

Efficient oxidation of sulfides using a molybdenum(VI)-dioxo complex containing an benzimidazole ligand

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ABSTRACT

For the first time, dioxomolybdenum(VI) complex with the general formula $[\text{MoO}_2\text{L}_2]$ containing a N-O bidentate ligands (HL=2-(o-aminophenyl)- benzimidazole) has been used for the oxidation of sulfides. Elemental analyses (carbon, hydrogen, nitrogen), FT-IR and Uv-Visible spectra and ^1H NMR analysis agree well with the proposed stoichiometry of the complex $[\text{MoO}_2\text{L}_2]$. A variety of sulfides were smoothly converted into the corresponding sulfoxide catalyzed by this molybdenum complex. The effect of the reaction conditions on the oxidation was studied by varying the amount of the catalyst, the amount of oxidant (UHP) and solvent type. Good yields with excellent selectivities were obtained in most cases.

Keywords: Dioxomolybdenum(VI) complex, Oxidation, Sulfide, UHP.

1. Introduction

The fact that molybdenum is an essential metallic element and exhibits significant enzymatic role in biochemical reactions especially in the oxidation of aldehydes, purines and sulfides [1-3] has created enormous interest to use the molybdenum complexes as biomimetic catalysts in the oxygenation of organic compounds [4-7].

Because sulfoxides can be easily transformed into a large variety of compounds by means of regio-selective ring-opening reactions, they are valuable auxiliaries in organic synthesis as well as in the preparation of biologically active compounds and a variety of functionalized products [8-15]. The catalytic oxidation of sulfides is a convenient method for the preparation of these valuable compounds [16-17]. Since then, a number of soluble molybdenum containing organic complexes with carboxylic acids, ketones, alcohols, glycols, amines, etc. have been synthesized and employed as homogeneous catalysts for the oxidation of various substrates [18-22]. The activity of these complexes varied markedly with the type of ligands and coordination sites [23-30]. Thus, we decided to use a dioxo-molybdenum (VI) benzoxazoline complex

containing an O-N bidentate ligand in the oxidation of sulfides using UHP as the oxidant (Scheme 1).

2. Experimental

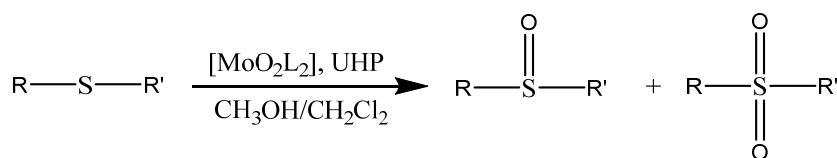
2.1. Materials and measurements

Chemical materials and solvents were purchased from the Fluka and Merck Chemical companies. 2-(o-aminophenyl)- benzimidazole (HL) and dioxomolybdenum(VI) complex with the general formula $[\text{MoO}_2\text{L}_2]$ were prepared according to the reported procedures [31, 32].

The elemental analysis (carbon, hydrogen, and nitrogen) of compounds were obtained from Carlo ERBA Model EA 1108 analyzer. FT-IR spectrum was obtained by using a Unicam Matson 1000 FT-IR spectrophotometer using KBr disks at room temperature.

UV-Vis spectrum was recorded on UV-Vis spectra were recorded by CARY 100 BioVARIAN UV-Vis spectrophotometer in methanol. Molar conductance of the ligands and its complex were determined in methanol (ca. 10^{-3} M) at room temperature using a Toa CM 405 conductivity meter. The ^1H and ^{13}C NMR spectra of the complexes in d^6 -DMSO were obtained using a Bruker FT-NMR 500 and 125 MHz spectrometer, respectively.

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Scheme 1. The oxidation of sulfides by the $[\text{MoO}_2\text{L}_2]/\text{UHP}$ catalytic system.

The reaction products of the sulfide oxidation were determined and analyzed by HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (phenyl methyl siloxane 30 m 320 μm 0.25 μm) and flame-ionization detector.

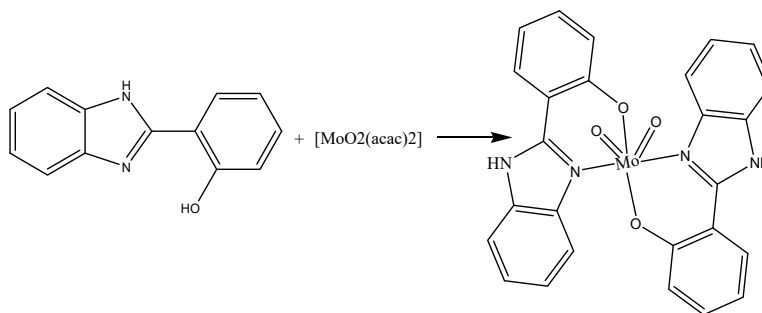
2.2. General procedure for oxidation of sulfides

In a typical experiment, to a solution of sulfide (0.2 mmol), chlorobenzene (0.2 mmol) as internal standard and catalyst (1×10^{-4} mmol) in a 1:1 mixture of $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ (1 mL) was added UHP (0.4 mmol) as the oxidant. The mixture was vigorously stirred at room temperature under air for the required time, and the course of the reaction was monitored using a gas chromatograph. Assignments of the products were made by comparison with authentic samples. All the reactions were run at least in duplicate.

3. Results and Discussion

3.1. Complex characterization

According to reported procedure, the reactions of $\text{MoO}_2(\text{acac})_2$ with corresponding ligands HL were carried out in 1:2 molar ratios in methanol to form complex MoO_2L_2 (Scheme 2). Elemental analyses agree well with the proposed stoichiometry of the complex. The I.R. spectrum of the complex indicates that the ligand, HL, is coordinated to the molybdenum ion via the azomethine nitrogen atom (shift of the azomethine $\nu(\text{C}=\text{N})$ band of the ligand from 1640 to 1614 cm^{-1}) and the broad band in the region 3285–3321 cm^{-1} due to OH vibrations, is absent from the spectra of the complex, indicating the deprotonation of this group on coordination with the metal atom (Fig. 1.) [33]. Also, the new band at 903 detected for complex $[\text{MoO}_2\text{L}_2]$ is assigned to the presence of the cisoid dioxometal moiety in the complex ($\nu_{\text{Mo}=\text{O}}$) [34].



Scheme 2. Synthesis of $[\text{MoO}_2\text{L}_2]$.

The ^1H NMR spectra of the free ligand and its Mo(VI) complex were recorded in DMSO-d_6 (See supplementary data). The spectra of the ligands LH exhibit a broad signal due to the OH proton respectively at $\delta = 12.38$ ppm, which is absent for the complex. The absence of this signal suggests that this proton has been lost via coordination this group with the metal atom. The multiplets in the region $\delta = 7.04$ – 8.13 ppm due to aromatic protons of the ring in the ligand and singlet in the region $\delta = 11.78$ ppm due to NH proton of ligand HL do not alter in the complexes, indicating the non-involvement of these groups in coordination [33]. The UV–Vis spectrum of complex $[\text{MoO}_2\text{L}_2]$ exhibits two bands in the electronic spectra, one in the UV region at ca. 285 and 297 nm and another at 337 and 331 nm in the visible region, respectively. These are arising due to ligand and ligand to metal charge transfer band (LMCT), respectively [32].

3.2. Catalytic reaction

3.2.1. Optimization of the sulfide oxidation conditions

To determine the optimal conditions for the catalytic oxidation of sulfides, the oxidation of methylphenyl sulfide (MPS) as probe substrate with UHP as an oxidant by using complex $[\text{MoO}_2\text{L}_2]$ was chosen as a model substrate. The influences of catalyst amounts, oxidant amounts and solvents on the reactivity of the catalyst were explored. Fig. 2 gives the yields of the methylphenyl sulfoxide obtained from the reaction using different solvents such as methanol, dichloromethane (DCM), acetone and n-hexane. In order to evaluate the best solvent for sulfide oxidation, different solvents were employed and among them, 1:1 mixture of $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ was the best for this protocol.

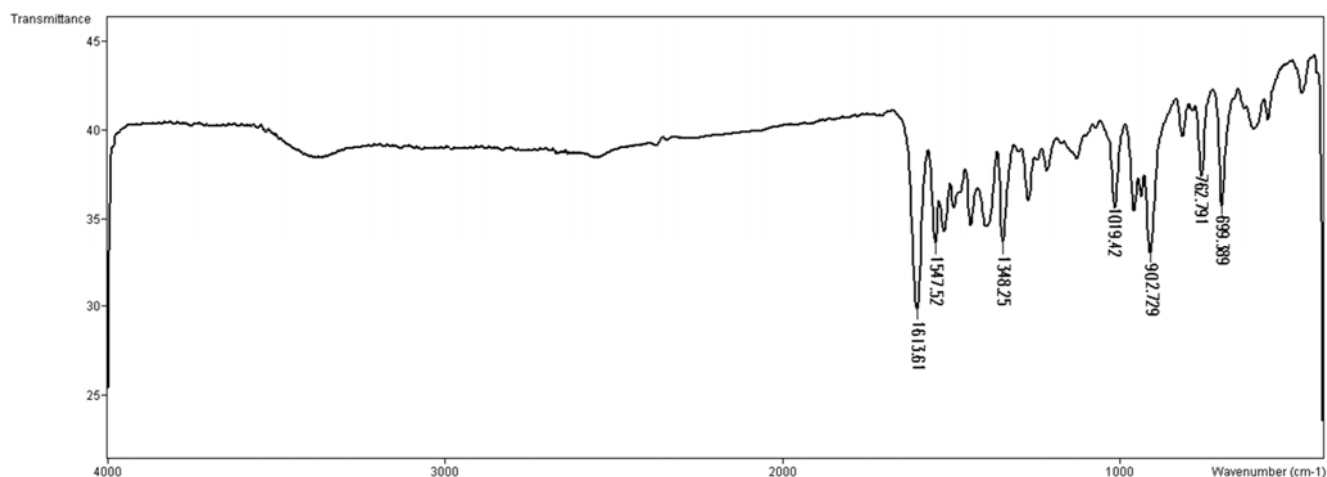


Fig. 1. IR spectrum of complex $[\text{MoO}_2\text{L}_2]$.

The effect of amount of the catalyst on the conversion of the MPS oxidation at room temperature for 15 min was studied. The results revealed that when the amount of catalyst increased to 0.002 mol, the conversion of MPS increased to 92% (Fig. 3). A high amount of the catalyst has almost no positive effect on the conversion MPS.

The amount of UHP could significantly affect the MPS conversion and selectivity to methyl phenyl sulfoxide (Fig. 4). When the amount of UHP increased from 0 to 1.0 mol, the conversion of MPS increased from 0 to 92%. With a further increase of UHP to 2.5 mol, the selectivity to methyl phenyl sulfoxide decreased from 100 to 54%, while the conversion of MPS increased from 92 to 100%.

A series of sulfides was subjected to the oxidation using $[\text{MoO}_2\text{L}_2]$ as the catalyst and UHP as the oxidant

(Table 1). Very good conversions of substrates were obtained for all cases (74-100%). Among the sulfides, arylalkyl (Table 1, entries 1 and 2), dibenzyl (Table 1, entry 5) and dialkyl (Table 1, entries 6-8) sulfide underwent clean and selective oxidation to the corresponding sulfoxide under air, in impressive selectivity (87- 100%). It was observed that aromatic and aliphatic sulfides underwent oxidation reactions more easily than diaryl substrates. The lowest conversion was obtained for diphenyl sulfide.

In order to show the merit and efficiency of the present catalytic system in comparison with recently reported protocols, we compared the results of the methylphenyl sulfide oxidation in the presence of other catalysts. As shown in Table 2, our catalytic system is superior to some of the previously reported catalysts in terms of reaction conditions and conversion.

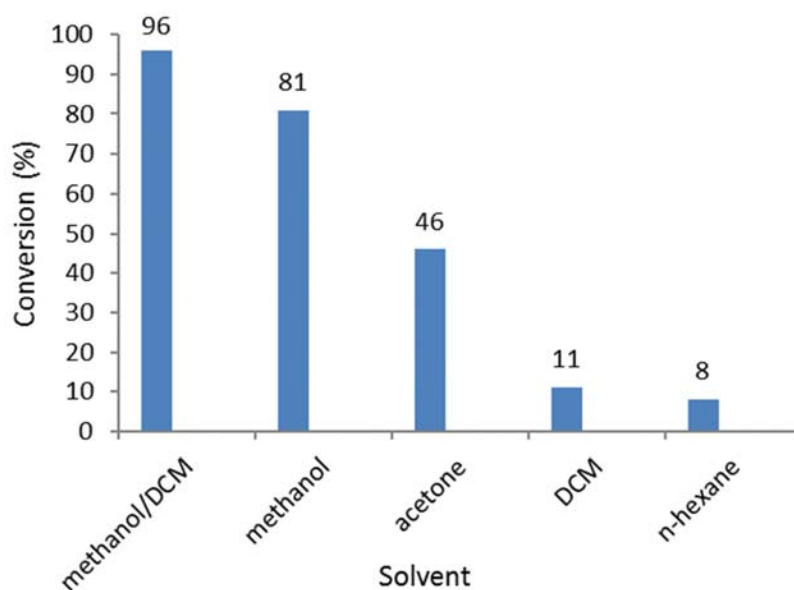


Fig. 2. The effect of different solvents in the oxidation of MPS.

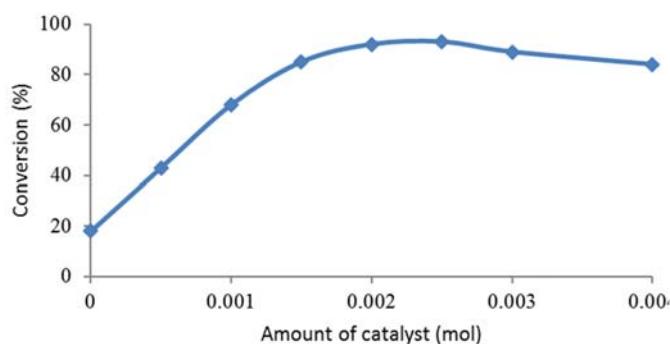


Fig. 3. The effect of amount of catalyst in the oxidation of MPS.

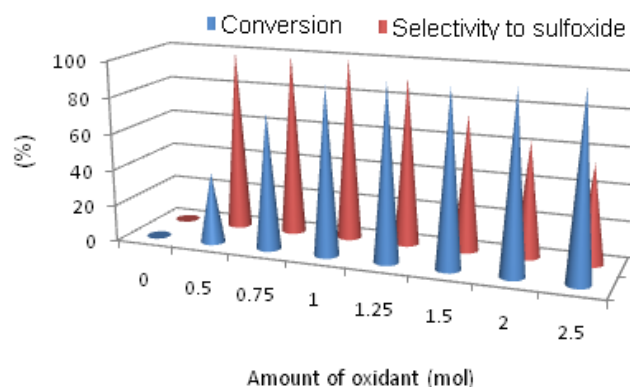


Fig. 4. The effect of amount of UHP in the oxidation of MPS.

In contrast to similar, previously reported systems, the catalytic system presented in this paper does not suffer from the harsh reaction conditions, such as using a large amount of catalyst (Table 2, entry 2), long reaction time (Table 2, entries 3 and 4),

and using an additive (Table 2, entries 3 and 4). As illustrated in Table 2, all dioxo-Mo(VI) complexes are almost equally effective sulfide oxidation catalysts in different conditions (Table 2, entries 1-4).

Table 1. Oxidation of sulfides catalyzed by [MoO₂L₂]/UHP.^a

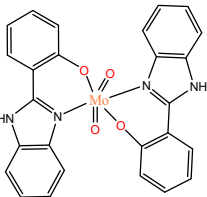
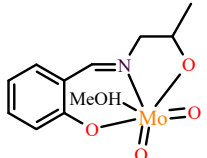
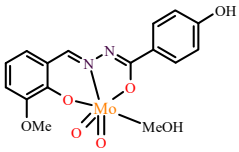
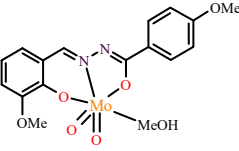
| Entry | Substrate | Conversion (%) ^b | Selectivity to sulfoxide (%) ^c |
|-------|-----------|-----------------------------|---|
| 1 | | 96 | 100 |
| 2 | | 91 | 87 |
| 3 | | 74 | 69 |
| 4 | | 88 | 85 |
| 5 | | 93 | 87 |
| 6 | | 96 | 100 |
| 7 | | 100 | 100 |
| 8 | | 84 | 100 |

^aThe molar ratios for catalyst:substrate:oxidant are 1:2000:4000. The reactions were performed in (1:1) mixture of CH₂Cl₂/CH₃OH (1 mL) under air at room temperature within 15 min.

^bThe GC yield (%) are measured relative to the starting sulfide.

^cSelectivity to sulfoxide = (sulfoxide%/(sulfoxide% + sulfone%)) × 100.

Table 2. Recently reported catalytic systems for the oxidation of sulfides by dioxo-Mo(VI) catalytic systems.

| Entry | Catalyst | Condition | Conversion (%) | Selectivity (%) | Ref. |
|-------|--|---|----------------|-----------------|-----------|
| 1 |  | 1 mol% of catalyst/ UHP/rt/15min | 97 | 94 | This work |
| 2 |  | 5 mol% of catalyst/ UHP/rt/30min | 92 | 100 | [35] |
| 3 |  | 1 mol% of catalyst/ H ₂ O ₂ /TMB/10°C/2h | 100 | 100 | [36] |
| 4 |  | 1 mol% of catalyst/ H ₂ O ₂ /TMB/10°C/2h | 100 | 100 | [36] |

4. Conclusions

The complex dioxo molybdenum (VI) containing bidentate O,N-donor benzimidazole ligand was prepared according to the reported procedure and was characterized using UV-Visible spectroscopy, NMR, IR and elemental analysis. The catalytic behavior of the complex was investigated in the oxidation of sulfides. The results show that dioxo-Mo(VI) complex is a very efficient catalyst for the oxidation of a variety of sulfides with full selectivity to sulfoxides.

Acknowledgment

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