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Theoretical investigation of the photochemical reaction mechanism of cyclopropenone decarbonylation

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Abstract
The gas-phase decomposition mechanism of the photochemical and thermal reaction of cyclopropenone leading to carbon monoxide and acetylene has been investigated theoretically. We employed the B3LYP, MP2, and CASSCF methods with the 6-311 + G** basis set to determine the pathways and the potential energy surface (PES) of this reaction. PES minima were characterized by the absence of any imaginary frequencies and compared with the transition states that contained single imaginary frequencies. The intrinsic reaction coordinate (IRC) method was used to find the minimum energy paths in which reactants and products were connected to the transition states. Activation barrier, thermodynamic, and IRC analyses were performed using the above three methods. Our computations indicated that the decomposition of cyclopropenone proceeds through a stepwise mechanism containing two transition states (TS1 and TS2) and an intermediate. The results show that TS1, the critical transition state, determines the rate of the cyclopropenone decomposition reaction. Therefore, we employed natural bond order (NBO) calculations to probe the structure of the intermediate. The calculations showed that the intermediate has resonance structures containing a carbene and a zwitterion. Our results are in good agreement with previous theoretical and experimental studies. © 2011 Taylor & Francis.

Author Keywords
CASSCF; cyclopropenone; NBO; solvent effect; transition state

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