

# Alkylations of benzene in room temperature ionic liquids modified with HCl

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## Abstract

Alkylations of benzene with dodecene and/or chloromethanes in the chloroaluminate room temperature ionic liquid modified with HCl as catalysts have been investigated. Different product distributions and enhanced activity, were respectively observed for these two alkylation reactions. This may be attributed to the superacidity of the ionic liquid induced by the presence of HCl. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Ionic liquids; Alkylation; Benzene; Superacidity

## 1. Introduction

Alkylation of benzene is one of the most important processes in chemical industry and more than 15 billion pounds per year of alkyl aromatics via the liquid acid catalysed alkylation of aromatics were produced. For example, liner alkylbenzene was produced by alkylation of benzene with C<sub>9</sub>–C<sub>14</sub> alkenes (average C number is 12) in the presence of HF or AlCl<sub>3</sub>. Alkylated products consisted of a series of long-chain alkylbenzene isomers in which the 2-phenyl isomer was desired product for its better emulsibility [1]. Phenylmethanes, including di- and triphenylmethane, have also been produced by alkylation of benzene with chloromethane using AlCl<sub>3</sub> as catalyst in industry. However, both of the processes have got some problems, such as formation of aluminate wastage, troublesome product recovery and purification, and catalysts can not be reused. Especially, for the

production of triphenylmethane, long reaction time was needed and only low yield was obtained, when AlCl<sub>3</sub> was used as catalyst [2,3]. Therefore, efforts to find environmentally benign catalytic processes have been made, for example, the alkylation of benzene over solid acid [4,5], heteropolyacids [6] and zeolites [7,8] has been reported. Solid catalysts, however, deactivated rapidly due to the build-up of coke.

Room temperature ionic liquids are being more and more regarded as relatively clean catalysts and solvents [9,10]. Recently, many organic reactions, including alkylation [11–13], epoxidation [14,15], hydrogenation [16], Suzuki cross-coupling reaction [17], aza-Diels–Alder reactions [18] and cracking reactions of polyethylene, [19] etc. have been reported to proceed in room temperature ionic liquid with excellent yields and selectivity. The alkylations of benzene with alkenes and chloromethane are kinds of Friedel–Crafts reactions catalysed by Lewis acidic catalysts. It was known that aluminium chloride-based ionic liquids can be Lewis acidic if the mole ratio of AlCl<sub>3</sub>: quaternary ammonium salt

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(such as 1-ethyl-3-methylimidazolium chloride or 1-butylpyridinium chloride) is  $>1.0$  [20], and a superacid may be formed, when protons were further added into the Lewis acidic ionic liquid [21,22]. Here, we first report alkylation of benzene with dodecene and/or chloromethanes in the aluminium chloride-based room temperature ionic liquids in the presence of HCl. The former reaction was carried out using the ionic liquids as catalyst in which HCl was artificially added, and the later was carried out using the ionic liquids in which HCl would be naturally produced during the reaction since one of the products of alkylation of benzene with chloromethane was HCl.

## 2. Experimental

### 2.1. Syntheses of ionic liquids

The room temperature ionic liquids, i.e. aluminium chloride + 1-ethyl-3-methylimidazolium chloride (EMIC), aluminium chloride + 1-butyl-3-methylimidazolium chloride (BMIC), aluminium chloride + 1-butylpyridinium chloride (BPC), and aluminium chloride + trimethylamine hydrochloride (TMHC) were employed in this work. The EMIC, BMIC and BPC were synthesised according to the previous literatures [12]. The ionic liquid containing HCl was prepared by stirring the ionic liquid under a HCl atmosphere for 25 min. Such a HCl atmosphere was obtained by flowing  $N_2$  through concentrated HCl and then dried by concentrated  $H_2SO_4$ . It was estimated that the partial pressure of HCl was about 140 mm Hg [23], under which the acidity of the ionic liquids was  $H = -15.8$  [22].

### 2.2. Alkylation of benzene and analysis

A certain amount of ionic liquid in which  $AlCl_3$  was 0.01 mol and the molar ratios of  $AlCl_3$  and quaternary ammonium salt were 1.8:1 to 2:1, was added into a 100 ml flask with magnetic stirrer. After evacuating for 30 min at calculated  $100^\circ C$  to remove a trace amount of water in the ionic liquid, benzene, 0.33 mol for the alkylation of benzene with 1-dodecene, or 0.3 mol for the alkylation of benzene with chloromethanes was charged into the reactor. Then, under stirring alkylation reagent, e.g. 1-dodecene (0.023 mol), dichloromethane or trichloromethane (0.02 mol) was dropwise added into the reactor after the reactor system was cooled to ambient temperature. The mixtures were stirred at 273–303 K for 5 min–8 h, depending on each specific reaction. For the purpose of comparison, same alkylation reactions were also carried out with anhydrous  $AlCl_3$  (0.01 mol) as catalyst. After the alkylation reaction, the upper unreacted benzene layer containing the alkylated products was separated from the ionic liquid in the bottom simply by decantation.

All analyses were carried out with a HP 6890/5973 GC/MS equipped with HP 5MS column,  $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ . The concentration of reactant and product was directly given by the system of GC/MS chemstation according to the area of each chromatograph peak.

## 3. Results and discussion

### 3.1. Alkylation of benzene with 1-dodecene

Results for alkylation of benzene with 1-dodecene over different catalysts were listed in Table 1. It can

Table 1  
Results of alkylation of benzene with 1-dodecene over different catalysts<sup>a</sup>

Entry	Catalyst	Molar ratios of EMIC/ $AlCl_3$	Product distributions				
			2-Phenyl	3-Phenyl	4-Phenyl	5-Phenyl	6-Phenyl
1	$AlCl_3$	–	26.7	20.1	17.4	18.0	17.8
2	$AlCl_3$ –EMIC	1:1.8	35.7	19.9	14.9	15.0	14.4
3	$AlCl_3$ –EMIC	1:2	34.7	20.1	14.7	15.8	14.6
4	$AlCl_3$ –EMIC + HCl	1:2	40.5	18.1	14.3	18.7	8.3

<sup>a</sup>  $AlCl_3$ : 0.01 mol, reaction time: 5 min, temperature: 293 K.

Table 2  
Results of alkylation of benzene with dichloromethane and trichloromethane

Entry	Catalyst	Alkylation reagents	Temperature (K)	Reaction time	Conversion (%)	Yield (%)
5	AlCl <sub>3</sub>	Dichloromethane	273	5 min	57	38.4
6	AlCl <sub>3</sub> -BMIC	Dichloromethane	273	5 min	99	96
7	AlCl <sub>3</sub> -BPC	Dichloromethane	273	5 min	99	95
8	AlCl <sub>3</sub> -TMHC	Dichloromethane	303	5 min	99	97
9	AlCl <sub>3</sub> -BMIC	Trichloromethane	303	1.5 h	23	21.6
10	AlCl <sub>3</sub> -BMIC	Trichloromethane	303	8 h	96	90
11	AlCl <sub>3</sub> -BPC	Trichloromethane	303	8 h	94	89
12	AlCl <sub>3</sub> -TMHC	Trichloromethane	303	8 h	96	91

be seen that almost 100% conversions of 1-dodecene were achieved over all the catalysts used within 5 min, but the resulted product distributions were different. As for anhydrous AlCl<sub>3</sub>, entry 1, the selectivity for 2-substituted isomer was remarkably lower than that in ionic liquid catalyst system composed of EMIC and AlCl<sub>3</sub> (entries 2 and 3), and the molar ratio of imidazole salt and AlCl<sub>3</sub> slightly affected the distribution of products. Since the benzene was in great excess, i.e. the mole ratio of benzene/1-dodecene = 14.3, by-products, which may be formed if the amount of 1-dodecene was excessive, such as dialkylated alkylbenzene or isomerisation and oligomerisation of 1-dodecene were not observed. It is worth to note that the selectivity of 2-substituted isomer was further increased, when the ionic liquids containing HCl was used as catalyst, entry 4. It is known that alkylation reaction is governed with the mechanism of carbenium ion. Strong polarity and electrostatic field of the ionic liquid used as catalyst and reaction medium may stabilise the intermediate of carbenium ion charged positively in the second C, and at same time, the reaction rate of alkylation may be further enhanced in the ionic liquid containing with small amount of HCl, thus, resulting in a remarkably high selectivity for 2-substituted isomer.

### 3.2. Alkylation of benzene with chloromethanes

Alkylations of benzene with di- and trichloromethane over different ionic liquid catalysts with the 2.0 molar ratio of AlCl<sub>3</sub>/quaternary ammonium salts are shown in Table 2. For the formation of diphenylmethane, it can be seen that dichloromethane conversion and diphenylmethane yield were quite low

with anhydrous AlCl<sub>3</sub> catalyst, entry 5, while, under same conditions, 99% of dichloromethane conversion and 95–96% of diphenylmethane yield were achieved with the ionic liquid as catalysts, entries 6–8. The formation of triphenylmethane in ionic liquid catalyst system was relatively difficult, i.e. only 23% of conversion was obtained, when the reaction has carried out for 1.5 h (entry 9). However, 96% dichloromethane conversion and 90% of the diphenylmethane yield were achieved if the reaction has carried out for 8 h, entries 10–12. This result is much better than that reported previously using anhydrous AlCl<sub>3</sub> as catalyst [2,3]. The experimental results also indicated that there were not much differences in the catalytic performance among the AlCl<sub>3</sub>-based MBIC, BPC and TMAC, indicating the cation part in the ionic liquids has little impact on the catalytic performance.

There may be two possible reasons for such high conversion and yield in ionic liquid used as catalyst: (1) the ionic liquid became superacidic as mentioned above during the reaction since HCl, as one of products, was formed; (2) the immiscibility of the resulted alkylated products with the ionic liquid should facilitate the reaction equilibrium shifting to the product side.

Though not shown here, the ionic liquids as catalyst could be repeatedly used as reported in previous literatures. For example, 98% of dichloromethane conversion and more than 95% of the diphenylmethane yield could still be maintained after the alkylation of benzene with dichloromethane was carried out in the same batch of ionic liquid catalyst for five times.

Another advantage of ionic liquid as catalyst was that the product could be easily separated with high purity. Since benzene was almost insoluble in ionic

liquids and phenylmethane is well soluble in benzene, the resulted products and the ionic liquid catalyst could be separated simply by the decantation of the upper excess benzene layer after the reaction. In the case of anhydrous aluminium chloride as catalyst, the reacted mixtures became deep reddish, and had to be washed with water after reaction, inevitably producing aluminate wastage.

#### 4. Conclusion

In summary, more favourable distributions of products for alkylations of benzene with dodecene and enhanced catalytic activity for alkylations of benzene with chloromethanes, were respectively achieved with aluminium chloride-based ionic liquid modified with HCl in comparison with anhydrous aluminium chloride catalyst. It could be a practical catalyst for alkylations of benzene with alkenes.

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