An expeditious solvent-free route to ionic liquids using microwaves

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A microwave-assisted preparation of a series of ambient temperature ionic liquids, 1-alkyl-3-methylimidazolium (AMIM) halides, that proceeds *via* efficient reaction of 1-methylimidazole with alkyl halides/terminal dihalides under solvent-free conditions, is described.

In addition to their role in electrochemistry[1] (electrolytes for battery, fuel cells *etc.*), heavy metal ion extraction,[2] phase transfer catalysis, and polymerization,[3] ionic liquids are emerging as a set of new green solvents, mainly as a replacement for conventional volatile organic solvents.[4] The use of a large excess of conventional volatile solvents required to run a chemical reaction is of ecological and economic concern. Ambient temperature ionic liquids encompassing 1,3-dialkylimidazolium cations (**A**) have shown great promise as an attractive alternative to conventional solvents.[5] The important properties of these ionic liquids are low volatility, negligible vapor pressure, ease of handling, accelerated reaction rates, potential for recycling, and compatibility with various organic compounds and organometallic catalysts.[6] Also, the products from reactions conducted in ionic liquids can be extracted very easily using various organic solvents. The preparation of 1,3-dialkylimidazolium halides *via* the conventional heating method in refluxing solvents requires several hours to afford reasonable yields and also uses a large excess of alkylhalides/organic solvents as the reaction medium.[7] In view of the emerging importance of the ionic liquids as reaction media[8] and our general interest in MW-assisted chemical processes,[9] we decided to explore the synthesis of ionic liquids using microwave (MW) irradiation under solvent-free conditions. Herein, we report an efficient method for the preparation of ionic liquids using microwave irradiation as the energy source by simple exposure of neat reactants in open containers to microwaves using an unmodified household MW oven. This solvent-free approach requires only a few minutes of reaction time in contrast to several hours needed under conventional heating conditions which uses an excess of reactants.

In an unmodified household MW oven it is not possible to vary the MW power. The reduction in power level simply entails that it operates at its full power but for a reduced period of time. A recently introduced household MW oven (Panasonic) equipped with inverter technology provides a realistic control of the microwave power to a desirable level. We examined the effect of microwave power on a set of reactions using 1-butyl bromide (1-BuBr) and 1-methylimidazole (MIM) as reactants (Table 1).† Upon microwave irradiation, the ionic liquid starts forming which increases the polarity of the reaction medium thereby increasing the rate of microwave absorption. The formation of ionic liquid could be monitored visibly in the reaction when it turns from clear solution to opaque and finally clear. It is observed that at elevated power levels evaporation of alkyl halide and partial decomposition/charring of the ionic liquid occurs possibly due to the localized heating of the ionic liquid, which eventually results in lower yields. To circumvent this problem, we conducted the reaction with intermittent heating and mixing at a moderate power level to provide better yields and cleaner ionic liquid formation.‡ After the first irradiation for 30 s at 240 W (~ bulk temperature 70–100 °C) the homogeneity of the reaction mixture changes due to formation of a small amount of ionic liquid. The reaction mixture is then taken out, mixed again for 10 s and then heated at the same power level for an additional 15 s. This step is repeated until the formation of a clear single phase ionic liquid product. At this stage, the unreacted starting materials are removed by washing with ether and the product dried under vacuum at 80 °C.

A series of ionic liquids prepared by microwave heating and the protocol is then compared with the similar preparation using conventional heating (oil bath at 80 °C). The comparative results are summarized in Table 2. Most of the halides used in this study have higher boiling points and are converted efficiently to ionic liquids under microwave irradiation. The relatively less reactive and low boiling reactants such as butyl chloride and 2-bromobutane (entries 1 and 4, Table 2) incurred loss due to evaporation and hence are used in excess quantity. The reactivity trend of halides is found to be in the order $I^- > Br^- > Cl^-$. Due to the high reactivity of the iodides excellent yields are obtained in all cases with minimum exposure time. The conventional methods reported in the literature generally use a large excess of alkyl halide–THF as solvents. The present method is eco-friendly and uses only stoichiometric amounts of reactants.

The preparation of ionic liquids bearing polycations are of recent synthetic interest.[10] We have prepared novel dicationic compounds (**B**) utilizing alkyl dihalides. The butyl and hexyl dicationic salts (entries 11–15, Table 2) are solids at rt. The corresponding octyl analogues with bromide/chloride as the anions are viscous liquids (entries 16 and 17, Table 2) whereas the iodo compound (entry 18, Table 2) is a solid. From the NMR data the dicationic salts generated from chloro and bromoalkanes (entries 11, 13, 14 and 16, Table 2) are slightly contaminated with the corresponding monocationic intermediate (< 5%). However, the diiodoalkanes, being reactive, afforded pure products. The purity of ionic salts prepared *via* microwave heating are found to be superior to those prepared *via* conventional heating methods, presumably due to inefficient mixing in the later, once the solid product (**B**) begins to form.§

The thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) data show that all ionic liquids

Table 1 Optimization of reaction conditions for preparation of ionic liquid using microwaves

No.	1-BuBr/ mmol	MIM/ mmol	MW-Power/W	Time/s	Yield (%)
1	1	1	120	60	42
2	1	1	120	120	62
3[a]	1	1	240	120	78
4[a]	1	1	360	60	76
5[a]	1	1	360	60	76
6	1	1	240	30 + 15 + 15 + 15	81
7[b]	1.1	1	240	30 + 15 + 15 + 15	86
8[b]	1.2	1	240	30 + 15 + 15 + 15	86

[a] Partial decomposition occurred at high power or extended irradiation time. [b] The reaction mixture was thoroughly mixed on a vortex mixer prior to irradiation.

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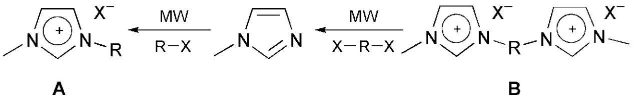
Table 2 Preparation of ionic liquids based on alkylimidazolium halides



Where X = Cl, Br, I

Entry	Alkylhalide (RX)	RX-mmol	MIM-mmol	MW-Time/s	Yield[a] (%)	Yield[b] (%) (time/h)
1	1-chlorobutane	4	2	30 + 15 + 15 + 15 + 15	76	50 (5)
2	1-bromobutane	2.2	2	30 + 15 + 15 + 15	86	76 (5)
3	1-iodobutane	2.2	2	30 + 10 + 10 + 10	92	93 (3)
4	2-bromobutane	4	2	30 + 15 + 15 + 15 + 15	71	61 (5)
5	1-chlorohexane	2.2	2	30 + 15 + 15 + 15 + 15	81	53 (5)
6	1-bromohexane	2.2	2	30 + 15 + 15 + 15	89	78 (5)
7	1-iodohexane	2.2	2	30 + 10 + 10 + 10	93	89 (3)
9	1-iodoheptane	2.2	2	30 + 10 + 10 + 10	94	95 (3)
10	1-bromooctane	2.2	2	30 + 15 + 15 + 15	91	73 (5)
11	1,4-dibromobutane	1	2.2	30 + 15 + 15 + 15	81	76 (5)
12	1,4-diiodobutane	1	2.2	15 + 15 + 10 + 10	91	89 (3)
13	1,6-dichlorohexane	1	2.2	30 + 15 + 15 + 15 + 15	82	56 (5)
14	1,6-dibromohexane	1	2.2	30 + 15 + 10 + 10	92	72 (5)
15	1,6-diiodohexane	1	2.2	15 + 15 + 10 + 10	85	97 (3)
16	1,8-dichlorooctane	1	2.2	30 + 15 + 15 + 15 + 15	78	72 (5)
17	1,8-dibromooctane	1	2.2	30 + 15 + 15 + 15	92	76 (5)
18	1,8-diiodooctane	1	2.2	15 + 15 + 10 + 10	94	93 (3)

[a] Using MW at power 240 W. [b] Using alternative heating method (oil bath at 80 °C). Entry, mp; 11, 67–69 °C; 12, 110–112 °C; 13, 85–87 °C; 14, 112–116 °C; 15, 149–150 °C; 18, 120–123 °C.

(Table 2) are pure and are free of any starting materials. These studies also establish that the compounds are thermally stable up to 280 °C and then start decomposing with complete decomposition occurring above 300 °C.¶

In conclusion, a solvent-free MW-assisted protocol is developed for the synthesis of ionic liquids in open containers using an unmodified household microwave oven. Essentially, the ionic liquids can be generated *in situ* and subsequent reactions conducted in the same pot.

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Notes and references

† In a typical reaction, 1-bromobutane (2.2 mmol) and MIM (2 mmol) are placed in a test tube, mixed thoroughly on a vortex Mixer (Fisher, Model 231) and the mixture is heated intermittently in an unmodified household MW oven (Panasonic NN-S740WA-1200W) at 240 W (30 s irradiation with 10 s mixing) until a clear single phase is obtained. The bulk temperature recorded is in the range 70 to 100 °C. The resulting ionic liquid is then cooled, washed with ether (3 × 2 mL) to remove unreacted starting materials and product dried under vacuum at 80 °C to afford 86% of 1-butyl-3-methylimidazolium bromide, ^{1}H NMR (250 MHz; D_2O), δ_H: 0.72 (t, CH_3), 1.15 (m, CH_2), 1.81 (m, CH_2), 3.71 (s, N-CH_3), 4.09 (m, N-CH_2), 7.38 (s, NCH), 7.43 (s, NCH), 8.7 (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), 49.51 (N-CH_3), 122.40 (NCH), 123.73 (NCH), 136.21 (N(H)CN). An experiment on a relatively large scale (22 mmol of 1-bromobutane and 20 mmol of MIM) afforded 87% yield.

‡ There are commercial microwave devices available that provide adequate mixing and control of reaction parameters such as temperature, pressure *etc.* For description see details at sites: http://www.cem.com; http://www.microcure.com and http://www.personalchemistry.com

§ The NMR spectra of the samples are recorded on a Brucker 250 MHz spectrometer using D_2O as solvent and $CD_3OD/CDCl_3$ as the standards. The new compounds are characterized by elemental analyses, ^{1}H and ^{13}C NMR. The data for a representative dicationic compound, entry 15, δ_H (250 MHz; D_2O) 1.29 (m, CH_2), 1.82 (m, CH_2), 3.71 (s, N-CH_3), 4.14 (m, N-CH_2), 7.38 (s, NCH), 7.43 (s, NCH), 8.7 (s, NC (H)N); δ_C: 24.99 (t, CH_2), 29.17 (m, CH_3), 36.18 (N-CH_2), 49.57 (N-CH_3), 122.35 (NCH), 123.64 (NCH), 135.97 (NC (H)N), (Calc. for $C_{14}H_{24}N_4I_2$: C, 33.49; H, 4.82; N, 11.16; Found. C, 33.69; H, 4.93; N, 11.68%).

¶ The TGA of the sample is performed by heating from 25 to 500 °C at a rate of 10 °C min^{-1} and DSC is conducted from 25 to 450 °C at a heating rate of 10 °C min^{-1}.

1 J. S. Wilkes, J. A. Levinsky, R. A. Wilson and C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263.
2 S. Dai, Y. H. Ju and C. E. Barnes, *J. Chem. Soc., Dalton Trans.*, 1999, 1201; A. E. Visser, R. P. Swatloski and R. D. Rogers, *Green Chemistry*, 2000, **2**, 1; A. E. Visser, R. P. Swatloski, W. M. Reichert, R. D. Rogers, R. Mayton, S. Sheff, A. Wierzbicki and J. H. Davis, Jr., *Chem. Commun.*, 2001, 135.
3 A. J. Carmichael, D. M. Haddleton, S. A. F. Bon and K. R. Seddon, *Chem. Commun.*, 2000, 1237.
4 T. Welton, *Chem. Rev.*, 1999, **99**, 2701.
5 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965.
6 J. D. Holbrey and K. R. Seddon, *Clean Products and Processes*, 1999, **1**, 223; J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765.
7 P. Volker, W. Bohm and W. A. Herrmann, *Chem. Eur. J.*, 2000, **6**, 1017.
8 For the recent commentary on the general utility of ionic liquids see: M. Freemantle, *Chem. Eng. News*, 1 January, 2001, p. 21; M. Freemantle, *Chem. Eng. News*, 15 May, 2000, p. 37; H. Carmichael, *Chem. Ber.*, January 2000, p. 36.
9 R. S. Varma, in *Green Chemistry: Challenging Perspectives*, ed. P. Tundo and P. T. Anastas, Oxford University Press, Oxford, 2000, pp. 221–244; R. S. Varma, *J. Heterocycl. Chem.*, 1999, **35**, 1565; R. S. Varma, *Green Chemistry*, 1999, **1**, 43.
10 S. I. Lall, D. Mancheno, S. Castro, V. Behaj, J. I. Cohen and R. Engel, *Chem. Commun.*, 2000, 2413.