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Reactivity of hydroxy-containing aromatic compounds towards electrogenerated hydroxyl radicals

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A B S T R A C T

A kinetic study on the oxidation of hydroxy-containing aromatic compounds by electrogenerated HO radical and simultaneous by direct electron transfer is presented. First order kinetics are used to describe consumption rates of hydroquinone, benzoic acid and hydroxybenzoic acid derivatives by galvanostatic electrolysis with simultaneous oxygen evolution at a Pt electrode. Linear correlations were established from the effect of electrolyses current density on k_{app}. The meaning of the intercept and slope is analyzed. A good agreement is found between intercept values and the apparent rate constants from potentiostatic electrolysis without O_2 evolution. Simultaneously, the slopes magnitude corroborate the relative reactivity order of species that was established considering the occurrence of positive charge densities on carbon atoms of the aromatic ring. Therefore, the present analysis provides kinetic information concerning both, the direct electron-transfer and the reaction with HO radical.

1. Introduction

Electrochemical methods have proved to be adequate for the destruction of organics in aqueous media. A significant number of researchers has sought new electrode materials and improved reactors design to optimize mineralization indexes. Boron-doped diamond (BDD) was the most used anode material for this purpose [1–7], allowing to an efficient decrease of the TOC (total organic content) of aqueous solutions containing test compounds, such as phenol [8,9], benzoic acid [10,11], bisphenol A [12] or gallic acid [13]. The efficiency of organics destruction, by means of their electrooxidation with simultaneous oxygen evolution, was attributed to the formation of HO radicals as intermediaries of water electrooxidation [14–16]. The formation of this radical was detected in assays using anodes of Ti/IrO₂, Ti/SnO₂ and Pt using a radical trap [15]. The following mechanism was proposed for the oxidation of organics mediated by HO radicals [17].

$$H_2O \xrightarrow{k_{HO}} HO^\bullet + H^+ + e^- \tag{1}$$

$$2HO^\bullet \xrightarrow{k_{O_2}} O_2 + 2H^+ + 2e^- \tag{2}$$

$$R + nHO^\bullet \xrightarrow{k_{R,\,HO}} Products \tag{3}$$

The adsorption of HO radicals at the anode surface has a significant effect on their reactivity. When they are strongly adsorbed they display lower reactivity, as it happens for Pt or IrO₂, whereas when the adsorption strength is weak, as it happens for BDD, the reactivity of electrogenerated radicals is important [7].

Although most of the available studies deal with high oxidation power anodes, the use of anodes with low oxidation power can have important applications particularly when a certain degree of selectivity is required for oxidation.

In a previous work [18] we have reported a kinetic study on the oxidation of two compounds (BA and 4-HBA) using BDD and Pt, where it was shown that consumption of species occurred mainly by reaction with electrogenerated HO radicals. Based on these results, a kinetic treatment was presented, considering the relative magnitude of the organics concentration towards $k_{R,HO}/k_{O_2}$, that allows the interpretation of concentrations decay during galvanostatic electrolysis.

In this work, a kinetic study on aromatic compounds oxidation by electrogenerated HO radical with simultaneous direct electron transfer is presented. The possibility of extending our previous analysis to electroactive compounds is quite relevant as a great number of organic compounds is electroactive, particularly the model compounds used in mineralization studies. Compounds used in this work were selected regarding the direct electron transfer reaction features namely, the number of electrons involved (one or two) and the stability of the formed products (semiquinone radical or quinones). Kinetic data is analyzed considering the presumed reactivity of these species suggested from charge density values on carbon atoms of the aromatic ring.

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2. Experimental

2.1. Chemicals

All reagents employed were of analytical grade: benzoic acid (BA; Prolabo), 4-hydroxybenzoic acid (4-HBA; BDH Chemicals), 2,3-dihydroxybenzoic acid (2,3-HBA; ACROS Organics), 2,4-dihydroxybenzoic acid (2,4-HBA; ACROS Organics), 2,5-dihydroxybenzoic acid (2,5-HBA; ACROS Organics), 3,4,5-trihydroxybenzoic acid (3,4,5-HBA; Sigma), hydroquinone (HQ; May & Baker, Ltd.), potassium chloride (Fluka), potassium ferrocyanide and potassium ferricyanide (José Gomes Santos), potassium dihydrogen phosphate and phosphoric acid (ACROS Organics). Methanol was of HPLC grade from Fisher Scientific.

2.2. HPLC

Oxidation reactions were monitored following the concentration decrease along galvanostatic electrolyses by HPLC. HPLC experiments were performed using a Jasco, PU-2080 Plus system equipped with a RP 18 column from Grace Smart (250 mm × 4.6 mm, 5 μm particle size) and using Clarity HPLC software from Jasco (Jasco 870/UV detector). A flow rate of 0.6 ml min^{-1} and a loop of 20 μl were used. A mixture of methanol, water and phosphoric acid (60:39:1) (v/v) was used as mobile phase. The detection wavelength was selected according to species: 210 nm for 2,3-HBA and 2,4-HBA; 230 nm for BA, 4-HBA and 2,5-HBA; and 280 nm for 3,4,5-HBA and HQ. The quantification was performed using calibration curves.

2.3. Electrochemical measurements

Voltammetric measurements and galvanostatic/potentiostatic electrolyses were performed using a potentiostat (Autolab type PGSTAT30, Ecochemie) controlled by GPES 4.9 software provided by Ecochemie.

2.3.1. Cyclic voltammetry

Cyclic voltammetry experiments were carried out from −0.25 to 1.4 V using an undivided three-electrode cell. The working electrodes were of glassy carbon (GC; 3 mm diameter disc electrode, CHI104, CH Instruments, Inc.) and of Pt (EM-EDI, Radiometer Analytical). An Ag/AgCl, 3.0 M (CHI111, CH Instruments, Inc.) was used as reference electrode and a Pt wire as counter electrode. The surface of the GC electrode was cleaned between scans by polishing with polycrystalline diamond suspension (3 F μm; Buehler) for ≈1 min. The Pt electrode was electrochemically cleaned in 0.10 M phosphate buffer pH 3.5 at the oxygen evolution region (0.02 A) during 600 s.

2.3.2. Electrolysis

Galvanostatic electrolyses were carried out using current densities from 50 to 1250 A m^{-2} in a two compartments cell separated by a glass frit membrane. The volume of the anodic compartment was 9.0 ml and the solution was mechanically stirred with a magnetic stir bar (300 rpm). The anode is made of a piece (20 mm × 10 mm) of Pt gauze (52 mesh woven from 0.1 mm diameter wire, 99.9%, from Alfa Aesar). Before each experiment the anode was cleaned electrochemically in 0.1 M phosphate buffer pH 3.5 during 600 s at a constant current of 0.02 A. The area of the Pt working electrode (5.6 cm^2) was determined in a chronoamperometry experiment using 1.00 mM of $K_3[Fe(CN)_6]$ in 0.1 M KCl [19].

Reported apparent rate constants from oxidation of hydroxybenzoic acid derivatives and of HQ were determined using data of at least two electrolyses and displayed uncertainties correspond to standard deviations.

2.4. Diffusion coefficients

Diffusion coefficients (D) were estimated from the slope of I_p vs. $v^{1/2}$ (regarding voltammetric data from 20 to 100 mV s^{-1}) for hydroxybenzoic acids derivatives whose first oxidation peaks involve a single electron. α values were estimated considering $(E_p - E_{p/2}) = 48/(\alpha \cdot n)$ (Table 1). The number of electrons of the first oxidation peak in Table 1 were obtained from literature [20–23]. As the homogeneous rate constants were not known, the selection of the scan rates was based on the fit to a linear dependence of I_p and $v^{1/2}$ in order to discard a pure kinetic behaviour (low scan rates) or distortions due to the capacitive current (higher scan rates). Despite a pure diffusion behaviour is not assured the introduced uncertainty is known to be low for EC processes [24]. Validation of determined D values cannot be performed as there are not available D values for most of the compounds analyzed. For 3,4,5-HBA the calculated value of D is in agreement with that reported elsewhere based on simulation results [22] with a deviation of 5%. Reported uncertainties were calculated using the standard deviation of the slope of I_p vs. $v^{1/2}$.

2.5. Hydrodynamics characterization of the electrolysis cell

The mass transport efficiency of the electrochemical cell was characterized by analysis of j–t curves from electrolyses (1.2 V) of 0.50 mM $K_4[Fe(CN)_6]$ in 0.15 M phosphate buffer pH 3.5 (Eq. (4)) [24].

$$\frac{j}{j_0} = \exp\left(-\frac{k_{app}A}{V}t\right) \tag{4}$$

where, A is the anode surface area, V is the volume of the solution in the anodic compartment, k_{app} is the apparent rate constant that characterizes the consumption of the substrate and t is time. As oxidation of $[Fe(CN)_6]^{4-}$ is a very fast one-electron transfer, the process is mass transport controlled and therefore $k_{app} = k_m$:

$$k_m = \frac{D}{\delta} \tag{5}$$

where, k_m is the mass transport coefficient and δ is the diffusion-layer thickness.

From Eq. (5) $\delta = 2.53 \times 10^{-3}$ cm was determined using $k_m = 3.04 \times 10^{-3}$ cm s^{-1} (evaluated from j–t curve of potentiostatic electrolysis) and $D = 7.7 \times 10^{-6}$ cm^2 s^{-1} (from voltammograms recorded in 0.15 M phosphate buffer pH 3.5 and using Cottrell equation). Calculated values of D for $[Fe(CN)_6]^{4-}$ is in agreement with that reported [25].

2.6. Charge density calculations

Charge density values were calculated using MarvinSketch, a Java based chemical editor, provided by platform ChemAxon. Representation of molecules was drawn also using MarvinSketch.

3. Results and discussion

Electrogeneration of HO radicals from water occurs at potentials higher than those required for oxidation of most hydroxybenzoic acid derivatives, therefore it is expected that their direct oxidation occurs simultaneously with the oxidation via HO radicals. Characterization of voltammetric response of these compounds is consequently relevant for interpretation of their oxidation kinetics.

3.1. Cyclic voltammetry and potentiostatic electrolysis

Cyclic voltammetry of 4-HBA, 2,3-HBA, 2,4-HBA, 2,5-HBA, 3,4,5-HBA and HQ in phosphate buffer pH 3.5 was carried out at Pt and