Zeolite-Assisted Oxidation of Sulfides with Sodium Bromite Trihydrate in Aprotic Solvents

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Synopsis. The title oxidation of a variety of sulfides was effectively performed in dichloromethane in the presence of H^+-exchanged zeolite F-9, affording the corresponding sulfoxides in good yields under mild and neutral conditions.

There are many classes of zeolites based on different framework compositions;[1] they have commonly intracrystalline pores through which a species, inclusive of inorganic cations, water, organic molecules with proper dimensions etc., can pass to and fro between the cavities and the external environment. Thus, the modification of a zeolite by cation exchange, implegnation, hydration, dehydration etc., can be easily performed, enabling a chemical transformation of a variety of reactive guest organic molecules. Zeolites have thus enjoyed important positions in petrochemical and oil-processing industries, and their application to syntheses of organic fine chemicals is currently being extended as well.[2]

Sodium bromite has been an asset to bleaching and desizing agents as a dilute aqueous solution due to its mild oxidative property. With the advent of high-purity solid $NaBrO_2$,[3] its synthetic potential as an oxidizing and brominating agent for organic substrates was enlarged upon by Kageyama[4—6] and Kajigaeshi[7—10] around 1983—1985.[11] However, their papers made no assessment of the efficacy of $NaBrO_2$ in organic solvents, and $NaBrO_2$ chemistry in water-free media is still unexplored.[12] Crucial to this is the negligible solubility of $NaBrO_2$ in organic solvents, except for lower alcohols, thus restricting the extensive use of this valuable reagent for organic synthesis. We have found that this problem could be circumvented by carrying out the reaction in organic solvents in the presence of a zeolite. This article describes some observations concerning sulfide oxidation with sodium bromite in aprotic solvents.

Results and Discussion

The oxidation can be performed readily by treating a sulfide with sodium bromite trihydrate (**1**, hereafter referred to simply as sodium bromite or $NaBrO_2$) in an aprotic solvent in the presence of optimally water-loaded H^+-exchanged zeolite F-9 ("wet" zeolite; vide infra). The reaction was followed by monitoring the consumption of a sulfide and the formation of the sulfoxide by GLC. For a comparison, although the reaction was also conducted in the absence or presence of commercial zeolite F-9 and the "dry" H^+-exchanged zeolite (vide infra), no perceptible reaction was observed. Additionally, the facility of the oxidation and selectivity of a sulfoxide were dependent on the water content of the zeolite; the use of a "wet" zeolite containing more or less water than that noted in Experimental resulted in an inferior conversion of the sulfide and/or selectivity of the sulfoxide. To obtain the optimum yield of a sulfoxide, as well as to suppress the overoxidation to the sulfone and any side reaction encountered sometimes in the oxidation with halides,[13—16] the present investigation was initiated by examining the effect of the reaction conditions on the yield of the sulfoxide.

The choice of the solvent is important to attain a satisfactory result, since the starting sulfide was mostly recovered, together with only a small amount of the sulfoxide, in ethyl acetate, tetrahydrofuran, benzene, and carbon tetrachloride, or, in some cases, overoxidation to the sulfone was observed even though a considerable amount of the sulfide still remained (hexane, chloroform, acetone, and acetonitrile). In a number of solvents examined, dichloromethane was selected on account of the high conversion of a sulfide and a high yield of sulfoxide; viz., upon oxidation of methyl phenyl sulfide (**2**) with equimolar **1** at room temperature for one hour, the sulfide **2** was consumed completely and the sulfoxide was exclusively formed (99%; GLC selectivity), with a faint trace of the sulfone.

The reaction temperature was found to be another important factor which effects the reaction. Indeed, although the oxidation proceeded extremely well at around 20—25 °C (so-called room temperature) in dichloromethane resulting in complete conversion of the sulfide **2** and selective formation of the sulfoxide (over 97%), virtually no or an inferior conversion was observed at the lower or higher temperature (-reflux), respectively; the phenomenon observed in the latter case may be related to the thermal lability of **1**.

On the basis of the above-mentioned observations, synthetic reactions of sulfoxides were carried out in dichloromethane and at room temperature. The present system was tested on various aromatic, aliphatic, and heterocyclic sulfides. In the first case, a *p*-substituent on the aromatic ring appreciably affects the ease with which its oxidation occurs. Especially, the electron-withdrawing group decreases the oxidizability of the sulfide (Entry 5); on the other hand, an electron-donating group facilitated the reaction (Entry 2). However, there is no serious dependence of the yields of the sulfoxides on the electronic nature of the *p*-substituents (Entries

Table 1. Zeolite-Assisted Oxidation of Sulfides with Sodium Bromite in Dichloromethane[a)]

Entry No.	Sulfides	$NaBrO_2$[b)] mmol	Time min	Sulfoxides[c)] %
1	PhSMe	1.0	60	82
2	p-$MeOC_6H_4SMe$	0.8	20	75
3	p-MeC_6H_4SMe	1.0	60	87
4	p-BrC_6H_4SMe	1.0	60	83
5	p-$NO_2C_6H_4SMe$	5.0	180	80
6	Ph_2S	5.0	300	75
7	$(PhCH_2)S$	1.5	60	67[d)]
8	$(CH_2=CHCH_2)_2S$	0.8	15	50
9	$(n\text{-}Pr)_2S$	0.8	30	79
10	$(i\text{-}Pr)_2S$	0.6	30	72
11	$(n\text{-}Bu)_2S$	0.8	30	80
12	$(s\text{-}Bu)_2S$	0.8	30	79
13	$(n\text{-}C_6H_{13})_2S$	0.8	60	75
14	$(n\text{-}C_8H_{17})SMe$	0.8	30	82
15	Tetrahydrothiophene	0.8	30	84
16	Tetrahydrothiopyran	0.7	30	68
17	Tetrahydrothiopyran-4-one	0.7	30	89
18	1,4-Thioxane	0.7	30	68

a) Under argon and at room temperature; 1 mmol of a sulfide, 1.0 g of the "wet" H^+-exchanged zeolite F-9, and 6 cm^3 of dichloromethane were used in every run. b) Sodium bromite trihydrate was used. c) Isolated yields. d) Isolated by recrystallization from ethanol.

2—5). Heterocyclic rings (Entries 15—18), oxo substituent (Entry 17), and ether linkage (Entry 18) are found to be intact under the reaction conditions. The allylic group also resists oxidation. However, only a moderate yield of the sulfoxide was obtained (Entry 8); this failure is ascribed to the extensive formation of the sulfone (25%; GLC selectivity), despite the fact that the starting sulfide remained unreacted (5.7%). Alkyl sulfides (Entries 9—14) are generally much more reactive than aryl sulfides (Entries 1—7), and their oxidation requires less oxidant and a shorter reaction time. The results are summarized in Table 1, in which the specific experimental conditions (concentration of sodium bromite and reaction time) for each sulfide are determined in terms of the reactivities of the sulfides and the selectivities and the yields of the sulfoxides.

In conclusion, the zeolite-assisted oxidation of a certain range of sulfides with sodium bromite trihydrate in dichloromethane can be readily performed under mild conditions, giving the corresponding sulfoxides in moderate to good yields. The unexpected failure of the "dry" H^+-exchanged zeolite in achieving an efficient reaction, however, means some remaining ambiguity regarding zeolite catalysis, since **1** is highly activated under acidic conditions.[4—6)] It is thus unlikely that the efficacy of a zeolite is determined simply by solid acid catalysis (either Brönsted or Lewis acidity) of it.[17)] However, it should not be doubted that the H^+-exchanged zeolite in combination with the optimum amount of water provides a reactive high-surface-area for **1**, causing the facile reaction, since **1** is insoluble in dichloromethane and no reaction takes place without a "wet" zeolite. From the experimental and practical aspects, an advantage of the present system is that it can be treated just like a zeolite-supported reagent without the need to preform the supported reagent; thus, the in situ $NaBrO_2$/zeolite procedure allows instant performance of the reaction and a facile isolation of the products by simply filtrating insolubles and evaporating the solvent. We hope that the present procedure might contribute to extend the scope of $NaBrO_2$ chemistry and the reagent's oxidative capability, since sodium bromite is cheap, safe to handle, and environmentally acceptable.

Experimental

The ^1H NMR spectra were measured with a JEOL PMX-60 spectrometer for solutions in either carbon tetrachloride or deuteriochloroform. The IR spectra were recorded for thin films (neat) or KBr disks on a JASCO A-100 spectrophotometer. GLC was performed on a Shimadzu GC-4C instrument with a 2 m column packed with 1.5% Silicone OV-17 on Shimalite WAW-DMCS, with temperature programming.

Starting Materials. All sulfides are commercially available and were used without purification after checking their purities by GLC. Sodium bromite trihydrate was a gift from Nippon Silica Industrial Co., Ltd. The "dry" H^+-exchanged zeolite was prepared by treating synthetic zeolite F-9 powder (Wako Pure Chemical Industries, Ltd.) with aqueous ammonium chloride, followed by thermal deammoniation at 250 °C.[18)] The "wet" H^+-exchanged zeolite was prepared by adding distilled water (2 g) in several portions to the "dry" zeolite (10 g), followed by vigorous shaking of the mixture upon every addition for a few minutes until a free-flowing powder was obtained.

Experimental Procedures. Ths following procedures are representative. The "wet" H^+-exchanged zeolite F-9 (1 g) and finely pulverized sodium bromite trihydrate (1 mmol) and dichloromethane (6 cm^3) were charged in a round-bottom flask. To this was added methyl phenyl sulfide (1 mmol) in a portion with magnetic stirring. The flask was flushed with dry argon in order to exclude any influence of autoxidation, and was then capped with a glass stopper or a silicone rubber septum, through which the supernatant was withdrawn by a microsyringe at intervals to monitor the reaction by GLC. The reaction mixture was vigorously stirred at room temperature until all of the starting sulfide was completely consumed (for an hour); n. b., efficient stirring is required to ensure a smooth and reproducible reaction. The whole mixture was transferred onto a sintered glass disk in order to separate the insolubles, which were thoroughly washed with dichloromethane (ca. 100 cm^3 of the solvent was used). The combined clear solvent was removed on a rotary evaporator under vacuum, leaving methyl phenyl sulfoxide contaminated with trace methyl phenyl sulfone. Chromatography on silica gel eluting with a mixture of hexane and ethyl acetate (2 : 1 by volume) afforded 82% of pure (by GLC) methyl phenyl sulfoxide.

The other tabulated sulfoxides, except for dibenzyl sulfoxide, were obtained as above. Dibenzyl sulfoxide was obtained by recrystallization of a crude material from ethanol; mp 135 °C (lit,[19] 134—135 °C). Identification of each sulfoxide was based on a comparison of its NMR and IR spectra, and GLC retention time with those of the authentic sample synthesized separately.

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