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Efficient Oxidation of Sulfides Catalyzed by Transition Metal Salts with Molecular Oxygen in the Presence of Aldehydes

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EFFICIENT OXIDATION OF SULFIDES CATALYZED BY TRANSITION METAL SALTS WITH MOLECULAR OXYGEN IN THE PRESENCE OF ALDEHYDES

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ABSTRACT: Oxidation of sulfides to sulfoxides and sulfones was achieved in moderate to high yields with a good selectivity, by using Fe_2O_3 , MnO_2 , $Cu(OH)_2$ and $Cu(OAc)_2$ as catalyst, with molecular oxygen in the presence of isovaleraldehyde under mild conditions.

The rich chemistry of sulfoxides and sulfones makes them very useful reagents in organic synthesis.¹ Therefore, there is continued interest in new and efficient syntheses of these kinds of compounds. Sulfoxides and sulfones are most generally prepared by oxidation of sulfides utilizing hydrogen peroxide, peracids and some other oxidizing agents. However, these oxidants are potentially explosive.² Recently, researches are actively elaborating safer and simpler oxidation processes. Much interest has been focused on the direct oxidation of some organic substrates by combined use of molecular oxygen and aldehydes in the presence of catalyst under mild reaction conditions.³ More recently, we have

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found that an $O_2/RCHO/Fe_2O_3$ system was an efficient oxidant for both the Baeyer-Villiger oxidation of cyclohexanone to ε -caprolactone and the epoxidation of cyclohexene.⁴ Here, we wish to report our subsequent study on the oxidation of sulfides to sulfoxides and sulfones using the above oxidant. The present system is a safe and very convenient method for the oxidation reaction of sulfides, compared with other oxidizing reagents.

$$R^{1}-S-R^{2}$$
 + RCHO + O₂ $\xrightarrow{Cat.}$ $R^{1}-S-R^{2}$ + $R^{1}-S^{0}-R^{2}$ + RCOOH

A typical reaction procedure for the oxidation of sulfides is as follows. A mixture of transition metal salt (0.1mmol), aldehyde (30mmol) and 1,2-dichloroethane (30ml) was placed into a four-necked flask with a reflux condenser and a thermometer and was vigorously stirred. Oxygen was bubbled into the stirred solution at 40°C for a while until the peroxide was produced (starch-iodide paper). Then sulfide (10mmol) was added to the above system. The resulting mixture was continuously stirred under bubbling of oxygen (1 atm) at 40°C for several hours. The catalyst was removed by filtration. Evaporation followed by column chromatography gave several products corresponding to those indicated above. Yields were determined by GC.

At first, the importance of the sacrificial aldehyde components in the oxidation system were examined in the Fe₂O₃-catalyzed oxidation of diethyl sulfide. In this model reaction it was found that the oxidation was strongly dependent on the nature of the aldehydes used. Of the aldehydes studied, isovaleraldehyde is the best. Increasing the amount of aldehyde had a positive effect on the products formation. The aldehydes used were converted into the corresponding acids under the reaction conditions. Notably, the effectiveness of

Entry	Aldehyde	R^1	R^2	Reaction	Yield ^a of oxidation	on products(%)
				time (n)	Sulfoxide	Sulfone
1	Me ₂ CHCH ₂ CHO	Et	Et	2	75 ^b	10 ^b
2	Me_2CHCH_2CHO	Ph	Me	1	81	8
3	Me_2CHCH_2CHO	Ph	Ph	4	65	trace
4	Me ₂ CHCHO	Et	Et	2	33 ^b	0.1 ^b
5	Me ₂ CHCHO	Ph	Me	1	55	0.3
6	Me(CH ₂) ₅ CHO	Et	Et	2	14 ^b	
7	Me(CH ₂) ₅ CHO	Ph	Me	1	41	trace
8	PhCHO	Et	Et	2	trace	
9	PhCHO	Ph	Me	1	8	

Table 1Effect of Various Aldehydes onthe Fe₂O₃-catalyzed Oxidation of Sulfides

^a Isolated yield. ^b GC yield.

aldehydes is different between the present oxidation example and those reactions reported by us⁴ in which benzaldehyde was the most effective. In the scrutiny of solvents in the diethyl sulfide oxidation with isovaleraldehyde, the solvent effect is remarkable and 1,2-dichloroethane has proved to be an excellent solvent, while benzene, carbon tetrachloride, 1,2-dichloropropane were less effective. The representative results of the Fe₂O₃-catalyzed oxidation of sulfides using the above combined system of an aldehyde, oxygen (1 atm) and 1,2-dichloroethane are summarized in Table 1. It should be pointed out here that the reactions occurred with good selectivity. Sulfoxides were predominant in all cases. After a prolonged reaction period, yields cannot be increased. In these reactions the other products were not detected and unreacted starting material was recovered. The reactions as shown in Table 1 did not proceed without using this catalytic system.

Furthermore, the catalytic activities of several transition metal salts have been examined for oxygenation of three sulfides with molecular oxygen in the

Entry	Catalyst	R ¹	R ²	Reaction time (h)	Yield ^a of oxidation Sulfoxide	on products(%) Sulfone
1	MnO ₂	Et	Et	2	72 ^b	4 ^b
2	MnO ₂	Ph	Ph	4	66	trace
3	Cu(OH) ₂	Et	Et	2	76 ^b	2 ^b
4	Cu(OH) ₂	Ph	Ph	4	47	trace
5	Cu(OAc) ₂	Et	Et	2	75 ^b	4 ^b
6	$Cu(OAc)_2$	Ph	Ph	4	76	trace
7	Fe ₂ O ₃	Et	Et	2	75 ^b	10 ^b
8	Fe ₂ O ₃	Ph	Me	1	81	8
9	Fe ₂ O ₃	Ph	Ph	4	65	trace

Table 2The Oxidations of Sulfides Catalyzed byTransition Metal Salts in the Presence of Isovaleraldehyde

a Isolated yield. b GC yield.

presence of isovaleraldehyde. The results are listed in Table 2. Fe₂O₃, MnO₂, Cu(OH)₂ and Cu(OAc)₂ have proved to be effective. The oxygenated product ratio of sulfoxides and sulfones, showed that the selectivities of the reactions using the above mentioned Cu(II) and Mn(II) catalysts were better than that of Fe₂O₃.

The present procedure was also successfully applied to the oxidation of pyridine. Fe₂O₃-catalyzed oxidation of pyridine afforded the pyridine N-oxide in 89% isolated yield by combined use of molecular oxygen (1 atm) and isovaleraldehyde in 1,2-dichloroethane, as shown in the following equation.

Although it is premature to explain clearly the mechanism of this valuable transformation at this stage, the oxidation might occur mainly by an organic

peracid generated from the reaction of an aldehyde with molecular oxygen in the presence of the transition metal salts. Subsequently, the peracid might react with the catalyst to afford the active species.^{3c} Further work on the precise mechanism and other applications of this type of oxidation method is actively in progress in our laboratory.

In conclusion, the O₂/Me₂CHCH₂CHO/Catalyst system is a convenient method for the oxidation of sulfides to sulfoxides and sulfones as well as the conversion of aldehydes into the corresponding carboxylic acid under mild conditions.

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