COMMUNICATION

Computational Study of the Photolysis of Salicylic Acid in the α C-O Bond Fission

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Abstract: In concert with the latest laser-induced fluorescence (LIF) experiment [J. Phys. Chem. A, 115 (2011), 5062-5068], we investigated the photolysis mechanics of salicylic acid (SA) with the α C-O bond fission by means of *ab initio* calculations. The potential energy curves of the ground and low-lying excited electronic states of SA were calculated by the time-dependent density functional theory (TD-DFT) at the B3LYP/6-311+ G (d,p) level. The nature of the transition state in the T_2 state was also characterized. The results of our calculations indicate that upon excitation of SA at 266/315-317 nm, the α C-O bond fission mainly occurs on the T_2 state with a considerable late exit barrier. This conclusion agrees with the LIF experimental observations.

The photochemical and photophysical processes in the photolysis of carboxylic acids have been investigated extensively [1-7] because it generates the OH radical, which is the most important chemical cleaning agent of the atmosphere [8]. Kumar et al. studied the photodissociation of saturated [1] and unsaturated [2, 3] carboxylic acids at 193 and 248 nm. They observed an appreciable amount of energy being channeled into the relative translation of OH and its co-fragment. Kwon et al. [4] and Naik et al. [5] studied the

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photolysis of acetic acid at 193 nm, respectively. They found that the dissociation takes place indirectly along the triplet surface via curve crossing with the reverse barrier in the exit channel. Recently, Yin et al. investigated the photodissociation of *o*-nitrobenzoic acid [6] and *p*-aminobenzoic acid [7] at different photolysis wavelengths. It was revealed that these acids undergo dissociation to produce the OH radical from the excited state with a considerable exit barrier.

In contrast to small molecules, photodissociation of polyatomic molecules may involve complex dynamics, from which one can obtain the dynamical information on the dissociation pathways and the nature of the dissociative state potential energy surface. Benzoic acid, as the simplest member of the aromatic carboxylic acid family, has been investigated both experimentally and theoretically to probe the mechanism of the nascent OH radical produced in the photolysis in recent years [9-13]. Li et al. [9] and Fang et al. [10] mapped the potential energy surfaces of the low-lying excited states of benzoic acid using the complete active space self-consistent field method. Combining the above theoretical calculations with the experimental observation [11,12], it was proposed that the α C-O bond fission from the S_1 state of benzoic acid is in competition with the fission from the T_2 state upon photolysis at the 266-284 nm; while it mainly occurs at the T_2 state at 284-294 nm, and the photon with a wavelength longer than 294 nm is unable to present the α C-O bond fission. Comparing to the clear mechanism of benzoic acid photodissociation leading to OH, it was vague that how the OH radical formed in the photolysis of salicylic acid (SA).

In this communication, as a continuation and extension of our latest study on the experimental photolysis of SA [14], we have carried out ab initio theoretical calculations to map the potential energy curves of the ground and low-lying excited electronic states of SA along the coordinate of the OH radical leaving employing the time-dependent density functional theory (TD-DFT) at the B3LYP/6-311+G(d,p) level and to characterize the nature of the transition state. According to the present computational results, a clarified mechanics of SA photolysis leading to OH formation is proposed.

Ab initio theoretical calculations were carried out, using the Gaussian 03 program [15], to investigate the photodissociation mechanics leading to OH formation in the photolysis of SA. The fully optimized geometries of SA, as well as the various possible intermediate products, the radical species, and the transition state structures (TS) were calculated at the B3LYP theory, using the 6-311+G(d,p) basis set. The electronic energies corresponding to the optimized geometries were calculated at the same level, including the zero-point energy (ZPE) correction. All TSs were ascertained by vibrational analysis calculations with only one imaginary frequency mode. Moreover, the vibrational mode with the imaginary frequency was verified to connect a specific pair of stationary points (reactants and products) by

performing the intrinsic reaction coordinate (IRC) calculations. To understand the dynamics of the α C-O bond fission in the carboxylic group leading to OH formation, potential energy curves were calculated as a function of the C_{13}–$O_{15}H_{16}$ bond length, using the TD-DFT theory at the B3LYP/6-311+G(d,p) level.

SA exists in several conformers of the ground state with respect to the internal rotation of the carboxyl group and the orientation of phenolic hydroxyl [16, 17]. Considering two main rotational isomers identified by the experimental infrared spectra [17], the phenolic OH acts as a proton donor to the carbonyl group in rotamer Ⅰ (see **Figure 1**) while the phenolic OH is a proton acceptor in rotamer Ⅱ. The rotamer Ⅰ is more stable in energy. It was also currently optimized at the B3LYP/6-311+G(d,p) level.
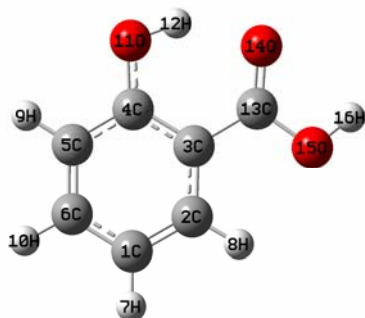

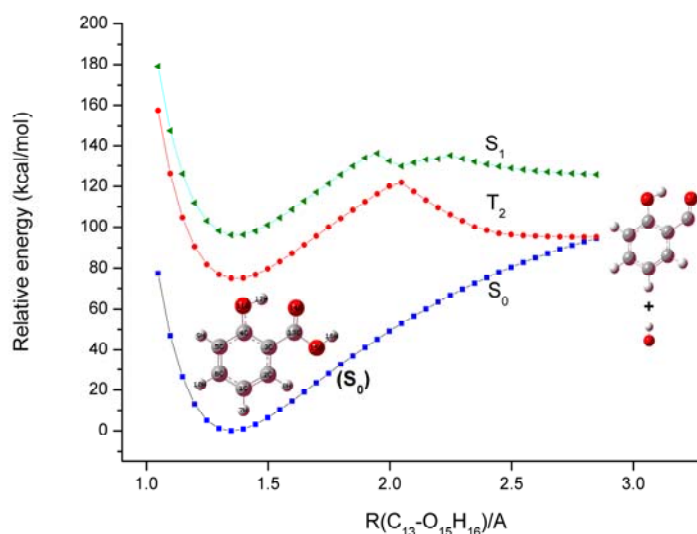**Figure 1:** The schematic structure and atomic labels of SA.

Figure 2: Potential energy curves of the ground and low-lying excited electronic states of SA along the coordinate of the OH radical leaving calculated with the time dependent B3LYP/6-311+G(d,p) method, partially cited from Ref 14. The geometry was frozen to the equilibrium position of the ground state except for variation in the C_{13}–$O_{15}H_{16}$ bond distance. Values were the relative energies at the S_0 minimum.

Our main purpose in this communication is to explain the photolysis mechanics of SA with the α C-O bond fission to form the OH radical. The experimentally employed photon energy is less than 315 nm (3.94 eV) [14], which can at most reach doorway state S_1. States

higher than S_1 are not our concern. The states below S_1 are S_0, T_1, and T_2. Similar to benzoic acid, the T_1 state of SA is a (π,π^*) transition, which is localized in the aromatic ring and correlates with the decarboxylation process. Therefore, for saving CPU time, we ruled out the T_1 state as the dissociating state for producing OH. Potential energy curves (PECs) of only the low-lying states (S_0, S_1, and T_2) were calculated by constraining the geometry of SA to the equilibrium position of the ground state with only the distance of the $C_{13}-O_{15}H_{16}$ bond varied, employing the TD-DFT method at the B3LYP/6-311+G(d,p) level, as presented in **Figure 2**. The relative energies of these states were as a function of the $C_{13}-O_{15}H_{16}$ bond distance, from 1.05 to 2.85 Å, at an interval of 0.05 Å. As can be seen in **Figure 2**, there are barriers in the $C_{13}-O_{15}H_{16}$ bond cleavage reaction on the PECs except the ground state. Between those barriers, the first barrier on the S_1 state (136.2 kcal/mol) is much higher than that on the T_2 state (121.8 kcal/mol). Hence, the competing dissociation on the T_2 state is a more favorable channel compared with the S_1 state.

It is well known that the structure of the TS can give helpful information on the exit channel dynamics during rupture of chemical bond. As mentioned above, the $C_{13}-O_{15}H_{16}$ bond cleavage of the T_2 state mainly gives rise to our desired OH fragment. The transition state on the T_2 state was successfully characterized according to the T_2 state curve, which was calculated to be 107.2 kcal/mol above S_0 minimum at the B3LYP/6-311+G(d,p) level. Comparing the barrier height of 121.8 kcal/mol to the above mapped T_2 state curve (constraining the geometry of S_0 with only the distance of the $C_{13}-O_{15}H_{16}$ bond varied), the calculated value of 107.2 kcal/mol herein represents the barrier height more reliable. **Figure 3** shows the optimized geometry of TS together with the structural parameters. The analysis of the displacement vectors associated with the imaginary frequency (300 cm^{-1}) and the IRC calculations confirm that the TS correlates with the products, the OH radical and HOC$_6$H$_4$CO. Careful inspection of **Figure 3** reveals that the structure of TS is of noncoplanarity with OH out of the aromatic ring. The breaking $C_{13}-O_{15}H_{16}$ bond in the TS is extended to 1.85 Å, implying the bond is almost broken. The structure of the other fragment HOC$_6$H$_4$CO in the TS is rather similar to that of the isolated fragment HOC$_6$H$_4$CO. Additionally, the $O_{15}-H_{16}$ bond length in the TS is calculated to be 0.97 Å, which is the same as that of the free OH radical. All of these indicate that the $C_{13}-O_{15}H_{16}$ bond fission process in the T_2 state has a late barrier. Thus, the fragments will be well separated after overcoming the barrier, having insufficient impact to couple the remaining energy into the vibrations of the photoproducts. Therefore, the TS structure illuminates the absence of vibrational excitation in the OH radical observed in the previous experiment [14].

Additionally, the experimentally observed Λ-doublet ratio of OH can provide the exit channel dynamics in the bond cleavage process. If the impulse is responsible for the

dissociation process, OH rotating in the plane containing the dissociating C_{13}–$O_{15}H_{16}$ bond axis as a result of in-plane dissociation would be expected. However, if the torsional motion of the parent molecule plays an important role upon dissociation, out-of plane dissociation takes place [18]. The measured Λ-doublet ratios in Ref. 14 showed preferential population of the $\Pi(A')$ state, indicating that impulse upon dissociation is converted into the OH rotation. Actually, our calculations reveal that it is the impulsive force mainly acts along the dissociating C_{13}–$O_{15}H_{16}$ bond in the TS. Furthermore, in the photodissociation of benzenesulfonic acid [19] and enolic-acethlacetone [20], the nonstatistical Λ-doublet ratio also suggests a nonplanar TS geometry for the OH channel. Thus, the calculated nonplanar structure of the TS also agrees with the experimental observation.
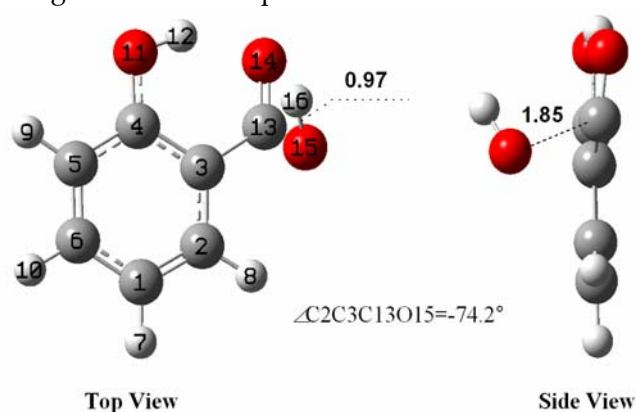

Figure 3: The optimized geometry of TS for OH elimination from the T_2 state calculated at the level B3LYP/6-311+G(d,p) of theory. The left is the top view, and the right one is the side view. The bond length and dihedral angle are in angstrom and degree, respectively.

According to the above discussion, the dissociative state of SA is mostly to be the T_2 state, and the experimental results [14] and the present computational findings strongly coincide much, i.e., (1) the very low internal energy distribution of OH (due to the presence of exit barrier in the T_2 state potential energy curve); (2) the absence of vibrational excitation in the OH radical (due to the existence of late barrier on the T_2 state); (3) the observed nonstatistical Λ-doublet ratio (due to the nonplanar structure of the TS). It is worthwhile to note that the barrier on the T_2 state is estimated to be 107.2 kcal/mol, which is about 9 kcal/mol higher than the experimental result (98.2±0.9 kcal/mol) [14]. For precise understanding of the mechanics of SA photodissociation leading to the OH product, theoretical calculations with a higher level on the potential surfaces along the reaction coordinate should be carried out.

The photolysis mechanics of SA in the α C-O bond fission was investigated by the

TD-DFT theory at the B3LYP/6-311+G(d,p) level calculated the potential energy curves of the ground and low-lying excited electronic states of SA. The nature of the transition state in the T_2 state was also characterized. The results of our present calculations indicate that upon excitation of SA at 266/315-317 nm, the α C-O bond fission mainly occurs on the T_2 state with a considerable late exit barrier, which agrees with the previous experimental observations.

Acknowledgements

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