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Effects of Axial Ligands on Oxidation Sites in One-electron Oxidation of Manganese(III) Porphyrins

MASAMOTO IWAIZUMI and HIROSHI KOMURO

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai 980, Japan

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There have been many investigations of the redox properties of metalloporphyrins aimed at understanding their role in widespread catalytic functions in biological systems and utilizing the complexes in model systems for mimicking the enzymatic reactions in natural processes. There is great interest now in the highly oxidized metalloporphyrins with their active oxidizing ability, and in the intermediates formed in the redox cycle of certain hemoproteins and photo-oxidation reactions of chlorophyll [1]. The electronic configuration of the redox products has been one of the main subjects of these investigations. Whether the reduction–oxidation site is located on the metal ion or the porphyrin ligand appears to depend mainly on the central metal and the reduction–oxidation step of each complex. In the case of one-electron oxidation of manganese(III) porphyrins, both metal-centered and ligand-centered oxidation have been reported [2–7]. In this communication we suggest that the axial ligand field plays an important role in determining whether the oxidation site is metal-centered or ligand-centered in the one-electron oxidation of manganese(III) porphyrins.

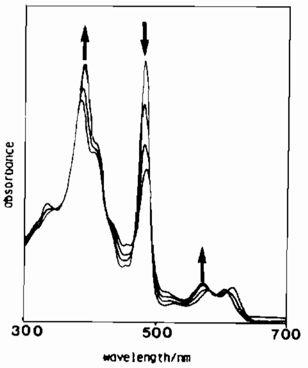

Fig. 1. Spectral change observed during electrochemical oxidation of $Mn^{III}TPPCl$ in dichloromethane containing TBAP.

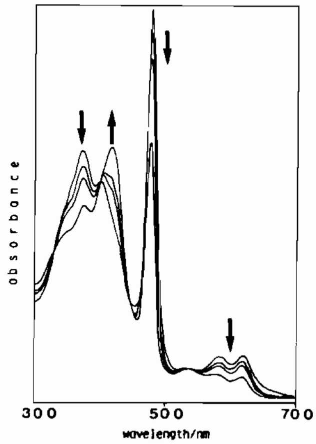

Fig. 2. Spectral change observed during electrochemical oxidation of $Mn^{III}TPPCl$ in dichloromethane containing TBAC.

In the present experiment, MnTPPX (X = OAc^-, Cl^-, NCS^-, or Br^-, TPP = tetraphenylporphyrinate) and MnOEPX (X = OAc^-, Cl^-, N_3^-, NCS^- or Br^-, OEP = octaethylporphyrinate) were electrochemically oxidized in dichloromethane using tetrabutylammonium perchlorate (TBAP) or tetrabutylammonium chloride (TBAC) as supporting electrolytes. The oxidation processes were monitored by UV-Vis spectra. Two different types of spectral changes were observed in the OEP and TPP complexes. Figures 1 and 2 show typical examples. The spectral changes of the type shown in Fig. 1 were observed when TBAP was used as a supporting electrolyte for both the OEP and TPP complexes. The spectral changes of the type shown in Fig. 2 were observed when TBAC was used as a supporting electrolyte and the electrolysis was carried out at low temperatures (below −40 °C). No spectral change was observed by electrolysis at room temperature for the TBAC system. This is due to the rapid reduction of the oxidized products to manganese(III) porphyrins; this was suggested by reversible UV-Vis spectral changes observed when the solutions electrolyzed at cool temperatures were allowed to return to room temperature. Replacement of the originally coordinated axial ligand X by the chloride ion was also suggested when TBAC was used for the complexes having NCS^- and Br^- as the axial ligand X. It is supposed therefore that the axial ligands in the oxidized products for the TBAP solution system are a combination of ClO_4^- and OAc^-, Cl^-, N_3^-, NCS^- or Br^- and, for the TBAC system, a combination of Cl^- and OAc^-, Cl^- or N_3^-.

The spectral features of the products shown in Fig. 1 are quite similar to those previously assigned to manganese(III) porphyrin cations [6, 7], and the features in Fig. 2 are similar to those of manganese(IV) porphyrins [2, 3]. The oxidized products of the type shown in Fig. 2 exhibit ESR spectra

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characteristic to the S = 3/2 metal ion corresponding to the manganese(IV) ion [3, 5, 8]; the fact that the products in this system are unstable at room temperature is consistent with characteristics reported for the manganese(IV) complexes. These facts indicate that the TBAP system produces manganese(III) porphyrin cations by one-electron oxidation, while the TBAC system produces manganese(IV) porphyrins. As the axial ligands in the latter system are considered to give stronger ligand fields than those in the former system, the experimental results indicate that strong ligand fields at the axial position yield metal-centered species, while weak axial ligand fields yield the manganese(III) porphyrin cations. It is likely that strong ligand fields elevate the d orbital levels and lead to the release of an electron from the metal d orbitals. It may be noted that the oxidation sites are interchangeable between the metal ion and the porphyrin ligand with replacement of the axial ligands; *i.e.*, it was observed that addition of equimolar TBAC to the solutions of manganese(III) porphyrin cations causes spectral changes similar to those of the manganese(IV) porphyrins, indicating the shift of the oxidation center from the porphyrin ligand to the central metal, associated with replacement of one axial ligand, ClO_4^-, by the chloride ion of TBAC.

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