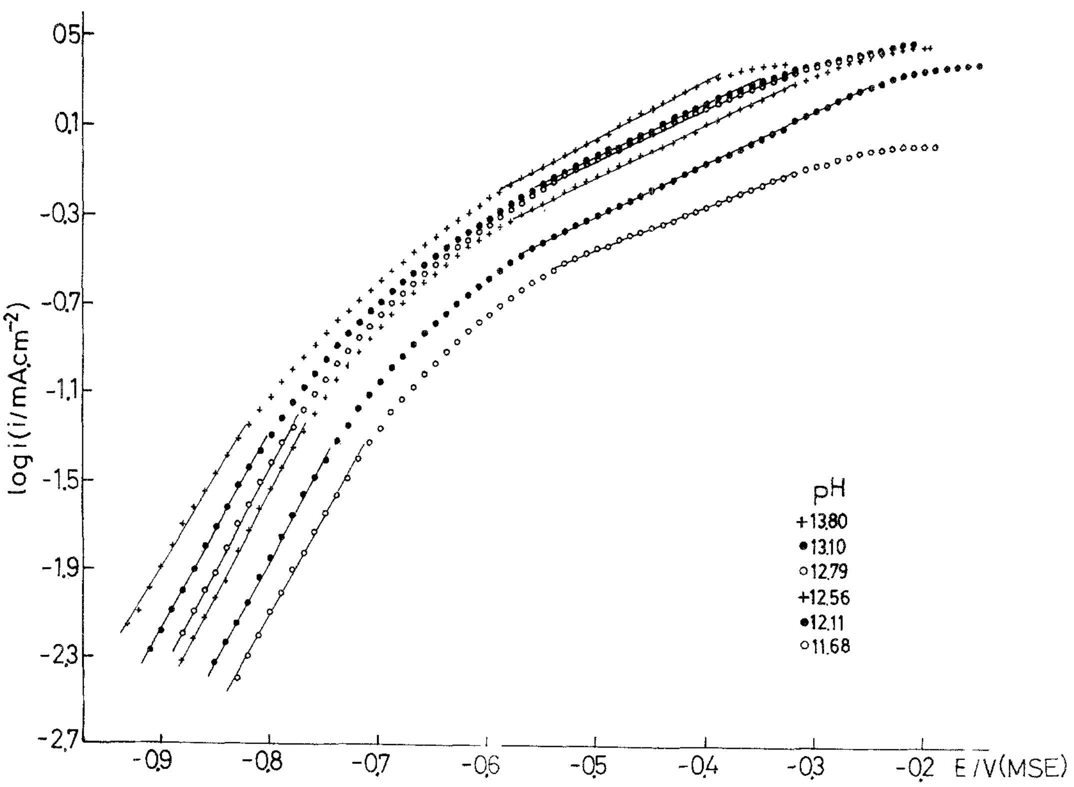


Fig. 5. Tafel slopes at different pH values ($C_{1,3}$ = 2 × 10^{-2} M, v = 5 mV s^{-1}, T = 25° C).

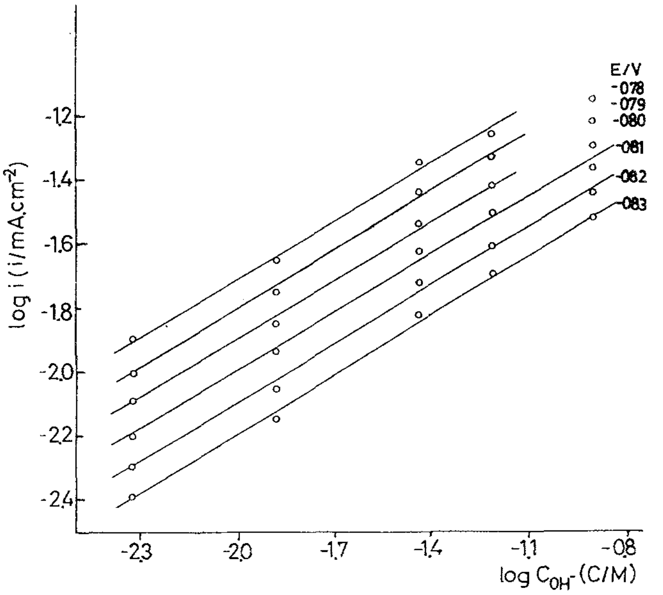


Fig. 6. Dependence of log i on log C_{OH} at constant potential ($C_{1,3}$ = 2 × 10^{-2} M, T = 25° C).

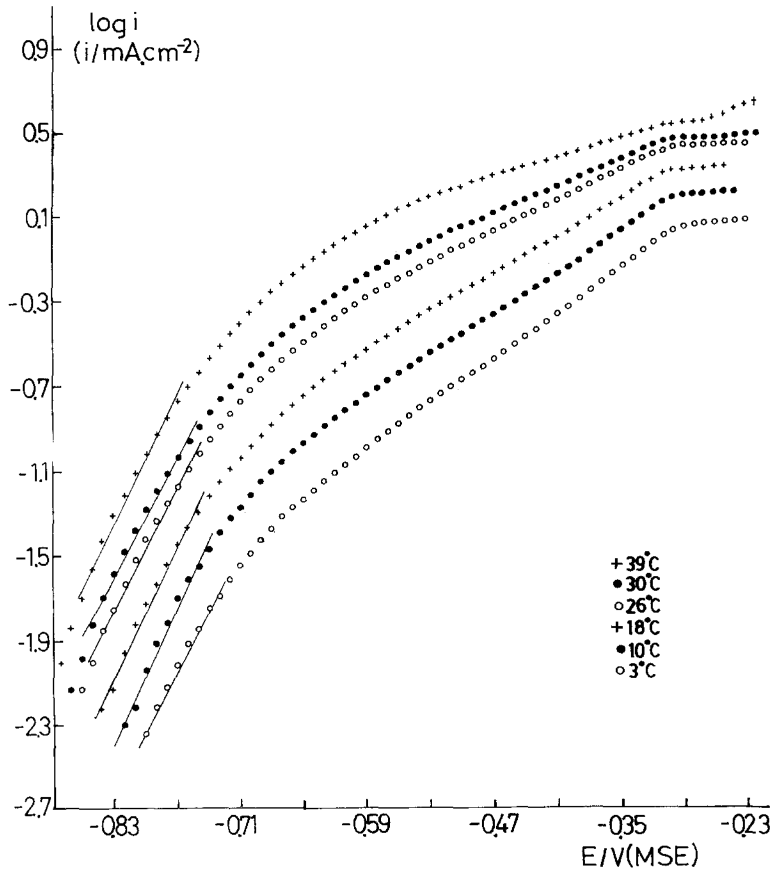


Fig. 7. Tafel slopes at different temperatures in 2×10^{-2} M 1,3-propanediol, pH = 13, v = 5 mV s^{-1}.

trolysis of the diol was carried out, by means of cyclic voltammetry, in alkaline medium, using 0.1 M KOH as supporting electrolyte. Diol concentration was 5×10^{-2} M. The potential limits were -1.20 and -0.23 V (vs MSE) and the sweep rate $v = 0.20$ V s^{-1}.

To gather the possible gases released during the electrolysis, a 2,4-dinitrophenylhydrazine solution was placed at the cell exit, and a yellow crystalline solid was obtained. 2,4-Dinitrophenylhydrazine is used for the identification of aldehydes and ketones, as the

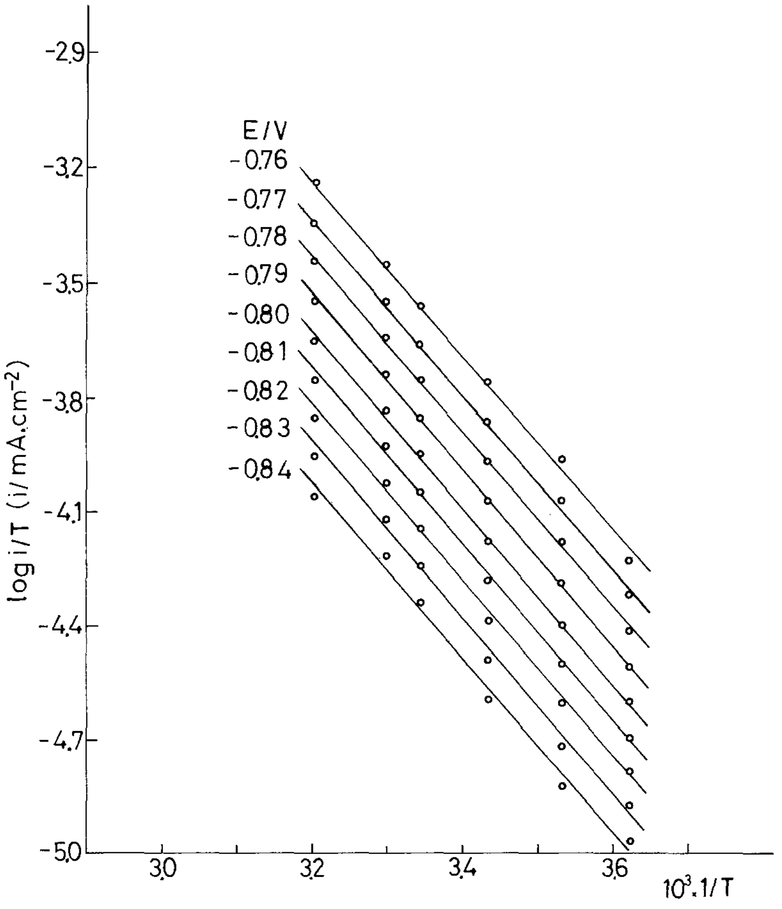


Fig. 8. Dependence of log i/T on $1/T$ at constant potential ($C_{1,3} = 2 \times 10^{-2}$ M, pH = 13).

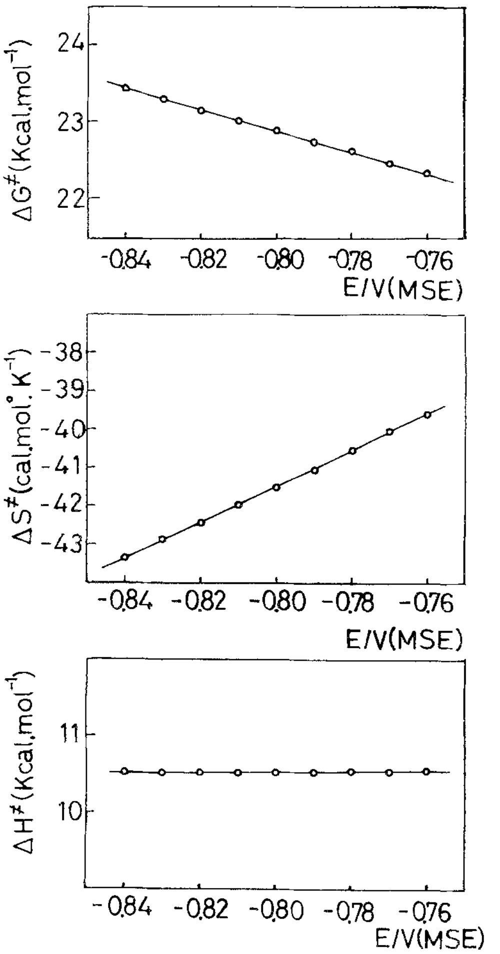


Fig. 9. (a) Variation of $\Delta H^{\neq}$ with the potential. (b) Variation of $\Delta S^{\neq}$ with the potential. (c) Variation of $\Delta G^{\neq}$ with the potential.

corresponding 2,4-dinitrophenylhydrazone is formed. The hydrazone colour gives an indication of the structure of the aldehyde or ketone it is derived from. So, a yellow colour is characteristic of aldehydes whose carbonyl group is not conjugated to another functional group, such as 3-hydroxypropanal. Identification was attempted by thin layer chromatography, NMR and infrared spectroscopy, but no results were obtained about the molecular structure of a possible aldehyde as an intermediate product of reaction. Likewise, in the determination of the melting point a change in colour was noticed at 144° C, then melting at 150° C. We can compare this result with one obtained from the literature for the 2,4-dinitrophenylhydrazone of propanal, which is orange at 148° C, red at 150° C and melts at 155° C. However, commercial dinitrophenylhydrazine melts at 201° C and a pure sample at 198° C.

For the determination of oxidation products by nuclear magnetic resonance (NMR) an electrolysis at pH = 14 and $C_{1,3} = 5 \times 10^{-1}$ M in deuterium oxide (99.8% pure) was carried out. The time calculated for the complete oxidation was 30 days for an average current of 14 mA. In the first place, a spectrum was produced after 15 days (Fig. 10). The bands A and B correspond to the initial product, 1,3-propanediol, and bands C and D to the oxidation product 3-hydroxypropanoic acid. It is possible to know, in an approximate way, the existing proportion in electrolysis between the initial product and the product resulting in oxidation. Considering that the ratio between the height of the integral lines of bands A and C is 9 : 1, it can be estimated that the 1,3-propanediol is in a proportion of 9 : 1 with respect to the 3-hydroxypropanoic acid. This is to say that the initial product is the predominant substance. On the contrary, in a second spectrum, made after a longer electrolysis time (30 days), the amount of 3-hydroxypropanoic acid had increased with respect to the initial product, the proportion being 2 : 3 (Fig. 11).

4. Discussion

The role of the OH⁻ ions adsorbed on the electrode surface, in the mechanism of the electrochemical oxidation, is indicated because (a) 1,3-propanediol is not oxidized in acid medium on the gold electrode and (b) the oxidation of 1,3-propanediol, in basic medium, takes place at sufficiently anodic potentials, where the electrode is partially covered by hydroxyl ions, this being the first step of the proposed oxidation mechanism.

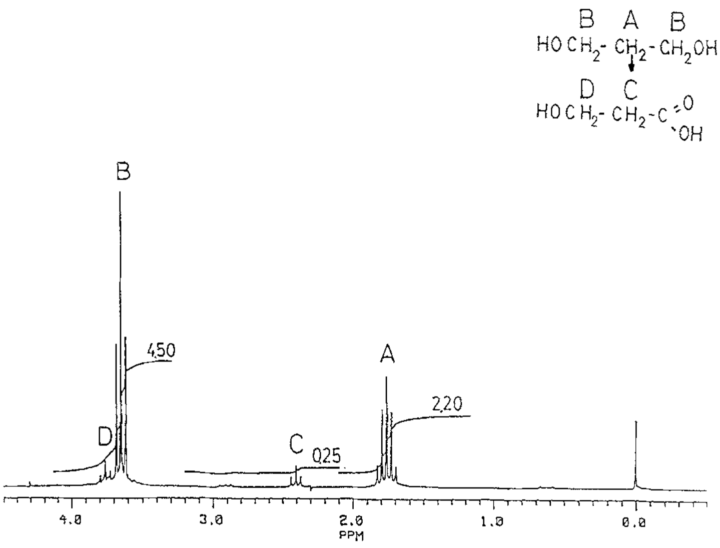


Fig. 10. Spectra ¹H of the electrolyte solution (5×10^{-1} M 1,3-propanediol in 1 M KOH) after electrolysis times (15 days) on gold electrode. $T = 25$° C.

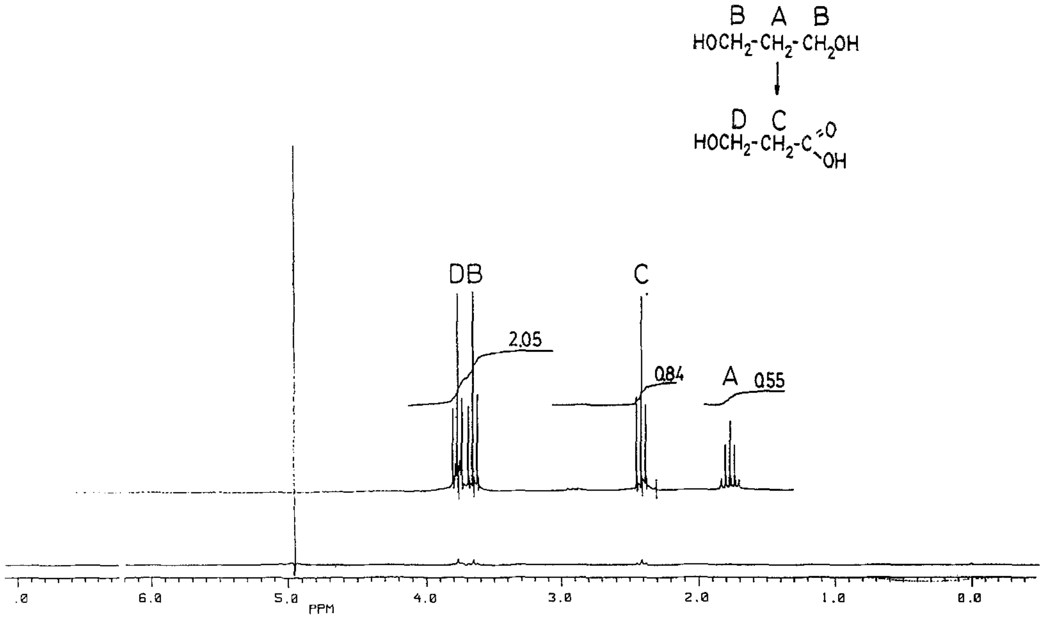


Fig. 11. Spectra ^{1}H of the electrolyte solution (5×10^{-1} M 1,3-propanediol in 1 M KOH) after electrolysis times (30 days) on gold electrode. $T = 25°$C.

Step 1

$$\mathrm{Au} + \mathrm{OH}^- \rightleftharpoons \mathrm{AuOH_{ads}} + e^-$$

If we suppose that the hydroxyl ions are adsorbed following a Frumkin isotherm, in quasi-equilibrium conditions, the following electrochemical isotherm is obtained:

$$\theta_{\mathrm{OH}}/(1 - \theta_{\mathrm{T}}) \times \exp[g(\theta)/RT] = k_1 C_{\mathrm{OH}} \exp FE/RT \qquad (1)$$

where function $g(\theta)$ has been defined considering that there are several adsorbed species on the electrode and, even though the adsorption energy is different for each of them, the variation rate of the different adsorption energies with the coverage is the same. So:

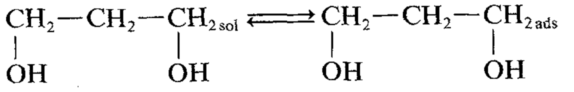
$$g(\theta) = f_{\mathrm{OH}} RT\theta_{\mathrm{OH}} + f_{\mathrm{R}} RT\theta_{\mathrm{R}} \qquad (2)$$

where θ_{R} is the gold surface fraction covered by a dehydrogenated radical and f is the factor of interaction between the adsorbed species.

The variation of i_{P} and E_{P} with the diol concentration together with the behaviour observed for these parameters with pH indicate that a coadsorption of the molecules of 1,3-propanediol and of the OH$^-$ ions on the electrode surface can take place in agreement with Holze and Beltowska-Brzezinska [9].

Consequently, the diffusion of 1,2-propanediol towards the electrode surface has been proposed as a second step of the mechanism, being adsorbed on the free sites following a Langmuir isotherm.

Step 2


$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_{2\,sol}}} \rightleftharpoons \underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_{2\,ads}}}$$

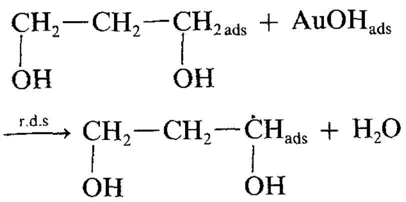
In quasi-equilibrium conditions we obtain:

$$\theta_{1,3} = k_2(1 - \theta_{\mathrm{T}})C_{1,3} \qquad (3)$$

θ_{T} being the addition of the coverage of the adsorbed species ($\theta_{\mathrm{T}} = \theta_{\mathrm{OH}} + \theta_{1,3} + \theta_{\mathrm{R}}$). $C_{1,3}$ is the concentration of propanediol in solution and k_2 the equilibrium constant for that step.

The third step supposes the homopolar breaking of the bond between hydrogen and carbon placed in position α with respect to the OH group, by means of an interaction with the AuOH coverage, to make up a dehydrogenated radical which is adsorbed following a Temkin isotherm.

Step 3


$$\underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\mathrm{CH_{2\,ads}}} + \mathrm{AuOH_{ads}} \xrightarrow{\mathrm{r.d.s}} \underset{\mathrm{OH}}{\mathrm{CH_2}}-\mathrm{CH_2}-\underset{\mathrm{OH}}{\dot{\mathrm{C}}\mathrm{H_{ads}}} + \mathrm{H_2O}$$

Supposing an activated adsorption both for OH$^-$ ions and for the radical, the rate equation is

$$v_3 = \vec{k}_3 \theta_{1,3} \theta_{\mathrm{OH}} \exp[(1 - \gamma)g(\theta)/RT] \times \exp[-\gamma g(\theta)/RT] \qquad (4)$$

where γ is the symmetry factor for the adsorption.

If the third step is rate determining the $g(\theta)$ function will be approximately

$$g(\theta) \approx f_{\mathrm{OH}} \theta_{\mathrm{OH}}$$

as θ_{R} will be very small. On top of this the steps 1 and 2 will be in quasi-equilibrium. For intermediate values of $\theta_{\mathrm{OH}} (0.2 \leqslant \theta_{\mathrm{OH}} \leqslant 0.8)$ Equation 1 becomes

$$\exp[g(\theta)/RT] = k_1 C_{\mathrm{OH}} \exp FE/RT \qquad (5)$$

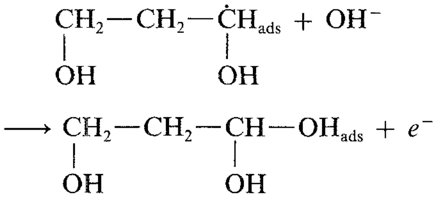
Substituting the function $g(\theta)$ as well as the $\theta_{1,3}$ value given in Equation 3 in the rate Equation 4 and neglecting the variation of the pre-exponential term with θ_{OH}, the rate equation for oxidation of 1,3-propanediol is obtained, in terms of current density

$$i_3 = \vec{k}_3 k_2 k_1^{1-2\gamma}(1-\theta_T)C_{1,3}C_{OH}^{1-2\gamma} \times \exp[(1-2\gamma)FE/RT] \qquad (6)$$

Equation 6 shows that the reaction order with respect to the concentration of 1,3-propanediol is one, coinciding with the experimental results obtained. Likewise, the activation coefficient, γ, can be directly calculated from the value of the order of reaction with respect to the hydroxyl ions concentration. With this γ value, the Tafel slope obtained is 98 mV per current decade. This value is comparable to those obtained from quasi-stationary measurements carried out either at constant pH and varying the diol concentration, or for a constant concentration of 1,3-propanediol and varying the pH, which are 110 and 106 mV, respectively.

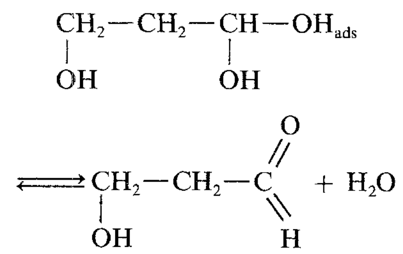
The steps following the rate determining step lead to the formation of 3-hydroxypropanal whose presence in solution could not be confirmed, although the formation of a yellow crystalline solid with 2,4-dinitrophenylhydrazine is an indication of its existence.

Step 4



$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{\dot{C}H_{ads}}} + OH^- \longrightarrow \underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{CH}}-OH_{ads} + e^-$$

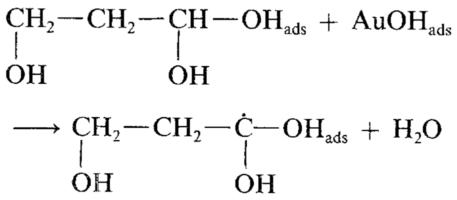
Step 5



$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{CH}}-OH_{ads} \rightleftharpoons \underset{OH}{\underset{|}{CH_2}}-CH_2-C\overset{\displaystyle O}{\underset{\displaystyle H}{}} + H_2O$$

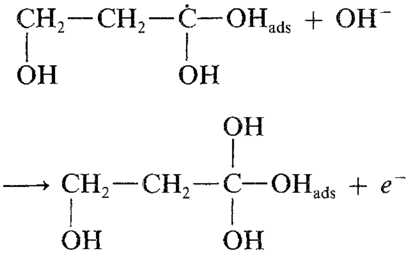
The later oxidation means the formation of 3-hydroxypropanoic acid, which has been identified by NMR.

Step 6



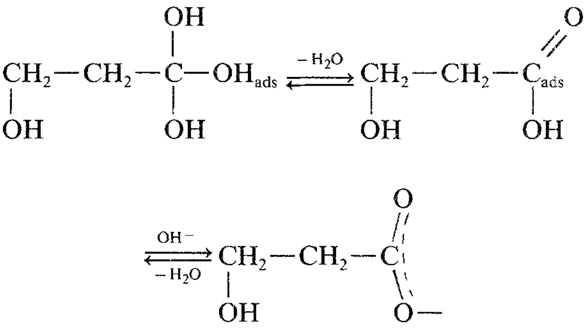
$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{CH}}-OH_{ads} + AuOH_{ads} \longrightarrow \underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{\dot{C}}}-OH_{ads} + H_2O$$

Step 7



$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\underset{OH}{\underset{|}{\dot{C}}}-OH_{ads} + OH^- \longrightarrow \underset{OH}{\underset{|}{CH_2}}-CH_2-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OH_{ads} + e^-$$

Step 8



$$\underset{OH}{\underset{|}{CH_2}}-CH_2-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OH_{ads} \xrightleftharpoons{-H_2O} \underset{OH}{\underset{|}{CH_2}}-CH_2-\overset{O}{\overset{/\!/}{\underset{OH}{\underset{|}{C_{ads}}}}} \xrightleftharpoons[-H_2O]{OH^-} \underset{OH}{\underset{|}{CH_2}}-CH_2-C\overset{\displaystyle O}{\underset{\displaystyle O^-}{}}$$

The oxidation could procede by breaking of the hydrogen of carbon (3) to yield 1,3-propanedioic acid. However, this oxidation product has not been identified. Probably, the 3-hydroxypropanoic acid has a similar behaviour in basic medium and on a gold electrode to that of glycolic acid [10], not being noticeably oxidized.

References

[1] H. Cnobloch, D. Groppel, H. Kohlmuller, D. Kuhl and G. Siemsen, in 'Power Sources 7' (edited by J. Thomson) (1979) Vol. 24, p. 389.

[2] F. Kadirgan, B. Beden and C. Lamy, *J. Electroanal. Chem.* **136** (1982) 119; **143** (1983) 135.

[3] E. Santos and M. C. Giordano, *Electrochim. Acta* **30** (1985) 871.

[4] E. Sokolova, *Electrochim. Acta* **24** (1979) 24.

[5] H. Huser, J. M. Leger and C. Lamy, *Electrochim. Acta* **30** (1985) 1409.

[6] S. N. Raicheva, *Z. Phys. Chem.* **264** (1983) 65.

[7] S. N. Raicheva, E. I. Sokolova, S. Kalcheva and W. Vielstich, 29th Meeting of the ISE, Budapest, 'Ext. Abstr.' (1978) p. 780.

[8] P. I. Iotov, S. V. Kalcheva, E. I. Sokolova and S. N. Raicheva, *Dok. Bulg. Akad. Nauk.* **39** (1986).

[9] R. Holze and M. Beltowska-Brzezinska, *J. Electroanal. Chem.* **201** (1986) 387.

[10] F. Kadirgan, Thesis, Université de Poitiers, (1983).