SCIENCE CHINA
Chemistry

• ARTICLES •

May 2010 Vol.53 No.5: 1102–1107
doi: 10.1007/s11426-010-0138-4

# Alkylation mechanism of benzene with 1-dodecene catalyzed by $Et_3NHCl$-$AlCl_3$

QI GuoPeng[1], JIANG Feng[1*], SUN XueWen[2] & ZHAO SuoQi[2]

[1]*School of Chemical Engineering, Tianjin University, Tianjin 300072, China*
[2]*State key Laboratory of Heavy Oil Processing, Petroleum University of China, Beijing 102249, China*

Received September 4, 2009; accepted November 25, 2009

The isotope exchange method was employed to investigate the catalytic mechanism of ionic liquid in alkylation of benzenes with olefins. It is proposed that alkylation was induced by the Lewis acid $AlCl_3$ which attracted π electrons of 1-dodecene to shift toward 1-carbon, thus forming a carbonium ion. The carbonium ion further reacted with benzenes to form a complex. Due to unstabilit of the complex, a deuterated ring proton was transferred into an electronegative 1-carbon of the side chain to substitute for the $AlCl_3$, accordingly 2-phenyldodecane was generated.

**ionic liquid, alkylation mechanism, deuteriobenzene, isotope exchange method**

## 1 Introduction

Ionic liquids as catalysts have been utilized in a wide variety of reactions, such as esterification, isomerization and alkylation. In order to effectively enhance the reaction process, investigation of the ionic liquid catalytic mechanism is necessary. Linear alkylbenzene (LAB), a surfactant intermedium, was typically synthesized through alkylation of benzenes with olefins catalyzed by acidic liquid or such solids as HF or $AlCl_3$. However these processes were regarded as being environmental unfriendly. Chloroaluminate ionic liquid used as the catalyst has been used for alkylation, facilitating separation of ionic liquid and products, having a low reaction temperature and high selectivity of 2-alkylbenzene [1–4]. For improved control of the reaction process, the catalytic mechanism of chloroaluminate ionic liquid has been extensively reported [5–10]. Smith *et al*. [11] found that arene was protonated by [Bmim]Cl-$AlCl_3$/HCl, suggesting that the reaction was catalyzed by Bronsted superacidity obtained from the reaction: arene + $Al_2Cl_7^-$ + HCl = arene-$H^+$ + 2$[AlCl_4]^-$. Yoo *et al*. [12] studied the alkylation of isobutane with 2-butene in [Bmim]Br-$AlCl_3$, and proposed that alkylation is induced by a Bronsted acid $[AlHCl_3]^+$ which was formed by association of $[Al_2Cl_7]^-$ with 2-H of imidazolium ring.

Though many studies concerning the mechanism of ionic liquids were reported, active substance that induces reaction remain ambiguous. In this work the isotope substitution method was employed to reveal the catalytic mechanism of ionic liquids. Alkylation of deuteriobenzene with 1-dodecene using $Et_3NHCl$-$AlCl_3$ as a catalyst was carried out, and then the product structures were analyzed by NMR and GC-MS. The reaction mechanism was determined by tracing the migration path of a D atom during the reaction process.

## 2 Experimental

### 2.1 Materials and the catalyst

$C_6D_6$, purity 99.6%, was purchased from Sigma-Aldirich. 1-dodecene, purity 99.9%, was obtained from Beijing

---

[*] Corresponding author (email: jiangfeng@tju.edu.cn)

Chemical Reagent Company. $Et_3NHCl-AlCl_3$ was synthesized according to previously reported methodology [13]. 0.5 mol Ethylamine hydrochloride was placed into a 250 mL round bottom flask with a stirrer, a reflux condenser equipped with a drying pipe and thermometer. 1 mol $AlCl_3$ in batches was introduced from a dosing funnel with the reaction temperature maintained at 40 °C. After all of the $AlCl_3$ had been added, the mixture was stirred at room temperature for 5 min, with the reaction subsequently carried out in a nitrogen atmosphere at 80 °C for 5 h.

### 2.2 Chemical reaction

A mixture of $C_6D_6$ (16.8 g) and 1-dodecene (5.6 g) in a molar ratio of 6:1 was placed into a three-necked flask into which 6.7 g of $Et_3NHCl-AlCl_3$ was introduced. The reaction mixture was continuously stirred at 30 °C for 15 min. The entire process was carried out in a nitrogen atmosphere. The liquid-liquid two phase formed when the reaction was terminated and upper layer liquid was decanted for analysis.

### 2.3 Analysis conditions

GC-MS analysis was carried out on a SSQ710V instrument. Samples were separated using anHP-5MS capillary column. The initial column temperature was maintained at 80 °C for 1 min, before being raised at the rate of 10 °C/min, and maintained at 300 °C for 10 min. The injection temperature was set at 290 °C, the transmisson line temperature was 250 °C, the split rate was 60 mL/min and the carrier pressure was 16 psi. Mass spectra were acquired over the mass range 35–350 amu; scan rate 1 scan/sec; energy ionization 70 eV.

All NMR spectra were recorded on a JNM ECA-600 (JEOL) instrument. The resonant frequencies for DEPT, $^2$D and two-dimensional NMR were respectively 150.91, 92.13, and 600.17 MHz. Analysis was carried out at 25 °C utilizing $C_6D_6$ as a solvent.

## 3 Results and discussion

The alkylation product was separated and identified by GC-MS. The GC spectrum is shown in Figure 1 where peaks are assigned to 6-, 5-, 4-, 3-, 2-phenyldodecane as the retention time is prolonged. Selectivity of dodecylbenzene isomers defined as $A_i/A_{\text{total isomer}}$ (*A*: peak area) are listed in Table 1.

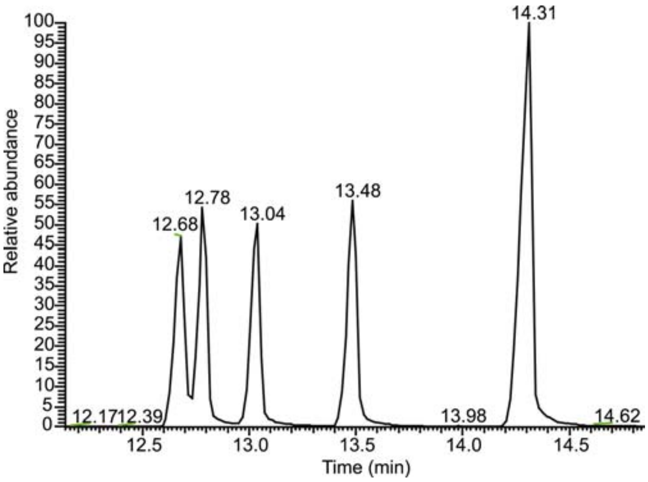


**Figure 1** GC spectrum of alkylation products of $C_6D_6$ with 1-dodecene.

**Table 1** Composition and selectivity of benzene products with 1-dodecene catalyzed by $Et_3NHCl-AlCl_3$

| Product composition | 2-LAB | 3-LAB | 4-LAB | 5-LAB | 6-LAB |
|---|---|---|---|---|---|
| Selectivity (%) | 39.3 | 19.8 | 13.9 | 13.8 | 13.2 |

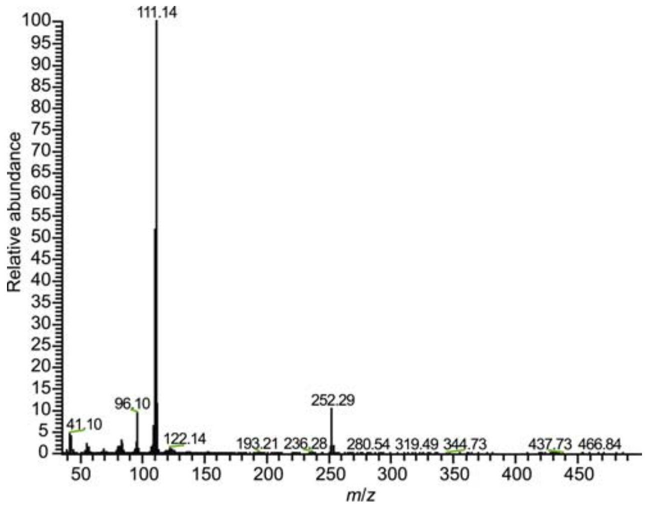
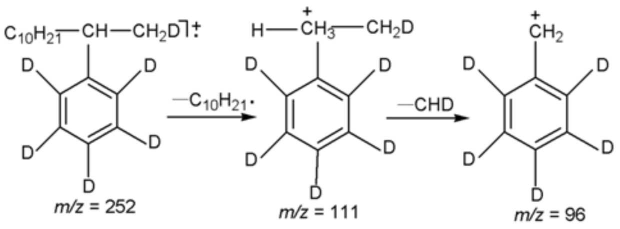


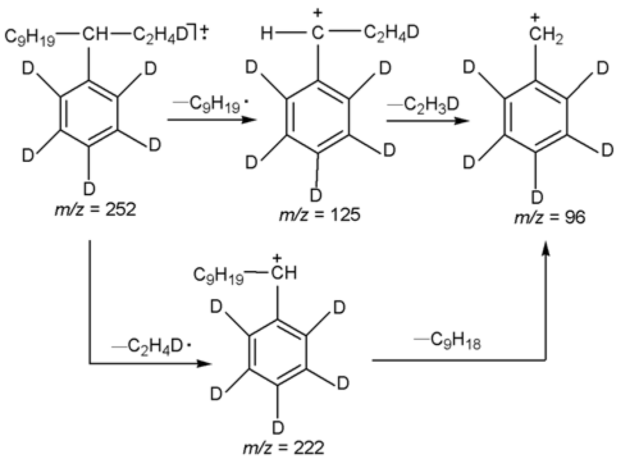
**Figure 2** Mass spectrum analysis of 2-phenyldodecane.

### 3.1 Determination of dodecylbenzene isomer structures

The MS spectrum of 2-phenyldodecane is shown in Figure 2 and the detailed MS analysis is listed in Scheme 1. The peak at *m/z* 252 corresponded to the molecular ion ($C_6D_5-C_{12}H_{24}D$). The peak at *m/z* 111 was assigned to the phenylethyl carbonium ion ($C_6D_5-C_2H_3D^+$) which resulted from the cleavage of $-C_{10}H_{21}$ from the molecular ion. Further cleavage of the phenylethyl ion and –CHD resulted in a benzyl carbonium ion of *m/z* 96 ($C_6D_5-CH_2^+$). MS analysis demonstrated that 2-phenyldodecane was part of a linear alkyl chain with a $-CH_2D$ group. Mass analysis of 3-phenyldodecane is shown in Figure 3. The MS analysis process of 3-dodecylbenzene is shown in Scheme 2. The peak at *m/z* 252 was assigned to the molecular ion ($C_6D_5-C_{12}H_{24}D$), and the cleavages of $-C_9H_{19}\cdot$, $-C_2H_4D\cdot$ from molecular ion resulted in fragment ions of *m/z* 125 and 222 ($C_6D_5-C_3H_5D^+$, $C_6D_5-C_{10}H_{20}^+$). Further loss of $-C_2H_3D$,



**Scheme 1** MS analysis of 2-phenyldodecane.



**Scheme 2** MS analysis of 3-phenyldodecane.

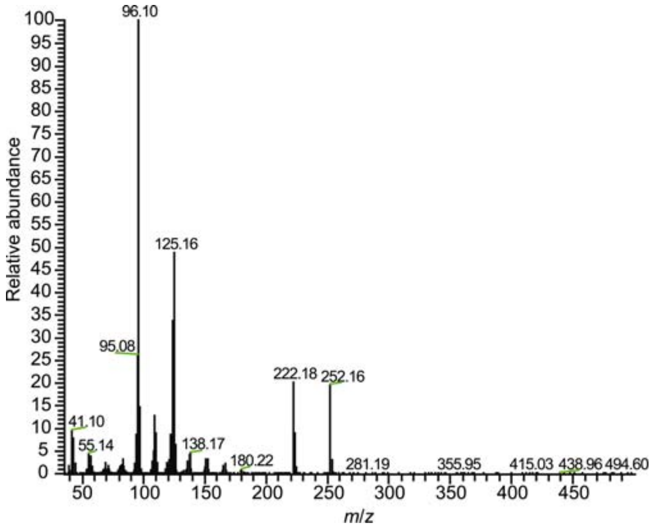


**Figure 3** Mass spectrum of 3-phenyldodecane.

–$C_9H_{18}$ from the two fragment ions formed the high-abundance peak at *m/z* 96 which was allocated to the benzyl carbonium ion ($C_6D_5$-$CH_2^+$). MS analysis demonstrated that 3-phenyldodecane possesses a linear side chain with a –$C_2H_4D$ group. Similar to the mass spectrum analysis of 2-, 3- phenyldodecane, 4-, 5- and 6- phenyldodecane were concluded to respectively have the group of –$C_3H_6D$, –$C_4H_8D$ and –$C_5H_{10}D$.

Because of the uncertainty of the D detailed position in the side chain of dodecylbenzene isomers, DEPT NMR was performed to ascertain the D position. The resulting spectrum is shown in Figure 4(a). The positive peaks in the range from 12.0 to 22.0 ppm corresponded to $CH_3$ with others in the range of 40.0–48.0 ppm corresponding to CH. All negative peaks were assigned to $CH_2$. Spectra around $\delta$ 12.0 and 22.0 ppm were enlarged to acquire the detailed structure and are respectively shown in Figure 4(b) and (c). In two figures the negative peaks were split into triple peaks which indicated that D exists in the –$CH_2$ group. Triple peaks in Figure 4(b) were attributed to the –$CH_2D$ of 3-–6- phenyldodecane and those in Figure 4(c) to the –$CH_2D$ of 2-phenyldodecane. The lower electron density of the –$CH_2D$ of 2-phenyldodecane is less than that of the –$CH_2D$ of the other isomers due to electron withdrawal from the benzene ring which results in the $CH_2D$ of 2-phenyldodecane shifting to the low field $\delta$ 22.0 ppm relative to that of the other isomers 12.0 ppm. Based on DEPT NMR analysis, D was determined to be connected to the 1-carbon of dodecylbenzene isomers.

Deuterium NMR was also performed to identify the D position in dodecylbenzene isomers with thespectrum shown in Figure 5. The peak at 1.1 ppm was assigned to the –$CH_2D$ of 2-dodecylbenzene, and peaks at 0.8 ppm corresponded to the –$CH_2D$ of 3- –6-phenyldodecane whose polarities were so similar that their peaks were overlaid. Deuterium NMR analysis further confirmed that D was located

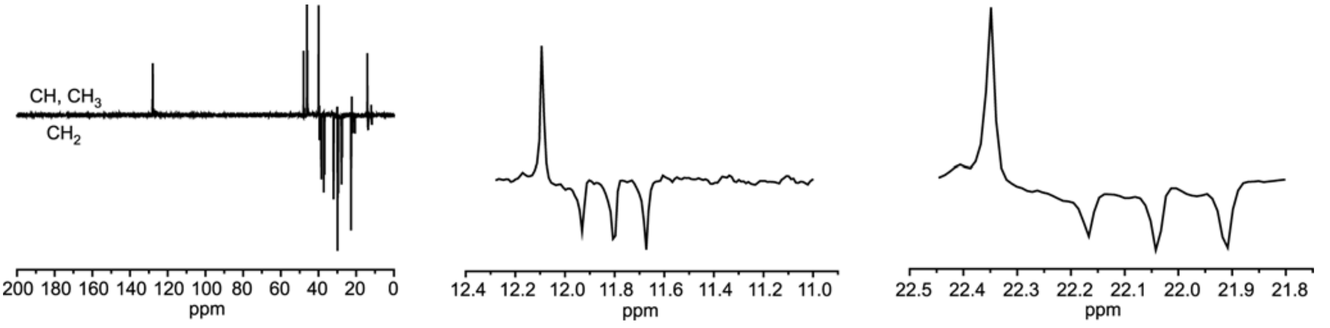


**Figure 4** (a) DEPT NMR spectrum of the product. (b) Partial view of DEPT NMR spectrum ranging from 11.0 to 12.4 ppm. (c) Partial view of DEPT NMR spectrum ranging from 21.8 to 22.5 ppm.

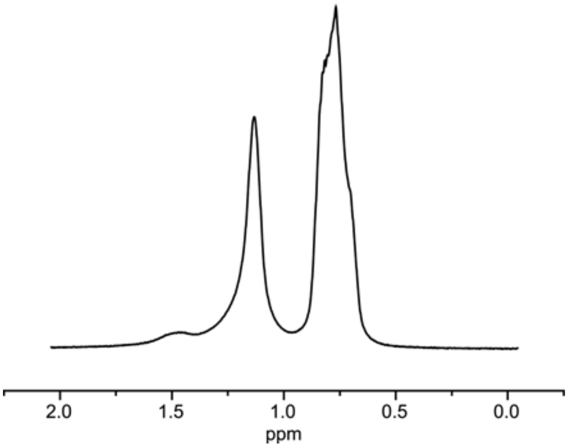


**Figure 5** Partial view of the Deuterium NMR spectrum of the benzene product with –dodecene catalyzed by $Et_3NHCl$-$AlCl_3$.

on the1-carbon of side chain of dodecylbenzene isomers.

HSQC analysis data is listed in Table 2. C, H chemical shifts of $CH_3$ of 2-phenyldodecane were 22.0 and 1.2 ppm higher than those of $CH_3$ with the other dodecylbenzene isomers at 12.0 and 0.8 ppm, which was consistent with $^{13}C$ and $^2D$ chemical shift in Figures 4(b), 4(c) and 5. The results tended to confirm the DEPT and Deuterium NMR analysis.

H-H COSY analysis was performed with the cross peak data summarized in Table 3. The cross peak between H($CH_3$) at 1.2 ppm and H(CH) at 2.6 ppm was determined to be the $CH_3CH$– group of 2-phenyldodecane. Coupling between the H($CH_3$) peak at 0.8 ppm and the H($CH_2$) peak at 1.5 ppm was confirmed to be the $CH_3CH_2CH$– group of 3-phenyldodecane.

The results of the HSQC and H-H COSY analysis accorded with that of $^2D$ and DEPT NMR. Theproduct structures, e.g., 2-, 3-phenyldodecane, were confirmed to be the structures shown in Figure 6.

## 3.2 Deduction of the catalytic mechanism of ionic liquids

There are two possible catalytic mechanisms within ionic liquids: the hydrogen proton or the Lewis acid catalytic mechanism. Therefore two pathways were proposed and the correct mechanism was obtained by comparing the deduced product structures with the analyzed ones.

### *3.2.1 H proton catalytic mechanism*

It was assumed that the reaction was induced by $H^+$ which attacked an unsaturated bond of 1-dodecene and formed $H_3C$-CH ⊕ -$C_{10}H_{21}$. $H_3C$-CH ⊕ -$C_{10}H_{21}$ reacted with benzene to form an unstable σ complex. As $D^+$ connected to the $sp^3$ hybridized carbon of σ complex ring, 2-phenyldodecane was generated. The reaction process catalyzed by $H^+$ is shown in Scheme 3.

The other isomers were formed by alkylation of benzene

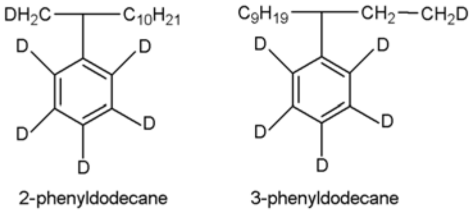


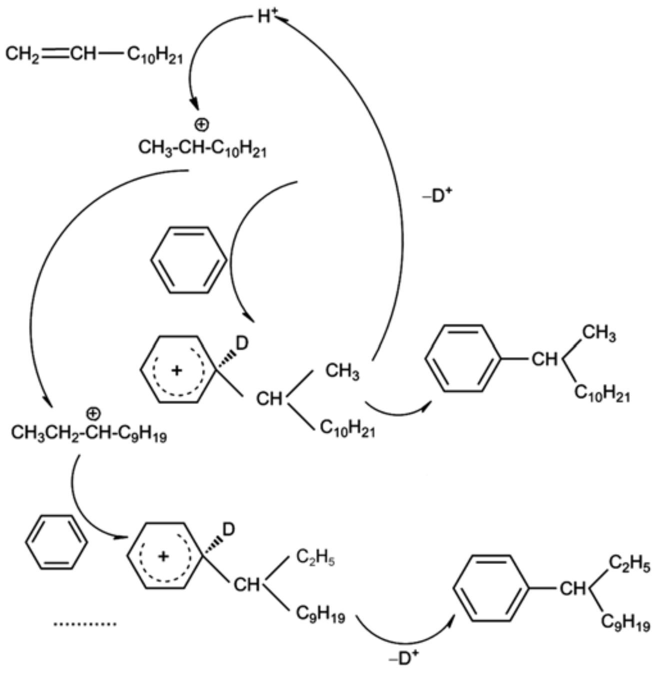
**Figure 6** Molecular structures of linear dodecylbenzene isomers.

**Table 2** Chemical shift of correlated $^{13}C$ and $^1H$ in the HSQC spectrum and the identification of the C-H of different groups

| Coupling between $^{13}C/^1H$ $\delta$(ppm) | C-H connection of the identified group |
|---|---|
| 22.0/1.2 | C-H of $CH_3$ of 2-dodecylbenzene |
| 12.0/0.8 | C-H of $CH_3$ of the other dodecylbenzene isomers |
| 22.0–32.0/1.1–1.2 | C-H of $CH_2$ |
| 38.0/1.5 | C-H of $CH_2$ connected to CH |
| 46.0/2.3 | C-H of CH |
| 48.0/2.2 | C-H of CH |
| 40.0/2.6 | C-H of CH |

**Table 3** Chemical shift of correlated H and H in the H-H COSY spectrum and the corresponding group

| Coupling between $^1H/^1H$ $\delta$(ppm) | Identified group |
|---|---|
| 2.6/1.2 | –$CHCH_3$ group of 2-phenyldodecane |
| 1.5/0.8 | $CH_2CH_3$ of 3-phenyldodecane |
| 1.2/0.8 | $CH_3CH_2$- of 4- ,5-, 6-phenyldodecane |
| 1.5/2.2–2.6 | –$CH_2CH$– |
| 1.5/1.2 | –$CH_2CH_2$– |



**Scheme 3** Catalytic mechanism of hydrogen proton in alkylation.

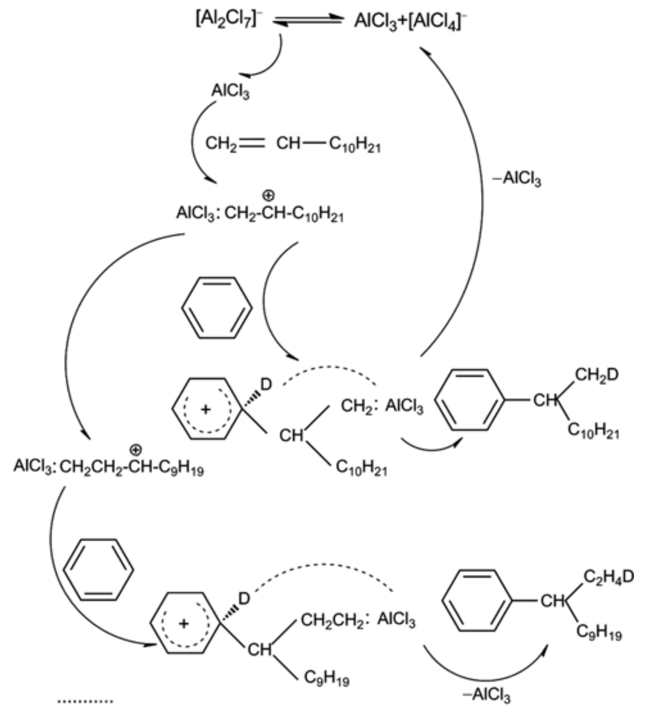
with the other carbonium ions which were obtained through rearrangement of $H_3C\text{-}CH\oplus\text{-}C_{10}H_{21}$. Due to a discrepancy in the deduced product structures (see products in Scheme 3) with those (linear dodecylbenzene isomers in Figure 6) obtained from MS and NMR analysis, the hydrogen proton catalytic mechanism was not established.

### 3.2.2 *Lewis acidity mechanism*

Quarmby *et al.* [14] reported that ionic liquids were lateral acids and could associate with such basic substances as acetone, to form adduct $B{:}AlCl_3$. Therefore it was proposed that alkylation was induced by the Lewis acid $AlCl_3$ which was obtained by the dissociation of $[Al_2Cl_7]^-$. The reaction process is illustrated in Scheme 4. Electron-withdrawal and the spatial effect of $AlCl_3$ made π electrons of 1-dodecene move forward to 1-carbon, and the carbonium ion ($AlCl_3\cdots CH_2\text{-}CH\oplus\text{-}C_{10}H_{21}$) was formed. The carbonium ion attacked benzene to form an unstable σ complex. Because $D^+$ was more electrophilic than $AlCl_3$, $D^+$ connected to the $sp^3$ hybridized carbon of a ring would shift to the electronegative 1-carbon of a side chain to substitute for $AlCl_3$, resulting in 2-phenyldodecane was generated.

The other isomers were formed by the reaction of benzene with the other carbonium ions which were obtained by the shift of the positive charge of $AlCl_3\cdots CH_2\text{-}CH\oplus\text{-}C_{10}H_{21}$. Based on the realization that product structures deduced from Lewis acid catalyst mechanisms were in accordance with ones obtained from GC/MS and NMR analysis, the Lewis acid $AlCl_3$ catalytic mechanism was recommended.

The Lewis acid mechanism also demonstrated that the selectivity of 2-phenyldodecane catalyzed by ionic liquid was higher than that by HF, which was attributed to the slower rearrangement rate of $AlCl_3\cdots CH_2\text{-}CH\oplus\text{-}C_{10}H_{21}$ than that of the carbonium ion $H_3C\text{-}CH\oplus\text{-}C_{10}H_{21}$.



**Scheme 4** Catalytic mechanism of Lewis acid $AlCl_3$ in alkylation.

## 4 Conclusions

The alkylation mechanism of benzene with 1-dodecene catalyzed by $Et_3NHCl\text{-}AlCl_3$ was investigated in the present work. The reaction of $C_6D_6$ with 1-dodecene using $Et_3NHCl\text{-}AlCl_3$ as a catalyst was carried out. The product was analyzed by employing NMR and GC-MS techniques, which confirmed that one D of the benzene ring was transferred to the 1-carbon of the linear chain of dodecylbenzene during the reaction process. Based on the above information, a mechanism was suggested that 1-dodecene reacted with the $AlCl_3$ obtained from the dissociation of an anion ion of ionic liquid ($[Al_2Cl_7]^-$), and formed the carbonium ion ($AlCl_3\cdots H_2C\text{-}CH\oplus\text{-}C_{10}H_{21}$). The carbonium ion further reacted with benzene to generate an unstable σ complex, and D+ connected to the sp3 -hybridized carbon of the ring of the σ complex which was transferred into an electronegative 1-carbon of a linear chain to replace $AlCl_3$, thereby generating 2-dodecylbenzene. The other isomers were generated by reaction of the rearranged carbonium ions with benzene.

*This work was supported by the National Natural Science Foundation of China (20676150).*

1 Qiao CZ, Zhang YF, Li CY. Activity and stability investigation of [BMIM][$\text{AlCl}_4$] ionic liquid as catalyst for alkylation of benzene with 1-dodecene. *Appl Catal A Gen*, 2004, 276: 61–66

2 Decastro C, Sauvage E, Valkenberg MH, Holderich WF. Immobilised ionic liquids as Lewis acid catalysts for the alkylation of aromatic compounds with dodecene. *J Catal*, 2000, 196: 86–94

3 Qiao K, Deng YQ. Alkylations of benzene in room temperature ionic liquids modified with HCl. *J Mol Catal A Chem*, 2001, 171: 81–84

4 Xin HL, Wu Q, Han M, Wang D. Alkylation of benzene with 1-dodecene in ionic liquids $[\text{Rmim}]^+\text{Al}_2\text{Cl}_6\text{X}^-$ (R = butyl, octyl and dodecyl; X = chlorine, bromine and iodine). *Appl Catal A Gen*, 2005, 292: 354–361

5 Trulove PC, Sukumaran DK, Osteryoung RA. Protons in acidic ambient-temperature chloroaluminate molten salts: Hydrogen-deuterium exchange between the imidazolium cation and hydrogen chloride. *J Phy Chem*, 1994, 98: 141–146

6 Sun XW, Zhao SQ. Alkylation mechanism of benzene with propylene catalyzed by ionic liquid under supercritical conditions (in chinese). *Acta Chim Sin*, 2008, 66: 471–473

7 Compell JLE, Johnson KE. The chemistry of protons in ambient-temperature ionic liquids: solubility and electrochemical profiles of HC1 in HCl:ImCl:$\text{AlC1}_3$ ionic liquids as a function of pressure (295 K). *J Am Chem Soc*, 1995, 117: 7791–7800

8 Schmerling L. Reactions of hydrocarbons ionic mechanisms. *Ind Eng Chem*, 1953, 45: 1447–1453

9 Whitmore FC. The common basis of intramolecular rearrangements. *J Am Chem Soc*, 1932, 54: 3274

10 Ma M, Johnson KE. Carbocation formation by selected hydrocarbons in trimethylsulfonium bromide-$\text{AlCl}_3$/$\text{AlBr}_3$-HBr ambient temperature molten salts. *J Am Chem Soc*, 1995, 117:1508–1513

11 Smith GP, Dworkin AS, Pagni RM, Zingg SP. Bransted superacidity of HC1 in a liquid chloroaluminate $\text{A1C1}_3$-1-ethyl-3-methyl-1*H*-imidazolium chloride. *J Am Chem Soc*, 1989, 111: 525–530

12 Yoo K, Nambodiri VV, Varma RS, Smirniotis PG. Ionic liquid-catalyzed alkylation of isobutane with 2-butene. *J Catal*, 2004, 222: 511–519

13 Zhao ZK, Qiao WH, Li ZS. Friedel-Crafts alkylation of methylnaphthalene in the presence of ionic liquids. *J Mol Catal A Chem*, 2004, 222: 207–212

14 Quarmby IC, Mantz RA, Goldenberg LM. Stoichiometry of latent acidity in buffered chloroaluminate ionic liquids. *Anal Chem*, 1994, 66:3558–3561