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Hydrogen transfer effect and reaction mechanism for catalytic hydrolysis of HCN in ionic liquids: A density functional theory study

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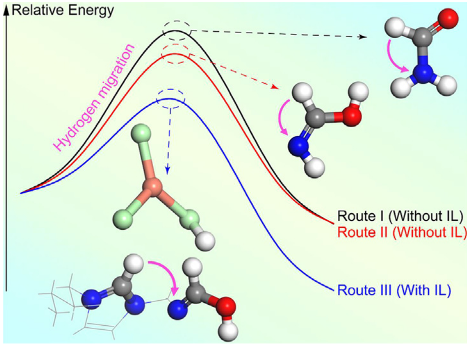
HIGHLIGHTS

- The formation of complex ($HCN\text{-}H_2O$) was caused by van der Waals forces.
- The controlling step for HCN hydrolysis was the migration of H from C–H to N–H bond.
- C-NH structure was conducive to the migration of H atom from C–H bond to N–H bond.
- IL changed the interaction among reactant molecules from van der Waals forces to chemical bond effect.
- IL changed the H atom migration and exchange actions among IL, HCN and H_2O molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

This report investigated the hydrogen transfer effect and reaction mechanism for HCN hydrolysis by IL ($[Bmim]^+[CuCl_3]^-$). Meanwhile, the influence of preferential break of O–H and C–H bonds in hydrolysis of HCN was investigated. The detailed reaction mechanisms were investigated by theoretical calculations. The results indicated that the formation of complex ($HCN\text{-}H_2O$) was an exothermic process and the process was caused by van der Waals forces. The controlling step for HCN hydrolysis was attributed to the migration of H from C–H to N–H bond. The migration of H atom from C–H bond to N–H bond under C-NH structure was easier than that under $C\text{-}NH_2$ structure. H_2O was firstly adsorbed with IL and then reacted with HCN. The addition of IL enhanced the adsorption effect among reactant molecules by changing the interaction from van der Waals forces to chemical bond effect. IL also decreased the maximum reaction energy barrier by changing H atom migration and exchange actions among IL, HCN and H_2O molecules. In general, ionic liquid is a kind promising catalyst for HCN hydrolysis in industrial application.

1. Introduction

Hydrogen cyanide (HCN), a kind poisonous liquid, boils at 26 °C [1]. It is commonly derived from the industrial tail gas emissions, such as closed carbide furnace tail gas [2–4]. As the main precursor of N_2O, it can lead to the destruction of ozone layer [5]. Meanwhile, it also can lead to the poison of catalyst and decrease the purity of raw material gas, such as CO in the tail gas [6–9]. Many methods have been used to remove HCN, such as adsorption [10–12], catalytic oxidation [13–15] and catalytic hydrolysis [16–18]. The catalytic hydrolysis method generates the fewer by-products under mild reaction conditions and the hydrolysis products (NH_3 and CO) can be used in other chemical

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industry as raw material gas [18]. Therefore, it has been used to remove HCN from industrial process.

In most previous studies, the hydrolysis removal of HCN is based on metal oxides [17] and modified carbon-based catalyst [18]. However, low life-time and low anti-poisoning ability are the main disadvantages for above catalysts. It leads to high operation cost and disposal problem of spent catalysts. As a kind of environmentally friendly material, Ionic liquids (IL) has been used for many catalytic reactions due to its high anti-poisoning ability and long life-time [19–25]. In the hydrolysis of HCN, –H and –OH groups play the important roles for hydrogen migration. Therefore, a suitable IL needs abundant hydrogen containing functional groups, such as –H and –OH groups. 1-butyl-3-methylimidazolium ($[Bmim]^+$) is the commonly used cationic provider and it can provide abundant hydrogen containing functional groups [26–28]. It is suitable for hydrolysis of HCN. In our previous study, Cu^{2+} is conducive to the hydrolysis of HCN [16]. Therefore, Cu^{2+} containing anion provider is suitable for hydrolysis of HCN, such as $[CuCl_3]^-$ [29–32]. As mentioned above, hydrogen migration effect is the key step for HCN hydrolysis. The detailed reaction mechanisms of hydrogen migration are different for different reaction environmental conditions. Jensen et al. investigated the reaction process of HCN hydrolysis by theoretical method [33]. The study showed that the mainly adsorption forms of reactants was $H_2O\cdots HCN$ by O···H adsorption interaction. Xia et al. investigated the reaction process of HCN hydrolysis in gas-phase environment by theoretical method [34]. The study showed that the H atoms in NH_3 can be derived from C atom or O atom. Although previous studies presented possible reaction pathways, the influence of preferential break of O—H and C—H bonds for hydrogen migration was not clear. Meanwhile, there were few studies focused on the gas-liquid phase reaction process for HCN hydrolysis. Furthermore, the effect of IL ($[Bmim]^+[CuCl_3]^-$) is an important factor for the hydrolysis of HCN. Therefore, it is valuable to investigate the detailed HCN hydrolysis reaction mechanisms and hydrogen migration effect by $[Bmim]^+[CuCl_3]^-$, and find out the hydrogen migration route in the liquid environment.

To this end, this report investigated the hydrogen transfer effect and reaction mechanism for HCN hydrolysis by IL ($[Bmim]^+[CuCl_3]^-$). Meanwhile, the influence of preferential break of O—H and C—H bonds in hydrolysis of HCN was investigated. The detailed reaction mechanisms were investigated by theoretical calculations. It could provide a theoretical foundation for the future industrial application. Meanwhile, it could provide a new research approach for hydrogen migration in the gas-liquid phase hydrolysis reaction.

2. Computational methods

All calculations in this work were performed using Dmol^3 program in the Material Studio 2017 software package and BlackHole2 computer system [35,36]. The hardware of BlackHole2 computer system includes 72 cores (Intel E5-2600V3 series), 64GB DDR4 RAM (Random Access Memory) and 2TB hard disk. Previous studies showed that GGA/PBE method was suitable for HCN and ionic liquid [37–40]. Therefore, in this work, the molecular geometries of the reactants, transition states (TS), intermediate complexes (IM), and products were calculated and optimized using the GGA/PBE method from density functional theory (DFT) [41]. A density functional semi-core pseudopotential method was used for the core electrons of Cu, and the all-electron method was used for the core electrons of H, C, N, O and Cl. A double-numeric quality basis set with polarization functions (i.e., DNP, version 3.5) was used. Unrestricted spin was chosen. The solvation effect was considered using solvation model COSMO with water to simulate the real situation. The tolerances of the SCF, energy, gradient and displacement convergence were 1.0×10^{-6} hartree (Ha), 1.0×10^{-5} Ha, 2.0×10^{-3} Ha/Å and 5.0×10^{-3} Å, respectively. Electronic and zero-point vibration energies (ZPVE) were calculated at the same level of theory. Linear synchronous transit/quadratic synchronous transit/conjugate gradient (LST/QST/CG) calculations were used to ensure that all of the transition states connected to the intended reactants and products. Transition states were identified by the presence of a single imaginary frequency, which corresponded to the reaction mode. To evaluate the reliability of calculation method and parameters, the geometries of monomers HCN and H_2O were calculated. The calculation results were showed in Fig. 1. According to these references [42–49], it can be found that the bond lengths of C—H bond and C≡N bond in HCN were at 1.065 ± 0.004 Å and 1.153 ± 0.003 Å, and the bond length of O–H bond in H_2O was at 0.961 ± 0.005 Å. Meanwhile, the bond angles of H—C—N in HCN and H—O—H in H_2O were at 180.0 ± 0.05° and 104.5 ± 0.08°. As shown in Fig. 1, the discrepancies of bond lengths and bond angles between the experimental and theoretical values are less than 0.003 Å and 0.1°, respectively [42–49]. The calculated results agreed with the available experimental results, which indicated that the selected calculation method and parameters were reliable and it met the requirements of our following calculation. The time of calculation for route I (without IL), II (without IL) and III (with IL) were 12 days, 14 days and 23 days respectively.

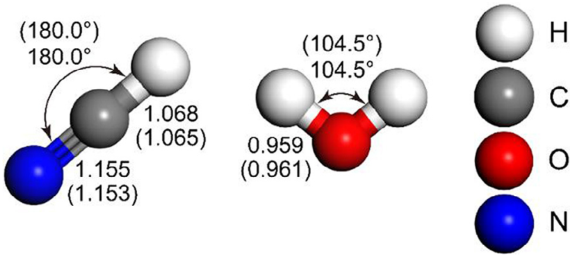

Fig. 1. Optimized geometries of HCN and H_2O (bond length in Å and angles in °, the experimental values are in brackets).

3. Results and discussion

3.1. Reaction mechanism of HCN hydrolysis without ionic liquids

Fig. 2 showed the reaction routes and mechanisms of HCN hydrolysis without ionic liquids. The imaginary frequencies of the transition states for HCN hydrolysis without ionic liquids were presented in Table S1. The relative energy of complex ($HCN\text{-}H_2O$) was −4.72 kcal/mol, and it indicated that the formation of complex ($HCN\text{-}H_2O$) was an exothermic process. Meanwhile, the process was caused by van der Waals forces. In the hydrolysis process of HCN, H atom could migrate from C—H bond and O—H bond to N—H bond. As the different migration pathways of H atom, the reaction routes could be divided into

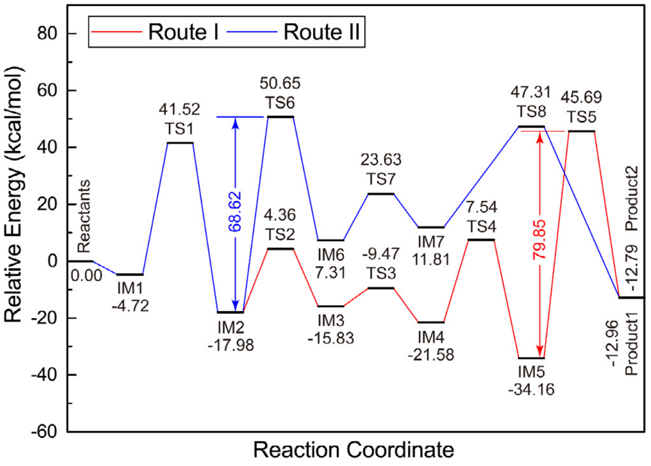

Fig. 2. Reaction routes and potential energy surface for HCN hydrolysis without ionic liquids.

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