

Synthesis of propionic acid at a gold electrode by electrochemical technique

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ABSTRACT: In recent years, catalytic properties of gold have played a major role in the chemistry of environmentally safe substances. In this study, propionic acid was synthesized using electrochemical oxidation on a gold plate electrode in potassium hydroxide. Five hours of electrochemical reaction at a constant voltage was carried out using the chronocoulometry method. Propionaldehyde was oxidized electrochemically to propionic acid as verified by the characterization data from high performance liquid chromatography and Fourier transform infrared spectroscopy. The proposed mechanism of the reaction showed the importance of the OH^- species in the synthesis reaction.

KEYWORDS: Propionaldehyde, chronocoulometry, HPLC, FTIR

INTRODUCTION

Propionic acid and its calcium, sodium, and potassium salts are widely used throughout the food industry as preservatives¹. As a preservative, propionic acid extends the shelf life of food products by inhibiting the growth of moulds and some bacteria^{2–4}. Although preservatives derived from propionibacterium fermentations are available, most propionic acid used in the food industry have been produced by petrochemical synthesis¹. Propionic acid is also useful as a chemical intermediate. It can be used to modify synthetic cellulose fibres. It is also used to make pesticides and pharmaceuticals products. The esters of propionic acid are sometimes used as solvents or artificial flavourings⁵. Large amounts of propionic acid were once produced as a byproduct of acetic acid manufacture using the Monsanto process⁶.

This study mainly aims to synthesize propionic acid from propionaldehyde by electrochemical means on a gold plate electrode. Poised as they are in the middle of the oxidation sequence of carbon, carbonyl compounds are capable of being reduced or oxidized by either gaining or losing an electron. Thus, aldehydes can be oxidized to carboxylic acids or reduced to alcohols, hydrocarbons, or diols⁷. There are two systems which are known for inserting oxygen to an α H–C–C=O position. First is the reaction of the molybdenum peroxide reagent, $\text{MoO}_5\text{PyHMPA}$ with a variety of ketones and esters at temperatures of -70°C to -40°C ⁸. The second is the use of SeO_2

for the oxidation of ketones and aldehydes to 1,2-dicarbonyl compounds⁹. However, the disadvantage of these methods is that the reactions require the use of stoichiometric amounts of reagents.

In this study, the gold plate electrode was used as the working electrode which also plays the role of a catalyst. Gold is characterized by its relatively weak adsorption properties which account for the poor catalytic activity of this electrode in acidic solutions. However, in the case of alkaline solutions, the gold electrode proves to be a more effective catalyst for dehydrogenation of organic compounds¹⁰. The catalytic activity of gold towards the electro-oxidation of many organic compounds is greater in an alkaline medium^{11,12}. For this reason a potassium hydroxide solution was chosen to be the electrolyte. In addition, gold has started to play a major role in green chemistry recently as it addresses 8 out of the 12 principles of green chemistry as which are to prevent waste, design less hazardous chemical syntheses, use renewable feedstocks, use catalysts, not to use stoichiometric reagents, maximize atom economy, use safer solvents and reaction conditions, increase energy efficiency, and minimize the potential for accidents¹³.

MATERIALS AND METHODS

Reagents

Potassium hydroxide and propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$) were purchased from Sigma. KOH solution was prepared by dissolving the reagent

in ultra pure water. Propionaldehyde was used throughout without further purification.

Electrode preparation

Gold metal in the form of a plate (99.99%, Aldrich Chemical Company) with a thickness of 0.5 mm was cut into 1 cm × 1 cm squares. The metal was attached with a silver wire in a glass rod. Silver conductive paint was then used to stick the wire onto the surface of the gold plate. Epoxy glue was then applied to cover the surface to avoid contact with the silver paint. The epoxy resins were used as they possess excellent adhesive properties and are resistant to weak alkalis¹⁴.

Electrochemical measurement

Universal Pulsar Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) completed with VoltMaster 4 software was used for electrochemical measurements. All experiments were carried out at room temperature. The cyclic voltammetry experiment and electrolysis were performed using a three electrodes system: gold plate as working electrode (anode), and platinum wire and saturated Calomel electrode (SCE) as the auxiliary and reference electrodes, respectively. The electrodes were housed in a single electrochemical glass cell with a capacity of 50 ml. High purity nitrogen gas was used for deaeration for at least 10 min prior to each run and to maintain an inert blanket during the measurements.

Product Analysis

Analysis of the reaction products was performed using high performance liquid chromatography (HPLC) completed with Waters 1515 Isocratic HPLC pump, C 18 column (150 mm × 5 μm) and Refractive Index (RI) detector. Acetonitrile in acetone was used as the mobile phase. Fourier transform infrared (FTIR) spectroscopy was performed in order to identify the product of the electrooxidation of propionaldehyde.

The electrolysis was conducted at a fixed potential of 300 mV for five hours. The products formed during the bulk electrooxidation of propionaldehyde were determined by comparing their retention times to those of pure reference products under the same analysis conditions. HPLC-RI method was used for the separation and characterization of the components using acetone-acetonitrile as the eluting solvent. Dual wavelength absorbance detector was used in this study and C18 (150 mm × 5 μm) as the column. The flow rate was 1 ml/min.

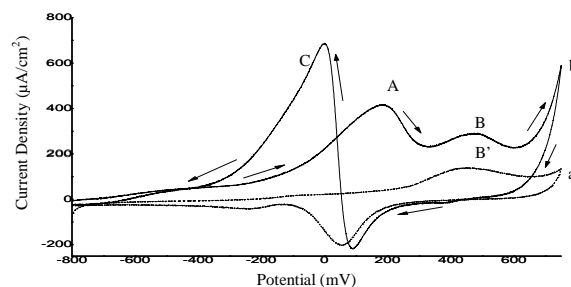


Fig. 1 Cyclic voltammogram of gold electrode in (a) 0.1 M KOH (dashed line) and (b) 0.1 M KOH + 0.20 M propionaldehyde (solid line). Scan rate: 50 mV/s.

RESULTS AND DISCUSSION

Voltammetry study

The voltammogram in Fig. 1 represents the oxidation of 0.20 M propionaldehyde on a gold electrode in 0.1 M KOH solution. There are three oxidation (anodic) peaks. Peaks A and B occur during positive sweep of potential. Peak C appears during the negative potential sweep.

Response of propionaldehyde

Peak B' indicates the surface oxidation¹⁵ which shows the hydroxide (OH^-) adsorption on the gold electrode surface forming a transient AuOH species. This adsorbed OH^- plays a governing role in the surface electrochemistry of Au in alkaline media¹⁶. The short-term species (OH^-) will be converted to surface oxide. The cathodic peak is the reduction of the gold oxide formed in the anodic scan¹⁷. The oxidation of propionaldehyde is not completely inhibited by the presence of the oxide layer of gold oxide, as shown by the fact that the intensity of peak B is higher than that of peak B'. Anodic peaks A and C appear before the 0.20 M propionaldehyde was introduced. These peaks are related to the oxidation of propionaldehyde. The onset for propionaldehyde oxidation occurs at a potential of around -100 mV for the SCE. The presence of the peak C indicates the reactivation of the surface oxide. After the oxidation peak, the catalytic oxidation peak decreased rapidly, and the oxidation peak was observed again at 10 mV. This behaviour is due to the passivated layer on the electrode surface of higher Au-oxides at a more positive potential¹⁸ of around 10 mV. This current (Peak C) originates from two contributions: the reduction of gold oxide and the oxidation of the reactant, i.e., the oxidation of the propionaldehyde species at the newly generated gold surface in our experiment¹⁹.

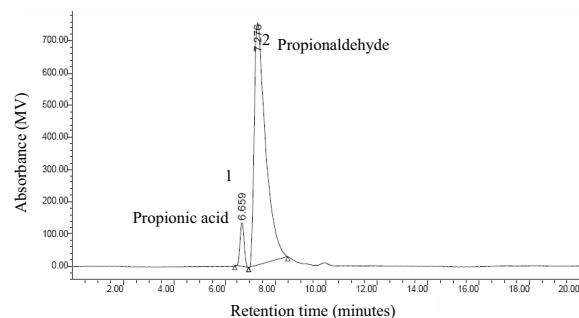


Fig. 2 Chromatogram of the product of the electrolysis of propionaldehyde.

HPLC and FTIR results

To identify the oxidation products, HPLC was used. A typical HPLC chromatogram (Fig. 2) for the oxidation products indicates that propionic acid was produced during the electrolysis of propionaldehyde. However, not all propionaldehyde was oxidized to propionic acid.

Products

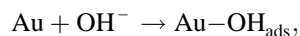
The principal products of the oxidation of C1, C2, C3, and C4 aldehydes are the respective carboxylic acids and CO_2 ²⁰. Carboxylic acids are known to be resistant towards chemical or electrochemical oxidation.

HPLC results indicate the presence of propionic acid in the product of the electrooxidation of propionaldehyde. The identified peaks indicate propionic acid at retention time of 6.659 min and propionaldehyde at 7.276 min.

From those FTIR spectra in Fig. 3, $\text{C}=\text{O}$ adsorption peaks were observed at 1640.91 and 1644.72 cm^{-1} . A very broad (strongly H-adsorbed) peak occurred at 3426.45 and 3427.17 cm^{-1} and 3427.17 cm^{-1} indicating the presence of OH^- . It usually overlaps the $\text{C}-\text{H}$ adsorption. This observation indicates the presence of the carboxyl group.

Electrooxidation of propionaldehyde on a gold plate electrode was successfully carried out in 0.1 M KOH resulting in propionic acid as the main product. The proposed mechanism for the reaction is shown in Fig. 4.

Previous experiments¹⁶ suggest a considerably polar behaviour of the $\text{Au}-\text{OH}^-$ bond and hence adsorption of OH^- on Au can be formally written as a partial charge transfer reaction:



where ads indicate directly chemisorbed species on Au. The $(\text{OH})_{\text{ads}}$ species on Au are usually hy-

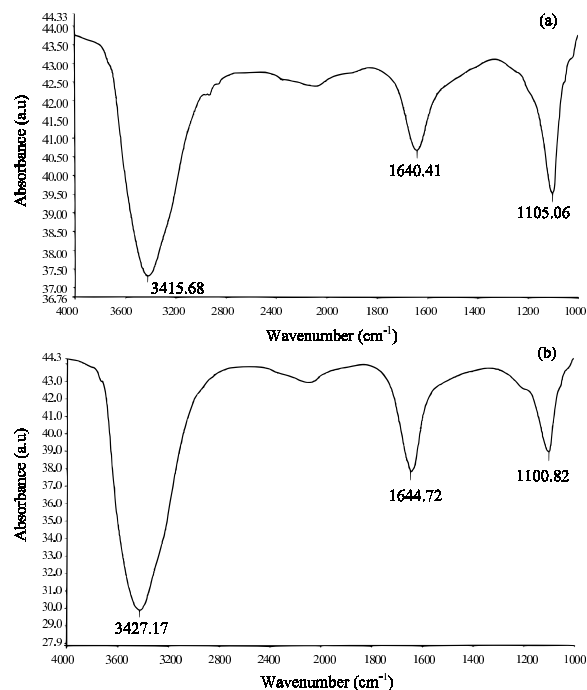


Fig. 3 Infrared spectra of (a) propionic acid (b) oxidation products.

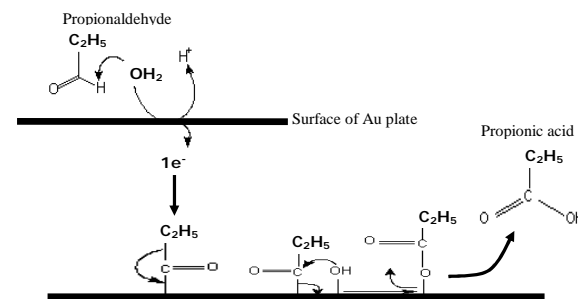
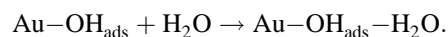


Fig. 4 The proposed mechanism of the oxidation of propionaldehyde on gold in alkaline media.

drated. Adsorption of H_2O on top of partially charged chemisorbed hydroxide species on Au can be formally written as:



CONCLUSIONS

This study proves the role of hydroxide species in the reaction path of synthesizing carboxylic acid from aldehyde. Gold is suitable to use as the catalyst in the production of carboxylic acid by means of heterogeneous system. This process provides an alternative method to easily and cleanly produce propionic acid.

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