

Ionic liquids as catalytic green solvents for cracking reactions

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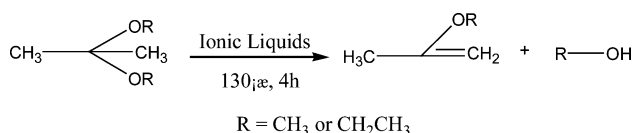
We demonstrate the use of room-temperature ionic liquids as catalysts and solvents for the cracking reaction of alkoxypropanes, eliminating the need for a volatile organic solvent and hazardous catalyst disposal.

Ionic liquids (ILs) are very attractive solvents because they have very low vapor pressure and are stable in a wide temperature range.^{1,2} Examples of their application in both reactions³ and separations⁴ have been demonstrated. The current emphasis on novel reaction media is motivated by the need for efficient methods for replacement of toxic or hazardous solvents and catalysts. The use of ionic liquids as novel reaction media may offer a convenient solution to both the solvent emission and the catalyst recycling problem.⁵ Although many types of reactions have been investigated in ionic liquids, the cracking reactions of alkoxypropanes are absent from the literature.

Alkoxypropenes are a highly valuable class of fine chemicals with applications in polymer formulations, surfactants, and drug delivery systems as well as general organic synthesis.^{6,7} They are key intermediates in the synthesis of vitamin E, vitamin A, clarithromycin and so on.⁸ Several methods are reported for the preparation of alkoxypropenes: for example, the reaction of alkynes with alcohols,⁹ pyrolysis or catalytic cracking with zeolites, aryl sulfonic acid.^{10–12} However, the employment of these methods is limited because the reaction must be carried out under severe conditions at higher pressure and temperature,^{13,14} or calls for the use of very toxic materials.¹⁵ Despite numerous attempts to overcome these drawbacks, no benign methods have appeared for the synthesis of alkoxypropenes so far. Therefore, it is important to synthesize alkoxypropenes in ionic liquids. This paper discloses the first novel catalytic method to allow the production of highly desired alkoxypropenes from the cracking reaction of alkoxypropanes in ionic liquids.

We have found that the cracking of alkoxypropanes to alkoxypropenes can be achieved with high yields in an ionic liquid system.

The cracking reactions of alkoxypropanes were investigated in several ionic liquids (Scheme 1). The choice of ionic liquids was motivated by their being the most widely used, and therefore the most widely available (see Fig. 1).



Scheme 1 Cracking reaction of alkoxypropanes.

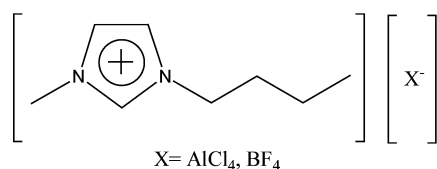


Fig. 1 Structure of the ionic liquids.

These reactions were carried out in a 100 ml volumetric flask set in a recirculating heated bath and stirred with a magnetic stir bar. In a typical reaction, alkoxypropane (0.5 mol) was added to preheated 1-butyl-3-methylimidazolium ([Bmim]) chloride–aluminium chloride (0.5 mol), and the mixture was stirred at 130 °C for several hours. During the reaction, alkoxypropene and alcohol were evolved from the surface of the reaction liquids, collected in a cold trap and analysed by gas chromatography (typical data are included in Table 1†). It should be noted that the addition of the alkoxypropane should be slow, letting the reaction take place on the surface of the ionic liquid, then most of the alcohol could be evaporated from the surface, otherwise the alcohol will react with the ionic liquid which would lead to the eventual decomposition of the ionic liquid.

The reaction appeared to be dependent on the ionic liquid anion used (ionic liquids tested included 1-alkyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium chloride–aluminium chloride) for a given temperature and time. The correlative data are listed in Table 1. It was seen that the catalytic activity was strongly affected by the anion of the ionic liquids. Good results were obtained with chloride–aluminium chloride anion. However, when tetrafluoroborate anion such as Bmim·BF₄ was used, the reaction was much slower and therefore product yields were significantly lower as compared to those obtained with chloride–aluminium chloride salts.

An important feature of these ionic liquids reactions is that there is no evidence for significant formation of ester. The ionic liquid process contrasts with the liquid cracking reactions carried out in the presence of *p*-toluenesulfonic acid where an ester is formed.

It should be noted that the temperature appeared to affect the reaction. Low temperature (< 100 °C) led to poor conversion levels. By contrast, the desired alkoxypropenes were obtained with good yields at 130 °C.

In order to investigate the influence of acids, several acidic cocatalysts were added, such as concentrated sulfuric acid (5 mol%) and solid acid. It should be noted that the addition of a proton source to an acidic chloride–aluminium chloride ionic liquid results in Brønsted superacidity of the proton.¹⁶ But the acidic cocatalyst made little difference to the outcome of the reaction.

However, the Lewis acidity affected the outcome dramatically. The Lewis acidity of these ionic liquids can be varied over a wide range by manipulating the relative amounts of organic base and AlCl₃. An AlCl₃ mole fraction less than 0.5 affords basic, *N* = 0.5

Table 1 The cracking reaction of 2,2-dimethoxypropane in ionic liquids

Entry	Solvents	<i>T</i> /°C	Conversion ^a (%)	Yield (%)
1	Bmim·AlCl ₃	130	75	70
2	Bmim·AlCl ₃	100	53	48
3	Bmim·AlCl ₃ + ^b	130	78	65
4	Bmim·BF ₄	130	9	7
5	Bmim·BF ₄ + ^b	130	35	26
6	Halohydrocarbon + ^c	200	43	34

^a Conversions after 4 hours. ^b Concentrated sulfuric acid. ^c *p*-toluenesulfonic acid.

gives neutral, and those greater than 0.5 afford acidic ionic liquids. The Lewis acidic species in such liquids is $[Al_2Cl_7]^-$, and its concentration in the liquid is a function of the mole fraction of $AlCl_3$.¹⁷ In an attempt to investigate the effect of Lewis acidity on the reaction, ionic liquids of different compositions were prepared. 2,2-Diethoxypropane and 2,2-dimethoxypropane were chosen as model substrates, and the conversions of the reactions were monitored in different ionic liquids at 130 °C. It is seen in Table 2 that with a larger N , there is a higher conversion.

The products of the reaction are all volatile compounds. Once the reaction is complete, heating is sufficient to remove products from the solvent.

The solvents can be reused up to six times, although with some loss of activity. Chloride–aluminium chloride salts showed a higher catalytic activity integrally maintained after four recyclings. The simple procedures as well as easy recovery and reuse of this novel catalytic system are expected to contribute to the development of more benign cracking reactions.

In summary, we have demonstrated the first cracking reaction of alkoxypropanes to alkoxypropenes in ionic liquids without the use of traditional volatile organic compounds (VOCs). The reactions proceed well in chloride–aluminium chloride ionic liquids and the alkoxypropenes are obtained in good yields. Further work is in progress to develop catalytic cracking reactions in ionic liquids.

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Table 2 Effect of Lewis acidity on the cracking reaction of alkoxypropanes in [Bmim]·AlCl₄ ionic liquids

N	Conversion (%) ^a	
	For 2,2-diethoxypropane	For 2,2-dimethoxypropane
0.50	12	13
0.60	44	46
0.67	69	71
0.70	72	73
0.73	73	75

^a Conversions after 4 hours.

Notes and references

† Bmim-BF₄ were synthesized and characterized following the procedures reported by Nishida *et al.*¹ Bmim-AlCl₃ was synthesized following the procedures reported by Wilkes *et al.*² The ionic liquids were dried under vacuum at 70 °C until the weight remained constant.

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