

Isolation and Characterization of Oxomanganese(V) Tetraphenylporphyrin Complex

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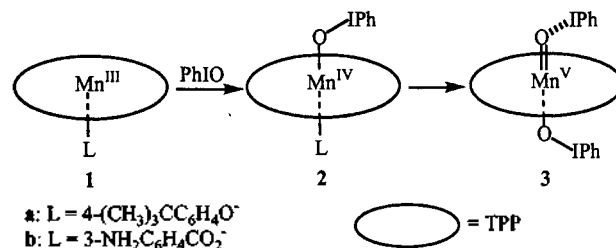
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Manganese(III) porphyrin complexes catalyze the oxidation of hydrocarbons with iodosylbenzene, hypochlorite and *m*-chloroperoxybenzoic acid as oxygen sources, which are good model compounds of cytochrome P-450. Because the study of the mechanism of the catalytic oxidation of hydrocarbons by the model compounds of cytochrome P-450 is useful as well as possible insight into the mechanistic features of oxidation of hydrocarbons by cytochrome P-450, it is a subject of great interest. Hill *et al.* investigated the oxidations of hydrocarbons by dimeric μ -oxomanganese(IV) tetraphenylporphyrin complex $[\text{ClMn(IV)TPP(OIPh)}]_2\text{O}$ and postulated that the active species was oxo pentavalent manganese tetraphenylporphyrin complex.¹ In addition, although the manganese(III) porphyrin-catalyzed epoxidations of alkenes with hypochlorite and *m*-chloroperoxybenzoic acid were studied by Meunier,² Collman,³ Notle,⁴ Bruice,⁵ and Groves,⁶ the detailed mechanisms of the epoxidations of alkenes were not fully established. However, it is generally agreed that the active species are the mixture of oxo tetravalent and pentavalent manganese porphyrins or oxo pentavalent manganese porphyrins. To date, the properties of active species are not characterized because oxo pentavalent manganese porphyrin complexes are not stable and could not be isolated. Although Groves⁷ and Harriman⁸ reported and claimed successful syntheses of oxo pentavalent manganese porphyrin complexes, these complexes are believed to be tetravalent manganese porphyrin complexes because their electronic absorption spectra display a Soret band near 420 nm and a shoulder band near 520 nm which are characteristic of tetravalent manganese porphyrin complex. We here report the isolation and characterization of oxo pentavalent manganese porphyrin complex.

Results and Discussion

We recently reported the generation of mono(iodosylbenzene)manganese(IV) tetraphenylporphyrin complexes **2** in the short time (<1 min) reaction of manganese(III) tetraphenylporphyrin complexes **1** with iodosylbenzene in dichloromethane at room temperature (Scheme 1).⁹ However, 'oxo-like' mono(iodosylbenzene) (tetraphenylporphinato) manganese(V) is observed to be formed in the longer time reaction. These results indicate that the oxidation of complexes **1** to the complex **3** proceeds *via* complexes **2**. The elemental analysis of the complex **3** shows a stoichiometry of two iodosylbenzenes per manganese porphyrin.

The electronic absorption spectrum of the complex **3** is shown in Figure 1. The complex **3** obtained from the reaction of **1a** and iodosylbenzene displays a Soret band at 407 nm and broad absorption bands at 379, 478, 582, and 618 nm. The spectrum of the complex **3** is distinctly different



Scheme 1.

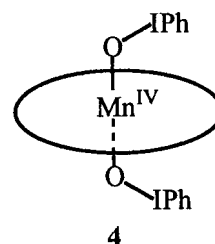


Chart 1.

from that of its precursors **2a** which display an intense Soret band at 422 nm and a broad shoulder band near 522 nm.⁹ The Soret band at 422 nm and broad shoulder band near 522 nm are characteristic of tetravalent manganese porphyrin complexes and are not observed in the absorption spectrum of the complex **3**. When the complex **3** was stored for 23 days at -20 °C, it was reduced to monomeric bis(iodosylbenzene)manganese(IV) porphyrin complex (**4**). Thus, it is clear that the complex **3** is in a higher oxidation state than Mn(IV). The complex **3** formed by the reaction between **1b** and iodosylbenzene showed the same electronic absorption spectrum.

The X-band ESR spectrum of the complex **3** as a solid powder at room temperature displays a broad resonance at $g_{\perp}=4.4$ and a resonance at $g_{\parallel}=2$. Thus, it is clear that the complex **3** is a monomeric manganese porphyrin complex.¹⁰ The magnetic susceptibility of the complex **3** shows a value for χ_g of 1.71×10^{-6} cgs units, which was determined in the solid state at 27 °C. On the basis of the equation $\mu_{eff}=2.83(\chi_m T)^{1/2}$, a value of $\mu_{eff}=2.5 \mu_B/\text{atom}$ of manganese, which only used a diamagnetic correction of -700×10^{-6} cgs units for the combined porphyrin ring,¹¹ was obtained. This value is close to the spin-only value expected for an S=1 system. This indicates that manganese in the complex **3** is in 5+ oxidation state.

The infrared spectrum of the complex **3** displays an intense absorption band at 584 cm⁻¹ which is characteristic of Mn-O-I stretch.¹⁰ The intense broad absorption band in the region of 810 cm⁻¹ is characteristic of Mn-O-Mn and is not

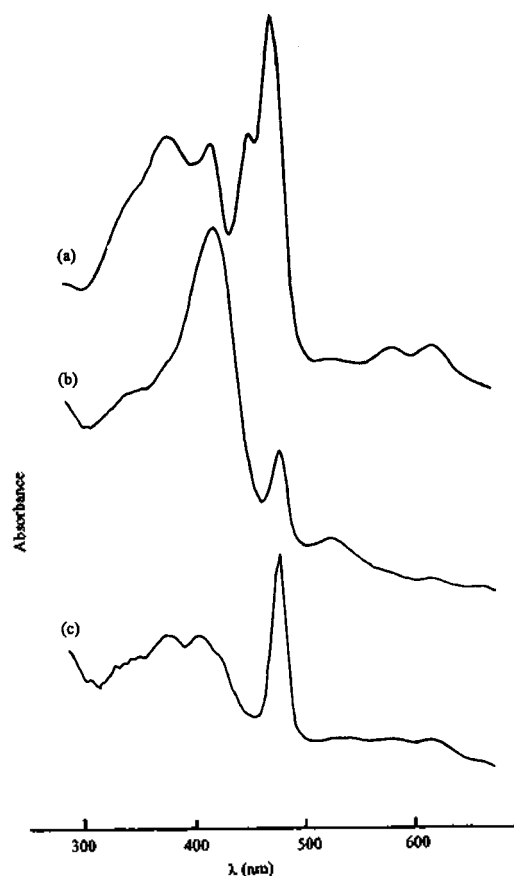


Figure 1. Electronic spectra of (a) 1a, (b) 4, and (c) 3.

present in the complex 3.¹⁰ Thus, it is clear that the complex 3 is a monomeric high-valent manganese porphyrin complex.

On the basis of the results and discussion described above, one possible structure for the complex 3 can be formulated. The elemental analysis of the complex 3 indicates a stoichiometry of two iodossylbenzenes per manganese porphyrin. The infrared spectrum indicates that the complex 3 is a monomeric iodossylbenzene manganese porphyrin complex. The electronic absorption spectrum indicates that the complex 3 is in a higher oxidation state than Mn(IV). The magnetic susceptibility indicates that manganese in the complex 3 is in 5+ oxidation state. Although IR spectrum shows that the complex 3 does not contain a discrete Mn=O unit, the oxygen and iodine of one iodossylbenzene seems to interact weakly each other. We propose, therefore, that the complex 3 is in pentavalent state and the possible structure of the complex 3 is $\text{PhI--O=Mn(V)TPP(OIPh)}$.

Experimental

General. Commercially available compounds were used without further purification except for the solvent, which was distilled by known methods before use. Iodossylbenzene,¹² tetraphenylporphyrin,^{13,14} and 1¹⁵ were prepared by known methods. Visible spectra were determined on a Shimadzu 2100 spectrophotometer. Infrared spectra were obtained by a Magna IR 550 infrared spectrophotometer. X-band ESR spectra were determined as a solid at room temperature using a JES-FE3AS ESR spectrometer. Magnetic susceptibility was determined on a Bruker BM4 Faraday balance.

Synthesis of 'oxo-like' mono(iodossylbenzene) (tetraphenylporphinato)manganese(V) (3) from the reaction of Mn(III)TPP(3-NH₂C₆H₄CO₂) (1b) with iodossylbenzene. To a solution of Mn(III)TPP(3-NH₂C₆H₄CO₂) (0.023 g, 0.03 mmol) in 5 mL of dichloromethane was added iodossylbenzene (0.100 g, 0.46 mmol). After the mixture was vigorously stirred at room temperature for 15 min, the resulting solution was cooled to -30 °C and filtered into hexane (100 mL) cooled to -30 °C. The filtration of the precipitates gives brown microcrystalline product. The solid was recrystallized from dichloromethane-hexane at -30 °C and dried *in vacuo* to give pure product (0.014 g, 48% yield). UV-vis (CH₂Cl₂) λ_{max} 330, 379, 407, 478, 582, 618 nm; IR (KBr) 584 (Mn-O-I) cm⁻¹. Anal. Calcd for C₅₆H₃₈N₄MnI₂O₂: C, 60.78; H, 3.45; N, 5.06; Mn, 4.96; I, 22.93. Found: C, 60.54; H, 3.32; N, 5.38; Mn, 4.35; I, 22.96.

The complex 3 was similarly isolated from the reaction of 1a (0.021 g, 0.026 mmol) with iodossylbenzene (0.100 g, 0.46 mmol) for 10 min reaction time. The pure product 3 was obtained in 50% yield. UV-vis (CH₂Cl₂) λ_{max} 330, 379, 407, 478, 582, 618 nm; IR (KBr) 584 (Mn-O-I) cm⁻¹. Anal. Calcd for C₅₆H₃₈N₄MnI₂O₂: C, 60.78; H, 3.45; N, 5.06; Mn, 4.96; I, 22.93. Found: C, 60.05; H, 3.66; N, 4.86; Mn, 4.71; I, 22.74.

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