Inorganica Chimica Acta

LETTER

Novel Ru(III)–dimethyl sulfoxide catalysts for the selective oxidation of thioethers to sulfoxides with molecular oxygen

R. S. Srivastava*, B. Milani, E. Alessio and G. Mestroni**

Dipartimento di Scienze Chimiche, Università di Trieste, via A. Valerio 22, 34127 Trieste (Italy)

(Received July 9, 1991; revised October 28, 1991)

In recent years, several attempts have been made to use transition metal complexes to promote the selective oxidation of thioethers to their sulfoxides using O_2 as oxidant. In particular, Riley and coworkers [1–6] screened a large number of Ru(II) and Ru(III) complexes and found that facile and selective O_2 oxidation of dialkyl-thioethers can be accomplished in alcohol solvents in the presence of *cis*-$RuCl_2(DMSO)_4$ (DMSO = dimethyl sulfoxide) as catalyst precursor. Alkyl-aryl substrates were more difficult to oxidize. Ru(III) derivatives such as $RuCl_3 \cdot nH_2O$ and *mer*-$RuCl_3(MeSPh)_3$ were found to be completely inactive.

The authors suggested that all-*trans*-$[RuCl_2(R_2SO)_2(R_2S)_2]$, generated *in situ*, is the Ru(II) complex involved in the catalytic cycle, the rate determining step being the oxidation of the Ru(II) complex by dioxygen (through an outer sphere process) to give hydrogen peroxide and a Ru(IV) derivative. The substrate is oxidized by H_2O_2 while Ru(II) is regenerated by reduction with the solvent alcohol [6].

$$R_1SR_2 + RCH_2OH + O_2 \xrightarrow{\text{catalyst}} R_1SOR_2 + RCHO + H_2O$$

Recently we have reported the synthesis, characterization and electrochemical behaviour of some new Ru(II) and Ru(III) complexes with DMSO, viz. *trans*-$[RuCl_2(DMSO)_4]$ (**1**) [7], $[(DMSO)_2H][trans\text{-}RuCl_4(DMSO)_2]$ (**2**), *mer*-$[RuCl_3(DMSO)_3]$ (**3**) [8, 9] and their analogous TMSO derivatives **4–6** (TMSO = tetramethylene sulfoxide) [10].

Experimental

Synthesis of the complexes

The known tested compounds were synthesized following the literature procedure [7, 8, 11].

mer-Trichlorobis(dimethyl sulfoxide)(methyl p-tolyl sulfide)ruthenium(III) (mer-$RuCl_3(DMSO)_2$(MePhSMe)) (7)

0.30 g of *mer*-$RuCl_3(DMSO)_3$ (0.678 mmol) was dissolved in 5 ml of dichloromethane. To the clear orange solution 1.0 ml of methyl *p*-tolyl sulfide (7.42 mmol) was added. The colour of the solution turned to red. After 1 h of stirring, at room temperature, a small amount of n-hexane was added. Orange crystals of the product formed within 24 h at 4 °C and were filtered off, washed with cold ethanol and vacuum-dried (yield 90%).

Anal. Calc. for $C_{12}H_{22}O_2S_3Cl_3Ru$ (M_r 501.91): C, 28.7; H, 4.4. Found: C, 28.6; H, 4.28%. Electronic spectra (λ_{max} (nm)) (in chloroform): 424, 359, 262. IR spectra (cm^{-1}) (KBr): 1111(s) ν(S–O) (DM*S*O); 916(s) ν(S–O) (DM*S*O) (DM*S*O = S-bonded dimethyl sulfoxide; DM*S*O = O-bonded dimethyl sulfoxide); 814(s) band attributable to the thioether; 500 ν(Ru–O); 421(m) ν(Ru–S); 332 ν(Ru–Cl).

mer-Trichlorodimethyl sulfoxide bis(methyl p-tolyl sulfide)ruthenium(III) (mer-$RuCl_3(DMSO)(MePhSMe)_2$) (8)

0.51 g of *mer*-$RuCl_3(DMSO)_3$ (1.15 mmol) was dissolved in 20 ml of methanol. To the clear orange solution 2.3 ml of methyl *p*-tolyl sulfide (17.08 mmol) were added. The colour of the solution turned to red. The solution was refluxed for 4.5 h; a solid was precipitated. The solid was filtered, washed with methanol, followed by diethyl ether and vacuum-dried (yield 85%). The solid was recrystallized with methanol to afford a light yellow compound.

Anal. Calc. for $C_{18}H_{26}OS_3Cl_3Ru$ (M_r 562.00): C, 37.5; H, 4.49. Found: C, 38.5; H, 4.66%. Electronic spectra (λ_{max} (nm)) (in chloroform solution): 407, 288, 258. IR spectra (cm^{-1}) (Nujol mull): 1111(s) ν(S–O) (DM*S*O); 812 and 802(s) band attributable to the thioether; 422(m) ν(Ru–S); 339 ν(Ru–Cl).

Procedure

All reactions were carried out in a Berghof stainless steel autoclave (100 ml) equipped with a Teflon liner, magnetic stirrer, manometer, heating mantel and temperature controller. In a typical reaction, the catalyst

*On leave from the Department of Chemistry, M.G. Degree College, Gorakhpur 273001, India.

**Author to whom correspondence should be addressed.

0020-1693/92/$5.00

TABLE 1. Turnover numbers, conversion % and selectivity for the catalytic dioxygen oxidation of methyl-*p*-tolyl sulfide with various catalyst precursors

Complex	Turnover number (cycles/h)[a]	Conversion (%)	Selectivity (%)
cis-$RuCl_2(DMSO)_4$	23	65	100
trans-$RuCl_2(DMSO)_4$	24	78	100
mer-$RuCl_3(DMSO)_3$	30	97	100
mer-$RuCl_3(DMSO)_2(MePhSMe)$	31	100	94
mer-$RuCl_3(DMSO)(MePhSMe)_2$	38	100	95
$K_2[RuCl_5(H_2O)]$	27	86	100

Reaction conditions: $T = 80$ °C; 100 psi O_2; solvent = MeOH (25 ml); [sub.]/[cat.] = 100; [cat.] = 1×10^{-3} M; time = 4.5 h.
[a]Average rate values calculated between $t = 0$ and $t = 1.5$ h of reaction.

precursor, the alcohol and the substrate were placed in the liner. The autoclave was then charged to the appropriate molecular oxygen pressure and heated to the required temperature (thermal equilibrium was usually reached in about 30 min). The reaction mixture was sampled periodically. Reaction samples were analyzed by using a DANI 6800 gas chromatograph equipped with a packed column CARBOWAX 20 M ($l = 2$ m; $\phi = 6$ mm) operating in temperature program.

Results and discussion

In the present communication, we report the catalytic behaviour of these complexes towards the above mentioned reaction. All the compounds are efficient catalysts for the selective dioxygen oxidation of thioethers, including the alkyl-aryl ones, to their sulfoxides, under rather mild conditions (60–80 °C, 100 psi O_2 in methanol).

Some selected results concerning the oxidation of alkyl-aryl thioethers are reported in Table 1.

trans-$RuCl_2(DMSO)_4$ is slightly more active than the *cis* isomer. Surprisingly, the Ru(III) derivative *mer*-$RuCl_3(DMSO)_3$ is also active, its catalytic activity being considerably more pronounced than that of *cis*-$RuCl_2(DMSO)_4$. Comparable catalytic activity is observed with the corresponding TMSO derivative.

Moreover two newly synthesized and characterized complexes, *mer*-$RuCl_3(DMSO)_2(MePhSMe)$ (**7**) and *mer*-$RuCl_3(DMSO)(MePhSMe)_2$ (**8**) are even more effective catalysts than their precursor, *mer*-$RuCl_3(DMSO)_3$. In fact 100% conversion with selectivities $\geq 94\%$ are easily obtained with these complexes. The higher activity of these complexes, in comparison to *mer*-$RuCl_3(DMSO)_3$, can be attributed to the lower number of coordinated DMSOs, which might have an inhibiting role. A remarkable decrease of the activity was in fact observed when the reaction was performed in the presence of increasing amounts of DMSO (or TMSO); the catalytic system became practically inactive at DMSO/Ru ratios higher than 20 (Fig. 1).

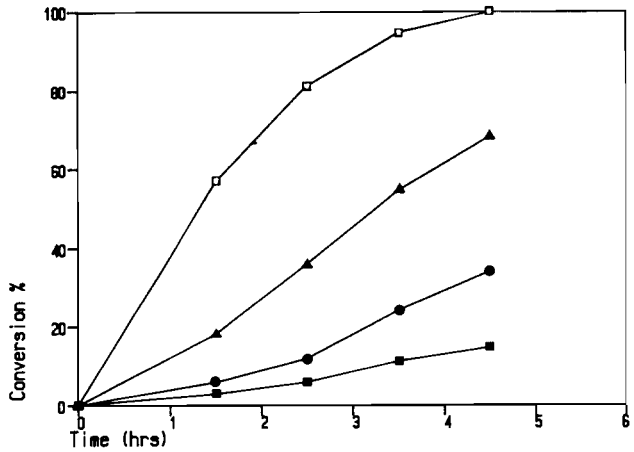

Fig. 1. Plot of conversion % vs. time for the catalytic dioxygen oxidation of methyl-*p*-tolyl sulfide with various catalysts precursors. Reduction conditions: see Table 1. □ $RuCl_3(DMSO)(MePhSMe)_2$; ▲ $RuCl_3(DMSO)(MePhSMe)_2$ + DMSO (Ru:DMSO = 1:6); ■ $RuCl_3(DMSO)(MePhSMe)_2$ + DMSO (Ru:DMSO = 1:22); ● $RuCl_3(TMSO)(MePhSMe)_2$ + TMSO (Ru:TMSO = 1:6).

Furthermore the known Ru(III) complexes *mer*-$RuCl_3(MeSAr)_3$ (Ar = phenyl, *p*-tolyl) [12] promote the oxidation of the corresponding thioethers to their sulfoxides with conversion > 99% in 4.5 h, under the same experimental conditions reported in Table 1.

Finally, $K_2[RuCl_5(H_2O)]$, albeit less active, is also a useful catalyst precursor for these reactions.

From the reported results it appears that all the Ru(III) complexes examined by us effectively promote the O_2 oxidation of thioethers and that the active species may not necessarily have two coordinated sulfoxides as proposed by Riley [6]. We suggest that the catalyst might be a pentacoordinated Ru(II) complex, $RuCl_2(R_2SO)_x(R_2S)_{3-x}$ ($x = 0, 1$), formed *in situ* through a fast monoelectronic reduction of the corresponding

Ru(III) derivatives*. Moreover owing to the availability of a vacant site on the metal center, the formation of an oxygen adduct cannot be ruled out and then an inner sphere mechanism cannot be rejected.

Acknowledgements

Financial support from M.U.R.S.T. (40% grant) and C.N.R. is gratefully acknowledged as well as T.W.A.S. for a research fellowship to R.S.S.

*Ru(III) derivatives undergo fast substitution and reduction reactions in the presence of mild reducing agents in aqueous solution.

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