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## ***N*-Hydroxyphthalimide-Catalyzed Oxidative Production of Phthalic Acids from Xylenes Using O<sub>2</sub>/HNO<sub>3</sub> in an Ionic Liquid**

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**Abstract:** A simple and mild process for oxidation of xylenes to phthalic acids using *N*-hydroxyphthalimide/O<sub>2</sub>/HNO<sub>3</sub> in an ionic liquid, wherein the ionic liquid can be successfully recovered and reused, is described.

**Keywords:** *N*-Hydroxyphthalimide, ionic liquid, nitric acid, oxidation, phthalic acid

### **INTRODUCTION**

The oxidation of xylenes to their corresponding di-acids is carried out on a large scale, and the product of oxidation, phthalic acids, are frequently used in polymer industries. Various methods exist for the oxidation of alkyl aromatic compounds, including oxidation with dioxygen, using a cobalt(II, III) catalyst,<sup>[1–4]</sup> periodate,<sup>[5]</sup> air,<sup>[6]</sup> or hypochlorite catalyzed by Ru(VIII) oxide.<sup>[7–9]</sup> All of these methods require either a quantitative amount of oxidizing agent or special instruments for carrying out the oxidation at high temperature and pressure.

With an ever-increasing quest for exploration of newer reactions in ionic liquids, herein we report the use of ionic liquids as a novel and

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recyclable polar reaction media for nitric acid oxidation of xylenes. Recent interest in the use of air and ionic liquids in organic synthesis<sup>[5,7]</sup> and the good solubility of gases (including oxygen) in these ionic solvents prompted us to use this reaction medium for aerobic oxidation.

Ionic liquids (ILs), composed entirely of ions with melting points less than 100°C, are emerging as promising and attractive alternatives because of their unique properties including low volatility, high polarity, stability over a wide temperature range, and capacity to dissolve a variety of organic, inorganic, and organometallic compounds.<sup>[10,11]</sup> Furthermore, a proper choice of cation and anion fine-tunes their miscibility with water and common organic solvents. Thus, ILs have been used as solvents in a wide range of organic reactions such as Diels–Alder,<sup>[12]</sup> Fridel–Crafts,<sup>[13]</sup> Heck,<sup>[14]</sup> Suzuki coupling reaction,<sup>[15]</sup> hydroformylation,<sup>[16]</sup> and hydrogenation.<sup>[17]</sup> However, only recently have the potential benefits of oxidation in ionic liquids been examined. Reported reactions include Ni(acac)<sub>2</sub>-catalyzed aerobic oxidation of aromatic aldehydes,<sup>[18]</sup> copper-2,2,5,5-tetramethyl pyrrolidine oxide-catalyzed aerobic oxidation of alcohols,<sup>[19]</sup> and palladium-catalyzed oxidation of styrene<sup>[20]</sup> and benzyl alcohol.<sup>[21]</sup>

We report a simple and mild process for oxidation of xylenes to phthalic acids using *N*-hydroxyphthalimide in an IL, wherein the IL can be successfully recovered and reused.

## RESULTS AND DISCUSSION

The process involves the oxidation of alkyl chains of xylene in the presence of nitric acid with good to excellent conversion. Thus, the oxidation of xylene takes place under Brosted acidic conditions, wherein xylene is admixed with nitric acid, *N*-hydroxyphthalimide (NHPI), and an IL. Nitric acid oxidizes the alkyl group and is in turn reduced to a lower valent form of nitrogen, which is unstable under the acidic condition and is reoxidized back to nitric acid by means of oxygen as the second oxidizing agent.

The recycling and reuse of the ionic solvent was accomplished by distillation. When H<sub>2</sub>O<sub>2</sub> was employed as a source of oxygen, a lesser yield of di-acid was obtained (Table 1, entry 12).

The conversion, selectivity, and yield of the oxidation under different conditions are summarized in Table 1. As shown in Table 1, TEMPO was successfully used as an initiator and co-oxidant agent. However, azo-bis-isobutyronitrile (AIBN) was found to be a poor initiator and co-oxidant (Table 1, entries 4 and 6). The reaction mixture was analyzed by gas chromatography (GC), for oxidation of *p*-xylene, and the amount

**Table 1.** Optimization of the reaction condition for oxidation of *p*-xylene<sup>a</sup>

Entry	HNO <sub>3</sub> / <i>p</i> -xylene ratio	Conv./sel. (%) <sup>b,c</sup>	Yield (%) <sup>c</sup>
1	0.3	62/60	41
2 <sup>d</sup>	0.3	36/47	21
3 <sup>e</sup>	0.3	38/40	18
4 <sup>f</sup>	0.3	6/32	Trace
5	0.6	78/82	62
6 <sup>g</sup>	0.6	82/74	68
7 <sup>i</sup>	0.6	98/98	96
8 <sup>h</sup>	0.6	98/90	88
9 <sup>h</sup>	0.6	96/89	85
10 <sup>h</sup>	0.6	95/86	82
11 <sup>h</sup>	0.6	88/85	74
12 <sup>j</sup>	0.6	50/30	18

<sup>a</sup>2 mmol *p*-xylene, HNO<sub>3</sub>, O<sub>2</sub>, 1.48 g bmim[OMS], 110°C, 1 atm, 6 h.

<sup>b</sup>GC conversion.

<sup>c</sup>Isolated yield and selectivity by weight of terephthalic acid to *p*-xylene and product mixture.

<sup>d</sup>1 mL of EtOAc was added to the IL.

<sup>e</sup>1 mL CHCl<sub>3</sub> was added to the IL.

<sup>f</sup>3 mol% AIBN was used as initiator.

<sup>g</sup>Tetramethylpyrrolidine N-oxide (TEMPO) was used as initiator.

<sup>h</sup>NHPI was used as initiator. Recycling experiment for [bmim]OMS.

<sup>i</sup>NHPI was used as initiator.

<sup>j</sup>H<sub>2</sub>O<sub>2</sub> 30% was used as the oxidizing agent.

of terephthalic acid was detected in 24 min with 96% area in the reaction mixture under optimized conditions. The results obtained for the oxidation of *m*- and *o*-xylene are shown in Table 2.

The yield and selectivity of the product was remarkably improved in the presence of NHPI. Although the role of NHPI in oxidation of xylenes by nitric acid in [bmim]OMS (1-butyl-3-methylimidazolium O-methyl-sulfate) is not clearly known, a plausible mechanism is proposed in Fig. 1. The initial step is abstraction of an H radical from NHPI by nitric acid, which results in a PINO radical. This radical is responsible for abstraction of benzylic hydrogen from xylene.<sup>[22–24]</sup> Then, the benzyl radical is attacked by oxygen to generate the hydroperoxide radical, which is converted to aldehyde by a nitrogen dioxide radical. Subsequent oxidation of the aldehyde results in carboxylic acid.

In conclusion, we have demonstrated that the NHPI/O<sub>2</sub>/HNO<sub>3</sub> system in [bmim]OMS is an efficient reactant system alternative to the old methods for production of terephthalic acid by oxidation of xylenes.

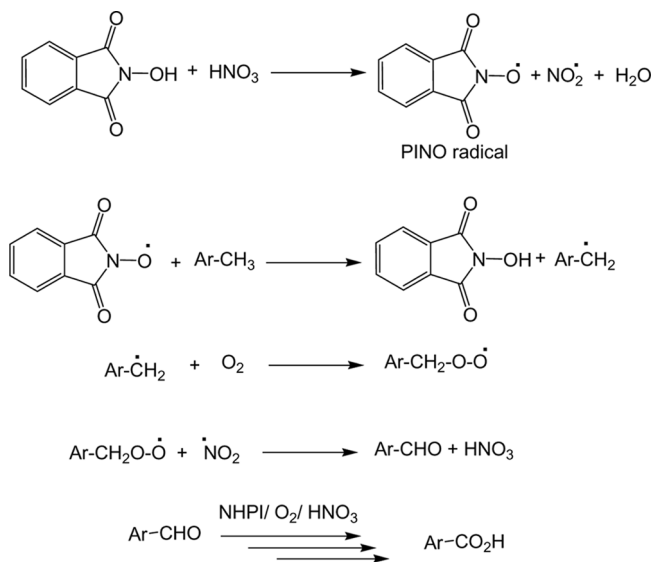
**Table 2.** Optimization of the reaction condition for oxidation of xylenes

Entry	Reactant	Products <sup>d</sup>	Yield (%)
1 <sup>a</sup>	<i>p</i> -Xylene	T	32
2 <sup>a</sup>	<i>o</i> -Xylene	P	23
3 <sup>a</sup>	<i>m</i> -Xylene	I	28
4 <sup>b</sup>	<i>p</i> -Xylene	T	41
5 <sup>b</sup>	<i>o</i> -Xylene	P	33
6 <sup>b</sup>	<i>m</i> -Xylene	I	36
7 <sup>c</sup>	<i>p</i> -Xylene	T	96
8 <sup>c</sup>	<i>o</i> -Xylene	P	71
9 <sup>c</sup>	<i>m</i> -Xylene	I	67

<sup>a</sup>40°C, 6 h.<sup>b</sup>60°C, 4 h.<sup>c</sup>110°C, 6 h.<sup>d</sup>T, terephthalic acid; I, isophthalic acid; P, phthalic acid.

## EXPERIMENTAL

Xylenes and the ILs used in this work were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Melting points



**Figure 1.** Proposed mechanism for oxidation of xylene to terephthalic acid by the NHPI/O<sub>2</sub>/HNO<sub>3</sub> system.

were measured on an Electrothermal 9100 apparatus. Elemental analyses for C and H were performed using a Heraeus CHN-O-Rapid analyzer. Infrared (IR) spectra were measured on a Shimadzu IR-460 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DRX-500 Avance instrument with dimethylsulfoxide (DMSO)- $d_6$  as solvent at 500.1 and 125.7 MHz, respectively. Mass spectra (MS) were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. GC analyses were performed on a Finnigan Trace GC Ultra Thermo GC analyzer.

### Typical Procedure for the Preparation of Terephthalic Acid

*p*-Xylene (2.14 g, 20 mmol), bmim[OMS] (1.48 g, 6.4 mmol), 67% nitric acid (1.08 g, 12 mmol), and NHPI (0.18 g, 0.6 mmol) were added under oxygen atmosphere to a 100-cm<sup>3</sup>, round-bottom flask, equipped with a magnetic stirrer and reflux condenser. The mixture was heated under reflux for 6 h. The flask was cooled, and the products were analyzed by GC. The signal from terephthalic acid was 96%. After adding 10 mL of H<sub>2</sub>O/acetone (4/1) to the reaction mixture, the precipitate was separated by filtration, washed with cold ethanol, and identified as terephthalic acid (3.18 g, 96%). When the filtrate was left in the refrigerator (−5°C) for 8 h, 0.08 g (3%) of a crystalline substance was formed, which was identified as 4-methylbenzoic acid. The second filtrate containing the IL was concentrated on a rotary evaporator (80°C, 50 mmHg) to remove all the organic solvents and reused as solvent for the next oxidation process by adding fresh *p*-xylene and nitric acid.

### Terephthalic Acid

White powder, mp > 300°C (decomp.). IR (KBr): 1730, 1602 cm<sup>−1</sup>.  $^1\text{H}$  NMR: 8.29 (s, 4H, 4CH), 13.60 (s, 2H, 2COOH).  $^{13}\text{C}$  NMR: 129.4 (4CH), 134.4 (2C), 166.7 (2COOH). Anal. calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>4</sub> (166.13): C, 57.84; H, 3.64; found: C, 57.97; H, 3.69%.

### Isophthalic Acid

Colorless crystals, mp 346–348°C. IR (KBr): 1770, 1665 cm<sup>−1</sup>.  $^1\text{H}$  NMR: 7.52 (m, 4H, 4CH), 12.60 (s, 2H, 2COOH).  $^{13}\text{C}$  NMR: 128.4 (2CH), 135.4 (2CH), 134.2 (2C), 166.7 (2COOH). Anal. calcd. for C<sub>8</sub>H<sub>6</sub>O<sub>4</sub> (166.13): C, 57.84; H, 3.64; found: C, 57.99; H, 3.61%.

### Phthalic Acid

Colorless crystals, mp 190–192°C (decomp.). IR (KBr): 1745, 1600  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 7.48 (d, 2H,  $^3J=7.9$  Hz, 2CH), 7.52 (d, 2H,  $^3J=7.9$  Hz, 2CH), 12.50 (s, 2H, 2COOH).  $^{13}\text{C}$  NMR: 128.2 (2CH), 132.2 (2CH), 136.4 (2C), 169.7 (2COOH). Anal. calcd. for  $\text{C}_8\text{H}_6\text{O}_4$  (166.13): C, 57.84; H, 3.64; found: C, 57.97; H, 3.69%.

### 4-Methylbenzoic Acid

Transparent crystals, mp 178–180°C. IR (KBr): 1775, 1650  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 2.42 (s, 3H,  $\text{CH}_3$ ), 7.24 (d, 2H,  $^3J=8.0$  Hz, 2CH), 8.11 (d, 2H,  $^3J=8.0$  Hz, 2CH), 11.60 (s, 1 H, COOH).  $^{13}\text{C}$  NMR: 21.4 ( $\text{CH}_3$ ), 128.9 (C), 129.5 (2CH), 129.8 (2CH), 143.4 (C), 167.7 (COOH). Anal. calcd. for  $\text{C}_8\text{H}_8\text{O}_2$  (136.15): C, 70.58; H, 5.92; found: C, 70.69; H, 5.88%.

### 2-Methylbenzoic Acid

White crystals, mp 257–259°C. IR (KBr): 1775, 1650  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 3.06 (s, 3H,  $\text{CH}_3$ ), 7.31 (m, 2CH), 7.48 (m, CH), 8.14 (m, CH), 11.54 (s, 1H, COOH). Anal. calcd. for  $\text{C}_8\text{H}_8\text{O}_2$  (136.15): C, 70.58; H, 5.92; found: C, 70.60; H, 5.89%.

### 3-Methylbenzoic Acid

Pale yellow crystals, mp 107–109°C. IR (KBr): 1785, 1680  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 2.44 (s, 3H,  $\text{CH}_3$ ), 7.41 (m, 2CH), 7.94 (m, 2CH), 11.80 (s, 1H, COOH).  $^{13}\text{C}$  NMR: 21.3 ( $\text{CH}_3$ ), 128.0 (C), 129.1 (CH), 129.4 (CH), 131.4 (CH), 133.8 (CH), 143.4 (C), 167.7 (COOH). Anal. calcd. for  $\text{C}_8\text{H}_8\text{O}_2$  (136.15): C, 70.58; H, 5.92; found: C, 70.59; H, 5.90%.

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