

Imidazolium salt assisted hydrolysis of 1-chloro-2,2,2-trifluoroethane

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Abstract

The use of imidazolium-based ionic liquids as promoters was found to be highly effective for the hydrolysis reaction of $\text{CF}_3\text{CH}_2\text{Cl}$ with aqueous potassium acetate to produce 2,2,2-trifluoroethanol (TFE). Among ionic liquids tested, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) showed the highest yield of TFE, over 90%, which is almost two times higher than that obtained in the absence of an ionic liquid. The integrity of imidazolium salt was maintained during the reaction, which was confirmed from the recycling studies and ^1H NMR spectroscopy.

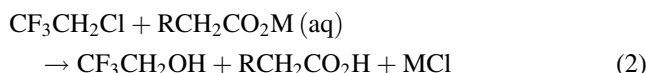
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1. Introduction

2,2,2-Trifluoroethanol (TFE) is widely used in many branches of chemistry and engineering as a working substance for heat pumps, a versatile solvent, and a raw material for further organic synthesis [1–4]. TFE is also considered to be a promising intermediate for non-chlorine containing CFC alternatives, such hydrofluorocarbon ethers, which have low global warming and zero ozone depleting potentials.

TFE can be prepared by the hydrolysis reaction of 1-chloro-2,2,2-trifluoroethane (HCFC-133a) in the presence of an aqueous alkali metal hydroxide or alkali metal salt of carboxylic acid as shown in Eqs. (1) and (2) [5,6].



where $\text{M} = \text{K}, \text{Na}$.

However, unlike the hydrolysis reaction of an alkyl halide to give the corresponding alcohol, the hydrolysis reaction of $\text{CF}_3\text{CH}_2\text{Cl}$, proceeds slowly, even at elevated temperatures, due to the presence of a highly electron withdrawing CF_3 group.

Recently, the use of ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆])

has been demonstrated as catalyst and solvent for the conversion of an alcohol to an alkyl halide [7,8]. With a hope that ionic liquids could also find a role in promoting the hydrolysis reaction of alkyl halides containing highly electron withdrawing functional groups like CF_3 , various ionic liquids were prepared and tested for their effects on the hydrolysis of $\text{CF}_3\text{CH}_2\text{Cl}$. Here we report that the use of imidazolium-based ionic liquid enhances significantly the reactivity of aqueous potassium acetate with $\text{CF}_3\text{CH}_2\text{Cl}$ to give TFE in high yield.

2. Results and discussion

To investigate the role of ionic liquids, the hydrolysis reactions of $\text{CF}_3\text{CH}_2\text{Cl}$ with aqueous potassium acetate were performed in DMF in the presence of various ionic liquids. As shown in Table 1, the hydrolysis reactions of $\text{CF}_3\text{CH}_2\text{Cl}$ produced TFE only in 42.7% yield together with the formation of 1.3% of trifluoroethyl acetate, an intermediate to TFE. Surprisingly, however, the use of small amounts of imidazolium-based ionic liquid increased the yield of TFE up to two times, depending on the types of ionic liquid employed. The ionic liquid added may act as a phase transfer catalyst, thereby facilitating the contact between $\text{CF}_3\text{CH}_2\text{Cl}$ and the potassium acetate [9,10]. The hydrolysis reaction was not affected by the variation of the cation, but strongly dependent on the type of anion. Among 1-butyl-3-methylimidazolium (bmim) salts, [bmim]Cl gave much higher yields of TFE in comparison with other imidazolium salts.

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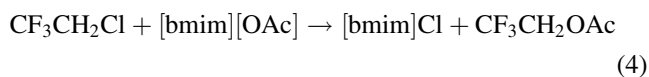
Table 1
Effect of ionic liquids on the hydrolysis of CF₃CH₂Cl with aqueous potassium acetate^a

Entry	Ionic liquid	Yield (%)	
		TFE	CF ₃ CH ₂ OAc
1	–	42.7	1.3
2	[bmim]Cl	91.3	2.6
3	[emim]Cl	87.3	2.4
4	[dmim]Cl	87.1	1.8
5	[bmim][BF ₄]	60.5	2.1
6	[bmim][OTf]	61.4	2.4
7	[bmim][PF ₆]	59.2	2.0
8 ^b	[bmim][OAc]	92.7	1.7
9	Bu ₄ NCl	67.4	2.1
10	Bu ₄ PBr	72.2	1.7

^a CF₃CH₂Cl, 50 mmol; CH₃CO₂K, 75 mmol; ionic liquid, 10 mmol; H₂O, 75 mmol; DMF, 30 ml, 180 °C, 3 h. [bmim], 1-butyl-3-methylimidazolium; [emim], 1-ethyl-3-methylimidazolium; [dmim], 1,3-dimethylimidazolium.

^b [bmim][OAc], 75 mmol. The hydrolysis reaction was conducted in the absence of CH₃CO₂K.

It is likely that [bmim]Cl reacts with potassium acetate to give [bmim][OAc], which in turn reacts with CF₃CH₂Cl and H₂O to produce TFE, as shown in Eqs. (3)–(5).



In fact, the hydrolysis reaction of CF₃CH₂Cl with aqueous [bmim][OAc] produced TFE in an high yield of 92.7% even in the absence of potassium acetate (Table 1, entry 8).

The conventional phase transfer catalyst, tetrabutylammonium chloride also exhibited some promotion effect for the hydrolysis reaction. However, it was observed that a large portion of the tetrabutylammonium chloride added was decomposed into tributylamine and butyl chloride under experimental conditions, thereby making the purification step more costly and prohibiting the recycling of tetrabutylammonium chloride [11]. Tetrabutylphosphonium bromide showed similar behavior to tetrabutylammonium chloride, decomposing into tributylphosphine and 1-bromobutane. The decomposed products, 1-chlorobutane and 1-bromobutane, were easily converted to 1-butanol by reacting with aqueous potassium acetate.

In contrast, imidazolium-based ionic liquids exhibited a remarkably high thermal stability. ¹H NMR spectra of the reaction mixtures containing [bmim][BF₄], [bmim][OTf] or [bmim]Cl (not shown here) revealed that the ionic liquid remained unchanged after the reaction. The stability of the imidazolium-based ionic liquid was confirmed further by recycling studies. Experiments were conducted using [bmim]Cl at 180 °C for 3 h, after which time the reaction mixture was filtered off to remove KCl. After removing

Table 2
Reuse of the [bmim]Cl for the hydrolysis of CF₃CH₂Cl^a

Number of reaction	Yield (%)	
	TFE	CF ₃ CH ₂ OAc
1	91.3	2.6
2	92.1	1.4
3	91.4	2.0
4	90.4	2.8
5	89.8	1.8

^a CF₃CH₂Cl, 50 mmol; CH₃CO₂K, 75 mmol; [bmim]Cl, 10 mmol; H₂O, 75 mmol; DMF, 30 ml, 180 °C, 3 h.

volatile organic compounds, CF₃CH₂Cl, TFE, acetic acid and 2,2,2-trifluoroethyl acetate, at 40 °C under vacuum, the resulting solution containing [bmim]Cl was reused for a further hydrolysis reaction with a fresh charge of CF₃CH₂Cl, potassium acetate, and water. As can be seen in Table 2, the yield of TFE remained almost unchanged even after five times of reuse, indicating that [bmim]Cl is, indeed, recyclable.

The hydrolysis reaction of CF₃CH₂Cl was influenced greatly by the amounts of [bmim]Cl used. Fig. 1 shows that the yield of TFE increased continuously with increasing amounts of [bmim]Cl up to the molar ratio of [bmim]Cl/CF₃CH₂Cl = 0.4, and remained unchanged thereafter. The formation of trifluoroethyl acetate was not affected greatly by the variation of the molar ratio of [bmim]Cl/CF₃CH₂Cl, suggesting that the reaction of trifluoroethyl acetate with water to produce TFE is an equilibrium reaction.

As can be seen in Table 3, the amount of potassium acetate also affected the hydrolysis of CF₃CH₂Cl. As the amount of potassium acetate increased from 1 to 5 molar equivalents of CF₃CH₂Cl, the yield of TFE increased from 75.7 to 97.7%.

The effect of solvents was investigated in the presence of [bmim]Cl and the results are listed in Table 4. Much higher yields of TFE were obtained in DMF, DMSO and 1-methyl-2-pyrrolidinone (NMP) than in γ -butyrolactone and CH₃CN. The lower TFE yields in γ -butyrolactone and CH₃CN can be ascribed to the low solubility of potassium acetate in these solvents. However, the promoting effect of [bmim]Cl was found to be more pronounced in γ -butyrolactone and CH₃CN when comparing TFE yields in the presence of [bmim]Cl with the one in the absence of the salt.

Table 3
Effect of CH₃CO₂K on the hydrolysis of CF₃CH₂Cl^a

Entry	Molar ratio ^b	Yield (%)	
		TFE	CF ₃ CH ₂ OAc
1	1	75.7	2.1
2	1.5	89.3	2.6
3	2	91.6	1.8
4	3	95.3	2.2
5	5	97.7	2.0

^a CF₃CH₂Cl, 50 mmol; [bmim]Cl, 10 mmol; H₂O, 75 mmol; DMF, 30 ml, 180 °C, 3 h.

^b Molar ratio: [CH₃CO₂K]/[CF₃CH₂Cl].

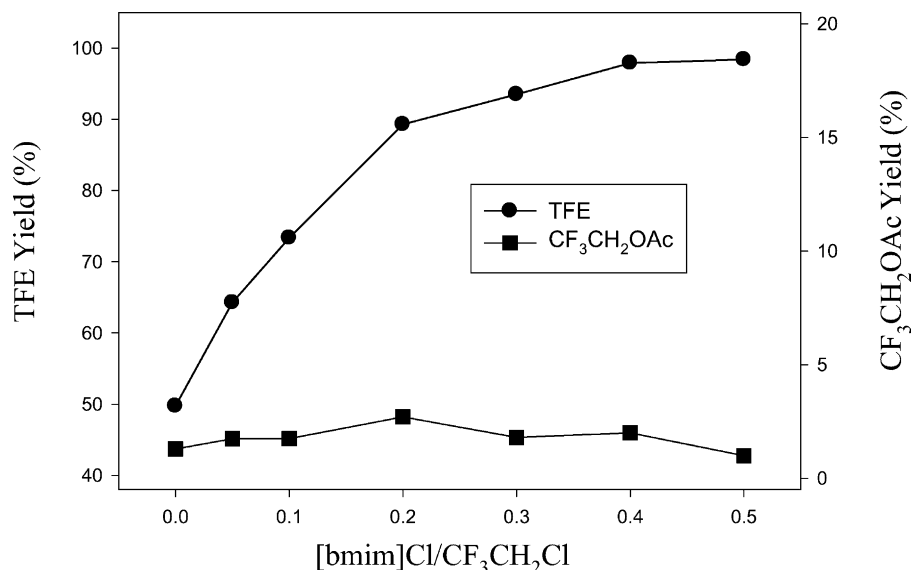


Fig. 1. Effect of molar ratio of [bmim]Cl/CF₃CH₂Cl on the hydrolysis of CF₃CH₂Cl. Conditions: CF₃CH₂Cl, 50 mmol; CF₃CO₂K, 75 mmol; H₂O, 75 mmol; DMF, 30 ml, 180 °C, 3 h.

Only trace amounts of TFE were formed in toluene and CH₂Cl₂, indicating the importance of solvent polarity in the hydrolysis reaction.

In summary, we have demonstrated the facile hydrolysis of CF₃CH₂Cl to produce TFE using aqueous potassium acetate in the presence of an imidazolium-based ionic liquid. The ionic liquids tested were stable enough to be recycled for further hydrolysis reaction.

3. Experimental

CF₃CH₂Cl (1-chloro-2,2,2-trifluoroethane) was purchased from Halocarbon Product Corp. Solvents, potassium acetate, tetrabutylammonium chloride, tetrabutylphosphonium bromide, and other reagents were obtained from Aldrich and used as received. Ionic liquids were prepared as described in the literature [12,13].

Table 4
Effect of solvent on the hydrolysis of CF₃CH₂Cl^a

Entry	Solvent	Yield (%) ^b	
		TFE	CF ₃ CH ₂ OAc
1	DMF	89.3 (42.7)	2.6 (1.3)
2	NMP ^c	80.9 (36.4)	2.3 (2.4)
3	DMSO	81.3 (35.0)	3.5 (2.7)
4	γ-Butyrolactone	51.1 (20.3)	3.7 (2.6)
5	CH ₃ CN	18.8 (5.6)	1.6 (2.0)
6	Toluene	Trace	–
7	CH ₂ Cl ₂	Trace	–

^a CF₃CH₂Cl, 50 mmol; CH₃CO₂K, 75 mmol; [bmim]Cl, 10 mmol; H₂O, 75 mmol; solvent, 30 ml, 180 °C, 3 h.

^b The numbers in parentheses are the results of the reactions conducted in the absence of [bmim]Cl.

^c NMP, 1-methyl-2-pyrrolidinone.

Hydrolysis reactions were conducted in a 100 ml stainless steel high pressure reactor with an electrical heating band. Potassium acetate (75 mmol), solvent (30 ml), H₂O (1.35 g, 75 mmol), 2-methyl pentanone (1 g, internal standard) and ionic liquid were charged into the reactor. After the mixture was cooled to 0 °C, CF₃CH₂Cl (50 mmol) was fed into the reactor through a sampling valve. The reactor was then heated to 180 °C and the reactants were stirred for 3 h. After cooling the reaction mixture to 0 °C, a sample of the liquid phase was analyzed using GC (HP 6890, FFAP, 25 m × 0.32 mm × 5 μm). The yields of TFE and CF₃CH₂OAc were determined by GC using an internal standard method. For the identification of the products, GC–MS (HP 6890N-5973 MSD) and NMR (Varian UNITYplus-300) were employed.

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