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CONFIRMAREA DFT A FORMĂRII COMPLECȘILOR CU TRANSFER DE SARCINĂ ÎN REACȚII ALE ACIZILOR ORGANICI ANTIOXIDANȚI CU RADICALII DPPH[•] ȘI ABTS^{•+}: ROLUL CRUCIAL AL SOLVENȚILOR

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Rezumat: Pe baza calculelor DFT s-a demonstrat că formarea complecșilor cu transfer de sarcină în reacțiile acizilor organici antioxidanți cu radicalii DPPH[•] și ABTS^{•+} se poate realiza în două etape. La prima etapă are loc transferul primar de protoni de la moleculele acizilor antioxidanți neutri la moleculele de solvent, ceea ce duce la formarea anionilor acizilor corespunzători. A doua etapă a reacțiilor de oxidoreducere studiate include formarea complecșilor corespunzători cu transfer de sarcină, care implică anioni acizi și transferul de electroni de la aceștia la radicalii protonați (DPPH[•]) sau încărcăți pozitiv (ABTS^{•+}), transformând astfel acești radicali în derivații lor diamagnetici.

Cuvinte cheie: antioxidanți, acizi alimentari, DPPH[•], ABTS^{•+}, complex cu transfer de sarcină, calcule DFT.

DFT EVIDENCE OF CHARGE TRANSFER COMPLEXES FORMATION IN REACTIONS OF ORGANIC ANTIOXIDANT ACIDS WITH THE DPPH[•] AND ABTS^{•+} RADICALS: THE CRUCIAL ROLE OF SOLVENTS

Abstract: Basing on the DFT calculations it was shown that the formation of the charge transfer complexes in reactions of organic antioxidant acids with the DPPH[•] and ABTS^{•+} radicals can be realized in two stages. At the first step, the primary proton transfer from molecules of neutral antioxidant acids to solvent molecules occurs, which leads to the formation of anions of the corresponding acids. The second stage of the studied redox reactions includes the formation of the corresponding charge-transfer complexes involving acid anions and electron transfer from them to protonated (DPPH[•]) or positively charged (ABTS^{•+}) radicals, thereby converting these radicals into their diamagnetic derivatives.

Keywords: antioxidants, food acids, DPPH[•], ABTS^{•+}, charge transfer complex, DFT calculations.

Introduction

The classical SPLET mechanism of antioxidant action of chemical compounds is based on the supposition that the proton transfer from an antioxidant molecule to an oxidant free radical particle is its first stage. The second stage of the given mechanism includes the following electron transfer which occurs between the two newly formed ions (the former antioxidant and the former oxidant molecules). Thus, the presence of active hydrogen atoms, which can abandon (at experimental conditions) the studied antioxidant molecules in the form of the corresponding protons, can indicate on

possibility of the SPLET mechanism. However, as it was shown in our recent [1] and previous [2] works, in the reactions of the certain antioxidant food acids with the radical $\text{ABTS}^{+\cdot}$ along with the reaction of dihydroxyfumaric acid (DHFA) with the radical DPPH^{\cdot} (see [2]) there is not any direct transfer of protons from molecules of the given acids to the above radicals.

In both these cases the corresponding redox reactions begin from the dissociation of these acids in the ethanol–water medium (see [1, 2]) and the formation of their anions in the studied solutions. Their former protons are bonded with molecules of solvents. Then, for the phenolic food acids their anions form charge transfer complexes with the radical cation $\text{ABTS}^{+\cdot}$ and transform it in its diamagnetic derivative. In the case of dihydroxyfumaric acid the protonation of the radical DPPH^{\cdot} occurs due to the passing of needed protons from protonated molecules of the solvents (ethanol and water) to the given radical [2].

In this work, we will demonstrate that such a two-step mechanism of antioxidant action can be called "quasi-SPLET" one, which is characterized by the following features: firstly, the absence of direct proton transfer from antioxidant acid molecules to the studied radicals, and secondly, the active participation of solvent molecules in both considered processes.

Computational details

All the electronic and geometry characteristics of the molecules of the studied acids and their complexes with DPPH^{\cdot} and $\text{ABTS}^{+\cdot}$ have been calculated by means of the DFT method using the Becke's three-parameter nonlocal-exchange functional [3] with the corresponding correlation functional proposed by Lee, Yang and Parr (B3LYP) in [4]. The full geometry optimization of the investigated compounds was carried out with the 6-31G* basis sets [5] which include polarization functions for all the atoms in the systems under consideration. All the studied molecular systems possessing unpaired electrons have been calculated by means of the unrestricted B3LYP method (UB3LYP). The calculations were performed by using of the GAUSSIAN09 program package [6].

Results and discussion

In the work [2] we have shown that the reaction between DPPH^{\cdot} and DHFA begins from the protonation of one of the heteroatoms of DPPH^{\cdot} by means of one of the free protons existing in the water-methanol solution of DHFA due to the electrolytic

dissociation of one of its carboxyl groups. In Figure 1 the calculated charges of some heteroatoms in the molecule DPPH[•] are presented.

The comparison of these charges indicates that the protonation of the DPPH[•] molecule will most likely be realized through its oxygen atom O4 (but not by means of the nitrogen atom N2). Besides, the atom N2 is spatially shielded by the bulk phenyl groups connected with N1. Preference for the protonation way via O4 as compared with that via N2 follows also from comparison of calculated values of the total energies of the two cation-radical systems: -1418.2152 a.u. and -1418.0283 a.u., respectively.

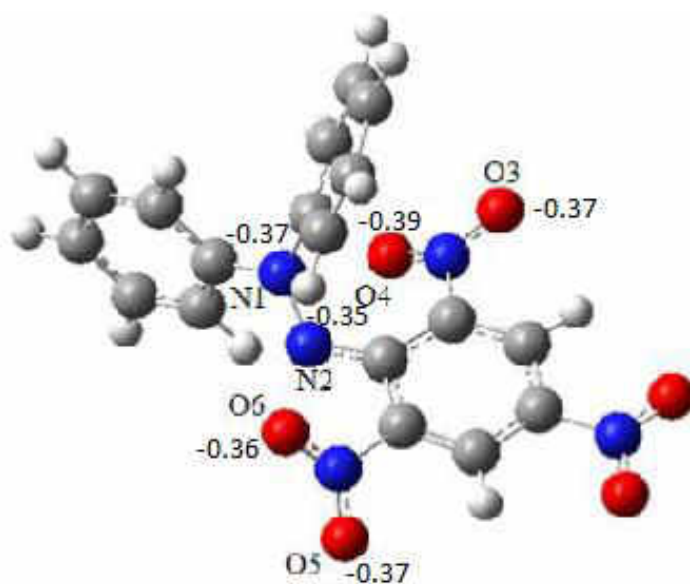


Fig. 1. The calculated charge values on some heteroatoms in the DPPH[•] molecule

Note also that calculations of the cation [DPPH-H]^{•+} whose additional proton is bonded with O4 allow one to understand the above mentioned color changes of DPPH[•] solutions. Indeed, in the DPPH[•] molecule the spin density of its unshared electron is mainly localized on the atom N2, while in the above [DPPH-H]^{•+} system it is mainly shared between the atom O3 and the nitrogen atom connected with O3 (Figure 1). One can expect that the ionic interaction between the cation-radical [DPPH-H]^{•+} and the anion of DHFA (hereafter [AH]⁻) formed due to electrolytic dissociation of the latter will be realized without any energy barrier at the room temperature. The quantum-chemical calculations of the whole system ([DPPH-H]^{•+}...[AH]⁻) indicate the formation of the charge-transfer complex (CTC) presented in Figure 2.

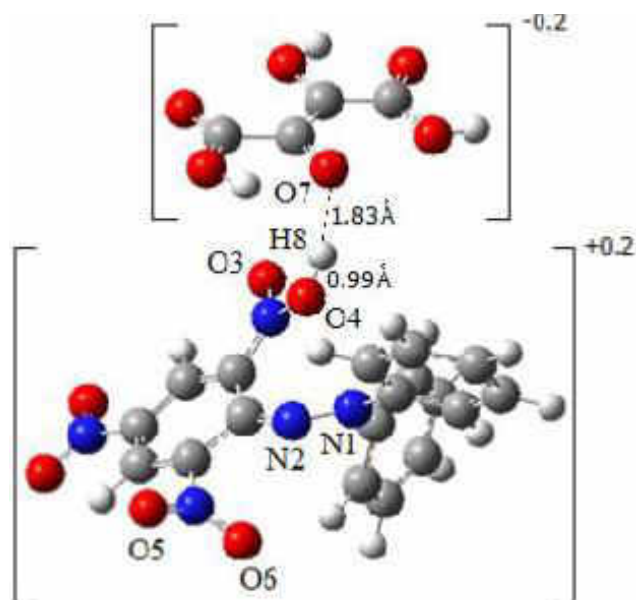


Fig. 2. The mutual geometry orientation and the summarized charges in the CTC between $[AH]^-$ and $[DPPH-H]^+$

Here it is to be noted (see Figure 2) that the formation of this CTC is accompanied by the transfer of the negative charge $0.8e$ from $[AH]^-$ to $[DPPH-H]^+$. The unshared spin density of the CTC is mainly localized on the carbon atoms belonging to the double $C=C$ bond of $[AH]^-$. The similar situation also takes place in the case, when the cation-radical $ABTS^{•+}$ interacts with phenolic food acids. The neutral molecules of these acids do not react with the cation-radical $ABTS^{•+}$ (see Figure 3 below).

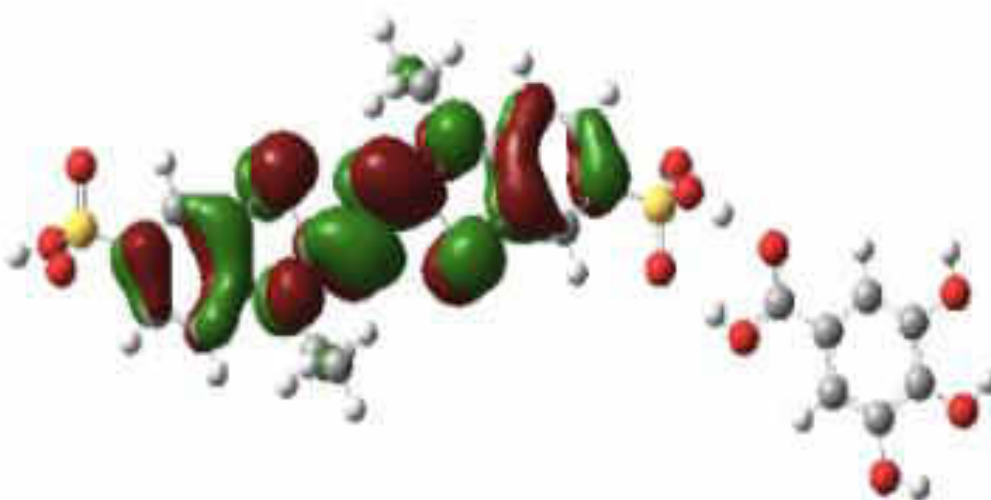


Fig. 3. The absence of the reaction between a neutral molecule of gallic acid and $ABTS^{•+}$

However, after their dissociation in the ethanol–water medium, the corresponding anions of these acids easily interact with ABTS^{•+} (see Figure 4 below and the work [1]).

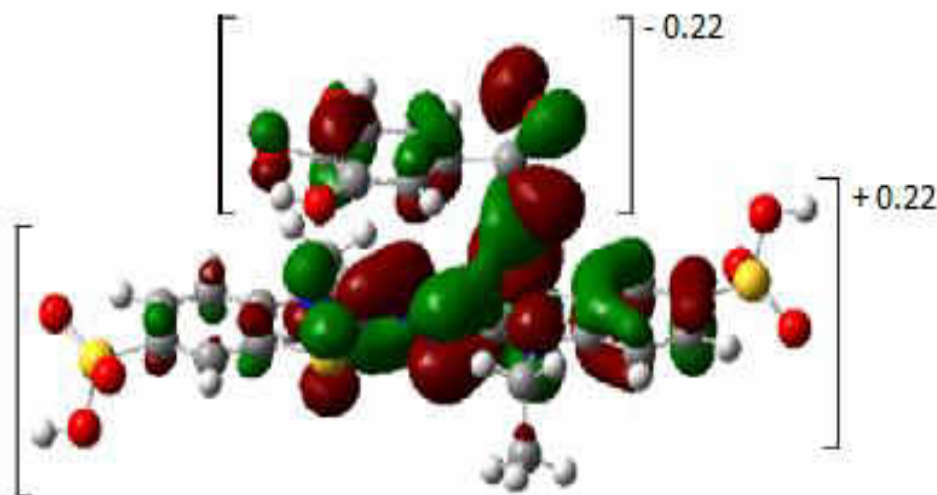


Fig. 4. The electronic density transition from an anion of gallic acid to ABTS^{•+} as a result of the formation of the CTC between the reacting particles

It can be seen that in this case the formation of this charge transfer complex is also accompanied by the transfer of the negative charge 0.78e from [AH]⁻ to ABTS^{•+}.

Conclusions

Basing on the DFT calculations it was shown that in both the cases considered, the primary proton transfer proceeds from neutral antioxidant acids molecules to solvent ones. At the same time, the second stages of the studied redox reactions include the formation of the corresponding charge transfer (electron transfer) complexes with the participation of the anions arising during their first stages. In this connection it seems to us reasonable that one can call such the type of antioxidant mechanism as „quasi-SPLET” one. I.e. the quasi-SPLET mechanism can be characterized by the following particularities: firstly, the absence of the direct transfer of protons from antioxidant molecules of the acids to the studied radicals; secondly, the active participation of solvents' molecules in both the processes: the passing of protons to the studied radicals (their protonation) and the formation of anions of acids, which, in their turn, take part (via the formation of the charge transfer complexes) in the process of donating of their electrons to the protonated (DPPH[•]) or positively charged (ABTS^{•+}) radicals and, therefore, transform these radicals in their diamagnetic derivatives.

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