Pergamon

Tetrahedron Letters 43 (2002) 5381–5383

TETRAHEDRON
LETTERS

An improved preparation of 1,3-dialkylimidazolium tetrafluoroborate ionic liquids using microwaves[†]

Vasudevan V. Namboodiri and Rajender S. Varma*

Clean Processes Branch, National Risk Management Research Laboratory, US Environmental Protection Agency, MS 443,
26 W. Martin Luther King Drive, Cincinnati, OH 45268, USA

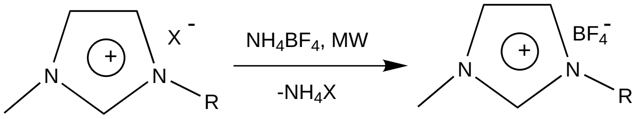
Received 6 June 2002; accepted 7 June 2002

Abstract—An efficient microwave protocol is described for the preparation of room temperature ionic liquids consisting of alkyl imidazolium cations bearing tetrafluoroborate as anions. © 2002 Elsevier Science Ltd. All rights reserved.

Room temperature ionic liquids (RTILs) are molten salts that are comprised of an array of heterocyclic cations[1] and various anions. They have received extraordinary attention due to their potential commercial applications in electrochemistry,[2] heavy metal ion extraction,[3] phase transfer catalysis and polymerization,[4] solubilization of materials[5] and as substitutes for common volatile organic solvents[6] including enzymatic reactions.[7] A vast majority of these ionic salts are stable solvents for a wide range of organic and inorganic materials and provide a polar alternative to biphasic systems. Other important attributes of these ionic liquids include negligible vapor pressure, potential for recycling, compatibility with various organic compounds and organometallic catalysts,[8] and ease of separation of products from reactions.

An efficient microwave-assisted preparation of 1,3-dialkylimidazolium halides has reduced the reaction time from several hours to a few minutes in a process that avoids the use of a large excess of alkyl halides/organic solvents as the reaction medium.[9] In view of the emerging importance of the ionic liquids as reaction media[10] and our general interest in microwave-assisted chemical processes,[8,11] we envisioned expediting the synthesis of ionic liquids bearing tetrafluoroborate

Table 1. Optimization of MW power level for the preparation of dialkyl imidazolium tetrafluoroborates



$[C_4MIM]Cl$ (mmol)	NH_4BF_4 (mmol)	MW-power (W)	MW-time (s)	Yield (%)
1	1.05	240	30+30+30+30+30	85
1	1.05	360	30+30+30+30+30	90
1	1.05	480	30+30+30+30+30	84[a]
1	1.05	240	30+15+15+15+15	81
1	1.05	360	30+15+15+15+15	84
1	1.05	480	30+15+15+15+15	90
20	21	360	60+60+30+30+30	91

[a] Partial decomposition.

Keywords: ionic liquids; 1,3-dialkylimidazolium tetrafluoroborates; microwave heating; solvent-free.

* Corresponding author. Fax (513)-569-7677; e-mail: varma.rajender@epa.gov

[†] Presented, in part, at the 223rd National ACS meeting, *Abst. I&EC 151*, Orlando, FL, 7–11 April 2002.

PII: S0040-4039(02)01075-4

anions using microwave (MW) irradiation under solvent-free conditions. Herein, we report an efficient method for the preparation of RTILs that involves exposing a mixture of imidazolium halides and ammonium tetrafluoroborate to microwaves in an unmodified household MW oven. This solvent-free approach requires only a few minutes of reaction time, in contrast to the several hours needed using conventional methods that require a large excess of organic solvent or expensive silver salts or aqueous tetrafluoroboric acid, which is difficult to handle.[12] A general schematic representation and the preparation of 1,3-dialkylimidazolium tetrafluoroborates are depicted below in Tables 1 and 2.

For these studies, a newer household MW oven (Panasonic NN-S740WA-1200) equipped with inverter technology that provides a better control of the MW power to a desired level was used. Initially, the effect of MW power level on the formation of 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4MIM][BF_4]$) from 1-butyl-3-methylimidazolium chloride ($[C_4MIM]Cl$) and ammonium tetrafluoroborate as reactants was examined (Table 1). The formation of ionic liquid could be monitored visibly in the reaction when the ammonium tetrafluoroborate crystals reacted and formed fine precipitates of ammonium halide. At elevated power levels, a partial decomposition or charring of the ionic liquid occurred possibly due to the localized overheating of ionic liquid, resulting in lower yields. To circumvent this problem, the reactions were conducted with intermittent heating at a moderate power level with mixing to obtain better yields and cleaner product formation. After the initial exposure for 30 s to MWs at power level P3 (360 W, bulk temperature ~80–110°C) the reaction mixture was taken out, mixed for 10 s and then heated at the same power level for an additional 30 s. This sequence was repeated until the formation of fine precipitate of ammonium halide ensued. At this stage, dry acetone was added, the ammonium salts were simply removed by filtration and the product was isolated by removal of acetone from the filtrate and then drying under vacuum at 60°C. The ionic liquids with alkyl chain length hexyl or higher are insoluble in water and can be purified very easily by washing with water followed by vacuum drying. The TGA and DSC analyses show that these ionic liquids are thermally stable up to 350°C and the spectral characteristics are in accordance with the literature reports.[12,13] The present method is general in nature and is suitable for the preparation of ionic liquids bearing alkyl chains of varying lengths (C_n) or different halides. The MW-assisted syntheses of a series of ionic liquids and comparison of these protocols with the corresponding preparations using conventional heating (oil bath at 90°C) are summarized in Table 2. Most of the halides used in this study are stable enough and are converted efficiently to the corresponding tetrafluoroborates under MW irradiation conditions. The ionic liquids comprised of longer carbon chains such as the octyl group required extended reaction time. The tetrafluoroborates obtained from the corresponding iodides are slightly colored and resisted complete decoloration even after repeated washings. The main advantages of this high yield method are use of a kitchen MW oven, faster generation of products, higher conversion and easier work up procedure compared to methods employing aqueous tetrafluoroboric acid.

In a representative reaction procedure, ammonium tetrafluoroborate (1.05 mmol) and butylimidazolium chloride (1.0 mmol) were placed in a test tube, mixed thoroughly using a vortex mixer and the contents were heated intermittently in the MW oven at power P3 corresponding to 360 W (30 s irradiation with 10 s mixing) until the dissolution of ammonium tetrafluoroborate crystals was completed and the formation of fine white precipitate of ammonium halide occurred. The bulk temperature recorded was in the range 80–110°C. The resulting ionic liquid $[C_4MIM][BF_4]$ was then cooled to room temperature, dry acetone was added and ammonium chloride and the unreacted starting materials were removed by filtration. Additional purification, if required, can be accomplished using the procedures described by Seddon et al.[12] The product was then dried under vacuum at 80°C to afford 1-butyl-3-methylimidazolium tetrafluoroborate (90%), ^{1}H NMR (250 MHz; acetone-d_6), δ_H: 0.98 (t, CH_3), 1.40 (m, CH_2), 1.95 (m, CH_2), 4.04 (s, N-CH_3), 4.30 (m, N-CH_2), 7.61 (s, NCH), 7.66 (s, NCH), 8.81 (s, N(H)CN); ^{13}C NMR δ_C 12.89 (t, CH_2), 19.02 (m, CH_3), 31.51 (m, CH_2), 35.86 (N-CH_2), 54.11 (N-CH_3), 122.40 (NCH), 123.83 (NCH), 136.61 (N(H)CN); ^{19}F NMR had a singlet at δ −152.80. The same experiment conducted via conventional heating (oil bath at 90°C for 3 h) afforded 28% of $[C_4MIM][BF_4]$. An experiment, on a

Table 2. Preparation of 1,3-dialkyl imidazolium tetrafluoroborates using microwaves[a]

Substrate (1 mmol)	MW-power (W)	MW-time (s)	Yield% MW (oil bath)
$[C_4MIM]Cl$	360	30+30+30+30+30	90 (28)
$[C_4MIM]Br$	360	30+30+30+30+30	92 (36)
$[C_4MIM]I$	240	30+30+30+30+30+30	92[b]
$[i\text{-}C_4MIM]Br$	360	30+30+30+30+30	91
$[C_6MIM]Cl$	360	30+30+30+30+30	89
$[C_6MIM]Br$	360	30+30+30+30+30	88
$[C_7MIM]I$	240	30+30+30+30+30+30	88[b]
$[C_8MIM]Cl$	360	60+60+30+30+30	89 (35)
$[C_8MIM]Br$	360	60+60+30+30+30	88

[a] NH_4BF_4 (1.05 mmol).

[b] Colored even after several washings but the NMR spectrum is in accord with the structure.

relatively large scale, starting from ammonium tetrafluoroborate (21 mmol) and [C_4MIM]Cl (20 mmol) afforded [C_4MIM][BF_4] (91%).

In conclusion, an expeditious MW-assisted protocol is developed for the synthesis of 1,3-dialkylimidazolium tetrafluoroborates using an unmodified household MW oven that is very practical and may provide a much faster and efficient route to this useful class of ionic liquids.

Disclaimer—This article was authored by U.S. Government employees as part of their official duties. In view of Section 105 of the Copyright Act (17 U.S.C. Section 105) the work is not subject to U.S. copyright protection. The views expressed in this article are those of the individual authors and do not necessarily reflect the views and policies of the U.S. Environmental Protection Agency. The use of trade names does not imply endorsement by the U.S. Government.

Acknowledgements

We thank Mr. Ballard Mullins for the TGA and DSC analyses. V.V.N. is a postgraduate research participant at the National Risk Management Research Laboratory administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the US Department of Energy and the US Environmental Protection Agency.

References

1. Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
2. Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.
3. (a) Visser, A. E.; Swatloski, R. P.; Rogers, R. D. *Green Chem.* **2000**, *1*, 1; (b) Visser, A. E.; Swatloski, R. P.; Reichert, W. M.; Mayton, R.; Sheff, S.; Wierzbicki, A.; Davis, J. H.; Rogers, R. D. *Chem. Commun.* **2001**, 135.
4. Carmichael, A. J.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237.
5. Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
6. Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965.
7. (a) Cull, S. G.; Holbrey, J. D.; Vargas-Mora, V.; Seddon, K. R.; Lye, G. J. *Biotechnol. Bioeng.* **2000**, *69*, 227; (b) Sheldon, R. A.; Maderia Lau, R.; Sorgedrager, M. J.; van Rantwijk, F.; Seddon, K. R. *Green Chem.* **2002**, *4*, 147.
8. (a) Holbrey, J. D.; Seddon, K. R. *Clean Products Processes* **1999**, *1*, 223; (b) Huddleston, J. G.; Willauer, H. D.; Swatloski, R. P.; Visser, A. E.; Rogers, R. D. *Chem. Commun.* **1998**, 1765.
9. (a) Varma, R. S.; Namboodiri, V. V. *Chem. Commun.* **2001**, 643; (b) Varma, R. S.; Namboodiri, V. V. *Pure Appl. Chem.* **2001**, *73*, 1309.
10. (a) Freemantle, M. *Chem. Eng. News* **2001**, *1 January*, 21; (b) Freemantle, M. *Chem. Eng. News* **2000**, *15 May*, 37.
11. (a) Varma, R. S. In *Green Chemistry: Challenging Perspectives*; Tundo, P.; Anastas, P. T., Eds.; Oxford University Press: Oxford, 2000; pp. 221–244; (b) Varma, R. S. *J. Heterocyclic Chem.* **1999**, *35*, 1565; (c) Varma, R. S. *Green Chem.* **1999**, *1*, 43; (d) Varma, R. S. *Pure Appl. Chem.* **2001**, *73*, 193.
12. Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc., Dalton. Trans.* **1999**, 2133.
13. (a) Wilkes, J. S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1992**, 965; (b) Fuller, J.; Carlin, R. T.; Osteryoung, R. A. *J. Electrochem. Soc.* **1997**, *144*, 3881; (c) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Brocker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156.