

New insight into the formation mechanism of imidazolium-based halide salts

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Abstract By performing density functional theory calculations, the Menshutkin reaction between the N-methyl imidazole with chloroethane is reexamined to rationalize the experimental discovery. The calculated results show that the reaction proceeds via a S_N2 mechanism with a barrier of $119.1 \text{ kJ mol}^{-1}$ which is much lower than that reported in previous literature according to a five-membered transition state mechanism. Moreover, it is found that the barrier is further reduced to 98.1 kJ mol^{-1} in toluene solution. The present result validates the experimental finding that the Menshutkin reaction for synthesizing N-alkyl imidazolium halide salts proceed smoothly at lower heating temperature.

Keywords Density functional theory · H-bond · Ionic liquid

Introduction

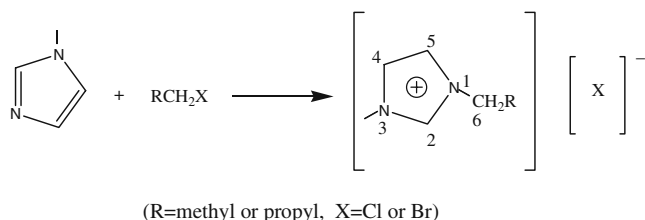
Ionic liquids (ILs), a class of novel compounds, are composed generally of organic cations and inorganic anions, which exhibit many excellent physicochemical properties [1, 2], such as low melting point, favorable solution capacity, high ionic conductivity, and particularly nonvolatile nature. ILs have been widely used as environmentally benign media in many fields of chemistry, including organic synthesis [3, 4], separation [5, 6], and biochemistry [7, 8]. Moreover, these natures can be

adjusted through varying the component cation, anion, and alkyl substituent on the cation to tailor a task specific ILs. Therefore ILs have been referred to as “designer solvents” [9] and elicited more and more interest in both academia and industry. To better understand the structures and properties of ILs, we have recently launched a theoretical project which aims at studying the mechanism of some important organic synthesis reactions catalyzed by imidazolium-based ILs by performing quantum chemical calculations, and the related results can be found elsewhere [10–18].

N-alkyl imidazolium halide salts are a kind of the most widely used ILs in experiments. So far, many published works have focused on their macroscopic properties [19–22], microscopic structures [23, 24], and catalytic mechanism [10, 11]. However, the research for their synthesis mechanism, as far as we know, is very limited, and many mechanistic aspects have not been elucidated yet. In experiments, imidazolium-based ILs are generally prepared via the Menshutkin reaction between N-alkyl imidazoles and alkyl halides (Scheme 1). This kind of reaction is environmentally friendly and easy to operate. To reveal microcosmic mechanism of the Menshutkin reaction at the atomic and subatomic scale, Li et al. [25] reported the theoretical study of the reaction of N-methyl imidazole with haloethane. They proposed two reaction pathways involving five-center transition states, as schematically shown in Scheme 2, where C2-H...Cl or C5-H...Cl H-bond is formed in transition states (I and II) along with the formation of C6-N bond and the cleavage of C6-Cl bond. However, their calculated energy barriers are as high as $\sim 200 \text{ kJ mol}^{-1}$. This seems to be inconsistent with the experimental observations that the reaction occurs very easily, and the N-alkylimidazolium halide salts can be obtained at lower heating temperature.

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Scheme 1 Sketch map indicating the synthesis of imidazolium-based halide ionic liquids

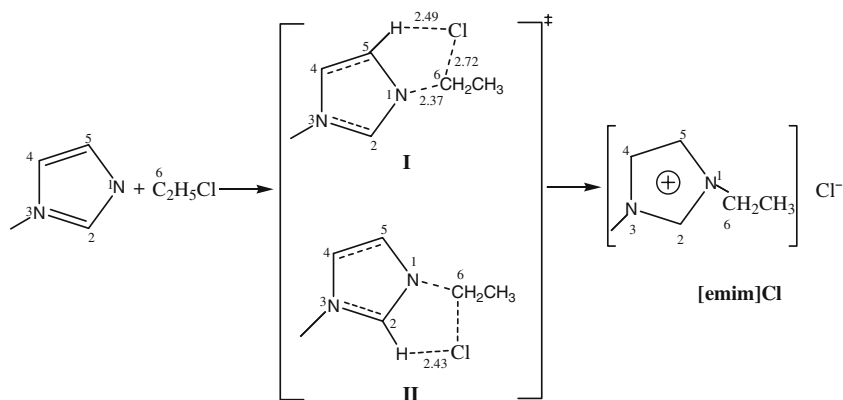
Therefore, in the present work we theoretically reexamine this kind of Menshutkin reactions to find out if there is any other energetically more favorable pathway.

As an example of this kind of reaction, herein, we studied the synthesis reaction of 1-ethyl-3-methyl imidazolium chloride ([emim]Cl) between methylimidazolium and chloroethane. For simplification, these two reactants are denoted as R1 and R2, respectively. The calculated results show a new pathway with a barrier of 119.1 kJ mol⁻¹, which is remarkably a much lower barrier than that by Li et al. [25]. The barrier is further reduced to 98.1 kJ mol⁻¹ when the solvent effect is taken into account. Our finding provides new insight into the mechanism details of the Menshutkin reaction.

Computational details

The geometrical optimization calculations reported in the present study were carried out at the B3LYP/6-31++G(d,p) level [26–28], as implemented in the Gaussian03 program package [29]. Frequency calculations at the same level of theory have also been carried out to verify all stationary points as minima (zero imaginary frequencies) or first-order saddle points (one imaginary frequency). The reaction pathways have been traced by performing intrinsic reaction coordinate (IRC) [30] calculations. The electronic properties for the relevant stationary points were illustrated based on the natural bond orbital (NBO) analysis [31, 32].

Scheme 2 Schematic shows for the transition states proposed in ref. [25]



The solvent effect was estimated by re-optimizing geometries in gas-phase using a self-consistent reaction field (SCRF) method [33–35] based on the polarizable continuum model (PCM) [36–38].

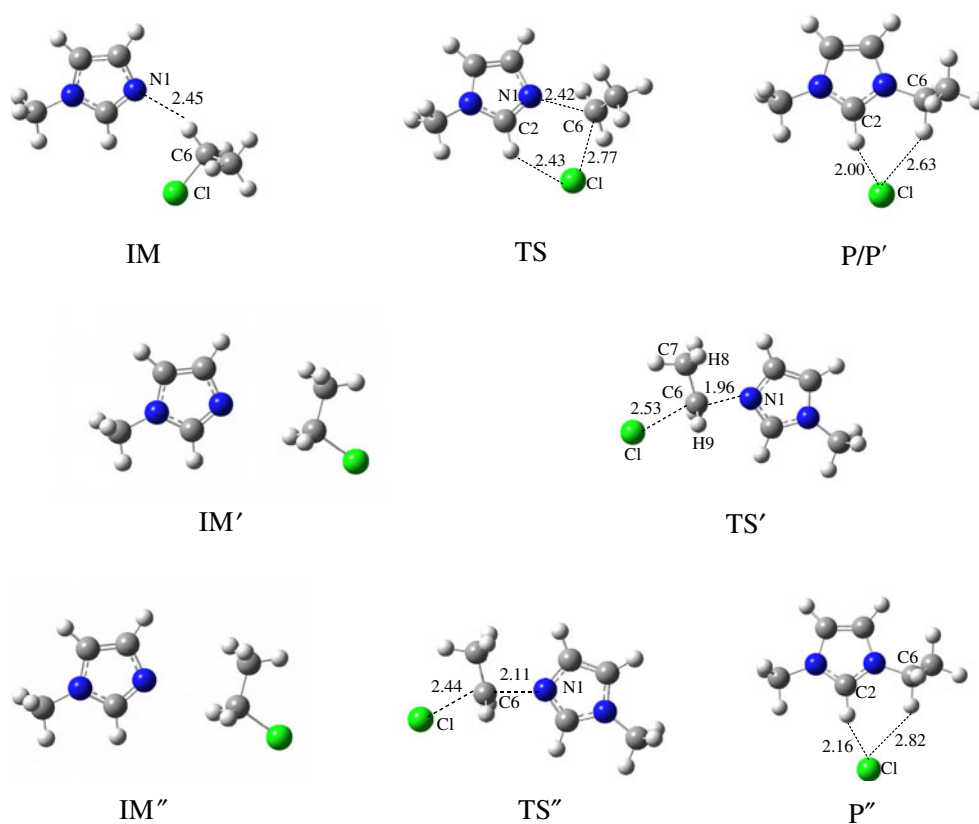
Results and discussion

In order to obtain comparable data, we first calculated the energy profile along the reaction pathway proposed by Li et al. [25]. The optimized structures for the intermediate (IM), transition state (TS), and product (P) involved in the reaction were shown in Fig. 1, the calculated potential energy surface along the reaction coordinate was given in Fig. 2 (see the black line profile).

We see that in TS the C6-N1 bond (2.42 Å) is forming and the C6-Cl bond (2.77 Å) is breaking, which can be confirmed by the transition vector corresponding to the imaginary frequency (427 i cm⁻¹). The C2-H...Cl H-bond distance is to be 2.43 Å. These structural parameters are geometrically very similar to those given by Li et al. [25], as shown in Scheme 1. The IRC calculations show TS connects IM and P. H-bonds are formed in these two structures: the C6-H...N H-bond with a distance of 2.45 Å in IM, and the furcated or two-centered H-bond with a distance of 2.00 Å for C2-H...Cl branch and a distance of 2.63 Å for C6-H...Cl branch in P. From the relative energies shown in Fig. 2, the TS is located to be 217.6 kJ mol⁻¹ higher than IM, and the overall reaction forming [emim]Cl is calculated to be exothermic by 3.6 kJ mol⁻¹. These results are in agreement with the early findings by Li et al. [25].

It is noted that the TS is a five-center transition state, where the N1 atom in the N-methyl imidazole acts as a nucleophilic center to attack the positive C6 atom at the side of Cl atom in R2. Such an attack way leads to large steric hindrance and so it is not surprising that the calculated barrier to reach the transition state is very high. Alternatively, to search for another more energetically

Fig. 1 Optimized structures of reactants, intermediates, and transition states along the two pathways. The distances are in angstroms



favorable pathway, we tried to optimize a new transition state, where the N1 atom in R1 attacks the C6 atom center at the back of the C-Cl bond in R2. After optimization, we did locate such a transition state structure, which is denoted as TS' in Fig. 1. Clearly, this is a typical S_N2 type transition state structure. IRC calculations from TS' give the reverse (IM') and forward minima (P', which has exactly the same geometry with P), as shown in Fig. 1. The calculated

relative energies were displayed in the red line profile in Fig. 2.

We find that in TS1' the C6-Cl bond (2.53 Å) is breaking and at the same time the N1-C6 bond (1.96 Å) is forming, which is confirmed by the transition vector corresponding to the imaginary frequency (427i cm^{-1}) which is mostly associated with the formation of N1-C6 bond and the cleavage of C6-Cl bond, and also by the calculated bond orders (0.15 for C6-Cl bond and 0.40 for N1-C6 bond). The Walden inversion of two hydrogen atoms on C6 atom was observed by determining the related dihedral angles. For example, $D_{H8-C7-C6-H9}$ angle changes from -58.64° in IM' to 38.29° in TS'.

As is shown by the red line profile in Fig. 2, the calculated barrier from IM' to TS' is 119.1 kJ mol^{-1} , which is lower by 98.5 kJ mol^{-1} than that from IM to TS. This fact indicates that the S_N2 pathway is energetically more favorable, and the calculated lower barrier is in accord with the easy preparation of N-alkyl imidazolium halide salts in experiments [25].

To estimate the influence of solvent on the reactivity, we further made calculations using the PCM approach, which is a computationally economic way. Toluene, an usual non-aqueous solvent used for the synthesis reaction [25, 39], is chosen as the model solvent with the dielectric constant being 2.38.

The structures of the intermediate, transition state, and product along the S_N2 pathway in toluene are very similar

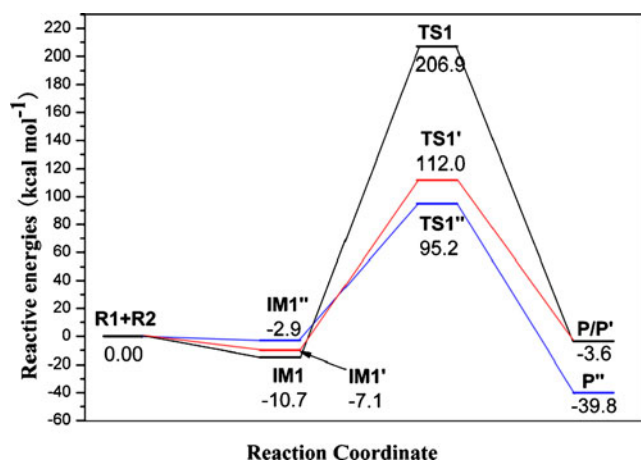


Fig. 2 Calculated electronic energy profiles for the synthesis of [emim]Cl. The red and blue lines are for the S_N2 pathway in gas phase and in toluene, and the black line is for the pathway proposed in ref. [25] in gas phase

to those in vacuum, which are denoted as IM'', TS'' and P'' in Fig. 1. We do not make comment on their geometrical characteristic again for simplification. Instead, our main concern is the relative energy differences between the PCM and gas phase calculations. The calculated relative energy for the reaction in toluene is shown in Fig. 2 again (see the blue line profile). The calculated barrier to reach TS'' is 98.1 kJ mol⁻¹, which is 21.0 kJ mol⁻¹ lower than that in vacuum. Furthermore, the overall reaction is calculated to be exothermic by 39.8 kJ mol⁻¹. These results are unsurprising because immersing the system in a polar dielectric medium favors to stabilizing the polar transition state. In other words, the solvent has important effects on the kinetic and thermodynamic properties of the Menshutkin reaction.

Conclusions

In summary, we have carried out a DFT study to reexamine the mechanism of the Menshutkin reaction between the N-methyl imidazole with chloroethane, an important reaction type synthesizing N-alkylimidazolium halide salts. The calculated results show a new S_N2 pathway with a barrier of 119.1 kJ mol⁻¹ in gas phase and a barrier of 98.1 kJ mol⁻¹ in toluene solution in solvent phase. This pathway is energetically much more favorable than that proposed in literature whose barrier was reported at ~200 kJ mol⁻¹ in gas phase calculations. The present results rationalize the early experimental findings and help us to better understand the synthesis mechanism of N-alkyl imidazolium halide salts.

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