DOI: 10.1002/ejoc.200900265

Borax-Catalyzed and pH-Controlled Selective Oxidation of Organic Sulfides by H_2O_2: An Environmentally Clean Protocol

Sahid Hussain,[a,b] Saitanya K. Bharadwaj,[a] Ravindra Pandey,[a] and Mihir K. Chaudhuri*[a,c]

Keywords: Sustainable chemistry / Acidity / Chemoselectivity / Oxidation / Sulfur

The selective oxidation of sulfides to sulfoxides and sulfones was achieved in high yields at room temperature with borax as a recyclable catalyst and H_2O_2 as the terminal oxidant by varying the pH of the reaction medium. The borax/H_2O_2 system can chemoselectively oxidize alkyl and aryl sulfides in the presence of oxidation-prone functional groups such as C=C, –CN, and –OH.

Introduction

The discovery of hydrogen carbonate catalyzed oxidation of organic sulfides[1] through peroxocarbonate (HCO_4^-) and the subsequent seminal contributions of Davies and coworkers[2] showing that borate is a better catalyst than HCO_4^- with rapidly formed peroxoborates, $HOOB(OH)_3^-$ and $(HOO)_2B(OH)_2^-$, being more reactive than HCO_4^-, and extending the pH functional range to the 8–12 region are very important developments in the realm of oxidation chemistry of organic sulfur. The examples to bear with this contention include oxidants like H_2O_2,[3] periodate,[4] peracids,[5] permonosulfate,[6] and peroxymonocarbonate.[1,7] It was suggested that a protic solvent facilitates the nucleophilic displacement of the carbonate in the case of HCO_4^- oxidations. Also, it was shown recently from ab initio calculations on the oxidation of $(CH_3)_2S$ by H_2O_2 in aqueous solutions[8] that the transition state involves O–O bond breaking with concurrent S–O bond formation, and that hydrogen transfer occurs after the system has passed the transition state. Solvent molecules or H_2O_2 (with higher concentration) can efficiently lower the activation barrier for the oxidative transformations. Insofar as the oxidation of organic sulfides by peroxoborate is concerned, the reactions generally proceed in a manner similar to other peroxo-based oxidants, for instance, by development of a positive charge on the sulfur atom in the transition state with the sulfide behaving as nucleophile, yet there is a succinct difference. The difference lies in mono and diperoxborates having the transition state earlier along the reaction coordinate[2] with relatively less positive charge being developed on the sulfur atom. This in turn emphasizes that proton transfer would play a significant role in the peroxoborate oxidation of organic sulfides. Indeed, it was proposed[2] that the lower extent of positive charge development on the sulfur atom for the reaction of peroxoborates was due to the greater importance of the proton transfer in stabilizing the transition state by peroxoborates. These results and those of Pizer and Tihal[9] on the effect of pH on the formation of different peroxoborates and the elegant reviews by McKillop and Sanderson[7b] on sodium perborate (SPB) oxidations in addition to our earlier experience in the synthetic peroxo–boron chemistry[10] caused us to perceive the possibility of borax-activated and pH-controlled selective oxidation of organic sulfides in a protic medium like MeOH or MeOH/H_2O. In a very recent study, Gomez et al.[11] suggested that SPB could be used for nucleophilic oxidation, whereas sodium percarbonate (SPC) could be used for electrophilic oxidation. It was further suggested that the influence of support might be relatively more pronounced than the oxidant.

Given the environmental acceptability, cost effectiveness, and ease of handling, the borax/H_2O_2 system offers an ideal combination for the chosen oxidations. A number of advantages for the use of peroxoborates,[7b] the vast chemistry and practical importance of sulfoxides and sulfones,[12] and the plethora of oxidizing agents[3–7,13] and catalysts[14,15] are well documented in the literature, thereby making any elaboration of these aspects redundant. Our main concern for the present work was the selective oxidation of organic sulfides in an environmentally clean and catalytic manner with

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[a] Department of Chemistry, Indian Institute of Technology Guwahati,
Guwahati-781039, India
[b] Department of Chemistry, Indian Institute of Technology Patna,
Patna-800013, India
[c] Tezpur University,
Tezpur-784028, India
Fax: +91-3712-267006
E-mail: mkc@iitg.ernet.in
mkc@tezu.ernet.in

H_2O_2 being the terminal oxidant. Herein, we report the results of our endeavor in the borax-catalyzed selective oxidation of organic sulfides by H_2O_2 in methanol at pH 6–7 and at pH 10–11.

Results and Discussion

In order to ascertain the optimum conditions, several reaction runs were carried out on methyl phenyl sulfide as the model substrate, each time with the substrate (2 mmol), H_2O_2 (35% aqueous solution, 6 mmol), and borax (0.2 mmol) in MeOH (2 mL) at different pH, as shown in Table 1. The pH of the reaction solution was adjusted by the careful addition of a 0.1 M NaOH solution. The control experiment without catalyst showed 65% conversion after 12 h to 85% sulfoxide and 15% sulfone. Use of four or five molar equivalents of H_2O_2, instead of three molar equivalents, at pH 6–7 reduced the reaction time by ca. 1 h; however, 15–20% of sulfone was formed along with the sulfoxide, thereby reducing the selectivity of the oxidation. The selective oxidation to sulfone, if desired, was best performed at pH 10–11 (Table 1).

From perusal of the distribution diagram of the peroxo–borate system presented by Pizer and Tihal[9] it is evident that at pH 6–7 mono and diperoxoborates, $(HO)_3BOOH^-$ and $(HO)_2B(OOH)_2^-$, respectively, occur in equal but relatively low concentration along with a very minute amount of inactive peroxoboric acid, $(HO)_2BOOH$. With the increase in pH to 10–11, peroxoboric acid disappears while both the peroxoborates occur in relatively higher concentrations, with the concentration of $(HO)_2B(OOH)_2^-$ being much higher. This indicates that a higher concentration of diperoxoborates favors sulfone formation over the corresponding sulfoxide.

Table 1. Optimization of pH for selective oxidation of methyl phenyl sulfide.

Entry	pH	Time [h]	Product(s)
1	6.0	5	Sulfoxide (80%)
2	6.0	6	Sulfoxide (90%)
3	7.0	6	Sulfoxide (92%)
4	7.5	6.5	Sulfoxide (85%)/Sulfone (15%)
5	8.0	6	Sulfoxide (75%)/Sulfone (25%)
6	9.0	6	Sulfoxide (35%)/Sulfone (65%)
7	10.0	2.5	Sulfone (93%)
8	11.0	2.5	Sulfone (93%)

In order to generalize the scope of the reaction, a series of structurally diverse sulfides were subjected to oxidation under the optimized reaction conditions, and the results are presented in Table 2. The reactions went on well to afford products in high yields. It is notable that the sulfides were chemoselectively oxidized in the presence of some oxidation-prone functional groups such as C=C, –CN, and –OH (Table 2, Entries 6–8). Sulfides containing a methyl ester group gave sulfone, along with its hydrolysis product in basic medium (Table 2, Entry 9).

Dibenzothiophene (DBT) and substituted DBT oxidations are rather difficult with standard oxidation procedures.[3b] However, upon treatment with the borax/H_2O_2 system some of these substrates were converted into the corresponding sulfoxides and sulfones (Table 2, Entries 12 and 13). Although we succeeded in oxidizing DBT and 4-methyl-DBT, our protocol did not work well for 4,6-di-

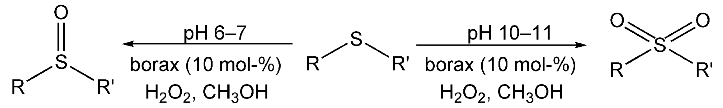

Table 2. Borax-catalyzed (0.1 equiv.) sulfide oxidation in MeOH by H_2O_2 at room temperature.

Entry	Substrate	pH 6–7		pH 10–11	
		Time [h]	Sulfoxide[a]	Time [h]	Sulfone[a]
1	$PhSCH_3$	6	92,83,[b] 94[c]	2.5	93, 85,[b] 95[c]
2	$PhSC_4H_9$	8	82	4	90
3	$PhSC_6H_{13}$	24	65	24	87
4	$C_2H_5SC_4H_9$	5	82	3	84
5	$C_4H_9SC_4H_9$	8	78	3.5	78
6	$PhSCH_2CH=CH_2$	8	85	6	90
7	$PhSCH_2CH_2CN$	7	85	6	88
8	$PhCH_2SCH_2CH_2OH$	5	90	–	–
9	$PhSCH_2CH_2CO_2CH_3$	5	92	5	62 + 25[e]
10	$PhSCH_2Ph$	8	90, 80,[b] 92[c]	3	94,78,[b] 97[c]
11	*p*-NO_2PhSCH_2Ph	6	88	2.5	95
12	Dibenzothiophene	10	55 + 42[d]	6	75
13	4-Methyldibenzothiophene	24	45 + 58[d]	24	75
14	4,6-Diethyldibenzothiophene	–	–	24	10

[a] Percent isolated yield. [b] Yield after fifth cycle. [c] Yield at 5-g scale. [d] Percent of sulfone. [e] Hydrolyzed product.

methyl-DBT. Only 10% oxidation was achieved after 24 h, possibly as a result of steric crowding by the methyl groups on DBT, which renders approach of the oxidant to the sulfur difficult, thereby causing problems (Table 2, Entry 14). It may be mentioned that with an increase in alkyl chain length of the sulfides, the rate of the reaction decreases. This may be due to orientation of the hydrophobic alkyl chain around the sulfur atom.

Recyclability of the catalyst was examined through a series of reactions with methyl phenyl sulfide by using the aqueous phase containing borax, obtained after extraction of the reaction mixture with ethyl acetate. This was charged with fresh substrate and H_2O_2 (3 equiv.) with adjustment of the pH of the solution. The catalyst could be reused for at least five reaction cycles with consistent activity. Importantly, the reaction can be performed on a relatively large scale (5 g) to give good yields (Table 2, Entries 1 and 10), which shows its potential for scale-up applications.

Conclusions

In conclusion, the present study presents a metal-free catalyst for the oxidation of sulfides to sulfoxides or sulfones at different pH values by using H_2O_2 as the oxidant in MeOH at room temperature. The borax/H_2O_2 system can be applied to the oxidation of alkyl and aryl sulfides in the presence of oxidation-prone functional groups such as C=C, –CN, and –OH. Refractory sulfides, viz., DBT and 4-methyl-DBT, are also capable of being oxidized quite effectively, though with less selectivity insofar as sulfoxidation is concerned. The oxidations of DBT substrates are especially important in the context of transportation fuel chemistry research targeting desulfurization of diesel and gasoline, for instance.

Experimental Section

General: Reagent-grade chemicals such as borax (E. Merck, India) and H_2O_2 were used as purchased. However, H_2O_2 was estimated by permanganometry before use. DBT, 4-methyl DBT, and 4,6-dimethyl DBT were purchased from Sigma Aldrich, India. Other organic sulfides were prepared by literature procedures. The products were characterized by comparing their spectroscopic data recorded with a Nicolet Impact-410 Fourier transform infrared spectrophotometer and a Varian-400 FT NMR spectrometer.

Oxidation of Organic Sulfides by H_2O_2/Borax: In a typical experiment, to a 25-mL flask equipped with a magnetic stirrer and H_2O_2 (6.0 equiv.) was added borax (0.2 equiv.) and MeOH (2 mL) followed by thioanisole (2 equiv.). To the resulting solution was added 0.1 M NaOH to maintain the pH of the solution at 10, and the mixture was stirred at room temperature for the time indicated in Table 2. The reaction was monitored by TLC (*n*-hexane/ethyl acetate, 9:1). After complete disappearance of the reactant, the product was extracted with ethyl acetate. To the ethyl acetate extract was added $Na_2S_2O_5$ to destroy the excess amount of H_2O_2, and the solution was then filtered and dried with anhydrous Na_2SO_4. The solvent of the pure fraction was evaporated, the product was fully dried, and the isolated yield was calculated. The aqueous phase containing borax, obtained after extraction of the reaction mixture with ethyl acetate, was reused with the addition of fresh substrate and H_2O_2 (3 equiv.) with adjustment of the pH value of the solution.

Acknowledgments

S. H. (2003–07) and S. K. B. thank the Council of Scientific and Industrial Research, New Delhi for research fellowships.

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Received: March 12, 2009