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Article

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DFT Study of Intermolecular Proton Exchange with Some Derivatives of Benzoic Acids

A theoretical study of proton transfer dynamics in complexes of some substituted benzoic acids with 3,6-di-tert-butyl-2-hydroxyphenoxyl (DTBPO) radical is presented. To elucidate the transfer mechanism, reaction pathways for various complexes of benzoic acid derivatives with DTBPO were modeled. The calculations were performed by the DFT method at the UB3LYP/6-31G+(d, p) level of theory using QST3, IRC procedures, in vacuum and toluene medium (PCM solvation model). Geometric and kinetic parameters of complexes with o-, p-, and m-isomers of nitrobenzoic and chlorobenzoic acids were calculated. Theoretically estimated activation barrier of 29-30 kJ/mol turned out to be approximately 30 % higher than the previously obtained experimental data. It was noted that in the case of o-isomers of aromatic acids the coplanarity of the transition state structure is violated, in contrast to the initial state. This leads to a change in the proton transfer mechanism. The dynamics of charge distribution, dipole moment and electrostatic potential in the studied complexes were analyzed. Based on the calculated data, it was shown that the studied intermolecular proton exchange process occurs throughout Hydrogen Atom Transfer (HAT), and not throughout Proton-Coupled Electron Transfer (PCET) mechanism.

Keywords: DFT, spin probe, nitrobenzoic acid, chlorobenzoic acid, 3,6-di-tert.butyl-2-hydroxyphenoxyl, radical, OH-acids, proton exchange, proton transfer, Hydrogen Atom Transfer (HAT).

Introduction

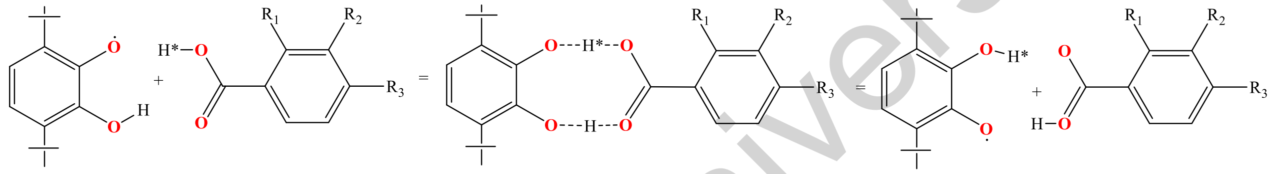
Reactions with proton transfer are widespread in living and non-living nature [1–5]. They arouse the unrelenting interest of researchers in relation to both proton transfer and proton exchange reactions [6–9]. The rate of such processes can have a wide range and can be studied by different methods, such as NMR spectroscopy for the diamagnetic and EPR spectroscopy for the paramagnetic systems [10–12]. The main advantage of these methods is the direct control over the reaction; however, they are also limited by the time interval available for research. This range includes $10–10^5$ c^{-1} for NMR, while for EPR it is within $10^6–10^9$ c^{-1}. However, even such a high time resolution does not allow one to fix the transition states formed during both intra- and intermolecular processes, since the lifetime of such states far exceeds the capabilities of these methods. The presence of a huge amount of experimental material on proton exchange in radical systems necessitates the application of computational chemistry methods to interpret these results [13–15]. Previously, we have obtained EPR experimental data on the kinetics of proton exchange between 3,6-di-tert-butyl-2-oxyphenoxyl (DTBPO) radical as a spin probe and a number of aromatic acids [16–18], which require theoretical interpretation. Kinetic parameters of intermolecular proton exchange for the systems m-nitrobenzoic acid — 3,6-di-tert-butyl-2-hydroxyphenoxyl and o-chlorobenzoic acid — DTBPO by dynamic EPR spectroscopy was obtained in toluene medium for which the proton exchange rate constant — 10^8 and 10^9 l/mol.s and activation parameters 22.7 and 23.9 kJ/mol, respectively [19]. Therefore, the aim of this work was to theoretically substantiate the previously obtained EPR data using a computational DFT study of proton exchange in systems containing the DTBPO radical and derivatives of nitrobenzoic and chlorobenzoic acids. The present work will provide more detailed information about the processes occurring in similar systems at different medium.

Computational Details

In this study density functional theory (DFT) computations with the UB3LYP [20, 21] functional and the 6-31G+(d, p) basis set, taking into account the dispersion with the original damping function D3 with the generation of electrostatic potentials, were used to optimize the structures of the initial, final as well as transition states of the complexes. The B3LYP functional is one of the most reliable methods to study the thermodynamics and kinetics of radical reactions [22, 23], this method is often used to assess the proton transfer radical reactions [24, 25]. The QST3 procedures were used to find the transition state, and the authenticity of the transition state was assessed by the presence of an imaginary frequency of normal vibrations along the reaction coordinate and its magnitude. The PES profile, the dynamics of charge distribution and dipole moment during the process under study were calculated using the Intrinsic Reaction Coordinate (IRC) procedure with optimization of all geometric parameters [26]. The effect of the solvent (toluene) was taken into account using the Polarizable Continuum Model (PCM) [27]. All calculations were carried out using the Gaussian 16 software [28], visualization of the obtained data was performed using the GaussView 6.0.16 graphical interface [29].

Results and Discussion

In general, the proton exchange reaction between the DTBPO radical and the studied benzoic acids can be represented by the following scheme:



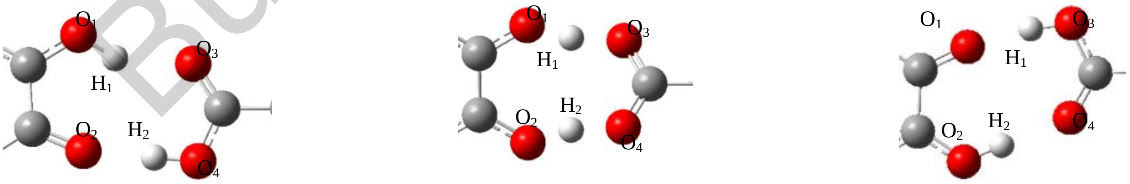
S1 TS S2

Scheme 1

where

R1 = R2 = R3 =H for unsubstituted benzoic acid;
R1 = NO_2 (or Cl), R2 = R3 =H for ortho-substituted benzoic acid;
R2 = NO_2 (or Cl), R1 = R3 = H for meta-substituted benzoic acid;
R3 = NO_2 (or Cl), R1 = R2 = H for para-substituted benzoic acid.

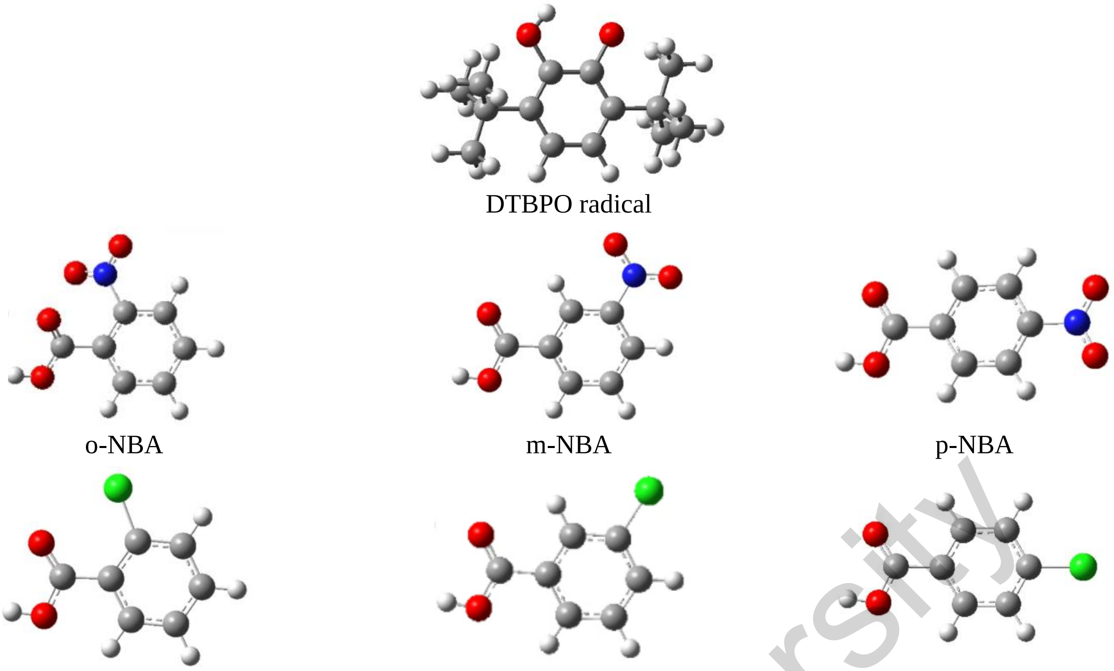
As can be seen from Scheme 1, proton exchange is facilitated by the formation of a cyclic complex between the DTBPO radical and the acid as the initial state S1 of the system (Fig. 1, *a*). The transition state TS of the system is characterized by approximately equal distance of both hydrogen atoms from the interacting molecules (Fig. 1, *b*). In the final state S2, the exchange of hydrogen atoms between the DTBPO radical and the acid is fixed (Fig. 1, *c*).



a) initial state (S1) b) transition state (TS) c) final state (S2)

Figure 1. Cyclic fragments of the complex between DTBPO radical and benzoic acid

Firstly, by employing UB3LYP/6-31G+(d, p) method, we have obtained optimized geometry structures for studied radical and acids: 3,6-di-tert-butyl-2-hydroxyphenoxyl (DTBPO) radical, o-nitrobenzoic (o-NBA), m-nitrobenzoic (m-NBA), p-nitrobenzoic (p-NBA), o-chlorobenzoic (o-ClBA), m-chlorobenzoic (m-ClBA) and p-chlorobenzoic (p-ClBA) (Fig. 2).



DTBPO radical

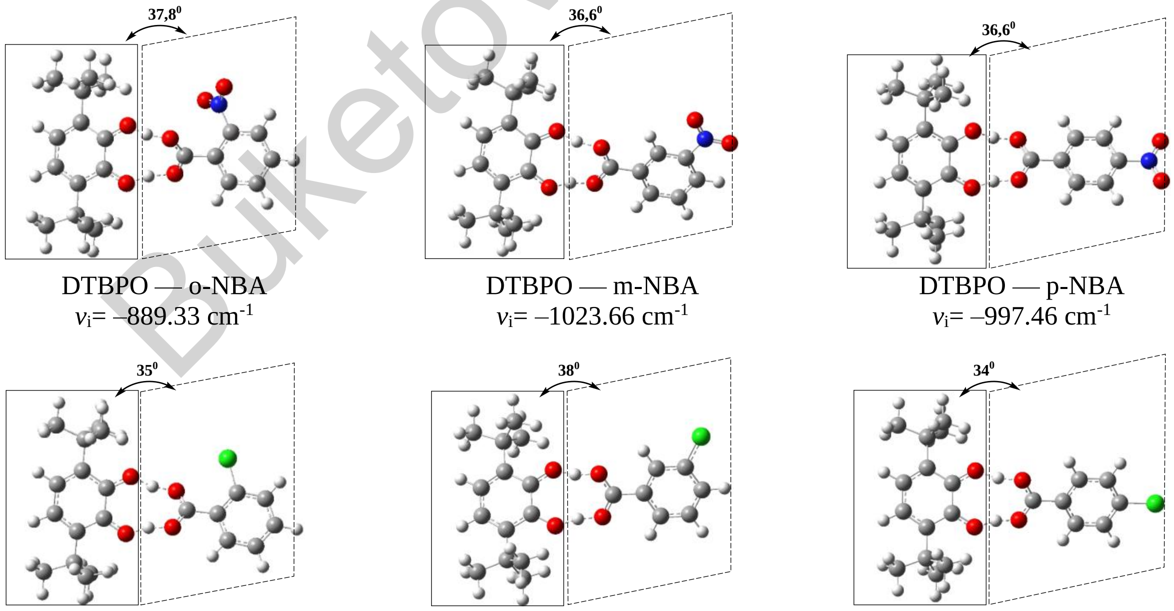
o-NBA m-NBA p-NBA

o-ClBA m-ClBA p-ClBA

Figure 2. Optimized structures of studied molecules

The spin probe 3,6-di-tert-butyl-2-hydroxyphenoxyl (DTBPO) radical was used as a partner in the proton exchange reaction. For this DTBPO radical, the kinetic data of intermolecular processes of proton transfer and exchange with various bases and acids in non-aqueous media were previously obtained by us using dynamic EPR spectroscopy [16–19].

The next step was to optimize the geometry of the initial S1, final S2, and transition TS states of the studied complexes between the DTBPO radical and benzoic acids (Fig. 3).



DTBPO — o-NBA
$\nu_i = -889.33$ cm^{-1}

DTBPO — m-NBA
$\nu_i = -1023.66$ cm^{-1}

DTBPO — p-NBA
$\nu_i = -997.46$ cm^{-1}

DTBPO — o-ClBA
$\nu_i = -1246.41$ cm^{-1}

DTBPO — m-ClBA
$\nu_i = -1240.77$ cm^{-1}

DTBPO — p-ClBA
$\nu_i = -1239.55$ cm^{-1}

Figure 3. TS structures of the DTBPO radical — benzoic acids proton exchange pathway.
ν_i — imaginary vibrational frequency

It should be noted that the planarity of the cyclic fragment is violated during the formation of the transition state. For example, if in the initial and final states the dihedral angle between the radical and acid parts of the complex is 0°, then in the transition state it is already equal to 37.8° in the case of the ortho-substituted acid isomer and 36.6° in the case of meta- and para -substituted isomers. It should be clarified that if in the case of an ortho-substituted acid the change is accompanied only by a distortion of the plane of the cyclic fragment, while for meta and para-substituted acids, the phenolic ring of nitrobenzoic acid also rotates. At the same time, the aromatic rings of the o-isomer of the acid and of the radical turned around by 9° relative to each other.

Similar change in the dihedral angle between the planes of the benzene rings of the radical and of the acid is observed in complexes with isomers of chlorobenzoic acids: the rotation angle is 35° in the case of o-ClBA, 38° in the case of m-ClBA, and 34° in the case of p-ClBA.

The obtained imaginary vibrational frequency of the transition state corresponding to the proton transfer are: –889.33 cm^{-1} for the o-NBA, –1023.66 cm^{-1} for the m-NBA, –997.46 cm^{-1} for the p-NBA and –1246.41 cm^{-1} for the o-ClBA, –1240.77 cm^{-1} for the m-ClBA, and –1239.55 cm^{-1} for the p-ClBA.

Some interesting for us geometrical parameters of the optimized structures of the studied complexes of the DTBPO radical with benzoic acids are presented in Tables 1-2 (the numbering of the atoms corresponds to Fig. 1).

Table 1

Bond lengths in the cyclic fragment of DTBPO — NBA complexes

	$R(O_1H_1)$, Å	$R(H_1O_3)$, Å	$R(O_2H_2)$, Å	$R(H_2O_4)$, Å	$R(O_1O_3)$, Å	$R(O_2O_4)$, Å
o-NBA						
S1	0.9916	1.78919	1.60677	0.99902	2.70052	2.60535
TS	1.13052	1.28989	1.13287	1.28364	2.40569	2.39966
S2	1.60164	1.00074	0.9924	1.76537	2.60223	2.68356
m-NBA						
S1	0.99262	1.77182	1.60938	0.99843	2.68551	2.60773
TS	1.14308	1.27078	1.14178	1.2718	2.39692	2.39703
S2	1.60301	0.99958	0.99277	1.76721	2.60259	2.68243
p-NBA						
S1	0.99241	1.77262	1.60743	0.99887	2.686	2.60626
TS	1.13999	1.27477	1.14001	1.27472	2.3978	2.39778
S2	1.60724	0.99885	0.99225	1.77409	2.60605	2.68807

Table 2

Bond lengths in the cyclic fragment of DTBPO — ClBA complexes

	$R(O_1H_1)$, Å	$R(H_1O_3)$, Å	$R(O_2H_2)$, Å	$R(H_2O_4)$, Å	$R(O_1O_3)$, Å	$R(O_2O_4)$, Å
o-ClBA						
S1	0.99491	1.73996	1.62713	0.9959	2.65933	2.62301
TS	1.19869	1.20249	1.19624	1.20579	2.38601	2.38647
S2	1.62474	0.99685	0.9952	1.74141	2.62158	2.66096
m-ClBA						
S1	0.99469	1.74959	1.61759	0.99683	2.66757	2.61442
TS	1.18599	1.216	1.18619	1.2162	2.38613	2.38619
S2	1.62098	0.99671	0.9947	1.749	2.61766	2.66685
p-ClBA						
S1	0.99506	1.74442	1.62433	0.99626	2.66334	2.62057
TS	1.20062	1.20038	1.20082	1.20041	2.38508	2.3854
S2	1.62367	0.99634	0.99509	1.74385	2.62	2.66291

Based on the data presented in Tables 1-2, an analysis of interatomic distances in complexes was made. It was shown that in the complexes of DTBPO radical with substituted NBA, the length of the hydrogen bridge in the initial molecules varies in a small range from 2.6 Å to 2.7 Å, while at the same time in the transition state $R(O_1O_2)$ is 2.4 Å. It was noted in the case of complexes between DTBPO radical and substituted

ClBA, that the length of the hydrogen bridge in the initial molecules varies in a small range from 2.62 Å to 2.66 Å, while in the transition state R(O_1O_2) is 2.38 Å.

The next step was to estimate the activation energy of the studied proton exchange process. Figures 4-5 show the calculated energies of minima and transition states for the studied complexes. The activation energy Δ*E* of the two-proton transfer between the structures of stable complexes S1 and S2 and the transition state TS are given in Table 3.

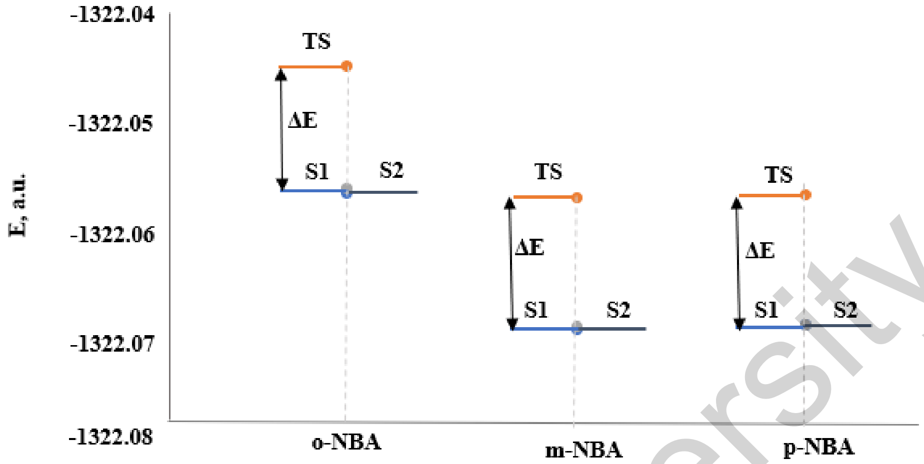


Figure 4. Energy minima and transition states for DTBPO — NBA complexes

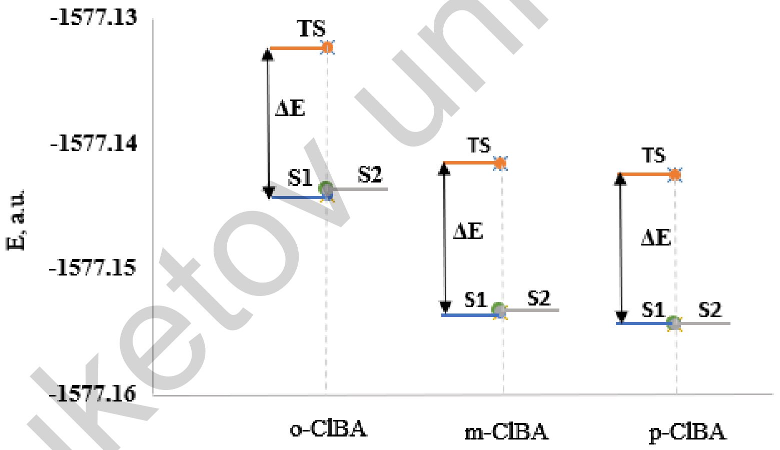


Figure 5. Energy minima and transition states for DTBPO — ClBA complexes

Table 3

Activation energy ΔE of the proton exchange process in intermolecular complexes of DTBPO radical and substituted benzoic acids

Acid	Δ*E*, kJ/mol		
	NBA (vacuum)	NBA (toluene)	ClBA (vacuum)
o-acid	29.55	30.20	30.33
m-acid	30.71	29.66	31.16
p-acid	30.79	29.65	30.99

As can be seen from Table 3, the activation kinetic characteristics increase in the series of complexes: o-NBA < m-NBA < p-NBA, while in complexes with ClBA the maximum value corresponds to the complex with m-ClBA. It can be seen from the calculated data that complexes with o-isomers of the studied acids are more stable. In the case of the o-isomers of the studied acids, we have a minimum activation barrier approximately equal to 29 kJ/mol, while in the case of the m-isomer ClBA, it is more than 30 kJ/mol. Previously obtained EPR spectroscopic data on proton exchange in toluene between DTBPO radical and m-NBA or o-ClBA acids have the following values of activation energy: ~ 22.7 kJ/mol and ~ 23.9 kJ/mol, respectively [29]. A comparison of the calculated and experimental values of the activation energy shows an almost 30 % excess of the first. We assumed that this may be due to the lack of the solvent effect and performed PCM calculations in the toluene medium for the DTBPO radical — o-NBA acid system (Table 3). However, calculations with a solvent did not lead to a significant decrease in the barrier. A decrease in the activation barrier by 1 kJ/mol was obtained in the case of the m- and p-isomers, while an increase by 0.5 kJ/mol was noted in the case of the o-isomer. Therefore, the reason is not only the solvent effect, but also a possible other mechanism of proton exchange, different from our model.

In order to better understand our proton exchange model, the next step was to study the change in charge distribution, dipole moment, electrostatic potential, and spin density in the DTBPO radical — o-NBA system during a reaction. Figure 6 shows the change in the charge distribution on the O and H interacting atoms of the DTBPO radical — o-NBA complex during the reaction.

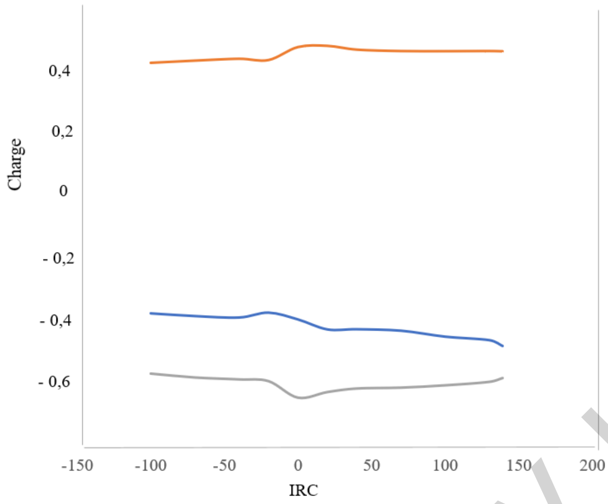


Figure 6. Charge distribution dynamics in the DTBPO radical — o-NBA complex. The blue line is the radical oxygen atom, the gray line is the acid oxygen atom, the red line is the acid hydrogen atom

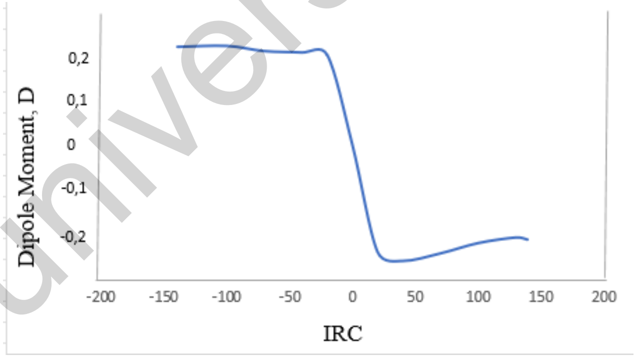


Figure 7. Dipole moment dynamics in the DTBPO radical — o-NBA complex

As can be seen in Figure 6, there is no charge transfer during the reaction. Thus, the charge on the H_2 acid hydrogen atom varies in the range from +0.42 to +0.46*e*, whereas the charge on the O_1 radical oxygen atom varies in the range from –0.38 to –0.48*e*, and the charge on the O_3 acid oxygen atom varies in the range from –0.57 to –0.65*e*. Comparison of the charge distribution dynamics in the system DTBPO radical — nitrobenzoic acids isomers with the phenoxy radical — phenol and 2,4,6-tri-tert-butylphenoxy radical — 2,4,6-tri-tert-butylphenol systems shows that the values of the studied system take intermediate position between the values of the unsubstituted phenoxy radical — phenol system and the benzyl radical — toluene system [30–31].

A similar analysis of the charge distribution dynamics for the complex of the semiquinone radical with chlorobenzoic acid showed, that the charge on the H_2 acid hydrogen atom varies in the range from +0.25 to +0.53*e*, while the charge on the O_1 radical oxygen atom varies from –0.28 to –0.59*e*, and the charge on the O_3 acid oxygen atom varies in the range from –0.32 to –0.59*e*. Such small changes in the charge distribution indicate that a hydrogen atom is transferred, but not a proton. It should be noted that earlier studies of the radical itself intramolecular tautomerism also showed the transfer of a hydrogen atom [32].

Based on the foregoing, we can assume that our computational model simulates the HAT mechanism for the process under study. Although it is possible that the proton exchange is simultaneously several competing mechanisms, including both the PCET mechanism and proton tunneling. This assumption will be tested in our future studies.

Next step was to analyze the dipole moment dynamics during proton exchange reaction in the DTBPO radical — o-NBA system (Fig. 7). As can be seen from the graph in Figure 7, the change in dipole moment was only 0.2 Debye. It can serve as another proof for the hydrogen atom transfer, since change in several units of the dipole moment is observed during the proton transfer [30]. A similar dependence is typical for other complexes.

The dynamics of the electrostatic potential was also studied during the proton exchange reaction in the DTBPO radical — o-NBA system (Fig. 8).

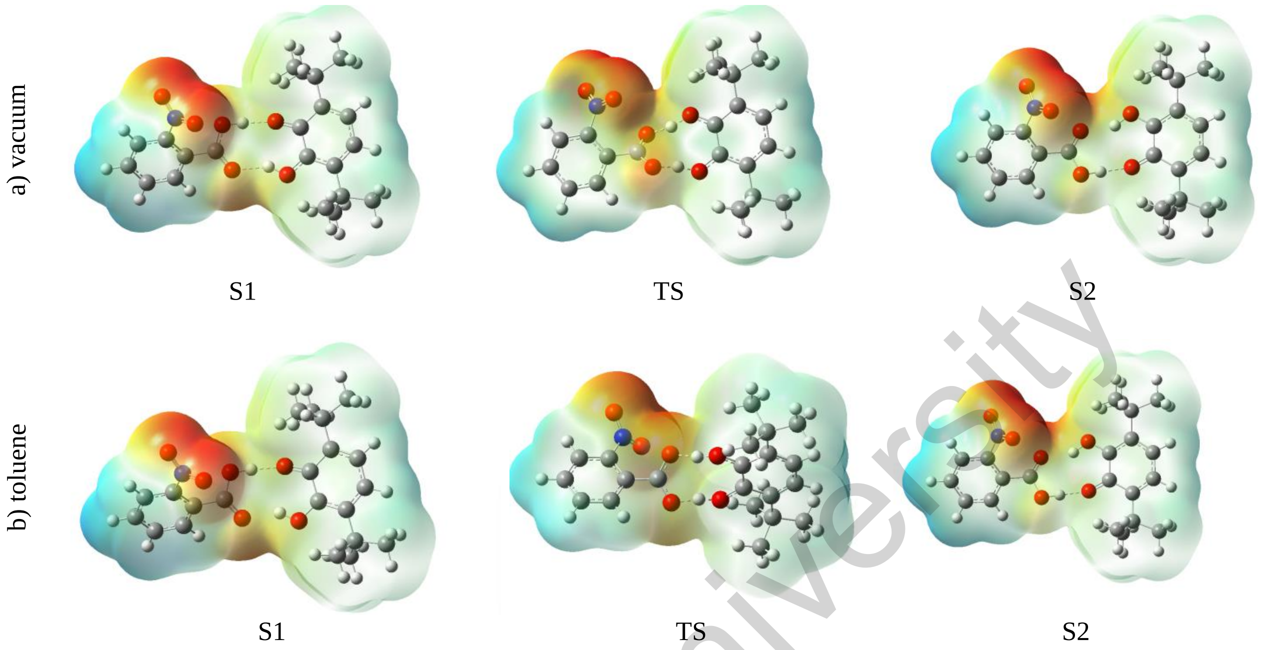


Figure 8. Electrostatic potential maps for the DTBPO radical — o-NBA complex.
Negatively and positively charged regions are marked in red and blue, respectively

As can be seen from the data presented in Figure 8, the excess electronic charge of the DTBPO radical — o-NBA system is localized mainly on the acid molecule. In the transition state (TS), an insignificant redistribution of the electrostatic potential is observed. This observation is consistent with the dynamics of dipole moment and charge distribution presented in Figures 6 and 7. Moreover, such changes are typical not only for the gas phase (vacuum), but also for the toluene medium, the geometry of the transition complex is also distorted in this case. The observed changes in electrostatic potentials emphasize the HAT mechanism in the DTBPO radical — o-NBA system and contrast it with the PCET mechanism in the phenoxyl — phenol complex [30–32].

At the final stage of the study, we analyzed the spin density dynamics during the proton exchange reaction in the DTBPO radical — o-NBA system (Fig. 9).

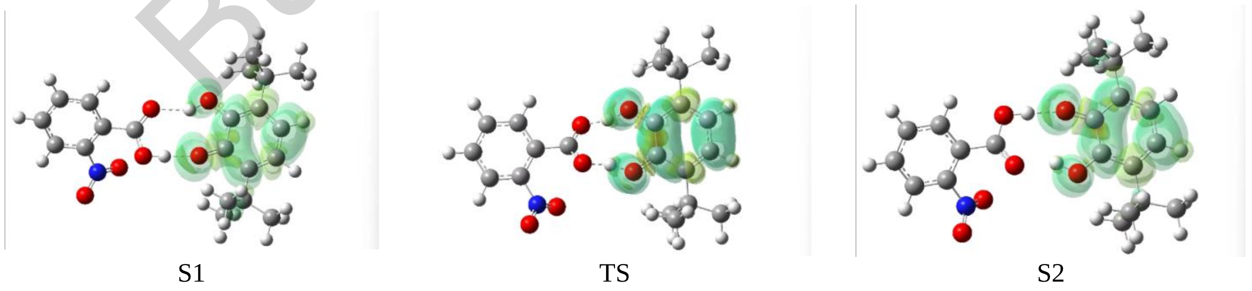


Figure 9. Spin density dynamics in the DTBPO radical — o-NBA system

As can be seen in Figure 9, the spin density is localized on the π-system of the radical benzene ring and does not pass over the acid molecule even in the transition state. It should be noted that in the transition state the spin density also extends on the both hydrogen atoms participating in the exchange process. These changes correspond to the dynamics observed in the experimental EPR spectra of the intermolecular proton exchange with DTBPO radical.

Conclusions

In this work, DFT modeling of proton exchange in DTBPO radical — substituted benzoic acids systems was performed for the purpose of its theoretical consideration. To study the mechanism of the proton exchange, the TS, QST3, IRC procedures, as well as the PCM model of the solvent effect (toluene) were used. Activation energy in the range of 29–30 kJ/mol for the proton exchange in DTBPO radical — substituted benzoic acids systems was estimated. The calculated activation energy is almost 30 % higher than the experimental value determined by EPR spectroscopy. This may be due to the limitations of the applied calculation model. An analysis of the dynamics of charge distribution, dipole moment, electrostatic potential, and spin density for the DTBPO radical — o-NBA system was performed. On the basis of the data obtained, a conclusion was made to confirm the Hydrogen Atom Transfer (HAT) model for the studied exchange reaction mechanism. Finally, these computational results and mechanism insights prove that DFT modeling is an effective method to study proton transfer process dynamics of similar systems.

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