

Study on the synthesis of quaternary ammonium salts using imidazolium ionic liquid as catalyst

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Abstract

Various tetramethyl ammonium salts and *N,N,N*-trimethyl-*N*-cyclohexyl ammonium salts with different anions were synthesized efficiently by a one-step reaction. The effects of the catalyst content, reaction temperature, and reaction time on the product yield were investigated. Under similar reaction conditions, the maximum yields of tetramethyl ammonium salts decrease corresponding to the anion type of the starting ammonium salts is Br^- , Cl^- , $\text{NO}_3^- > \text{F}^-$, $\text{SO}_4^{2-} > \text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , OAc^- . For the *N,N,N*-trimethyl-*N*-cyclohexyl ammonium salts with anions such as Br^- , Cl^- , and NO_3^- , quantitative yields (>99%) can be achieved at 413 K within 8 h or at 443 K for 2 h. The yield of *N,N,N*-trimethyl-*N*-cyclohexyl ammonium acetate reaches the maximum (95.7%) at 443 K for 8 h, while the carbonate yield reaches 95.0% at 453 K for 8 h. Quantitative yield of *N,N,N*-trimethyl-*N*-cyclohexyl ammonium sulfate is obtained at 443 K for 8 h. © 2006 Elsevier B.V. All rights reserved.

Keywords: Quaternary ammonium salts; Ammonium salts; Aminium salts; Dimethyl carbonate; Ionic liquid; Catalyst

1. Introduction

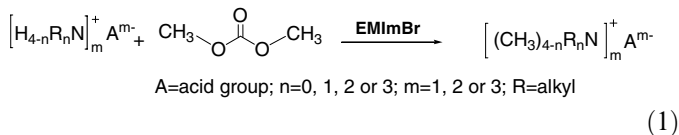
The chemistry of ionic liquids or room-temperature molten salts is at an incredibly exciting stage in its development [1–11]. Quaternary ammonium salts that have been proven to be one potential group for ionic liquids have been synthesized and studied intensively [12–20]. Generally, the initial step in the synthesis of quaternary ammonium salts is the quaternization of an amine or amide by an alkyl source, for example, alkyl halide [21,22]. The anions of those salts formed by direct quaternization as described before are quite limited. Among them, chloride and bromide anions are most commonly reported. In many cases, where it is impossible to form the desired anion directly by the quaternization reaction, an anion-exchange procedure is necessary. Alternatively, it is done by the addition of a metal salt $\text{M}^+[\text{A}]^-$ with precipitation of M^+X^- or

by displacement of the original ion by a strong acid $\text{H}^+[\text{A}]^-$ with release of H^+X^- [1,23]. It deserves attention that those salts obtained by anion-exchange are possibly contaminated with a small amount of X^- ions unless the exchange reaction is fully completed, which places particular demands on the preparative work. Thus, it would be desired to have a method by which a variety of quaternary ammonium salts with different anions could be directly synthesized via a one-step reaction.

During our study on quaternary ammonium salts, we initiated a new method for synthesizing them from ammonium or aminium salts and dimethyl carbonate via a one-step reaction, as shown in reaction (1). Since that the aminium salts can be easily prepared by the neutralization of aqueous solutions of an amine with an acid, using aminium salts as substrates allows us to design the cations and anions synchronously for the quaternary ammonium salts by choosing an appreciate amine and an acid with desired anion. On the other hand, choosing dimethyl carbonate, which is of low toxicity and environmentally benign [24], as the methyl source for the quaternization is also of importance.

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1-Ethyl-3-methyl imidazolium bromide (EMImBr) has been proved to be an efficient catalyst for this reaction in our previous work. In the current study, our efforts focus on investigating the effects of the catalyst content, reaction temperature, and reaction time on the product yield by employing ammonium salts and *N*-cyclohexylammonium salts with different anions as substrates.



2. Experimental

EMImBr was prepared according to the procedure described in literature [25]. The *N*-cyclohexylammonium salts were prepared by neutralizing cyclohexylamine with stoichiometric amount of corresponding acids, and then dried in vacuum. In a typical reaction, ammonium bromide (2.0 mmol), dimethyl carbonate (8.0 mmol), and EMImBr (0.8 mmol) were charged into a stainless steel autoclave (inside volume 3.0 mL), and then the reactor was heated to 443 K and kept at this temperature for 8 h to carry out the reaction. As no solvent was used, large amount of solid product was formed after reaction. Thereby, the pure tetramethylammonium bromide was obtained by simple filtration and washing with acetone for several times afterwards. However, if the quaternary ammonium salt was synthesized from a starting salt with an anion other than Br^- , the product purified this way is contaminated with Br^- that was from the catalyst. In the product quantification, we did not do separations for the products. The mixture was directly dissolved in D_2O to prepare a solution and analyzed on a NMR spectrometer. The calculations of the quaternary ammonium salts yields were based on the peak areas of hydrogen atoms (supporting information available).

3. Results and discussion

From Fig. 1, we can find that the yields of tetramethylammonium salts with different anions vary quite differently with the increase of the mole percent of EMImBr (based on the reaction content in the autoclave). Obviously, when the reactant is ammonium nitrate, the mole percent of EMImBr influences the product yield dramatically. The yield varies within the wide range from 25% to 96% with the mole percent of EMImBr increasing from 2.1% to 8.5%. As for ammonium chloride and ammonium bromide, no apparent variation trend in the yield is presented. The yield always remains higher than 93% within the investigated mole percent range of the catalyst. Compared to the above two salts, obvious variation can be observed in the ammonium fluoride case. The yield increases to the maximum value when the mole percent of EMImBr is 7.8% and then decreases. The amount of catalyst also influences the tetra-

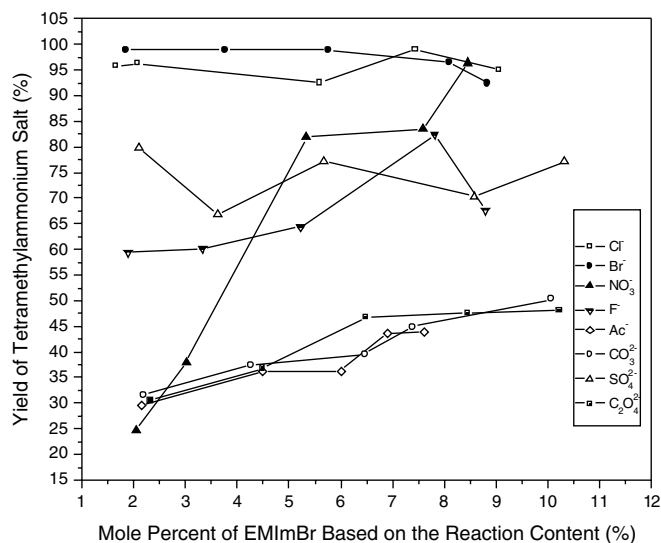


Fig. 1. The yields of tetramethylammonium salts with different anions vary with the catalyst amount (ammonium salt 2.0 mmol, dimethyl carbonate 8.0 mmol, 443 K, 8 h).

methylammonium sulfate yield, but interestingly the yield fluctuates from 67% to 80% with the increase of catalyst amount. When ammonium acetate, ammonium carbonate, or ammonium oxalate is employed as reactant, the variation trend is similar, where the yield increases gently with the increase of the mole percent of EMImBr. It can also be found that under similar reaction conditions, the maximum yields of those tetramethylammonium salts decrease corresponding to the anion type of the starting ammonium salts is Br^- , Cl^- , NO_3^- > F^- , SO_4^{2-} > $C_2O_4^{2-}$, CO_3^{2-} , OAc^- .

The influence of reaction temperature and reaction time on the quaternary ammonium salt yields is also investigated by employing *N*-cyclohexyl ammonium salts as

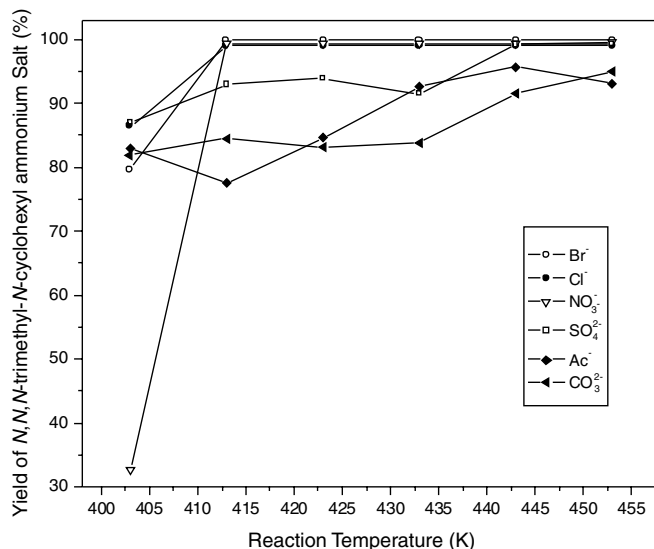


Fig. 2. The effect of temperature on the yields of *N,N,N*-trimethyl-*N*-cyclohexyl ammonium salts (ammonium salt 2.0 mmol, dimethyl carbonate 12.0 mmol, 8 h).

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