Revealing the catalytic mechanism of an ionic liquid with an isotope exchange method

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Abstract: The alkylation mechanism catalyzed by an ionic liquid (as a Lewis acid) may be different from the traditional alkylation mechanism catalyzed by Brønsted acid, especially as their initiation steps are still not clear. In this paper, an isotope exchange method is used to investigate the catalytic mechanism of AlCl_3 /butyl-methyl-imidazolium chloride ionic liquid in the alkylation of benzene with 1-dodecene. The proposed catalytic mechanism was confirmed by analysis of ionic liquid before and after reaction and of the alkylation products of deuterated benzene (C_6D_6) with 1-dodecene. The proposed mechanism consists of the equilibrium reaction between $[\text{Al}_2\text{Cl}_7]^- + \text{H}^+$ and $[\text{AlHCl}_3]^+ + [\text{AlCl}_4]^-$, in which the Brønsted acid $[\text{AlHCl}_3]^+$ is supplied by the reaction of 2-H on the imidazolium ring and $[\text{Al}_2\text{Cl}_7]^-$. The alkylation reaction is initiated by the Brønsted acid $[\text{AlHCl}_3]^+$ which reacts with 1-dodecene to form a carbonium ion, then the carbonium ion reacts with benzene to form an unstable σ complex, leading to the formation of 2-phenyldodecane.

Key words: Catalytic mechanism, ionic liquid, isotope exchange method, alkylation, deuterated benzene

1 Introduction

The use of ionic liquids (IL) as an alternative to conventional hazardous solvents has received very considerable attention for its applications in electrochemistry (Hussey, 1988; Wilkes et al, 1982), liquid/liquid separations (Swatloski et al, 2002b; Blanchard et al, 1999), extractions (Huddleston et al, 1998), catalysis (Swatloski et al, 2002a; Cole et al, 2002; Zhao et al, 2002), biocatalysis (Cull et al, 2000; Sheldon et al, 2002), and polymerization (Hardacre et al, 2002b; Carmichael et al, 2000). Ionic liquids are benign and stable solvents for a wide range of organic and inorganic materials (Nara et al, 2001; Green et al, 2000). The advantages of ionic liquids include negligible vapor pressure, potential for recycling, compatibility with various organic compounds and organometallic catalysts, and ease in separation of reaction products (Welton, 1999). Ionic liquids with strong acidity can be used as acid catalysts for alkylation processes. In addition, the physical and chemical properties of an ionic liquid can be adjusted by varying its organic cation and inorganic anion. The organic cation controls the solubility, density and viscosity of the ionic liquids. The properties of the liquid ion vary significantly with various alkyl groups used as cations. The acidity of the ionic liquid depends on the metal halide used and the ratio of metal halide to organic base (Welton, 1999; Seddon, 1997). Hence, to gain insights into ionic-liquid-catalyzed alkylation

reaction processes, it is necessary to understand the catalytic mechanism of ionic liquids.

Alkylation of benzene with linear C_{10} - C_{14} olefins is an established industrial process. The linear alkylbenzene (LAB) products are used as intermediates in the production of surfactants and detergents. At present, the acid catalysts used in the commercial alkylation process are hydrofluoric (HF) acid and sulfuric acid (H_2SO_4), which are corrosive and hazardous substances. Attempts have been made to use AlCl_3 IL as catalyst for alkylation reactions. It has been shown that AlCl_3 IL can lower the alkylation reaction temperature, has a high selectivity to 2-alkylbenzene, and can be separated easily from the alkylate products (Qiao et al, 2004; Decastro et al, 2000; Qiao and Deng, 2001; Xin et al, 2005). Albermale (formerly Akzo-Nobel) developed IL alkylation catalysts with triethylamine hydrochloride and aluminium chloride, which can be economic alternatives to imidazolium-based salts (Hope et al, 2004). These IL's were designed specifically for catalyzed alkylation of benzene with 1-dodecene (Sherif et al, 1998), and had a higher 2-dodecylbenzene yield than the conventional HF catalyst. A large number of investigations have been conducted studying the mechanism of AlCl_3 IL catalyzed alkylation (Trulove et al, 1994; Sun and Zhao, 2008; Compell and Johnson, 1995; Schmerling, 1953; Whitmore, 1932; Ma and Johnson, 1995). Smith et al (1989) reported that arene was protonated by butyl-methyl-imidazolium chloride ($[\text{bmim}]\text{Cl}$)- AlCl_3/HCl , indicating that the alkylation was catalyzed by strong Brønsted acid, as shown in the following reaction:

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Received March 14, 2011

As there was trace water in the reaction system, so HCl was produced by hydrolysis of ionic liquid. According to this interpretation, if there was no water in the system, the ionic liquid cannot catalyze the alkylation.

It is known that the strong Lewis acid $[\text{Al}_2\text{Cl}_6\text{Br}]^-$ can react with hydrogen atoms at the 2-position of an imidazolium ion to form a Brønsted acid (Arduengo et al, 1991; Gifford and Palmisano, 1987). Yoo et al (2004) examined the alkylation of isobutane with 2-butene using methyl-imidazolium bromide $([\text{mim}]\text{Br})-\text{AlCl}_3$, and postulated that the alkylation reaction was catalyzed by the Brønsted acid $[\text{AlHCl}_3]^+$ which was formed from the association of $[\text{Al}_2\text{Cl}_7]^-$ with H^+ , which is dissociated from 2-H of an imidazolium ring. However, there is no conclusive evidence for it, only an inference. Although the IL catalyzed alkylation reactions have been extensively investigated, the reaction mechanism of the initiation step is still not clear.

In this paper, an isotope substitution method was used to investigate the reaction initiation of IL catalyzed alkylation of deuterated benzene (C_6D_6) with 1-dodecene using $[\text{bmim}]\text{Cl}-\text{AlCl}_3$ catalyst. The reaction mechanism was determined by tracking the path of the deuterium atom during the reaction process.

2 Experimental

2.1 Materials

Deuterated benzene (C_6D_6 , 99.6% purity) was obtained from Sigma-Aldrich Corporation (USA), 1-dodecene (99.9% purity) and anhydrous AlCl_3 were from Beijing Chemical Reagent Company, China.

2.2 Preparation of ionic liquid

Butyl-methyl-imidazolium chloride ($[\text{bmim}]\text{Cl}$) was prepared the reaction of dried and redistilled N-methylimidazolium with a slight molar excess of 1-chlorobutane in a stainless-steel autoclave (Munson et al, 2002). The autoclave was sealed and pressurized with nitrogen to 0.51 MPa. It was then heated to 90 °C for 18 h. After the reaction, the autoclave was cooled to room temperature. The material in the autoclave was transferred to a rotary evaporator, in which the unreacted chloro-butane and 1-methylimidazole were removed by nitrogen stripping at 95 °C for 18 hours. The reaction product was washed with acetonitrile. The washed product composed of $[\text{bmim}]\text{Cl}$ was vacuum-dried at 105 °C to remove the residual solvent and water.

The $[\text{bmim}]\text{Cl}/[\text{AlCl}_3]$ ionic liquid was prepared by adding anhydrous AlCl_3 to $[\text{bmim}]\text{Cl}$ in a 2:1 molar ratio. The reaction mixture was continuously stirred for 12 h at room temperature. The entire process was carried out in a glove box under a nitrogen atmosphere to avoid hydrolysis of AlCl_3 . The resulting $[\text{bmim}]\text{Cl}/[\text{AlCl}_3]$ ionic liquid was stored in a dry inert atmosphere. Before use, the $[\text{bmim}]\text{Cl}/[\text{AlCl}_3]$ ionic liquid was dried with 3A molecular sieves to keep the moisture content below 10 $\mu\text{g/g}$.

2.3 Alkylation of benzene with 1-dodecene

A 200 mL autoclave reactor was equipped with two glass

windows, a gas inlet valve, a sample exit line, a magnetic stirrer, and a piston for controlling the reactor pressure. The autoclave was put in a temperature-programmed oven. Prior to the experiment, the autoclave was purged with nitrogen and then evacuated. The $[\text{bmim}]\text{Cl}/[\text{AlCl}_3]$ ionic liquid (25 mL) was put into the reactor and then heated to 30 °C. Then, 150 mL of dodecene- C_6D_6 mixture (molar ratio 1:10) was charged into the reactor using a plunger pump at 500 mL/h. The alkylation reaction was carried out for 10 min while the mixture was stirred at 650 rpm. Subsequently, the reaction product and catalyst were decanted from the reactor and let stand for 15 min. Then the reaction product and catalyst were transferred to a separation funnel, in which the reaction product and catalyst were separated into upper and lower phases, respectively. The reaction product and catalyst were collected for analysis.

2.4 Analysis method

The reaction product was examined by gas chromatography (GC) analysis. A temperature programmed GC (SP-3420, Beijing Beifen Analysis Equipment Technology Co., Ltd, China) was equipped with a flame ionization detector (FID) and an OV-101 capillary column (0.32 mm in diameter $\times$ 50 m in length). The temperature of the GC was raised from 50 °C to 250 °C at 10 °C/min, and then maintained at 250 °C for 20 min.

Qualitative analysis of the product was carried out in a SSQ710V GC mass spectroscope (MS) (Agilent company, USA). Samples were separated using a HP-5MS capillary column. The initial column temperature was set at 80 °C and kept at 80 °C for 1 min and then increased to 300 °C at 10 °C/min and kept at 300 °C for 10 min. The sample injection temperature was 290 °C and the temperature in the sample transmission line was 250 °C. The flow rate of helium carrier gas was 60 mL/min at 0.11 MPa. Mass spectra were collected over the mass range of 35-350 amu at 1 scan per second at 70 eV energy ionization.

All the NMR spectra were recorded on a JEOL JNM ECA-600. The resonant frequencies for distortionless enhancement by polarization transfer (DEPT) was 150.9134 MHz. Analysis of 2-H intensity in the imidazolium ring of ionic liquid before and after reaction was carried out at 25 °C. The resonant frequencies for ^{27}Al -NMR were 150.9134 MHz and analysis temperature was 80 °C. Spectra were acquired at a sweep-width of 31250.0 Hz. The analysis samples were dissolved in C_6D_6 , with a concentration of 0.5 wt%. Et_3Al was used as a reference.

A ZDJ-3S Karl-Fischer (Beijing Xianquweifeng Company, China) was used to determine the trace content of water in the $[\text{bmim}]\text{Cl}/[\text{AlCl}_3]$ ionic liquid catalyst.

3 Results and discussion

3.1 Catalytic function of water-free ionic liquid

In the conventional HF or H_2SO_4 catalyzed alkylation processes, the acid catalyst function of HF and H_2SO_4 is Brønsted acid. The Brønsted acid provides H^+ directly which acts as an initiator to catalyze the alkylation reaction via the

carbocation mechanism. However, the ionic liquid is a Lewis acid which cannot provide H^+ directly. Generally, ionic liquid catalyzed alkylation reactions were considered to be initiated by solvated H^+ , which is dissociated from HCl produced by hydrolysis of $AlCl_3$. But the ionic liquid and reactants were dehydrated before reaction, so hydrolysis of $AlCl_3$ would not occur, and HCl would not be produced, as a result, nonsolvated H^+ existed in the system. According to the above interpretation, the alkylation reaction cannot occur. But the actual case was completely different.

The GC spectrum of alkylation products of C_6D_6 with 1-dodecene is shown in Fig. 1. It can be seen that different peaks appear in Fig. 1. These spectrum peaks are assigned as 6-, 5-, 4-, 3-, 2-phenyldodecanes, respectively, with increasing retention time. This indicated that the alkylation reactions can still occur using water-free ionic liquid as catalyst. To better understand the catalytic mechanism of the ionic liquid, it is essential to determine the source of initiator.

Fig. 1 GC spectrum of alkylate products of C_6D_6 with 1-dodecene

3.2 The acidity of different H in ionic liquid

There are various possible H ion sources in the ionic liquid. To determine which acts as the initiator of the alkylation reaction, the [bmim]Cl solution was subjected to anhydrous potassium hydroxide (KOH) alcohol solution titration. Fig. 2 shows the FT-IR spectra of [bmim]Cl before and after KOH titration. The adsorption band intensity at

Fig. 2 FT-IR spectra of [bmim]Cl ionic liquid before (a) and after (b) anhydrous KOH alcohol solution titration.

$1600-1700\text{ cm}^{-1}$ increased remarkably, indicating the shear deformation vibration of H_2O (Lu and Deng, 1989). This showed that water was formed as a result of reaction of the H of the ionic liquid with the OH^- of KOH anhydrous solution, indicating the proton acidity of the ionic liquid.

To determine the acidity of the various H atoms of the ionic liquid, the 1H NMR method was employed to analyze the solution of [bmim]Cl before and after KOH titration. The 1H NMR spectra in Fig. 3 show that the intensity of 4,5-H chemical shift at 8 ppm on the imidazolium ring was reduced slightly and the 2-H chemical shift at 9.5 ppm disappeared completely after KOH titration. The intensity of the H chemical shift at 1.0-2.0 ppm on alkyl chain did not change. This indicates that the 2-H on the imidazolium ring has a significant proton acidity and its acidity is stronger than those of 4,5-H on the imidazolium ring and H on alkyl chain. This result is consistent with that reported by Arduengo et al (1991).

The effect of the $AlCl_3$ content of the ionic liquid on the 2-H chemical shifts was also investigated, and it was found that the 2-H chemical shifts were shifted downfield with increasing $AlCl_3$ content. This suggests that the 2-H on the imidazolium ring of the ionic liquid can be disengaged easily. So solvated H^+ or its complex must exist in the system, and act as a Brønsted acid to initiate the alkylation. The results are shown in Fig. 4.

Fig. 3 1H NMR spectra of [bmim]Cl before (a) and after (b) KOH titration

Fig. 4 The effect of AlCl₃ content on chemical shift

3.3 Catalytic mechanism of the ionic liquid

In order to determine the form of the initiator in the system, the structure of the ionic liquid was analyzed using Al-NMR.

Fig. 5 shows the Al-NMR spectra of ionic liquid before and after alkylation. It can be seen that the increased abundance of [AlCl₄]⁻ was at the expense of [Al₂Cl₇]⁻ after the alkylation reaction. This suggests that [AlCl₄]⁻ and [Al₂Cl₇]⁻ are in equilibrium:

Hence, the form of Brønsted acid is [AlHCl₃]⁺ which acts as an initiator to catalyze the alkylation, and the H in

[AlHCl₃]⁺ is disengaged from 2-H on the imidazolium ring. The proposed reaction mechanism is shown in Fig. 6.

Fig. 5 Structure of ionic liquid before and after alkylation reaction

Fig. 6 Catalytic mechanism of Brønsted acid in the alkylation reaction

3.4 Examination of the mechanism of alkylation catalyzed by ionic liquid

According to the above mechanism, the Brønsted acid $[\text{AlHCl}_3]^+$ reacted first with dodecene to form the carbonium ion, then the carbonium ion further reacted with benzene to generate an unstable σ complex, and deuterium D^+ ion on the ring of the σ complex was transferred to $[\text{AlHCl}_3]^+$ to replace H and form $[\text{AlDCl}_3]^+$. Since C_6D_6 was used as a reactant, if the proposed mechanism is correct, deuterium would appear in the alkyl chain of products. To ascertain the position of deuterium in the alkyl chain, DEPT NMR analysis was conducted. Figs. 7 and 8 are the expanded DEPT NMR spectra at $\delta 11.0$ – 12.4 ppm and $\delta 21.8$ – 22.5 ppm, respectively. The negative peaks were split into three peaks, indicating deuterium in the $-\text{CH}_2\text{D}$ group. The three peaks in Fig. 7 were assigned to $-\text{CH}_2\text{D}$ of 3- and 6-phenyldodecanes, whereas those in Fig. 8 assigned to $-\text{CH}_2\text{D}$ of 2-phenyldodecane. The results showed that deuterium was at the first carbon of the dodecylbenzene isomers.

To examine the proposed catalytic mechanism of the ionic liquid catalyst in the alkylation reaction, GC-MS analysis of various reaction products were performed. Figs. 9 and 10 show the MS spectra of 2-phenyldodecanes and 3-phenyldodecanes, respectively. The two molecular ion peaks of 2-alkyl-dodecane appeared at m/z 251 and 252. The relative abundance of 2-alkyl-dodecane with m/z 251 was

Fig. 7 Enlarged DEPT NMR spectrum at δ 11.0 to 12.4 ppm

Fig. 8 Enlarged DEPT NMR spectrum at δ 21.8 to 22.5 ppm

Fig. 9 Mass spectrum of 2-alkyl-dodecane

lower than that with m/z 252. This suggests that the 2-alkyl-dodecanes at m/z 251 and 252 are isomers: $\text{C}_6\text{D}_5\text{-C}_{12}\text{H}_{25}$ and $\text{C}_6\text{D}_5\text{-C}_{12}\text{H}_{24}\text{D}$, respectively.

The spectrum peaks at m/z 110 and 111 in Fig. 9 are phenylethyl carbonium ions $\text{C}_6\text{D}_5\text{-C}_2\text{H}_4^+$ and $\text{C}_6\text{D}_5\text{-C}_2\text{H}_3\text{D}^+$, respectively, which are cleavages of $-\text{C}_{10}\text{H}_{21}^+$ from the molecular ion. Further cleavage of the phenylethyl ion and $-\text{CH}_2^+$ and $-\text{CHD}^+$ resulted in a benzyl carbonium ion of m/z 96 ($\text{C}_6\text{D}_5\text{-CH}_2^+$). The MS analysis showed that the 2-alkyl-dodecane was a part of a linear alkyl chain with a $-\text{CH}_2\text{D}$ group.

The two molecular ion peaks of 3-alkyl-dodecane appeared at m/z 251 and 252. The m/z 252 peak is assigned to the $\text{C}_6\text{D}_5\text{-C}_{12}\text{H}_{24}\text{D}$ molecular ion. The cleavages of $-\text{C}_9\text{H}_{19}^+$ and $-\text{C}_2\text{H}_4\text{D}^+$ from the molecular ion resulted in fragment ions of m/z 125 ($\text{C}_6\text{D}_5\text{-C}_3\text{H}_5\text{D}^+$) and 222 ($\text{C}_6\text{D}_5\text{-C}_{10}\text{H}_{20}^+$). Further loss of $-\text{C}_2\text{H}_3\text{D}^+$ and $-\text{C}_9\text{H}_{18}^+$ from the two fragment ions formed the high-abundance peak at m/z 96 which is assigned to benzyl carbonium ion ($\text{C}_6\text{D}_5\text{-CH}_2^+$). The MS analysis showed that the 3-phenyldodecane has a linear side-chain with a $-\text{C}_2\text{H}_4\text{D}$ group. Similar MS spectrum analysis also showed that $-\text{C}_3\text{H}_6\text{D}$, $-\text{C}_4\text{H}_8\text{D}$ and $-\text{C}_5\text{H}_{10}\text{D}$ groups existed in 2-, 3-phenyldodecane, and 4-, 5- and 6-phenyldodecane.

To further examine the proposed overall reaction mechanism, the ionic liquid was separated from the alkylation products of C_6D_6 with 1-dodecene and to catalyze the alkylation C_6H_6 with 1-dodecene. The result is shown in Fig. 11.

Fig. 10 Mass spectrum of 3-phenyldodecane

Fig. 11 MS spectrum of 2-alkyl-dodecane produced from alkylation of C_6H_6 with 1-dodecene

If the proposed mechanism was followed, carbonium ion $[AlDCl_3]^+$ must be the initiator in the ionic liquid at the beginning of the alkylation reactions of C_6H_6 with 1-dodecene. The relative abundance of alkyl-dodecane at m/z 246 must be higher than that at m/z 247. The results in Fig. 10 showed that 2-alkyl-dodecane had two peaks at m/z 246 and m/z 247 and the relative abundance of alkyl-dodecane at m/z 246 is higher than that at m/z 247. Therefore, it is concluded that a carbocation provides the mechanism of alkylation reactions catalyzed by ionic liquid, in which the Brønsted acid $[AlHCl_3]^+$ is the reaction initiator, not traditional H^+ .

4 Conclusions

Based on above information, it may be concluded that the alkylation catalyzed by $AlCl_3$ ionic liquid follows a carbocation mechanism. Brønsted acid $[AlHCl_3]^+$ which produced by 2-H on the imidazolium ring reacting with $[Al_2Cl_7]^-$ acts as initiator instead of traditional H^+ . $[AlHCl_3]^+$ reacted with dodecene first to form a carbonium ion. Then the carbonium ion further reacted with benzene to generate an unstable σ complex, and D^+ on the ring of the σ complex was transferred into ionic liquid to replace 2-H, thereby generating different dodecylbenzenes.

Acknowledgement

We are grateful for financial support from the National Natural Science Foundation of China (NSFC, 2052010). We also thank the other members of the consortium for the interesting discussions.

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(Edited by Zhu Xiuqin)