

Spectroelectrochemistry of salicylaldehyde oxidation



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ABSTRACT

The advances in knowledge of the oxidation mechanism of salicylaldehyde are important in understanding its role and conversion in the involved oxidative degradation, synthesis and aerobic metabolism processes. The electrochemical oxidation of salicylaldehyde was investigated in different pH media using cyclic voltammetry, *in situ* UV–vis spectroscopy and cyclic voltabsorptometry based on a long optical-path thin-layer electrochemical cell. ATR-FTIR spectroscopy was used for characterization of the oxidation products deposited on the electrode surfaces. Time-derivative cyclic voltabsorptograms were obtained at the characteristic wavelengths of salicylaldehyde and the soluble oxidized salicylaldehyde, for comparative discussion with the corresponding cyclic voltammograms. Two couples of redox peaks, subsequent to the main oxidation peak of salicylaldehyde, were observed on the voltabsorptograms but nearly indistinguishable on the voltammograms. Salicylaldehyde was initially oxidized to reactive phenoxyl radicals, followed by a series of transformation steps leading to different final products. A parallel-consecutive reaction mechanism was proposed for the pH-dependent formation of a deposited polyester and two trace amounts of soluble quinoid products.

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1. Introduction

Salicylaldehyde (*o*-hydroxybenzaldehyde) is a common highly-functionalized arene that has often been used as analysis reagent, spices and gasoline additive. It is also a key precursor in organic synthesis of a variety of chelating agents and other chemicals. Because of its widespread application, salicylaldehyde becomes an organic pollutant that finds its way into the water system through pharmaceutical medications, cosmetic products, and agricultural chemicals [1]. Also, salicylaldehyde naturally occurs in grape, tomato, cinnamon, milk and milk products, beer, coffee and tea. It has been found to be an intermediate formed during the aerobic metabolism of some polycyclic aromatic hydrocarbons [2–4].

Salicylic acid is one of the possible oxidation products of salicylaldehyde. Electrochemical oxidation of salicylic acid [1,5–12] and acetylsalicylic acid [13–15] has been widely investigated focusing on the electrochemical removal and degradation [1,5–7], electrochemical detection [8–11,13,14], electro-polymerization [7,12] and electro-oxidation mechanism [9,15]. Salicylic acid and its derivatives have also been used as an electrode modifier for the determination of trace copper(II) in water [16], the amperometric

nonenzymatic determination of glucose free of interference [17], and for the visible light photoelectrocatalytic degradation of *p*-nitrophenol [18]. However, only a few reports are available on electrochemical oxidation of salicylaldehyde [1,5]. Chen et al. studied the kinetics of electrochemical oxidation of salicylic acid and salicylaldehyde in 0.5 M H₂SO₄ at a Ti/IrO₂-SnO₂-Sb₂O₅ electrode [1] and of their photoelectrochemical oxidation on titanium dioxide nanotube arrays [5] using *in situ* UV–vis spectroscopy. They revealed the impact of temperature, initial concentration, current density and supporting electrolyte etc. on the degradation kinetics. The electro-oxidation pathway of salicylaldehyde is currently unclear and deserves further study for better understanding its role and conversion in the involved oxidative degradation, synthesis and aerobic metabolism processes.

A combination of cyclic voltammetry (CV) and cyclic voltabsorptometry (CVA) allows simultaneously measuring the potential-dependent current and absorbance [19,20]. The light-absorbing reactant, intermediates and products involved in the electrochemical processes can be followed photometrically by setting the corresponding characteristic wavelengths. The time-derivative cyclic voltabsorptometry (DCVA) presents the data curves in a shape resembling that of the corresponding CV curves, providing direct comparison between the CV and DCVA peaks. Unlike the CV peaks, the DCVA peaks may be caused not only by electrochemical reaction but also by chemical conversion. Moreover, no charging/discharging background signals are

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recorded on the DCVA curves, which may improve the response to the electrochemical and chemical processes.

The CVA has generally been used along with an optically transparent electrode, in a light incident mode perpendicular to the electrode surface. In the present work, the CVA technique was used with a long path-length thin-layer electrochemical cell to investigate the electrochemical oxidation of salicylaldehyde in acidic, physiological and alkaline pH media. This thin-layer cell, in a light incident mode parallel to and close to the electrode surface, allows monitoring soluble intermediates and products generating from an opaque electrode. The use of long path-length greatly improves the sensitivity of detection of the analytes present in the thin-layer solutions. Enhanced responses are therefore obtained to the potential- and pH-dependent formation and reduction of the soluble products.

2. Experimental

2.1. Chemicals and solutions

Reagent grade salicylaldehyde (98%+ pure) from Guangfu (Tianjin, China) was used as received. Spectrograde graphite powder (320 mesh) and spectrograde paraffin wax (solidification point 62–65 °C) from Shanghai Chemical Works were used for preparing the graphite paste electrode. Graphite sheet was from Aida-hengsheng (Tianjin, China). Other chemicals were of analytical grade from China-Reagent group. All solutions were prepared with doubly-distilled water from an all-glass distillation apparatus. Salicylaldehyde stock solution was prepared with ethanol and water in a volume ratio of 1:4 by means of ultrasonic agitation, and then kept at 4 °C in a refrigerator. The supporting electrolytes with various pH values were a mixture of 0.2 M Britton-Robinson (BR) buffered solution and 0.5 M KCl. High pure N₂ was used for solution deaeration.

2.2. Apparatus, electrodes and cells

Cyclic voltammetry and spectroelectrochemistry were carried out on a CHI660C electrochemical workstation (Chenhua, Shanghai, China). UV-vis spectroscopic and photometric measurements were carried out on an UV-2500 spectrophotometer (Shimadzu, Japan) to monitor the soluble reactants and products under potentiostatic and potentiodynamic conditions. Attenuated total reflectance (ATR)-FTIR spectra were recorded on a Vertex 80 infrared spectrometer coupled to a Hyperion 2000 IR microscope (Bruker Optics).

The three-electrode system was composed of a graphite working electrode, a KCl-saturated Ag/AgCl reference electrode (0.195 V vs. SHE, self-made) and a platinum wire counter electrode. The graphite working electrode used for the conventional voltammetric measurements was a disk solid graphite paste electrode (GPE) with a smaller geometrical area of 0.049 cm², whereas the electrode for the thin-layer electrochemical experiments was a quadrate graphite sheet electrode with a larger area of 0.77 cm². The graphite paste electrode was selected because of its advantages of low background currents, low noise and fast base line stabilization, and its preparation was described previously [21,22].

A conventional single-compartment cell was used for the voltammetric measurements. A thin-layer spectroelectrochemical cell was self-made, using a standard quartz photometric cell with 10 mm optical path length as the cell body. The schematic view of the thin-layer cell can be found in literature [23]. The incident light beam parallels to the working electrode and goes through the thin-layer electrolyte solution (0.2 mm thick) on the electrode surface.

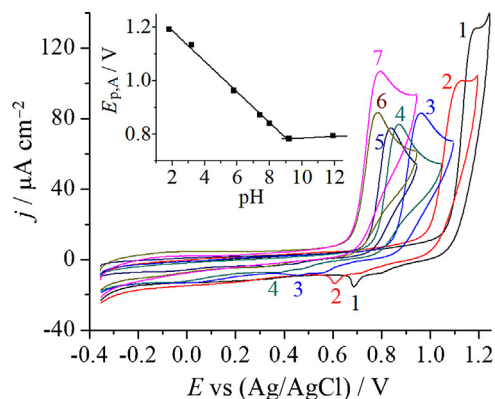


Fig. 1. CVs of 100 μM salicylaldehyde in different pH buffers. pH (1→7): 1.8, 3.2, 5.8, 7.4, 8.0, 9.2 and 11.9. Scan rate 100 mV s⁻¹. Inset: pH dependence of the anodic peak potential.

2.3. Procedures

Salicylaldehyde solutions were bubbled with high pure N₂ for about 15 min to remove dissolved oxygen before being put into the electrochemical cells. The working electrode was polished carefully with 800 grit emery paper. Before each run, the working electrode was cleaned and activated by repetitive cyclic scans between 0.0 and 1.6 V in 0.1 M NaHCO₃ solution until only the background current remained. Considering the adsorption of salicylaldehyde on graphite electrode, a pre-accumulation step was always performed in open circuit for 60 s. All the experiments were carried out at room temperature (22 ± 1 °C).

The UV-vis absorption spectra were recorded while the thin-layer solution was electrolyzed at a constant potential. Blank BR buffers were used for the spectral baseline correction. Cyclic voltammetry was performed at a certain wavelength to follow the absorbance changes of species in the thin layer solution. The ATR-FTIR spectra were recorded *ex situ* for characterizing oxidation products deposited on the electrode surfaces. The spectra were collected with 64 scans and at a resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammetric behavior of salicylaldehyde was examined in a wide pH range of 1.8–11.9. The cyclic voltammograms recorded using the GPE shows one anodic peak (Fig. 1), corresponding to the oxidation of salicylaldehyde. The anodic peak current density ($j_{p,A}$) first decreased and then increased with increasing pH, showing a minimum peak current at pH 8.0. The anodic peak potential ($E_{p,A}$) shifted negatively with increasing pH until reaching pH 9.2, following a linear relationship $E_{p,A}/V = 1.3008 - 0.0571 \text{ pH}$ ($R = -0.99837$) (the inset of Fig. 1). The equation slope of -57 mV per pH unit supports a reaction mechanism involving an equal number of electrons and protons. At the pH values greater than 9.2, the peak potential did not depend on the pH of media, suggesting the absence of proton transfer in these pH conditions. The pK_a values of salicylaldehyde, phenol and benzaldehyde are about 8.37, 9.99 and 14.90 at 25 °C [24]. Accordingly, the initial electro-oxidation should occur at the phenolic group of salicylaldehyde, through one-electron one-proton transfer for the undissociated molecules but only one-electron transfer for the deprotonated phenolate anions.

The corresponding cathodic peaks were extremely small (Fig. 1), indicating the poor reversibility of salicylaldehyde oxidation. The

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