

# An advantageous tetrameric titanium alkoxide/ionic liquid as a recyclable catalyst system for the selective oxidation of sulfides to sulfones

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## Abstract

The quantitative oxidation of organic sulfides to sulfones with 30% aqueous hydrogen peroxide (3:1 molar ratio of H<sub>2</sub>O<sub>2</sub>/sulfide) at room temperature using the known titanium alkoxide Ti<sub>4</sub>[(OCH<sub>2</sub>)<sub>3</sub>CMe]<sub>2</sub>(*i*-PrO)<sub>10</sub> (**1**) as a catalyst is reported. Mixtures of sulfone/sulfoxide are obtainable with lower H<sub>2</sub>O<sub>2</sub>/sulfide ratios. Catalyst **1** can be used in a solvent, such as methanol or acetonitrile or it can be immobilized in solution in room temperature ionic liquids (RTILs), from which the product sulfone is extracted with ether, thus, allowing the 1/RTIL system to be recycled. With some substrates, approximately 30% faster reaction rates are seen in a 1/RTIL system compared with **1** in methanol. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Titanium; Oxidation; Sulfides; Sulfones; Ionic liquids; Hydrogen peroxide

## 1. Introduction

Sulfones are useful reagents in organic synthesis and they are also valuable synthetic intermediates for the construction of chemically and biologically important molecules [1]. Thus, the oxidation of sulfides to sulfoxides or sulfones has been the subject of extensive studies, and a variety of procedures for their preparation are available [2–18]. Among preparations of sulfones, the most important employ sulfide oxidations, and oxidizing agents used for this purpose include nitric acid [7], KMnO<sub>4</sub> [4], MnO<sub>2</sub> [5], NaClO<sub>4</sub> [6], *m*-chloroperbenzoic acid [7], sodium metaperiodate [8], bromine [9], dinitrogen tetroxide [10], oxaziridine [11], benzeneseleninic peracid [12], *tert*-butyl hydroperoxide [13], sulfinyl peroxy compounds [14], iodosobenzene diacetate [15] and 4-methylmorpholine *N*-oxide/osmium tetroxide [16]. Unfortunately, most of these reagents are not amenable to medium or large scale syntheses because of the low oxidizing oxygen content, formation of environmentally damaging by-products, and/or high cost. Although molecular oxygen in the presence of 2-methylpropanal and Co(II) complexes has also been used for the oxidation of sulfides [17], a large excess of aldehyde is required. Very recently, molec-

ular oxygen has been employed as a stoichiometric oxidant in the presence of potassium osmate to catalyze such oxidations [18], but the toxicity and relatively high cost of this metal compound are major drawbacks to this approach.

Aqueous hydrogen peroxide (30%) is an ideal oxidant in view of its high effective-oxygen content, its eco-friendly by-product (water), its relative safety in storage and operation, and its comparatively low cost of production and transportation [19]. These advantages have spurred the development of useful procedures for the hydrogen peroxide oxidation of sulfides catalyzed by tungsten systems, such as H<sub>2</sub>WO<sub>4</sub> [20], [C<sub>5</sub>H<sub>5</sub>N(*n*-C<sub>16</sub>H<sub>33</sub>)]<sub>3</sub>PO<sub>4</sub>[W(O)(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub> [21], and Na<sub>2</sub>WO<sub>4</sub>/[*n*-C<sub>4</sub>H<sub>9</sub>]<sub>4</sub>N]Cl [22], and also by Na<sub>2</sub>MoO<sub>4</sub>/[*n*-C<sub>4</sub>H<sub>9</sub>]<sub>3</sub>PO [23], Ti(III)Cl [24] and CH<sub>3</sub>ReO<sub>3</sub> [25]. However, there remains considerable room for improved protocols, because many of these procedures require the use of chlorohydrocarbon solvents which are health and environmental hazards [13b,21,22,23]. In order to address this issue, Noyori and co-workers reported the oxidation of sulfides to sulfoxides and sulfones with 30% H<sub>2</sub>O<sub>2</sub> using Na<sub>2</sub>WO<sub>4</sub> under solvent and halogen-free conditions [26]. The requirement for the added presence of a phosphonic acid promoter, and the acidic quaternary ammonium salt [CH<sub>3</sub>(*n*-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N]HSO<sub>4</sub> makes this process cumbersome, however. Moreover, the catalyst could not be recovered for recycling.

Recyclable heterogeneous oxidation catalyst systems are preferred over homogeneous analogues, especially in the case of

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metal catalysts that generate copious amounts of heavy metal waste. In efforts to meet environmental and technical requirements, many heterogeneous systems for the selective oxidation of sulfides to sulfoxides or sulfones have been employed which consist of supported reagents or catalysts [27]. For example, the titanium silicates TS-1 and TS-2 [27g] promote sulfide oxidation in the presence of hydrogen peroxide, but the use of bulky sulfides was precluded by their limited access to the active Ti sites. In order to overcome this limitation, mesoporous materials have been used. Thus, Ti-MCM-41 allows the oxidation of bulky sulfides using hydrogen peroxide or *tert*-butylhydroperoxide, although only mixtures of sulfoxides and sulfones were obtained [28]. Recently, Choudary et al. reported a useful alternative approach that employs tungstate-exchanged layered double hydroxides for the hydrogen peroxide oxidation of thioethers. A disadvantage of this method is that it entails the formation of mixtures of products [27j].

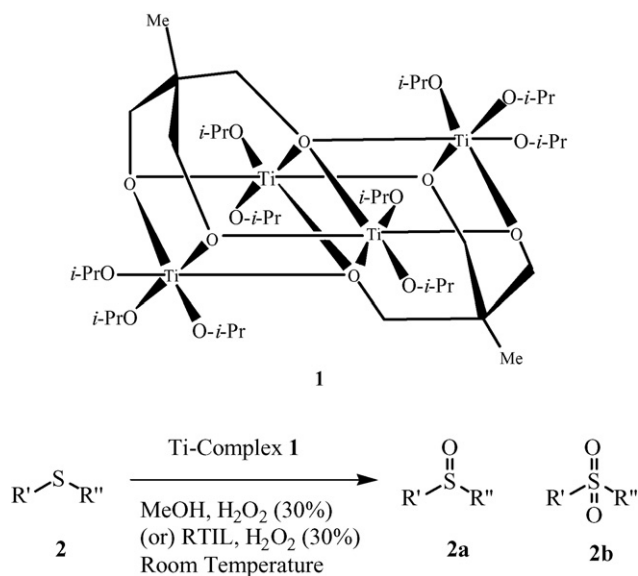
With the currently growing trend toward increased environmental responsibility, there is considerable incentive to find new catalytic systems that are efficient, recyclable and environmentally friendly. In recent years, room-temperature RTILs have attracted growing interest because of their useful properties such as thermal stability, high ionic conductivity, negligible vapor pressure, tolerance towards air and moisture, low corrosive nature and a large electrochemical window [29,30]. Depending on the anion and the alkyl group of imidazolium RTILs, for example, carbonyl compounds, alcohols, alkyl halides, supercritical CO<sub>2</sub> (scCO<sub>2</sub>) and transition metal complexes can be solubilized in these liquids, although some imidazolium RTILs are poorly miscible with dialkyl ethers, alkanes, water and scCO<sub>2</sub> [29,31]. Numerous examples of the usefulness of RTILs in catalysis and biocatalysis [32] have been reported [33] and they are also capable of replacing traditional organic solvents (OS) in aqueous-OS biphasic systems, including those used for the selective extraction of metal ions from aqueous solution in aqueous-OS biphasic systems [34,35] and for OS extraction from scCO<sub>2</sub> in OS-scCO<sub>2</sub> biphasic media [36,37]. Applications of imidazolium RTILs have also been found in gas chromatography [38] as stationary phases, in electrochemistry [39] as solvents and electrolytes, and in pervaporation procedures [40].

We report here a novel, efficient and recyclable catalytic approach to the room temperature oxidation of sulfides to sulfones by cheap, nonpolluting and reasonably stable hydrogen peroxide in the presence of a catalytic amount of titanium complex **1**. The reaction can be carried out in methanol or acetonitrile. Because the rates are nearly the same in both solvents, these solvents were used interchangeably. RTILs were also employed to immobilize the catalyst, thus, allowing both the solvent and the catalyst to be recycled (Scheme 1).

## 2. Experimental

### 2.1. General

All reactions were performed in oven-dried glassware in an argon atmosphere using standard Schlenk techniques. All solvents were collected from a Grubbs-type solvent purification



Scheme 1.

system and kept over 4 Å molecular sieves. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian VRX-300 NMR spectrometer using standard procedures. The chemical shifts are referenced to the residual peaks of CDCl<sub>3</sub> (7.26 and 77.23 δ ppm in <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively). Silica gel (J.T. Baker, 40–140 mesh) was used for column chromatography. Aqueous H<sub>2</sub>O<sub>2</sub> (30%) was purchased from Fisher chemicals, and Ti(O-*i*-Pr)<sub>4</sub>, 1,1,1-*tris*(hydroxymethyl)ethane, bromobutane, 1-methylimidazole, NaBF<sub>4</sub> and the organic sulfides were purchased from Aldrich and were used without further purification. RTIL **3** was synthesized according to a literature procedure [30e] and its <sup>1</sup>H NMR spectrum corresponded to that reported by others [31a] RTILs **4** and **5** were purchased from Solvent-Innovation and were used without further purification. Catalyst **1** (prepared in 88% yield) was synthesized following the method in our earlier report [41].

### 2.2. General procedure for the oxidation of organic sulfides in methanol

To a stirred solution of sulfide (2 mmol) and **1** (5 mol%) in methanol (5 mL), was added an aqueous solution of 30% (w/w) hydrogen peroxide (0.66 mL, 6 mmol) in 2–3 portions at room temperature. After completion of the reaction (which was followed by TLC), a small amount of MnO<sub>2</sub> was added to decompose unreacted H<sub>2</sub>O<sub>2</sub>. The reaction mixture was filtered to remove solid MnO<sub>2</sub>, and the product was then extracted with diethyl ether (3 × 10 mL). The extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to afford the product. Analytically pure compound was obtained after column chromatography (silica gel, using hexane/ethyl acetate 90:10, v/v).

### 2.3. General procedure for the oxidation of sulfides in RTILs

An RTIL (4.0 mL) and catalyst **1** (5 mol% based on the sulfide) were premixed in an oven-dried Schlenk flask equipped with a magnetic stirring bar. This procedure was carried out

under an argon atmosphere in a glove bag. The resultant solution was degassed by pumping under reduced pressure (200 mTorr) for 10 min and then the flask was filled with argon. Sulfide (2 mmol) was then introduced in the case of a liquid. (In the case of a solid, the sulfide was dispersed into the RTIL with stirring giving a cloudy solution.) Addition at this point of 30% (w/w) hydrogen peroxide (0.66 mL, 6 mmol) in 2–3 portions at room temperature via syringe gave a homogeneous solution. The reaction mixture was then vigorously stirred for the time indicated. The extent of the reaction was monitored by TLC. After complete conversion,  $3 \times 10$  mL portions of diethyl ether were introduced via cannula for product extraction, after which the mixture was allowed to stir for 10 min after each portion was added. After separation and settling of the RTIL/I phase had occurred (0.5–1 h) the supernatant ether layer was removed through a cannula and then the ether solution was evaporated on a rotavapor apparatus to obtain the crude sulfone. After, the RTIL/I phase was separated from the product, the RTIL/I phase was placed under reduced pressure (200 mTorr for 2 h) to remove water (formed from decomposition of the hydrogen peroxide) and traces of ether used in the extraction. Fresh substrate and hydrogen peroxide were then added for recycling.

All the compounds synthesized herein are listed below with literature citations since they are all known compounds. Our  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data are in good agreement with those recorded in the literature.

#### 2.4. Spectral data for all compounds

##### 2.4.1. Methyl phenyl sulfone [26] (Table 5, entry 1)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.05 (s, 3H), 7.57–7.60 (m, 3H), 7.93–7.96 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  45.12, 127.97, 129.99, 134.32, 141.22.

##### 2.4.2. Benzyl sulfone [42] (Table 5, entry 2)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.13 (s, 4H), 7.40 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  58.47, 127.97, 129.43, 131.32.

##### 2.4.3. Di-tert-butyl sulfone [26] (Table 5, entry 3)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.47 (s, 18H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  25.74, 64.43.

##### 2.4.4. Ethyl phenyl sulfone [27] (Table 5, entry 4)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  1.23 (t, 3H,  $J=7.44$  Hz) 3.07 (q, 2H,  $J=7.44$  Hz), 7.53–7.68 (m, 3H), 7.88–7.90 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  7.19, 50.33, 127.93, 128.99, 133.42, 138.24.

##### 2.4.5. Diphenyl sulfone [26] (Table 5, entry 5)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.47–7.56 (m, 6H), 7.93–7.96 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  127.60, 129.32, 133.26, 141.54.

##### 2.4.6. Dibenzothiophene-5,5-dioxide [26] (Table 5, entry 6)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  7.53–7.56 (m, 2H), 7.62–7.67 (m, 2H), 7.67–7.84 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  121.76, 122.32, 131.75, 134.06, 137.85.

##### 2.4.7. Benzyl phenyl sulfone [43] (Table 5, entry 7)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.3 (s, 2H), 7.06 (d, 2H,  $J=6.9$  Hz), 7.23–7.31 (m, 3H), 7.42–7.47 (m, 2H), 7.60–7.64 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  62.63, 128.32, 128.38, 128.51, 128.63, 130.56, 133.46, 137.58.

##### 2.4.8. 4-(Phenylsulfonyl)-2-butanone [44] (Table 5, entry 8)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.18 (s, 3H), 2.90 (t,  $J=7.8$  Hz, 2H), 3.34 (t,  $J=7.8$  Hz, 2H), 7.55–7.67 (m, 3H), 7.89–7.92 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  30.0, 36.0, 50.6, 128.1, 129.5, 134.1, 139.0, 203.9

##### 2.4.9. Methyl 3-(phenylsulfonyl)propionate [44a] (Table 5, entry 9)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.73 (t,  $J=7.44$  Hz, 2H), 3.40 (t,  $J=7.44$  Hz, 2H), 3.64 (s, 3H), 7.56–7.68 (m, 3H), 7.90–7.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  27.3, 51.1, 52.4, 127.8, 129.1, 133.7, 138.1, 170.1

##### 2.4.10. 2-(Phenylsulfonyl)ethanol [26] (Table 5, entry 10)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.41 (br, 1H),  $\delta$  3.33 (t,  $J=5.25$  Hz, 2H), 3.98 (t,  $J=5.25$  Hz, 2H), 7.56–7.60 (t,  $J=6.96$  Hz, 2H), 7.66–7.72 (m, 1H), 7.92–7.95 (d,  $J=7.08$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  56.30, 58.30, 128.02, 129.56, 134.17, 139.04.

##### 2.4.11. Phenyl vinyl sulfone [42] (Table 5, entry 11)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  6.02 (d,  $J=9.66$  Hz, 1H), 6.48 (d,  $J=16.47$  Hz, 1H), 6.65–6.70 (m, 1H), 7.52–7.88 (m, 3H), 7.90–7.91 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  127.5, 127.6, 129.1, 133.4, 138.2, 139.3.

##### 2.4.12. Allyl phenyl sulfone [42] (Table 5, entry 12)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.79 (d,  $J=7.44$  Hz, 2H), 5.10 (d,  $J=16.95$  Hz, 1H), 5.30 (d,  $J=10.26$  Hz, 1H), 5.73–5.82 (m, 1H), 7.51–7.66 (m, 3H), 7.84–7.87 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  60.61, 124.3, 124.4, 128.2, 128.8, 133.51, 138.0.

##### 2.4.13. 3-(Phenylsulfonyl)propionitrile [44a] (Table 5, entry 13)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.84 (t,  $J=7.44$  Hz, 2H), 3.41 (t,  $J=7.44$  Hz, 2H), 7.60–7.76 (m, 3H), 7.92–7.94 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  12.23, 51.35, 116.15, 128.5, 130.02, 134.97, 137.74.

##### 2.4.14. Benzyl methyl sulfone [44b] (Table 5, entry 14)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.75 (s, 3H), 4.25 (s, 2H), 7.41 (s, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75.5 MHz):  $\delta$  38.74, 60.98, 128.01, 128.85, 130.25.

### 3. Results and discussion

Titanium(IV) isopropoxide is a useful catalyst in the asymmetric oxidation of sulfoxides in the Sharpless protocol which employs *tert*-butyl hydroperoxide as the oxidant [45]. Compound **1** could be advantageous in this reaction, in that it is stable

Table 1  
Effect of oxidant in the oxidation of thioanisole catalyzed by **1** in methanol

| Entry | Oxidant                             | Time   | Conversion (%) <sup>a</sup> | 2a/2b   |
|-------|-------------------------------------|--------|-----------------------------|---------|
| 1     | H <sub>2</sub> O <sub>2</sub> (30%) | 15 min | 99                          | 2b Only |
| 2     | Oxone <sup>®b</sup>                 | 48 h   | 99                          | 2a Only |
| 3     | TBHP                                | 3 h    | 99                          | 52:48   |

All reactions were carried out with 2 mmol of substrate, 6 mmol of oxidant and 5 mol% of catalyst in 5 mL of MeOH at room-temperature.

<sup>a</sup> Based on <sup>1</sup>H NMR spectroscopic integration.

<sup>b</sup> 2KHSO<sub>5</sub>·KHSO<sub>4</sub>·K<sub>2</sub>SO<sub>4</sub>.

in the atmosphere at ambient temperature over short periods of time compared with Ti(O*i*Pr)<sub>4</sub> which is a fuming liquid under the same conditions. It may be added that **1** is easily made in 88% yield by combining one equivalent of commercially available 1,1,1-*tris*(hydroxymethyl)ethane and excess Ti(O*i*Pr)<sub>4</sub> in THF [41]. Moreover, it would be advantageous to use hydrogen peroxide as a less expensive oxidizing agent for the oxidation of sulfides to sulfoxides and sulfones. The catalytic activity of **1** was initially compared with the three oxidants in Table 1 for the methanolic oxidation of thioanisole. It is clear from this table that hydrogen peroxide is the best of these three oxidizing agents for this reaction.

When Ti(O*i*Pr)<sub>4</sub> was used as the catalyst in the oxidation of thioanisole, sulfone was exclusively obtained in 99% conversion in 10 min using 5 mol% of catalyst in methanol. Upon increasing to 12.5 mol% of the catalyst in methanol, the conversion to sulfone was completed within 5 min. The completion time of this reaction was the same when it was carried out in the RTILs. It should be noted that the Ti(O*i*Pr)<sub>4</sub>/RTIL took on a milky appearance in the presence of Ti(O*i*Pr)<sub>4</sub>, whereas this was not the case with **1** (see below). From Table 2, it is seen that 6 mmol of H<sub>2</sub>O<sub>2</sub> (30%) is required to obtain sulfone selectively with two millimoles of substrate. Although good conversion was obtained with lower concentrations of 30% H<sub>2</sub>O<sub>2</sub>, mixtures of sulfoxide and sulfone are formed. The data in Table 3 show that the ratio of sulfoxide:sulfone was 33:67 after quantitative conversion was achieved at 0 °C (Table 3, entry 2) whereas after quantitative conversion at –20 °C, the ratio of sulfoxide:sulfone was 16:84 (Table 3, entry 4). However, sulfoxide formation was considerably higher at 84% conversion (Table 3, entry 3). These data support the known faster rate of the first oxidative step compared with the second [46].

Table 4 shows the effect of titanium concentration (mol%) on the activity and selectivity of thioanisole oxidation. The use of 2.5 mol% of titanium catalyst leads to formation of a mixture of

Table 2  
Selectivity for the conversion of thioanisole to the corresponding sulfoxide/sulfone as a function of hydrogen peroxide concentration in the presence of catalyst **1**

| Entry | 30% H <sub>2</sub> O <sub>2</sub> (mmol) | Time (min) | Conversion (%) <sup>a</sup> | 2a/2b   |
|-------|--|------------|-----------------------------|---------|
| 1     | 1.5                                      | 30         | 84                          | 81:19   |
| 2     | 6  | 15         | 99                          | 2b Only |

All reactions were carried out with 2 mmol of substrate and 5 mol% of catalyst in 5 mL of MeOH at room temperature.

<sup>a</sup> Based on <sup>1</sup>H NMR spectroscopic integration.

Table 3  
Effect of temperature in the oxidation of thioanisole catalyzed by catalyst **1**

| Entry          | Temperature | Time (min) | Conversion (%) <sup>a</sup> | 2a/2b   |
|----------------|-------------|------------|-----------------------------|---------|
| 1 <sup>b</sup> | R.T.        | 15         | 99                          | 2b Only |
| 2              | 0 °C        | 30         | 99                          | 33:67   |
| 3              | –20 °C      | 15         | 84                          | 80:20   |
| 4              | –20 °C      | 30         | 99                          | 16:84   |

All reactions were carried out with 2 mmol of substrate, 0.66 mL (6 mmol) of aqueous hydrogen peroxide (30%) and 5 mol% of catalyst in 5 mL of acetonitrile.

<sup>a</sup> Based on <sup>1</sup>H NMR spectroscopic integration.

<sup>b</sup> This entry was repeated with MeOH as solvent and the same result was obtained.

Table 4  
Effect of concentration of catalyst **1** on the 2a/2b ratio in the hydrogen peroxide oxidation of thioanisole

| Entry | Concentration (mol%) <b>1</b> | Time   | Conversion (%) <sup>a</sup> | 2a/2b              |
|-------|-------------------------------|--------|-----------------------------|--------------------|
| 1     | 2.5                           | 1.0 h  | 99                          | 62:38              |
| 2     | 2.5                           | 1.0 h  | 97                          | 88:12 <sup>b</sup> |
| 3     | 5                             | 25 min | 99                          | 75:25              |
| 4     | 8                             | 20 min | 99                          | 88:12              |

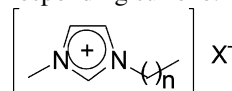
All reactions were carried out with 2 mmol of substrate, 0.33 mL (3 mmol) of aqueous hydrogen peroxide (30%) and different mol% of catalyst in 5 mL of acetonitrile at room temperature unless specified otherwise.

<sup>a</sup> Based on <sup>1</sup>H NMR spectroscopic integration.

<sup>b</sup> Reaction conducted at 0 °C.

products (Table 4, entry 1), while using 3 mmol of H<sub>2</sub>O<sub>2</sub> (30%) with 2 mmol of substrate (entry 2 in Table 4) shows that 2.5 mol% of catalyst at 0 °C leads to the formation of a major amount of sulfoxide in contrast to the minor amount given in entry 2 of Table 3, for which 5 mol% of catalyst was used instead of 2.5 mol%. With 5 and 8 mol% of **1** (entries 3 and 4, respectively) only 20–25 min were required for quantitative conversion, with an expected high selectivity for the sulfoxide.

Encouraged by these results, we immobilized catalyst **1** in three imidazolium RTILs (**3–5**) resulting in 99% conversion in 10 min under the conditions given in Table 3 (footnote) except that 2 mL of RTILs were used in place of acetonitrile. All three RTILs show very similar activity in the room temperature oxidation of thioanisole but the rates are 2–11 times faster than those of homogeneous and heterogeneous catalysts reported so far [21,25,27,28]. The same conclusion was drawn when the three RTILs were used for diphenyl sulfide, which is a more difficult substrate to oxidize and which took 2 h for complete conversion to the corresponding sulfone.



n = 1, X = BF<sub>4</sub> **3**

n = 3, X = BF<sub>4</sub> **4**

n = 3, X = PF<sub>6</sub> **5**

Recycling of the homogeneous [BMIM]BF<sub>4</sub>/**1** catalytic system was carried out by extracting the product from the RTIL/**1**/sulfone reaction solution with ether, followed by vacuum pumping the [BMIM]BF<sub>4</sub>/**1** system to remove water formed in the oxidation process, and then adding fresh hydrogen perox-

Table 5  
Oxidation of sulfides to sulfones catalyzed by cat 1 using aqueous H<sub>2</sub>O<sub>2</sub> (30%)

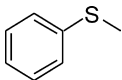
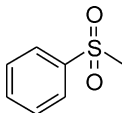
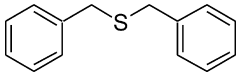
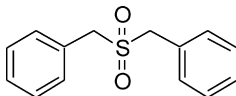
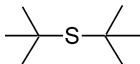
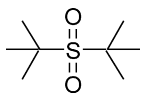
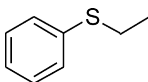
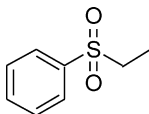
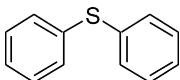
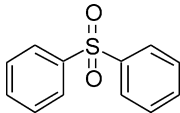
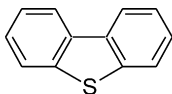
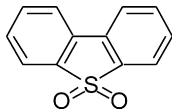
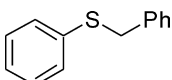
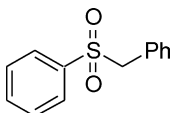
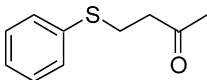
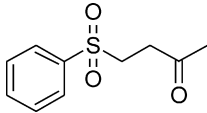
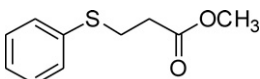
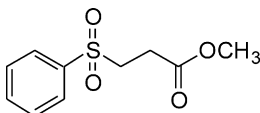
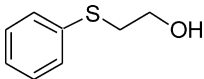
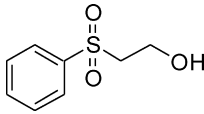
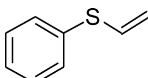
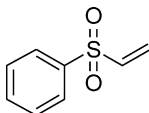
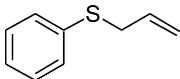
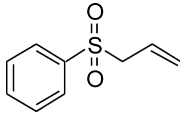
| Entry | Sulfide   | Product   | Cat1/MeOH time (h)<br>conv (%) <sup>a</sup> | Cat 1/(BMIM)BF <sub>4</sub><br>time (h) | Isolated yield (%) <sup>b</sup> |
|-------|---|---|---|---|---------------------------------|
| 1     |    |    | 15 min<br>94 <sup>c</sup>                   | 10 min                                  | 95                              |
| 2     |    |    | 2.5   | 2.5                                     | 93                              |
| 3     |    |    | 1.0   | 1.0                                     | 93                              |
| 4     |    |    | 2.0   | 2.0                                     | 98                              |
| 5     |    |    | 2.0   | 2.0                                     | 91                              |
| 6     |   |   | 2.0   | 2.0                                     | 89                              |
| 7     |  |  | 2.0   | 2.0                                     | 90                              |
| 8     |  |  | 2.0   | 1.5                                     | 90                              |
| 9     |  |  | 2.5   | 2.0                                     | 91                              |
| 10    |  |  | 3.0   | 3.0                                     | 91                              |
| 11    |  |  | 3.0   | 2.5                                     | 87                              |
| 12    |  |  | 2.0   | 2.0                                     | 91                              |

Table 5 (Continued)

| Entry | Sulfide | Product | Cat1/MeOH time (h)<br>conv (%) <sup>a</sup> |    | Cat 1/(BMIM)BF <sub>4</sub><br>time (h) | Isolated yield (%) <sup>b</sup> |
|-------|---------|---------|---|----|---|---------------------------------|
| 13    |         |         | 2.0   | 99 | 2.0                                     | 91                              |
| 14    |         |         | 1.5   | 99 | 1.0                                     | 94                              |

Reaction conditions: all reactions were carried out with 2 mmol of substrate, 5 mol% of catalyst in 5 mL of MeOH or 4 mL of RTIL, 0.66 mL (6 mmol) of aqueous hydrogen peroxide (30%).

<sup>a</sup> Based on <sup>1</sup>H NMR spectroscopic integration.

<sup>b</sup> After column chromatography using the RTIL method.

<sup>c</sup> Isolated yield after column chromatography.

ide and substrate. Thus, the catalyst was reused six times without loss of activity and selectivity using the conditions given in Table 3 (footnote) except that 2 mL of RTILs were employed in place of acetonitrile.

We also compared the reusability of the [BMIM]BF<sub>4</sub> system with [BMIM]BF<sub>4</sub>/Ti(OiPr)<sub>4</sub> in the oxidation of thianisole. Although this reaction gave a 99% conversion to sulfone in 10 min in the first run, more time was required from the second cycle onwards. Thus, the reaction times for the second to the sixth cycle are 20, 40, 90, 105 and 150 min, respectively, under the same reaction conditions.

The [BMIM]BF<sub>4</sub>/1 catalyst system is advantageous for the oxidation of sulfides in terms of its higher activity compared with the [BMIM]BF<sub>4</sub>/Ti(OiPr)<sub>4</sub> system. Furthermore, upon the addition of hydrogen peroxide to the latter system, a milky suspension formed which gradually became a turbid solution. This was not the case with the [BMIM]BF<sub>4</sub>/1 solution, which became pale yellow and became only slightly turbid after six cycles. The turbidity is probably associated with the formation of titanium dioxide via hydrolysis, since it is well-known that titanium alcoholates are hydrolyzed stepwise, ultimately forming titanium dioxide [47]. Nevertheless, the nature (e.g., homogeneous and/or heterogeneous) of the active titanium species responsible for the oxidation of sulfides in the solution phase remains uncertain [48].

The use of RTILs as a solvent in the oxidation of sulfides is an attractive alternative to the use of environmentally undesirable chlorinated organic solvents [17b,21,46]. It is worth noting that the 6 cycles we achieved with the [BMIM]BF<sub>4</sub>/1 catalyst system is somewhat better than the maximum of 4 or 5 cycles reported by previous investigators using heterogeneous oxidation catalysts for this reaction [18,27j].

In an effort to establish the scope of our protocol, a series of sulfides with a variety of sulfur substituents were oxidized and the results are presented in Table 5. In our protocol, thioanisole requires only 15 min in methanol and 10 min in the RTIL, while homogeneous catalytic procedures recorded in the literature require from 1 to 3 h [21,25,27g,28], including experiments carried out at elevated temperatures for this transformation

[27g,28]. It is also seen in Table 5 that sulfides with aliphatic substituents oxidize more quickly (entries 1 and 3). Interestingly, thioanisole is exceptionally quick to oxidize, perhaps because of considerable steric accessibility of the sulfur to the catalytically active form of the catalyst (see below). A dialkyl sulfide (Table 5, entry 3) is more easily oxidized than the diaryl sulfides in this table, perhaps because of minimal steric hindrance of the methyl group.

Although the oxidation of diphenyl sulfide requires a higher temperature compared with the other aryl sulfides [26], the present method represents a relatively easy catalytic oxidation of this compound to diphenyl sulfone in a one-pot reaction that gives a quantitative yield in a manner that allows the catalyst to be recycled (Table 5, entry 5). Interestingly, some sulfides reacted at a faster rate in the RTIL/1 system compared with 1 in methanol as the solvent (Table 5, entries 1, 8, 9 and 11).

Our approach is a significant improvement over the aforementioned homogeneously catalytic procedure reported by Noyori and co-workers [26] using an analogous reaction employing Na<sub>2</sub>WO<sub>4</sub>, a phosphonic acid promoter and an acidic quaternary ammonium salt; a non-recyclable procedure that must be carried out at elevated temperatures in order to achieve good yields. Catalyst 1 is also a more efficient catalyst for the oxidation of sulfides than various metal anion-exchanged layered double hydroxides and their homogeneous analogues [27j].

The oxidation of dibenzothiophene is of current interest because of its presence in diesel fuel as a cause of acid rain and airborne particulate material [49]. Oxidation of thiophenes in fuels followed by extraction of the sulfone products is one of the few better methods available for sulfur removal. Such oxidations can be carried out using heterogeneous mixed oxide and titania-containing molecular sieve systems [49] and require prolonged reaction times (at least 5 h) and higher temperatures (50–70 °C). The present protocol involving a recyclable medium provides quantitative yields of dibenzothiophene sulfone at room temperature in a considerably shorter reaction time (Table 5, entry 6). After appropriate improvement in recyclability, is conceivable that the methodology reported here could be adapted to

the removal of sulfur-containing compounds from petroleum-derived fuels.

Interestingly, allyl and vinyl phenyl sulfides were selectively oxidized to their corresponding sulfones without epoxide formation (Table 5, entries 11 and 12). No aldehyde formation was observed in the oxidation of 2-hydroxyethyl phenyl sulfide (Table 5, entry 10). Thus, many functional groups such as nitrile (Table 5, entry 13), ester (Table 5, entry 9), keto (Table 5, entry 8), benzyl (Table 5, entries 2 and 7), alcohol (Table 5, entry 10) and alkene (Table 5, entries 11 and 12) are preserved under our reaction conditions.

Our novel RTIL/1/H<sub>2</sub>O<sub>2</sub>/sulfide reaction mixture is a solution, thus, allowing catalysis to occur rapidly in a homogeneous medium. The novelty of our approach is that not only does the RTIL act as a propitious solvent for the titanium alkoxide catalyst **1**, hydrogen peroxide, the organic sulfide substrate and the sulfone product (a diverse set of solutes), but it quite selectively retains the catalyst after efficient extraction of the product with ether. The RTIL also retains water formed in the reaction, which is removed under reduced pressure.

As a catalyst for oxidation, **1** probably takes part in the usual peroxo chemistry of titanium [48], reacting with H<sub>2</sub>O<sub>2</sub> to form a peroxotitanium intermediate such as TiOOH. Oxidation is then believed to proceed via oxygen transfer from the titanium to the nucleophilic sulfide, with initial formation of a sulfoxide that can further react with another molecule of a peroxotitanium species to form a sulfone.

#### 4. Conclusions

The present methodology, in which **1** is used for the first time as an oxidation catalyst in either methanol or an RTIL, represents the first protocol that permits a one-pot rapid and mild oxidation of sulfides to sulfones. The broad range of sulfides converted to sulfones by the [BMIM]BF<sub>4</sub>/**1** catalyst system (including bulky sulfones) coupled with excellent room temperature conversion rates and recyclability over five cycles, renders the [BMIM]BF<sub>4</sub>/**1** catalyst system at least competitive, if perhaps not superior to all heterogeneous and homogeneous catalysts reported so far. Catalyst **1**, which is easily made in high yield from titanium isopropoxide and trimethylol ethane, possesses two major advantages over titanium isopropoxide, namely, stability toward hydrolysis and greater recyclability.

#### Supplementary material

Copies of <sup>1</sup>H and <sup>13</sup>C NMR of all sulfones products in this work.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2007.02.053.

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