Oxidation of cumene hydroperoxide on glassy carbon electrodes in aqueous solution and its interaction with ascorbic and gallic acids

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ABSTRACT

The cumene hydroperoxide oxidation on glassy carbon electrodes involves an irreversible one-electron transfer to peroxide and phenoxy radicals, being the main end products hydroquinone and acetone. The overall oxidation mechanism occurs in two steps: formation of acetone and a phenoxy radical, and the reaction of this phenoxy radical with water, getting stability by oxidizing into p-benzoquinone The interaction of such radicals with ascorbic and gallic acids decreases the oxidation signal of cumene hydroperoxide in differential pulse voltammetry. This decrease, due to the scavenging of the radicals formed after the electron transfer, is related to the antioxidant activities. So, it is possible to substitute the mercury as a probe for the electrochemical determination of antioxidant activity.

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1. Introduction

Antioxidants can be primary, if they block the generation of free radicals [1], secondary, if they repress the propagation of radicals, hinder the production of ROS (reactive oxygen species), and impede the activation of carcinogens in the metabolism [2,3], and tertiary, when they repair the harm produced by free radicals or when they wipe out damaged molecules [4,5].
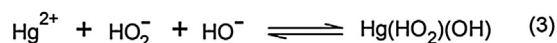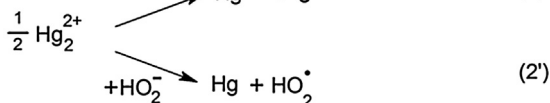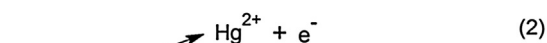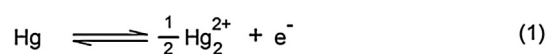
The antioxidant activity of natural products can be assessed by means of different methods, both direct and indirect [6]. Among these methods, electrochemical measurements have been proposed as a short-time assay for checking the antioxidant character of many organics [7,8]. In this way, cyclic voltammetry was used with phenolic acids, flavonoids, cinnamic acids etc [9–11], their oxidation potentials being compared to evaluate the differences in their antioxidant activities. The aptitude of a molecule to donate electrons is related to its antioxidant character and also to low oxidation potentials, which sequence of values are well correlated with the order in antioxidant activity measured by non-electrochemical techniques as the DPPH• radical scavenging [12]. Mostly of these experiments were performed on glassy carbon electrodes.

In another approach, the antioxidant character of components of foods was primarily determined using the anodic oxidation reaction of hydrogen peroxide on mercury by polarographic [13–17] and voltammetric (differential pulse) [18] techniques. Polarographic chriteria for the determination of antioxidant capacity have been developed [19–22].

Differential Pulse Voltammetry of hydrogen peroxide solutions on mercury electrodes was used to determine the activity of secondary antioxidants (radical scavengers) [18,23]. In this case, mercury is oxidized to Hg(I) and Hg(II) ions with the formation of traces of hydroperoxide radical, which interacts with the radical scavengers in diverse extent due to the different nature of the molecular reactivity. So, the scavenging activity of each antioxidant can be related to the concentration making the area of the DPV peak decrease in a 10%. This was also extended to mixes of compounds with scavenging activity and to extracts of several condiments.

The method is based in the following oxidation pathways [23]:

$$Hg \rightleftharpoons \frac{1}{2} Hg_2^{2+} + e^- \tag{1}$$

$$\frac{1}{2} Hg_2^{2+} \nearrow Hg^{2+} + e^- \tag{2}$$

$$\searrow +HO_2^- \quad Hg + HO_2^• \tag{2'}$$

$$Hg^{2+} + HO_2^- + HO^- \rightleftharpoons Hg(HO_2)(OH) \tag{3}$$

In such scheme AO represents the antioxidant; in its absence, only traces of Hg(I) reacts via reaction 2′. After the addition of AO, the hydroperoxyde radical produced in reaction 2′ is scavenged and this reaction decreases the concentration of the Hg(I) ion which give Hg(II) ion through reaction 2. Thus, less electrons are involved in the overall process and the overall oxidation current decreases. The subsequent DPV peak lowering as the antioxidant concentration increases has a lower limit: just a 50% of the area that was measured in the absence of AO. Intermediate values (from 10%% to 50%) can be easily related to the antioxidant activity.

Cumene hydroperoxide is a colorless to pale yellow liquid used mainly in the production of acetone and phenol [24–26]. It is a strong free radical source and, consequently, a catalyst for rapid polymerization, in particular with redox systems, a curing agent for unsaturated polyester resins, an initiator for polymerization of styrene and acrylic monomers and, finally, a chemical intermediate for dicumyl peroxide [27]. When it is heated or exposed to the light, it can originate fire, or even explode, due to its very fast decomposition.

The aim of this paper was, first, to propose an oxidation scheme for cumene hydroperoxide in aqueous solutions and, second, to show that this process can substitute hydrogen peroxide as electrochemical probe of antioxidant activity, using inert electrodes as GCE replacing the mercury electrodes.

2. Experimental

2.1. Materials

Cumene hydroperoxide (CHP), Ascorbic acid, Gallic acid and Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) were from Sigma-Aldrich. CHP, 80%, was of technical grade. All the other reagents used were at least of analytical quality. The rest of reagents used were from Merck. All chemicals were used without further purification.

Supporting electrolytes were solutions of acetic and phosphoric acids, for pH < 8.5, or phosphoric and boric acids, for pH > 8.5, with concentrations of 0.1 mol·L^{-1} in each component. Ultrapure water type I (resistivity 18.2 MΩ.cm at 25 °C) obtained from a Millipore-Milli Q system was used. The ionic strength was adjusted to 0.5 M with solid KNO$_3$ and the pH was adjusted with solid NaOH. Stock solutions were stored in darkness at 277 K to avoid decomposition.

2.2. Electrochemical measurements

A CHI650A electrochemical workstation from IJCambria was used for the electrochemical measurements. The glassy carbon electrode (GCE) was from IJCambria (area = 7.5 mm^2). The reference electrode was a Metrohm 6.0733.100 Ag | AgCl | KCl (3 m) and the auxiliary electrode was a platinum rod. Solutions were purged with purified nitrogen for at least 10 min to eliminate the oxygen that could originate undesired redox reactions on the electrode. The parameters selected in differential pulse voltammetry (DPV) were: pulse amplitude 0.05 V, pulse width 0.05 s and pulse period 0.2 s.

2.3. Electrode conditioning

Before each experiment, the glassy carbon electrode was polished with silicon carbide paper, followed by a diamond (0.25 μm) slurry and alumina (0.3 and 0.05 μm) slurries. Residual polishing was removed from the surface by the sonication of the electrode in a water bath for 30 minutes. After rinsed with distilled water thoroughly, it was applied a potential of +1.7 V under stirring in 0.2 m phosphate solution of pH 4.7 for 300 s, and then the electrode was scanned between +0.2 and +1.5 V at 0.1 V/s until a steady-state current-voltage curve was obtained.

The concentration of cumene hydroperoxide in the cell was $1 \cdot 10^{-3}$ M and the temperature was kept at 298 K. The reproducibility of the measurements was ensured by repeating the experiments and the standard deviations of the data were less than 5%.

3. Results and discussion

To cover the goal of using the cumene hydroperoxide oxidation for checking antioxidant activities, it is necessary to assess the production of free radicals in the electrode process. As far as the authors know, the electrooxidation process of CHP has not been examined in the literature. For this reason, the first work done was an electrochemical characterization of such process.

The cyclic voltammograms of CHP uniquely present one oxidation peak in the whole pH range studied as is shown in Fig. 1. In this figure the voltammograms recorded at very acidic pH values are not represented to avoid confusion caused by the great number of curves. The absence of reduction peaks at potentials near the oxidation peak indicates that the overall process is irreversible.

In the whole pH range studied, 1.0-12.3, the peak potential shifted towards less positive values in a roughly linear manner, with a slope of –125 mV per pH unit. The acid-base dissociation reaction of CHP has a value of 12.6 [28], this meaning that the undissociated CHP is the form present in the solution. So, it is clear that the pH-dependence of the voltammetric peak is due to this acid dissociation reaction preceding the oxidation reaction.

In addition, at constant pH, the peak potential is independent of the CHP concentration. The peak intensity is independent of the pH, and below CHP concentrations of $2 \cdot 10^{-3}$ M, the current is proportional to the CHP concentration.

All the above data indicate that the electrochemical process is of first-order with respect to CHP, consisting of an irreversible one-electron transfer preceded by the dissociation of an H$^+$ ion and followed by the rest of chemical-electrochemical reactions to give the oxidation products.

Finally, the current function $I_p/v^{1/2}$ is independent of $v^{1/2}$ at low scan rates, this meaning that adsorption processes, if they exist, are weak or inexistent.

As stated in the introduction section, the end products of the acid-catalyzed decomposition of CHP are phenol and acetone.
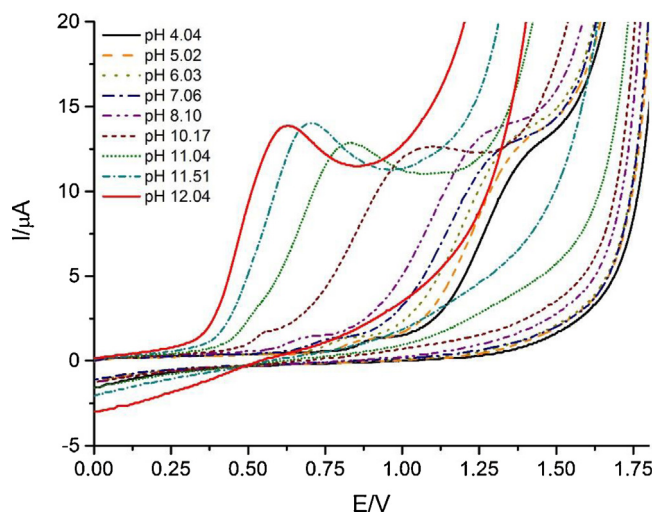

Fig. 1. Cyclic voltammograms of $1 \cdot 10^{-3}$ M cumene hydroperoxide at different pH values.