

## Stability of [Bmim]PF<sub>6</sub> as Catalyst-Solvent in Esterification Reactions

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Ionic liquids have been widely used as reaction media. However, investigations on the stability of an ionic liquid, [Bmim]PF<sub>6</sub> in the acid-catalysis reactions are scarcely reported. Taking the esterification of benzyl alcohol or cycloolefins with acetic acid as probe reactions, we investigated the effects of reaction conditions including substrates, atmosphere, water content, reaction temperature, reaction time and types of reactions on the stability of [Bmim]PF<sub>6</sub>. Results indicate that inert atmosphere, dry environment, less reactive substrates and lower reaction temperature are beneficial for avoiding the decomposition of [Bmim]PF<sub>6</sub> but are of low conversion or poor selectivity.

**Key Words:** [Bmim]PF<sub>6</sub>, Stability, Decomposition, Acid-catalysis, Esterification.

### INTRODUCTION

Stable room-temperature ionic liquids have been used as novel reaction solvents<sup>1-12</sup>. As a neutral ionic liquid, [Bmim]PF<sub>6</sub> shows wide spread applications in many reactions<sup>3-8</sup>. The thermal stability of 1-alkyl-3-methylimidazolium phosphates has been extensively studied<sup>13-18</sup>. However, vast majority of the reported data are the temperatures of the onset of degradation (weight loss) based on fast (10 or 20 °C/min) thermogravimetric analysis (TGA) scans, collected under dry nitrogen. The decomposition reaction is too slow to allow equilibration at certain temperature. The heat transfer in the ionic liquid is slow, hence the temperature in the ionic liquid may lag behind. When [Bmim]PF<sub>6</sub> is used as a solvent or a catalyst in a reaction, the substrates, atmosphere, reaction temperature and reaction time could significantly affect the stability of the ionic liquid. Therefore, results obtained under different reaction conditions are different. So far, little is known about the influence of reaction conditions on the stability of [Bmim]PF<sub>6</sub> ionic liquid in acid-catalysis reactions.

Recently, Salunkhe<sup>19</sup> and Shen *et al.*<sup>20</sup>, reported that the neutral ionic liquid [Bmim]PF<sub>6</sub> is an efficient acidic catalyst in Pechmann condensation and *t*-butylation of phenol reactions. It is generally recognized that water is able to enhance the rate of the decomposition of [Bmim]PF<sub>6</sub>. It has been reported that HF might be present in [Bmim]PF<sub>6</sub> due to the relatively facile decomposition of PF<sub>6</sub> anion in the presence of a trace amount of water<sup>18</sup>. Therefore, HF generated from the ionic liquid may be responsible for the acceleration of the reaction. This prompts us to investigate the activity and stability of [Bmim]PF<sub>6</sub> in the

esterification reaction, which is known as a typical acid-catalysis reaction. It should be emphasized that room temperature ionic liquids generally contain varying degrees of water, unless rigorous drying protocols and inert environments are employed. Water is still present in [Bmim]PF<sub>6</sub> as we studied, even after a moderate drying procedure. In this work, [Bmim]PF<sub>6</sub> is prepared and denoted as "dry" ionic liquid, water content is about 0.02 %<sup>15</sup>. Our interest in the stability of [Bmim]PF<sub>6</sub> initially is aroused by the unusual behaviours under different conditions (*e.g.*, water content, reaction temperature). It is further enhanced when it was found that reaction type and the environment also have a significant influence on the stability of [Bmim]PF<sub>6</sub> ionic liquid in the probe esterification reactions.

### EXPERIMENTAL

All the solvents and chemicals used were commercially available and used without further purification unless otherwise specified. Karl-Fischer analysis was used to measure the amount of water in the reactant material. The Karl-Fischer analyzer used was a 787 KF Titrino metrohm water detecting instrument.

**Preparation of [Bmim]PF<sub>6</sub>:** 1-Butyl 3-methylimidazolium chloride (5.22 g, 0.03 mol) was dissolved in 100 mL of acetone in a 250 mL round bottom flask equipped with a stirrer. Then KPF<sub>6</sub> (5.52 g, 0.03 mol) was added and the solution was stirred for 24 h at room temperature. The resulting precipitate of KCl was filtered and acetone was removed under reduced pressure to obtain a yellow coloured liquid, which is denoted as "dry" ionic liquid.

**Procedure:** In a typical reaction, benzyl alcohol (1.05 g), acetic acid (1.20 g) and 1 g of ionic liquid were added into a 50 mL three-necked round bottom flask which was immersed in an oil bath and fitted with a water cooled condenser. In the next reaction, cyclic olefins (10 mmol), acetic acid (1.20 g) and 1 g of ionic liquid were introduced into a 90 mL autoclave and allowed to react. The identities of the products were confirmed by GC-MS. After the reaction, the ionic liquid could be recovered by extraction using Et<sub>2</sub>O and heat treatment under vacuum (80 °C, 5 mmHg) for 1 h.

## RESULTS AND DISCUSSION

Table-1 shows the results of the esterification of benzyl alcohol with acetic acid conducted in [Bmim]PF<sub>6</sub>. It is clear that the influence of reaction temperature on the stability of [Bmim]PF<sub>6</sub> is rather significant (entries 1-5). At 25 or 40 °C, reaction hardly takes place and the appearance of the reaction mixture remains unchanged. When the reaction was performed at 60 °C for 4 h, white fumes and white solid was observed and the reaction mixture appears strong acidic. Obviously, [Bmim]PF<sub>6</sub> was unstable and decomposed. The GC data show 98 % alcohol conversion and 100 % selectivity to the corresponding ester. The white fumes consist of HF and other species. Rogers *et al.*<sup>18</sup> reported that the white solid was 1-butyl-3-methylimidazolium fluoride monohydrate [Bmim]F·H<sub>2</sub>O, which was characterized by the identification of single crystal X-ray diffraction, as a crystalline decomposition product from hydrolytic degradation of [Bmim]PF<sub>6</sub>. It should be noted that although the mass loss in [Bmim]PF<sub>6</sub> is difficult to quantitize, the changes in its appearance indicates moderate to high level of degradation. When the temperature was enhanced to 80 or 100 °C, the same phenomena indicating the decomposition of [Bmim]PF<sub>6</sub> was observed within a shorter reaction time. Furthermore, the main products were ethers instead of esters. As we known, stronger acidity leads to the ethers (entries 4 and 5). Further investigations show that prolonged reaction

time increases the decomposition of [Bmim]PF<sub>6</sub> (entry 6) and the presence of N<sub>2</sub> atmosphere (entries 7 and 8) could avoid the decomposition of [Bmim]PF<sub>6</sub>. As our expected, the addition of water promotes whereas the addition of 3A molecular sieve (M.S.) suppresses the decomposition of the [Bmim]PF<sub>6</sub> (entries 9-12).

The FTIR spectra of the fresh and the recovered [Bmim]PF<sub>6</sub> (Table-1, entries 2 and 4) are shown in Fig. 1. The recovered ionic liquid (Fig. 1b) after 4 h reaction at 40 °C has a similar pattern as the prepared, whereas the ionic liquid (Fig. 1c) after 4 h reaction at 80 °C shows a big difference with the fresh one (Fig. 1a) and the characteristic peak of [Bmim]PF<sub>6</sub> could not be observed. The results elucidate that most of the ionic liquid has been decomposed in this case.

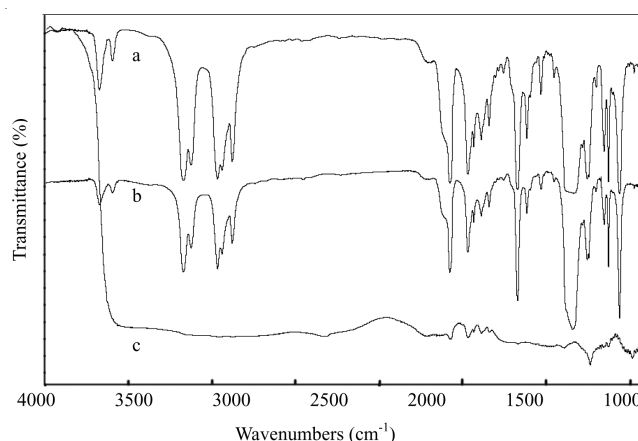
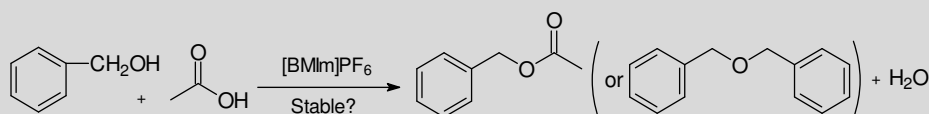


Fig. 1. FT-IR spectra of (a) fresh [Bmim]PF<sub>6</sub>; (b) recovered [Bmim]PF<sub>6</sub> (Table-1, entry 2, reaction at 40 °C after 4 h); (c) recovered [Bmim]PF<sub>6</sub> (Table-1, entry 4, reaction at 80 °C after 4 h)

The esterification reaction of dicyclopentadiene with acetic acid, in which no water produced, was also conducted in [Bmim]PF<sub>6</sub> (Table-2). It is also found that reaction time, reaction temperature, water content and atmosphere play

TABLE-1  
REACTION OF BENZYL ALCOHOL WITH ACETIC ACID IN [Bmim]PF<sub>6</sub>



Entry	Temp. (°C)	Time (h)	Atmosphere	[Bmim]PF <sub>6</sub> <sup>a</sup>	Appearance <sup>b</sup>	pH Test	Conc. <sup>c</sup> (%)	Sel. (%)	
								Ester	Ether
1	25	4	Air	Dry	A	Neutral	–	–	–
2	40	4	Air	Dry	A	Neutral	2	100	–
3	60	4	Air	Dry	B	Acidic	98	100	–
4	80	4	Air	Dry	B	Acidic	100	8	92
5	100	4	Air	Dry	B	Acidic	100	2	98
6	40	24	Air	Dry	B	Acidic	95	100	–
7	60	4	N <sub>2</sub>	Dry	A	Neutral	–	–	–
8	80	4	N <sub>2</sub>	Dry	B	Acidic	100	13	87
9	25	4	Air	1.0 mL H <sub>2</sub> O	A	Neutral	3	100	–
10	40	4	Air	1.0 mL H <sub>2</sub> O	B	Acidic	90	100	–
11	80	4	Air	1 g 3A M.S.	A	Neutral	6	100	–
12	100	2	Air	1 g 3A M.S.	A	Neutral	10	100	–

a: Dry: a water amount of about 190 ppm; 1 g 3A MS: a water amount of about 85 ppm. They were measured by Karl-Fischer analysis. b: A: colorless liquid; B: white fume and white solid were produced. c: Conversion of benzyl alcohol.

TABLE-2  
REACTION OF CYCLOOLEFINS WITH ACETIC ACID IN [Bmim]PF<sub>6</sub>



Entry	Temp. (°C)	Time (h)	Cycloolefins	Atmosphere	[Bmim]PF <sub>6</sub> <sup>a</sup>	Appearance <sup>b</sup>	pH test	Conc. (%) <sup>c</sup>
1	40	4	Dicyclopentadiene	Air	Dry	A	Neutral	–
2	60	4	Dicyclopentadiene	Air	Dry	B	Acidic	85
3	80	4	Dicyclopentadiene	Air	Dry	B	Acidic	100
4	40	24	Dicyclopentadiene	Air	1.0 mL H <sub>2</sub> O	A	Neutral	–
5	60	4	Dicyclopentadiene	N <sub>2</sub>	Dry	A	Neutral	6
6	80	4	Dicyclopentadiene	N <sub>2</sub>	Dry	B	Acidic	77
7	80	4	Dicyclopentadiene	Air	1g 3A M.S.	C	Weak acidic	18
8	100	4	Cyclohexene	Air	1.0 mL H <sub>2</sub> O	A	Neutral	–

a: Dry: a water amount of about 190 ppm; 1 g 3A M.S.: a water amount of about 85 ppm. They were measured by Karl-Fischer analysis. b: A: colorless liquid; B: white fume and white solid were produced, C: no obvious white fume or white solid were observed but the color of the reaction mixture turned to dark. c: the selectivity to the corresponding ester are all > 99 %.

important roles in the stability of the studied ionic liquid and the tendencies are similar with the esterification of benzyl alcohol (entries 1-7). Especially, when less active substrate cyclohexene was used as alkyl donor (entry 8), no product could be distinctly detected by GC/MS analysis and the recovered ionic liquid remains unchanged.

The experiments provide more realistic assessment of the stability of [Bmim]PF<sub>6</sub> in esterification reaction, however, such experiments cannot be reduced to a single number that reflects the stability. Also noteworthy is the investigation of ionic liquids under reaction conditions is in its infancy and the affecting factors are much more varied and complex than what is possible with simple TGA scans.

### Conclusion

In summary, the stability of [Bmim]PF<sub>6</sub> as catalyst-solvent in acid-catalysis reactions is very different from that determined by other techniques such as TGA. Taking the esterification of benzyl alcohol or cycloolefins with acetic acid as probe reactions, it is found that reaction conditions including substrates, atmosphere, water content, reaction temperature, reaction time and types of reactions show significant effects on the stability of [Bmim]PF<sub>6</sub>. Inert atmosphere, dry environment and/or less reactive substrates and lower reaction temperature are beneficial for avoiding the decomposition of [Bmim]PF<sub>6</sub> but are of low conversion or poor selectivity.

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