Anodic Oxidation Of Propanol on Platinized Platinum Electrode

by

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Anodic Oxidation Of Propanol On Platinized Platinum Electrode

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ABSTRACT

The investigation of the anodic oxidation of propanol at platinized platinum in 1 N H₂SO₄ solution by cyclic linear sweep gives the following results: In the cathodic sweep an anodic peak related to the formation of adsorbed intermediate oxidation product of propanol is observed. This adsorbed intermediate inhibits the adsorption of hydrogen. The saturation coverage of hydrogen at platinized platinum electrode in 1 N H₂SO₄ containing 3.10⁻⁴ M to 3.10⁻²M. propanol is equal to 0.4. Adsorbed product is oxidized at 0.35 V. The second oxidation of propanol occurs at 0.45 V. The anodic reaction order of propanol is equal to 0.5. The kinetic of oxidation mechanism is explained with the aid of Langmuir isotherm for dissociative adsorption. Propanol oxidation also occurs at the Pt–O formation region. Adsorbed intermediate is the poisoning specie for propanol oxidation.

INTRODUCTION

The anodic oxidation of alcohols on noble metals in aqueous solutions has been the subject of several studies [1–6], as alcohols are attractive fuels in fuel–cell technology. In order to increase the catalytic activity of electrodes or the rate of alcohol oxidation, the electrode reaction mechanism must be known.

We chose our electrode as platinized platinum because its behaviour at different potentials is relatively well known and decided to employ propanol as reagent because most of the studies were done on methanol.

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EXPERIMENTAL

1. The electrochemical cell;

The employed electrochemical cell consists of three compartments for the counter, working and reference electrode separated by stopcocks. The volume of the electrolyte in the working electrode compartment amounted 150 ml. Counter and working electrodes consisted of platinized platinum. For platinizing, platinum electrode was potentiostated at 250 mV / r.h.e in chloroplatinic acid solution for approximately thirty minutes. After washing with doubly distilled water, oxidized in 1 N Na₂SO₄ solution at oxygen evolution potential and then reduced at hydrogen evolution potential for five minutes successively. Saturated calomel electrode was used as a reference. All solutions were prepared with p.a. chemicals and doubly distilled water. Propanol concentration was varied between 3.10⁻⁴ M and 3.10⁻²M. The solutions were deaerated by bubbling with oxygen free nitrogen. During the experiments, the room temperature was 16°C. All the potentials given in this work were reported relative to the hydrogen electrode.

2. Measuring Unit.

Current–potential measurements were performed under potentiostatic control using Taccussel 30.01 potentiostat in combination with Taccussel UAP–3 Unit and EPL 2 recorder. Current–potential curves were recorded in the potential range from 0.0 V to 1.42 V at the sweep rates of 2.5, 5, 10 and 25 mV/sec for propanol in 1 N H₂SO₄.

3. Pretreatment of the electrode.

Before each of the experiment repetitive current–potential curves were obtained in 1 N H₂SO₄ solution between 0.0 V and 1.42V at a sweep rate of 10 mV/sec until the obtained surface layer diagram corresponded to those previously recorded. Subsequently the electrode was introduced into the measuring cell. Sometimes the electrode potential was varied between the starting potential 0.0V to 0.4V and then reversed to zero volt again in 1 N H₂SO₄. This procedure was done repetitively until reproducible curves were obtained.

After the electrode had been used, stored in 1 N H₂SO₄ in short–circuit with saturated calomel electrode.
The area of the working electrode was determined to 79.7 cm² by measuring the hydrogen coverage at different sweep rates.

RESULTS

1. Hydrogen Region:

Fig. 1 represents the part of the current–potential diagrams obtained for 1 N H₂SO₄ solution containing 3.10⁻⁴ M to 3.10⁻² M propanol. The sweep rate was 25 mV/sec. On the cathodic part of the diagram obtained for 1 N H₂SO₄, two peaks appear. The first and the second peaks show the strongly and weakly adsorbed Pt–H layer respectively. On the anodic region two peaks are also observed for the desorption of corresponding adsorbed Pt–H layer [7]. A comparision surface layer diagrams obtained in 1N H₂SO₄ containing propanol with surface layer diagram obtained only in 1N H₂SO₄ solution shows that hydrogen peaks, especially strongly bounded Pt–H layer are inhibited by propanol adsorption. Similar surface layer diagrams were obtained for the sweep rates 2.5 mV/sec, 5 mV/sec and 10 mV/sec. Anodic and cathodic charges in hydrogen region were calculated by measuring the areas under the curves in Fig. 1. For each propanol concentration, anodic and cathodic charges are equal and taken as the Adsorption and desorption of Pt–H layer.

Fig. 2 shows the dependence of hydrogen coverage on the propanol concentration at different sweep rates. Θ₃ is the ratio of the adsorption (or desorption) charge in hydrogen region for 1N H₂SO₄ solution containing propanol to the adsorption (or desorption) charge for only 1N H₂SO₄ solution. As can be seen from Fig. 2 Θ₃ decreases with propanol concentration and reaches to a constant value of 0.4 for each sweep rate. At which concentration Θ₃ reaches to constant value depends on sweep rate.

As can be seen from Fig. 1 in the anodic region there is a weakly pronounced peak at 0.35 V on the curves obtained for 1 N H₂SO₄ containing 3.10⁻³ M to 3.10⁻² M propanol. An examination of Fig. 1 and Fig. 2 shows that up to 3.10⁻³ M propanol the decrease of hydrogen coverage with propanol is rather high and there is no anodic current in the reverse scan only the current in the double layer region decreases. For higher propanol concentration anodic
Fig. 1. Part of the current-potential curves obtained for 1 N H$_2$SO$_4$ solution containing 3.10$^{-3}$M to 3.10$^{-7}$M propanol for hydrogen region. The sweep rate was 2.5 mV/sec.

—- 1 N H$_2$SO$_4$ containing 3.10$^{-3}$M, —— 5.10$^{-3}$M, —…… 7.10$^{-3}$M, —— 10$^{-3}$M, —— 3.10$^{-7}$M, —-x-x-- 5.10$^{-7}$M, —— — 7.10$^{-7}$M, x—x—-x 10$^{-7}$M —— — 3.10$^{-7}$M propanol.
Fig. 2. The dependence of hydrogen coverage on the propanol concentration at different sweep rates.

\[ \Delta \text{ 25 mV/sec,  } \bullet \text{ 10 mV/sec,  } \square \text{ 5 mV/sec,  } \times \text{ 2.5 mV/sec.} \]
current begins to pass in the cathodic sweep after PtO reduction and the step at 0.35 V is seen in the anodic region. We proposed that adsorbed intermediate product of propanol is formed during the passage of anodic current in the cathodic sweep. This adsorbed product inhibits the formation of Pt-H layer. The oxidation of adsorbed product occurs at 0.35 V (process I).

2- Double Layer and Oxide Region.

Fig. 3 represents the part of the current-potential diagrams obtained for 1 N H₂SO₄ solutions containing 3.10⁻⁴ M to 3.10⁻² M propanol for double layer and oxide region of platinum. The sweep rate was 2.5 mV/sec. The current increases at 0.45 V and passes a maximum (process II) at 0.55 V and then shows a minimum at approximately 0.75 V where the Pt-O formation begins. After 0.8 V curves obtained in 1 N H₂SO₄ solutions containing 3.10⁻⁴ M to 3. 10⁻³ M propanol are the same as the curve obtained in 1 N H₂SO₄ solution, only the plateau current (process III) at 1.2 V increases. The peak potential of process II increases with propanol concentration and shifted to more anodic potentials. After 5.10⁻³ M propanol, process II overlaps the beginning of Pt-O formation region. In Fig. 4 is shown the cathodic potential sweeps at a rate of 2.5 mV/sec for 1N H₂SO₄ containing 3.10⁻⁴ M to 3. 10⁻² M propanol solutions. In the cathodic sweep an anodic peak (mentioned in the preceding paragraph) is observed which is typical for many electrochemically oxidizable organic compounds after the Pt-O layer is reduced. The peak current increases with propanol concentration.

DISCUSSION

For irreversible diffusion controlled reactions, the maximum peak current of a current-potential diagram is given by [8,9]

\[ i_p = 3.10^5 \times n \left( \frac{RT}{b'F} \right)^{\frac{1}{2}} \times \frac{D}{v} \times C \]  

(1)

where \( b' = \frac{RT}{\alpha n_a F} \) and \( n \) is the total number of electrons exchanged per propanol molecule. \( n_a \) is the transferred electron number at the rate determining step.
Fig. 3. Part of the current-potential curves obtained for 1 N H₂SO₄ solutions containing 3 × 10⁻⁵M to 3 × 10⁻²M propanol for double layer and oxide region. The sweep rate was 2.5 mV/sec.

--- 1 N H₂SO₄ --- 3 × 10⁻⁵M, --- 5 × 10⁻⁶M, ...
--- 7.10⁻⁵M, --- 7.10⁻⁴M --- 3 × 10⁻²M --- 3 × 10⁻⁵M
--- 7.10⁻⁷M, --- 3 × 10⁻⁷M, --- 3.10⁻²M propanol.
Fig. 4 The cathodic potential sweeps at a rate of 2.5 mV/sec for 1 N H₂SO₄ containing 3.10⁻⁷M to 3.10⁻¹M propanol.
According to (1) the peak current should increase proportionally to the square root of the sweep rate. This is represented for various propanol concentration for process II in Fig. 5. As can be seen, equation (1) is fulfilled for low sweep rates. Fig. 6 shows the current-potential curves obtained at different sweep rates for 1 N H₂SO₄ containing 5.10⁻³M propanol. Adsorption of intermediate oxidation product of propanol in place of strongly bounded hydrogen atoms is a slow process since at high sweep rates (25 mV/sec) adsorption peak of strongly bounded H atoms is obtained but at low sweep rates (2.5 mV/sec), it disappears.

In the case of diffusion and charge transfer controlling the rate of reaction the peak potential varies with the sweep rate according to

$$E_p = E_o + \nu b' [0.780 + \ln \nu^{1/2} (D_0/b')^{1/2} - 1 \ln k_s]$$  \hspace{1cm} (2)

Here, $E_o$ denotes the standard potential and $k_s$ heterogeneous rate constant at the standard potential. Equation (2) can be simplified as follows

$$E_p = 0.5 b \log \nu + \text{const.}$$  \hspace{1cm} (3)

$b = 2.303 b'$ and all constant terms summarized into cont.

Fig. 7 represents plots of $E_p$ v.s $\log \nu$ for 1 N H₂SO₄ containing 5.10⁻⁴, 5.10⁻³ and 3.10⁻² M propanol for process II. From the slopes of these lines one obtains $(dE_p/d \log \nu) = 120$ mV and, therefore a value for the Tafel slope of $b = 240$ mV. This value is in good agreement with the result obtained from quasi stationary (2.5 / sec) current potential diagrams will be given later.

Furthermore for irreversible diffusion controlled reactions, the peak current varies with peak potentials according to [8]

$$i_p = 0.227 n F C \text{ks} \exp \left[ - \frac{1}{b'} \left( E_p - E_o \right) \right]$$  \hspace{1cm} (4)

Thus, the plot of $E_p$ v.s $i_p$ is independent of $\nu$ with the slope $b = 2.303 b'$. Fig. 8 represents $E_p$ v.s log $i_p$. The slopes of these lines are 255 mV very close to the obtained Tafel slope.

According to eq. (1), $i_p$ is expected to increase linearly with the propanol concentration. This is not fulfilled for the propanol oxidation for process II. Therefore, it has to be assumed that propanol adsorbed on the electrode surface before a reaction takes place.
Fig. 5. Peak current against square root of the scan rate on Pt in 1 N H₂SO₄ for different propanol concentrations.
Fig. 6. Current-potential curves obtained at different sweep rates for 1 N H₂SO₄ containing 5.10⁻³M propanol. . . . . 25 mV/sec, ...... 10 mV/sec, --- 5 mV/sec, ——— 2.5 mV/sec.
Fig. 7. Peak potential against logarithm of sweep rate. (□) for 1 N H₂SO₄ + 3.10⁻³M propanol, (○) for 1 N H₂SO₄ + 5 10⁻³M propanol, (△) for 1 N H₂SO₄ + 5.10⁻³M propanol.
Fig. 8. Peak potential against logarithm of peak current for different propanol concentration. (x) 3.10⁻⁻M, (□) 10⁻⁻M, (△) 7.10⁻⁻M, (□) 3.10⁻⁻M, (●) 7.10⁻⁻M, (△) 3.10⁻⁻M
The Langmuir isotherm was derived for adsorption of small particles, each occupying a single site on the surface. For dissociative chemisorption a slightly modified form of the same isotherm is applicable \[2\], namely

\[
\frac{\theta}{1-\theta} = K^{\frac{1}{2}} \cdot \frac{1}{p}. \tag{5}
\]

For low coverage and adsorption from solution we can write equation (5)

\[
\theta = K' \cdot C^\frac{1}{2} \tag{6}
\]

For the adsorption case equation (1) can be written as

\[
i_p = 3.105n \left( \frac{RT}{b'F} \right)^{\frac{1}{2}} D^{\frac{1}{2}} \theta_p \tag{7}
\]

Inserting eq. (6) in eq. (7) and defining \(A\) as

\[
A = 3.105n \left( \frac{RT}{b'F} \right)^{\frac{1}{2}} D^{\frac{1}{2}} \theta_p \tag{8}
\]

is obtained.

In Fig. 9 \(\log i_p\) is plotted against \(\log C\) for different sweep rates and agreement with (8) is seen to be good with the experimental uncertainties taken into account. The slopes of these lines are equal to 0.5 as expected.

The electrochemical reaction order can be determined from the concentration dependence of the current density at a constant potential. However, the employed potential must be located in the validity range of the Tafel line. Then the reaction order is obtained from the measured current–density as a function of the concentration \[10\].

\[
\left[ \frac{d \log i}{d \log C_p} \right] = \frac{Z_p}{n} \neq \frac{RT}{p \cdot E} \tag{9}
\]

Fig. 10 shows the Tafel relation for different concentrations. The slopes of the Tafel lines are constant (250 mV) within the investigated range of propanol concentration. From Fig. 11 the reaction order for propanol is equal to 0.48. Since the Tafel slope \(b\) is equal to
Fig. 9 Log-log plot of peak current at process II against propanol concentration at different sweep rates. (×) 25 mV/sec, (□) 10 mV/sec, (▲) 5 mV/sec, (○) 2.5 mV/sec.
Fig. 10 Anodic Tafel lines of propanol oxidation for different concentrations on Pt in 1N H₂SO₄. The sweep rate was 2.5 mV/sec. (□) 3.10⁻⁷M, (▲) 10⁻⁷M, (x) 7 10⁻³M, (o) 5 10⁻³M propanol.
Fig. 11. Log-log plot of current density and concentration at constant potential.
\[
\frac{2.303 \, RT}{x \, n_a \, F} = \frac{0.059}{x \, n_a} \quad \text{at } 25^\circ \text{C}, \text{ zna values can be calculated from the Tafel slopes.}
\]

<table>
<thead>
<tr>
<th>From</th>
<th>Tafel slope, mV</th>
<th>zna value</th>
<th>Reaction Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>equation (2)</td>
<td>240</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>equation (4)</td>
<td>255</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>equation (8)</td>
<td>—</td>
<td>—</td>
<td>0.5</td>
</tr>
<tr>
<td>equation (9)</td>
<td>250</td>
<td>0.23</td>
<td>0.48</td>
</tr>
<tr>
<td>and Fig. 10</td>
<td></td>
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</table>

The calculated \((zna)\) values show that \(n_a\), the transferred electron number at the rate determining step must be equal at least to one. In this case \(x\) is equal to 0.25. It is smaller than the common value of symmetry factor \(\beta = 0.5\). Also, the fractional order of reaction indicates the role of adsorption. The results summarized above suggest the following mechanism for process II.

The first step represents dissociative adsorption

1. Step

\[
\begin{align*}
Pt + C_2H_5 & \xrightarrow[k_1]{\text{H}} C_2H_5^- \xrightarrow[k_{-1}]{\text{H}} C_2H_5OH \quad \text{(10)}
\end{align*}
\]

2. Step

\[
Pt \, (H) \xrightarrow[k_2]{\text{Pt}} Pt + H^+ + e^- \quad \text{(11)}
\]

If we assume the second step as rate determining, the rate of the second step can be written as \(v_2 = k_2 \theta_H \phi \kappa \Delta \Phi / RT\) \quad \text{(12)}

\(\Delta \Phi\) is the potential difference according to the arbitrary selected reference potential, \(x\) is the transfer coefficient. For the quasisteady-state case from the first step

\[
k_1 \, (1-\Theta_H) \, (1-\Theta_p) \, C_p = k_{-1} \, \Theta_H \, \Theta_p. \quad \text{(13)}
\]

for \(\Theta_H = \Theta_p\).

\[
\frac{\Theta_H^2}{(1-\Theta_H)^2} = \frac{k_1}{k_{-1}} \cdot C_p = K_1 \cdot C_p \quad \text{(14)}
\]
For small $\Theta_H$ values eq. (14) can be written as $\Theta_H = \sqrt{K_1} C_p^{1/2}$ so

$$\nu_2 = k_2 \sqrt{K_1} C_p^{1/2} e^{\alpha_\Phi \Delta \Phi / RT}$$

(15)

Equation (15) gives the order of reaction as 0.5 which is in accordance with the experimental value.

Low values for $\alpha$ and high Tafel slopes were explained with two energy barrier model [11].

$$\Delta \Phi_T = \Delta \Phi_1 + \Delta \Phi_2$$

$$i = i_o \exp (\alpha_e \Delta \Phi_T / RT)$$

$\alpha_e$ is the effective transfer coefficient and defined as

$$\alpha_e = \frac{\beta_1}{\beta_1 + \beta_2}$$

$\beta_1$, $\Delta \Phi_1$, and $\beta_2$, $\Delta \Phi_2$ are the symmetry factors and potential differences of the first and second energy barriers respectively.

For $\beta_1 = \beta_2 = 0.5$ effective transfer coefficient found as 0.25.

We propose two energy barriers for hydrogen ionization reaction (2. step). First, is the energy barrier of the hydrogen ionization reaction itself and the second is the electron transfer in the film of adsorbed intermediate P. Adsorbed radical layer is present on the electrode surface during the charge transfer of the second step, because the desorption rate of adsorbed intermediate P. is probably smaller than the rate of second reaction.

If we take $\alpha = 0.25$ in eq. (15), Tafel slope $\frac{d \Delta \Phi}{d \log \nu_2} = 240$ mV is obtained.

Following mechanism can be thought for the desorption of adsorbed intermediate P.

$$\text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt OH} + e^- + \text{H}^+$$

(16)

$$\text{Pt OH} + \text{C}_3\text{H}_5 - \text{C} \rightarrow \text{C}_2\text{H}_5 - \text{C} = \text{O} + \text{H}_2\text{O} + \text{Pt}$$

(17)

In the oxide region a reaction between Pt – O layer and propanol can be thought since the reduction current of Pt – O peak decreases as the propanol concentration is increased. (see Fig. 3 and 4).
In order to determine the currents due to the propanol oxidation in process III, it is necessary from the measured currents to subtract the PtO layer formation current. This was done by subtracting the current in the potential range from 1.0 V to 1.4 V measured in the sweep in 1 N H₂SO₄.

The corrected current values were plotted against concentrations at constant sweep rate and against square root of the sweep rate at constant concentration. (Fig. 12 and 13). \( i_p - \sqrt{v} \) linear variation shows that propanol oxidation at the PtO formation region is a diffusion controlled process. As can be seen from Fig. 12 \( d \log i / d \log C = 0.97 \) is taken as unity.

According to the above results, a reaction mechanism between the PtO and propanol which gives the order of reaction as unity can be thought.

\[
\text{Pt} + C_2H_5 - CH_2OH \xrightarrow{r,d} \text{PtOH} + C_2H_5 - \bigodot \bigodot \text{HOH} \quad (18)
\]

\[
\text{Pt OH} \rightleftharpoons \text{PtO} + H^+ + e^- \quad (19)
\]

\[
\text{Pt OH} + C_2H_5 - \bigodot \bigodot \text{HOH} \leftarrow C_2H_5 - \bigodot \bigodot \bigodot \text{C} + H_2O + \text{Pt} \quad (20)
\]

Reaction (18) is the rate determining step for process (III). If the propanol concentration is high reaction (20) also takes place and PtO reduction peak tends to disappear. In the cathodic sweep anodic oxidation of propanol takes place after the PtO layer is reduced. The reaction mechanism for this region must be the same as the reaction mechanism at process II, because the potential ranges of process II and the anodic reaction in the cathodic sweep coincide to each other and approximately the same relation between the \( \log i_p - \log C \) is found (Fig. 14).

The adsorbed radical \( P \) formed according to reaction (10) in the reverse sweep inhibites the hydrogen adsorption.

\[
\text{H}
\]

As a result, adsorbed radical \( P \) (\( C_2H_5 - \bigodot \bigodot \text{OH} \)) is the poisoning specie for propanol oxidation.
Fig. 12. Log-log plot of current density and concentration for process III at different sweep rates. (△) 25 mV/sec, (□) 10 mV/sec, (▲) 5 mV/sec, (○) 2.5 mV/sec.
Fig. 13 Peak current of process III against square root of the scan rate on Pt in 1 N HSO₄.
Fig. 14. Log-log plot of anodic peak current in the cathodic sweep against propanol concentration.
ÖZET

Propanolun 1 N H₂SO₄ içinde platinlenmiş platin elektrottaki anodik oksidasyonunun dönüştümlü voltametri ile incelemesi aşağıdaki sonuçları verir. Katodik süpürmede propanolün adsorbe ara oksidasyon ürününün oluşumu ile ilgili bir anodik tepe gözlenir. Bu adsorbe ara ürün hidrojen adsorpsiyonunu öner. 3.10⁻⁴ ila 3.10⁻² M propanol içeren 1 N H₂SO₄ içinde Pt -Pt de hidrojenin doygunluk kaplaması 0.4 dür. Adsorbe ara ürün 0.35 V da redükleştir. Propanolün ikinci oksidasyonu 0.45 V da olur. Propanolün anodik reaksiyon mertebe 0,5 dır. Kinetik oksidasyon mekanizması dissozisatif adsorpsiyon için verilen Langmuir izotermi yar-dımıyla açıklanmıştır. PtO oluşma bölgesinde de propanol oksidasyonu cereyan eder. Adsorbe ara ürün propanol oksidasyonunu inhibe eder.