

# Immobilization of HX: [Hmim]X as Halogenating Agent, Recyclable Catalyst and Medium for Conversion of Alcohols to Alkyl Halides

WU, Hai-Hong(吴海虹) SUN, Jing(孙靖) YANG, Fan(杨帆)  
TANG, Jie\*(汤杰) HE, Ming-Yuan(何鸣元)

Department of Chemistry, East China Normal University, Shanghai 200062, China

HX is immobilized by reaction of halogen acid with methylimidazole, and the formed ionic liquid [Hmim]X was used as halogenating agent, catalyst as well as medium for conversion of alcohols to alkyl halides. Excellent yields were obtained. The halides produced could be easily separated from the reaction mixture via simple decantation, and the ionic liquid [Hmim]X could be regenerated conveniently by adding equivalent of halogen acids followed by removal of water.

**Keywords** halogenation, ionic liquid, alcohol, alkyl halide

## Introduction

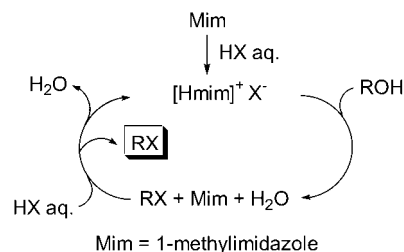
The conversion of alcohols into the corresponding alkyl halides is one of the most described transformations in organic synthesis.<sup>1</sup> A widely used method for this transformation involves the treating of alcohol with halogen acids or sodium halide and a large excess of concentrated sulfuric acid,<sup>2</sup> which caused environmental problems. Although halogen acids could be also used as halogenating agents and acidic catalysts, a mass of water in halogen acids influenced the reaction equilibrium. Meanwhile, the application was limited for its strong volatility and serious corrosiveness.

Ionic liquids (IL), with thermal stability and without effective vapor pressure, have been recognized as a possible environmentally benign alternative to chemical volatile solvents in some industrial processes. Therefore, exploration of industrial application potential of ionic liquids has recently become an exciting area of research.<sup>3-8</sup> So far ionic liquids are mostly used as solvents or media for organic reactions, however, their utility as reactant, such as nucleophile, has rarely been reported. Ren<sup>9</sup> investigated the transformation of alcohols to their corresponding alkyl halides using [Bmim]X as halogenating agent. But the reaction still needed Brønsted acid, concentrated sulfuric acid or CH<sub>3</sub>SO<sub>3</sub>H as catalyst. Moreover, the IL [Bmim]X, which had been converted to [Bmim]HSO<sub>4</sub> or [Bmim]CH<sub>3</sub>SO<sub>3</sub> after the reaction, was difficult to regenerate. Nguyen reported the conversions of fatty alcohols to alkyl bromides and iodides in ionic liquids, such as [Bmim]X and [Omim]X. However, the acidic catalyst *p*-toluene sulfonic acid

(PTSA) was still needed, and no chlorinating reaction was investigated. Most of all, large amount of traditional organic solvents, hexane and acetone, were used for the isolation and the recycling of the ionic liquid.<sup>10</sup>

We have reported an environmentally friendly and efficient procedure for esterification using a Brønsted acidic IL, 1-methylimidazolium tetrafluoroborate ([Hmim]BF<sub>4</sub>), as recyclable catalyst and solvent.<sup>11</sup> Herein, we developed a novel procedure for the conversion of alcohols to the corresponding alkyl halides (Scheme 1): HX was immobilized by reaction of halogen acid with methylimidazole, and the formed Brønsted acidic IL [Hmim]X was used as halogenating agent, recyclable catalyst and medium. The [Hmim]X could be regenerated conveniently by adding equivalent of HX followed by removal of water. The halides can be easily separated from the reaction mixture via simple decantation.

**Scheme 1**



The halogenations of some alcohol substrates were investigated in IL [Hmim]Cl, [Hmim]Br and [Hmim]I. The results are summarized in Table 1. As shown in Table 1, the reactions of primary alcohols, such as

\* E-mail: jtang@chem.ecnu.edu.cn; Fax: 021-62232100

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*n*-octanol, benzyl alcohol, gave very satisfactory yields. Whether chlorination or bromination, so much as iodination obtained the corresponding halides with almost quantitative yields (98%—99%, Entries 1—3, 10—12). For halogenations of hexanediol, a primary di-alcohol, the corresponding dihalides were also obtained with 98%—99% yields (Entries 13—15). So the process was quite effective for halogenating of primary alcohols, and few rearrangement and dehydration products were detected. It should be pointed out that the use of [Hmim]I must be protected by N<sub>2</sub> and at lower temperature for the mixture was darkened due to air-oxidation of iodide (Entries 3, 6, 9, 12 and 15).

**Table 1** Conversion of alcohols to alkyl halides in [Hmim]X<sup>a</sup>

Entry	Alcohol	X	Temp./°C	Time/h	Yield <sup>b</sup> /%
1	<i>n</i> -Octanol	Cl	120	12	99
2	<i>n</i> -Octanol	Br	120	12	99
3	<i>n</i> -Octanol	I	60	20	98 <sup>c</sup>
4	<i>sec</i> -Octanol	Cl	120	12	75
5	<i>sec</i> -Octanol	Br	120	12	85
6	<i>sec</i> -Octanol	I	60	20	94 <sup>c</sup>
7	Cyclohexanol	Cl	120	12	99
8	Cyclohexanol	Br	120	12	99
9	Cyclohexanol	I	60	12	85 <sup>c</sup>
10	Benzyl alcohol	Cl	120	12	99
11	Benzyl alcohol	Br	120	12	99
12	Benzyl alcohol	I	60	12	99 <sup>c</sup>
13	Hexandiol	Cl	120	12	98 <sup>d</sup>
14	Hexandiol	Br	120	12	98 <sup>d</sup>
15	Hexandiol	I	60	12	99 <sup>c,d</sup>

<sup>a</sup> All reactions were conducted using 10 mL of ionic liquid [Hmim]X, 10 mmol of alcohols, and the ionic liquid was reused. <sup>b</sup> Isolated and detected by GC/MS. <sup>c</sup> The reaction was protected by atmosphere N<sub>2</sub>. <sup>d</sup> Dihalide.

In comparison of the reactions for secondary alcohols, cyclohexanol gave better yields than *sec*-octanol, a chain alcohol. As shown in Table 1, both chlorination and bromination of cyclohexanol gave the corresponding halides in excellent yields (99%, Entries 7 and 8). However, iodination of cyclohexanol only gave cyclohexyl iodide in 85% yield with 15% yield of dehydration product (Entry 9). With regard to *sec*-octanol, satisfactory result (94% yield) for iodination was obtained (Entry 6), while only 75% and 85% yields of *sec*-octyl chloride and *sec*-octyl bromide were achieved for chlorination and bromination, respectively (Entries 4 and 5).

However, as for halogenation of tertiary alcohol with [Hmim]X, the major product was corresponding alkene, such as that the iodination of *tert*-butanol gave only 18% yield of *tert*-butyl iodide with 82% of dehydration

products, *iso*-butene and its oligomers.

The difference of the solubility between the substrate and product is crucial for this procedure. The substrate alcohol is easily dissolved in [Hmim]X resulting in a homogeneous reaction system. Along with the progress of the reaction, the produced halide, which is insoluble in [Hmim]X, was liberated successively from the reaction system, promoting the reaction equilibrium towards the product. Meanwhile, the [Hmim]X is an ammonium salt, and its hydrophilicity is also favorable for the reaction.

The [Hmim]X, as halogenating agent and medium, was largely excessive in the reaction, and therein the part as reagent was transformed into methylimidazole after the reaction. The methylimidazole was dissolved in the product halide, so the product could not be isolated directly. By addition of equivalent of halogen acid, stirring and decanting, the methylimidazole was transformed to [Hmim]X again. Then the halide could be easily separated from the reaction mixture via simple decantation, and the ionic liquid [Hmim]X could be regenerated conveniently by removal of water. Hence, for the whole process, the reaction consumed equivalent of halogen acid and alcohol to produce halide and water.

In conclusion, the halogen acid was immobilized in methylimidazole forming IL [Hmim]X. With the properties of Brønsted acidic acid, thermal stability and negligible vapor pressure, [Hmim]X could be used as halogenating agent, acidic catalyst as well as medium for conversion of alcohol to halide. It was very convenient to prepare and reuse all the time. The procedure is very practical for the preparation of primary and secondary halides. The studies on stereochemistry of the halogenation reactions are underway.

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