



Radical sites in humic acids: A theoretical study on protocatechuic and gallic acids



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ARTICLE INFO

Article history:

Received 1 October 2013

Received in revised form 16 January 2014

Accepted 17 January 2014

Available online 26 January 2014

Keywords:

Protocatechuic acid

Gallic acid

Humic acids

DFT

EPR

Solvation

ABSTRACT

Protocatechuic and gallic acids (PCA/GA) were used as models for studying the radical sites in humic acids. Neutral, anionic, and anion radical conformers were investigated by means of density functional theory in gas phase and solvent, respectively. For the most stable radical structures electron spin density and EPR parameters such as g -tensors and isotropic hyperfine coupling constants (HFCCs) were calculated using the B3LYP functional. Additionally, the performance of several other popular functionals of the DFT theory including BP86, B97D, M06, TPSS, TPSSh and B2PLYP was evaluated. Obtained g -tensors are strongly anisotropic having two principal components (g_{xx} , g_{yy}) lying in the plane of the aromatic ring. The difference between the g -tensors of PCA and GA anion radicals are minimal. Inclusion of environmental effects (explicit consideration of hydrogen bonds plus continuum solvation) has a significant impact on g -tensor components and HFC constants shifting their values closer to available experimental data. In summary, good agreement of the B3LYP results with experiment is obtained and from the set of the additional DFT functionals used only the hybrid variant of the TPSSh functional provides good results. The calculated values of g -tensors and HFCCs support the hypothesis that polyphenolic fragments are main sources of transient and native radical sites in structurally complex humic acids.

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1. Introduction

Humic acids (HAs) represent a group of large organic macromolecules with high structural and functional complexity and strongly varying properties. They constitute an important part of the soil matrix and are involved in various biochemical and chemical environmental processes. It is well documented that the major polar part of HAs is composed of functional groups such as carboxylic, phenolic, hydroxyl, carbonyl, and quinoidic [1]. Carboxylic and phenolic functionalities represent an important source for the production of charged and radical sites and are dominant in hydrogen bonds and metal binding. It is also believed that stable radical sites play a key role in numerous free-radical reactions resulting in a transformation of soil organic matter [1,2]. The radical sites in HAs are classified as stable (native) and short-lived (transient) [3,4]. It was shown that the existence of different radical sites is pH dependent and native radical sites transform to transient with increasing pH [3–6].

The complexity of humic acids makes their complete structural characterization extremely difficult. However, it was shown previously that relatively small, well-defined organic molecules may serve as useful representative models of the humic acid macromolecules in studying radical centers in HAs [7–12]. In particular, it has been suggested to use hydroxybenzoic acid derivatives such as gallic (3,4,5-trihydroxybenzoic) acid (GA) and protocatechuic (3,4-dihydroxybenzoic) acid (PCA) as such models [13,14]. It was demonstrated by means of various experimental techniques [15–18] that the GA radicals resemble quite closely the properties of stable radical sites in humic acids. For example, HPLC, FTIR, UV/Vis, and EPR methods were used in the study of a model humic acid synthesized from GA [15]. Other experimental (IR, far-IR, and Raman) and theoretical (quantum-chemical, B3LYP functional) investigations also indicated that water presence in the crystal structure had a strong effect on the vibrational spectra of crystalline GA [16]. Theoretical and experimental investigations of protonated and deprotonated radical forms of PCA were performed in several works [19–22]. It was concluded that partially protonated radical species of PCA can be used as a suitable model of the native radicals present in humic acids, whereas fully deprotonated PCA radical species can be used as model of the transient radicals. Observed

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differences between calculated g -parameters for protonated and deprotonated model radicals were similar to those observed for humic acids allowing to attribute the stable radicals to protonated semiquinones and the short-lived radicals to deprotonated forms [19]. Witwicki et al. [20,22] showed that explicit consideration of water molecules in the first hydration sphere in a combination with an implicit solvation method improved a prediction of g -tensor and isotropic hyperfine constants. Hatzipanayioti et al. [21] studied oxidized, oxygenated, and dimeric forms of PCA using DFT calculations and their structural and spectroscopic parameters (UV/Vis and NMR) were calculated. They determined the conditions for the existence of protonated, fully deprotonated, and/or oxygenated semiquinones of PCA, respectively.

EPR spectroscopy provides valuable parameters (e.g. hyperfine coupling constants, HFCC) of the electronic structure of radicals. By comparison of experimental and theoretical data is possible to gain insight into the particular structures of radicals. The isotropic term (a_{iso}) of HFCC is a function of the Fermi contact interaction of the unpaired electron with nucleus, and strongly depends on the spin density at the nucleus position [23]. The prediction of a_{iso} represents a difficult task for quantum chemistry because it requires an accurate wave function in the vicinity of nucleus of the interest. Very good predictions can be achieved by highly accurate *ab initio* methods but the size of the molecular systems is limited due to the computational demand [24]. Numerous EPR studies at the DFT level led to the consensus that hybrid DFT functionals provide, on average, very good predictions for organic radicals [24,25]. From the hybrid functionals, the highest popularity achieved B3LYP [26,27]. Despite of its undeniable success, this functional also has certain limitations and in DFT field new improved functionals are systematically developed such as meta-GGA types [28] or so-called 'double hybrid' functionals [29].

This work is dedicated to the accurate and systematic characterization of the radical properties of PCA and GA by means of computed electron spin densities and EPR parameters by using the B3LYP functional, particularly g -tensors and HFCCs. All possible anion radicals are studied in order to mimic both types of radical sites in humic acids (native and transient) [2]. The effect of environment on the radical sites is represented by explicit insertion of water molecules around GA and PCA moieties. Long range interactions are included by additionally using a polarizable continuum model. Furthermore, in the addition to the B3LYP method, we compare the performance of several popular DFT functionals in the prediction of the EPR parameters of the PCA/GA anion radicals (see details in following section). The calculated EPR parameters are interpreted in term of available experimental data for the PCA/GA species and humic acids as well.

2. Computational details

The PCA molecule (Fig. 1a) has three acidic hydrogen atoms having pK_a values of 4.35 (carboxylic group), 8.79 and 13.00 (two phenolic OH groups). Similarly, gallic acid (Fig. 1b) has four ionizable groups with pK_a of 4.27 (carboxylic group), 8.70, 11.45 and >13 (three phenolic OH groups) [30]. Therefore, depending on pH , PCA has a neutral and three anionic structures and GA has a neutral and four anionic structures, respectively. Our work comprises the study of all structures and conformers of protocatechuic acid – closed shell neutral H3-PCA (Fig. 1a), mono- and dianions ($[\text{H2-PCA1}]^-$ and $[\text{H-PCA1}]^{2-}$), and mono- and dianion radicals ($[\text{H-PCA1}]^{\cdot-}$ and $[\text{PCA1}]^{2\cdot-}$). In case of gallic acid, the following structures were investigated – neutral H4-GA (Fig. 1b), mono-, di-, and trianions ($[\text{H3-GA}]^-$, $[\text{H2-GA}]^{2-}$, and $[\text{H-GA}]^{3-}$), and corresponding mono-, di- and trianion radicals ($[\text{H2-GA}]^{\cdot-}$, $[\text{H-GA}]^{2\cdot-}$, and $[\text{H-GA}]^{3\cdot-}$). All structures were optimized by means

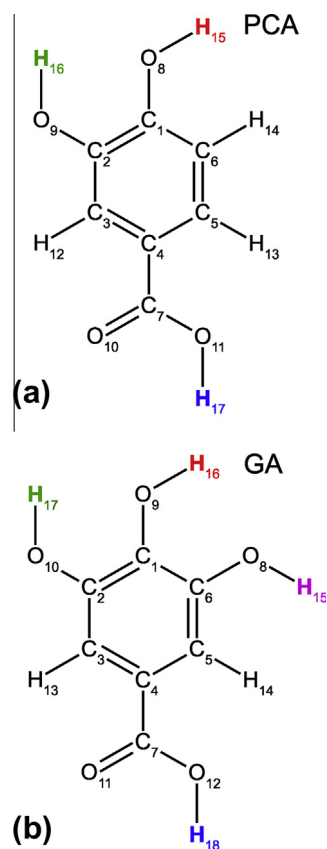


Fig. 1. Schematic structure and numbering of atoms of PCA (a) and GA (b) molecules. Colored atoms indicate which protons/hydrogen atoms are removed in the formation of anion radicals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of DFT calculations using the B3LYP [26] hybrid functional employing triple zeta valence plus polarization (TZVP) basis set [31,32]. It was shown many times in the literature that the B3LYP functional provides reliable structural results on various organic molecules including phenoxy radicals [16,33–35]. For example, the B3LYP geometry of gallic acid (GA) has been in a very good accordance with the experimental structural data of GA molecular crystal [16]. All geometries were optimized without symmetry constraints and were characterized as a true minimum by harmonic vibrational analysis. Water solvent effect (dielectric constant $\epsilon = 78.39$) was computed in a framework of the self-consistent reaction field polarized continuum model (SCRF-PCM) [36]. However, molecules such as PCA and GA have polar functional groups ($-\text{OH}$ and $-\text{COOH}$) and continuum solvent models are not able to describe the capability of these functional groups to form directional hydrogen bonds with solvent molecules (i.e. the formation of first hydration shell) or with heterogeneous polar environment in complex humic acids structures. This deficiency of continuum solvent models can be overcome by using a microsolvation model (explicit insertion of water molecules in a proximity of polar functional groups) and to perform for such models continuum solvent calculations (global solvation) [37,38]. Therefore, for the most stable conformers, microsolvated models were created. The number of water molecules was selected in a way that all proton donor/acceptor sites of the polar functional groups of PCA and GA species were saturated. The final cluster models contained 6 (PCA) and 7 (GA) water molecules, respectively. These models were fully optimized in a gas phase (microsolvation only, *MS* abbreviation will be used) using the same method and basis set as for isolated molecules. The explicitly hydrated anion radical species were obtained

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