



A UV–vis study of the effects of alcohols on formation and stability of Mn(por)(O)(OAc) complexes

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ABSTRACT

Interactions of three different (acetato) (tetraarylporphyrinato) manganese (III) Mn^{III}(por) with tetra-*n*-butylammonium hydrogen monopersulfate (*n*-Bu₄NHSO₅), in the presence of excess tetra-*n*-butylammonium acetate (*n*-Bu₄NOAc) and in the absence or presence of various alcohols (alcohols = CH₃OH, C₂H₅OH, *i*-C₃H₇OH, *t*-C₄H₉OH) in CH₂Cl₂, were monitored by their UV–vis spectral changes, under identical conditions, at room temperature. (Acetato) (tetrakis(pentafluorophenyl)porphyrinato) manganese (III) Mn^{III}(tpfpp)(OAc) and (acetato) (tetramesitylporphyrinato) manganese (III) Mn^{III}(tmp)(OAc) produced their corresponding high valent Mn(tpfpp)(O)(OAc) and Mn(tmp)(O)(OAc) both in the absence or presence of alcohols. Whereas, (acetato) (tetraphenylporphyrinato) manganese (III) Mn^{III}(tpp)(OAc) only generated Mn(tpp)(O)(OAc) in the presence of less bulky alcohols. In the absence of alcohols or in the presence of *t*-C₄H₉OH, the UV–vis spectra displayed a very weak sign of formation of Mn(tpp)(O)(OAc) complex. It was observed that alcohols generally increased the rate of formation of Mn–oxo species in accordance with their acidity or hydrogen bonding strength, and enhanced the stability of Mn–oxo complexes, as their size increases. Attempts are made to explain these effects. A mechanistic scheme is also suggested for the decomposition of HSO₅[−] to O₂ and HSO₄[−], through the formation and dimerization of Mn–oxo species.

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1. Introduction

Generation and reactivity of high valent manganese–oxo porphyrin complexes, as the active site models of cytochrome P-450 enzymes, have attracted attention for over two decades [1–7]. An important objective in the study of such reactive intermediates is to elucidate the nature of the factors that may determine their chemical properties. However, gaining insights into the reactivity pattern of the manganese–oxo complexes of porphyrin, has often been hampered by their transient nature. Recently, we have shown that alcohols can play a critical role in defining the stability and reactivity of two different [Mn(por)(O)(im)]⁺ species, formed by tetra-*n*-butylammonium periodate (*n*-Bu₄NIO₄), as a mild oxidant [8]. In this study we have compared the generation and stability of three stereoelectronically different Mn(por)(O)(OAc) complexes (Fig. 1) by employing tetra-*n*-butylammonium hydrogen monopersulfate (*n*-Bu₄NHSO₅), as a strong oxidant, and by using the oxidatively stable OAc[−] axial ligand, in the presence or absence of various alcohols, under identical conditions. In particular, this work has provided new conditions for the generation of

Mn(tpfpp)(O)(OAc), which was not possible by *n*-Bu₄NIO₄ [8]. A mechanistic scheme has also been tentatively proposed, for the first time, for catalytic decomposition of HSO₅[−] to O₂ and HSO₄[−] by mediation of Mn^{III}(por), through formation and possible coupling of high valent Mn(por)(O)(OAc) complex.

2. Experimental

2.1. Materials

All the solvents were distilled under nitrogen prior to the use. Dichloromethane was purified by distillation over P₂O₅ and/or CaH₂ and stored over molecular sieves (Linde 4A). Methanol (99.8%), ethanol (99.6%), and *i*-propanol (99.5%) were purchased from Merck or Fluka. *t*-Butanol (99.4%), was obtained from Aldrich. Deionized, double-glass distilled water was used for all the experiments. A constant temperature bath was employed to maintain the temperature at 25 ± 2 °C.

The free base porphyrin ligands, H₂TPP [9], H₂TMP [10] and H₂TPFPP [11] were prepared in accordance with the previously reported methods. Manganese was inserted by standard routes [12,13]. The synthesis of tetra-*n*-butylammonium peroxymonosulfate was achieved by the known procedures [14,15]. Since the oxidizing ability of *n*-Bu₄NHSO₅ diminishes with time, the freshly

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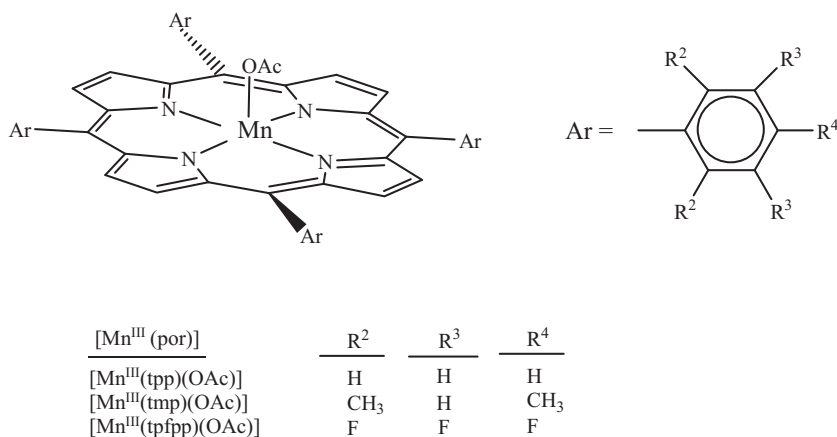


Fig. 1. (Acetato) (tetraarylporphyrinato) manganese (III) complexes used in this study.

prepared oxidant was refrigerated and used within three days. *Caution:* *n*-Bu₄NHSO₅ should be considered as a potentially explosive compound. *n*-Bu₄NOAc was prepared by using the known method [16].

2.2. General procedure

Stock CH₂Cl₂ solutions of Mn^{III}Por (2 ml, 1.2 × 10⁻⁵ M), *n*-Bu₄NOAc (48 μL, 0.25 M) and *n*-Bu₄NHSO₅ (1–96 μL, 0.25 M) were added into a 1-cm UV cell. If alcohol was needed, then 50 μL was added to the UV-cell before the addition of *n*-Bu₄NHSO₅. For this study, the best molar ratio of Mn^{III}(por)/*n*-Bu₄NOAc/*n*-Bu₄NHSO₅ was found to be 1/500/100.

The electronic absorption spectra were recorded on a MultiSpect-1501 Shimadzu spectrophotometer.

3. Results and discussion

3.1. Mn^{III}(tpfpp)(OAc)

The UV-vis spectra for interaction of Mn^{III}(tpfpp)(OAc) with *n*-Bu₄NHSO₅ in the presence of *n*-Bu₄NOAc under Mn^{III}(por)/*n*-Bu₄NOAc/*n*-Bu₄NHSO₅ molar ratio of 1/500/100 in CH₂Cl₂, at room temperature, are presented in Fig. 2. Addition of *n*-Bu₄NOAc to CH₂Cl₂ solution of Mn^{III}(tpfpp)(OAc) (Soret, λ_{max} = 474 nm) gave a broad Soret band (λ_{max} = 466 nm) with a shoulder, reflecting the

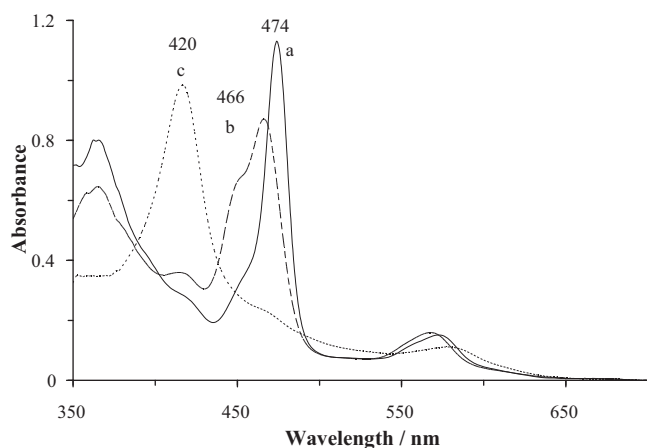


Fig. 2. UV-vis spectra for interaction of Mn^{III}(tpfpp)(OAc) with *n*-Bu₄NHSO₅: Mn^{III}(tpfpp)(OAc) (2.4 × 10⁻⁵ mmol) in CH₂Cl₂ (2 mL, 1.2 × 10⁻⁵ M) (a); (a) + *n*-Bu₄NOAc (1.2 × 10⁻² mmol) (b); (b) + *n*-Bu₄NHSO₅ (2.4 × 10⁻³ mmol) (c), at 25 ± 2 °C.

formation of six coordinate [Mn^{III}(tpfpp)(OAc)₂]⁻ complex in equilibrium with Mn^{III}(tpfpp)(OAc). Addition of *n*-Bu₄NHSO₅ to this solution resulted in a new Soret band (λ_{max} = 420 nm), concomitant with complete disappearance of 466 nm band, in ca. <45 s. The 420 nm band, which is related to the formation of high valent Mn(tpfpp)(O)(OAc) [17,18], remained virtually intact for ca. 2000 s, and then decayed slowly with reappearance of the 466 nm band. However, the 420 nm band disappeared completely after 24 h and the 466 nm band was mostly recovered, indicating total decomposition of HSO₅⁻ and some degradation of the Mn^{III}(por).

Changing solely the molar ratio of HSO₅⁻/Mn^{III}(por), causes a dramatic effect on the formation rate and the lifetime of Mn-oxo complex (Fig. 3). For HSO₅⁻/Mn^{III}(por) = 10, complete conversion of Mn^{III}(por) to Mn-oxo complex occurred in ca. 1200 s, while for HSO₅⁻/Mn^{III}(por) ≥ 300 it happened instantly. For all HSO₅⁻/Mn^{III}(por) ≥ 10, after complete conversion of Mn^{III}(por) to Mn-oxo, the intensity of the 420 nm band remained virtually unchanged for a limited period of time, increasing from ca. 300 s (HSO₅⁻/Mn^{III}(por) = 10) to >10,000 s (HSO₅⁻/Mn^{III}(por) ≥ 300). These results indicate that both the formation rate and the lifetime of Mn-oxo complex enhance as HSO₅⁻/Mn^{III}(por) ratio increases. It may also be concluded that, in the time span wherein the intensity of the 420 nm band is fixed, the system is under a steady state condition, and the rate of generation of Mn-oxo complex and its decay rate to Mn^{III}(por) and O₂ are equal.

Furthermore, it was found that the intensities of 466 and 420 nm bands are inversely related in the course of decomposition of HSO₅⁻, in the presence of Mn^{III}(tpfpp)(OAc), under the molar ratio of HSO₅⁻/Mn^{III}(por) = 10 (Fig. S1). After complete decomposition

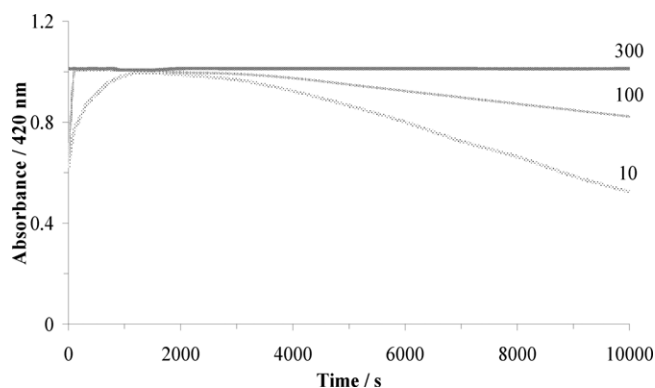


Fig. 3. Changes in the Soret band intensities of Mn(tpfpp)(O)(OAc) (λ_{max} = 420 nm) versus time/s, for three different HSO₅⁻/Mn^{III}(tpfpp)(OAc) molar ratios (i.e., 10, 100, 300), at 25 ± 2 °C.

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