Pergamon

TETRAHEDRON

Tetrahedron 57 (2001) 8391–8394

Reactions in clay media: photooxidation of sulfides by clay-bound methylene blue

D. Madhavan and K. Pitchumani*

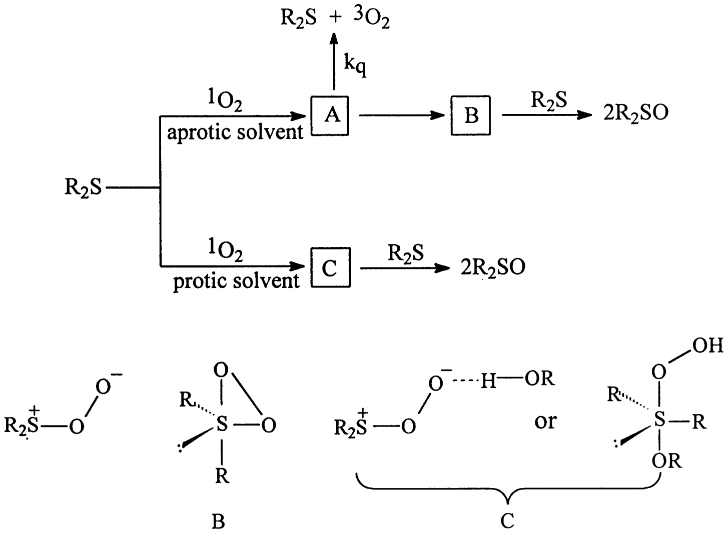
School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

Received 9 May 2001; revised 11 July 2001; accepted 8 August 2001

Abstract—Photooxidation of dialkyl and alkyl aryl sulfides to the corresponding sulfoxides with clay-bound methylene blue is studied in acetonitrile. A significant increase in sulfoxide/sulfone ratio and a marginal increase in cooxidation of a second sulfide molecule are observed. The results are explained in terms of a suitable mechanism involving persulfoxide and thiadioxirane intermediates. © 2001 Elsevier Science Ltd. All rights reserved.

The reaction between singlet oxygen and sulfides to give the corresponding sulfoxides has attracted considerable interest[1–3] in view of its synthetic and biological implications. The course of the reaction depends on the medium.[4] In aprotic solvents, the interaction with singlet oxygen leads mainly (>95%) to physical quenching and oxygenation is inefficient, however, the efficiency increases at lower temperature. Two discrete intermediates are proposed under these conditions. The first one with electrophilic character, is quenched by diphenyl sulfoxide and the other one which has nucleophilic character is quenched by diphenyl sulfide. In a protic polar solvent such as methanol, on the contrary, chemical reaction predominates over physical quenching and a single intermediate (quenched by both Ph_2S and Ph_2SO) is proposed.[3,4] The identified intermediates are the persulfoxide A, the thiadioxirane B in aprotic media and an adduct of A with ROH (C, which may be a hydrogen-bonded persulfoxide or a sulfurane) for the reaction in methanol (Scheme 1).

A survey of recent literature[3–5] shows instances of supported sensitizers for the generation of singlet oxygen. A resin-bound rose bengal is used for aqueous photooxidation by Foote et al.[5] Photooxidation of organic sulfides using dicyanoanthracene covalently grafted on silica using visible light is reported.[6] An efficient oxidation of stilbenes by



Scheme 1. Mechanism of sulfide photooxidation by singlet oxygen.

Keywords: photooxidation; sulfides; clay-bound methylene blue.

* Corresponding author. Tel.: +91-452-858246, fax: +91-452-859181; e-mail: pit12399@yahoo.com

PII: S0040-4020(01)00834-1

Table 1. The percentage conversion and SO_2/SO ratio in sulfide oxidation by singlet oxygen mediated by MB–Bentonite composite

Sulfide	[Sulfide] (M)	Time (min)	Conversion (%)	SO_2/SO ratio
Di(*n*-butyl) sulfide	0.01	5	11	–/100
Di(*n*-butyl) sulfide	0.01	15	21	–/100
Di(*n*-butyl) sulfide	0.01	30	45	–/100
Di(*n*-butyl) sulfide	0.01	45	71	6/94
Di(*n*-butyl) sulfide	0.01	60	96	8/92
Di(*n*-butyl) sulfide	0.01	120	98	11/89
Di(*n*-butyl) sulfide	0.10	120	11	10/90
Di(*n*-butyl) sulfide	0.05	120	19	11/89
Di(*n*-butyl) sulfide	0.005	120	100	–/100
Di(*n*-butyl) sulfide	0.001	120	100	–/100
Di(*n*-butyl) sulfide[a]	0.01	60	42	14/86
Methyl phenyl sulfide	0.01	120	4	–/100
Methyl *para*-tolyl sulfide	0.01	120	25	–/100

The ratio of sulfide to dye is 20:1; studied in acetonitrile medium.

[a] Corresponds to solution irradiation.

zeolite-bound dyes involving an electron-transfer pathway is reported by Ramamurthy et al.[7] In the photooxidation of pentamethylene sulfide $(CH_2)_5S$ and thiolane $(CH_2)_4S$ by methylene blue doped NaY zeolite, Clennan et al.[8] have proposed the persulfoxide intermediate A, stabilized in the highly electrostatic environment of zeolite cage, as the single intermediate. The zeolite medium also precludes the hydrogen abstraction necessary to form B from A. Their results are consistent with competitive trapping by both sulfoxide (R_2SO) and the sulfide (R_2S). In the oxidation of diphenyl sulfide, it is proposed[8] that the reaction occurs by electron-transfer from diphenyl sulfide to singlet oxygen to give a sulfide radical cation–superoxide ion pair, which then collapses to the persulfoxide intermediate A (which is also competitively trapped by sulfoxide, but with reduced efficiency). These interesting findings coupled with our interest in using clays and modified clays as media for organic reactions have prompted us to undertake this investigation.

1. Results and discussion

In the present study, sulfides such as di(*n*-butyl) sulfide, methyl phenyl sulfide and methyl *para*-tolyl sulfide are found to be oxidized by singlet oxygen generated from bentonite-bound methylene blue as the sensitizer in oxygen saturated acetonitrile medium, and the corresponding sulfoxides are formed as major products. Among the three, di(*n*-butyl) sulfide is oxidized more efficiently and the other two are oxidized at slower rates. In other solvents, like *n*-hexane, methanol, dichloromethane and chloroform, no reaction is observed and thus acetonitrile is found to be the solvent of choice for the oxidation of sulfides. The percentage conversion of sulfides at regular time intervals and the corresponding sulfone/sulfoxide ratio are summarized in Table 1. It has also been found that with the increasing concentration of the sulfide, the percentage conversion decreases and the optimum level of oxidation corresponds to a sulfide:dye ratio of 20:1. The oxidation is also efficient in a surfactant-pillared bentonite clay, containing bound methylene blue as sensitizer.

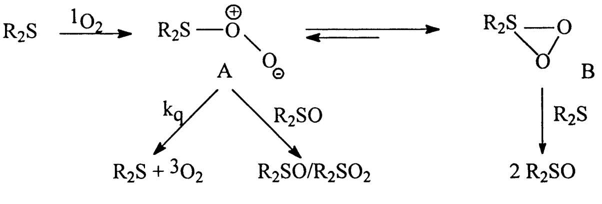
Addition of a second less reactive sulfide has resulted in an increase in its oxidation. For example, methyl phenyl sulfide which is oxidized to an extent of only 8% is oxidized to 28% in the presence of the more reactive di(*n*-butyl) sulfide. However, the same is not true with sulfoxides, as the addition of diphenyl sulfoxide to the reaction medium has no effect on the oxidation of sulfide/sulfoxide.

Control experiments show that there is no oxidation in the absence of either methylene blue or oxygen, and also that bleaching of methylene blue bound to clay does not occur. Addition of anthracene, nitrobenzene, 2-naphthol and *N*,*N*-dimethylaniline has no effect on the overall yield of sulfoxide and this rules out an electron-transfer pathway. However a dramatic decrease in the yield of sulfoxide is observed when iodide ion (from 100 to 12%) and β-carotene (from 100 to 30%) are added.

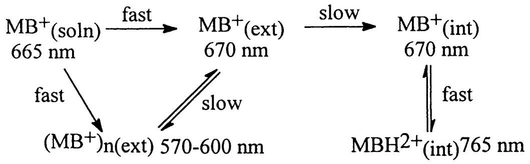
When our results of sulfide oxidation are compared with the oxidation of sulfide in zeolites,[8] some interesting differences are observed: (a) competitive trapping of intermediate A by sulfoxide does not occur (as in low $[R_2S]$ in zeolites) and, in fact, a small increase in yield of sulfone is observed with an increase in $[R_2S]$ (Table 1) and (b) Ph_2S does not undergo any oxidation under the experimental conditions and this rules out any electron-transfer pathway.

We believe that the decreased mobility within the restricted environment of the zeolite supercage ensures greater contact between the sensitizer and the substrate which favours an electron-transfer route. This is in contrast to the present study, wherein the substrate moves relatively more freely.

These observations have prompted us to visualize the following mechanism for R_2S oxidation (Scheme 2) involving a predominant energy-transfer route. It is likely that the persulfoxide intermediate A, may not be as



Scheme 2. Mechanism of sulfide photooxidation by singlet oxygen in bentonite clay.



Scheme 3. Nature of the methylene blue species in solution and upon adsorption onto montmorillonite clays.[10]

efficiently stabilized as in zeolite and is in equilibrium with the thiadioxirane intermediate B. The presence of sulfide (R_2S) shifts the equilibrium towards B leading to formation of mainly sulfoxide.

It is relevent to note here that a systematic time-dependent spectrophotometric study of the interaction of methylene blue with montmorillonite clay[9] provides valuable information about the nature of the dye species. The four bands of methylene blue at 575, 610, 670 and 760 nm are ascribed[10] to dimer and higher aggregates (first two peaks), monomer and J band of the dimer, respectively (Scheme 3). Upon addition, dyes are adsorbed on the external surface of the clays as induced aggregates $[(MB^+)_{n(ext)}]$ or as monomers $[MB^+_{(ext)}]$. A slower desorption followed by deaggregation tends to carry the methylene blue into the clay interlayer $[MB^+_{(int)}]$ and the sequence of steps in Scheme 3 is proposed.

Diffuse reflectance spectra of methylene blue–bentonite aggregate (Fig. 1) shows a peak at 674 nm, indicating that the deaggregation has indeed occurred in the present study also, and this suppression of aggregate formation of methylene blue in clays facilitates efficient oxidation. It is also proved by another study[11] that most methylene blue molecules can exist as monomers on the clay in suspensions of low loadings.

The other advantages of using clay-bound sensitizer, besides suppression of formation of H aggregates are, (a) the dye can be recycled, (for example, even after reusing three times the efficiency is still more than 80% for the oxidation of di(*n*-butyl) sulfide), (b) the sensitizer can easily be added and removed from the medium with no loss of efficiency. It is also more stable towards bleaching in the bound state and is thus an environmentally friendly sensitizer, (c) work-up is much easier as removal of the dye from the reaction mixture is now unwarranted and (d) the dye can be used as sensitizer in a medium in which it is not soluble.

The observed results have prompted us to extend the oxidation studies to other systems also. Systematic preliminary investigations have shown that this novel clay-bound sensitizers also oxidizes electron-rich phenols (cresols, 2,6-di-*t*-butylphenol), quinols, α-naphthol and also anthracene (to 9,10-anthraquinone) efficiently. Further studies to extend the scope of this work to other functional groups are in progress.

2. Experimental

The bentonite clay and di(*n*-butyl) sulfide were purchased from Aldrich. Methyl phenyl sulfide and methyl *para*-tolyl sulfide were prepared as per reported procedures.[12] Methylene blue and acetonitrile were supplied by E. Merck and were of A.R. grade. Acetonitrile was further purified by distillation after drying with activated silica gel.[13]

The Na^+-exchanged bentonite clay was prepared by stirring 1 g of the natural clay with 25 mL of 1 M sodium chloride solution for three days and was filtered, washed well with water and dried at 95°C overnight. Bentonite bound methylene blue was prepared by stirring 6 g of the Na^+-exchanged bentonite clay with 150 mL of a 100 ppm dye solution for three days. It was filtered, washed well with distilled water and dried at 140°C for six hours. Analysis of the washings showed that about 90% of the dye was adsorbed. It was characterized by UV-diffuse reflectance (Fig. 1) and FT-IR spectra (methylene blue intercalated bentonite shows absorption at 3113 and 2925 cm^{-1} (absent in Na^+–bentonite). In addition, OH stretching frequencies at 3635 and 3445 cm^{-1} are shifted to 3628 and 3450 cm^{-1}, respectively).

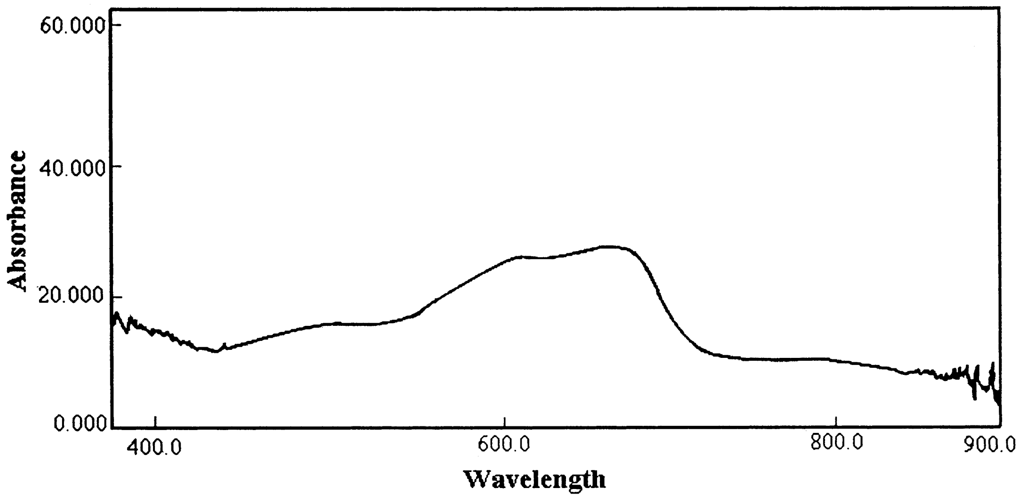


Figure 1. Diffuse reflectance spectra of bentonite-bound methylene blue.

In a typical oxidation, 200 mg of the clay-sensitizer composite and 5 mL of 0.01 M sulfide solution in acetonitrile were purged with high purity oxygen for 15 min. The oxygen saturated reaction mixture was then sealed and irradiated as a slurry under a 1000 W tungsten–halogen lamp through a 12 M sodium nitrite filter solution,[8] with stirring for the required time. After filtration of the solvent, the clay sample was extracted again with acetonitrile. The combined reaction mixture was concentrated under reduced pressure and was analyzed by a Shimadzu-17A GC (SE-30 10% capillary column—FID detector—high purity nitrogen as the carrier gas). The products were identified by coinjection with authentic samples. In all the experiments, retention time of the starting material was taken as the internal reference.

Acknowledgements

We thank Professor V. Ramamurthy, Tulane University, USA for recording the UV-diffuse reflectance spectra. Financial assistance from Department of Science and Technology (DST), New Delhi is gratefully acknowledged.

References

1. For a few selected reviews see: (a) Foote, C. S. In *Singlet Oxygen*, Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p. 139. (b) Clennan, E. L. *Sulfur Rep.* **1996**, *19*, 171. (c) Clennan, E. L. *Tetrahedron* **2000**, *56*, 9151. (d) Ando, W.; Takada, T. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC: Boca Raton, 1985; Vol. 3, p. 1. (e) Bellus, D. *Adv. Photochem.* **1979**, *11*, 105. (f) Jenson, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI: Greenwich, CT, 1995; Vol. 4, p. 49.
2. (a) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795. (b) Foote, C. S.; Denny, R. W.; Weaver, L.; Chang, Y.; Peters, J. W. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 139. (c) Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1982**, *104*, 49. (d) Clennan, E. L.; Oolman, K. A.; Yang, K.; Wang, D. X. *J. Am. Chem. Soc.* **1992**, *114*, 3021. (e) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191. (f) Murray, R. W.; Jindal, S. L. *Photochem. Photobiol.* **1972**, *16*, 147. (g) Monroe, B. M. *Photochem. Photobiol.* **1979**, *29*, 761. (h) Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 3511.
3. (a) Bonesi, S. M.; Mella, M.; d'Alessandro, N.; Aloisi, G. G.; Vanossi, M.; Albini, A. *J. Org. Chem.* **1998**, *63*, 9946. (b) Clennan, E. L.; Wang, D.; Clifton, C.; Chen, M. F. *J. Am. Chem. Soc.* **1997**, *119*, 9081. (c) Toutchkine, A.; Clennan, E. L. *J. Org. Chem.* **1999**, *64*, 5620. (d) Bonesi, S. M.; Albini, A. *J. Org. Chem.* **2000**, *65*, 4532. (e) Bonesi, S. M.; Torriani, R.; Mella, M.; Albini, A. *Eur. J. Org. Chem.* **1999**, 1723.
4. (a) Liang, J. J.; Gu, C. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717. (b) Jenson, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478. (c) Jenson, F.; Greer, A.; Clennan, E. L. *J. Am. Chem. Soc.* **1998**, *120*, 4439. (d) Jenson, F. *J. Org. Chem.* **1992**, *57*, 6478. (e) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677. (f) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 494.
5. Prat, F.; Foote, C. S. *Photochem. Photobiol.* **1998**, *67*, 626.
6. Soggiu, N.; Cardy, H.; Jiwan, J. L. H.; Leray, I.; Soumillon, J.Ph.; Lacombe, S. *J. Photochem. Photobiol.* **1999**, *124*, 1.
7. Li, X.; Ramamurthy, V. *Tetrahedron Lett.* **1996**, *37*, 5235.
8. Zhou, W.; Clennan, E. L. *J. Am. Chem. Soc.* **1999**, *121*, 2915.
9. Gessner, F.; Schmitt, C. C.; Newmann, M. G. *Langmuir* **1994**, *10*, 3749.
10. (a) Bergmann, K.; O'Konski, C. T. *J. Phys. Chem.* **1963**, *67*, 2169. (b) Bodenheimer, W.; Heller, L. *Isr. J. Chem.* **1968**, *6*, 307. (c) Yariv, S.; Lurie, D. *Isr. J. Chem.* **1971**, *9*, 553.
11. Iwasaki, M.; Kita, M.; Ito, K.; Kohno, A.; Fukunishi, K. *Clays Clay Miner.* **2000**, *48*, 392.
12. (a) Obermeyer, J. *Berichte* **1887**, *20*, 2918. (b) Vogel, A. I. *J. Chem. Soc.* **1948**, 1822. (c) Fehnel, C. A.; Carmackm, M. *J. Am. Chem. Soc.* **1949**, *71*, 84. (d) Barkenbus, C.; Kelly, B. *J. Chem. Educ.* **1945**, *22*, 356. (e) de la Mare, P. B. D.; Vernon, C. A. *J. Am. Chem. Soc.* **1956**, *78*, 41. (f) Price, C. C.; Stacy, G. W. *J. Am. Chem. Soc.* **1946**, *68*, 498. (g) Mauthner, F. *Berichte* **1906**, *39*, 3594.
13. Vogel, A. I. *Textbook of Practical Organic Chemistry*; 5th ed.; Longmann group UK: Essex, 1989; p. 410.