

COMMUNICATION

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

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Received 30 December 2012; Accepted (in revised version) 23 January 2013

Special Issue: Guo-Zhong He Festschrift

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 T₂ 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 T₂ state with a considerable late exit barrier. This conclusion agrees with the LIF experimental observations.

AMS subject classifications: 65D18, 68U05, 68U07

Key words: Salicylic acid, α C-O bond, OH radical, TD-DFT, B3LYP/6-311+G (d, p)

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