APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 769–771
DOI: 10.1002/aoc.222

NOTE

Selective oxidation of thioethers to sulfoxides with molecular oxygen mediated by rhodium(III)–dimethylsulfoxide complexes

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A rhodium–dimethylsulfoxide-promoted catalytic oxidation of a thioether to sulfoxide is studied. Screening of different rhodium complexes reveals moderate to excellent catalytic properties for the oxidation of thioethers using molecular oxygen as an oxidant. The scope of this reaction is discussed. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: rhodium; catalysis; thioether; sulfoxide; oxidation

Received 9 February 2000; accepted 31 January 2001

INTRODUCTION

Several attempts have been made to promote transition-metal-mediated selective oxidation of thioethers to sulfoxides in the presence of molecular oxygen as an oxidant. Ruthenium(II) and ruthenium(III) complexes containing dimethylsulfoxide (DMSO) are found to be active catalysts for the selective oxidation of thioethers to the corresponding sulfoxides in alcohol solvent.[1–6] The net stoichiometry observed is shown in Eqn [1]:

$$R_1SR_2 + RCH_2OH + O_2 \rightarrow R_1SOR_2 + RCHO + H_2O \qquad (1)$$

It has been suggested[6] that an active intermediate complex, *trans*-$[RuCl_2(R_2SO)_2(R_2S)_2]$ is generated *in situ* when the *cis*-$RuCl_2(DMSO)_4$ complex is used as a catalyst precursor. The rate-determining step is the oxidation of ruthenium(II) by oxygen through an outer-sphere mechanism to generate hydrogen peroxide and a ruthenium(IV) species. The substrate, in turn, is oxidized by hydrogen peroxide, and ruthenium(II) is regenerated by reduction with alcohol.[6]

Recently, we have reported the selective oxidation of thioethers to sulfoxides using molecular oxygen as an oxidant in the presence of a series of ruthenium complexes;[7] our continued interest in transition-metal–DMSO complexes prompted us to investigate the catalytic behavior of Rh–DMSO complexes. We now report in this paper a significantly improved metal-catalyzed procedure for the oxidative preparation of a sulfoxide from a sulfide and molecular oxygen using mainly rhodium complexes as the catalyst.

RESULTS AND DISCUSSION

A series of rhodium complexes has been screened as a catalyst for the selective oxidation of thioethers to sulfoxides. All the compounds are moderate to efficient catalysts for the selective oxidation of thioethers to their corresponding sulfoxides, under mild conditions (80–110 °C, 100 psi molecular oxygen in methanol). That the Rh–DMSO complexes **5** and **6** act as catalysts in the selective oxidation of sulfides to sulfoxides prompted us to determine if chiral derivatives of **5** and **6** could effect enantioselective oxidation of prochiral sulfides. Various combinations of temperature, oxygen pressure and solvent for the proposed catalytic reaction were tried. The optimum conditions were found to be 110 °C, 6.80 atm molecular oxygen in methanol as solvent. Alkyl–aryl substrates were more difficult to oxidize. A pronounced solvent effect was observed (Table 1).

The results of the reaction between methyl *p*-tolyl sulfide and molecular oxygen catalyzed by Rh–DMSO complexes, such as $H(DMSO)_2]$

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Table 1 Rhodium-catalyzed oxidation of methl *p*-tolyl sulfide

Run	Catalyst	Solvent	Yield (%)	Selectivity (%)
1	$[RhCl_4(DMSO)_2][(DMSO)_2]H$	Methanol	93	100
2	*mer*-$RhCl_3(DMSO)_3$	Methanol	96	100
3	$[Rh(CH_3COO)_2H_2O]_2$	Methanol	58	58
4	$[RhCl(1{,}5\text{-hexadiene})]_2$	Methanol	80	92
5	*mer*-$RhCl_3(DMSO)_2(pMeC_6H_4SMe)$	Methanol	100	100
6	*mer*-$RhCl_3(DMSO)(pMeC_6H_4SMe)_2$	Methanol	100	100
7	*mer*-$RhCl_3(DMSO)_3$	Ethanol	74	100
		2-propanol	49	49

$[RhCl_4(DMSO)_2]$ (**1**), *mer*-$RhCl_3(DMSO)_3$ (**2**), $[Rh_2(AC)_4]\cdot 4H_2O$ (**3**), $[RhCl(hd)]_2$ (**4**), *mer*-$RhCl_3(DMSO)_2(pMeC_6H_4SMe)$ (**5**) and *mer*-$RhCl_3(DMSO)(pMeC_6H_4SMe)_2$ (**6**), are presented in Table 1.

It is observed that the newly synthesized catalysts **5** and **6** are very efficient in comparison with other catalysts employed under the same experimental conditions (Table 1). In fact, 100% conversion and selectivity are easily obtained with these complexes. A slightly higher reactivity of complexes **5** and **6**, in comparison with the precursor, *mer*-$RhCl_3(DMSO)_3$, may be attributed to the lower number of coordinated DMSO molecules, which might have an inhibitory effect. Indeed, a remarkable decrease in catalytic activity was observed when the reaction was performed in the presence of increasing increments of DMSO. An analogous behavior was also observed in the Ru–DMSO system.[8] The catalytic system becomes ineffective at DMSO/Rh ratios higher than 22 (Fig. 1).

From these results it appears that all the rhodium(III) complexes screened effectively promote the molecular oxygen oxidation of thioethers. Though the mechanistic details of the catalysis are presently under investigation, studies involving the catalytic intermediate need further investigation. It is not clear whether rhodium behaves similarly to ruthenium[1–6] and interacts with molecular oxygen to generate a rhodium adduct that leads to catalysis. It is also uncertain if peroxide adducts form, by inner-sphere electron transfer, or if outer-sphere processes occur, and whether one- or two-electron transfer processes are operative. However, the present results indicate that the availability of a vacant site on the metal center forms an oxygen adduct that may initiate the catalytic cycle *via* an inner-sphere mechanism (Fig. 1). However, the outer-sphere mechanism proposed by Riley and Lyon[6] still cannot be ruled out.

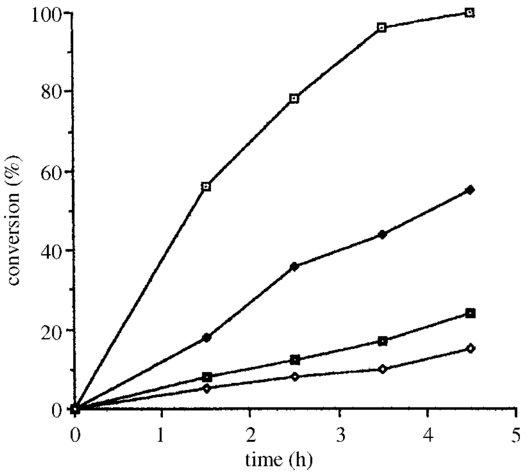

Figure 1 Plot of percentage conversion for the molecular-oxygen-catalyzed oxidation of methyl *p*-tolyl sulfide with various rhodium catalyst precursors: ⊡ $RhCl_3(DMSO)(pMeC_6H_4SMe)_2$; ◆ $RhCl_3(DMSO)(pMeC_6H_4SMe)_2$ + DMSO (Rh:DMSO = 1:6); ◘ $RhCl_3(DMSO)(pMeC_6H_4SMe)_2$ + DMSO (Rh:DMSO = 1:10); ◇ $RhCl_3(DMSO)(pMeC_6H_4SMe)_2$ + DMSO (Rh:DMSO = 1:22).

EXPERIMENTAL

Synthesis of the complexes

$H(DMSO)_2][RhCl_4(DMSO)_2]$ (**1**), *mer*-$RhCl_3$ $(DMSO)_3$ (**2**), $[Rh_2(AC)_4]\cdot 4H_2O$ (**3**), $[RhCl(hd)]_2$ (**4**), compounds were prepared following the literature procedure.[8–12]

mer-Trichlorobis(dimethyl sulfoxide)(methyl *p*-tolyl sulfide) rhodium(III) [*mer*-$RhCl_3(DMSO)_2(pMeC_6H_4SMe)$ (5)]

mer-$RhCl_3(DMSO)_3$ (0.30 g, 0.676 mmol) was dissolved in dichloromethane (10 ml). To the clear solution 1.0 ml, 7.42 mmol, of methyl *p*-tolyl sulfide was added. The resulting mixture was stirred at room temperature overnight. The solution was concentrated and a small amount of hexane was added. A red compound was obtained, filtered, washed with cold dichloromethane and vacuum dried.

Anal. Calc. for $C_{12}H_{22}Cl_3O_2RhS_3$ (503.767): C, 28.6; H, 4.4. Found: C, 28.62; H, 4.36%. IR spectra (cm^{-1}) (KBr): ν(S—O) 1132, 910 (s, DMSO); ν(Rh—S); 436 (m); ν(Rh—Cl) 350 (s); ν(Rh—O) 485 (m).

mer-Trichloro(dimethyl sulfoxide) bis(methyl *p*-tolyl sulfide) rhodium(III) [*mer*-$RhCl_3(DMSO)(pMeC_6H_4SMe)_2$ (6)]

mer-$RhCl_3(DMSO)_3$ (0.30 g, 0.676 mmol) was dissolved in methanol (20 ml). To the heterogeneous orange mixture 1.4 ml, 7.42 mmol, of methyl *p*-tolyl sulfide was added. The resulting mixture was refluxed for 5 h to produce a red solution. This solution was concentrated and a small amount of hexane was added, resulting in a yellow–orange crystalline compound, which was filtered, washed with cold ethanol and vacuum dried. Yield 60%.

Anal. Calc. for $C_{18}H_{26}Cl_3ORhS_3$ (563.847): C, 38.2; H, 4.53. Found: C, 38.34; H, 4.64%. IR spectra (cm^{-1}) (KBr): ν(S—O) 1142, 1098 (s, DMSO); ν(Rh—S); 430 (m); ν(Rh—Cl) 347 (s); ν(Rh—O) 483 (m).

Procedure for catalytic reaction

The Rh–DMSO complex (0.044 mmol), methyl *p*-tolyl sulfide (2.2 mmol) and methanol (25 ml) were introduced in a 100 ml steel autoclave. The autoclave was purged and then pressurized to 6.8 atm with molecular oxygen and was placed in a preheated oil bath at 100 °C. Thermal equilibrium is normally reached within 30 min. An aliquot of the reaction mixture was withdrawn hourly and analyzed [150 °C ($T_i = 6$ min)–190 °C ($T_f = 10$ min) with a 10 °C min^{-1} ramp] by either a DANI 6800 GC or an HP 5890 GC equipped with a packed carbowax column.

Acknowledgements We thank Professor August Gallo of our department for helpful discussions. A part of this work was done at the University of Trieste, Italy.

REFERENCES

1. Riley DP. *Inorg. Chem.* 1983; 1965.
2. Riley DP, Shumate RE. *J. Am. Chem. Soc.* 1984; **106**: 3179.
3. Riley DP, Oliver JD. *Inorg. Chem.* 1986; **25**: 1814.
4. Riley DP, Oliver JD. *Inorg. Chem.* 1986; **25**: 1821.
5. Riley DP, Oliver JD. *Inorg. Chem.* 1986; **25**: 1825.
6. Riley DP, Lyon III J. *J. Chem. Soc. Dalton Trans.* 1991; 157.
7. Srivastava RS, Milani B, Alessio E, Mestroni G. *Inorg. Chim. Acta.* 1992; **191**: 15.
8. Winkhaus G, Singer H. *Ber.* 1966; **99**: 3602.
9. Alessio E, Faleschini P, Santi ASO, Mestroni G, Calligaris M. *Inorg. Chem.* 1993; **32**: 5756.
10. James BR, Morris RH. *Can. J. Chem.* 1980; **58**: 399.
11. James BR, Morris RH, Einstein FWB, Willis A. *J. Chem. Soc. Chem. Commun.* 1980; 31.
12. Winkhaus G, Ziegler P. *Z. Anorg. Allgem. Chem.* 1967; **350**: 51.