**RESEARCH ARTICLE****STUDY OF THE ADSORPTION OF REACTION INTERMEDIATES RESULTING  
OF THE ELECTROOXIDATION OF PROPANEDIOLS ON  
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**Abstract**

The study of the electrocatalytic oxidation of 1,2-propanediol and 1,3-propanediol on electrodes of platinum and gold in acid or basic aqueous medium was carried out in previous publications [1,2], by cyclic voltammetry and in situ infrared reflectance spectroscopy. In order to confirm the proposed reaction mechanisms during the electrooxidation of the two isomers of propanediol, similar studies on the reaction intermediates which can be formed were performed under the same conditions by cyclic voltammetry and in situ infrared reflectance spectroscopy. The reaction intermediates studied are: hydroxyacetone, lactic acid and malonic acid. SPAIR spectra show that, on platinum in acid medium, hydroxyacetone, acetic and formic acid and CO<sub>2</sub> are obtained. In alkaline medium, acetaldehyde and formic acid are detected on platinum and formic, lactic and acetic acids are detected on gold electrode. The results obtained in this study clearly confirm the different paths for these mechanisms.

**Keywords:** Propanediol ; Electrochemical oxidation ; *In situ* IR Reflectance Spectroscopy

**Introduction**

The electrocatalytic oxidation of small organic molecules, especially those coming from biomass, principally alcohols, has been studied for understanding the role of different experimental parameters [3] and also for finding the most reactive molecules for applications as fuels in fuel cells. Sokolova [4] studied the electrooxidation of propanediols on platinum in sulfuric acid medium. Horanyi and al [5] studied the oxidation of 1,2-propanediol on platinized platinum in sulfuric acid medium and proposed a reaction mechanism which included the rupture of the C-C bond. Some studies of our laboratory by electrolysis and HPLC of 1,2-propanediol on platinum in acidic medium have

shown the presence of hydroxyacetone, lactic, pyruvic, acetic and formic acids and traces of CO<sub>2</sub> [6].

Alonso and Gonzalez-Velasco [7] show that the oxidation of the 1,2-propanediol on gold electrode in alkaline media leads to lactic, acetic and formic acids. The electrooxidation of a series of vicinal and terminal aliphatic diols ranging from ethanediol to hexanediol and in particular 1,2-propanediol at a polycrystalline gold electrode in alkaline electrolyte solution has been studied by Luczak and al [8]. These authors have calculated the adsorption free energy for these products: in one part, the longer

the carbon chain is, the higher the adsorption free energy is and in another part, this adsorption free energy is increased for terminal diols. In other paper from the same authors [9], it is shown that the electrooxidation of the diols on gold electrode in alkaline solution depends of the strength carbon chain and alcohol function position.

The study of phenomena that occur at the electrode / electrolyte interface during an electrocatalytic reaction, requires new methods of investigation such as spectroscopic techniques. Infrared spectroscopy in situ reflection in its different variants is particularly interesting because it allows collecting vital information about the nature and structure of adsorbed and / or products of the reaction intermediates. Two methods were mainly used in this work: SPAIRS (Single Potential Alteration Infrared Reflectance Spectroscopy) and SNIFTIRS (Subtractively Normalized Interfacial Fourier Transform Infrared Reflectance Spectroscopy) using a Fourier transform spectrometer.

The detailed writing of electrocatalytic oxidation mechanisms of the isomers of propanediol on platinum and gold electrode in acid and alkaline media has been presented in previous publications [1, 2]. Therefore, and in order to justify the better the choice of the different reaction pathways that have been proposed, SPAIRS of spectra relating to the adsorption and oxidation of some reaction products identified as hydroxyacetone, lactic and malonic acids are recorded between 1000 and 3100  $\text{cm}^{-1}$  in the same conditions as for propanediols.

## 2. EXPERIMENTAL

### 2.1 Electrochemical measurements

The electrochemical equipment used to record cyclic voltammograms consists of a LB81 bank potentiostat, a PPRI Hi-Tek waveform generator, and a BD90 Kipp & Zonen XY recorder. The electrochemical cell was a classical one with a smooth bead, obtained by the melting of a wire of platinum or gold as the working electrode, a glassy carbon plate as the counter electrode and a reversible hydrogen electrode (RHE) as the reference electrode. The supporting electrolyte is prepared from ultrapure water (Millipore Milli Q system) and suprapur Merck products (sulphuric acid and sodium hydroxide) and propanediols, hydroxyacetone, lactic and malonic acids (Aldrich).

### 2.2 Infrared reflectance spectroscopy

A Fourier transform infrared spectrometer (Bruker IFS 66v), equipped with a special reflectance device allowing the observation of reflectance spectra at the electrode/electrolyte interface, with an IR lights beam passing entirely through a vacuum purged atmosphere, was used. A Globar source and a nitrogen cooled mercury cadmium telluride (MCT) detector (Infrared associates) were used. A detailed description can be found in previous papers [10-12]. A special three electrode spectroelectrochemical cell was designed with a  $\text{CaF}_2$  IR transparent window allowing the beam to pass through a thin electrolyte layer (a few micrometers) before reflection at the electrode surface. The reference electrode is a reversible hydrogen electrode (RHE) and the counter electrode is a vitreous carbon plate. The working electrode is a platinum or a gold disc, with a diameter of 0.6 cm, polished to a mirror finish with fine alumina, up to 0.5  $\mu\text{m}$ , and fixed to the top of a syringe.

Two types of IR reflectance experiments were carried out ; single potential alteration infrared reflectance spectroscopy (SPAIRS) and subtractively normalised interfacial Fourier transform infrared reflectance spectroscopy (SNIFTIRS).

With the SPAIRS technique [13], the electrode surface reflectivities were recorded each 100 mV during the first slow voltammetric scan (1  $\text{mV s}^{-1}$ ). Each spectrum resulted from the coaddition of 128 interferograms. The acquisition required 20 s, i.e. over ca 20 mV. Spectra were normalised as:

$$\frac{\Delta R}{R} = \frac{R_{E_i} - R_{E_{ref}}}{R_{E_{ref}}}$$

where  $R_E$  is the reflectivity taken during the voltammetric scan and  $R_{E_{ref}}$  is the reflectivity recorded at the most negative potential (50 mV (RHE)).

With the SNIFTIRS method, reflectivities were obtained at two electrode potentials (frequency of potential modulation of 0.025 Hz) and coadded 50 times at each potential. Final spectra were normalised as :

$$\frac{\Delta R}{R} = \frac{R_{E_2} - R_{E_1}}{R_{E_1}} \text{ with } E_2 - E_1 = 300\text{mV} .$$

## 3. RESULTS

### 3.1. Spectrum of hydroxyacetone

These spectroscopic experiments were performed with 0.1 M hydroxyacetone. Similar experiments done with 1 mM show the same bands with weaker intensity.

For the SPAIRS experiment, voltammograms of platinum or gold in acid (0.5 M H<sub>2</sub>SO<sub>4</sub>) and alkaline (0.1 M NaOH) media in the presence of 0.1 M hydroxyacetone were recorded during the first cycle at 1 mV s<sup>-1</sup>. The acquisition of spectra was, between 50 and 1600 mV(RHE) for the platinum and between 50 and 1750 mV(RHE) for the gold electrode, each 100 mV, in p-polarization.

#### 3.1.1. On a platinum electrode.

In acid medium, SPAIR spectra were calculated with the reference taken at 50 mV(RHE) and are represented in Figure 1. It is interesting to note that no trace of CO is observed, while the band at 2345 cm<sup>-1</sup> attributed to CO<sub>2</sub> is present from 750 mV (RHE). This indicates that the CO<sub>2</sub> comes from the direct oxidation of hydroxyacetone via the formation of formaldehyde and / or formic acid (first peak at 550 mV / RHE). From the second oxidation peak (1150 mV / ERH) bands at 1280, 1370 and 2622 cm<sup>-1</sup> are added to that at 1720 cm<sup>-1</sup> and are clearly assigned to acetic acid.

#### 3.1.2 On a gold electrode in alkaline medium.

The Figure 2 show the voltammogram of gold in the presence of hydroxyacetone in the NaOH medium and the corresponding SPAIRS spectra. From the potential of 1250 mV (RHE) at the end of the rise of oxidation peak, the band at 2345 cm<sup>-1</sup> attributed to CO<sub>2</sub> was observed. The presence, from the lowest potential of the positive band (opposite direction to that of CO<sub>2</sub>) and 1750 cm<sup>-1</sup> attributed to the carbonyl group >C = O, reflects consumption hydroxyacetone during oxidation. On the other hand, no presence of CO is observed. The spectral domain 1000 - 1250 cm<sup>-1</sup> also has several bands corresponding to the consumption of hydroxyacetone.

### 3.2 SPAIRS of lactic acid

#### 3.2.1 On a platinum electrode in H<sub>2</sub>SO<sub>4</sub> medium.

Analysis of SPAIRS spectra recorded during the electrocatalytic oxidation of lactic acid on a platinum electrode in H<sub>2</sub>SO<sub>4</sub> medium (Figure 3) shows the presence of the band of CO<sub>2</sub> from 750 mV (RHE)

corresponding at the beginning potential of oxidation. From 1050 mV (RHE), the bands at 1720 cm<sup>-1</sup> and 1390 cm<sup>-1</sup> begin to appear and are attributed to acetic acid. No band attributed to CO adsorbed was observed.

#### 3.2.2 On a gold electrode in a basic medium.

The voltammogram of gold in the presence of lactic acid in the alkaline medium and the SPAIRS spectra corresponding are shown in Figure 4. These spectra shows the presence of the band of CO<sub>2</sub> at 2345 cm<sup>-1</sup> from 1250 mV (RHE) or just after the oxidation peak during the positive variation of potential. Bands at 1400 and 1360 cm<sup>-1</sup> appear from 950 mV (RHE) are attributed to carbonates.

### 3.3 SPAIRS spectra of malonic acid

#### 3.3.1 On a platinum electrode in acidic medium.

In H<sub>2</sub>SO<sub>4</sub> medium (Figure 5), SPAIRS spectra of malonic acid show the presence of band of CO<sub>2</sub>, water and some bands for malonic acid. In basic medium, in addition to the bands of water and malonic acid, those assigned to the carbonates are also visible.

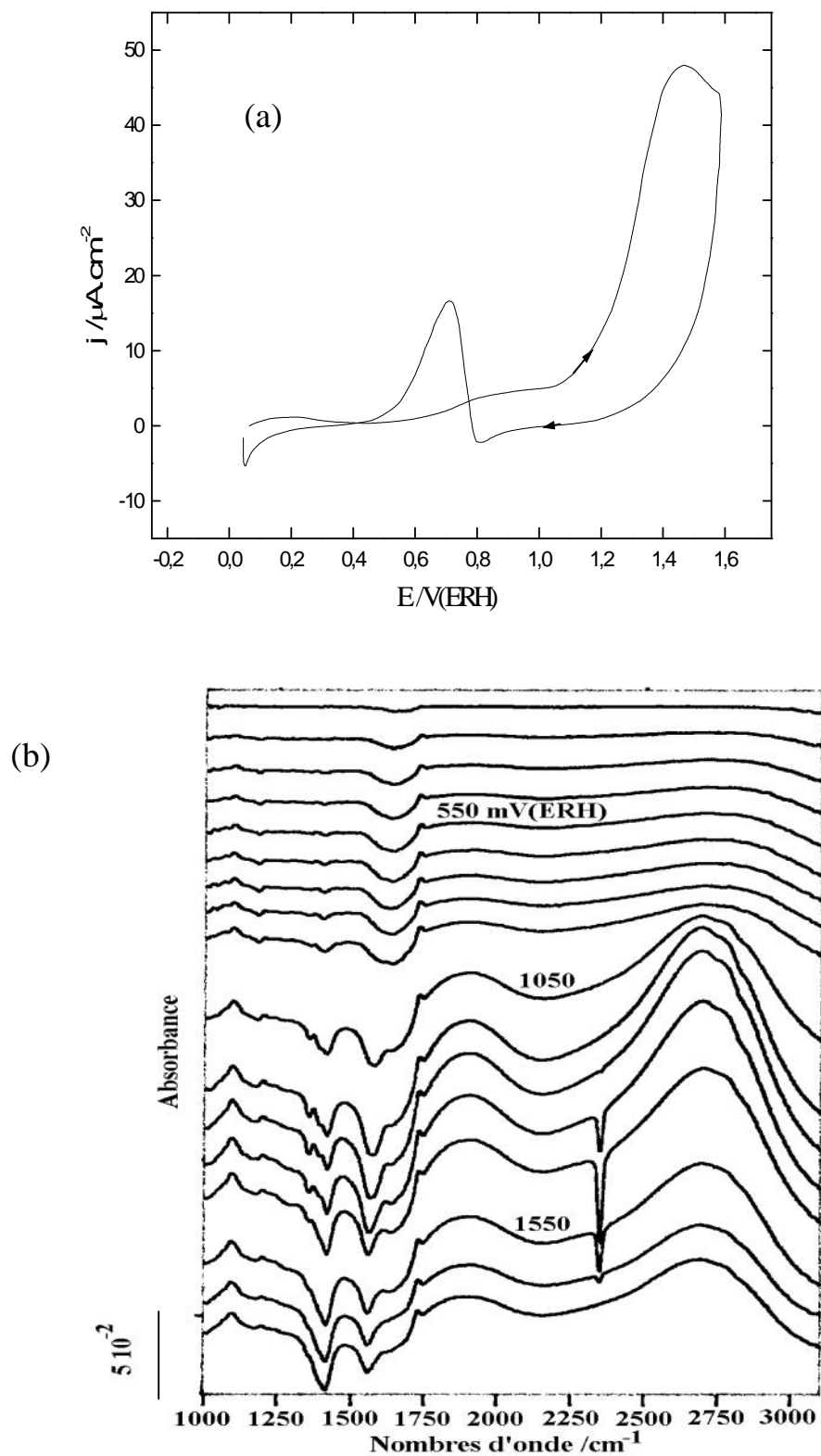
#### 3.3.2 On a gold electrode in a basic medium.

On the gold electrode in NaOH medium, no oxidation of malonic acid by voltammetry was observed, and the SPAIRS spectra recorded show only the bands of the water (Figure 6).

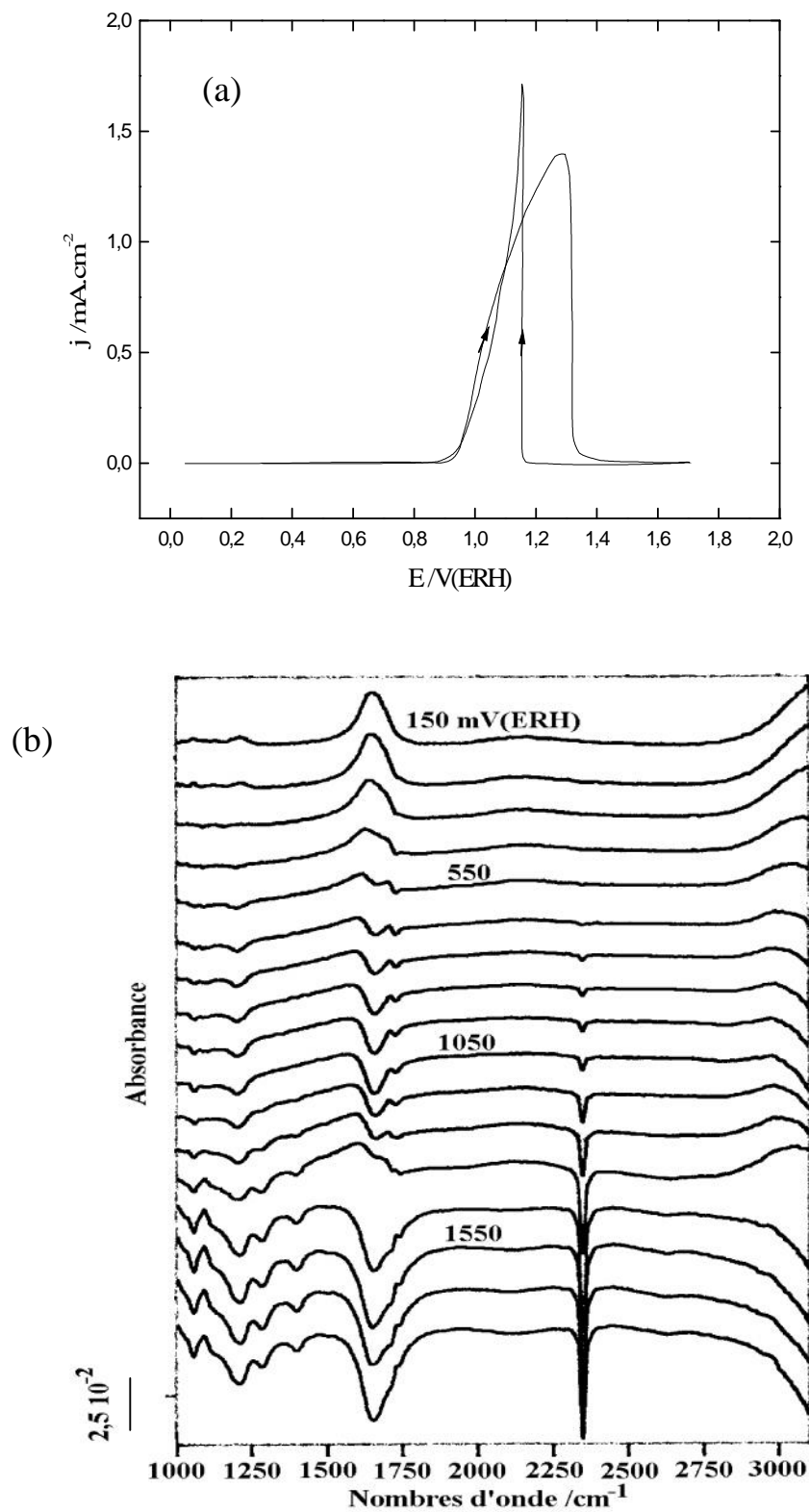
## 4. DISCUSSION.

On platinum electrode, in acid or alkaline medium, both propanediols have a dissociative chemisorptions.

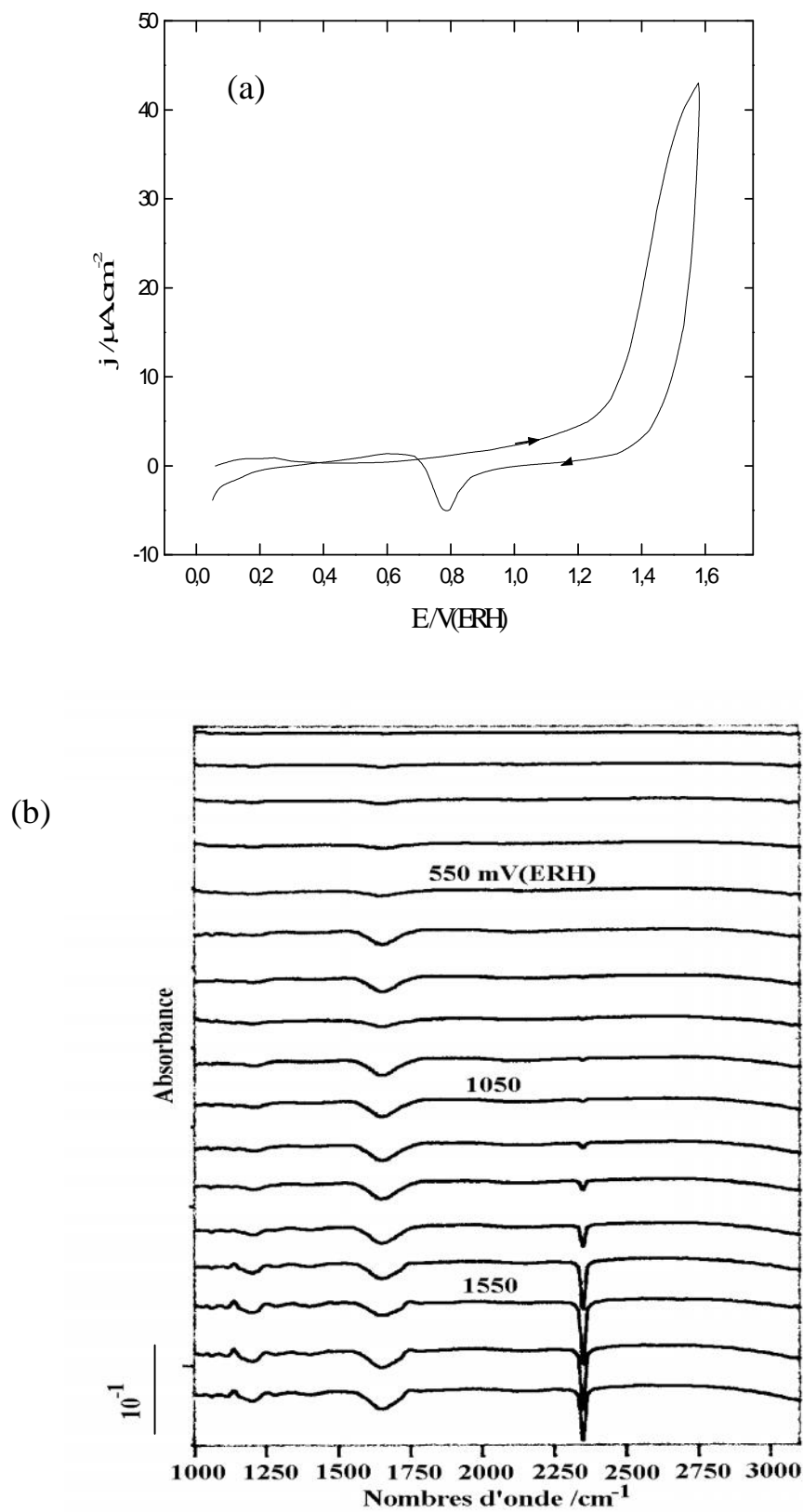
On gold electrode, in basic medium, the propanediols are oxidized. In spite of a big oxidation peak of the 1,3-propanediol on gold, no IR absorption band are observed i.e. principally, no CO and no CO<sub>2</sub> are detected. The main conclusion is the 1,3-propanediol chemisorptions is not dissociative and all reaction oxidation products are C3 molecules. For the 1,2-propanediol oxidation, the electrochemical process is totally different, CO is not detected, and on the other hand, carbonyl species and CO<sub>2</sub> are clearly observed during all the process (adsorption, oxidation and after the oxidation).



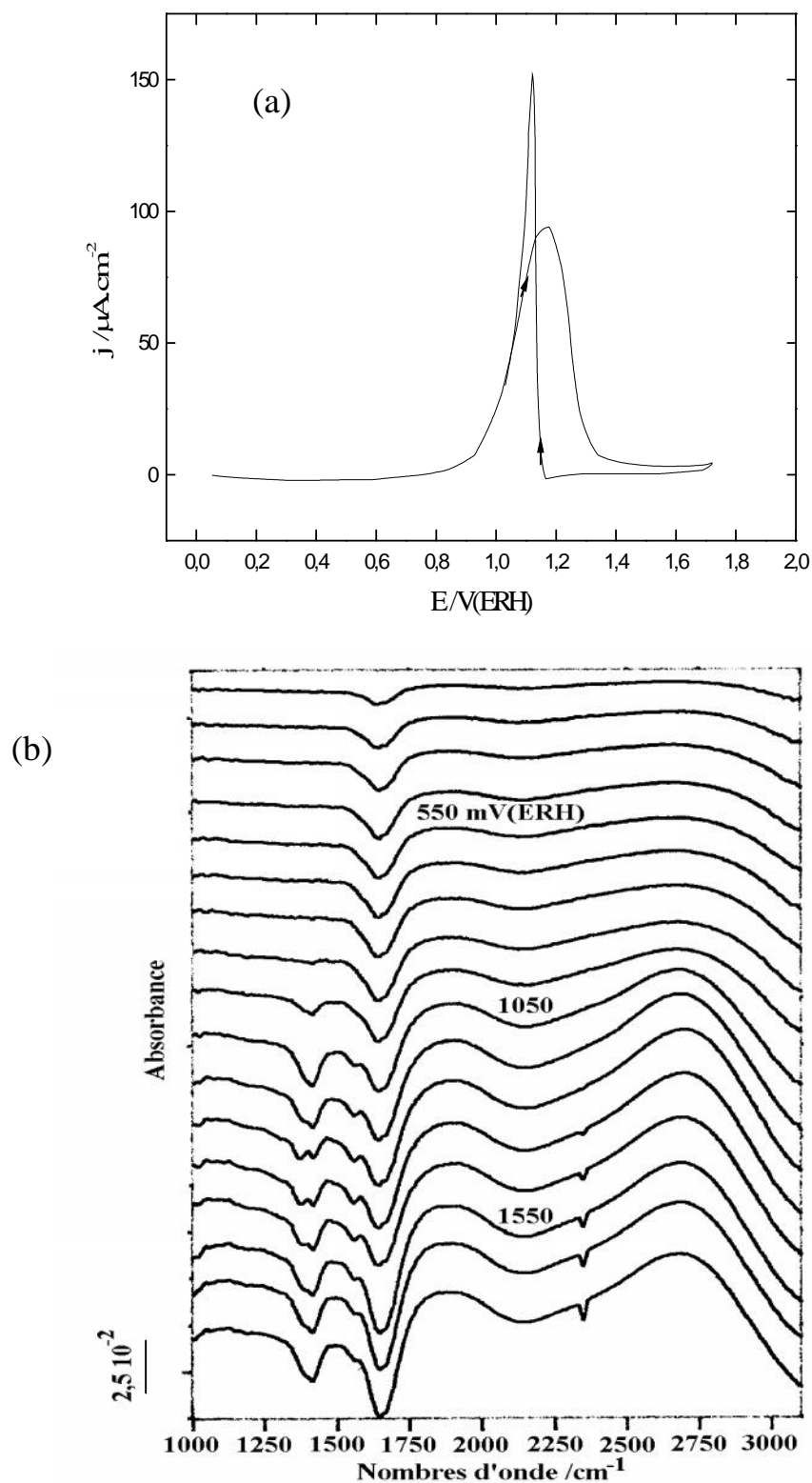
**Figure 1 :** (a) Voltammogram of platinum in  $\text{H}_2\text{SO}_4$  0,5 M, recorded at  $1 \text{ mV}\cdot\text{s}^{-1}$  in presence of the hydroxyacetone 0,1 M ; (b) SPAIRS spectra corresponding, polarisation p



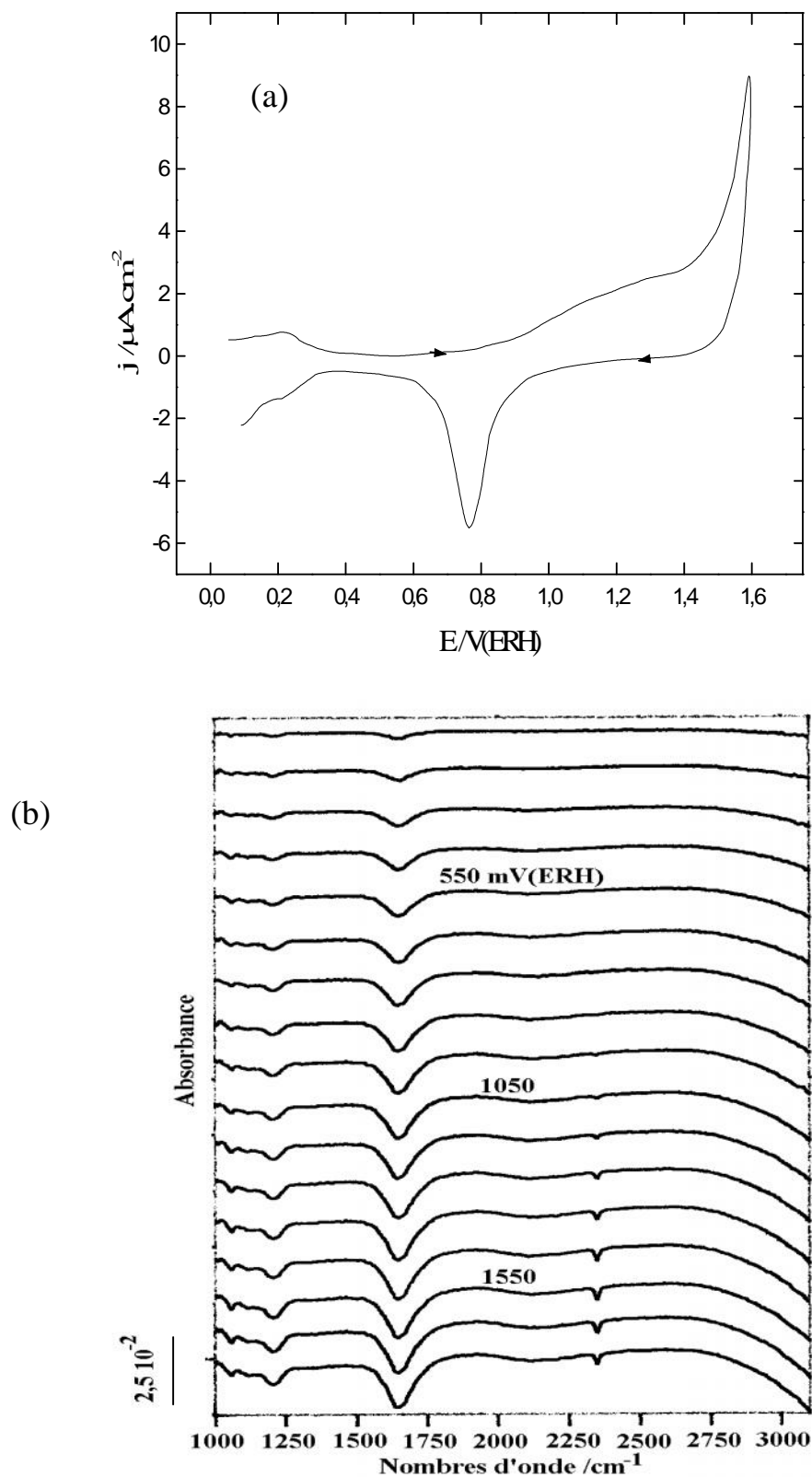
**Figure 2:** (a) Voltammogram of platinum in NaOH 0.1 M, recorded at  $1 \text{ mV}\cdot\text{s}^{-1}$  in presence of the hydroxyacetone 0,1 M ; (b) SPAIRS spectra corresponding, polarisation p.



**Figure 3 :** (a) Voltammogram of platinum in  $\text{H}_2\text{SO}_4$  0,5 M, recorded at  $1 \text{ mV}\cdot\text{s}^{-1}$  in presence of the lactic acid 0,1 M ; (b) SPAIRS spectra corresponding, polarisation p.

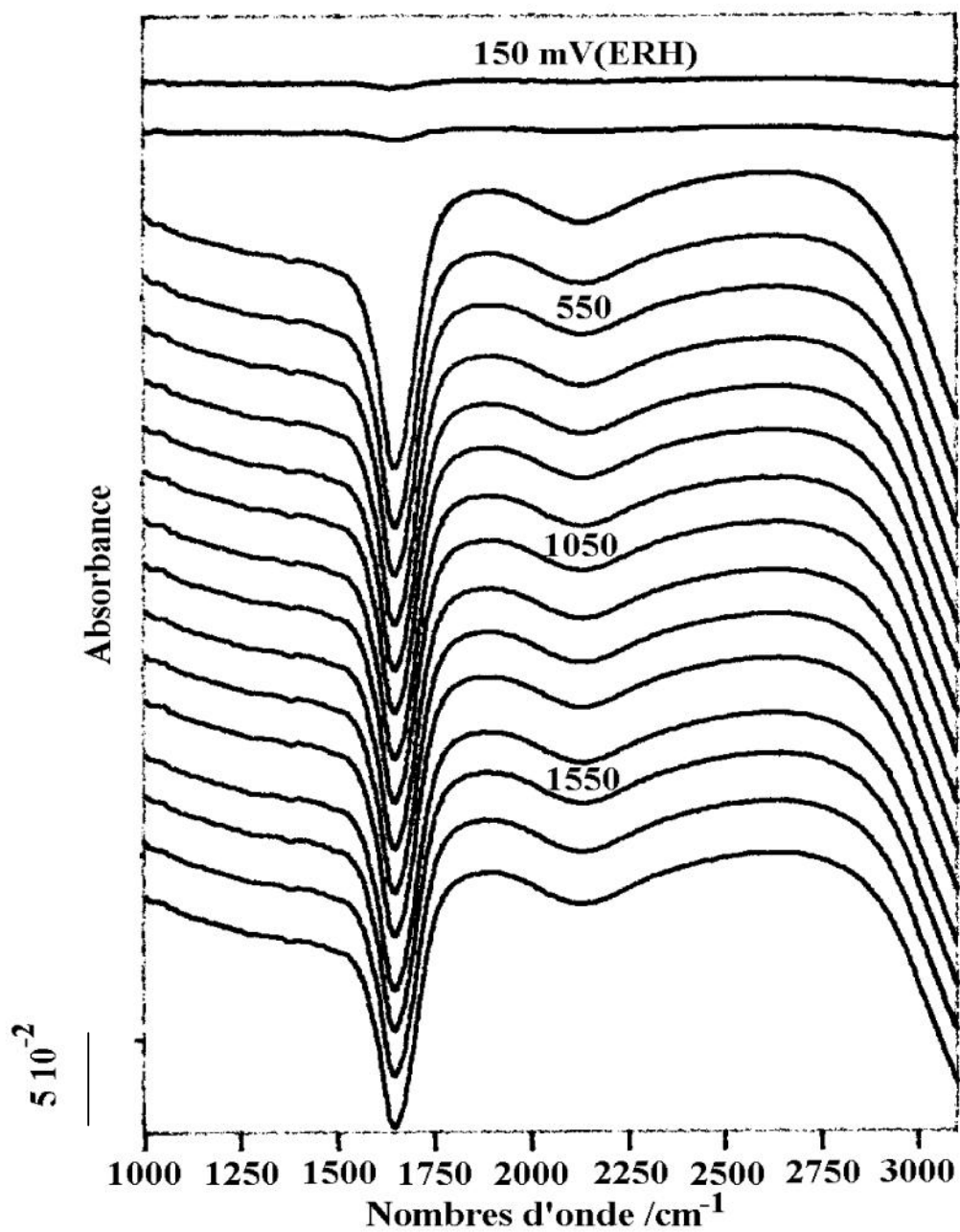


**Figure 4 :** (a) Voltammogram of gold in NaOH 0.1 M, recorded at  $1 \text{ mV}\cdot\text{s}^{-1}$  in presence of the lactic acid 0,1 M ; (b) SPAIRS spectra corresponding, polarisation p.



**Figure 5 :** (a) Voltammogram of platinum dans  $\text{H}_2\text{SO}_4$  0,5 M, recorded at  $1 \text{ mV}\cdot\text{s}^{-1}$  in presence of malonic acid 0,1 M ; (b) SPAIRS spectra corresponding, polarisation p.





**Figure 6** : SPAIR spectra of 0.1 M malonic acid in 0.1 M NaOH on a Au electrode at various potentials -  $R_{\text{Eref}}$  taken at 50 mV (RHE) - p polarization - 128 interferograms

By electrolysis [2, 6] and IR spectroscopic results, identified products are therefore: on platinum, the electrooxidation of 1,3-propanediol leads to the formaldehyde, formic acid, malonic acid and CO<sub>2</sub>, on the gold electrode it leads especially to the malonic acid. While the electrooxidation of 1,2-propanediol on platinum leads to the hydroxyacetone, lactic, pyruvic and acetic acid, on the gold electrode it leads to formic, lactic and acetic acid.

1,2-Propanediol and 1,3-propanediol have the same formula but one of them (1,3-PD) is a symmetrical molecule and the other hand (1,2-PD) is an asymmetrical molecule. Also, the adsorption atoms are different and mean to different process and reaction products. The 1,3-propanediol has twice the same primary alcohol function. Several reaction paths are possible and from spectroscopic and electrolysis results, two reactional diagrams for the two propanediols are proposed including the different intermediates, adsorbed species and reaction products. The mechanisms proposed for the electrooxidation of 1,2-propanediol and 1,3-propanediol are presented in the last articles [1, 2]. In order to complete this work, SPAIRS have been performed during the oxidation of hydroxyacetone, lactic and malonic acid on a platinum and gold electrode in acid and alkaline media. These spectra show the presence of the absorbance band of CO<sub>2</sub>. This seems in agreement with the proposed mechanism, in which CO<sub>2</sub> results from the oxidation of hydroxyacetone, lactic and malonic acid.

#### 4.1 . Mechanism of the electrocatalytic oxidation of the 1,3-propanediol

The 1,3-propanediol is oxidized on platinum electrodes in acid and alkaline media, and on gold electrodes in alkaline medium only. The behavior of 1,3-propanediol on gold and platinum is totally different, from both the electrochemical and spectroscopic points of view, but the current densities are much larger on gold in alkaline medium.

From the spectroscopic results, the occurrence of different species was proved: adsorbed CO (both CO<sub>L</sub> and CO<sub>B</sub>), carbonyl group and CO<sub>2</sub> on platinum. Conversely, on gold, no CO<sub>ads</sub> was detected. This leads to two conclusions: the 1,3-propanediol adsorption is dissociative on platinum

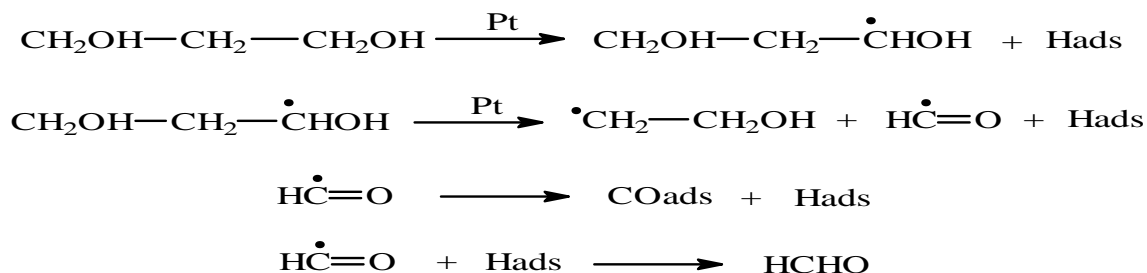
but not on gold. Thus, the reaction products will be C1, C2 and C3 molecules on a platinum electrode, and only C3 molecules on a gold electrode. Adsorbed CO species, which are formed at low potentials, are poisoning species. The absorption band at 1720 cm<sup>-1</sup>, attributed to a carbonyl group C=O from an aldehyde or an acid, is practically seen in the three cases Pt/H<sub>2</sub>SO<sub>4</sub>, Pt/NaOH and Au/NaOH. The band of CO<sub>2</sub> is detected only on a platinum electrode in acid medium. In alkaline medium, bands from carbonate species are detected by SPAIRS. On a gold electrode, no band of CO<sub>2</sub> is observed. The presence of CO<sub>2</sub> confirms the dissociative adsorption of 1,3-propanediol on platinum.

The 1,3-propanediol is a symmetric molecule, so that two possibilities for the first adsorption step can be considered: adsorption by the terminal carbon, i.e. OH-CH<sub>2</sub>-CH<sub>2</sub>-\*CH-OH and/or adsorption by the oxygen of an alcohol function OH-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-\*O; the adsorption by the central carbon is excluded totally (steric hindrance). By considering the adsorption by a carbon atom, two paths can be taken into account (figure 7): (path A), where there is no dissociation of the carbon skeleton of the organic molecule, leading to reaction products such as 3-hydroxy propanal, -lactic acid and malonic acid which is one of the product obtained during prolonged electrolysis [16]. In the second path (called B), the adsorption can be more complex (on two sites or more) and leads to the dissociation of the molecule with breaking of the C-C bond and then to the formation of CO<sub>ads</sub> species (poisoning species detected by IR). At the same time, formaldehyde and formic acid can be produced. For potentials greater than 0.4 V(RHE) the oxidation peak becomes very intense and CO<sub>2</sub> appears as a final product.

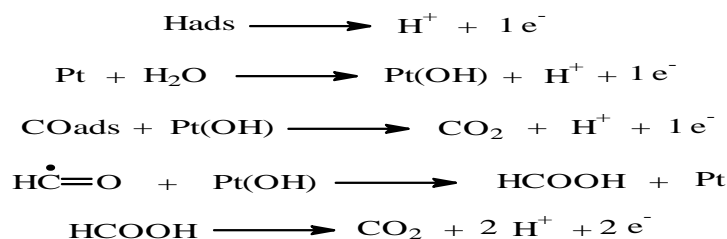
By the considering the second hypothesis, adsorption by the oxygen atom, only one path can be possible, (path C), with formation of aldehyde (3-hydroxypropanal) as in the path A. finally, a fourth path (D) can be proposed to explain the formation of the C=C bond by dehydration of 1,3-propanediol as detected by the band at 1610 cm<sup>-1</sup> on IR spectra. The final product would be acrylic acid.

The different ways of the electrocatalytic oxidation of 1,3-propanediol on Platinum electrode are therefore:

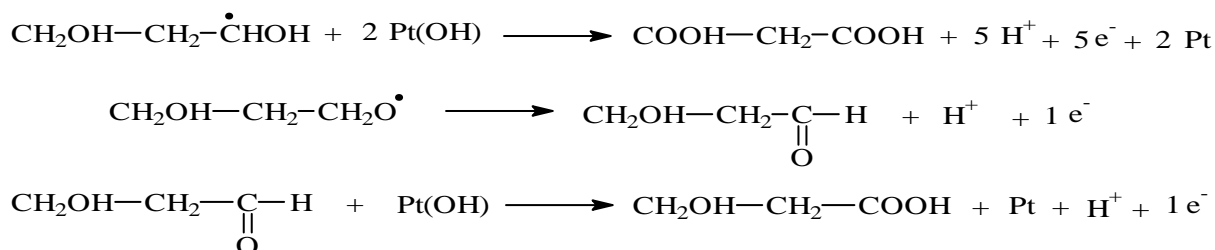
↳  $E < 0,4$  V(RHE) dissociative adsorption:



↳  $E > 0,4$  V(RHE) oxidation of adsorbed products :



For the oxidation to products at three carbons without dissociative adsorption we have



then:

Finally,  $\text{CO}_2$  species can also result from the oxidation of malonic acid and lactic acid as it was observed in SPAIRS experiments performed from those products on a platinum electrode. All these results mechanistic are transcribed in Figure 7.

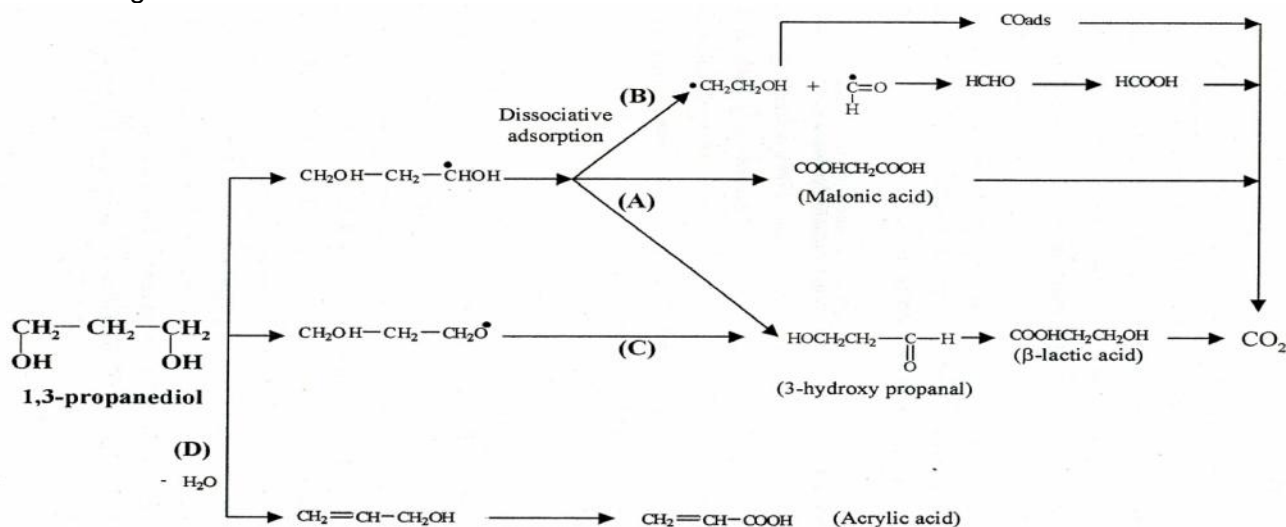


Figure 7. Mechanism of the electrocatalytic oxidation of the 1,3-propanediol

## 4.2 Mechanism of the electrocatalytic oxidation of the 1,2-propanediol

All these results have shown during the chemisorption of 1,2-propanediol on platinum electrode in acid medium the formation of hydroxyacetone, lactic acid, pyruvic acid, acetic acid, adsorbed CO, carbonyl species and CO<sub>2</sub>. The three ways A, B and C can be considered for this electrochemical process.

The 1,2-propanediol is an asymmetric molecule having two alcohol functions : primary and secondary alcohol functions. Also, several possibilities for the 1,2-propanediol adsorption can be considered : adsorption from the <sup>1</sup>C carbon having the alcohol function CH<sub>3</sub> - CH(OH) - <sup>•</sup>CH(OH), from the <sup>2</sup>C carbon CH<sub>3</sub> - <sup>•</sup>C(OH) - CH<sub>2</sub>OH and / or from the <sup>3</sup>C carbon <sup>•</sup>CH<sub>2</sub> - CHOH - CH<sub>2</sub>OH.. The adsorption can also be from the oxygen atom, i.e two possibilities: adsorption by <sup>1</sup>O : CH<sub>3</sub> - CHOH - CH<sub>2</sub>O<sup>•</sup> and CH<sub>3</sub> - CHO<sup>•</sup> - CH<sub>2</sub>(OH). Only three adsorption ways can be kept, see figure 8. The way called way A begins with the CH<sub>3</sub> - CHO<sup>•</sup> - CH<sub>2</sub>(OH) radical and can give the

hydroxyacetone without dissociation of the molecule, then acetic and formic acids. Another way, called way B, gives the CH<sub>3</sub> - CHOH - CH<sub>2</sub>O<sup>•</sup> radical, then 2-hydroxy-propanal which can be dissociated in adsorbed CO and CH<sub>3</sub> - <sup>•</sup>CH(OH), this last one can give acetaldehyde and acetic acid and / or still be dissociated to form formaldehyde and CO then formic acid. CO and formic acid are oxidized in CO<sub>2</sub>.

From the CH<sub>3</sub> - CH(OH) - <sup>•</sup>CH(OH) radical of the third way called way C, two paths are possible, path Ca without dissociation of the radical and lactic acid and pyruvic acid can be obtained. The path Cb, with the break of the bond C - C, and CH<sub>3</sub> - <sup>•</sup>CHOH and CO are formed. From this, the path Cb continues like the way B.

Another pathway (called D) for 1,2-propanediol dehydration can be considered, leading to different products in C3 molecule. Such a kind of C=C bond was reported during the oxidation of 1,3-butanediols and 1-butanol [14, 15]. This possibility, although weak, can be considered.

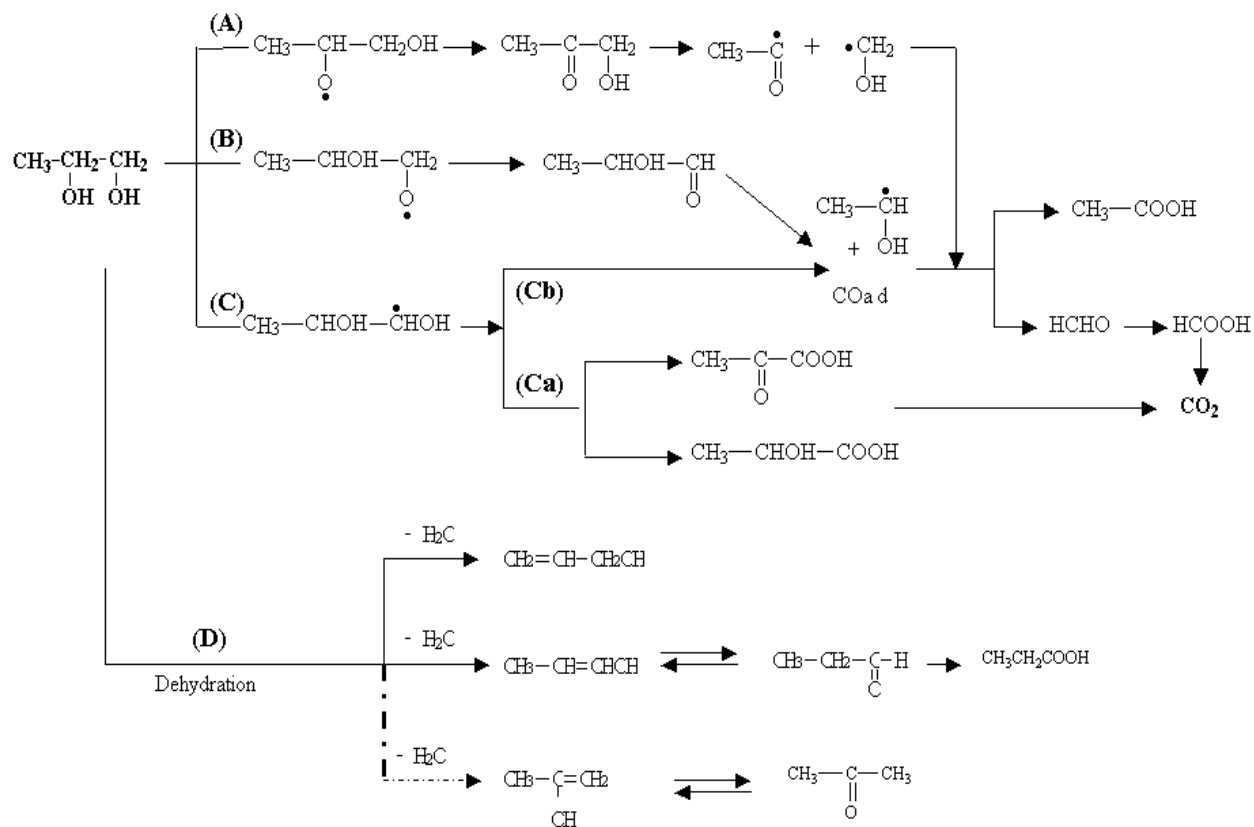
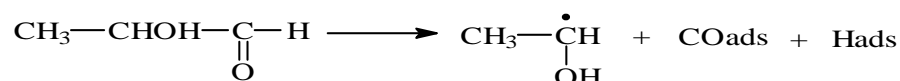
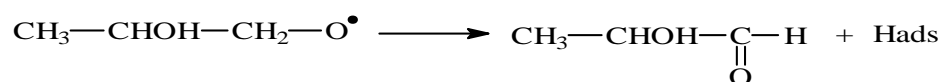
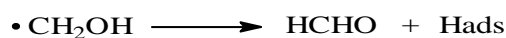
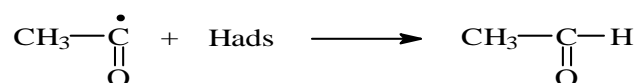
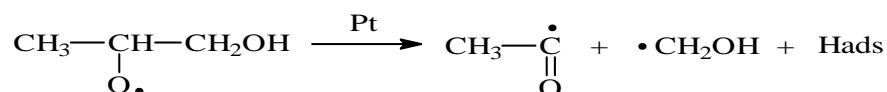
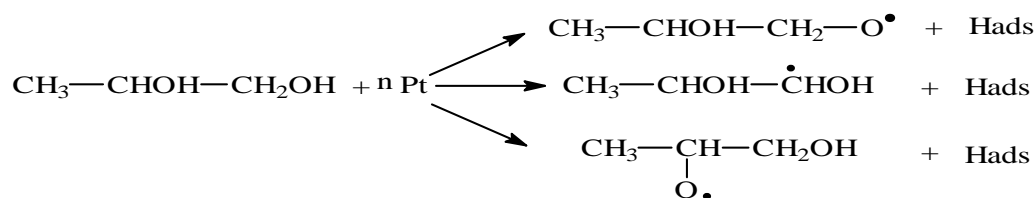


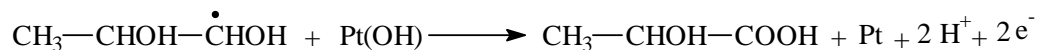
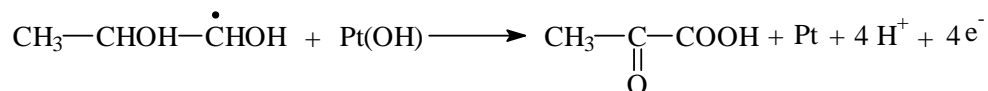
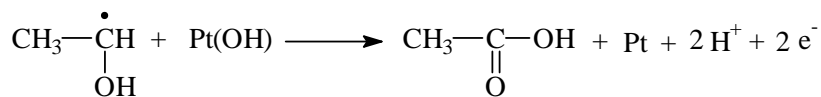
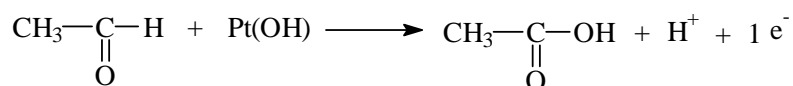
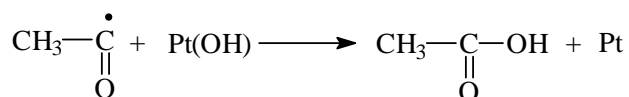
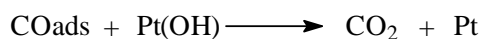
Figure 8. Mechanism of the electrocatalytic oxidation of the 1,2-propanediol

The different ways of the electrocatalytic oxidation of 1,2-propanediol on Platinum electrode are therefore:

↳  $E < 0,4 \text{ V(RHE)}$



↳  $E > 0,4 \text{ V(RHE)}$



## 5. CONCLUSIONS

To better justify the different paths leading to the reactional mechanism that we are going to propose, some SPAIRS experiments were realized by taken like reactifs the molecules identified like intermediate products. Three molecules were studied : hydroxyacetone, lactic and malonic acids. It is well known that acetic acid is not oxidized on platinum or gold electrodes. SPAIR spectra show that, from hydroxyacetone on platinum in acid medium, acetic and formic acid and CO<sub>2</sub> are obtained. In alkaline medium, acetaldehyde and formic acid are detected on platinum and formic, lactic and acetic acids are detected on gold electrode.

Several important new results are reported in this work. Firstly, it is found through spectroelectrochemical measurements that the process of electrooxidation of 1,3-propanediol on gold and platinum electrodes are different. indeed, on gold, there is no dissociation of 1,3-propanediol, and only path A is possible, while, on a platinum electrode, the dissociative chemisorption of the diol leads rather to paths B and C (figure 7). secondly, FTIR measurements reveal, besides the presence of CO adsorbed species, small amounts of formaldehyde, malonic acid and CO<sub>2</sub>.

The dissociative chemisorption of 1,2-propanediol on gold or platinum electrode leads to paths A, B, C and D (figure 8).

From the voltammetric, spectroscopic and electrolysis results, it is possible to derive some conclusions about the reactional mechanism of the electrocatalytic oxidation of propanediols on platinum and gold electrodes in alkaline and acid media. The mechanisms of these electrocatalytic reactions greatly depend on the nature of the electrode material, which determines the structure of adsorbed intermediates.

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