

Hydrogen Atom or Proton Transfer in Neutral and Single Positive Ions of Salicylic Acid and Related Compounds

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Abstract: The nature of the process “hydrogen atom” or “proton” transfer reaction in neutral and single positive ions of salicylic acid, *o*-hydroxybenzaldehyde, and salicylaldehyde has been studied using the B3LYP density functional method. Single-point calculations at the CCSD(T) level have also been performed. For neutral systems, the reaction corresponds to a proton transfer process coupled with an important electronic transfer, which leads to a compound with nonzwitterionic character. A similar behavior is observed for ionized π radical cations. In ionized σ states, however, the process is that of a hydrogen transfer. In all cases, π ionization strengthens the initial H-bond and favors the reaction. For some of the systems the proton transfer occurs spontaneously.

I. Introduction

Hydrogen transfer processes play a very important role in many fields such as biochemistry and acid–base catalysis.¹ In some cases, the nature of the process, “proton” or “hydrogen atom” transfer is clear. For example, the proton transfer reaction in the ground and excited states of neutral systems leads to the formation of an ionic pair if the process is intermolecular or to the zwitterionic form if it is intramolecular. On the other hand, the hydrogen abstraction by a radical is a clear example of hydrogen atom transfer.

For radical cations, proton transfer reactions can also take place if the ionization is localized on the proton-donor group, which leads to the formation of distonic species.² For these systems the proton transfer reaction is more favorable than for the neutral analogues, due to an increase of the acidity of the ionized monomer and to the fact that the proton transfer does not imply a creation of charges but a transfer of a positive charge.³ If ionization takes place in the acceptor group, the proton transfer reaction becomes very unfavorable.^{2b,3a,b,d}

For certain systems, however, it is especially difficult to determine whether a proton or a hydrogen atom transfer has occurred. Special attention has been devoted to the excited-state isomerizations of heteroaromatic systems, which in most cases show a reverse isomerization on the ground-state surface after the excited state decays, leading to a complete cyclic

process. This reaction type has been denoted “hydrogen atom” or “proton” transfer according to the degree of charge transfer.⁴

The salicylic acid and related compounds are some of the systems for which the nature of the intramolecular transfer in excited states has been more extensively debated. Given that the acidity of phenol and the basicity of the ester group increase upon excitation,⁵ the first interpretation of the dual emission spectrum of methyl salicylate⁶ assumed an equilibrium between the initial excited-state system and a zwitterionic form originating from the proton transfer reaction.⁷ A similar interpretation, given 25 years later, suggested a zwitterionic structure for the Stokes-shifted fluorescence.⁸ The process was referred to as electronically excited state intramolecular proton transfer (ESIPT). However, later studies showed that the fluorescence decay rate constant is only slightly dependent on the dielectric constant of the solvent.⁹ Therefore, the existence of the zwitterionic form has been questioned, and more recent studies suggest that the red-shifted fluorescence corresponds to an enolic neutral form, arising from the ketonic isomer after the transfer of an hydrogen atom accompanied by an important electronic and structural reorganization.¹⁰ This is confirmed by experimental femtochemistry studies which have shown that the motion of the hydrogen takes place within 60 fs, while the OH bond stretch would give 13 fs for the motion.¹¹ Moreover,

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experimental studies showed that the ultraviolet fluorescence does not correspond to the non-proton transferred intramolecular hydrogen-bonded structures, but to other isomeric rotamers,¹⁰ which suggests that the proton transfer process is spontaneous in the excited state. Other experimental studies have been performed for salicylic acid,¹² *o*-hydroxybenzaldehyde¹³ and *o*-hydroxyacetophenone,¹⁴ and salicylideneaniline.^{5,15}

Theoretical studies for the $\pi \rightarrow \pi^*$ excited state of salicylic acid and related compounds using semiempirical and low level ab initio methods, provided a double-well energy profile.¹⁶ The inclusion of dynamical correlation energy dramatically changes these profiles in such a way that only one minimum appears.^{16d-g} The most recent calculations at the CASPT2 level using CIS geometries show that the only minimum corresponds to a nontransferred form with an OH bond length 0.15 Å larger than that determined for the equilibrium ground-state structure. The experimental Stokes shift of the fluorescence is explained from the rearrangement of the H-chelate ring and so, without considering any transfer process.^{16f} Nagaoka et al., however, on the basis of the nodal properties of the wave function, emphasized the importance of the geometrical reorganization of the benzene skeleton for understanding the experimental results.^{13d,17}

To our knowledge, only two studies have been performed for the ionized states of the *o*-hydroxybenzaldehyde system by means of photoelectronic spectroscopy and ab initio calculations.^{17,18} The experimental results indicate that the potential surface of the first ionic state is distorted from that of the ground state. Low level ab initio calculations determine an ionized structure for which the hydrogen atom lies almost equidistant to the carbonylic and hydroxylic oxygens.

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In this paper, we study the nature of the process, “hydrogen atom” or “proton” transfer reaction, in neutral and radical cations of salicylic acid, *o*-hydroxybenzaldehyde, and salicylidimine. We have chosen these systems since the reaction becomes more favorable along this set of systems. We have also performed calculations for the more simple 3-hydroxy-2-propenoic acid, 3-hydroxy-2-propenal (malonaldehyde), and 3-hydroxy-2-propenimine systems, which have the same functional groups as the larger systems but without the aromatic ring. Calculations for these smaller systems will allow us to analyze the role of the aromatic ring in the process and to calibrate the methods used for the larger systems.

II. Computational Methods

Molecular geometries of the considered species have been optimized using the nonlocal three-parameter hybrid exchange B3LYP density functional method¹⁹ and the 6-31+G(d,p) basis set.²⁰ Harmonic vibrational frequencies of the different stationary points have been calculated at the same level.

We have chosen the B3LYP method since it has proved to provide accurate geometries and harmonic vibrational frequencies for a wide variety of hydrogen-bonded systems.²¹ In particular, for different radical cations, the UB3LYP method has been shown to perform much better than the more computationally demanding UMP2 one,^{3c,d,22} due to the fact that the perturbation expansion converges slowly when the UHF reference function has large spin contamination.²³ In contrast, UB3LYP does not overestimate spin polarization, which has been related to spin contamination.²⁴ However, in certain special cases, such as symmetrical radical cations, the B3LYP method has been shown to overestimate the stability of these systems.^{3e,25} This is attributed to an overestimation by the exchange functional of the self-interaction part of the exchange energy due to the delocalized electron hole.^{3e} Because of that, to confirm the B3LYP results, we have performed single-point calculations at the coupled cluster level with single and double excitations and a perturbative estimate of the triple excitations (CCSD-(T))²⁶ at the B3LYP equilibrium geometries using the same 6-31+G(d,p) basis set. In these CCSD(T) calculations we have correlated all the electrons except the 1s-like ones.

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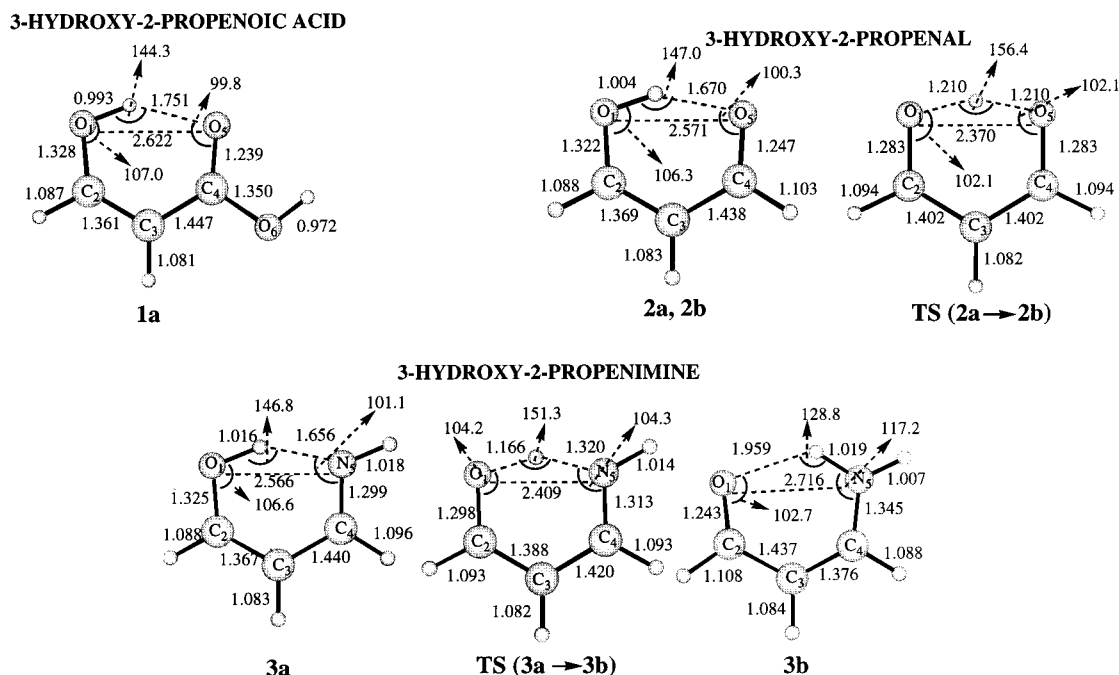


Figure 1. B3LYP-optimized geometries of the stationary points of neutral 3-hydroxy-2-propenoic acid, 3-hydroxy-2-propenal, and 3-hydroxy-2-propenimine. Distances are in angstroms, and angles are in degrees.

The nature of the proton or hydrogen atom transfer in the different compounds has been analyzed using the natural population analysis of Weinhold et al.²⁷ Density functional calculations have been performed with the Gaussian94 package.²⁸ Open-shell calculations at the CCSD(T) level have been carried out with the MOLPRO-96 program using a spin-restricted formalism.²⁹

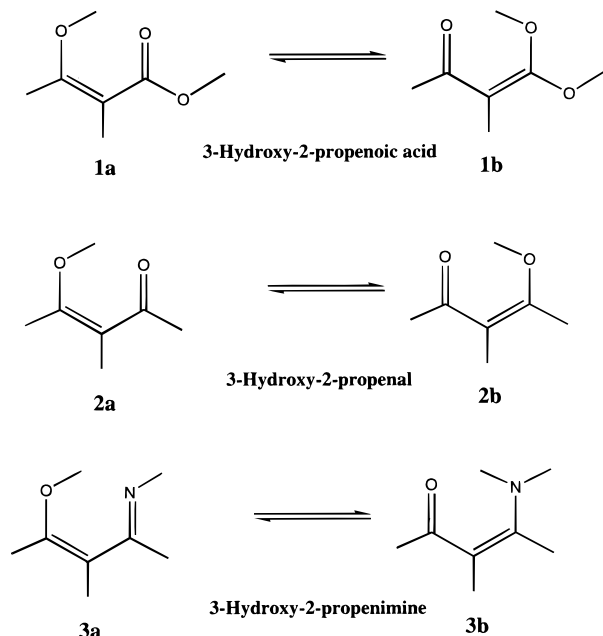
III. Model Systems

The three-model systems considered and their corresponding intramolecular reactions are shown in Scheme 1.

For each system we have investigated the two isomers implied in the reaction as well as the transition state connecting them. Figure 1 shows the B3LYP geometrical parameters of the stationary points, minima, and transition states found for the neutral systems.

The optimized structures of the radical cations are shown in Figure 2. In all cases optimizations have been performed for the lowest ionic state ($^2A'$). In addition, for the 3-hydroxy-2-propenal system we have also studied the process in the excited $^2A'$ state. The comparison between the $^2A''$ and $^2A'$ states for this system will allow us to get a deeper insight into the nature of the process, that is, to discuss whether the process is a

Scheme 1



“hydrogen atom” or a “proton” transfer reaction. The reaction energies and the energy barriers for the neutral and cationic systems are given in Table 1.

Let us first analyze the neutral systems. For 3-hydroxy-2-propenoic acid, we have only found one minimum on the potential energy surface, the one corresponding to the enol tautomer (**1a**). Any attempt to optimize the keto tautomer (**1b**) has collapsed to the enol one (**1a**). This fact was to be expected considering the instability of gem diols. It can be observed in Table 1 that the energy difference (7.9 kcal/mol) between the enolic minimum (**1a**) and the keto tautomer, the latter obtained by fixing the O_5-H distance, is significant. For 3-hydroxy-2-propenal (malonaldehyde), we have localized one minimum, which corresponds to both the reactant and product, due to the symmetry of the system, and the transition state of the reaction.

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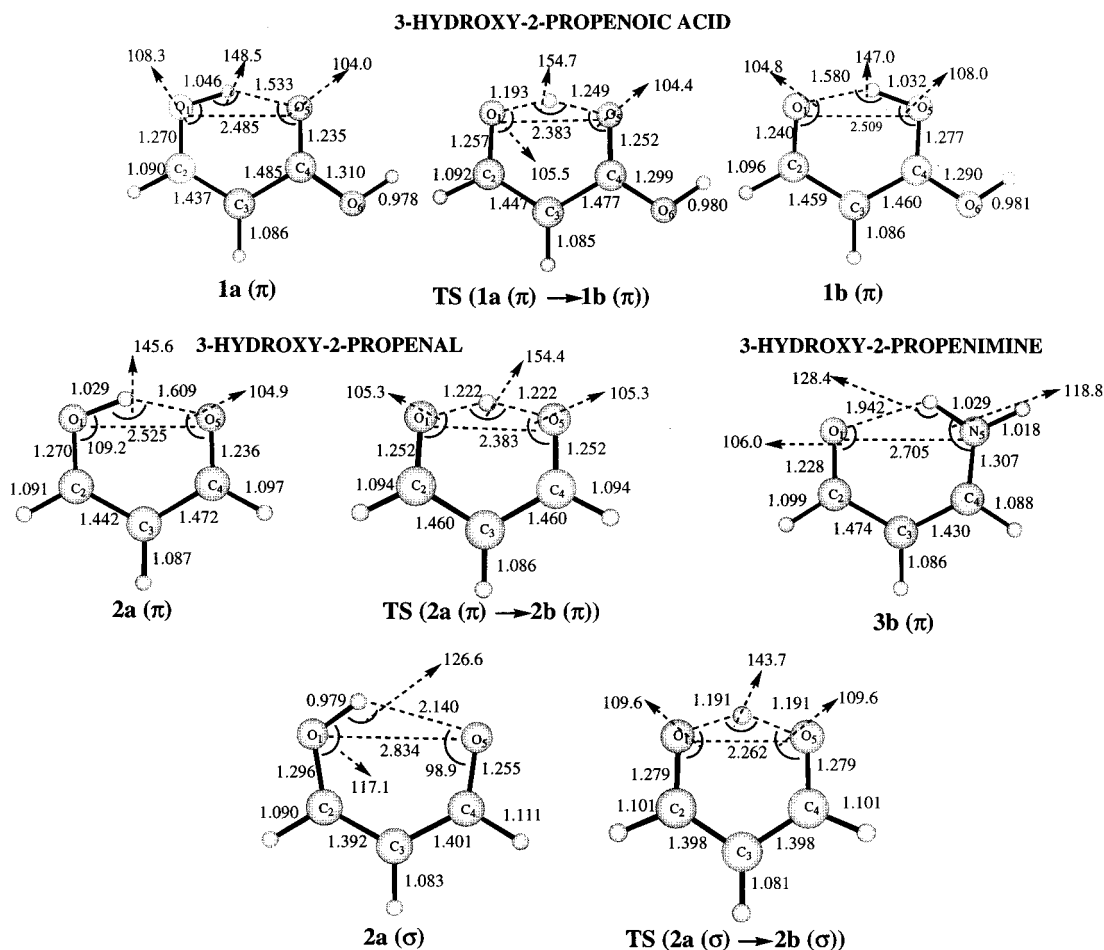


Figure 2. B3LYP-optimized geometries of the stationary points of 3-hydroxy-2-propenoic acid, 3-hydroxy-2-propenal, and 3-hydroxy-2-propenimine radical cations. Distances are in angstroms, and angles are in degrees.

For 3-hydroxy-2-propenimine, we have localized the reactant, product, and transition state.

Many theoretical studies have been performed for neutral malonaldehyde and the transition state of the hydrogen exchange.³⁰ Our B3LYP results are in good agreement with those reported at the correlated MP2 level.^{30c} In particular, the computed B3LYP hydrogen bond H–O₅ distance (1.670 Å) is very similar to the MP2 (1.678 Å) value determined with the 6-311G(d,p) basis set.^{30m} This value is also in a very good agreement with the experimental one (1.68 Å),³¹ in contrast to what is obtained at the Hartree–Fock level, which predicts a much larger hydrogen bond distance (1.88 Å).^{30c} Very similar geometrical parameters between B3LYP and MP2 are also

obtained for the transition state.^{30m} To our knowledge, no geometrical parameters at a correlated level have been reported for the other two systems.^{16g,32}

Whereas B3LYP performs well for determining the geometrical parameters of the stationary points, it seems to underestimate the energy barrier of the reaction compared to highly correlated methods such as the CCSD(T) one (see Table 1). Previous studies for malonaldehyde found a similar behavior when comparing the B3LYP result (2–3 kcal/mol) with the very accurate G2 one (4.3 kcal/mol).^{30m} Both our CCSD(T) value (4.5 kcal/mol) and the G2 one are in very good agreement with the experimental results.³² This underestimation by B3LYP was attributed to an overestimation of the correlation energy that produces an excessive degree of conjugation in the backbone of malonaldehyde. The same tendency is observed for 3-hydroxy-2-propenimine. This system shows a smaller energy barrier than the malonaldehyde one due to the exothermicity of the reaction and in agreement with Hammond postulate. This exothermicity was to be expected considering the instability of imine systems.

The lowest ionized state (²A'') arises from removing the electron from the π HOMO orbital (see Figure 3). The second ionic state (²A') corresponds to the ionization of the σ sub-HOMO orbital. For the sake of comparison we have also considered this state in the case of malonaldehyde. First of all, it should be noted that ionization changes significantly the topology of the potential energy surface. That is, for 3-hydroxypropenoic acid we have located the two isomers, reactant **1a**

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Table 1. Reaction Energies and Energy Barriers for the Model Systems (in kcal/mol)

system	system	ΔE			ΔE^\ddagger		
		B3LYP	CCSD(T)	CCSD(T)/ZPE	B3LYP	CCSD(T)	CCSD(T)/ZPE
neutral	1	7.9 ^a	9.9	-	-	-	-
	2	0.0	0.0	0.0	2.5	4.5	2.1
	3	-8.0	-6.5	-6.5	1.3	3.6	1.1
ionized π	1	-0.9	-1.3	-1.3	0.6	0.9	-1.1
	2	0.0	0.0	0.0	1.3	1.6	-0.4
	3	-12.9 ^b	-14.6	-	-	-	-
ionized σ	2	0.0	0.0	0.0	8.7	11.3	8.0

^a Value determined optimizing the **1b** structure with the O₅-H distance frozen at 1.0 Å. ^b Value determined optimizing the **3a** (π) structure with the O₁-H distance frozen at 1.0 Å.

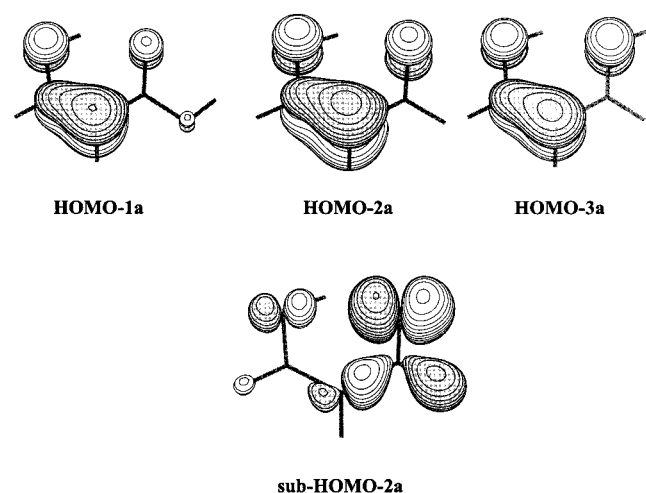


Figure 3. HOMO orbital of the enol form of 3-hydroxy-2-propenoic acid, 3-hydroxy-2-propenal, and 3-hydroxy-2-propenimine and sub-HOMO orbital of 3-hydroxy-2-propenal.

(π) and product **1b** (π), of the reaction, in contrast to the neutral system for which only the **1a** structure was found to be a minimum. On the other hand, ionization of 3-hydroxy-2-propenimine produces the spontaneous transfer of the hydrogen, and so only one minimum **3b** (π) is obtained. These differences come from the larger stabilization of the keto tautomer as compared to the enol one, after ionization (see below).

It can be observed in Figure 2 that π ionization strengthens the H-bond. Moreover, the two C-C bond distances increase, whereas the C-O ones decrease becoming more similar. These changes can easily be understood considering the nodes observed in the HOMO orbital from which the electron is removed. That is, the distances between centers with an antibonding combination decrease upon ionization while those with a bonding character increase. Natural population analysis indicates that spin density is mainly localized in the central carbon (0.66), which agrees with the geometrical changes observed. The radical character in the central carbon is maintained in the product and transition state and is stabilized by π electron donor substituents by resonance, which is more effective in the keto tautomer: in 3-hydroxy-2-propenoic acid because the keto structure has two hydroxyls acting as electron donors while in 3-hydroxy-2-propenimine because the amino group is a better donor than the hydroxyl one.

As can be observed in Table 1, the energy barrier of the π -ionized malonaldehyde is smaller than that of the neutral compound. This was to be expected since the strength of the H-bond is correlated with the energy barrier. Moreover, the geometrical changes involved in the reaction are smaller in the cationic π system than in the neutral one. Although the B3LYP energy barrier is again somewhat smaller than the CCSD(T)

one, the differences in this case are smaller than those observed for the neutral system. Thus, we expect the B3LYP method to be reliable enough when studying the larger ionic systems. Including the zero-point correction the transition state becomes more stable than the reactant or product and so, the transition-state structure would be the most populated one in this ionic state. Therefore, the experimental electron attachment study of this ionic structure could provide some structural information on the neutral transition state, similarly to what happens in an anion photodetachment spectra.³⁴

A very different situation is observed if ionization is produced in the sub-HOMO σ orbital. In this case, the intramolecular H-bond is weakened. This is due to the fact that this orbital has an important contribution of the electron pair of the proton acceptor oxygen (see Figure 3). The population analysis confirms that the spin density (0.84) is mainly located on this atom. Thus, ionization decreases its basicity, which produces an important increase of the H-bond distance and as a consequence, the energy barrier is significantly larger than that obtained for the π cationic system (see Table 1).

IV. Salicylic Acid and Related Compounds

Scheme 2 shows the reactions of the three systems considered.

The B3LYP geometrical parameters of the minima and transition states of the neutral and π radical cations are given in Figures 4 and 5, respectively. The reaction energies and energy barriers are given in Table 2.

The results obtained for the neutral systems indicate that the presence of the aromatic ring significantly stabilizes the reactant structures through resonance. Since the aromaticity is lost in the product, the proton transfer process becomes less favorable. A comparison of Tables 1 and 2 shows that the reaction energies for the neutral systems are about 9–11 kcal/mol more endothermic in the aromatic systems than in the model ones. Similar results have been found in all the theoretical studies performed for these systems in the ground state.¹⁶ As a consequence, the hydrogen transferred minimum for the *o*-hydroxybenzaldehyde system disappears and the reaction for salicylaldehyde becomes endothermic. The effect of resonance in the reactants is also

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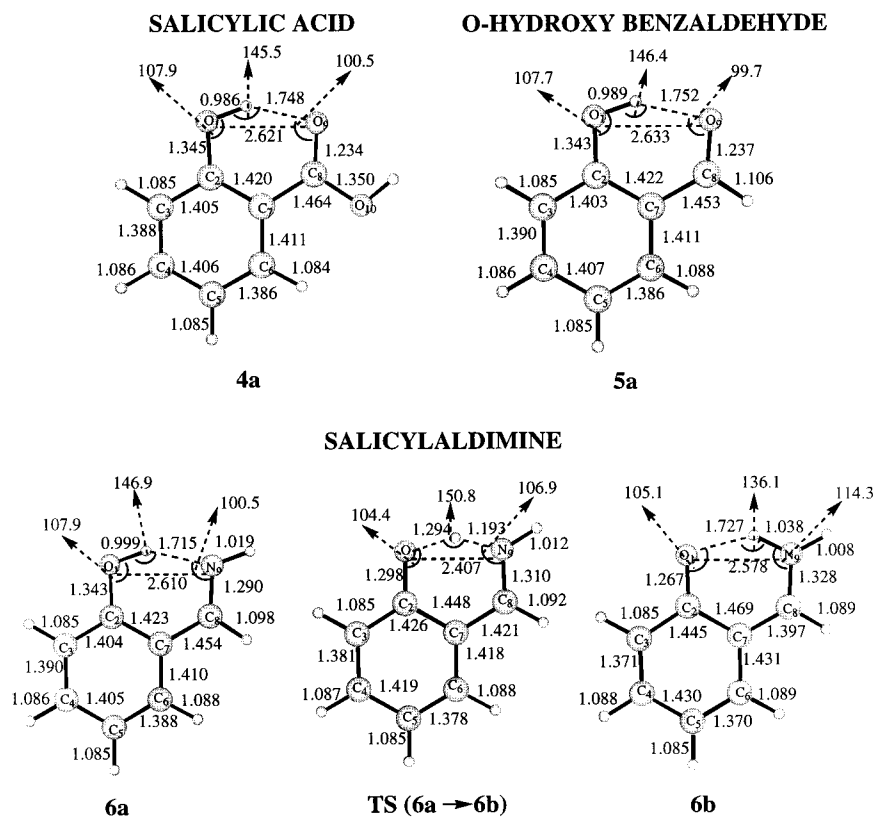
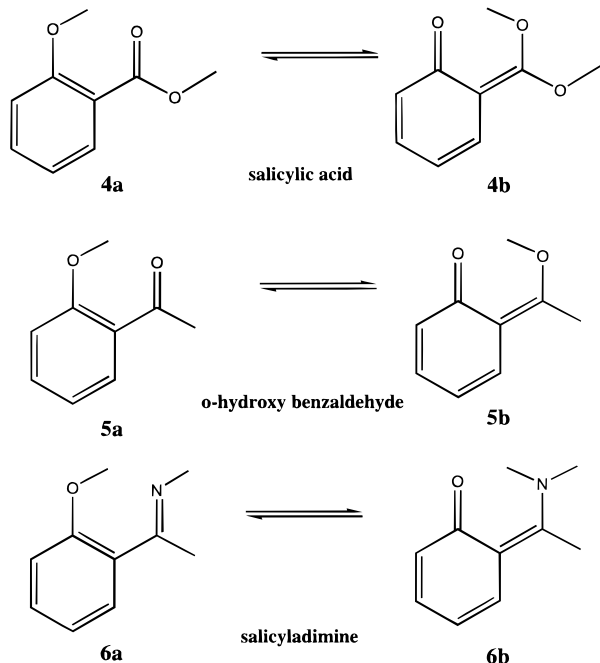


Figure 4. B3LYP-optimized geometries of the stationary points of neutral salicylic acid, *o*-hydroxybenzaldehyde, and salicylaldehyde. Distances are in angstroms, and angles are in degrees.

Scheme 2



seen from a geometrical point of view since the C_2-C_7 distances are always much larger than their analogous C_2-C_3 of the model systems. Moreover, it can be observed in Figure 4 (structure **6b**), the only minimum localized for the products, that aromaticity is lost after the hydrogen transfer since the difference between the shorter and larger C-C bonds is more pronounced, which is indicative of the formation of a quinoidal structure.

As for the model systems, the lowest ionic state (${}^2A'$) arises from ionizing the HOMO orbital, which is of π nature. The

geometry changes produced upon ionization can be understood by looking at the HOMO orbital shown in Figure 6. This orbital has a similar nodal plane than the one present in the model systems. Thus, ionization produces similar geometry changes: the two C-O bond distances become more equal and the intramolecular H-bond is strengthened. In addition to this nodal plane, there is a second one in the benzenic ring. Figure 5 shows that the C_3-C_4 and C_6-C_7 bond distances become significantly smaller than the other C-C bonds which increase upon ionization, in agreement with the bonding and antibonding character between the different atoms of the ring in this orbital. These structures show some degree of quinoidal character in accordance to a loss of aromaticity. The population analysis shows that the spin density mainly lies on C_5 . Overall, we could say that the changes upon ionization are similar to those found previously for the model systems with the exception that now the radical character does not remain in the central carbon C_7 since it spreads to the C_3 (0.24) and C_5 (0.39) positions of the benzenic ring.

Table 2 shows that ionization favors the reaction. This is due to the fact that the reactant loses more aromaticity than the products and, as found for the model systems, to the fact that resonance stabilization is more effective in the products. However, for salicylic acid we have only localized one minimum for the reactant at the B3LYP level. The potential energy surface is very flat at the product region and any attempt of optimization of this structure collapsed to the reactant. Since the B3LYP method tends to underestimate the energy barrier, CCSD(T) calculations might provide a shallow minimum for this structure. However, due to the size of the system such optimizations are not feasible at present.

The *o*-hydroxybenzaldehyde radical cation is the only system that has been previously studied both from an experimental and theoretical point of view. For this system, we have localized

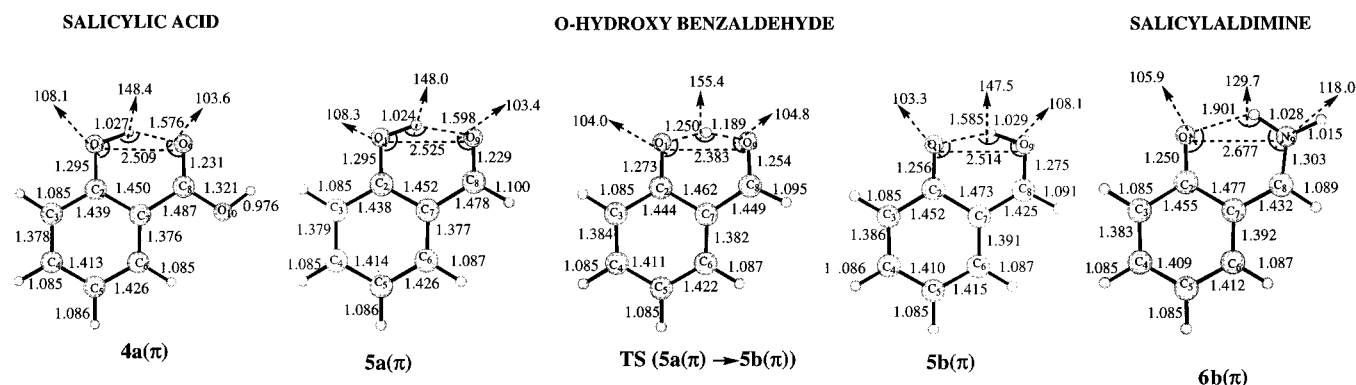


Figure 5. B3LYP-optimized geometries of the stationary points of salicylic acid, *o*-hydroxybenzaldehyde, and salicylaldimine radical cations. Distances are in angstroms, and angles are in degrees.

Table 2. Reaction Energies and Energy Barriers for Salicylic Acid and Derivatives (in kcal/mol)

system	4	ΔE			ΔE^\ddagger		
		B3LYP	CCSD(T)	CCSD(T)/ZPE	B3LYP	CCSD(T)	CCSD(T)/ZPE
neutral	4	17.0 ^a			-		
	5	11.3 ^a			-		
	6	3.7			5.5		
ionized π	4	3.3 ^a			-		
	5	1.1	2.7	1.3	2.0	3.5	2.7
	6	11.8 ^b			-		

^a Values determined optimizing the **4b**, **5b**, and **4b** (π) structures with the O₉-H distance frozen at 1.0 Å. ^b Value determined optimizing the **6a** (π) structure with the O₁-H distance frozen at 1.0 Å.

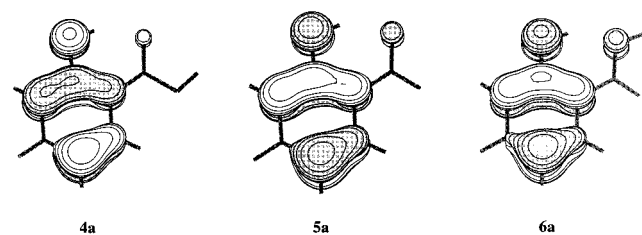


Figure 6. HOMO orbital of the enol form of salicylic acid, *o*-hydroxybenzaldehyde, and salicylaldimine.

the reactant, product, and transition state of the reaction. Because of that, this is the only large system for which we have performed single point calculations at the CCSD(T) level. As found for the model systems, the B3LYP energy barrier is somewhat smaller than the CCSD(T) one. However, the double-well energy profile is the same at both levels of calculations with and without correcting for the zero-point energy. Therefore, these results predict the existence of the H transferred species for this system which could be detected in an experimental study. It is also interesting to note that the energy barrier is somewhat larger than the one found for the analogous model system. This is due to the more important structural reorganization when the aromatic ring is present.

Experimental studies have provided a value of 8.83 eV for the vertical ionization of *o*-hydroxybenzaldehyde. Our computed B3LYP result (8.77 eV) is in very good agreement with the experimental one. Moreover, the experimental spectrum is very similar to that of phenol. However, the first ionization band of phenol is structured while that of *o*-hydroxybenzaldehyde is structureless, suggesting a strong geometry reorganization of the system upon ionization. The comparison between structures **5a** in Figures 4 and 5 shows that important geometry changes take place after ionization. In particular, the H-bond distance decreases significantly. Presently, there are no experimental studies that confirm the existence of the H transferred structure determined by our theoretical results.

Salicylaldimine is a very interesting system since the absolute minimum of the neutral and cationic systems correspond to different species. Consequently, ionization produces the proton transfer process spontaneously, which after the attachment of an electron would easily produce the reverse isomerization, leading to a cyclic process.

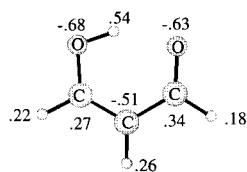
In summary, the present work has shown that we can change the topology of the potential energy surface by ionization. In all cases, ionization favors the H transfer process. However, whereas for salicylic acid the product minimum does not exist, for *o*-hydroxybenzaldehyde, both the reactant and product are stable and for salicylaldimine the H transferred structure is the only minimum on the potential energy surface.

V. Proton or Hydrogen Atom Transfer

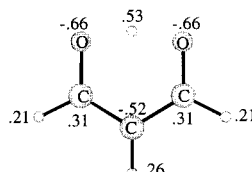
Let us now discuss the nature of the process: “hydrogen atom” or “proton” transfer. For neutral systems, the intramolecular reaction does not lead to the formation of compounds with zwitterionic character. For π radical cations, the changes of charge distribution along the reaction are small. Thus, one could think that the process corresponds to a hydrogen atom transfer. On the other hand, the population analysis shows that in all cases there is a high positive charge (0.55) on the hydrogen atom along the process, which would suggest that the reaction corresponds to a proton transfer.

The analysis of the results has shown that there are two different situations: one in which the process takes place in a four-electron/three-center system and another one in which the process proceeds through a three-electron/three-center interaction. The first situation corresponds to the neutral and π -ionized systems. In these cases, the net atomic charges of the two oxygens involved in the reaction are very similar. Since the charges of these oxygens remain almost constant along the reaction, the process may be viewed as the transfer of the partial positive charge on H; that is, as a proton transfer process. However, in a typical proton transfer process, despite some σ

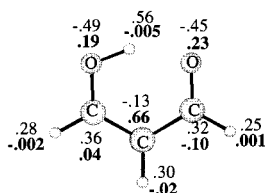
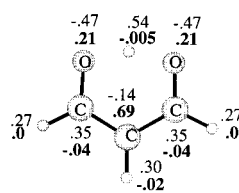
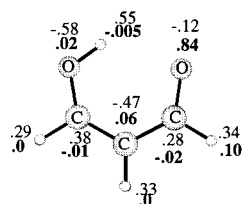
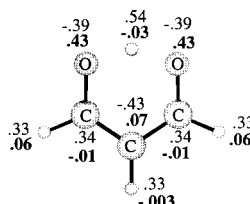
3-HYDROXY-2-PROPENAL



2a, 2b



TS (2a → 2b)

2a (π)TS (2a (π) → 2b (π))2a (σ)TS (2a (σ) → 2b (σ))

O-HYDROXY BENZALDEHYDE

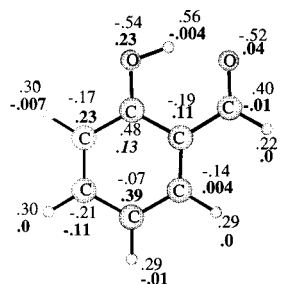
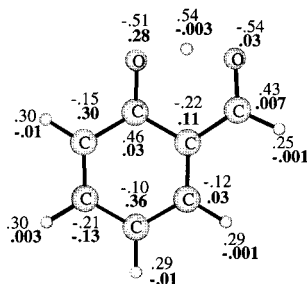
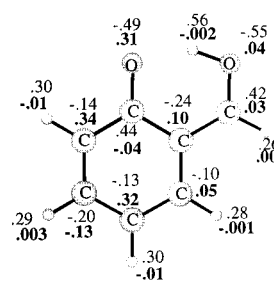
5a(π)TS (5a(π) → 5b(π))5b(π)

Figure 7. Population analysis for neutral and radical cation of 3-hydroxy-2-propenal and radical cation of *o*-hydroxybenzaldehyde. Net atomic charges are in plain text and spin densities are in bold text.

charge relaxation, the net atomic charge of the donor oxygen is expected to increase, whereas that of the acceptor oxygen is expected to decrease. This does not happen in the present systems, as can be observed in Figure 7, because the increase of σ electron density at the proton donor oxygen and the decrease of σ density at the proton acceptor oxygen induce a π polarization that compensates the σ electronic changes. That is, there is a π electronic transfer from the donor oxygen to the acceptor one through the conjugated π system, in such a way that the final compound has no zwitterionic character for the neutral system and no important changes in the net atomic charge distribution are observed for the π radical cations. The proton donor acts as electron donor and the proton acceptor acts as electron acceptor. Calculations for the deprotonated π ionized *o*-hydroxybenzaldehyde confirm the exaltation of the electronic donor character of the proton donor oxygen. In fact, the electron density on this atom decreases compared to that in the reactant, whereas that of the benzenic ring increases. Similar σ - π polarization effects were found by Wiberg et al.³⁰ⁿ in a

study of the origin of the acidity of enols and carboxylic acids. In summary, the process in neutral and cationic π systems can be viewed as a proton transfer process coupled with an electronic transfer through the conjugated system.

The second situation, three-electron/three-center interaction, appears for the ionized σ radical cations. As has been previously mentioned, σ ionization is mainly produced in the acceptor oxygen and so the spin density is mainly localized in this atom and there is an important decrease of the negative atomic charge. Since the final situation has the radical character on the initially donor oxygen, the process corresponds to a radical hydrogen atom transfer. The hydrogen atom supports a positive charge similar to the previous systems due to the fact that the O-H bond is polarized, but overall there is not a positive charge transfer from the donor to the acceptor oxygen.

V. Conclusions

The nature of the process "hydrogen atom" or "proton transfer" reaction in neutral and radical cations of salicylic acid,

o-hydroxybenzaldehyde, and salicylaldehyde has been studied using the B3LYP density functional approach. We have also performed calculations for the more simple 3-hydroxy-2-propenoic acid, 3-hydroxy-2-propenal (malonaldehyde), and 3-hydroxy-2-propenimine systems, which have the same functional groups as the larger systems but without the aromatic ring.

For neutral and ionized π systems, the reaction corresponds to a proton transfer process coupled with an important electronic polarization. The oxygen that loses the proton increases its electron donor character, whereas the proton acceptor atom increases its electronic acceptor character. The proton transfer process is accompanied by an electron transfer through the conjugated system so that the resulting product has no zwitterionic character for the neutral system and no important changes in the net atomic charge distribution are observed for the π radical cations. In these cases the reaction takes place through a four-electron/three-center system.

However, if ionization takes place in the highest σ orbital, the process proceeds through a three-electron/three-center interaction and the reaction can be viewed as the transfer of a hydrogen radical atom.

The ionization of the system to the π electronic state increases the acidity of the proton donor oxygen and decreases the basicity

of the proton acceptor. Because the increase of acidity is the most important effect, ionization strengthens the initial H-bond and favors the reaction so that, the transfer can occur spontaneously in some cases. The presence of the aromatic ring, stabilizes the reactant compared to the product which has some quinoidal character. This stabilization is larger in the neutral systems than in the cationic ones, because ionization implies a decrease of the aromaticity in the system.

Overall the most important results of our study is that the proton transfer process is produced much more easily in the ionized π state than in the ground state similar to what is observed for certain excited states. Over many years, several experimental works have studied the intramolecular proton transfer processes in excited states of salicylic acid derivatives. We expect the present work will encourage similar studies for ionized states.

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