CATALYTIC O₂-OXIDATION OF THIOETHERS TO SULFOXIDES USING RUTHENIUM(VI) DIOXO PORPHYRIN SPECIES

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Received 7 January 1989; accepted 21 February 1989

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 O₂ 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 O₂-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 C₆H₆ or C₆D₆ in a specially designed cell for UV/vis measurements [10], or in an NMR tube, in a glovebox under N₂. The cell and NMR tube were then handled subsequently by attachment to a vacuum-line; addition of O₂

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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)(OSET₂)₂ with S-bonded sulfoxide were isolated by evaporating to dryness benzene solutions of 1 (10 mg, ~10⁻⁵ mol in 1.5 mL) containing Et₂S (10 μL, ~10⁻⁴ mol) that had reacted 12 h at room temperature; the resulting micro-crystalline solid was dried at 80 °C at ~10⁻³ torr for 24 h. [Calc. (found) for C₆₄H₇₂O₂NgS₂Ru-C₆H₆:C 71.70 (71.50), H 6.71 (6.91), N 4.78 (5.00); ν(SO) for S-bonded Et₂SO = 1165 cm⁻¹ [11].] Benzene was distilled over CaH₂ prior to use; thioethers (Aldrich or Fairfield Chemicals) were passed through neutral alumina (activity 1) and vacuum-distilled; the grade of cylinder-O₂ 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 O₂ or whether the O₂ 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. ¹H NMR spectra were obtained on C₆D₆ solutions with a Varian XL-300 spectrometer.

3. Results and discussion

In situ samples of 1 react with the R₂S thioethers (R₂ = Et₂, nBu₂, and decylmethyl) to generate initially, in a slow k₁ step, Ru(TMP)(OSET₂)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] = (2.0–4.0) × 10⁻⁶ M with [R₂S] = (2.5–50) × 10⁻² M (fig. 1); the observed pseudo-first order rate constants were strictly proportional to the thioether concentration, and the second-order k₁ 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(OSR₂)(OSET₂) species 3 and then the bis(S-bonded) derivative Ru(OSR₂)₂, 4. Species 2–4 were characterized in solution by ¹H NMR (see below), while 4 (R = Et) was also isolated as a benzene solvate. The final UV/vis spectrum of the 1/Et₂S solutions corresponded to that of 4 {λₘₐₓ(log ε): 423 (5.42), 510 (4.38)}.

Monitoring the reaction of 1 (~6 × 10⁻³ M) with Et₂S (~6 × 10⁻³ M) in C₆D₆ at 20 °C by ¹H 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 –CH₂– protons of Et₂SO, as in the free ligand [11], are seen to be magnetically inequivalent, and appear as multiplets (approximately sextets centred at δ = -1.46 and -1.80) as the AB