

## Regioselectivity for Nitrochlorobenzene Preparation Over Imidazolium Ionic Liquids Media Using Nitric Acid

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Nitrochlorobenzene could be regioselective prepared over imidazolium ionic liquids media by using nitric acid as nitrating agents. A variety of ionic liquids, [Hmim]HSO<sub>4</sub>, [Hmim]NO<sub>3</sub> and [Hmim]CF<sub>3</sub>COO were prepared for the improvement of mononitrochlorobenzene isomers. It was found that a high *para* isomer was achieved when employing [Hmim]HSO<sub>4</sub>. Ionic liquids could be conveniently reused for five times by filtration with excellent yield of mono-nitration products and *para*-selectivity.

**Key Words:** Chlorobenzene, Nitric acid, Ionic liquids, Nitration, Regioselectivity.

### INTRODUCTION

Aromatic nitro compounds are important starting materials for the manufacture of various industrial products such as pharmaceuticals, dyes, intermediates, explosives and plastics. Industrial preparation processes for the compounds are carried out by employing a mixture of nitric acid and sulfuric acid predominantly yielding *ortho* and *para* substituted products by using mono-substituted benzenes as substrates. But in this way, a major problem associated with the mentioned technology is that the use of corrosive strong acid mixtures generates large amounts of spent acids, oxidation and organic byproducts because of poor selectivity, which are very costly to treat and not of environmental economy. In order to overcome the problems, researchers have paid much attention to catalytic nitration using solid acid<sup>1-6</sup>, especially the reaction on zeolite and molecular sieve *etc.* catalysts<sup>7-15</sup>. Therefore, some novel ways for the manufacture of nitro compounds were developed<sup>16-18</sup>.

Over the past few years room-temperature ionic liquids have received attention for their promise as alternative reaction media because of their convenient physical properties (non-volatile, non-flammable, wide liquid range) and favourable solvation behaviour, which make them useful as 'clean or green' solvents. Such liquids have been explored as solvents and/or catalysts in some reactions. Of these reactions, reaction rates were enhanced even though the reasons are not always clear. The nitration of aromatics in ionic liquids should therefore be of interest to both academic and industrial researchers.

There were some reports for the use of ionic liquids<sup>19-24</sup>. As part of our continuing interest in the development of clean chemical processes, in particular, regioselective preparation of nitro aromatic compounds, we utilized ionic liquids in an attempt to develop the clean and green method. The ionic liquids selected were [Hmim]HSO<sub>4</sub>, [Hmim]NO<sub>3</sub>, [Hmim]CF<sub>3</sub>COO, which were applied to the synthesis of nitrochlorobenzene with aromatic chlorobenzene as substrate by using nitric acid nitrating reagent in mild conditions.

## EXPERIMENTAL

All of the starting materials were chemical purity grade or above. HPLC (Shimadzu LC-10Avp Plus using 30 volume of distilled water to 70 volume of methanol as eluent.) were utilized to determine nitro isomers and chlorobenzene conversion using *n*-dodecane as internal standard. IR spectra were recorded in cm<sup>-1</sup> (KBr) (Hitachi IR meter 260-10).

**Preparation of ionic liquids:** Ionic liquid, [Hmim]HSO<sub>4</sub>, was synthesized according to procedures in the literature, *i.e.*, sulfuric acid (98 %, 5.10 g, 0.05 mol) was diluted with water (5 mL) in low temperature and then the mixture was added dropwise to stirred N-methylimidazole (4.09 g, 3.95 mL, 0.05 mol) cooled to 0 °C in low temperature bath over 1 h. The reaction mixture was stirred for 1 h at 0 °C and warmed to room temperature for 2 h. The aqueous solvents were removed in vacuum below 75 °C to give the product as colourless oil. [Hmim]NO<sub>3</sub> and [Hmim]CF<sub>3</sub>COO were the same synthesized as above. IR (KBr, cm<sup>-1</sup>): [Hmim]HSO<sub>4</sub>, 3346(m), 3150(m), 2872 (m), 1655(w), 1587(w), 1446 (w), 1191(s), 1082(s), 1044(s), 849(s), 583(s); [Hmim]NO<sub>3</sub>, 3435(m), 3149(m), 2860(m), 1632(w), 1585(w), 1548(w), 1385(s), 1084(w), 827(w), 756(w), 626(m); [Hmim]CF<sub>3</sub>COO, 3435(m), 3153(m), 2866(m), 1675(s), 1425(m), 1204(s), 832(m), 721(m), 630(m), 517(w).

**Nitration of chlorobenzene with HNO<sub>3</sub> in ionic liquids:** To a round-bottomed flask containing a stirred mixture of the ionic liquids and chlorobenzene (4.00 g), nitric acid (6.92 g, 65 %) was added dropwise for defined time at defined temperature. On completion of reaction, the product was extracted with ethyl acetate, washed sequentially with 5 % sodium bicarbonate aqueous solution and water to neutral. The ionic liquid was further reused after dried in vacuum below 75 °C to remove the aqueous solvents.

## RESULTS AND DISCUSSION

Nitrochlorobenzenes are usually formed in three nitro isomers (**Scheme-I**) when employing chlorobenzene as substrate under all present nitration processes developed. Similarly, the three nitro isomers were also detected in present ionic liquid systems. Some results were shown in Table-1. The obvious effects on substrate conversion and products selectivity from the ionic liquids were observed as compared with that of a small substrate conversion with low selectivity exist in the reaction without

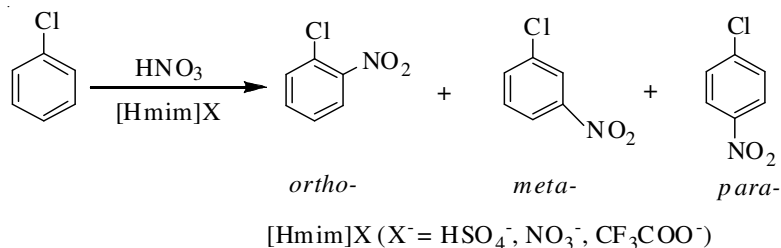
**Scheme-I:** Formation of nitro chlorobenzene

TABLE-1  
NITRATION OF CHLOROBENZENE WITH NITRIC  
ACID (65 %) IN THE PRESENCE OF ILs

No.	IL	IL (g)	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)	Selectivity (%)		<i>para/ortho</i>
							<i>para</i>	<i>ortho</i>	
1	–	–	60	5	55.2	52.9	71.6	28.4	2.52
2	– <sup>a</sup>	–	60	5	69.8	62.9	71.7	28.3	2.53
3	[Hmim]HSO <sub>4</sub>	0.3	60	5	63.4	57.5	72.8	27.2	2.67
4	[Hmim]HSO <sub>4</sub>	0.6	60	5	62.8	59.2	73.3	26.7	2.75
5	[Hmim]HSO <sub>4</sub>	1.0	60	5	60.4	55.8	72.1	27.9	2.58
6	[Hmim]HSO <sub>4</sub>	1.3	60	5	57.7	54.7	76.5	23.5	3.26
7	[Hmim]HSO <sub>4</sub>	1.6	60	5	62.1	52.4	73.4	26.6	2.76
8	[Hmim]HSO <sub>4</sub>	1.3	60	8	60.3	55.4	73.7	26.3	2.80
9	[Hmim]HSO <sub>4</sub>	1.3	50	5	47.7	42.8	74.2	25.8	2.87
10	[Hmim]HSO <sub>4</sub>	1.3	70	5	63.3	59.5	73.0	27.0	2.70
11	[Hmim]HSO <sub>4</sub>	1.3	80	5	66.6	62.2	72.8	27.2	2.67
12	[Hmim]NO <sub>3</sub>	1.0	60	5	53.4	43.8	72.2	27.8	2.60
13	[Hmim]CF <sub>3</sub> COO	1.4	60	5	48.9	41.1	73.0	27.0	2.70
14	[Hmim]CF <sub>3</sub> COO	1.4	60	6	43.6	37.7	72.7	27.3	2.66
15	[Hmim]CF <sub>3</sub> COO	1.4	70	5	55.4	47.5	72.2	27.8	2.60
16	[Hmim]NO <sub>3</sub>	0.5	60	5	62.2	52.7	72.6	27.4	2.66
17	[Hmim]NO <sub>3</sub>	0.5	60	8	64.6	54.4	71.0	29.0	2.45
18 <sup>b</sup>	[Hmim]HSO <sub>4</sub>	1.3	60	5	50.3	49.4	76.2	23.8	3.20

<sup>a</sup>The reaction was conducted the traditional nitric (3.46 g, 65 %) and sulfuric(3.66 g, 98 %) acids. <sup>b</sup>A recovered [Hmim]HSO<sub>4</sub> was reused for five times.

ionic liquid (No. 1), although the better conversion of chlorobenzene with nitric and sulfuric acids mixture was observed at the expense of poor selectivity. Addition of the ionic liquids brought about increase of reaction activity and preferential formation of *para* isomer in all cases. Of three ionic liquids, the [Hmim]HSO<sub>4</sub> appeared the best *para* selectivity, up to a *para/ortho* ratio of 3.26, which probably is because [Hmim]HSO<sub>4</sub> can further provide one proton as Brønsted acid to promote nitric acid to form active agent nitronium ion favour to nitration reaction. And with increase of the reaction temperature to 80 °C from 50 °C, the chlorobenzene conversion was increased to 66.6 % from 47.7 %. Although increasing the temperature for accelerating the reaction is apparently favourable, the selectivity towards *para*-nitrochlorobenzene decreased to a *para/ortho* ratio of 2.67.

The reusability of [Hmim]HSO<sub>4</sub> in the preparation of nitrochlorobenzene was examined (No. 18). [Hmim]HSO<sub>4</sub> recycled for five times in reaction did not show obviously characteristic changes. Nitration reaction was still towards *para* regioselectivity but the yield was lost about several percentages. This indicated that [Hmim]HSO<sub>4</sub> has excellent reusability for preparing *p*-nitrochlorobenzene.

### Conclusion

The present work shows that nitration of simple aromatics using nitric acid in ionic liquids proceeds successfully with better *para*-selectivity favour to the preparation of *para*-nitrochlorobenzene instead of conventional nitric acid-sulfuric acid mixture. Furthermore, the use of ionic liquid used for a substitute of sulfuric acid is of environmental economy for industrial element. The ionic liquid could be recycled by easily work up, however, their reaction activity could be paid some attentions.

### REFERENCES

1. K.R. Sunajadevi and S. Sugunan, *Catal. Commun.*, **6**, 611 (2005).
2. S.K. Bharadwaj, S. Hussain, M. Kar and M.K. Chaudhuri, *Catal. Commun.*, **9**, 919 (2008).
3. S.K. Bharadwaj, S. Hussain, M. Kar and M.K. Chaudhuri, *Appl. Catal. A: General*, **343**, 62 (2008).
4. K.R. Sunajadevi and S. Sugunan, *Mater. Lett.*, **60**, 3813 (2006).
5. D. Vassena, A. Kogelbauer and R. Prins, *Catal. Today*, **60**, 275 (2000).
6. A.S. Khder and A.I. Ahmed, *Appl. Catal. A: General*, **354**, 153 (2009).
7. S.P. Dagade, S.B. Waghmode, V.S. Kadam and M.K. Dongare, *Appl. Catal. A: General*, **226**, 49 (2002).
8. S.S. Kim, T.J. Pinnavaia and R. Damavarapu, *J. Catal.*, **253**, 289 (2008).
9. R.J. Kalbasi, M. Ghiaci and A.R. Massah, *Appl. Catal. A: General*, **353**, 1 (2009).
10. S. Bernasconi, G.D. Pirngruber and A. Kogelbauer, *J. Catal.*, **219**, 231 (2003).
11. K. Smith, T. Gibbins and R.W. Millar, *J. Chem. Soc. Perkin Trans. I*, 2753 (2000).
12. T. Esakkidurai and K. Pittchumani, *J. Mol. Catal. A: Chem.*, **185**, 305 (2002).
13. T.J. Kwok and K. Jayasuriya, *J. Org. Chem.*, **59**, 4939 (1994).
14. X. Peng, H. Suzuki and C. Lu, *Tetrahedron Lett.*, **42**, 4357 (2001).
15. K. Smith, S. Almeer and S.J. Black, *J. Chem. Soc. Chem. Commun.*, 2748 (2001).
16. X. Peng, N. Fukui, M. Mizuta and H. Suzuki, *Org. Biomol. Chem.*, **1**, 2326 (2003).
17. M. Mascal, L. Yin, R. Edwards and M. Jarosh, *J. Org. Chem.*, **73**, 6148 (2008).
18. N.S. Nandurkar, M.D. Bhor, S.D. Samant and B.M. Bhanage, *Ind. Eng. Chem. Res.*, **46**, 8590 (2007).
19. R. Rajagopal and K.V. Srinivasan, *Ultrasonics Sonochem.*, **10**, 41 (2003).
20. K. Smith and S. Liu, *Ind. Eng. Chem. Res.*, **44**, 8611 (2005).
21. E. Dal and N.L. Lancaster, *Org. Biomol. Chem.*, **3**, 682 (2005).
22. K.K. Laali and V.J. Gettwert, *J. Org. Chem.*, **66**, 35 (2001).
23. D. Fang, Q. Shi, J. Cheng, K. Gong and Z. Liu, *Appl. Catal. A: General*, **345**, 158 (2008).
24. J.D. Holbrey and K.R. Seddon, *J. Chem. Soc. Dalton Trans.*, **2133**, 21 (1999).