

Electrochemical and spectral studies on the catalytic oxidation of nitric oxide and nitrite by high-valent manganese porphyrins at an ITO electrode

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Abstract

Catalytic oxidation of nitric oxide and nitrite by water-soluble manganese(III) meso-tetrakis(*N*-methylpyridinium-4-yl) porphyrin (Mn(III)(4-TMPyP) was first studied at an indium-tin oxide (ITO) electrode in pH 7.4 phosphate buffer solutions. A stepwise oxidation of Mn(III)(4-TMPyP) through high-valent manganese porphyrin species has been observed by electrochemical and spectroelectrochemical (OTTLE) techniques. The formal potential of 0.63 V for the formation of O=Mn(IV)(4-TMPyP) has been estimated from OTTLE data. The product, oxoMn(IV) porphyrin, was relatively stable decaying slowly to Mn(III)(4-TMPyP) with a first-order rate constant of $3.7 \times 10^{-3} \text{ s}^{-1}$. O=Mn(IV)(4-TMPyP) has been found to oxidize NO catalytically at potentials about 70 mV more negative than that previously reported for O=Fe(IV)(4-TMPyP) with good selectivity against nitrite. Nitrite was catalytically oxidized at potentials higher than 1.1 V presumably by O=Mn(V)(4-TMPyP). O=Mn(IV)(4-TMPyP) was observed as an intermediate species. Nitrate has been confirmed to be a final product of the electrolysis at 1.2 V, while at 0.8 V nitrite left unchanged, demonstrating that O=Mn(IV)(4-TMPyP) could not oxidize nitrite. A possible schemes of the catalytic oxidation of NO by O=Mn^{IV}(4-TMPyP) and NO₂⁻ by O=Mn(V)(4-TMPyP) have been proposed.

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1. Introduction

Since 1987 when nitric oxide had been recognized as an endothelium-derived relaxing factor for the first time [1], a wide range of its physiological functions have been discovered [2–6]. Nitric oxide is known to be one of the factors in signaling functions in the central and peripheral nervous system and in vascular endothelium, inflammatory and degenerative diseases, immune response, septic shock, Parkinson's and Alzheimer's diseases. Certain metabolites of NO (peroxynitrite and nitrous anhydride) can be cytotoxic or mutagenic when present in sufficiently high concentrations. Selective and in situ monitoring of NO providing reproducible and quantitative data is essential to draw solid conclusions on its functions and their regulation. One of the most promising

methods of NO monitoring is electrochemical detection using different modified electrodes. The most recently updated review by Bedioui on this subject is available [7].

In the past 12 years since Malinski and Taha first designed the so-called porphyrinic sensor for nitric oxide detection [8], metalloporphyrins became one of the most widely exploited species for the preparation of electrochemical NO sensors. A wide range of different metalloporphyrins including nickel [8–11], iron [12–15], cobalt [16,17], manganese [18–20], and some other metal complexes [21,22] have been found to serve as effective catalysts for the oxidation or reduction of nitric oxide. The nature of this catalysis has not been clearly understood, however, especially in the case of oxidation reactions. The role of the metal ion in catalysis is also questionable still. Nickel and iron porphyrins are undoubtedly leaders in the field of electrochemical detection of NO.

It has been previously reported that iron porphyrins could catalyze an electrooxidation of nitric oxide and nitrite through

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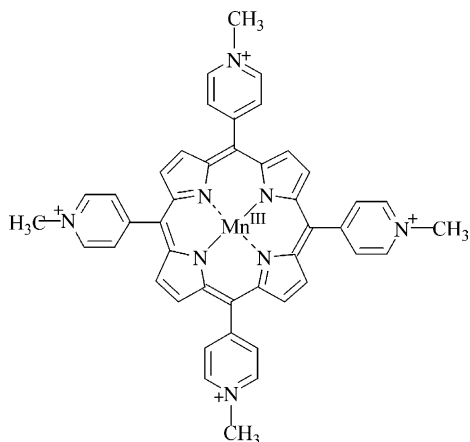


Fig. 1. Chemical structure of Mn(4-TMPyP).

the formation of high-valent complexes, namely oxo-iron(IV) and oxo-iron(IV) porphyrin π -cation radical species, respectively [13,15]. Manganese porphyrins can also form high-valent species by the electrochemical oxidation [23]. Although high-valent manganese porphyrins are well known catalysts in many oxidation processes like an epoxidation of olefins and a hydroxylation of alkanes [24–31] and usually show similar or better catalytic properties than their iron analogs, their possible catalytic activities in the electrooxidation of NO or/and nitrite have not been studied yet. Diab et al. [19,20] reported the preparation of NO sensor utilizing pyrrole functionalised manganese porphyrin. The authors did not discuss the mechanism of that catalysis and any possible active species that could be responsible for the observed catalytic current, however.

The present study has been carried out in order to clarify the effect of manganese porphyrin on the electrooxidation of nitric oxide at an indium-tin oxide (ITO) electrode. Water-soluble manganese(III) meso-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (Mn(III)(4-TMPyP) (Fig. 1.) was used in this study. Oxidation of nitrite as the species that always coexist with nitric oxide in real systems was also studied under the same conditions. The data were compared with those obtained previously for Fe(4-TMPyP).

2. Experimental

2.1. Chemicals

Preparation of manganese porphyrin was based on the methods reported by Pasternack et al. [32] and Barley et al. [33]. An insertion of manganese cation into free base meso-tetrakis (*N*-methylpyridinium-4-yl)porphyrin (H₂(4-TMPyP), Aldrich) has been achieved by refluxing an aqueous solution of the latter with an excess of MnCl₂·4H₂O (Wako) under the flow of nitrogen. The completion of the reaction was checked by spectrophotometry. Resulting solution was let to cool down and saturated solution of NaClO₄ (Wako)

was added to precipitate Mn(4-TMPyP) perchlorate. Solution was kept in a refrigerator over the night and the precipitate was collected then by filtration, washed by methanol, dried in air and recrystallized from methanol.

Phosphate buffer solutions (PBS, 0.05 M) with pH 7.4 were prepared by mixing 0.05 M solutions of analytical grade NaH₂PO₄ and Na₂HPO₄ (Nacalai Tesque). The pH was adjusted by using digital pH-meter (TOA, HM-30 V). All aqueous solutions were prepared from twice distilled water. Solutions were deaerated before each measurement by bubbling ultra pure argon gas (99.9999% min., Nippon Sanso).

Nitric oxide solutions were prepared by bubbling 1% NO in argon gas mixture (Nippon Sanso) into deaerated solutions before each measurement. Molar concentrations of NO in the resulting solutions were estimated from the reported saturated solubility of about 2 mM for nitric oxide in pH 7.4 PBS [34] and Ostwald's solubility coefficient for a given pressure of NO. For 1% NO gas mixture, saturated concentration of NO was estimated roughly 20 μ M. Sodium nitrite (NaNO₂, Wako) was used in experiments on nitrite electrooxidation.

2.2. ITO electrode

As we reported earlier, electroconductive indium-tin oxide (ITO) had been found to be a very promising material for the studies on the electrooxidation of nitric oxide and nitrite [13,15]. It demonstrated one crucial advantage over the glassy carbon (GC) electrode in such studies. Both NO and nitrite could be oxidized at a GC and other carbon materials easily enough to make catalytic effect of the porphyrin not so obvious. Oxidation of NO and NO₂⁻ at an ITO electrode occurred at more positive potentials and showed lower currents than those obtained using a GC electrode, especially in the case of nitrite. On the other hand, the electrochemical behavior of Mn(4-TMPyP) was similar at both electrodes. This made the catalysis easy to clarify.

A special attention should be paid to ensure that electrode surface was cleaned thoroughly prior each experiment. It has been found that hydrophilic surface of an ITO electrode could absorb charged porphyrin complexes. In fact, some amounts of absorbed porphyrin could be detected at cyclic voltammograms obtained by transferring working electrode from the solution containing porphyrin into a pure PBS. On its first use (or after not using for a while), the ITO electrode was sonicated in acetone for 15 min, followed by rinsing with water, ultrasonic cleaning in a mixture of 6 M aqueous NaOH and ethanol (1:1), and rinsing with water again. Electrode was kept in PBS solution between measurements and was exposed to alkaline treatment described above every time before experiments.

2.3. Electrochemical and spectroelectrochemical experiments

Electrochemical data were collected by BioAnalytical Systems (BAS) model BAS 100 B/W electrochemical work-

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