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Ab initio molecular dynamics simulation study of dissociative electron attachment to $C_6H_5(CH_2)_nCl$ ($n = 0, 1, 2, 3, 4$)

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ABSTRACT

The C—Cl bond cleavages induced by electron attachment to 1-chloroalkyl benzenes [$C_6H_5(CH_2)_nCl$, $n = 0, 1, 2, 3, 4$] are investigated with ab initio molecular dynamics simulations. The fragment Cl^- is generated and the C—Cl bond cleavage time decreases with the increasing length of the alkyl chain. In the dissociative electron attachment processes, the incoming electron is initially captured to the local π^* virtual orbital of the phenyl group and then transfers to the anti-bond σ^* orbital of the remote C—Cl moiety; the variation of the C—Cl bond cleavage times shows a similar trend of the dissociation thresholds of $C_6H_5(CH_2)_nCl + e^- \rightarrow C_6H_5(CH_2)_n^\bullet + Cl^-$.

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1. Introduction

Dissociative electron attachment (DEA), $e^- + AB \rightarrow A + B^-$, can produce the neutral (A) and anionic (B^-) fragments for the gas- or condense-phase molecule (AB) [1,2]. If the target AB (for example, unsaturated hydrocarbon) has the low-lying virtual π^* orbital, the incoming electron e^- is easily captured and temporally occupies at the π^* orbital of a local group, and then transfers to the anti-bond orbital σ^* of another local moiety of AB. The electron transfer efficiency of $\pi^* \rightarrow \sigma^*$ is regarded as an important role in breaking the σ bond [3–9]. For chloro/bromoalkyl-substituted alkenes [4–7] and benzenes [8,9], the production efficiency of the halogen anionic fragment ($X^- = Cl^-$, Br^-) was found to decrease with the increasing length of the alkyl chain. The authors further concluded that the electron transfer or π^*/σ^* coupling was always much weaker between two remote local bonds than that for two vicinities [3–9]. This through-space mechanism about the electron transfer has been widely accepted as a general rule controlling the DEA to the unsaturated hydrocarbons, nucleic acids and their derivatives.

In this work, we perform ab initio molecular dynamics simulations for the C—Cl bond cleavages in the DEA processes of 1-chloroalkyl benzenes [$C_6H_5(CH_2)_nCl$, $n = 0, 1, 2, 3, 4$], and the present results indicate that the C—Cl bond dissociation becomes faster for the longer alkyl chain. Our finding is obviously contrary to the previous understanding [3–9]. A complete description of the DEA to the unsaturated hydrocarbons is demanded.

2. Computational method

As shown in Fig. 1, the geometries of all conformers of $C_6H_5(CH_2)_nCl$ ($n = 0, 1, 2, 3, 4$) were optimized at B3LYP/6-31G* level of density functional theory. Eight conformers were 0I, 1I, 2I, 3I, 4I, 2II, 3II and 4II, and no imaginary frequencies were found for these stable conformers. 1II, 2III, 3III and 4III conformers had one imaginary frequency within C_s symmetry. These unstable conformers were proved to be the transition-state structures corresponding to the chloroalkyl-group rotations, on the basis of the conformer searching calculations along the intrinsic reaction coordinate. The larger basis set (for example, 6-311+G*) could lead to some artificial results [5], thus 6-31G* was also used for calculations for anionic molecules $C_6H_5(CH_2)_nCl^-$ and in the dissociation simulations. The vertical attachment energy (VAE) value of the neutral conformer was determined with the energy difference, $VAE = E[C_6H_5(CH_2)_nCl^-] - E[C_6H_5(CH_2)_nCl]$, over the molecular geometry of the neutral, where E is the total electronic energy of the neutral or anionic molecule. The dissociation threshold of $C_6H_5(CH_2)_nCl + e^- \rightarrow C_6H_5(CH_2)_n^\bullet + Cl^-$ was predicted with the energy difference between $E[C_6H_5(CH_2)_nCl]$ and the total

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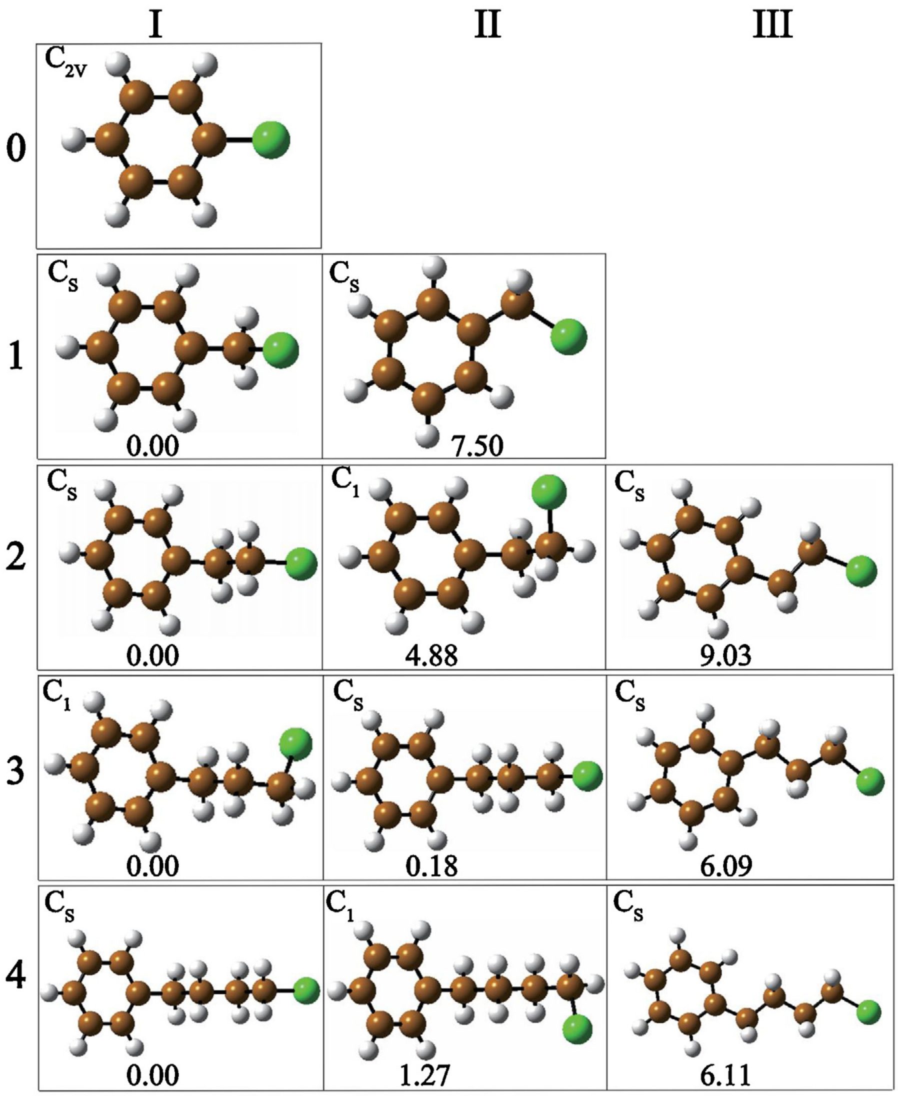

Fig. 1. Molecular structures (symmetries assigned) and the relative energies (in kJ mol^{-1}) of the neutral $C_6H_5(CH_2)_nCl$. Hydrogen, carbon and chlorine atoms are colored in white, brown and green, respectively.

energy of the anionic fragment Cl^- and free radical $C_6H_5(CH_2)_n^\bullet$ at their electronically ground states. The geometries of $C_6H_5(CH_2)_n^\bullet$ were also optimized at the B3LYP/6-31G* level.

The lowest unoccupied molecular orbital of the neutral molecule showed the predominant character of π^* localized at the benzene ring, and thus the low-energy incoming electron would occupy this π^* orbital in the vertical attachment. The following structural and energetic evolvements would start with this local resonant state of $C_6H_5(CH_2)_nCl^-$. Ab initio molecular dynamics simulations were carried out with the atom-centered density matrix propagation method [10–12] [ADMP-B3LYP/6-31G(d)]. In the ADMP approach, the one-electron density matrix was expanded in an atom-centered (Gaussian) basis and was propagated as electronic variables; all electrons of the system were treated in quantum chemistry scheme without resorting the pseudopotentials and the deviation from the Born–Oppenheimer surface could be controlled precisely without the resulting mixing of fictitious and real kinetic energies [10–12]. As shown in our previous study, this method was successfully applied in the simulations of the $\pi^* \rightarrow \sigma^*$ electron transfer in the DEA to dialanine [13]. In the first scheme, the dynamic evolution was initiated from the Franck–Condon region of the vertical electron attachment to the neutral target. There were no internal motions of the molecular anion $C_6H_5(CH_2)_nCl^-$ at the beginning point with the neutral structure, and the atomic motions in the following steps were due to the energy difference between the energy of $C_6H_5(CH_2)_nCl^-$ gained from the vertical attachment and the threshold of dissociation to $C_6H_5(CH_2)_n^\bullet + Cl^-$. Here we also considered another scheme where the internal motions of $C_6H_5(CH_2)_nCl^-$ at the beginning point were mimicked with the atomic motions of $C_6H_5(CH_2)_nCl$ at the vibrationally ground state. In this scheme, the atomic motions, including the molecular geometries and the initial velocity of each atom in $C_6H_5(CH_2)_nCl^-$ were stochastically selected from the neutral after 400 fs ADMP simulations of $C_6H_5(CH_2)_nCl$ at the vibrationally ground state. In each of two schemes, the time step was 0.2 femtosecond (fs), and the time scale of simulations was about 200 fs. No dissociation pathways were constrained in the simulations. All quantum chemistry calculations were performed with GAUSSIAN 09 program [14].

3. Results and discussion

As shown in Fig. 1, the unstable conformers 1II, 2III, 3III and 4III as the transition states are higher in energy than their corresponding stable conformers. The relative energies (in kJ mol^{-1})

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