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On the dramatic increase with chain length of the oxidazability of linear saturated aliphatic alcohols on gold in alkaline media

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ABSTRACT

The electrooxidation of linear saturated aliphatic alcohols from C1 to C8 on gold in alkaline media has been studied by cyclic voltammetry and with an electrochemical quartz crystal microbalance. The current density of alcohol oxidation very markedly increased and, correspondingly, the onset potential decreased, with increasing chain length, that is, with initially slightly increasing, and then constant, pKa. We attribute this oxidazability increase with chain length to the increasing hydrophobicity of the alcohol. Effectively, a molecular dynamics simulation of the hydration of alcohols and alcoholates shows that the hydrophobicity of the alcohols increases with increasing chain length. The higher activity of gold for the oxidation of organic, and also inorganic (CO), compounds in alkaline media is well known, and should be due to an activation of the gold surface by OH adsorption, and not to a change of the compounds themselves, the (majority) neutral alcohol being the oxidized species both in acid and alkaline media. At the potentials at which 1-heptanol oxidation starts, the mass in both base electrolyte and in 1-heptanol is at a minimum, or nearly so, which shows that water is driven away from the surface of gold prior to the oxidation of both gold and 1-heptanol.

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1. Introduction

The electrochemical oxidation of small alcohols continues to be actively investigated because of their possible use as renewable energy sources in fuel cells. The oxidation of methanol, the most studied alcohol, yields CO_2 and HCOOH or HCHO, depending on methanol concentration, electrode roughness, and time of electrolysis [1,2], whereas for ethanol it is very difficult to reach the complete 12-electron oxidation [3]. Recently, electrodes with catalysts that favour the homolytic cleavage of the C-C bond, although with small yields, have been reported [4]. The oxidation of methanol, which is strongly poisoned by chemisorbed CO, has been studied preferentially in acidic media using Pt electrodes. Gold is known to be a good oxidation catalyst in alkaline media, in which it has been used for studying the oxidation of methanol, ethanol, isopropanol, and glucose; ethylene glycol and glycerol have also been studied because of their high boil points and low toxicity [5–7]. Glassy carbon electrodes modified with a composite of Pd nanoparticles with chitosan have shown high activity for the electrooxidation of methanol, ethanol, and isopropanol in alkaline media [8]. And Estudillo-Wong et al. [9] used a TiO_2/C composite as support for Pd nanoparticles, concluding that at Pd/TiO_2–C the OH groups adsorbed at the TiO_2 sites increased the kinetics of methanol oxidation.

The origin of the high activity of gold in alkaline media remains a matter of debate. Recently, Ren *et al.* [10] concluded from an H-D kinetic isotope study that the cleavage of the α-H from the C-H bond is the rate- determining step (rds) for alcohol electro-oxidation on Au, whereas on Pd the rds would depend on the structure of the alcohol. Kwon et al. [11] reported that the onset potential for the oxidation on Au in 0.1 M NaOH of several alcohols with pK_a's ranging from 13.6 (sorbitol) to 18 (iso-butanol) increased linearly with their pK_a. They concluded that alcoholate was the only reacting species. Strmcnik et al. proposed that non-covalent interactions between hydrated alkali metal cations $M^+(H_2O)_x$ and adsorbed OH (OH_{ad}) species increase in the same order as the hydration energies of the corresponding cations ($Li^+ >> Na^+ > K^+ > Cs^+$), this trend being inversely proportional to the activity of Pt for methanol oxidation, which suggests that the OH_{ad}–$M^+(H_2O)_x$ clusters block the platinum active sites [12].

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At pH 11 the oxidation of methanol on gold is negligible [6]. In a previous work we reported that in a pH 11 carbonate/hydrogen carbonate buffer electrolyte the activity of gold was high for benzyl alcohol (BA), lower for ethylene glycol, and very low for 1-propanol and 1-butanol [13]. The double-layer capacity with BA was about one third of that for the aliphatic alcohols, which points to an expulsion of water from the Au surface due to the hydrophobic character of BA, suggesting that BA removes water molecules from the electrode surface, which should facilitate its electrooxidation. Similar results were obtained when the gold electrode was modified with Ni-based compounds [14], especially with poly-NiTSPc films, which rendered gold more hydrophobic.

In the present work the oxidation in alkaline solutions of the C1 to C8 linear saturated aliphatic alcohols, whose pK_a's are practically independent of the chain length, was studied in order to determine if acidity plays a role in their oxidazability or, as is the case with benzyl alcohol, if the hydrophobicity of the molecule plays a critical role.

2. Experimental

2.1. Reagents

Methanol, ethanol, 1- and 2-propanol, NaOH, Na_2CO_3, and $NaHCO_3$ were analytical grade from Merck, whereas 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol, also analytical grade, were from Sigma Aldrich.

Supporting electrolytes were 0.1 M NaOH or a 0.088 M Na_2CO_3 + 0.012 M $NaHCO_3$ buffer electrolyte, pH 11. All the solutions were freshly prepared with twice distilled water (conductivity near 2 $\mu S\,cm^{-1}$). The experiments were carried out at room temperature under a nitrogen atmosphere.

2.2. Electrochemical equipment

The measurements were carried out with an Autolab electrochemical work station, provided with an Elchema Electrochemical Quartz Crystal Microbalance (EQCM), and the corresponding Nova 1.10 software for the acquisition and treatment of the electrochemical data. Two types of gold electrodes were used: a gold disc electrode from CHInstruments (d = 0.2 cm) and a 10 MHz AT-cut quartz crystal with a thin film of gold (0.25 cm^2 geometrical area, and 0.24 cm^2 resonant area), Au/Q. As the adhesive layer for Au on the Au/Q electrodes a thin layer of Cr was used. The mass change data were directly registered using a constant of 4.4 ng $Hz^{-1}\,cm^{-2}$, based on Sauerbrey's equation, which is valid only under rather strict conditions. A Pt wire was used as counter electrode. Potentials were measured against an Ag/AgCl/0.3 M KCl electrode (CHInstruments), located in a vertical tube containing a 0.1 M Na_2SO_4 solution, and with a closed glass stopcock to avoid chloride diffusion into the cell. The potentials are usually referred to the Reversible Hydrogen Electrode, RHE, in order to directly compare catalytic activities independently of the solution pH. Current densities (j) are referred to the geometrical area. The roughness factor, R_F, is the ratio of the electrochemically active area determined from the gold oxide reduction charge, taking 400 $\mu C\,cm^{-2}$ for the reduction of a monolayer of AuO [15], to the geometric area. The roughness factor of the CHI Au electrode was 1.64 in 0.1 M NaOH, and about 3.0 for the Au/Q electrode (R_F was determined for each quartz crystal used). Before each experiment the Au disc electrode was polished with 0.1 μm alumina, sonicated for 10 min. and cycled in base electrolyte until its typical CV was again obtained. The same procedure, but for the polishing, was applied to the Au/Q electrode. All the experiments were run in duplicate.

2.3. Molecular Dynamics simulation

All alcohols were built with the Gaussian view software. The ChelpG charges for all atoms were assigned using the B3LYP/6-31G** basis set in Gaussian 03 software [16]. The Molecular Dynamics (MD) simulations were performed using NAMD 2.6 [17] with the Charmm33b1 force field [18]. Methanol, ethanol and propanol were put into a water box 40 × 40 × 40 $Å^3$ with about 1900 water molecules. We added NaCl 0.1 M and applied a cutoff of 10 Å for non-bonded interactions. We performed 250 ps of water equilibration, 10000 steps of minimization and 50 ps of heating from 0 K up to 310 K before each MD simulation. For each simulation 1 ns long Molecular Dynamics simulations were carried out. The temperature was kept constant using Langevin's method (310 K). All graphical analyses (Radial Distribution Function, RDF) were performed with the VMD software [19] using a correction parameter of monomer, added into the Charmm Force Field with a CcpNmr ACPYPE web server [20].

3. Results and Discussion

3.1. Cyclic voltammograms of C1 to C7 linear aliphatic alcohols in alkaline solutions

The CVs at 0.005 V s^{-1} of the Au disc in 0.1 M NaOH also 10 mM in methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-heptanol and 1-octanol are shown in Fig. 1. The alcohols were admitted to the cell at open circuit. The use of a homologous series eliminates possible singularities of polyhydric and branched alcohols.

The irreversible oxidation of gold starts at about 1.2 V_{RHE}, with a maximum at 1.39 V_{RHE}, and the formed gold oxide is reduced in a peak with a maximum at 1.13 V_{RHE}. Two anodic peaks, A1 in the positive scan and A2 in the negative scan, are due to the oxidation of the alcohol. The peak current density of both peaks A1 and A2 increases with the number of the carbon atoms up to 1-heptanol, and decreases abruptly for 1-octanol, because it is almost insoluble [21]. So, while the CV for methanol was but slightly higher than that in base, for 1-heptanol the peak current density, 0.8 mA cm^{-2}, was within a factor of 2 of that calculated for a diffusion-limited irreversible oxidation [22]

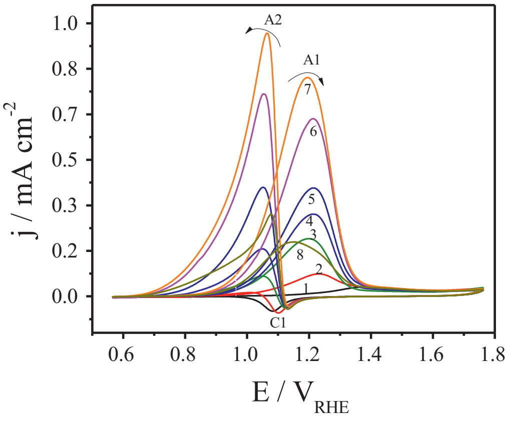

Fig. 1. Cyclic voltammograms at 0.005 V s^{-1} of a gold disc in 0.1 M NaOH, also 10 mM in: (1) methanol; (2) ethanol; (3) 1-propanol; (4) 1-butanol; (5) 1-pentanol; (6) 1-hexanol; (7) 1-heptanol and (8) 1-octanol. Roughness factor: 1.64.

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