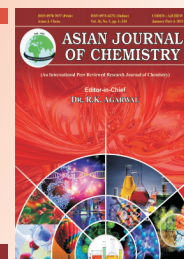




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## Novel Oxidation of Hydrogen Sulfide by Dimethyl Sulfoxide in Presence of $\beta$ -Cyclodextrin

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Dimethyl sulfoxide is used as an oxidizing agent to oxidize hydrogen sulfide to solid sulfur at room temperatures and normal pressures, in which,  $\beta$ -cyclodextrin plays an important role in this reaction. In this work, when GC-MS, SEM and FTIR spectroscopic techniques were used for inspection of spectral changes of  $\beta$ -cyclodextrin, dimethyl sulfoxide solution with increasing  $H_2S$  concentration, the results suggest that  $H_2S$  was oxidated by dimethyl sulfoxide in the presence of  $\beta$ -cyclodextrin and dimethyl sulfide, water, and sulfur can be identified. The results of this work can be used to provide important reaction mechanism of  $H_2S$  with dimethyl sulfoxide in the presence of  $\beta$ -cyclodextrin with potential industrial application of  $\beta$ -cyclodextrin-dimethyl sulfoxide solution.

**Keywords:** Dimethyl sulfoxide, Hydrogen sulfide,  $\beta$ -Cyclodextrin, Dimethyl sulfide.

### INTRODUCTION

The versatility of dimethyl sulfoxide as a solvent medium in organic reactions has received widespread attention in recent several decades<sup>1,2</sup>. In some cases, the ability of dimethyl sulfoxide to act as an oxidation in the course of reaction has been recognized. Dimethyl sulfoxide was found to oxidize *n*-propyl, *n*-butyl and tetramethylene sulfides to the corresponding sulfoxides in yield of 59, 55 and 58 %, respectively. The conditions employed involved heating the sulfide with a 50 % molar excess of dimethyl sulfoxide at 160-175 °C for several hours<sup>3</sup>. Kornblum and collaborators<sup>4</sup> had reported the successful oxidation of several phenacyl halides with dimethyl sulfoxide. Subsequent addition of the carbonyl component and appropriate reaction temperature, time and product isolation complete the process. Researchers had reported the some reactions of S(-2) with dimethyl sulfoxide in the presence of catalysts. The needed changes are an increase in the amount of halogen or hydrogen halide catalyst to about twice the number of moles of L-cystine and a significantly lower reaction temperature. The combinations DL-cysteic acid-dimethyl sulfoxide and DL-homocysteic acid with both dimethyl sulfoxide and tetramethylene sulfoxide were also checked. The corresponding molecular complexes were obtained; though, with DL-homocysteic acid, these were syrups from which it appeared that the compounds slowly crystallized<sup>5</sup>. The explanation for formation of these compounds would appear to lie in the ability of the oxygen of sulfoxides such as dimethyl sulfoxide and tetramethylene sulfoxide to serve as a proton acceptor<sup>6</sup>. Success

of the oxidation of dithiols depends on slow addition to an excess of dimethyl sulfoxide to avoid polymerization. Thiols ( $RSH$ ,  $ArCH_2SH$ ,  $ArSH$ ) can be oxidized to disulfides ( $R-S-S-R$ , *etc.*) by dimethyl sulfoxide. Reactivity depends upon the acidity of the thiol ( $ArSH > ArCH_2SH > RSH$ ). Aromatic thiols are oxidized spontaneously at room temperatures, whereas higher temperatures are required for oxidation of aliphatic thiols<sup>7,8</sup>. The oxidation of disulfides to sulfonic acids by dimethyl sulfoxide has been described. Unfortunately, several similar sulfides did not react appreciably with dimethyl sulfoxide under these conditions and attempts to catalyze the reactions with acid were unsuccessful. Especially,  $H_2S$  is satisfactory oxidation is not accomplished without modification of the procedure.

Removal of hydrogen sulfide ( $H_2S$ ) from gases is required for reasons of health, safety and corrosion during transmission and distribution and to prevent pollution with sulfur dioxide ( $SO_2$ ) upon combustion of the gases. Several different types of processes are in use for treating "sour" gases containing the acid component of  $H_2S$ . Possible gas-treating applications are many and varied and the selection of a truly optimum treatment method is a complex process, such as incineration, adsorption or chemical scrubbing. Because of the favorable absorption and desorption properties for acid gases in industrial processes, organic solvents have become the subject of increasing interests in recent years<sup>9-13</sup>. Wei and his coworkers have paid great attention to the alcohol system to remove acidic gases for several years<sup>14-17</sup>. In the present work, we tried to develop a new system for the absorption of  $H_2S$  by using dimethyl sulfoxide and a

novel reaction of  $\text{H}_2\text{S}$  with dimethyl sulfoxide was observed in the presence of  $\beta$ -cyclodextrin.

In the hope of finding a mild enough oxidizing agent we attempted the following oxygen reaction, using dimethyl sulfoxide as an oxygen donor. The present procedure is attractive not only for its simplicity and general applicability, but also because dimethyl sulfoxide plays a double role of oxidizing agent and solvent. Furthermore,  $\beta$ -cyclodextrin has been used as a cyclic component in the construction of supramolecular architectures because of well-defined ring structure. We wish herein to report the novel oxidation of  $\text{H}_2\text{S}$  by dimethyl sulfoxide in the presence of  $\beta$ -cyclodextrin. In this work, it is known that  $\text{H}_2\text{S}$  can be oxidized by using dimethyl sulfoxide in the presence of  $\beta$ -cyclodextrin. In addition the by-product of the reaction, dimethyl sulfide, water and sulfur were identified by various spectroscopic techniques.

### EXPERIMENTAL

Analytical grade dimethyl sulfoxide and  $\beta$ -cyclodextrin are purchased from Beijing Reagent Company. Capillary column for GC-MS/MS on QMS with an Rtx-5 MS capillary column (30 m  $\times$  0.25 mm i.d; 0.25  $\mu\text{m}$  film thickness) was used. Helium (purity 99.999 %) was the carrier gas with a constant flow of 1 mL/min. The inlet temperature was maintained at 200  $^\circ\text{C}$ . The initial temperature was 40  $^\circ\text{C}$ , held for 10 min; ramped at 25  $^\circ\text{C}/\text{min}$  up to 220  $^\circ\text{C}$  and held for 5 min. Data were collected using GC/MS analysis software. A Hitachi (Japan) S-3400N Scanning Electron Microscope (SEM) was used. FTIR spectra were recorded on a Bruker VECTOR22 FTIR spectrometer with a resolution of 1  $\text{cm}^{-1}$  at 298 K in the range from 4000 to 400  $\text{cm}^{-1}$ . The spectrometer possesses auto-align energy optimization and a dynamically aligned interferometer and fitted with a constrigent  $\text{BaF}_2$  pellet for the measurement of aqueous solution, an OPUS/IR operator and IR source. A base line correction was made for the spectra that were recorded in air; and then 15 mL solution was used on the FTIR spectrometer in every one of measurements and the thin layer of samples are less than typically 2  $\mu\text{m}$  thickness.

**Measurements:** 0.8000 g of  $\beta$ -cyclodextrin is dissolved in 100 mL dimethyl sulfoxide and mix well-distributed, at room temperatures and normal pressures, accessing with  $\text{H}_2\text{S}$ , while the solution gradually becomes yellow. The solution still presents yellow and rather with some kind of yellow precipitation, after about 24 h. On the other hand, there is no yellow precipitate if dimethyl sulfoxide is bubbled into  $\text{H}_2\text{S}$  without the presence of  $\beta$ -cyclodextrin.

### RESULTS AND DISCUSSION

The contrast test was performed in the absence of  $\beta$ -cyclodextrin. In the contrast test, no sulfur was found after 2 days.

A photograph shows the precipitated sulfur for 24 h in the presence of  $\text{H}_2\text{S}$  (Fig. 1) in the presence of  $\beta$ -cyclodextrin. After in the presence of  $\text{H}_2\text{S}$  the color changes of  $\beta$ -cyclodextrin dimethyl sulfoxide solution from colorless to yellow could be due to a reaction of dimethyl sulfoxide with  $\text{H}_2\text{S}$ . To confirm the reaction process the  $\beta$ -cyclodextrin dimethyl sulfoxide solutions in the presence of  $\text{H}_2\text{S}$  were analyzed by SEM, FTIR and GC-MS techniques.

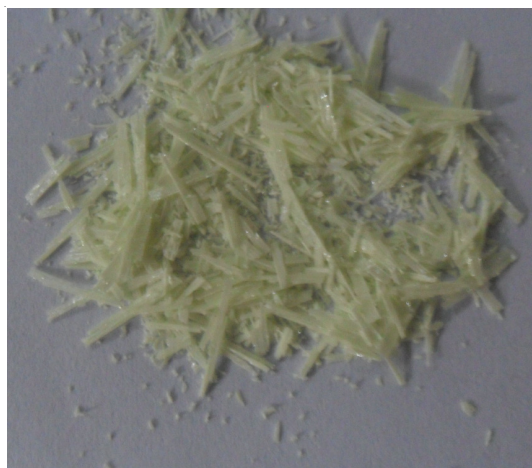


Fig. 1. Photograph of the formed sulfur

A scanning electron microscope (SEM) is used to study the surface morphology of the precipitate, which reveals that sulfur ether can be identified (Fig. 2a,b). In Fig. 1a, it illustrates that the precipitate is inclined trapezium shape. It is also found that the size of the crystal is about 800  $\mu\text{m}$ . Fig. 1b shows energy spectrum pattern of the precipitate film. It is identified that the precipitate is elemental sulfur.

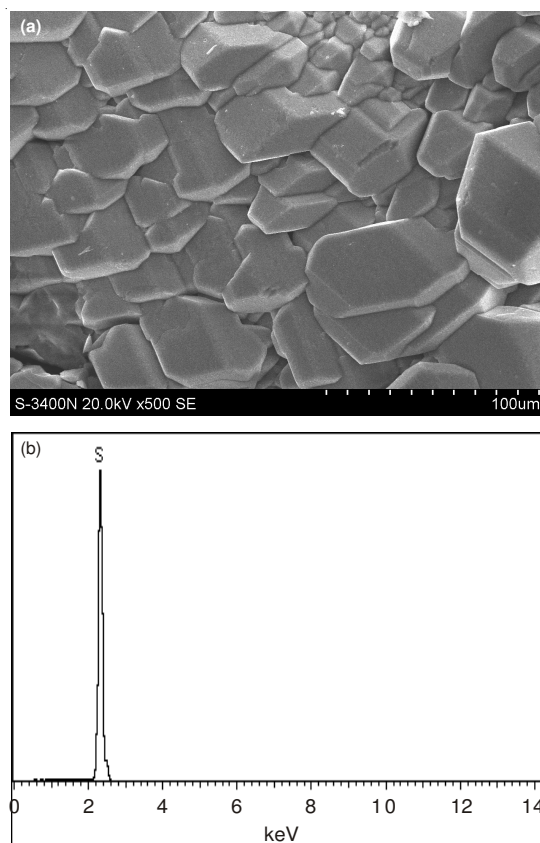


Fig. 2. (a) SEM micrograph of the surface; (b) energy spectrum pattern of the precipitate film

Liquid supernatant is analyzed by GC-MS method and results are shown in Fig. 3a,b, which undergoes an intramolecular hydrogen transfer to give the observed carbonyl product plus dimethyl sulfide.

