

# Selective air oxidation of dimethyl sulfide to dimethyl sulfoxide catalysed by aminopolycarboxylatoruthenium(III) complex

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## Abstract

Reactions of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  (L = aminopolycarboxylate ligands viz. edta, pdta, hedtra) with dimethylsulfide (DMS) and dimethylsulfoxide (DMSO) were studied by using spectrophotometric, electrochemical and kinetic methods.  $[\text{Ru}^{\text{III}}\text{L}(\text{DMS})]$  complexes formed by the interaction of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  and DMS undergo oxidation when exposed to air to yield DMSO and  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  back. Under identical condition  $[\text{Ru}^{\text{III}}\text{L}(\text{DMSO})]$  complexes do not undergo any further oxidation to produce dimethyl sulfone. © 1997 Elsevier Science B.V.

*Keywords:* Oxidation; Dimethylsulfide; Dimethylsulfoxide; Aminocarboxylate; Catalysis

## 1. Introduction

The selective oxidation of sulfides to sulfoxides is of current interest [1] because of the synthetic versatility of sulfoxides [2]. Selectivity in the oxidation of sulfides with metal oxo reagents [3–5] was not observed because the sulfoxides also undergo further oxidation to produce sulfones. Riley and co-workers studied the oxidation of sulfides to sulfoxides by  $\text{O}_2$  catalysed with dihaloruthenium(II) complexes [6] which reportedly give sulfoxide/sulfone ratios parallel to those observed in the  $\text{H}_2\text{O}_2$  oxidation of sulfides [7]. The potential catalytic ability of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  in the oxidation of organic substrates [8–10] prompted us to undertake this work. In an earlier communication [11] prelimi-

nary results on the oxidation of dimethylsulfide was reported from this laboratory. It was felt necessary to carry out more work, in particular the interaction of aminopolycarboxylate complexes of ruthenium(III) with dimethylsulfoxide to know about the selectivity of the catalytic system.

We now wish to report herein the results of spectrophotometric, electrochemical and kinetic studies on the reactions of different  $\text{LRu}^{\text{III}}(\text{H}_2\text{O})$  complexes (where L = EDTA, PDTA, HEDTRA) with dimethyl sulfide (DMS) and dimethyl sulfoxide (DMSO). Our goal was to develop a catalytic route for selective oxidation of DMS to DMSO with molecular oxygen.

## 2. Experimental

$\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  complexes (Fig. 1) were prepared by following the published procedure

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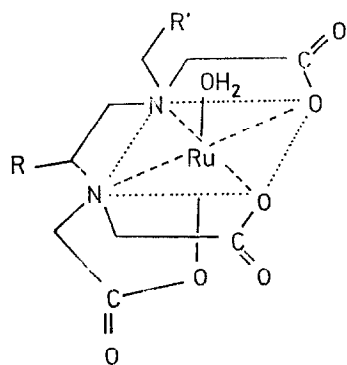


Fig. 1. Structural representation of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  complex. R = H, R' =  $\text{COO}^-$ ; L = EDTA; **1a**. R =  $\text{CH}_3$ , R' =  $\text{COO}^-$ ; L = PDTA; **1b**. R = H, R' =  $\text{CH}_2\text{OH}$ ; L = HEDTRA; **1c**.

[12,13] and characterised. All other chemicals used were of A.R. grade. Double distilled water and purified dioxan were used throughout the experiments. Absorption spectra were recorded on a Shimadzu UV-vis 160 A spectrophotometer coupled with a TCC-240A temperature controller. Electrochemical studies were carried out with a PAR 174A electrochemical instruments. A glassy carbon working electrode and a standard calomel electrode (SCE) as reference were used for this purpose. Fast kinetic studies were performed spectrophotometrically on a HI-TECH stopped-flow instrument. Slow kinetics were studied by using conventional mixing techniques. The reaction products were identified and analysed by HPLC (Waters Instruments) method.

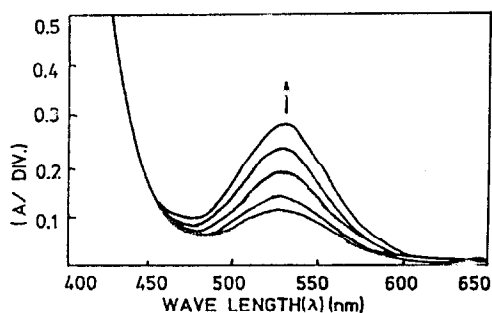
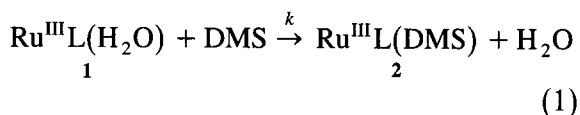


Fig. 2. Formation of  $\text{Ru}^{\text{III}}(\text{EDTA})(\text{DMS})^\pm$  complex in 1:1 water-dioxan medium  $[\text{Ru}^{\text{III}}] = 1 \times 10^{-3}$  M,  $[\text{DMS}] = 1 \times 10^{-3}$  M, pH = 5.1,  $T = 25^\circ\text{C}$ .

### 3. Results and discussion

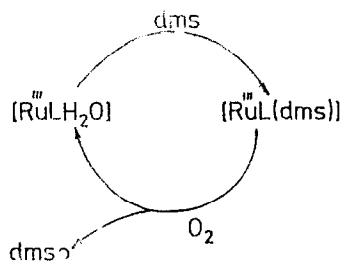
In Fig. 2 is shown a representative spectral change attributed to the formation of  $\text{Ru}^{\text{III}}(\text{DMS})$  complex (Pink colour) in the reaction of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  with DMS in absence of  $\text{O}_2$  (Eq. (1)). An intense band observed in the visible region ( $520 < \lambda_{\text{max}} < 530$  nm) is assigned to the characteristic LMCT band of coordinated sulfur ligand in  $\text{Ru}(\text{III})$ -edta type complexes [14]



Electrochemical studies (cyclic voltammetry) of  $\text{Ru}^{\text{III}}\text{L}(\text{DMS})$  complexes exhibited a pair of quasi-reversible cathodic and anodic peaks ( $\Delta E_p = 80\text{--}100$  mV) and the values of  $E_{1/2}$  corresponding to the  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couple in  $[\text{RuL}(\text{DMS})]$  complexes were found to be in the range  $-0.16 < E_{1/2} < -0.14$  (vs. SCE). Kinetic studies of the formation of  $\text{Ru}^{\text{III}}\text{L}(\text{DMS})$  complexes (**2**) showed that the formation of **2** is a first order to the complex **1** concentration. The values of the pseudo first order rate constant were found to increase linearly with the increase of  $[\text{DMS}]$ . Formation rate constant ( $k$ ) values ( $2.2 < k < 4.3 \text{ M}^{-1} \text{ s}^{-1}$ ) and activation parameters ( $8 < \Delta H^\ddagger < 10 \text{ kcal mol}^{-1}$ ;  $-43 < \Delta S^\ddagger < -40$  e.u.) are in favour of an associatively mode of activation proposed for the formation of  $[\text{Ru}^{\text{III}}\text{L}(\text{DMS})]$  complexes (Eq. (1)).

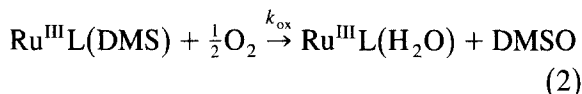
### 4. Air-oxidation of DMS to DMSO. Homogeneous catalysis

Purging oxygen into the pink solution of **2** caused gradual change in the colour (pink to pale yellow) which accompanied the oxidation of DMS to DMSO (Eq. (2)) as revealed by HPLC analysis. The rate of oxidation was found to be of first order with respect to complex **2**



Scheme 1.

and one-half order with respect to dissolved oxygen concentrations.

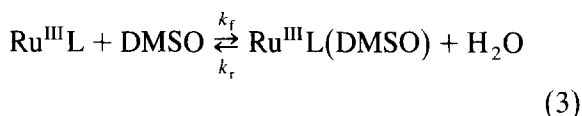


The values of rate constant fall in the range  $2.1 \times 10^{-3} < k_{\text{ox}} < 3.0 \times 10^{-3} \text{ s}^{-1}$ . Addition of fresh dms revives the pink colour which is again changed to pale-yellow upon exposing to air. Several numbers of catalytic cycles (Scheme 1) were performed under the employed condition.

## 5. Reaction of 1 with DMSO

The  $\text{Ru}^{\text{III}}\text{L}(\text{DMSO})$  complex is formed by the reaction of  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  with DMSO present in excess. In contrast to the other sulfur bound  $\text{Ru}^{\text{III}}\text{-L}$  complexes [7] which are charac-

terised with their strong ligand-to-metal charge transfer (from coordinated sulfur to ruthenium) in the visible region, the  $\text{Ru}^{\text{III}}\text{L}(\text{DMSO})$  complex (hereafter designed as  $\text{Ru}^{\text{III}}\text{-S}$ ) exhibits this particular charge transfer band in the near UV region (380–390 nm) [15]. The spectral shift to higher energy for the S-bound sulfoxide ligand, which is a very weak  $\sigma$ -donor, is consistent with the earlier observation [16] reported for the  $[\text{Ru}^{\text{III}}(\text{bipy})(\text{tepy})(\text{DMSO})]$  complex. Stopped-flow kinetics studies revealed that the formation of the  $\text{Ru}^{\text{III}}\text{L}(\text{DMSO})$  complex takes place in a reversible reaction as outlined below.



The values of  $k_f$  and  $k_r$  are estimated fall in the range  $0.40 < k_f < 12 \text{ M}^{-1} \text{ s}^{-1}$  and  $0.9 < k_r < 6 \text{ s}^{-1}$ , respectively. Electrochemical studies (Fig. 3) also confirmed that  $\text{Ru}^{\text{III}}\text{L}(\text{DMSO})$  complexes is very weak and undergoes hydrolysis ( $k_r$  step in Eq. (3)) under employed conditions. Furthermore, oxidation of  $\text{Ru}^{\text{II}}\text{L}(\text{DMSO})$  species ( $\text{Ru}^{\text{II}}\text{-S}$ ) occurs at positive potentials (0.339 as shown in Fig. 3) for which oxidation of coordinated DMSO by dioxygen is not effected under specified conditions.

In conclusion, the results of the present investigation explore the possibility of a facile catalytic route for selective oxidation of DMS to DMSO by air catalysed by amino polycarboxylate complexes of ruthenium(III). It is worth mentioning here that aryl sulfides were found to be much less reactive with  $\text{Ru}^{\text{III}}\text{L}(\text{H}_2\text{O})$  complexes.

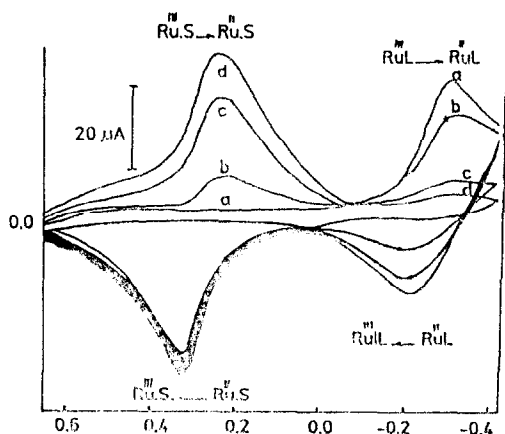


Fig. 3. CV of  $\text{Ru}^{\text{III}}(\text{HEDTRA})$  in the presence of DMSO [ $\text{Ru}^{\text{III}}] = 1 \times 10^{-3} \text{ M}$ ,  $[\text{DMSO}] =$  (a) 0.0, (b) 0.7, (c) 0.14 and (d) 5 M, scan rate  $200 \text{ mV s}^{-1}$ .

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