

A DFT study on the double bond migration of butene catalyzed by ionic pair of 1-ethyl-3-methyl-imidazolium fluoride

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Received 14 February 2005; in final form 28 May 2005

Available online 22 June 2005

Abstract

The double bond migration of butene catalyzed by 1-ethyl-3-methyl-imidazolium fluoride (EmimF) has been studied using quantum chemical method. The geometries of reactant, transition state and product for the isomerization have been optimized by density functional theory (DFT) at the B3PW91/6-31G(d,p), 6-311++G(d,p) and aug-cc-PVDZ levels. The computed results show that the 4-H atom on imidazole ring of EmimF has a good catalytic activity to the double bond migration of butene and the catalytic reaction of 1-butene to 2-butene is a synergetic and elementary process. The apparent activation energy of isomerization is about 197 kJ/mol.

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1. Introduction

It is well known that recent years the room temperature ionic liquids (RTILs) have exhibited many special properties such as negligible vapor pressure, low melting point, large liquid range, powerful solubility and high catalytic activity [1–3]. These properties can be adjusted and controlled to a certain extent by changing the anion, cation, or substituent groups on the cation. Some detailed reviews of these properties for RTILs have been reported in the Chemical Review and other journals [4–6]. The acidified ionic pair of 1-ethyl-3-methyl-imidazolium fluoride (EmimF) is one kind of typical ionic liquid [7]. It has been used as recyclable solvents, catalysts and reaction medias [8,9]. Some experimental studies have focused on measuring the local structure and property of RTILs [10–12], but a general fundamental understanding of how these properties depend on the chemical composition and structure of RTILs is still

lacked of. One of the handicap preventing the wide application of RTILs is the shortage of physical property data, so the theoretical studies have attracted much attention to the relations between structure and properties of ionic liquid [13,14]. Some quantum chemical calculation at the different computing levels about the electronic structure of RTILs such as 1-ethyl-3-methyl-imidazolium cation (Emim⁺) and 1-butyl-3-methyl-imidazolium cation (Bmim⁺) has been carried out [15,16]. However, the reaction mechanism catalyzed by RTILs has not been studied using quantum chemical methods from the literature to the best of our knowledge. We have started the primary researches on the butene isomerization catalyzed by the cation of Emim⁺ using the B3LYP method of density functional theory [17]. The transition state of double bond migration of butene catalyzed by single cation of Emim⁺ has been found. However, it is still ambiguous whether the hydrogen atom on imidazole ring in ionic liquid has good catalytic activity to the butene isomerization. In this Letter, the catalysis of the 4-H proton on the imidazole ring of 1-ethyl-3-methyl-imidazolium fluoride (EmimF) ionic pair has

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been studied by using the B3PW91 method of density functional theory (DFT) with three kinds of basis. The microscopic 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 initial structures of all the concerned molecules of butene isomerization were first established by molecular mechanical method. Then the geometries of reactants, transition state and products were fully optimized at the B3PW91/6-31G(d,p), 6-311++G(d,p), and aug-cc-PVDZ levels. B3PW91 method was chosen because lower energy barrier can be got than that of B3LYP, which was also suggested by Luthi's work [18]. Through computing the eigenvalues of force constant matrices of the geometries the vibrational analysis was performed and the zero-point energies (ZPEs) were obtained. According to the numbers of imaginary frequency the geometries of equilibrium state or transition state were verified. The intrinsic reaction coordinates (IRCs) were calculated from the starting point of transition state to

the reactant and the product, respectively. All the quantum chemical calculations were finished by GAUSSIAN 03 [19] software package.

3. Results and discussions

According to the experimental studies, the isomerization of 1-butene (marked as B1) to 2-butene (marked as B2) could be taken place only if the catalyst existed in the reaction system. Here the ionic pair of EmimF was regarded as catalyst of butene isomerization. The physical image of the double bond shift of butene catalyzed by EmimF included three steps. First, 1-butene was adsorbed on the 4-H atom of the imidazole ring of EmimF, and a supermolecule (marked as B1-EmimF) formed. Then, B1-EmimF transformed to another supermolecule (marked as B2-EmimF) through a transition state (marked as TS), and B2-EmimF could be also regarded as the product formed by 2-butene adsorbed on the 4-H atom of the imidazole ring of EmimF. Finally, the supermolecule B2-EmimF was desorbed and the single molecule of 2-butene and EmimF was formed. This meant that the catalyst EmimF was restored and B2

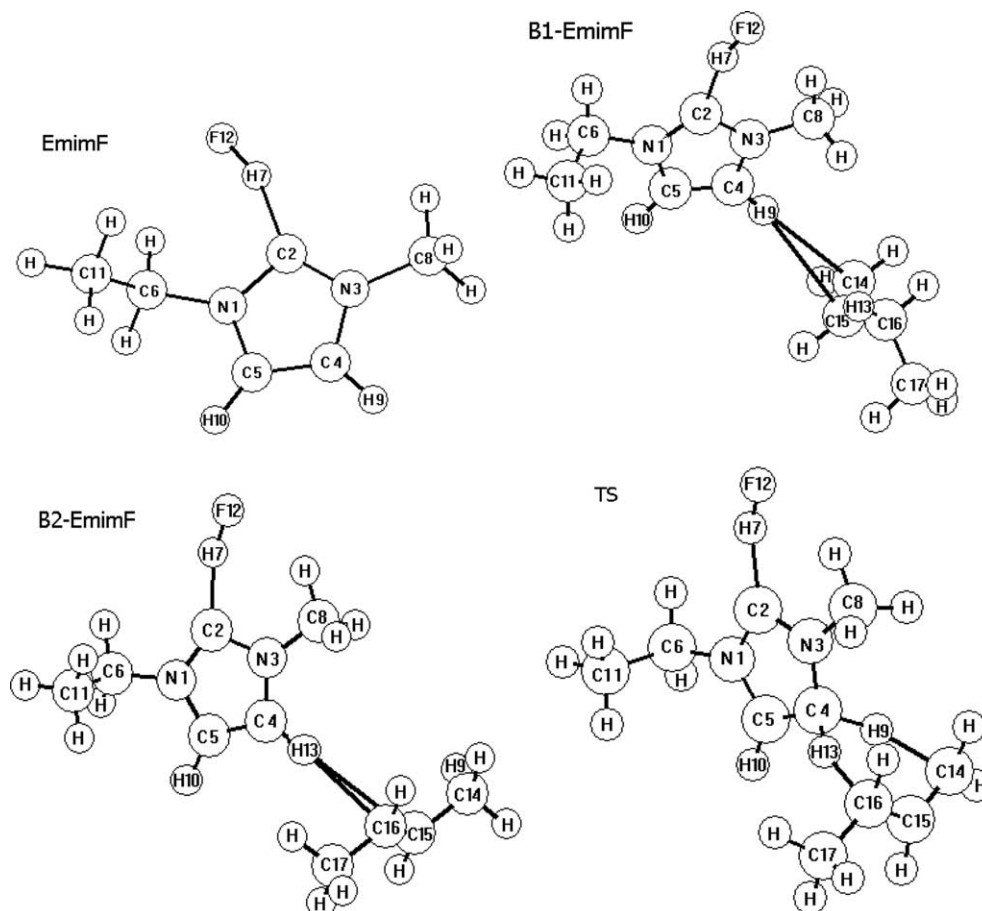


Fig. 1. Molecular structure models of EmimF, B1-EmimF, B2-EmimF and TS.

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