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Editor's Choice

Automated exploration of isomerization and dissociation pathways of ethylene sulfide cation by the global reaction route mapping method

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ABSTRACT

Isomerization and dissociation reaction pathways of $C_2H_4S^+$ associated with photoionization of *c*-C_2H_4S have been explored on the potential energy surfaces by the global reaction route mapping (GRRM) method. Reaction channels yielding $C_2H_3S^+$, HCS^+, H_2S^+, $C_2H_3{}^+$, and $C_2H_2S^+$ were disclosed. Calculated values of energy barriers to transition states and direct dissociation energies gave theoretical supports to recent synchrotron radiation experiments generating HCS^+ and $C_2H_3S^+$.

1. Introduction

Photoionization process by vacuum ultraviolet (VUV) light has been studied for the investigation of electronic structure of molecules, clusters or solid surface. After the electron emission from molecules by photoionization, dissociation to ionic and/or neutral fragments can be induced [1]. Reaction pathways leading to dissociation depend on the excess energy and the excited electronic or vibrational states over the ionization threshold. Tunable photon sources in synchrotron radiation facilities have been utilized to observe the photon energy dependence for products such as fragment ions. The composition of reaction products can be determined by a mass spectrometer. However, it is difficult to determine the structures of the products and the energy barriers to transition states (TSs) toward isomerization only by the mass detection. Ab initio quantum chemical calculation may elucidate chemical reaction pathways including dissociation or isomerization. The global reaction route mapping (GRRM) method can automatically explore reaction pathways including TSs on potential energy surfaces (PESs) [2–4] and the comparison between the experimental results and the theoretical results obtained by the GRRM method can attract interest by experimental researchers as well as help them for analysis of observed ionic fragments.

Upon irradiation of photons, cyclic molecular systems undergo various processes such as ring-opening and production of radicals or ions. Ethylene sulfide (*c*-C_2H_4S), which is the smallest sulfur-containing three-membered heterocyclic ring structure, was studied for theoretical calculations of ring-opening process [5,6] and photodissociation [7,8] which can occur by irradiation of ultraviolet light. Also, dissociation process upon ionization was observed [9,10]. As for the electronic structure of *c*-$C_2H_4S^+$, photoelectron spectra were observed [11–13] and the first ionization energy (IE) was determined to be 9.051 eV [14].

With the synchrotron radiation, photoionization of *c*-C_2H_4S and the following processes have been studied by the time-of-flight method with threshold photoelectron photoion coincidence (TPEPICO) spectroscopy by Fang and co-workers [14,15]. As increasing the energy of VUV light, intensity change of fragment ions of CH_3CS^+ and HCS^+ was measured by using a TPEPICO technique, and appearance energies (AE) of $C_2H_3S^+$, HCS^+, H_2S^+, $C_2H_3{}^+$, and $C_2H_2S^+$ were determined from the TPEPICO spectra at 10.71, 11.13, 11.96, 12.58, and 13.07 eV, respectively [14,15]. Furthermore, they found a substantial TS in a dissociation pathway from the most stable isomer CH_3CHS^+ to $C_2H_3S^+ + H$ with kinetic energy release (KER) distribution of $C_2H_3S^+$ and calculations of quasi-equilibrium theory (QET) and a pure impulsive model [14]. From the AE of $C_2H_3S^+$ and the IE of *c*-C_2H_4S, they determined height of the TS barrier (ca. 1.66 eV = 10.71–9.051) [14]. On the other hand, the dissociation channel of $HCS^+ + CH_3$ was interpreted as a direct pathway from the most stable isomer CH_3CHS^+ without a TS on the basis of the KER distribution of HCS^+ and QET calculations [14]. The threshold dissociation energy was determined to be ca. 2.08 (=11.13–9.051) eV from the AE of HCS^+ and the IE of *c*-C_2H_4S [14].

The isomerization pathways of *c*-$C_2H_4S^+$ into the most stable isomer CH_3CHS^+ via TSs before dissociation into $C_2H_3S^+ + H$ and $HCS^+ + CH_3$ were calculated with the G3 method by Fang and co-workers [14]. In this study, isomerization and dissociation pathways after ionization of *c*-C_2H_4S on the ground ionic state have

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been searched by the GRRM method [2–4]. Obtained theoretical energies of TSs and dissociation channels (DCs) have been compared with AE or estimated TS energies of fragment cations by the synchrotron radiation experiments [14,15]. The GRRM has been applied to cationic systems and clusters [16–18] in order to estimate energy barriers of TSs and dissociation energies.

2. Computational methods

Reaction pathways of c-$C_2H_4S^+$ on the doublet PES were searched by the GRRM method [2–4]. All electronic state calculations in the present study were performed by using the GAUSSIAN 09 program [19]. Initially, a stable equilibrium structure (EQ) of c-$C_2H_4S^+$ was determined by geometry optimization. Reaction pathways starting from the optimized geometry of c-$C_2H_4S^+$ were explored at the level of M06-2X/6-31G by the GRRM11 program [20]. Searched stationary points were automatically confirmed as EQs or TSs by inspecting vibrational modes with no or only one imaginary frequency, respectively. Zero-point vibrational energies (ZPE) were obtained for each structure at the level of M06-2X/6-31G. All energies in the present study were corrected with ZPE. The GRRM program automatically recognizes DCs, when reaction pathways reach dissociating regions where the distance between fragments exceeds the threshold value estimated from atomic radii [20]. For obtaining refined energies, single-point calculations were done for each geometry of EQs, TSs, and DCs at the level of MP4/6-311++G(d,p).

3. Results and discussions

The automated GRRM search on the doublet PES starting from c-$C_2H_4S^+$ resulted in 83 isomers (EQs) and 301 TSs, 218 DCs at the

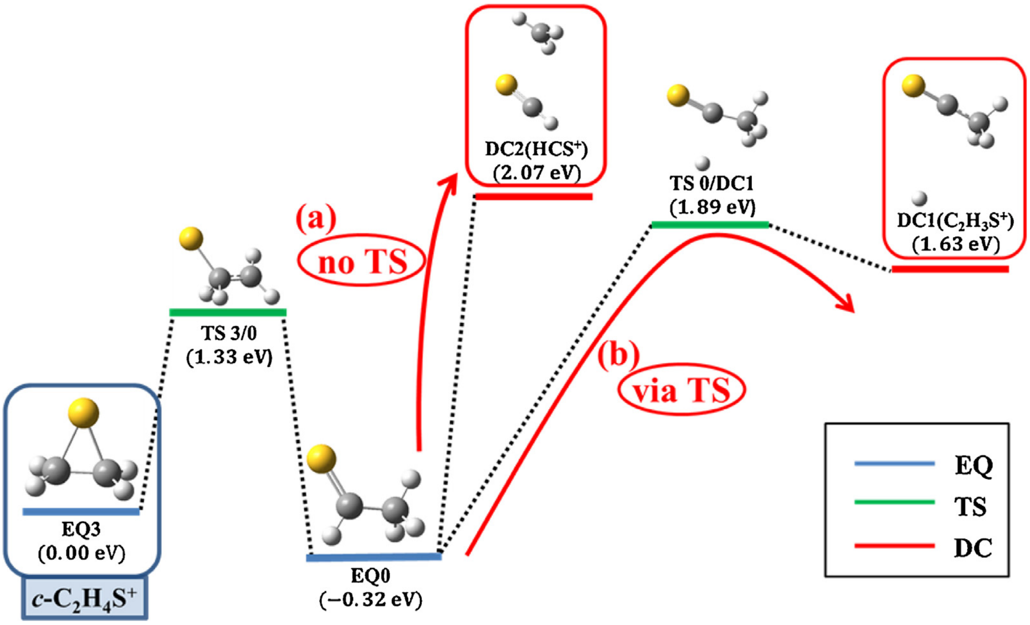

Figure 1. Dissociation pathways for c-$C_2H_4S^+$ (EQ3) → (a) HCS^+ + CH_3 and (b) $C_2H_3S^+$ + H after isomerization of c-$C_2H_4S^+$ (EQ3) into CH_3CHS^+ (EQ0).

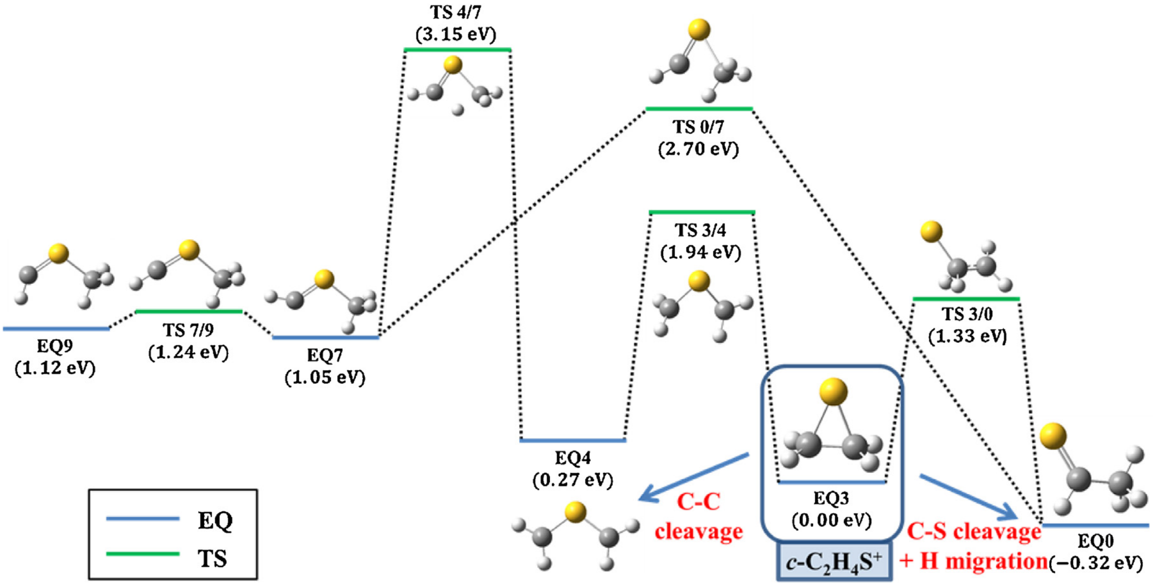

Figure 2. Ring-opening pathways for isomerization of c-$C_2H_4S^+$ (EQ3) into (left-hand side path) $CH_2SCH_2^+$ (EQ4) by C—C bond cleavage and (right-hand side path) CH_3CHS^+ (EQ0) by C—S bond cleavage and H migration.