

RESEARCH ARTICLE

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Understanding the decomposition reaction mechanism of chrysanthemic acid: a computational study

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Abstract

Background: Chrysanthemic acid (**CHA**) is a major product from the photodecomposition of pyrethrin which is an important class of pesticide compounds.

In the following paper, Hybrid density functional theory (DFT) calculations of the potential energy surface (PES) for three possible channels decomposition of chrysanthemic acid (cis-trans isomerization, rearrangement and fragmentation) have been carried at the B3LYP/6-311+G** level of theory. DFT was employed to optimize the geometry parameters of the reactants, transition states, intermediates and products based on detailed potential energy surfaces (PES).

Results: Our results suggest that all three pathways of **CHA** are endothermic. DFT calculations revealed that the activation barriers for cis-trans isomerization are low, leading to a thermodynamically favorable process than other two pathways. We also investigated the solvent effect on the PES using the polarizable continuum model (PCM). In addition, time-dependent density functional theory (TDDFT) calculations showed that these reactions occur in the ground state rather than in an excited state.

Conclusion: The rearrangement process seems to be more favorable than the decomposition of **CHA** to carbene formation. The solvent effect calculations indicated no changes in the shape of the PES with three continua (water, ethanol and cyclohexane), although the solvents tend to stabilize all of the species.

Background

Pesticides are essential products in everyday life. The natural pyrethrin insecticides have the desirable environmental properties of being both non-toxic to mammals and non-persistent [1,2]. Experimental studies have been reported that pyrethrins degrade rapidly when exposed to sunlight [3]. Chrysanthemic acid [2, 2-dimethyl-3-(2-methyl-1-propenyl)] is one of the products from pyrethrin photodecomposition and is widely used as the acidic part of synthetic pyrethroid insecticides [4-9]. The photochemical degradation of the acid components of pyrethrins has been examined in numerous studies. Sasaki et al. [10] and Ueda and Matsui [11] found that carbons 1 and 2 (Scheme 1) of the main cyclopropane group are cleaved, subsequently leading to the formation

of a diradical according to Elliot and Janes [12]. The photochemistry of simple cyclopropanes has been examined by several workers [13-18] and the fundamental photochemical transformations are generally observed. For instance, the photodegradation of pyrethrins in sunlight is rapid and results in the isomerization of the side-chains, photooxidation to a variety of carboxylic acids, and isomerization of the cyclopropane acids.

The main objective of this project was to carry out a theoretical study to determine the reaction mechanism of the decomposition of chrysanthemic acid. This investigation may improve our knowledge about the potential energy surface (PES) of these important compounds. We explored the potential energy surfaces of the ground state and the lowest singlet and triplet excited states and the interplay between them. DFT calculations have been used successfully in calculating transition structures [19] and the reaction parameters of various reactions, such as pericyclic rearrangements, cycloadditions

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