Research paper

Energy-decomposition analysis of ion-neutral complexes along reaction coordinates of unimolecular proton-transfer reaction in gas phase: Comparison between 2-butanol radical ion and protonated 2-ethoxypropane ion

Natsuhiko Sugimura, Yoko Igarashi, Reiko Aoyama, Toshimichi Shibue

Materials Characterization Central Laboratory, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

A R T I C L E   I N F O

Article history:
Received 22 June 2017
In final form 22 August 2017
Available online 24 August 2017

Keywords:
Energy-decomposition analysis
Density-functional theory
Ion-neutral complex
2-Butanol
2-Ethoxypropane

A B S T R A C T

An energy-decomposition analysis clarified the physical origins that change in gas-phase unimolecular proton-transfer reactions via ion-neutral complexes of the 2-butanol radical ion and protonated 2-ethoxypropane ion. In the bond cleavage and new bond-formation parts of the reaction coordinates, exchange and polarization energies provide a major source of the attraction. In the ion-neutral complex-formation part of the reaction coordinate, different major attractive sources, dispersion, and electrostatic energies were observed. The physical origins of weak interaction in the ion-neutral complexes were affected by the local charges and distances between the ion moieties and the neutral moieties.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Ion-neutral complexes include concepts of π-complexes, hydrogen-bonded complexes, and ion-dipole complexes as intermediates in the unimolecular reaction of organic molecules in the gas phase, and these have been discussed theoretically and experimentally [1–11]. The ion-neutral complex was first postulated to understand the unusual reactivity of certain metastable ions that dissociate after partial transmission through the mass spectrometer [12–15]. Based on these studies, the following reactions were elucidated. The two moieties of the ion-neutral complexes are not connected by a covalent bond but are bound by attractive interactions. The separation between the charged and neutral moieties is sufficient to allow for their rotation with respect to one another, and they may react with each other by hydrogen-transfer reactions that constitute the most common evidence of ion-neutral-complex-mediated processes [16–21]. However, a direct observation of the ion-neutral complex formation is difficult. Therefore, little knowledge exists on the weak intermolecular interaction that dominates the ion-neutral complex formation.

Recently, ab initio calculations have become a powerful method for the theoretical study of weak intermolecular interactions [22–24]. Su et al. developed a local-molecular-orbital energy-decomposition analysis (LMOEDA) [25]. This method separates the total interaction energy between two molecules into electrostatic, exchange, repulsion, polarization, and dispersion energies:

$$\Delta E_{\text{Total}} = \Delta E_{\text{Electrostatic}} + \Delta E_{\text{Exchange}} + \Delta E_{\text{Repulsion}} + \Delta E_{\text{Polarization}} + \Delta E_{\text{Dispersion}}$$

The LMOEDA method has been used to study the physical origins of molecular interactions in the gas phase [26–29]. Electrostatic interactions are Coulombic electrical interactions between static charged atoms or molecules. Exchange (attractive) and repulsive interactions are associated with the Pauli Exclusion Principle. Polarization interactions result from the orbital relaxation energy, and dispersion interactions result from the electron correlation energy; both are attractive interactions. These interactions are considered to be of two types: long- and short-range interactions. Electrostatic, polarization, and dispersion interactions are long-range interactions, and their interaction energies are proportional to the inverse power of the interaction distance. In contrast, exchange and repulsive interactions are short-range interactions, with interaction energies that are related exponentially to the interaction distance [30].

To investigate changes in the physical origin of the interaction in the proton-transfer reaction via an ion-neutral complex in the gas phase, we had to obtain a series of ion structures along the
reaction coordinates. An energy path that connects the initial and final states with the greatest statistical weight is termed the minimum-energy path. The nudged-elastic-band (NEB) method is efficient at calculating the minimum-energy path [31–35]. The NEB method calculates the minimum-energy path between given initial and final states and involves constructing a set of images between the initial and final states. A common analogy of the NEB method is that of throwing a rope over a mountain pass and dragging it back and forth to locate the lowest elevation path.

A combination of the LMOEDA and NEB methods allowed us to investigate non-covalent weak interactions in the ion-neutral complexes along their reaction coordinates.

This study investigated the non-covalent weak intermolecular interactions that dominate the ion-neutral complex formation as unusual unimolecular reactions in the gas phase. The unimolecular proton-transfer reaction via ion-neutral complexes along their reaction coordinates was explored by energy-decomposition analysis. The originality of this work was to analyze changes in physical origins of the interaction in an ion-neutral complex along the reaction coordinates. In the theoretical study, two simple model molecules of the 2-butanol radical and protonated 2-ethoxypropane ions were used to compare the physical origins of ion-neutral complexes. To the best of our knowledge, these molecules are one of the simplest molecules that form radical ion-neutral and protonated ion-neutral complexes, respectively. The moderate molecular size allowed us to perform calculations at our theoretical calculation facility, and their unimolecular proton-transfer reaction mechanisms in the gas phase have been studied in detail [36].

2. Methods

2.1. Theoretical calculations

The molecular structures of the initial and final states of fragmentation were optimized using density-functional theory restricted/unrestricted M06-2x/6-31+G(d,p). M06-2x is a hybrid meta-exchange-correlation and high-nonlocality functional for applications that involve main-group thermochemistry, kinetics, noncovalent interactions, and electronic excitation energies to valence and Rydberg states [37].

Calculations of the minimum-energy path to find the structures of ion-neutral complexes along their reaction coordinates were performed using the NEB method [31–35] in the Reaction plus Pro program [38] with the restricted/unrestricted M06-2x/6-31+G(d,p) calculation using Gaussian 09 [39]. Twenty-five interpolations (spring interactions between the initial and final states) were applied to the force energy between the interpolations. The transition-state structures were optimized using the synchronous transit guided quasi-Newton (STQN) method [40]. All the molecular-structure calculations in Gaussian 09, which is the self-consistent field method, were applied to obtain a more accurate set of orbitals, and then the Schrödinger equation was solved again with these calculations until the self-consistent field results converged within 0.004 eV. LMOEDA analyses [25] were performed at the restricted/unrestricted M06-2x/6-31+G(d,p) computational level to partition the interaction energies with a general atomic and molecular electronic-structure system program [41]. Calculations were performed at the Materials Characterization Central Laboratory, Waseda University (Tokyo, Japan) [42].

3. Results and discussion

Fig. 1 shows the proposed unimolecular proton-transfer reactions of the (a) 2-butanol radical and (b) protonated 2-ethoxypropane ions via ion-neutral complexes in the gas phase [36]. Both unimolecular reactions show single hydrogen transfer via ion-neutral complexes. The two moieties of the ion-neutral complexes are not connected by a covalent bond but are bound by attractive interactions. The separation between the charged and neutral moieties is sufficient to allow their rotation with respect to one another, and they react with each other by hydrogen-transfer reactions.

We input the initial and final ion structures in the unimolecular proton-transfer reaction in Fig. 1 into the NEB method to find the minimum-energy path. Fig. 2a and b shows the optimization process to determine the minimum-energy path for the unimolecular proton-transfer reactions of the 2-butanol radical ion and the protonated 2-ethoxypropane ion via ion-neutral complexes in the gas phase using the NEB method.

These optimizations are based on minimizing the energy of the coarse loop that consists of 25 interpolations between the initial and final states to a slope that is perpendicular to the potential-energy surface. The initial and final molecular structures were calculated as movable images, and they were optimized to find more stable structures. Finally, we obtained a minimum-energy path that consisted of 25 discrete ion structures as reaction coordinates. An illustration of the reaction coordinates that were constructed using the NEB method is shown in Fig. S1 (Supporting information).

The principal advantage of the NEB method is that it provides energy barriers using only the optimized initial and final molecular structures. The energy barrier that corresponds to the proton-transfer reaction of the 2-butanol radical and protonated 2-ethoxypropane ions was approximately 0.72 eV and 1.41 eV, respectively.

The saddle-point structures in the reaction coordinates could be candidates for the transition states. The synchronous transit-guided quasi-Newton (STQN) method [40] was used to determine the structures of the transition states. The STQN method provides precise and optimized structures for transition-state structures that correspond to the proton-transfer reaction of 2-butanol radical and protonated 2-ethoxypropane ions. The transition-state structures were found to have only one imaginary frequency.

Fig. 3 shows the transition-state structures of (a) 2-butanol radical and (b) protonated 2-ethoxypropane ions. The atomic charges of the transition-state structures were estimated by natural population analysis [43]. In the transition-state structures of (a) the 2-butanol radical ion, the total charges of the 1-hydroxyethan-1-yl moiety and the ethyl radical were 0.96 e and 0.04 e, respectively. This result supports the theory that the unimolecular proton-transfer reaction of the 2-butanol radical occurred via an ion-neutral complex. The dispersion energy and electrostatic energy between the two moieties in the transition state were −0.39 eV and −0.24 eV, respectively.

In the transition-state structures of the (b) protonated 2-ethoxypropane ions, the total charges of the propane-2-yl moiety and the ethyl radical were 0.94 e and 0.06 e, respectively. This result confirms that the unimolecular proton-transfer reaction of protonated 2-ethoxypropane ions occurred via an ion-neutral complex. The dispersion energy and electrostatic energy between the two moieties in the transition state were −0.37 eV and −0.97 eV, respectively.

We defined the geometrical parameters and distance definition of the ion-neutral complexes in the unimolecular proton-transfer reaction of the 2-butanol radical and protonated 2-ethoxypropane ions in the gas phase. The geometrical parameters are the bond distances between atoms where bonds are cleaved and the bond distances between newly formed atoms.

In the ion-neutral complex-structure unimolecular proton-transfer reaction of the 2-butanol radical ion, the cleavage bond
دریافت فوری
متن کامل مقاله

امکان دانلود نسخه تمام متن مقالات انگلیسی
امکان دانلود نسخه ترجمه شده مقالات
پذیرش سفارش ترجمه تخصصی
امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
امکان دانلود رایگان ۲ صفحه اول هر مقاله
امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
دانلود فوری مقاله پس از پرداخت آنلاین
پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات