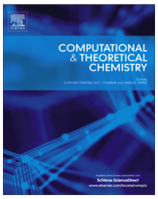
Computational and Theoretical Chemistry 1067 (2015) 7–12

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Theoretical study on the activity of hydrogen atom of imidazolium ring in ionic liquids

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ARTICLE INFO

Article history:
Received 19 April 2015
Received in revised form 24 May 2015
Accepted 25 May 2015
Available online 5 June 2015

Keywords:
Ionic liquids
Pentene
Activity
Isomerization
DFT

ABSTRACT

The double-bond isomerization of 1-pentene catalyzed by [Emim]BF$_4$ ionic liquid and the interaction relationship of the [Emim]BF$_4$ ion pair have been studied by using density functional theory (DFT) at the B3LYP/6-31G(d,p) level. The obtained results reveal that the [Emim]$^+$ and BF$_4^-$ ions exist in the form of the ion pairs in the ionic liquid system, and only two stable structures are obtained. The isomerization process of 1-pentene on [Emim]BF$_4$ ionic liquids proceeds via a concerted reaction pathway. The hydrogen atom transfer is accompanied by the migration of the intramolecular double bond. The ionic liquid acts as a proton donor, while it also favors the proton abstraction. The adsorption energies of 1-pentene on the 2-position and 4-position hydrogen atoms of the imidazolium ring are -11.32 and -7.42 kJ/mol, respectively. The apparent activation energies of the double-bond isomerization for 2-position hydrogen atom and 4-position hydrogen atom are 196.91 and 214.64 kJ/mol, respectively. Those indicate that two kinds of hydrogen atoms of the imidazolium ring have both catalytic activities, but the activity of 2-position hydrogen atom is much higher than the one of 4-position hydrogen atom.

1. Introduction

Ionic liquids (ILs) have recently attracted considerable worldwide attention as environmentally benign solvents and catalysts [1–3]. ILs are room temperature fluids composed entirely of ions, typically large organic cations based on alkylimidazolium or alkylpyridinium ions and small inorganic anions such as BF$_4^-$, PF$_6^-$, N(CF$_3$SO$_2$)$_2^-$, etc. They have no detectable vapor pressure and therefore exhibit favorable solvent properties for new homogeneous catalytic reactions and other chemical production processes with respect to "green chemistry". By changing the anion or the alkyl chain on the cation, a wide variation in properties such as hydrophobicity, viscosity, density and solvation can be obtained. Many organic reactions, including alkylation [4,5], epoxidation [6,7], hydrogenation [8], Suzuki cross-coupling reaction [9], etc. have been performed in room temperature ionic liquid with excellent yields and selectivity.

In alkylation reaction, ionic liquid is not only as solvent but also as co-catalyst. In addition, some of the ionic liquids can even act as catalysts. For example, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF$_4$) or hexafluorophosphate ([Bmim]PF$_6$) is used as catalysts for the Biginelli condensation reaction under solvent-free conditions [10], and 1-Butylimidazolium tetrafluoroborate ([Hbim]BF$_4$) is found to be the best ionic liquid for the Friedlander heteroannulation reaction [11]. These indicate that both cations and anions in the ionic liquids play an important role in the reaction process. Sun et al. [12] have found that the significant Brønsted acid properties of the 2-position H of 1-*n*-butyl-3-methylimidazolium chloride ([Bmim]Cl) by titration, FT-IR, and ^{1}H NMR analysis, and proposed a typical carbocation mechanism for the alkylation of benzene with ethylene catalyzed by [Bmim]Cl/FeCl$_3$. The research of catalytic mechanism of ionic liquids helps us the search for novel applications of ILs in the chemistry field. However, not much research has been performed on the details of the mechanisms of the reactions occurring in these media or catalysts, and possible changes that are involved in comparison to conventional solvents. The theoretical studies have attracted much attention to the relations between structure and properties of ionic liquid [13–15].

Because the double-bond isomerization of alkenes is very fast processes that requires weaker acid sites [16], alkenes as probe molecules can be used to investigate the Brønsted acid properties of H atom of imidazolium ring. The primary researches on the butene isomerization catalyzed by the cation of Emim$^+$ had been finished using the density functional theory, but the influence of anion on the reaction is not considered [17]. In this letter, we have studied the reaction mechanism of the double-bond isomerization

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http://dx.doi.org/10.1016/j.comptc.2015.05.025
2210-271X/

of 1-pentene catalyzed by [Emim]BF_4 ionic liquid by using the B3LYP method of density functional theory. The microcosmic physical image of atomic shift of the isomerization has been described by means of the intrinsic reaction coordinates at the scale of atomic structure.

2. Computational methods

The geometries of the reactant, [Emim]BF_4 ionic liquid, transition state and product were fully optimized at the B3LYP/6-31G (d,p) level of theory [18]. Vibrational frequencies were calculated at the same level to identify the nature of the stationary points and obtain the zero-point-energy (ZPE) corrections. The vibrational frequencies were scaled with a factor of 0.9614 [19]. The reaction trajectories were determined by the intrinsic reaction coordinate (IRC) methods [20,21]. All calculations were performed by using the Gaussian 03 program [22].

3. Results and discussion

3.1. Interaction of [Emim]BF_4 ion pair

The [Emim]BF_4 ion pair calculations are initiated by placing the cation in several different positions relative to the imidazolium ring. These positions included above and below the ring and at the side of the imidazolium ring. Regardless of the starting point, only two final structures are obtained. Fig. 1 shows the optimized structures of the [Emim]BF_4 ion pair (marked as EA and EB, respectively). The corresponding geometrical parameters are summarized in Table 1. For structure EA, it can be found that the four H—F distances (F1—H5, F2—H5, F2—H4 and F3—H4 bonds, respectively) are less than the H—F van der Waals of 2.7 Å [23], while the six H—F distances (F1—H2, F2—H2, F3—H2, F3—H3, F2—H6 and F1—H1 bonds, respectively) in structure EB are less than the H—F van der Waals. This means that hydrogen-bonded interactions occur between the F atoms on the anion and the C—H moieties on the imidazolium cation.

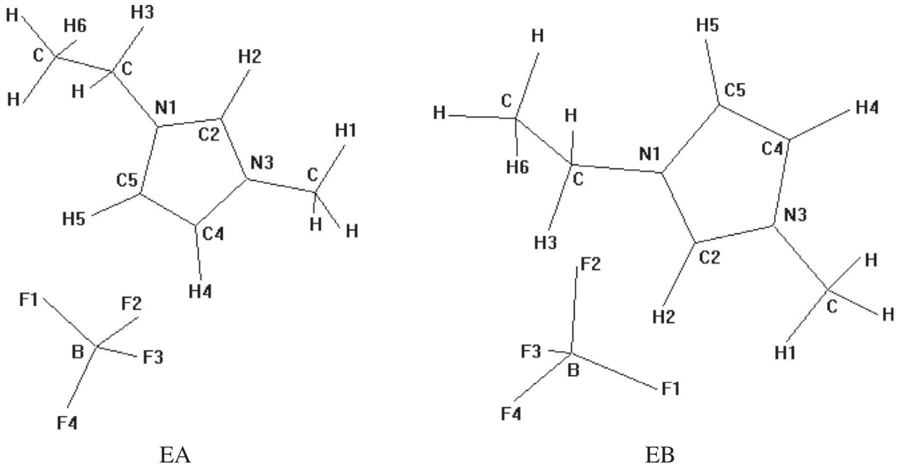
Table 1
Main optimized geometric parameters of the BF_4^-, $Emim^+$, EA and EB for [Emim]BF_4 ion pair (bond lengths in Å and bond angles in °).

	BF_4^-	$Emim^+$	EA	EB
B—F1	1.410		1.431	1.428
B—F2	1.410		1.429	1.415
B—F3	1.410		1.407	1.436
B—F4	1.410		1.375	1.367
C2—H2		1.079	1.078	1.081
C2—N3		1.339	1.342	1.336
C2—N1		1.338	1.341	1.335
C5—N1		1.382	1.381	1.385
C4—N3		1.383	1.381	1.386
C4—C5		1.364	1.364	1.363
C5—H5		1.079	1.086	1.078
C4—H4		1.079	1.083	1.078
F1—H5			1.985	
F2—H5			2.684	
F2—H4			2.592	
F3—H4			1.901	
F1—H2				2.130
F2—H2				2.571
F3—H2				1.946
F3—H3				2.306
F2—H6				2.267
F1—H1				2.164
N3—C2—N1		109.0	108.2	108.8

From the ion pair structure, the hydrogen bonds in configuration EA are more than in configuration EB. From the distribution of charge, charges of the anion and cation partially transfer. The charge distribution in structure EA (−0.7749 to +0.7749 e) is significantly different from the one in structure EB (−0.8324 to +0.8324 e). The interaction energy of the ion pair is defined as the difference between the energy of the ionic system and the sum of the energies of the pure cation and anion. The interaction energy of the [Emim]BF_4 ion pair are summarized in Table 2. As can be seen in Table 2, the interaction energy ($-402.94\ \mathrm{kJ\ mol^{-1}}$) for the structure EB is much lower than the one for the structure EA ($-343.30\ \mathrm{kJ\ mol^{-1}}$), which indicates that the hydrogen bonds and electrostatic effects in structure EB is much stronger. Therefore, the structure EB is more stable than the structure EA. It further illustrates that the stabilization of the 2-position hydrogen atom on the imidazolium ring is much stronger than the one of the 4 or 5-position hydrogen atom, and the chances of EB configuration in ionic liquids is more than the one of EA configuration. In general, the interaction energies of the ion pairs in two configurations are very great, therefore the cation–anion exists in the form of ion pair in the ionic liquid system.

3.2. Catalytic activity of hydrogen atom of imidazolium ring

The imidazolium ring of [Emim]BF_4 ionic liquid has two different kinds of hydrogen atoms, 2-position H and 4 or 5-position H. Pentene as a probe molecule is used to investigate the catalytic activity of two different H atoms of imidazolium ring. Figs. 2 and



EA EB

Fig. 1. Molecular structures for [Emim]BF_4 ion pair.