



## Oxidation of Organic Sulfides with Clay-supported Iodosylbenzene as Oxygen Donor

Pothiraj Kannan,<sup>a</sup> Ranganathan Sevvil,<sup>b</sup> Seenivasan Rajagopal,<sup>a\*</sup>  
Kasi Pitchumani<sup>\*\*</sup> and Chockalingam Srinivasan<sup>b\*</sup>

<sup>a</sup>School of Chemistry and <sup>b</sup>Department of Materials Science,  
Madurai Kamaraj University, Madurai-625 021, India

**Abstract :** Alkyl, aryl and diaryl sulfides afford excellent yields of sulfoxides with PhIO supported on natural (montmorillonite, KSF and bentonite clay) as well as cation-exchanged clays of K10-montmorillonite in acetonitrile suspension and also in solid state. A ligand coupling mechanism for this facile oxidation is proposed. © 1997 Elsevier Science Ltd.

Syntheses of sulfoxides have been the subject of considerable research, partly due to their importance of sulfoxides as useful intermediates in organic chemistry.<sup>1</sup> Though several oxidants have been employed for the oxidation of sulfides, it is desirable to have a simple and convenient method for the exclusive preparation of sulfoxides without further oxidation.<sup>2</sup> The present work describes the efficient oxidation of sulfides to sulfoxides (without over-oxidation to sulfones) in dry K10-montmorillonite/PhIO in the solid state as well as in the presence of acetonitrile, in good yield. This illustrates the efficiency of clays and clay-based reagents as catalysts<sup>3</sup> in organic reactions.

Uncatalysed oxidation of organic sulfides using PhIO as the oxidant is known to be very slow.<sup>4</sup> We have also noticed that during the kinetics of oxidation of organic sulfides by PhIO, complexes of Cr, Ru and Mn act as catalysts.<sup>5</sup> Here we report the efficient catalytic role of clay instead of metal complexes in the PhIO oxygenation of organic sulfides. The superiority of clays over metal complexes as catalysts stems from the faster rate, easier work-up, good yield and reusability. This is also the first report with PhIO as the oxygen donor upon heterogenization in a clay interlayer.

### RESULTS AND DISCUSSION

The oxidation of sulfides with PhIO to the corresponding sulfoxides is carried out in clay interfaces in the solid state as well as in a suspension of acetonitrile. Typically clay and PhIO are intimately mixed. Sulfide is then added to this mixture which is shaken periodically after every 10-15 minutes. The results of the oxidation of sulfides with a 1:1 and 1:2 ratio of clay and PhIO are presented in Table 1. In the case of alkyl aryl sulfides, the presence of electron releasing substituents in both the benzene ring and alkyl group favors a significant increase in the oxidation in the solid state as well as in solution (Table 1). However, when electron withdrawing substituents are introduced in the benzene ring, there is no marked decrease in the yield of sulfoxides. An increase in the yield of sulfoxide is obtained with an increase in the [PhIO]. The oxidation is facile in K10-mont. as well as with other natural clays namely KSF and bentonite. When the same reaction is carried out in cetyltrimethylammonium chloride (CTAC) and 3-aminopropyltriethoxysilane pillared clays, there is no reaction in either case. In these clays, after intimate

Table 1.

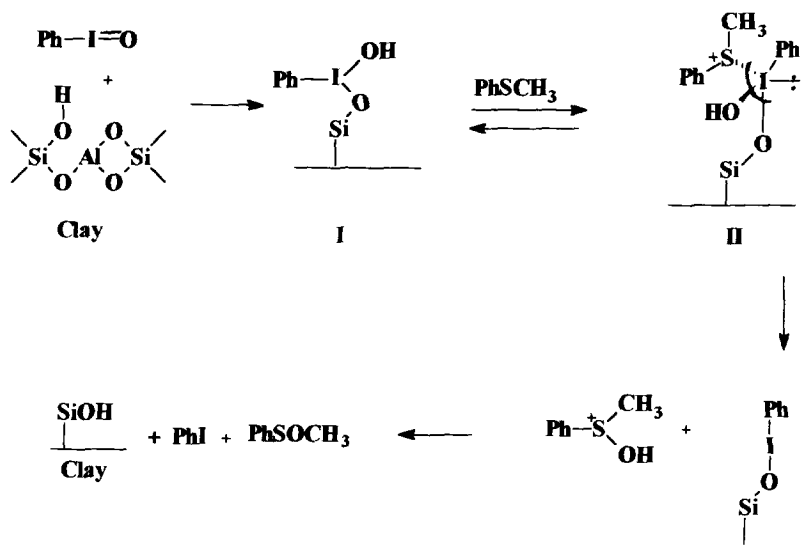
Oxidation of  $p\text{-X-C}_6\text{H}_4\text{SR}$  to  $p\text{-X-C}_6\text{H}_4\text{-SOR}$  in the presence of clay catalyst<sup>a</sup>

| Substrate                  |  | Catalyst                   | Reaction time (h) | % of sulfoxide in solid mixture | % of sulfoxide in a suspension of solid mixture in CH <sub>3</sub> CN |
|----------------------------|--|----------------------------|-------------------|---------------------------------|---|
| X                          | R  |                            |                   |                                 |   |
| 1:1 ratio of clay and PhIO |  |                            |                   |                                 |   |
| H                          | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 45                              | 54  |
| H                          | -CH <sub>3</sub>                                 | K10-mont. <sup>b</sup>     | 5                 | No reaction                     | No reaction   |
| H                          | -CH <sub>3</sub>                                 | K10-mont. <sup>c</sup>     | 5                 | No reaction                     | No reaction   |
| H                          | -CH <sub>3</sub>                                 | K10-mont.-Na <sup>+</sup>  | 5                 | 37                              | 49  |
| H                          | -CH <sub>3</sub>                                 | K10-mont.-H <sup>+</sup>   | 5                 | 46                              | 55  |
| H                          | -CH <sub>3</sub>                                 | K10-mont.-Al <sup>3+</sup> | 5                 | 46                              | 55  |
| H                          | -CH <sub>3</sub>                                 | K10-mont.-Cr <sup>3+</sup> | 5                 | 41                              | 50  |
| H                          | -CH <sub>3</sub>                                 | K10-mont.-Cu <sup>2+</sup> | 5                 | 42                              | 52  |
| H                          | -CH <sub>2</sub> CH <sub>3</sub>                 | K10-mont.                  | 5                 | 56                              | 59  |
| H                          | -CH(CH <sub>3</sub> ) <sub>2</sub>               | K10-mont.                  | 5                 | 87                              | 100   |
| H                          | -(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | K10-mont.                  | 5                 | 53                              | 51  |
| p-Ome                      | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 89                              | 100 <sup>d</sup>  |
| p-COOH                     | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 43                              | 89  |
| p-Cl                       | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 50                              | 90  |
| H                          | -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>   | K10-mont.                  | 5                 | 76                              | 90  |
| p-Cl                       | -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>   | K10-mont.                  | 5                 | 65                              | 86  |
| H                          | -C <sub>6</sub> H <sub>5</sub>                   | K10-mont.                  | 5                 | 37                              | 78  |
| H                          | -CH <sub>3</sub>                                 | KSF                        | 5                 | 37                              | 50  |
| H                          | -CH <sub>3</sub>                                 | Bentonite                  | 5                 | 25                              | 35  |
| 1:2 ratio of clay and PhIO |  |                            |                   |                                 |   |
| H                          | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 100                             | ---   |
| H                          | -CH <sub>2</sub> CH <sub>3</sub>                 | K10-mont.                  | 4.5               | 100                             | ---   |
| H                          | -CH(CH <sub>3</sub> ) <sub>2</sub>               | K10-mont.                  | 3.5               | 100                             | ---   |
| H                          | -(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> | K10-mont.                  | 5                 | 80                              | ---   |
| p-Ome                      | -CH <sub>3</sub>                                 | K10-mont.                  | 3                 | 100                             | ---   |
| p-COOH                     | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 90                              | ---   |
| p-Cl                       | -CH <sub>3</sub>                                 | K10-mont.                  | 5                 | 98                              | ---   |
| H                          | -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>   | K10-mont.                  | 3.5               | 100                             | ---   |
| p-Cl                       | -CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>   | K10-mont.                  | 3.5               | 93                              | ---   |
| H                          | -C <sub>6</sub> H <sub>5</sub>                   | K10-mont.                  | 5                 | 80                              | ---   |

<sup>a</sup>Reaction in suspension state in the duration of 40 min; <sup>b</sup>CTAC pillared clay; <sup>c</sup>3-Aminopropyltriethoxy-silane pillared clay; <sup>d</sup>kept only for 25 min.

mixing, the sulfide prefers to stay in the hydrophobic (lipophilic) region and PhIO in the hydrophilic region. This limits the contact between these two reagents and consequently there is no reaction.

We propose the following mechanism for the oxidation. Iodosylbenzene, upon heterogenization into the clay microenvironment, combines with the acidic sites (generated upon the hydrolysis of Si--O--Al bonds), to produce a hydroxy-[silyloxy]-iodobenzene intermediate (I), which reacts more readily with sulfides than PhIO itself (Scheme 1). Subsequent ligand coupling within the hypervalent intermediate (II) produces sulfoxide and iodobenzene. The ligand coupling reaction<sup>6</sup> appears to be more pronounced when the central atom of the two coupling ligands is a highly polarizable heteroatom and such reactions



Scheme 1

on sulfur,<sup>7,8</sup> iodine<sup>9</sup> and phosphorus<sup>10</sup> have been studied in detail and are common reactions in various fields of organic chemistry.

In a recent report,<sup>11</sup> a similar facile oxidation of sulfides to sulfoxides using iodosylbenzene catalysed by benzeneselenenic acid has been carried out. Ligand coupling in the hypervalent iodine intermediate is given as the reason for the facile oxidation. It is interesting to note that the reaction is, however, not catalysed by the other protic acids such as acetic acid and benzoic acid.<sup>11</sup> In our case also,  $\text{H}^+$ -exchanged clay reacts at the same rate as that of natural as well as other cation-exchanged clays. The absence of any acceleration in reaction with  $\text{H}^+$ -exchanged (extralattice Bronsted acidity) and other cation-exchanged (Lewis acidity) clays substantiates the proposed mechanism, in which the Bronsted acidity generated upon the hydrolysis of Si-O-Al bond is responsible for the efficient oxidation. The

presence of acetonitrile(which may aid mixing of the reagents), facilitates ligand coupling and subsequent elimination of sulfoxide by shifting the equilibrium towards the product (Scheme 1). Restricted movement of the reagents, may also be the cause of the slower reaction in the solid state.

This is the first report of the oxidation of sulfide to sulfoxide using PhIO as the oxygen donor in the clay interfaces. The superiority of clays over the metal complexes as catalyst is established by the following experiments. We have carried out the same reaction using Cr(III)-salen complex (salen is the ligand obtained from salicylaldehyde and ethylenediamine) as the catalyst instead of clay and this slows down the reaction to 5%. When we studied the reaction by adding the metal complex to the clay and PhIO mixture, the yield of sulfoxide is again lowered (~10% conversion). This reduction in the yield may be due to the blocking of some of the active sites in clay interfaces by the metal complex.

In conclusion, the oxidation of sulfides with PhIO/dry K10-montmorillonite system in the solid state and suspended acetonitrile readily affords sulfoxides. This system is superior to the metal complex catalysed oxidation reactions. All the reagents used are inexpensive and safe to handle, the clay can be reused and the reaction can be carried out under mild conditions. Though this system could be treated just like a clay-supported reagent,<sup>12</sup> permitting a facile isolation of sulfoxides, it does not require the tedious preparation of supported reagent.

## EXPERIMENTAL SECTION

*Materials.* All the organic sulfides,<sup>3h,13</sup> chromium(III)-salen complex<sup>14</sup> and PhIO<sup>15</sup> were prepared by standard procedures. Cation-exchanged montmorillonite clays were prepared by stirring 1g of natural clay with 25 ml of 1 M aqueous solution of the appropriate salt (nitrate or chloride) for three days. It was then filtered, washed repeatedly with distilled water and dried at 60°C.

Cetyltrimethylammonium chloride pillared clay was prepared by mixing 6 g of sodium exchanged clay in 50 ml of 0.15M of cetyltrimethylammonium chloride at 53°C for 100 h with stirring. It is then filtered, washed repeatedly with distilled water and dried at 95°C for over night. The 3-aminopropyltriethoxysilane pillared clay was prepared as described by us recently.<sup>3h</sup>

*General Procedure for Oxidation of Sulfides.* Clay (0.050 g) was intimately mixed with (0.045g)  $8.64 \times 10^{-3}$  mole of PhIO in a 50 ml stoppered conical flask, and then  $8.64 \times 10^{-3}$  mole of sulfide was added to the above mixture which is shaken periodically at regular intervals of 10 - 15 minutes. The reaction mixture was kept at room temperature for 5 h and then extracted with 20 ml of chloroform. In another set of experiments  $8.64 \times 10^{-3}$  mole of the sulfide was dissolved in 2.5 ml of acetonitrile in a 50 ml round bottomed flask, and then the clay containing PhIO was added and stirred for 40 min. The work-up is similar to solid state reaction.

In each case the reaction mixture was analysed in a Shimadzu LC-8A modular h.p.l.c. system (reverse phase column ODS, UV-detector at 258 nm) using 70% methanol as the mobile phase. Sulfoxides were identified by comparing with the authentic samples, prepared by literature methods.<sup>16</sup>

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