Investigation of Markovnikov reactions of alkenes via ABEEM-σπ model

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ABSTRACT

Electrophilic additions of HCl to a series of asymmetric alkenes in the gas phase have been investigated in the light of the ABEEM-σπ model and high-level *ab initio* method. We demonstrated well the regioselectivity of the electrophilic reactions by means of the ABEEM-σπ model on the basis of local HSAB principle and maximum hardness principle. According to the charge distribution in the initial state of alkenes not only regioselectivity has been explained reasonably, but also an interesting phenomenon has been observed that alkenes with electron-donating substituents show a clear regioselectivity, but those with electron-withdrawing ones do not display a clear preference for anti-Markovnikov or Markovnikov addition.

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1. Introduction

Electrophilic addition to alkenes is one of the most widely studied reactions. It is well known that the chemistry of alkenes depends mainly on the characteristic double bond between two carbon atoms. There are many theoretical studies on the addition of alkenes [1–7]. Electrophilic addition to alkenes is characterized by two important properties, reactivity and regioselectivity of the addition reaction. Regioselectivity has been proposed to follow the empirical Markovnikov's rule [8], i.e., the addition of an acidic proton to a double bond of an alkene yields a product where the proton is bound to the carbon atom bearing the largest number of hydrogen atoms. As regards reactivity, electron-donating substituents increase the reactivity, whereas electron-withdrawing ones decrease it. But there are some exceptions to Markovnikov's rule. For instance, the electrophilic additions to alkenes that contain strongly electron-withdrawing groups preferentially form the anti-Markovnikov product [9].

Numerous theoretical studies have focused on electrophilic additions to alkenes. For example, the regioselectivities of the addition reaction to olefins can be explained with the frontier molecular orbital theory [6]. In terms of the core-electron spectroscopy and theory [5], Sæthre, Thomas and Svensson have pointed out that both regiospecificity and reactivity are quantitatively related to core-ionization energies. They have also noticed that a significant difference between Markovnikov and anti-Markovnikov addition is due to the charge distribution in the initial state of the olefin and not due to the different abilities of the molecules to delocalize

the added charge in the transition state. The electrostatic potential as well as the electron density distribution in a molecule for better accounting for the regiospecificity of Markovnikov reactions has been emphasized by Hessley [4]. Suresh, Koga and Gadre found that the substituents can be classified as electron donating and withdrawing via molecular electrostatic potential (MESP) surrounding the π-region of several alkenes [3]. They investigated correlation between the Hammentt σ_p and π-region MESP CPs (the most negative-valued MESP point) of alkenes. Recently, the Markovnikov regioselectivity has been well studied via the density functional theory reactivity descriptors by Aizman and coworkers in the light of an activation model [2]. In the more recent studies, the regioselectivity and reactivity of the alkenes for electrophilic addition reactions have been well demonstrated by Molecular Face theory [1]. Theoretical studies as well as the experimental works indicated that Markovnikov addition reaction proceeds via reactants initially forming a weakly bound T-shaped ethylene-hydrogen halide complex, then passing through a transition state to the ultimate addition products [7].

On the basis of DFT [10–12] and electronegativity equalization principle [10], we developed the ABEEM-σπ model [13–15], which explicitly considered the structure of double bonds that is quite essential for the modeling of organic and biological systems. In the previous study, we have successfully used it to produce the charge distributions of polypeptides [13], and well investigated the regio- and stereoselectivity of Diels–Alder reactions [14,15], etc. In this paper, the regioselectivity of the electrophilic reactions of HCl to a series of asymmetric alkenes has been investigated in terms of charge distribution, Fukui function value and hardness obtained via the ABEEM-σπ model on the basis of local HSAB principle and MHP.

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2. Methodology

2.1. The ABEEM-σπ model

Within ABEEM-σπ model, the molecular electron density is partitioned as single bond atom region, double bond atom region, single bond region, σ bond region and π bond region of the double bond, and lone-pair electron region, respectively. In the ABEEM-σπ model, molecular properties and reactivity are investigated through discussing perturbation of the total molecular energy with respect to the number of electrons and the external potential. Under the condition of perturbation, the sensitivity coefficient demonstrates a variation of the properties of a molecular system. In this paper, we mainly investigated three sensitivity coefficients, Fukui function, local softness and global hardness.

Based on Fukui function, global softness and local hardness, we obtain:

$$s(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial \mu}\right)_v = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_v \left(\frac{\partial N}{\partial \mu}\right)_v = f(\vec{r}) \cdot S \quad (1)$$

where μ is the chemical potential and S is the global softness. And another important property is global hardness η

$$\eta = \frac{1}{2S} = -\frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right)_v \quad (2)$$

Here, χ is the electronegativity. According to the electronegativity equalization principle and the definition of hardness, one has

$$2\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_v = -\left(\frac{\partial \chi_a}{\partial N}\right)_v = \cdots = -\left(\frac{\partial \chi_m}{\partial N}\right)_v = \cdots$$

$$= -\left(\frac{\partial \chi_{a-b}}{\partial N}\right)_v = \cdots = -\left(\frac{\partial \chi_{m=n}}{\partial N}\right)_v = \cdots \quad (3)$$

Moreover, through a series of derivation, and in terms of the definition of Fukui function, we have

$$2\eta = 2\eta_a^* f_a + C_a \sum_{a-b} f_{a-b} + D_a \sum_{lp \in a} f_{lp} + k\left[\sum_{b \neq a} \frac{f_b}{R_{a,b}} + \sum_m \frac{f_m}{R_{a,m}} \right.$$

$$\left. + \sum_{g-h \neq a-b} \frac{f_{g-h}}{R_{a,g-h}} + \sum_{\sigma m=n} \frac{f_{\sigma m=n}}{R_{a,\sigma m=n}} + \sum_{\pi m=n} \frac{f_{\pi m=n}}{R_{a,\pi m=n}} + \sum_{lq \neq a} \frac{f_{lq}}{R_{a,lq}}\right] \quad (4)$$

Similarly, we can get five analogous equations concerning the single bond region, double bond atom region, σ bond region and π bond region of the double bond, and lone-pair electron region. These six equations, along with the normalization condition of Fukui function, can be solved to give the molecular hardness values, and Fukui function values of each region in the molecule if all the parameters in these equations have been calibrated.

In this paper, the parameters have been determined through trimming based on the parameters of the literature [13,14], the correction coefficient k has been still taken 0.57, which is coincident with the value determined by Yang et al. in the ABEEM model.

2.2. Quantum chemical method

Electrophilic additions of HCl to ethene, propene and 2-methyl-propene (substituents X = H, CH₃, (CH₃)₂, respectively) in the gas phase were investigated at different levels of theory (refer to Ref. [1]). The calculated activation energies with zero-point energy correction and the experimental values are listed in Table 1 (refer to Ref. [1]). The calculated activation energy at B3LYP/6-311 + G(3df,2p), CCSD(T)/aug-cc-pVDZ//B3LYP/6-311 + G(3df,2p) and MP2/6-311 + G(3df,2p) levels of theory agree well with the experimental values [5], and the good linear correlations between the calculated activation energies $E^{\#}_{cal}$ and experimental values $E^{\#}_{exp}$ (correlation coefficients are 0.9930, 0.9956 and 0.9984, respectively) have been obtained. The MP2/6-311 + G(3df,2p) method can predict better activation energies compared with the experimental values, which suggests that the theory correctly predicts the overall trend in the values. Therefore, all the electrophilic additions have been studied at MP2/6-311 + G(3df,2p) level of theory. In addition, vibrational frequencies were calculated to identify the obtained stationary points as either equilibrium structures or transition states. The intrinsic reaction coordinate (IRC) routes were performed for the 15 electrophilic addition reactions. The zero-point energies (ZPEs) for all structures were obtained at MP2/6-311 + G(3df, 2p) level of theory.

3. Results and discussion

3.1. Ab initio activation energies

Electrophilic additions of HCl to a series of asymmetric alkenes in the gas phase have been investigated by means of an *ab initio* method. On the one hand, theoretical studies [1,2,5] indicate that regiospecificity of electrophilic additions is due to charge distribution in the initial states of alkenes. On the other hand, the studies on reactions in the gas phase can usually obtain intrinsic reaction mechanism. Hence, the activation energies and energies of the TSs of the Markovnikov and anti-Markovnikov additions for the reactions considered in the gas phase have been calculated at MP2/6-311 + G(3df, 2p) level of theory, and the corresponding calculated values are listed in Table 2. For the alkenes with the substituents CH₃, (CH₃)₂, CH₂CH₃, CHCH₂, OCH₃, OH and Cl, the activation energies of Markovnikov addition routes are much lower than those of anti-Markovnikov addition routes, indicating that Markovnikov additions are mainly reaction routes for these reactions. But for the alkenes with the substituents CHO, COOH, CN and COF, the activation energies of anti-Markovnikov addition routes are slightly lower than those of Markovnikov addition routes, indicating that these reactions may slightly prefer anti-Markovnikov addition routes. Note that the three geometries of the alkenes with the substituents NO₂ and CH₃, which include cis- and trans- geometry (denoted by NO₂CH₃-cis and NO₂CH₃-trans, respectively), and both NO₂ and CH₃ bounding to a carbon atom of the double bond (denoted by NO₂CH₃), have been investigated. The activation energies of anti-Markovnikov addition routes of the former are slightly lower than those of Markovnikov addition routes, but the activation energy of Markovnikov addition route of the latter is lower than that of anti-Markovnikov addition route.

In addition, the effect of the solvent was examined using PCM. The activation energies of the reactions considered were recalculated at MP2/6-311 + G(3df, 2p) level of theory using PCM based on the geometries in the gas phase, and are listed in Table 3. It is seen from Table 3 that the trends of the Markovnikov or anti-Markovnikov additions do not change for these reactions. The reactions for the alkenes with the substituents CH₃, (CH₃)₂, CH₂CH₃, CHCH₂, OCH₃, OH, Cl and NO₂CH₃ still prefer Markovnikov addition routes. And the reactions for the alkenes with the substituents CHO, COOH, CN, COF, NO₂CH₃-cis and NO₂CH₃-trans still slightly prefer anti-Markovnikov addition routes.

3.2. Study on regioselectivity via the ABEEM-σπ model

3.2.1. Charge distributions in the initial state of alkenes

According to density functional theory (DFT), the electron density of a molecular system determines all properties of a molecular system [11]. Therefore, the charge distributions of a molecular