



## Short communication

# Fenton-like oxidation of small aromatic acids from biomass burning in atmospheric water and in the absence of light: Identification of intermediates and reaction pathways



Patrícia S.M. Santos <sup>a,\*</sup>, M. Rosário M. Domingues <sup>b</sup>, Armando C. Duarte <sup>a</sup>

<sup>a</sup> CESAM (Centre for Environmental and Marine Studies) & Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

<sup>b</sup> Mass Spectrometry Centre & QOPNA, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

## HIGHLIGHTS

- The main oxidation intermediates produced are also small aromatic compounds.
- The intermediates show more hydroxyl groups linked to benzene ring than precursors.
- The hydroxylation is the main step on the oxidation of small aromatic compounds.
- A double step of decarboxylation/hydroxylation may originate poly-hydroxybenzenes.

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## ABSTRACT

A previous work showed that the night period is important for the occurrence of Fenton-like oxidation of small aromatic acids from biomass burning in atmospheric waters, which originate new chromophoric compounds apparently more complex than the precursors, although the chemical transformations involved in the process are still unknown. In this work were identified by gas chromatography-mass spectrometry (GC-MS) and by electrospray mass spectrometry (ESI-MS) the organic intermediate compounds formed during the Fenton-like oxidation of three aromatic acids from biomass burning (benzoic, 4-hydroxybenzoic and 3,5-dihydroxybenzoic acids), the same compounds evaluated in the previous study, in water and in the absence of light, which in turns allows to disclose the chemical reaction pathways involved. The oxidation intermediate compounds found for benzoic acid were 2-hydroxybenzoic, 3-hydroxybenzoic, 4-hydroxybenzoic, 2,3-dihydroxybenzoic, 2,5-dihydroxybenzoic, 2,6-dihydroxybenzoic and 3,4-dihydroxybenzoic acids. The oxidation intermediates for 4-hydroxybenzoic acid were 3,4-hydroxybenzoic acid and hydroquinone, while for 3,5-dihydroxybenzoic acid were 2,4,6-trihydroxybenzoic and 3,4,5-trihydroxybenzoic acids, and tetrahydroxybenzene. The results suggested that the hydroxylation of the three small aromatic acids is the main step of Fenton-like oxidation in atmospheric waters during the night, and that the occurrence of decarboxylation is also an important step during the oxidation of the 4-dihydroxybenzoic and 3,5-dihydroxybenzoic acids. In addition, it is important to highlight that the compounds produced are also small aromatic compounds with potential adverse effects on the environment, besides becoming available for further chemical reactions in atmospheric waters.

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## 1. Introduction

Biomass combustion is an important primary source of particles

in the global atmosphere, and the biomass burning constituents are worthy of concern due to their effects on atmospheric chemistry (Rosenfeld et al., 2008), climate (Chand et al., 2006), aquatic and terrestrial ecosystems (Silva et al., 2015), and human beings (Wegesser et al., 2009). Furthermore, the constituents directly emitted by biomass burning events have different lifetimes due to the various chemical reactions that occur in the atmosphere. Those

\* Corresponding author.

E-mail address: [patricia.santos@ua.pt](mailto:patricia.santos@ua.pt) (P.S.M. Santos).

reactions can take place both on the surface of particulate matter and inside water droplets (e.g., mist, fog, and clouds), and yield intermediates that often play a key role in atmospheric chemistry (Vione et al., 2006). However, as the chemical transformations that occur in the atmosphere still contain a high level of uncertainty, the identification of intermediate compounds of atmospheric reactions becomes of utmost importance to understand the mechanistic of reactions, but also because it helps to foresee hazardous consequences for the environment.

A recent work of Santos and Duarte (2015) evaluated the Fenton-like oxidation of three small aromatic acids (benzoic, 4-hydroxybenzoic and 3,5-dihydroxybenzoic acids) from biomass burning in water, by ultraviolet–visible and molecular fluorescence spectroscopies, and showed that even in the absence of light there is a production of new chromophoric compounds that are subsequently degraded. Moreover, the same study showed that for the three aromatic acids the new chromophores presented fluorescent bands at similar excitation wavelengths, 330/340 nm and 400 nm, suggesting the formation of similar compounds. In order to evaluate these hypothesis, the present work aims at identifying the intermediate compounds formed during Fenton-like oxidation of three small aromatic acids, benzoic, 4-hydroxybenzoic, and 3,5-dihydroxybenzoic acids, in water and in the absence of light, which in turns allows to disclose the reaction pathways that occur with the oxidation of the aromatic acids in atmospheric waters. For such, the experimental conditions used in this work were chosen to mimic atmospheric waters as much as possible, according to the work of Santos and Duarte (2015), and the identification of the intermediate compounds was evaluated by gas chromatography-mass spectrometry (GC-MS) and by electrospray mass spectrometry (ESI-MS).

## 2. Material and methods

The Fenton-like oxidation of benzoic, 4-hydroxybenzoic and 3,5-dihydroxybenzoic acids in water and in the absence of light was performed as reported by Santos and Duarte (2015). Briefly, the concentration of acids used was  $2 \times 10^{-5}$  M, the concentration of iron (III) was  $5 \times 10^{-6}$  M, and the concentration of hydroxide peroxide was  $10^{-4}$  M. These concentrations of iron (III) and hydrogen peroxide are within the ranges found in the atmospheric aqueous phase (Vione et al., 2006). A pH value of 4.5 was chosen to perform the reactions, since it promotes the reaction for the three compounds (Santos and Duarte, 2015), and it is also within the typical values of pH for atmospheric droplets (Seinfeld and Pandis, 1998). The pH of solutions was adjusted with sulphuric acid and sodium hydrogen carbonate (Pignatello et al., 2006). Hydrogen peroxide was prepared and added to the model solutions immediately after the adjustment of pH in order to initiate the reaction. Then, solutions (20 mL in a glass flask of 50 mL) were placed in an incubator at 20 °C with agitation of 300 rpm and in absence of light until the time of stopping the reaction. The choice of the reaction time for identifying the oxidation intermediates was based on the fluorescence data of the previous study of Santos and Duarte (2015), when it was observed the presence of the highest fluorescence intensity for the highest number of new fluorescent bands: 24 h for the benzoic acid; 6 h for the 4-hydroxybenzoic acid; and 1 h for the 3,5-dihydroxybenzoic acid.

The reaction intermediates were separated and identified by gas chromatography-mass spectrometry (GC-MS) according to the methodology used by Deng et al. (2006) for the benzoic acid. The extraction of compounds was carried out by extracting 2 times 7.5 mL of each sample three times with 1.5 mL of ethyl acetate by vortexing for 1 min in a 10-mL glass tube (after pH adjustment to 1.0 by addition of 0.50 M HCl). The top organic layers were removed

and pooled in another glass tube. The ethyl acetate extracts were dried under nitrogen flow. The extracts were derivatized by adding 50  $\mu$ L of pyridine, 50  $\mu$ L of the derivatization reagent N,O-bis(triethylsilyl)trifluoroacetamide (BSTFA) and 10  $\mu$ L of trimethylchlorosilane (TMCS), and heated at 70 °C for 1 h. Then, the extracts were analysed using a Shimadzu Corporation GC/MS-QP5050A, equipped with a ZB-5MSi fused silica capillary column and helium as a carrier gas. For analysis the injector temperature and the interface temperature were both at 280 °C, and the injection volume was 1.0 mL in the splitless mode. The column temperature was programmed as follows: 80 °C for 1 min, increased at a rate of 10 °C/min until 200 °C, followed by 20 °C/min until 280 °C, and was kept at 280 °C for 2 min. The mass spectra were scanned from  $m/z$  50–700. The identification of compounds was performed by comparing GC retention times and mass spectra of authentic standards for the initial aromatic acids, and comparing the mass spectra of intermediate compounds with mass spectral libraries, where only similarities higher than 85% were accepted. The presence of the identified compounds by GC-MS in the extracts was confirmed by electrospray ionization mass spectrometry (ESI-MS) in negative mode, in a linear ion trap mass spectrometer LXQ (Thermo Finnigan, San Jose, CA, USA). The dry extracts were solubilized with 200  $\mu$ L of chloroform and 200  $\mu$ L of acetone, and were introduced through direct infusion (mixture of 3  $\mu$ L of extract and 197  $\mu$ L methanol), and the ESI conditions in negative mode were as follows: flow rate of 8  $\mu$ L/min; electrospray voltage of 4.7 kV; capillary temperature of 275 °C and the sheath gas flow of 25 units. An isolation width of 0.5 Da was used with a 30 ms activation time for MS/MS experiments. Full scan MS spectra and MS/MS spectra were acquired with a 50 ms and 200 ms maximum ion injection time, respectively. Normalized collision energy TM (CE) was varied between 23 and 26 (arbitrary units) for MS/MS. Data acquisition and treatment of results were carried out on an Xcalibur Data System (version 2.0).

## 3. Results and discussion

Fig. 1 shows the chromatograms obtained by GC-MS analysis of the derivatized extracts resulting from the Fenton-like oxidation of benzoic, 4-hydroxybenzoic, and 3,5-dihydroxybenzoic acids (BA, 4-HBA and 3,5-DHBA, respectively) for 24 h, 6 h, and 1 h, respectively.

The following oxidation intermediates were identified for the benzoic acid experiment: 2-hydroxybenzoic, 3-hydroxybenzoic, 4-hydroxybenzoic, 2,3-dihydroxybenzoic, 2,5-dihydroxybenzoic, 2,6-dihydroxybenzoic, and 3,4-dihydroxybenzoic acids. Deng et al. (2006) also found these intermediate compounds through the iron-catalyzed photochemical reaction of benzoic acid in water, which suggest that they are important intermediates of both type of reactions in atmospheric liquids. Moreover, it was suggested in such study that the hydroxyl ( $\cdot$ OH) radicals may attack the ortho, meta, and para positions of benzoate ions ( $C_6H_5COO^-$ ) leading to the formation of mono- and/or di-hydroxybenzoic acids, which seems to have also occurred with the Fenton-like oxidation of benzoic acid in the absence of light (Fig. 2a)).

For the 4-hydroxybenzoic acid the oxidation intermediates identified were the 3,4-dihydroxybenzoic acid and hydroquinone (HQ). Rivas et al. (2001) also found these intermediates, among others, in the Fenton oxidation of 4-hydroxybenzoic acid, and they suggested the occurrence of a decarboxylation step in the mechanism of formation of hydroquinone, which possibly also occurred in the present study (Fig. 2a). Moreover, it is important to note that the compounds 4-hydroxybenzoic acid and 3,4-dihydroxybenzoic acid were also identified as oxidation intermediates of benzoic acid, and they may be considered as secondary and tertiary products of the Fenton-like oxidation of benzoic acid, respectively.

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