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Research paper

Theoretical study of charge-remote fragmentation along the reaction coordinate of 1,4-hydrogen elimination in the gas-phase: Energy barrier and mechanism

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Density functional and Møller-Plesset perturbation approaches were applied to charge-remote fragmentation along the reaction coordinate of 1,4-hydrogen eliminations in the gas-phase. The mechanisms and energy barriers of the reactions are discussed. The calculations indicate that 1,4-hydrogen elimination via an aromatic-like six-atom transition state structure is energetically favorable with no involvement of the charge site. Cleavage of C—C and C—H bonds and the formation of H—H bonds occur simultaneously, and the energy barrier of this reaction is 4.01 eV. Energy decomposition analysis predicts a repulsive interaction between the formed H_2 and the remaining substituents.

1. Introduction

One unusual type of gas-phase ion decomposition, termed charge-remote fragmentation, occurs at sites that are physically remote from the location of the charge site. In these charge-remote fragmentations, the charge must be stable in its location within the gas-phase molecules and not be able to move to the reaction site. The ions are usually closed shell, and are introduced into the gas-phase by chemical ionization or fast atom bombardment ionization. For many systems, high-energy collision activations are required to cause the charge-remote fragmentation [1–7].

Charge-remote fragmentations have principally been applied using tandem sector mass spectrometry or double-focusing mass spectrometry. However, following the demise of sector and double-focusing mass spectrometry, there has been a marked decline in the application of high-energy collision activation. Despite this, the introduction of time of flight (TOF) mass spectrometry specifically designed for high-energy collision activation, TOF/TOFMS, has triggered renewed interest in high-energy fragmentation processes [8]. For example, matrix-assisted laser desorption ionization (MALDI) with high-energy collision activation TOF/TOFMS has been applied to induce charge-remote fragmentations and enable structural characterization of lipids, sulfated steroids, lithiated fatty acids, and fullerene derivatives [8–11].

Charge-remote fragmentation as gas-phase ion decompositions are a class of structurally informative reactions that can be applied to determine structure and identify unknowns. Charge-remote fragmentations along an alkyl chain occur as thermal-like 1,4-hydrogen eliminations to give both an alkene and unsaturated charged species containing the functional group (Fig. 1). The characteristic loss of the C_nH_{2n+2} alkenes indicate the length of the hydrocarbon chain and the location of important structural features, such as double bonds, branch points, and functional groups [1–7].

In contrast to the number of published experimental studies, few theoretical studies are available in the literature. Limited examples include semi-empirical AM1 molecular orbital calculations and Hartree-Fock calculations using a STO-3G basis set, which were used to demonstrate the cyclic elimination mechanisms and energy requirements for some charge-remote fragmentations [12].

We, therefore, conducted a theoretical investigation to attempt to answer some basic questions: (1) Are there important interactions between the charge and reaction site? (2) Are two C-H bonds and one C-C bond cleaved simultaneously or is the cleavage in two steps? (3) What interaction is the physical origin of the energy between the formed H_2 and the remaining substituents in the elimination process?

Our theoretical investigation also triggered our interest in high-energy fragmentation processes in high-energy collision activations using MALDI TOF/TOFMS. This study used density functional

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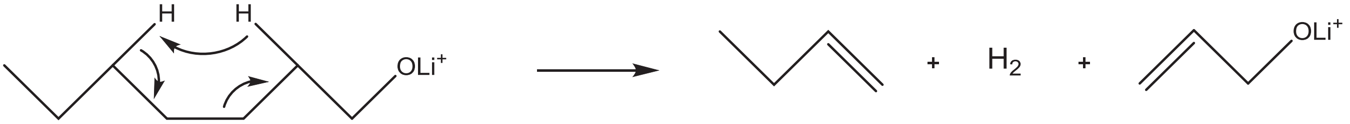

Fig. 1. 1,4-hydrogen elimination mechanism of 1-heptanol cationized with lithium.

theory and Møller-Plesset perturbation theory to investigate 1,4-hydrogen elimination using the simple model of 1-heptanol cationized with lithium.

2. Methods

The molecular structures of the initial and final states of fragmentation were optimized using density functional theory with the M06-2X/6-31+G(d,p) combination of method and basis sets. M06-2X is a hybrid meta exchange-correlation and high-nonlocality functional suitable for applications that involve main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states [13]. The transition state structures were optimized by the synchronous transit guided quasi-Newton (STQN) method [14] using density functional theory and Møller-Plesset (MP2) perturbation theory [15]. The reaction coordinate was calculated using an intrinsic reaction coordinate (IRC) scheme [16,17]. The STQN method, IRC calculation, atomic charge analysis and bond order analysis were performed using the Gaussian 09 suite of programs [18]. Calculation of the zero-point energy corrected activation energies of the transition states was performed and compared using the MP2, M06-2X, CAM-B3LYP [19] and WBD97XD [20] calculation methods with 6-31G+(d,p), 6-311G+(d,p), and 6-311G++(2d,p) basis sets.

Localized molecular orbital energy decomposition analysis (LMOEDA) [21] was performed at the restricted M06-2X/6-31+G (d,p) computational level to partition the interaction energies with a general atomic and molecular electronic-structure system program [22].

3. Results and discussion

The transition state structure for the 1,4-hydrogen elimination from 1-heptanol cationized with lithium (Fig. 2) was optimized using the STQN method. The transition state agrees with previous experimental results [1–3].

The reaction coordinate of the 1,4-hydrogen elimination from 1-heptanol cationized with lithium (Fig. 3) was calculated using the intrinsic reaction coordinate (IRC) approach. The IRC is defined as the minimum energy reaction pathway in mass-weighted Cartesian coordinates between the transition state of a reaction and its reactants and products [16,17]. The reaction coordinate provided a minimum energy path and 80 discrete ion structures.

The minimum energy path in Fig. 3 indicates the energy barrier to activation of the 1,4-hydrogen elimination from 1-heptanol cationized with lithium. The zero-point energy corrected activation energies were calculated by the difference in energy between aromatic-like six-atom transition state structure and the optimized structure of 1-heptanol cationized with lithium. The zero-point energy corrected activation energies at the different computational levels are summarized in Table 1.

Siegel [12] calculated the minimum activation energy for 1,4-hydrogen elimination as 4.0 eV, and reduced it to 2.7 eV in consideration of overestimation. Herein, we ascertain that although it tends to decrease in value when larger basis sets are employed, DFT method provided the energy range 3.80 – 3.95 and MP2 method provided 3.59 – 3.77 eV. Ideally, these values should be confirmed by the CCSD(T) method [23], which iteratively includes single and double substitutions and perturbatively incorporates the triple substitutions, is known as the gold-standard in quantum chemistry [24].

We used CCSD(T) electronic energies based upon the MP2 geometries with MP2 zero-point energy corrections and the resulting barrier height at this CCSD(T)//MP2 method is 4.01 eV.

Noteworthy is the difference in activation energy between reported experiment and theoretical estimation (this study) of the 1,4-hydrogen elimination. By experiment the internal-energy barrier for 1,4-hydrogen elimination was estimated as being in the range 1.3–1.9 eV [2]. This was on the basis that the changes in fragmentation favor release of the alkali metal cation. Wyscoki and Ross estimated the activation energy for charge-remote loss of C_nH_{2n+2} to be less than 3.0 eV [4].

We applied frequency analysis to the 1,4-hydrogen elimination from 1-heptanol cationized with lithium. The calculated wavenumber corresponding to the Li—O bond stretch was 607.1 cm^{-1}; the wavenumber corresponding to the transition state (imaginary frequency) was 885.3 cm^{-1}; and the wavenumber corresponding to the C—C bond stretch (simple bond cleavage) was 1152.9 cm^{-1}. Lee et al. achieved the bond-selective dissociation of a polyatomic cation using an appropriate mid-infrared wavelength. The wavelength dependence of the dissociation shows that resonant vibration excitation does play a role in the dynamics of strong field dissociation. An energetically disfavored elimination was strongly enhanced using an appropriate wavelength with polarization along a target bond [25]. Cheng and Gross have proposed an energy distribution diagram to describe the competition between 1,4-hydrogen elimination and simple cleavage. They demonstrated that several pathways are simultaneously involved in charge-remote fragmentation, and the preference for certain pathways is determined by the internal energy of the compound itself and the ionization and activation energies that are applied to it [6].

The collision activation results in a relatively broad internal-energy distribution [26]. The broad internal-energy distribution would convert into a broad distribution of stretching vibration energies, and the shape of this distribution affects the bond-dependent dissociation. From these considerations, we believe that the experimental results 1.3–1.9 eV [2], 3.0 eV [4] and our theoretical calculations 4.01 eV do not contradict each other. The density functional theory and MP2 approaches simply calculated the energy barrier corresponding to 1,4-hydrogen elimination via an aromatic-like six-atom transition state, experimental results consider the energy distribution.

The reaction coordinate in Fig. 3 provided 80 discrete ion structures. From these, we analyzed changes in the atomic charge, bond length, and bond order as the reaction proceeds along the coordinates. Fig. 4 shows atomic charge profiles along the reaction coordinate of 1,4-hydrogen elimination from 1-heptanol cationized with lithium. The atom labels and numbers correspond to those in Fig. 2. No changes observed in the atomic charge of lithium (Li18), oxygen (O16), and hydrogen (H17) correspond to the charge site of the cationized lithium. Atomic charge changes were observed only at the reaction site. These results clearly indicate that the charged site is not involved in the 1,4-hydrogen elimination even with a relatively short alkyl chain. The 1,4-hydrogen