Theoretical investigation of the thermal decomposition of imidazolium ionic liquids with different halides ions

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A B S T R A C T

The ionic liquids (ILs) are green solvents with numerous applications in technology and science. Among the physical properties of the ILs which have a great effect on their application, thermal stability is an important issue which has been discussed in this paper. Kinetics aspect of thermal decomposition of the ILs is considered as a scale of thermal stability. The ILs which have been studied here are composed of 1-hexyl-3-methylimidazolium cation with halide anion [Hmim][X], (X = F, Cl, Br). Three probable paths for thermal decomposition of ILs have been proposed. The first and second paths are the SN2 mechanism in which there are two possible sites on the imidazolium ring position, methyl and hexyl chain. Third path is E2 mechanism which is initiated from hexyl chain. In the case of [Hmim][X] (X = Cl, Br), since the first path has a lower activation energy, it occurs faster than the second path, while in the case of [Hmim][F], path B has a lower barrier than path A and occurs faster. Energy analysis for three studied ILs, showed that [Hmim][Br] with $E_a = 137.5$ kJ mol^{-1} is decomposed faster than other ILs.

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1. Introduction

In the recent years, Ionic liquids (ILs) due to their especial properties are used in industry as an alternative to organic solvents [1–3]. These properties include the low melting point, no flammability and thermal stability [4,5]. The structure of the ILs is composed of the organic cations and organic/inorganic anions [6]. Because of the variety of the cations and anions, ILs have enormous diversity [7,8]. Because of this diversity, a great deal of researches have been done on their properties tuning [9, 10].

Papaiconomou and coworker's synthesized seven imidazolium and pyridinium ILs for determination of their properties in the separation of the heavy metals in the waste water [11]. Another important application of the ILs is CO_2 adsorption [12–18], which has been reported by Zhang and coworkers using a new class of amine ILs [19]. In their research, 1,3-di[2-aminoethyl]-2-methylimidazolium bromide was investigated. Under the effect of pressure, temperature and CO_2 concentration and based on the experimental and theoretical data, they proposed that this ILs is a good alternative for industrial application.

Another research was done by Wang on 1-ethyl-3-methylimidazolium Lysine, [Emim][Lys], which stabilizes polymethylmethacrylate (PMMA) absorbent [20]. The creation of the IL-PMMA system increases the capacity of the CO_2 adsorption. The obtained activation energy of two suggested steps are 4.1 and 4.3 kJ

mol^{-1}, which indicates that CO_2 adsorption occurs quickly. Considering a high capacity of CO_2 adsorption and suitable thermal stability predicted that this system is a better choice for CO_2 adsorption.

According to the mentioned researches, thermal stability of the ILs is an important factor in the selection of ILs for industrial applications; therefore the research on the thermal stability of the ILs is of a great importance [21].

Rui and coworkers have done a kinetic study on the thermal decomposition of 1-butyl-3-methylimidazolium dicyanamide IL [22]. They used isothermal and non-isothermal gravimetric methods (TGA) to analyze the thermal stability of this IL. A good thermal stability within an activation energy value of 150 ± 3 kJ mol^{-1} has been obtained [23].

Some groups of the ILs based on carboxylate anion have been considered by the Clough group [24] including 1-ethyl-3-methylimidazolium acetate, [Emim][OAC], experimentally and theoretically. According to the obtained data, thermal decomposition has been done through a nucleophilic substitution (SN2) mechanism. Activation energy, which has been determined by using the TGA technique, showed a low thermal stability of this IL [25].

Chamberu research group investigated thermal stability of [Emim][Br] (1-ethyl-3-methylimidazolium Bromide) by density function theory (DFT) method [26]. According to the obtained data, they proposed that thermal decomposition occurs though a SN2 mechanism.

Hao and coworkers investigated thermal decomposition of alilimidazolium ILs [27]. For thermal decomposition of this IL, they proposed and analyzed two paths using the DFT method. In the first path, chloride anion attacks to methyl chain with an activation energy in the range of 123–124 kJ mol^{-1}. On the second path, the anion attack

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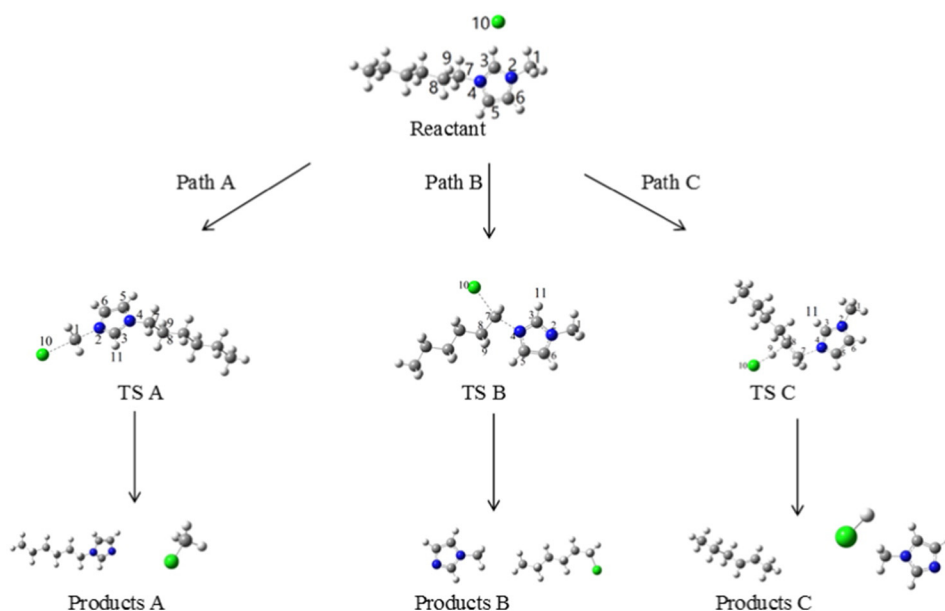
Scheme 1. Proposed mechanisms for thermal decomposition of [Hmim][X](X = F, Cl, Br) ILs.

to allyl chain with an activation energy in the range of 120–122 kJ mol^{-1}. According to the obtained results, allyl chain attack is more favorable than methyl chain. The thermal stability of this ILs has been studied using the TGA technique. Based on the TGA data good thermal stability for cellulose dissolving has been confirmed.

With the aim of thermal stability analysis of the IL nanostructures through the reaction mechanism elucidation [28], in this work, a group of the ILs with a fixed cation and variable anions have been theoretically studied. By using different computational procedures such as natural charge and vibrational frequency analysis within the topological properties, different paths have been considered for thermal decomposition process and discussed. The ILs in this research are as follows:

1-Hexyl-3-methylimidazolium Fluoride [HMIM][F],1-hexyl-3-methylimidazolium Chloride [HMIM][Cl], 1-hexyl-3-methylimidazolium Bromide [HMIM][Br].

2. Computational details

DFT calculations were used for optimization of the structures of the studied ILs. In order to have an estimation of the zero point vibrational energy and thermodynamic parameters, frequency calculations have been done for all of the stationary points. Transition state (TS) structures were characterized by using the transit guided quasi-Newton (SQTN) method [29].

All calculations were performed using the M06-2X functional within 6-311++G(d, p) basis set as implement in Gaussian 09 [30]. Natural bond orbital (NBO) analysis [31] was taken into account for ILs to obtain

the electron distribution on the atoms and the donor–acceptor interactions of the reactants and TS structures. Also, by this procedure charge transfer has been studied for thermal decomposition of the ILs. For determination of the topological properties at the bond critical point (BCP) quantum theory of atoms in molecules (QTAIM) analysis has been applied [32,33] using the AIM 2000 [34].

3. Results and discussion

Three different paths have been proposed for thermal decomposition of the halide ILs. Paths A and B are the nucleophile substitutions, while path C proceeds through an elimination mechanism. A halide ion attacks to the methyl and hexyl groups of the studied ILs on paths A and B, respectively. Therefore, their corresponding products will be different too, as shown in Scheme 1. According to this scheme, the products of the path C are hexane, hydrogen halide and 1-methylimidazolium.

3.1. Structural analysis

The optimized structures of the reactants, products and TSs have been shown in Fig. S1. After optimization of the structures in the gas phase, main geometrical parameters were evaluated and reported in Table 1.

According to Table 1, in path A, X—C (X = F, Cl, Br) bond length has been decreased while C—N has been increased at the TS. Calculated average $\Delta r^{\dagger}$, which means the activated bond length (bond length changes

Table 1
Bond lengths comparison between the reactants and TSs in the gas phase at the M062X/6-311++G(d,p) level.

		[Hmim][F]			[Hmim][Cl]			[Hmim][Br]	
	Bond	Reactant	TS	Bond	Reactant	TS	Bond	Reactant	TS
Path A	N2—F10	3.47	4.35	Cl10—N2	3.19	4.35	Br10—N2	3.31	4.35
	N2—C1	1.45	1.84	Cl10—C1	3.43	2.51	Br10—C1	3.61	2.51
	C1—F10	3.74	2.51	N2—C1	1.45	1.84	N2—C1	1.45	1.84
Path B	F10—H9	5.54	1.28	Cl10—N4	4.15	4.32	N4—C2	1.46	1.97
	N4—C7	1.46	1.80	Cl10—C7	4.52	2.43	C7—Br10	3.62	2.60
	F10—C7	4.14	2.03	C7—N4	1.46	1.94	Br19—N4	3.31	4.48
Path C	F10—H9	5.54	1.28	C4—N7	1.46	1.95	–	–	–
	C7—C8	1.52	1.49	Cl10—H9	4.49	1.60	–	–	–
	C7—N4	1.45	1.52	C8—H9	1.09	1.37	–	–	–