

Sulfonylation reactions of aromatics using FeCl₃-based ionic liquids

M.V. Alexander, A.C. Khandekar, S.D. Samant*

Applied Chemistry Division, Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400019, India

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Abstract

Friedel–Crafts sulfonylation of benzene and its derivatives was carried out using FeCl₃-based ionic liquids. These liquids serve as an efficient media as well as Lewis acid catalyst, furnishing good yields of sulfones, under mild conditions. In pursuit of development of a catalytic system, we have studied the use of these ionic liquids, in catalytic amounts for a range of substrates, under conventional conditions. The use of these liquids as an aid for microwave heating and as effective catalysts for sulfonylation was also studied.

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1. Introduction

The sulfonylation of arenes using sulfonyl chlorides is a modification of the Friedel–Crafts acylation reaction [1] and has wide applicability, as aryl sulfones can be effectively synthesized via this route. Organosulfones are versatile synthons and have attracted a great deal of interest recently, due to their importance in fields as diverse as agrochemicals [2], pharmaceuticals [3], and polymers [4]. Their immense utility in medicinal chemistry has resulted in development of their synthesis in various academic laboratories and process development groups. Among Friedel–Crafts (FC) type reactions, sulfonylation possess is an important problem in catalysis [5–12].

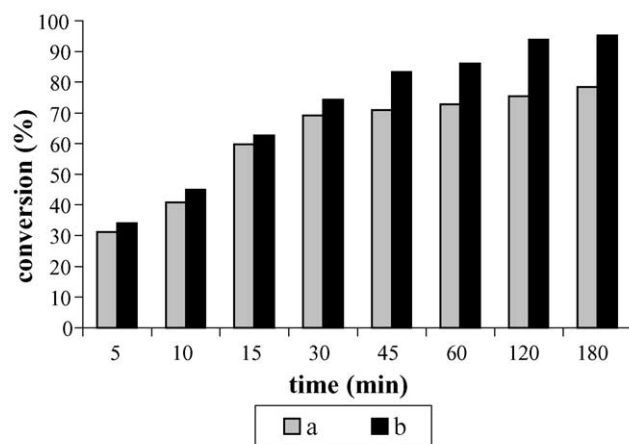
Among the recent developments in catalysis, the use of ionic liquids has been an exciting and burgeoning area of research [13]. Ionic liquids with their unique miscibility, high thermal stability and miniscule vapour pressure are valuable alternatives for the wide range of traditional solvents available. The liquids that manifest Lewis acidic character have been thoroughly studied (especially the chloroaluminates).

Several properties of these solvents can be effectively tuned by simply varying the anion, cation or the substituent groups on the cation. Ionic liquids are thus referred to, as ‘green’ replacements for various organic solvents.

Microwave activation as a non-conventional energy source has become a very popular and useful technology in organic chemistry [14–17]. From the perspective of microwave chemistry, one of the points of key importance is the high polarity of ionic liquids. They absorb microwave irradiation in a very efficient manner and thus can be employed as effective microwave coupling agents, when microwave transparent solvents or substrates are used.

Our initial forays into the use of these liquids include the investigation of Friedel–Crafts benzylation reaction in chloroaluminate ionic liquid [18]. Our subsequent work [19–24] led to the extension of their use in different organic transformations. The low tolerance towards moisture in organoaluminates, necessitating the use of glove box and Schlenk techniques has hindered extensive progress in research. This problem can be overcome by replacing aluminium with less reactive metals. Anhydrous ferric chloride in this regard is a valuable and cheaper alternative. Recently, Freeman and coworkers published the details of their investigation towards ionic liquids derived from FeCl₂ or FeCl₃ and

* Corresponding author. Tel.: +91 22 2414 5616; fax: +91 22 2414 5614.
E-mail address: mva.sds@yahoo.co.in (S.D. Samant).



^a Reaction of benzene with benzene sulfonyl chloride at 30 °C, for 3 h.

^b Reaction of benzene with *p*-toluene sulfonyl chloride at 30 °C, for 3 h.

^c *Reaction Conditions:* The reactions were performed with sulfonyl chlorides (2.5 mmol), benzene (3.0 mmol), ionic liquid (3.0 mmol) and conversion monitored by GC analysis.

Fig. 1. Sulfonylation of benzene, with benzene sulfonylchloride and *p*-toluene sulfonyl chloride using [bmim]Cl-FeCl₃ ionic liquid (*N* = 0.6).

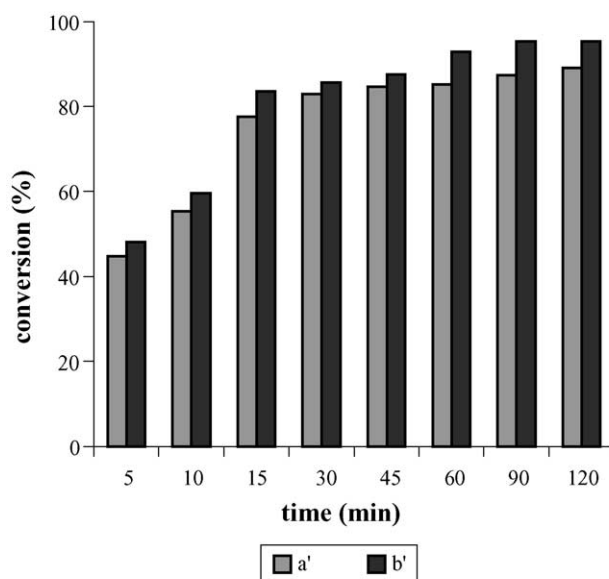
1-butyl-3-methylimidazolium chloride, i.e. [bmim]Cl [25]. In our initial disclosure, we carried out the Biginelli condensation and the Ferrier rearrangement in these FeCl₃-based ionic liquids [26].

The present work was aimed to study the feasibility of the FeCl₃-based ionic liquids for Friedel–Crafts sulfonylation reaction under mild conditions and further to exploit the ionic nature of these liquids for microwave irradiation (Scheme 1).

2. Experimental

2.1. Materials

All starting materials, including anhydrous iron (III) chloride, were commercially available from M/s s. d. Fine Chemical Ltd., Mumbai and Rankem, India, and used without any further purification. 1-Chlorobutane and 1-methylimidazole

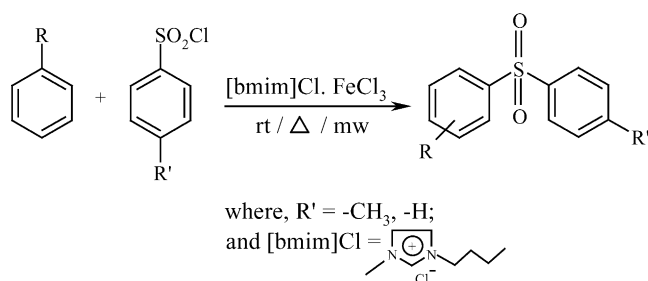


^{a'} Reaction of toluene with benzene sulfonyl chloride at 30 °C, for 2 h.

^{b'} Reaction of toluene with *p*-toluene sulfonyl chloride at 30 °C, for 2 h.

^c *Reaction Conditions:* The reactions were performed with sulfonyl chlorides (2.5 mmol), toluene (3.0 mmol), ionic liquid (3.0 mmol) and conversion monitored by GC analysis.

Fig. 2. Sulfonylation of toluene, with benzene sulfonyl chloride and *p*-toluene sulfonyl chloride using [bmim]Cl-FeCl₃ ionic liquid (*N* = 0.6).



Scheme 1. Friedel–Crafts sulfonylation of benzene and its derivatives using benzene sulfonyl chloride and *p*-toluene sulfonyl chloride, using [bmim]Cl-FeCl₃ ionic liquid.

were obtained from Merck Schuchardt, and Lancaster, respectively. The microwave instrument used for the study was a Microwave Accelerated Reactor system (MARS 5) vessel procured from CEM Corporation, USA.

2.2. Preparation of ionic liquid

1-Butylpyridinium chloride [bpy]Cl and 1-butyl-3-methylimidazolium chloride [bmim]Cl were prepared under microwave irradiation, by a procedure developed in our laboratory [24]. The different compositions of ionic liquids based on FeCl₃ were prepared by simply varying the amounts of the prepared [bpy]Cl and [bmim]Cl with anhydrous FeCl₃ [25].

2.3. Reaction procedure for the sulfonylation of arenes under mild conditions

To a weighed quantity of ionic liquid ($N = 0.6$, 6 mmol), was added *p*-toluene sulfonyl chloride or benzene sulfonyl chloride (5 mmol) and an arene (5.5 mmol). All the reactions are performed on a 5-mmol scale with respect to the sulfonylating agent, unless otherwise stated. The reaction mixture was stirred magnetically, at the specified temperature (30 or 50 °C). On complete consumption of the sulfonylating agent (as observed by TLC analysis), the reaction mixture was quenched by using 6 M HCl in cold conditions. In certain cases, a solid product was obtained, which was filtered, washed with sat. NaHCO₃, water and further subjected to GC analysis and purification procedures. Oth-

erwise, the resultant solution was extracted with ethyl acetate ($3 \times 10 \text{ cm}^3$) and the combined organic extracts were washed successively with sat. NaHCO₃ ($2 \times 5 \text{ cm}^3$) and water (10 cm^3), dried over anhydrous Na₂SO₄ and then concentrated under reduced pressure. The crude extract was assayed on GC, so as to monitor the conversion and isomer distribution. Whenever required, the products were purified by column chromatography so as to afford the pure sulfone, which were well characterized by physical constants and spectral data.

2.4. Procedure for sulfonylation of arenes using catalytic amounts of ionic liquid under conventional conditions

To a weighed quantity of ionic liquid ($N = 0.6$, 5–10 mol%), was added *p*-toluene sulfonyl chloride or benzene sulfonyl chloride (5 mmol) and an arene (10.0 mmol). All the reactions are performed on a 5-mmol scale with respect to the sulfonylating agent, unless otherwise stated. The flask was then fitted with a reflux condenser (cold water) and a calcium chloride tube. The reaction mixture was stirred magnetically at temperatures relative to the boiling points of the respective substrates. On complete consumption of the sulfonylating agent (observed by TLC analysis), the reaction mixture was quenched by using 6 M HCl in cold conditions and subjected to similar treatment as mentioned in Section 2.3 to obtain the pure sulfone.

2.5. Procedure for sulfonylation of arenes using catalytic amounts of ionic liquid under microwave irradiation

To the weighed amount of ionic liquid ($N = 0.6$, 5–10 mol%) in a flask, *p*-toluene sulfonyl chloride or benzene sulfonyl chloride (5 mmol) and arene (10 mmol) were added. The flask was then fitted with a reflux condenser (cold water) and a calcium chloride tube. The reaction mixture was stirred magnetically and irradiated in a CEM (MARS 5) reactor system, under an incident power of 300 W, under both standard control and ramp conditions (mentioned in Table 6). At the end of the irradiation, the reaction mixture was cooled, quenched with 6 M HCl, analyzed and further subjected to same treatment as mentioned in Section 2.3, to obtain the pure sulfone.

2.6. Analysis


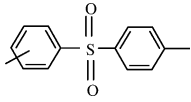
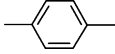
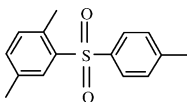
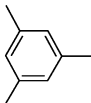
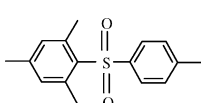

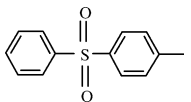
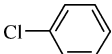
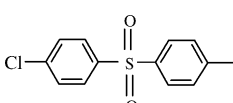
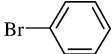
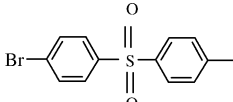
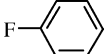
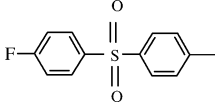
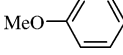
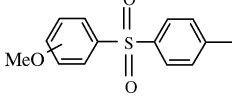
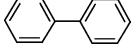
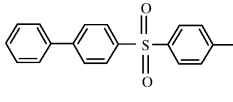

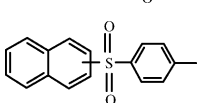
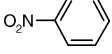
An Eshika gas chromatograph equipped with a flame ionization detector (FID) was employed for the analysis. The detector temperature was maintained at 300 °C. The column was programmed with an initial temperature of 150 °C and was increased thereafter to 270 °C at the rate of 15 °C min⁻¹. The column used for this purpose was a liquid phase SE-30 (length 2 m).

Table 1
Effect of increasing amount of FeCl₃ on sulfonylation reaction of benzene, using [bmim]Cl-FeCl₃ ionic liquid^a

[bmim]Cl/ [FeCl ₃]	Mole fraction of FeCl ₃ (N)	Conversion (%)	
		C ₆ H ₅ SO ₂ Cl	<i>p</i> -CH ₃ -C ₆ H ₅ SO ₂ Cl
1.5:1.0	0.40	–	–
1.3:1.0	0.43	–	–
1.0:1.0	0.50	–	–
1.0:1.3	0.57	64	68
1.0:1.5	0.60	72	85

^a Reaction conditions: The reactions were performed with sulfonyl chlorides (2.5 mmol), benzene (3.0 mmol) and ionic liquid (3.0 mmol) for 1 h, at 30 °C and conversion monitored by GC analysis.

Table 2
Sulfonylation of benzene and its derivatives using [bmim]Cl-FeCl₃ ionic liquid (*N* = 0.6), with *p*-toluene sulfonyl chloride^a

Entry	Substrate	Product	Temperature (°C)	Time (h)	Yield ^b (%)
1			30	2.0	89 ^c
2			30	2.0	93
3			30	1.0	95
4			30	3.0	82
5			30	8.0	76
6			50	5.0	68
7			30	8.0	79
8			50	3.0	84 ^c
9			50	2.0	87
10			50	3.0	71
11		-	50	12.0	-

^a Reaction conditions: *p*-toluene sulfonyl chloride (5.0 mmol), substrate (6.0 mmol) and ionic liquid (*N* = 0.6, 6.0 mmol).

^b Isolated yields of pure products.


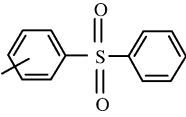

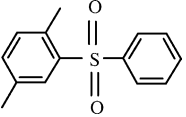
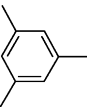
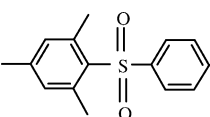

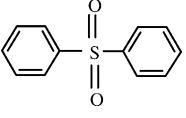
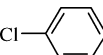
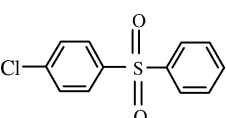
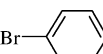
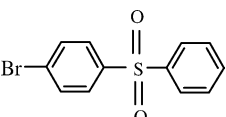
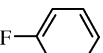
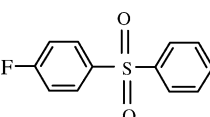
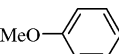
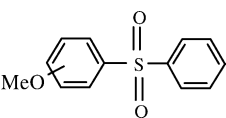
^c Isomeric ratio (o:p) based on GC analysis (39:61—entry 1 and 43: 57—entry 8).

3. Results and discussion

At room temperature, iron (III) chloride forms ionic liquids with [bmim]Cl from a composition of 1.0/1.9 to 1.7/1.0 [25]. Preliminary Mossbauer measurements indicate that the addition of FeCl₃ to [bmim]Cl leads to an equilibrium mixture that could contain FeCl₃, Fe₂Cl₆, [bmim]⁺[FeCl₄]⁻ and [bmim]⁺[Fe₂Cl₇]⁻, depending on the molar ratio of [bmim]Cl and FeCl₃ [27]. The Raman scattering results [25] indicate that FeCl₃ behaves much like

AlCl₃, first forming [FeCl₄]⁻ and then [Fe₂Cl₇]⁻ as the ratio exceeds 1.0/1.0, i.e. *N* = 0.5, where *N* is the apparent mole fraction of FeCl₃. The Raman spectrum of the liquid containing an [FeCl₃]/[bmim]Cl ratio of 1.0 to 1.5 showed peaks at 120, 333 and 384 cm⁻¹, which correspond to [FeCl₄]⁻ species as a solid or in solution. However, when the ratio is greater than 1, i.e. 1.5/1.0, the spectrum reveals the presence of [FeCl₄]⁻ (333 cm⁻¹) and new peaks at 370 and 420 cm⁻¹, which can be attributed to [Fe₂Cl₇]⁻.

Table 3
Sulfonylation of benzene and its derivatives using [bmim]Cl-FeCl₃ (*N* = 0.6), with benzene sulfonyl chloride^a

Entry	Substrate	Product	Temp (°C)	Time (h)	Yield ^b (%)
1			30	3.0	86 ^c
2			30	2.0	92
3			30	1.0	91
4			30	8.0	78
5			30	10.0	66
6			50	6.0	69
7			30	10.0	74
8			50	5.0	73 ^c

^a Reaction conditions: benzene sulfonyl chloride (5.0 mmol), substrate (6.0 mmol) and ionic liquid (*N* = 0.6, 6.0 mmol).

^b Isolated yields of pure products.

^c Isomeric ratio (o:p) based on GC analysis (51:49 – entry 1 and 45:55—entry 8).

3.1. Sulfonylation of arenes under mild conditions

The acidity of these ionic liquids can be varied over a wide range, by manipulating the relative amounts of [bmim]Cl and FeCl₃. To study the effect of increasing amounts of the Lewis acid in the liquid, we undertook screening of different compositions of [bmim]Cl and FeCl₃ ranging from 1.5/1.0 (*N* = 0.4) to 1.0/1.5 (*N* = 0.6). For these studies, benzene was chosen as a model substrate (Table 1). Sulfonylation of benzene did not take place in basic and neutral melts, at 30 °C. This led to the conclusion that FeCl₃ in its complexed form, i.e. [FeCl₄]⁻, was not effective at lower temperature. However, with gradual increase in the acidity, subsequent increase in the rate of conversion was observed.

The extent of conversion of benzene and toluene with benzene sulfonyl chloride and *p*-toluene sulfonyl chloride (Figs. 1 and 2) was studied. The reactions showed that the conversions gradually increased with time up to 60–90 min and then remained almost constant. Pyridinium-based ionic liquids led to rather similar results. As the imidazolium-based ionic liquids are well characterized, we decided to carry out all our studies in these solvents.

The reaction of benzene and its derivatives with both the sulfonylating agents are detailed in Tables 2 and 3. Variation in the sulfonylating agent does not cause any significant difference in results. Most of the substrates exhibited enhanced reactivity, furnishing excellent yields of sulfone. The synthesis of diphenyl sulfone, an important intermediate for

Table 4

Sulfonylation of benzene and its derivatives using catalytic amounts of [bmim]Cl-FeCl₃ ionic liquid (*N* = 0.6), with *p*-toluene sulfonyl chloride and benzene sulfonyl chloride^a

Entry	Substrate	Product	mol.% of iL	Temperature/time	Yield ^b (%)
1			5.0	110 °C/1 h	90 ^c
2			5.0	110 °C/1 h	84 ^c
3			5.0	135 °C/30 min	92
4			5.0	135 °C/30 min	86
5			5.0	120 °C/30 min	93
6			5.0	120 °C/30 min	89
7			5.0	80 °C/8 h	83
8			10.0	80 °C/8.5 h	70
9			10.0	120 °C/12 h	62
10			10.0	120 °C/12 h	58
11			5.0	100 °C/1 h	88

^a Reaction conditions: sulfonyl chloride (5.0 mmol), substrate (10.0 mmol) except in case of biphenyl (5.0 mmol) and catalytic amount of ionic liquid (*N* = 0.6).

^b Isolated yields of pure products.

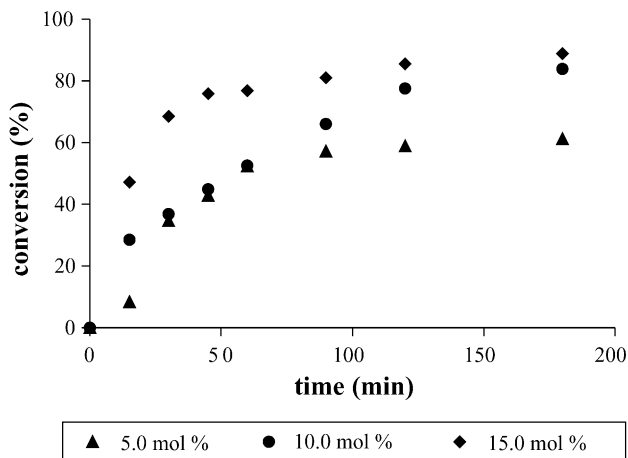
^c Isomeric ratio (o:p) based on GC analysis (33:67—entry 1 and 38:62—entry 2).

Dapsone (antileprosy drug), could be achieved at 30 °C. Aromatic halides like fluorobenzene ($\sigma_p^+(\text{F}) = -0.07$) and chlorobenzene ($\sigma_p^+(\text{Cl}) = +0.11$) could be easily converted at 30 °C, to the corresponding sulfones with excellent *para* selectivity. However, bromobenzene ($\sigma_p^+(\text{Br}) = +0.15$) required slightly higher temperature, i.e. 50 °C to give the corresponding (4-bromophenyl)-*p*-tolylsulfone. Of particular interest are aromatics like biphenyl and naphthalene, which were converted to the corresponding sulfones using this methodology under these milder conditions. Thus, FeCl₃-

based ionic liquids served as efficient solvent cum catalysts for the sulfonylation reactions under mild conditions.

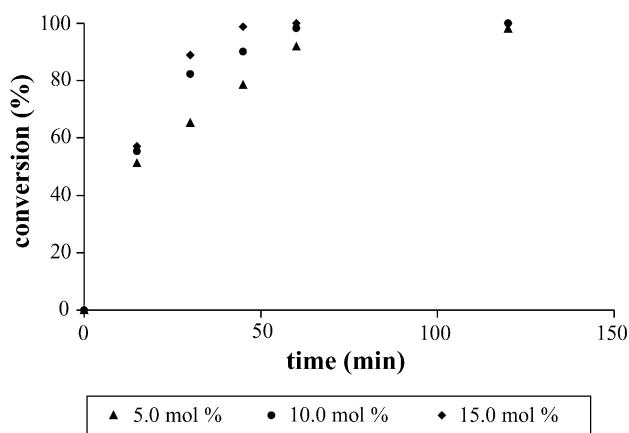
3.2. Sulfonylation of arenes using catalytic amounts of ionic liquid under conventional conditions

We also evaluated the effect of this FeCl₃-based ionic liquid in small amounts, at higher temperatures. The initial experimentations were carried out with 10 mol% of ionic liquid (*N* = 0.4, 0.5, 0.6) using benzene and TsCl, at 80 °C.



^a Reaction Conditions: The reactions were performed with *p*-toluene sulfonyl chloride (2.5 mmol), benzene (5.0 mmol) using varying amount of ionic liquid, at 80 °C for 3 h and conversion monitored by GC analysis.

Fig. 3. Effect of increasing molar proportion of the [bmim]Cl·FeCl₃ ionic liquid (*N* = 0.6) on the sulfonation of benzene with *p*-toluene sulfonyl chloride, at 80 °C.



^a Reaction Conditions: The reactions were performed with benzene sulfonyl chloride (2.5 mmol), toluene (5.0 mmol) using varying amount of ionic liquid, at 110 °C for 2 h and conversion monitored by GC analysis.

Fig. 4. Effect of increasing molar proportion of the [bmim]Cl·FeCl₃ ionic liquid (*N* = 0.6) on the sulfonation of toluene with benzene sulfonyl chloride, at 110 °C.

Table 5

Microwave heating effects of adding catalytic amount of [bmim]Cl·FeCl₃ ionic liquid (*N* = 0.6), to the various substrates used in the sulfonation reaction^a

Substrate used ^b	Boiling point (°C)	Temperature without ionic liquid (°C)	Temperature with ionic liquid (°C)
Benzene	78	53	90
Toluene	110	56	124
<i>p</i> -Xylene	133	57	149
Mesitylene	120	57	118
Chlorobenzene	133	71	146
Bromobenzene	158	73	158

^a Reaction conditions: substrate (10.0 mmol) and catalytic amount (5 mol%) of ionic liquid (*N* = 0.6).


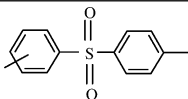

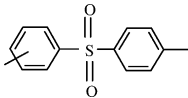
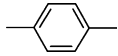
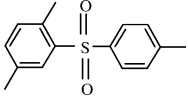
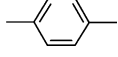
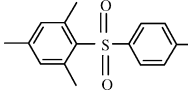

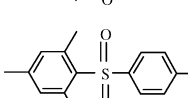

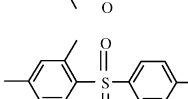

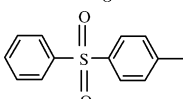
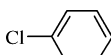
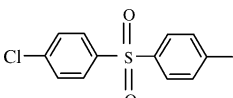
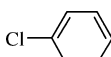
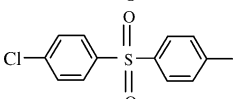
^b The substrates were irradiated at 300 W in a CEM make MARS 5 microwave oven, at full power for a period of 1.0 min.

As anticipated, no conversion to the corresponding sulfone was observed, in the basic and neutral melts, even at higher temperature. However, a gradual increase in the conversion was noted as the acidic ionic liquid was introduced. These results are in complete agreement with those observed at 30 °C. We decided to carry out further investigations into the use of catalytic amounts of acidic FeCl₃-based ionic liquids, for sulfonylation of arenes. We studied the effect of increasing molar proportion of the liquids, for two different sets of reaction. Benzene and toluene were subjected to sulfonylation reaction with the different sulfonylating agents at temperature, relative to their boiling points (Figs. 3 and 4). Significant rate enhancements were observed with an increase in the molar proportion of the ionic liquid. Consequently, 5 mol% of the ionic liquid was chosen for reactive substrates and relatively higher amounts for a few electron-deficient arenes. The results are summarized in Table 4.

3.3. Sulfonylation of arenes using catalytic amounts of ionic liquid under microwave irradiation

Further insight into the use of ionic liquid as an aid for microwave heating [28] was examined using the optimized results obtained from the above set of experiments. It is clearly seen from Table 5 that ionic liquids have a dramatic effect on the heating of all substrates studied, with temperatures much higher than the boiling point being achieved in relatively short period of time. The details of reaction conditions for the various substrate combinations are mentioned in Table 6. Substantial reduction in time was observed, when microwaves were used as a source of heating. The reactions are extremely clean, giving good yields of the corresponding sulfone, though moderate refinement in this regard is required and is being pursued.

Table 6
Sulfonylation of benzene and its derivatives using catalytic amounts of [bmim]Cl·FeCl₃ ionic liquid (*N* = 0.6), with *p*-toluene sulfonyl chloride, under microwave irradiation^a

Entry	Substrate	Product	Mol% of IL	Temperature/time	Yield ^b (%)
1			5.0	110 °C/5 min	65 ^c
2			5.0	160 °C/3 min	90 ^c
3			5.0	135 °C/5 min	68
4			5.0	165 °C/3 min	87
5			5.0	120 °C/5 min	74
6			5.0	165 °C/3 min	91
7			5.0	80 °C/30 min	36
8			10.0	133 °C/15 min	29
9			10.0	150 °C/15 min	64

^a Reaction conditions: *p*-toluene sulfonyl chloride (5.0 mmol), substrate (10.0 mmol) and ionic liquid (*N* = 0.6).

^b Isolated yields of pure products.

^c Isomeric ratio (o:p) based on GC analysis (34:66 – entry 1 and 11:89 – entry 2). ^dThe substrates were irradiated at 300 W in CEM make MARS 5 microwave oven, both under standard control and ramp conditions.

4. Conclusions

We have developed a radically improved version of the classical reaction for sulfonylation of aromatic systems with *p*-toluene sulfonyl chloride and benzene sulfonyl chloride as sulfonylating agents. The best results are realized and the utility of the FeCl₃-based ionic liquids both as solvent and catalyst are satisfactorily justified. Further, we have also demonstrated the potential of ionic liquids as efficient aid for microwave heating and believe that it could offer significant advantages to chemists attempting to improve rates and yields of reactions run in non-polar solvents.

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