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Electro-oxidation of D-mannose on platinum, gold and nickel electrodes in aqueous medium

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Abstract

The oxidation of D-mannose is studied on platinum, gold and nickel in alkaline medium. The electro-reactivity of this compound and the rate determining step of the reactions were determined by cyclic voltammetry. Lead adatoms have important effect on the oxidation of D-mannose on platinum electrode. Five folder of increase in current densities was observed after the addition of 10^{-6} M Pb^{2+}. Electrolyses carried out on upd-lead modified platinum, and gold electrodes show good conversion yields (75% and 80%, respectively) and reasonable selectivities towards mannonic acid. High amount of cleavage products were detected at the end of the electrolysis at nickel electrode. The reactivity-functional group relationship has been discussed considering the results of the electrolyses.

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1. Introduction

As our fossil raw materials are irrevocably decreasing and as the pressure on our environment is building up, the progressive changeover of chemical industry to renewable feedstocks for their raw materials emerges as an inevitable necessity. By far, the most important class of organic compounds in terms of volume produced are carbohydrates, as they represent roughly 75% of the annually renewable biomass of about 200 billion tons [1]. Of these, only a minor fraction (ca. 4%) is used by man, the rest decays and recycles along natural pathways. The bulk of the annually renewable carbohydrate biomass are polysaccharides. Accordingly, the constituent repeating units of these polysaccharides i.e. cellulose, hemicellulose, constitute the actual carbohydrate raw materials for basic organic chemicals. Keeping this goal in mind the electro-oxidation of D-mannose in alkaline medium was investigated. D-Mannose is a freely available sugar which can be obtained from the hemicellulosic part of the biomass. The galactoglucomannans, the main hemicelluloses in softwoods, are composed of a linear backbone of β-D-mannopyranose and β-D-glucopyranose (in a ratio approximately 1:4) linked by 1,4′-glycosidic bonds [2]. The catalytic and electro-catalytic oxidation of mannose has been the subject of relatively few investigations. The catalytic oxidation of mannose on gold catalysts, among other hexoses, has been studied by Mirescu et al. [3]. The authors reported that the Au/TiO_2 (0.45%) catalyst allow the transformation of D-mannose to its corresponding aldonic acid with 95.5% selectivity. The electro-catalytic oxidation of D-mannose and some other monosaccharides were investigated by Ben Aoun et al. [4], in order to determine the electro-catalytic activity of metal adatoms onto gold single crystal surfaces toward the electro-oxidation of sugars. Torto et al. [5] investigated the electrochemical oxidation of some mono- and disaccharides including D-mannose at copper rotating disk electrodes in alkaline medium. They reported that the number of electrons (n) transferred during the oxidation of the monosaccharides, was approximately 12. The aim of this work is to evaluate the electro-reactivity of D-mannose at different metal electrodes. Considering the

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results of long-term electrolyses and related mechanistic aspects some reaction schemes are tentatively proposed.

2. Experimental

2.1. Electrochemical setup

A thermostated three-electrode glass cell was used during the voltammetric study, while a two compartment glass cell separated by an ion exchange membrane (Ionac MA 3475) was employed for the electrolyses. The saturated calomel electrode and a platinum plate were used as reference and counter electrodes, respectively. Working electrodes for cyclic voltammetry were a nickel disc 99.98% (0.5 cm^2), a platinum 99.99+% (0.1 cm^2) and gold, 99.99+% (0.1 cm^2) spheres (GoodFellow). All the electrode activities are given in current densities, the active area being estimated from the hydrogen adsorption for the platinum electrode and the oxygenated species adsorption for the gold electrode. The geometric area is used for nickel electrode. Before each experiment, solutions were deaerated with pure argon (U Quality from L'Air Liquid). The platinum and gold electrodes were cleaned before each experiment with boiled deionized water and if necessary with H_2SO_4 solution (50%). The nickel disc electrode was polished using alumina powder. The cleanness of the surfaces and solutions was tested prior each experiment by recording voltammograms in the supporting electrolyte alone. Platinum, gold and nickel foils (6.5 mm × 6.5 mm × 0.25 mm each), purchased from GoodFellow, were used for the electrolyses.

The electrochemical instrumentation consisted of a potentiostat/galvanostat from Amel Instruments coupled to a microcomputer (Pentium II/500 MHz) through a AD/DA converter. The Labview software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for generating and applying the potential program as well as acquiring data such as current intensities.

2.2. Chemicals and reagents

The supporting electrolytes were prepared with ultrapure water (18 MΩ cm, Barnsted E-pure system), sodium hydroxide (Merck, pro analysi) sodium carbonate (Merck, pro analysi), sodium hydrogen carbonate (Merck, pro analysi) and sulfuric acid (Merck, extra pure). D-Mannose was purchased from Aldrich (97%). The aqueous solutions of HPLC references were prepared from Aldrich products. Lead nitrate (Riedel-de Haen, puriss.) was used to provide lead adatoms.

2.3. Product analysis

The identification of reaction products was carried out by gas cromatography (GC) using a CP-Sil 8 (Crompack) capillary column (95% dimethyl–8% diphenyl polysiloxane bonded, 30 m, 0.25 mm i.d. and 0.25 μm film thickness) and a FID detector. The electrolytic solutions were treated before analysis according to the following procedure. The electrolyzed solutions were neutralized using Dowex 200 (Dow Chemicals) a cation exchange resin, in order to obtain an aqueous solution of electrolyzed material free from inorganic ions. The water was removed by lyophilization to leave dry samples of electrolyzed material. This material was trimethylsilylated using Supelco HMDS + TMCS + Pyridine, 3:1:9 (Sylon HTP) Kit, as described in Ref. [6]. Authentic samples of D-mannose and of the expected reaction products were also trimethylsilylated and their chromatographic data were used for the product identification.

The quantitative analysis of reaction products was performed using two chromatographic setups: high performance liquid chromatography (HPLC) using an isocratic pump and a double on line detection including an UV–Vis detector and refractometer and ionic chromatography (IC, Dionex) using conductivity detector. The product partition was carried out on ion exchange columns: Aminex HPX-87 H from Biorad for HPLC and AS11-HC from Dionex for IC.

3. Results and discussion

3.1. Oxidation of D-mannose at platinum, gold and nickel electrodes

The voltammograms of platinum in presence of 10 mM D-mannose in 0.1 M H_2SO_4, in carbonate buffer (pH 10) and in 0.1 M NaOH are given in Fig. 1. D-Mannose appears to be very weakly oxidized in 0.1 M H_2SO_4 and the overall current densities increase with an increase of pH. During the positive potential sweep the oxidation of D-mannose in 0.1 M NaOH medium starts at −0.9 V vs. SCE (Fig. 1c). This value corresponds to a potential range where no oxygenated species is present on the electrode surface. The maximum current densities for the oxidation peak labeled A reach 0.13 mA cm^{-2} at −0.75 V vs. SCE. A second oxidation wave (B) with a maximum of 0.35 mA cm^{-2} at −0.22 V vs. SCE appears when the platinum electrode begins to be oxidized. Thus, the oxidation corresponding to the peak B seems to need the presence of adsorbed hydroxyl at the electrode surface. A third peak (C) with a lower current density by comparison to the previous one (0.26 mA cm^{-2} at 0.10 V vs. SCE) is observed at more positive potentials. During the negative potential sweep the voltammogram displays an oxidation peak (D) with a maximum of 0.10 mA cm^{-2} at −0.40 V vs. SCE. The voltammogram of platinum in presence of 10 mM mannonic acid in 0.1 M NaOH medium was shown in Fig. 2. The absences of oxidation peaks at potentials up to −0.4 V and higher to −0.1 V vs. SCE show the connection between the aldehyde group and the processes involved in these potential regions. Considering some other papers on the oxidation of some mono- and disaccharides [7–11], the reaction pathways for these processes can be tentatively presented. The first oxidation peak may be

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