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# CATALYTIC $O_2$-OXIDATION OF THIOETHERS TO SULFOXIDES USING RUTHENIUM(VI) DIOXO PORPHYRIN SPECIES

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Ruthenium(VI) dioxo porphyrin species in benzene act as stoichiometric oxygen-atom transfer reagents toward alkyl thioethers to give the sulfoxide; the systems become catalytic in the presence of dioxygen at room temperature, but turn-overs are limited by formation of substitution-inert bis(S-bonded sulfoxide) complexes.

## 1. Introduction

Interest in selective catalytic oxidations utilizing dioxygen as oxidant remains intense, particularly in aspects of oxidation processes of the mono- [1,2] and dioxygenase type [3,4]. The 'sterically hindered' *trans*-dioxo species Ru(TMP)$(O)_2$, 1 (TMP = the dianion of meso-tetramesitylporphyrin), readily generated using $O_2$ as the oxo source [3,4], is proving to be a useful dioxygenase-type system in which both O-atoms are transferred, for example, to olefins to generate epoxides [3,5]. We have initiated studies on 1 for the $O_2$-oxidation of other substrates such as thioethers and aliphatic and aromatic alcohols; a particular aim is the selective oxidation of thioethers to sulfoxides, a reaction of some industrial importance [6,7]. This communication describes such an oxidation and presents kinetic and activation parameter data for the O-atom transfer process; the studies were first described at a homogeneous catalysis symposium [8].

## 2. Experimental

The Ru(TMP)$(MeCN)_2$ complex was prepared from Ru(TMP)(CO) by photolysis in MeCN as described earlier [9]. A few mg of the MeCN complex were dissolved in $C_6H_6$ or $C_6D_6$ in a specially designed cell for UV/vis measurements [10], or in an NMR tube, in a glovebox under $N_2$. The cell and NMR tube were then handled subsequently by attachment to a vacuum-line; addition of $O_2$

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readily generated solutions of Ru(TMP)$(O)_2$ 1 [3,4], and thioether was added subsequently via a serum-cap. Samples of Ru(TMP)$(OSEt_2)_2$ with S-bonded sulfoxide were isolated by evaporating to dryness benzene solutions of 1 (10 mg, $\sim 10^{-5}$ mol in 1.5 mL) containing $Et_2S$ (10 $\mu$L, $\sim 10^{-4}$ mol) that had reacted 12 h at room temperature; the resulting micro-crystalline solid was dried at 80 °C at $\sim 10^{-3}$ torr for 24 h. [Calc. (found) for $C_{64}H_{72}O_2N_4S_2Ru \cdot C_6H_6$: C 71.70 (71.50), H 6.71 (6.91), N 4.78 (5.00); $\nu$(SO) for S-bonded $Et_2SO$ = 1165 $cm^{-1}$ [11].] Benzene was distilled over $CaH_2$ prior to use; thioethers (Aldrich or Fairfield Chemicals) were passed through neutral alumina (activity 1) and vacuum-distilled; the grade of cylinder-$O_2$ used did not affect the kinetic data for the reaction between 1 and the thioethers, and the UV/vis kinetic data were identical whether the reaction solution was maintained under $O_2$ or whether the $O_2$ was replaced by Ar (after forming 1). UV/vis spectra were run on a thermostated Perkin-Elmer 552 A, and IR spectra on a Nicolet 5DX FT instrument. $^1$H NMR spectra were obtained on $C_6D_6$ solutions with a Varian XL-300 spectrometer.

## 3. Results and discussion

In situ samples of 1 react with the $R_2S$ thioethers ($R_2$ = $Et_2$, $^nBu_2$, and decylmethyl) to generate initially, in a slow $k_1$ step, Ru(TMP)$(OSR_2)_2$, 2, in which both sulfoxides are O-bonded; the reaction is first-order in both Ru and thioether, and presumably goes via the monooxo intermediate shown (Scheme 1). The kinetics were determined by monitoring the UV/vis spectral changes at [Ru] $\approx (2.0–4.0) \times 10^{-6}$ M with [$R_2S$] = $(2.5–50) \times 10^{-2}$ M (fig. 1); the observed pseudo-first order rate constants were strictly proportional to the thioether concentration, and the second-order $k_1$ rate constants for three thioethers are shown in table 1.

Subsequent, much slower UV/vis spectral changes occur, and these are attributed to successive conversions to the mixed Ru$(OSR_2)(OSR_2)$ species 3 and then the bis(S-bonded) derivative Ru$(OSR_2)_2$, 4. Species 2-4 were characterized in solution by $^1$H NMR (see below), while 4 (R = Et) was also isolated as a benzene solvate. The final UV/vis spectrum of the $1/Et_2S$ solutions corresponded to that of 4 {$\lambda_{max}$(log $\epsilon$): 423 (5.42), 510 (4.38)}.

Monitoring the reaction of 1 ($\sim 6 \times 10^{-3}$ M) with $Et_2S$ ($\sim 6 \times 10^{-3}$ M) in $C_6D_6$ at 20 °C by $^1$H NMR allows for observation of 2, 3 and 4; the complete spectrum of 4 is shown in fig. 2, and that of a mixture of 2 and 3 in the high-field region is shown in fig. 3. Spectral assignments are given in table 2. The relative intensities of the singlets for the pyrrole protons in the 8.5–8.7 ppm range readily reveal the proportions of 2–4 present. For 4, the $-CH_2-$ protons of $Et_2SO$, as in the free ligand [11], are seen to be magnetically inequivalent, and appear as multiplets (approximately sextets centred at $\delta = -1.46$ and $-1.80$) as the AB

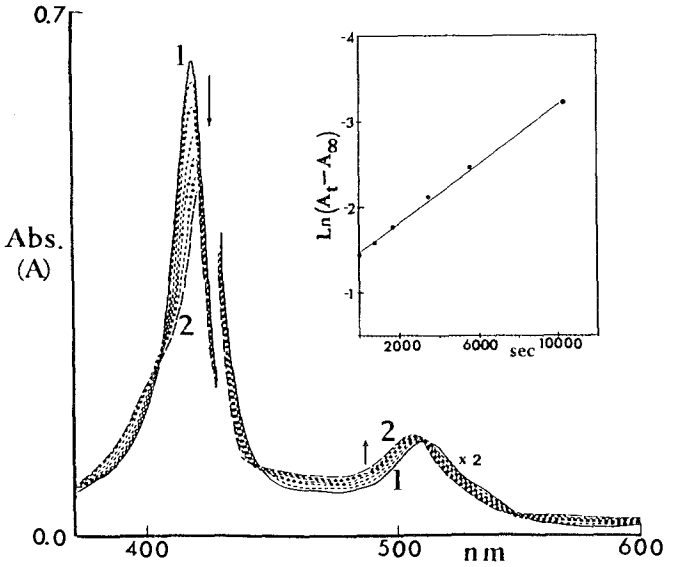
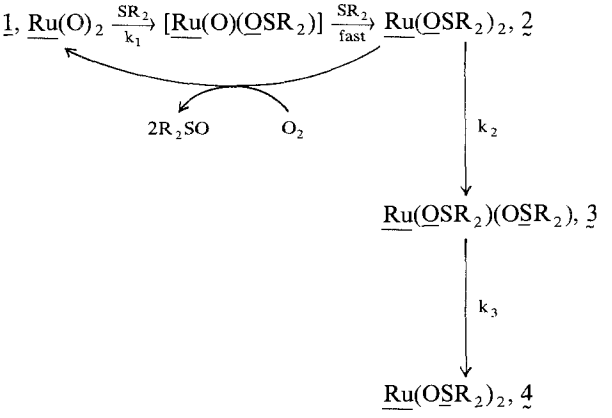



Fig. 1. UV/vis spectral changes observed for the reaction $\underset{\sim}{1} \rightarrow \underset{\sim}{2}$ in $C_6H_6$ at 20 °C; [Ru] ~ $3\times10^{-6}$ M, [$Et_2S$] = $4.6\times10^{-2}$ M. Inset shows pseudo-first order plot for the disappearance of $\underset{\sim}{1}$.

Table 1
Second order rate constants for O-atom transfer from Ru(TMP)$(O)_2$ to alkyl thioethers at 20 °C

| Thioether | decylmethyl | di-*n*-butyl | diethyl |
|---|---|---|---|
| $k_1$, $M^{-1}s^{-1}$ | 0.11 | 0.012 | 0.0075 |

moiety of an $ABX_3$ system; the $-CH_3$ protons approximate as a triplet ($\delta = -1.00$). The spectrum shown in fig. 3 taken under the conditions shown pertains to a mixture of $\underset{\sim}{2}$ and $\underset{\sim}{3}$ before appreciable amounts of $\underset{\sim}{4}$ are formed; by using




Scheme 1. (Ru = Ru(TMP).)

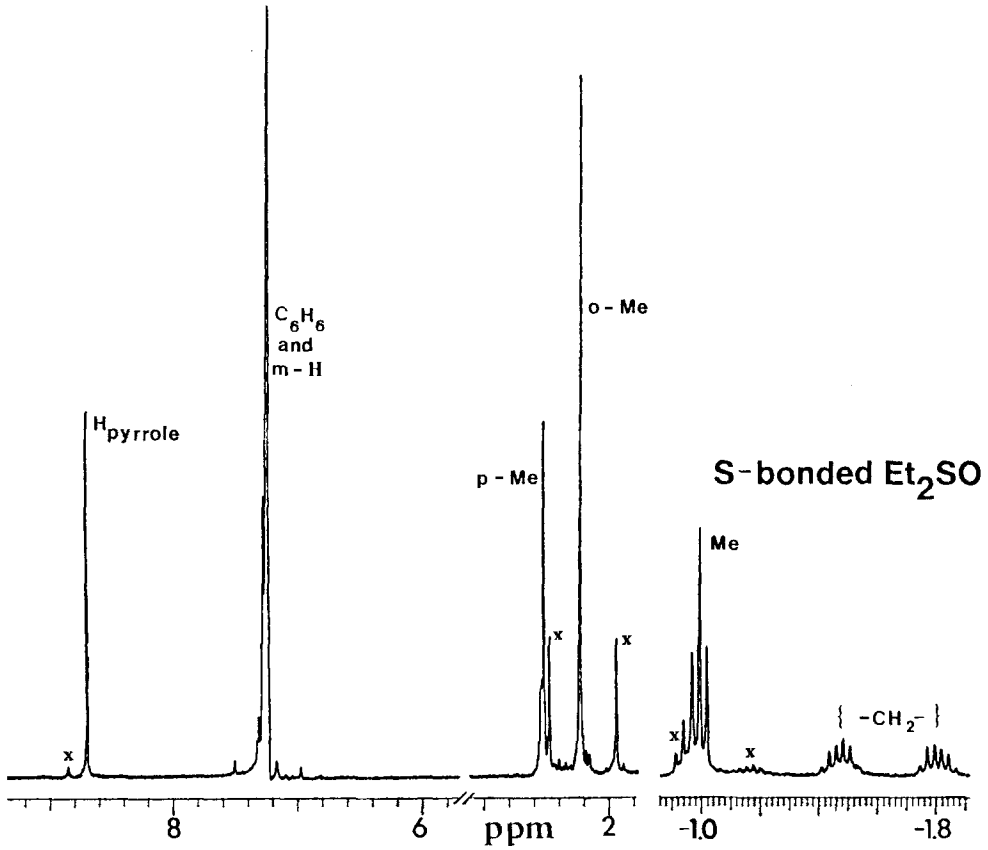



Fig. 2. The room temperature $^1H$ NMR spectrum of Ru(TMP)($OSEt_2$)$_2$, 4, in $C_6D_6$. Isolated sample or final *in situ* reaction product of scheme 1; this *in situ* sample formed after ~ 2 days shows also signals from a slowly formed, unknown species x, and a MeCN signal ($\delta \sim 1.2$) from precursor Ru(TMP) (MeCN)$_2$.

selective decoupling and the relative integration intensities, we assign the peaks as shown in the figure.

The $-CH_2-$ protons of the O-bonded $Et_2SO$ in 2, and in 3, appear as quartets (coupled to the adjacent Me) and thus the theoretically expected magnetic inequivalence is too small to be observed, which is not unprecedented for O-bonded $Et_2SO$ systems [11]. The $-CH_3$ protons of 2 appear as the expected triplet, while in 3 the two types of methyls (from the O- and S-bonded sulfoxides) appear as partially overlapping triplets. The $-CH_2-$ protons of the S-bonded sulfoxide within 3, as in 4, are magnetically inequivalent and appear as multiplets ($\delta = -1.30, -1.59$).

Of interest, Meyer's group has reported on the oxidation of $Me_2S$ by the Ru(IV)-oxo complex, $[Ru(bipy)_2(py)O]^{2+}$, via O-atom transfer [6]; the O-atom transfer step was similarly 1st order in both Ru and $Me_2S$ with $k = 13.0\ M^{-1}\ s^{-1}$ in MeCN at 20 °C, the rate being 100–2000 times faster than those measured at

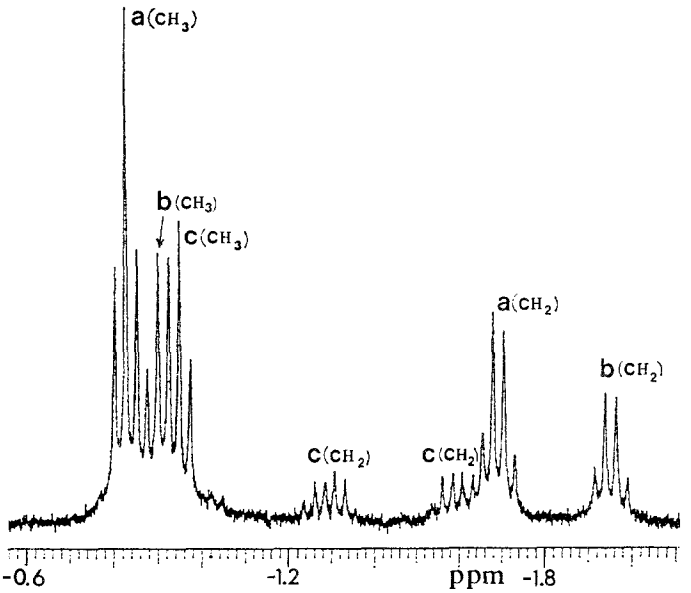



Fig. 3. High-field region of $^1$H NMR spectrum (room temperature) of a mixture of 2 and 3 (scheme 1, R = Et); a are signals for 2; b and c are signals for O- and S-bonded $Et_2SO$, respectively, within 3. [1] = [$Et_2S$] = $6\times10^{-3}$ M, $2\frac{1}{2}$ h reaction time.

20 °C in our work. Nevertheless, a subsequent isomerization of the initially formed $[(bipy)_2(py)Ru\text{-}OSMe_2]^{2+}$ to give the S-bonded analogue was also a feature of their work. It is surprising that in our Ru(VI)-dioxo system, the first O-atom transfer step ($k_1$) is slower than the second O-atom transfer that generates the detected species 2; the $^1$H NMR and UV/vis spectral changes rule out any possibility that the slow step being monitored is the conversion of Ru(OSEt$_2$)O to 2.

If the O-atom transfer occurs via electronic coupling induced by strong $\nu$(Ru = 0) vibrational motion [6,12], the findings imply that this process occurs more readily with $(Et_2SO)Ru^{IV}=O$ than with the $O=Ru^{VI}=O$ species 1. Groves and Ahn [13] have formed the $Ru^{IV}$(TMP)O species in situ by treatment

Table 2
$^1$H NMR shifts ($\delta$, ppm) for the pyrrole protons and the coordinated diethyl sulfoxide ligands [a]

| Complex | $H_{pyrrole}$ | $-CH_3$ | $-CH_2-$ |
|---|---|---|---|
| 1 | 9.07 | – | – |
| 2 | 8.50 | −0.82 | −1.69 q |
| 3 | 8.60 | −0.90, −0.95 | −1.30 m, −1.59 m, 1.95 q |
| 4 | 8.68 | −1.00 | −1.46 m, −1.80 m |

[a] $CH_3$ signals are triplets; q = quartet, m = multiplet; in 2 and 4, the porphyrin plane is a mirror plane, and one singlet is observed for the ortho-Me groups (~ 2.2 ppm) and one for the meta-protons (~ 7.3 ppm) of the mesityl groups; in 3, there is no such mirror plane, and two singlets are observed in each of these regions for the ortho- and meta-groups.

of 1 with $PPh_3$; here, the phosphine oxide product does not coordinate and their data imply that 1 is a much more potent oxo-transfer agent than the 5-coordinate Ru(TMP)O. The role of the trans, axial ligand L in $LRu^{IV}(TMP)O$ species within O-atom transfer is clearly critical, and these systems offer an excellent route into models for the biologically important oxoiron(IV) porphyrins [13,14].

The thioether oxidation rates (table 1) are seen to increase with increasing alkyl chain length; further data (more extensive series of thioethers, activation parameters) are needed before such a reactivity trend can be rationalized. The aromatic-containing methyl p-tolylsulfide did not react with benzene solutions of 1 at 20 °C. Preliminary activation parameters for $k_1$ for the $Et_2S$ system ($\Delta H^{\ddagger} \sim 50$ kJ $mol^{-1}$, $\Delta S^{\ddagger} \sim -120$ $JK^{-1}$ $mol^{-1}$) are comparable with those for O-atom transfer from $[Ru(bipy)_2(py)O]^{2+}$ to $Me_2S$ ($\Delta H^{\ddagger} \sim 34$ kJ $mol^{-1}$, $\Delta S^{\ddagger} \sim -110$ $JK^{-1}$ $mol^{-1}$).

In the presence of a 10 to 100-fold excess of $Et_2S$, solutions of 1 (at $\sim 6 \times 10^{-3}$ M) under 1 atm $O_2$ at 20 °C do catalyze the $O_2$-oxidation to generate selectively the sulfoxide $Et_2SO$, but after a turn-over of ~ 5 after 20 min catalysis was suppressed; at this stage 4 is present, and we find this species to be substitution-inert. Thus 4 remains as such in MeCN and THF, under Ar or $O_2$, and there is no ligand exchange. The catalysis likely occurs via 2, the more labile O-bonded sulfoxides [15] being lost with concomitant regeneration of 1 (scheme 1). Higher turn-overs (~ 15) are realized at 65 °C but now the porphyrin ligand undergoes degradation perhaps via reactivity with the O=Ru=O moiety in an intermolecular process. Preliminary studies indicate that another sterically hindered system *trans*-$Ru(OCP)(O)_2$(OCP = the dianion of meso-tetra(2,6-dichlorophenyl)porphyrin) is more oxidation resistant and a better catalyst for $Et_2S$ oxidation.

The $Ru^{VI}$ dioxo species also generate *p*-quinone from phenol, and dehydrogenate 2-propanol to give acetone, and are thus proving to be versatile oxidants; coupled with their ready generation from $O_2$, the species and their reactivity represent a major advance in $O_2$-oxidation chemistry. The thioether oxidations are very different in type to those effected by $O_2$-oxidation of Ru(II) thioether complexes via outer-sphere electron transfer [16,17]. It should be noted here that the bis(thioether) species $Ru(TMP)(SR_2)_2$ are readily formed *in situ* from solutions of $Ru(TMP)(MeCN)_2$. The $^1H$ NMR spectrum in $C_6D_6$ of the $Et_2S$ complex reveals a single triplet at $\delta - 0.82$, and a single quartet at $\delta$: $-1.70$ for the $-CH_3$ and $-CH_2-$ protons of coordinated thioether, respectively; such solutions are unreactive toward $O_2$ at 20 °C.

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