Evaluation of Ferryl Formation by Electrocatalytic Oxidation of Alkene Using Luminol Chemiluminescence

Mohammad Sohel RANA* and Keietsu TAMAGAKE

Faculty of Pharmaceutical Sciences, Okayama University; Okayama 700—8530, Japan.
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Electrochemical formation of ferryl porphyrin was examined by electrocatalytic oxidation of alkene by measuring luminol chemiluminescence using a flow-injection method. Emission was observed both below the reduction potential of Fe[III]TMPyP (−0.08 V at pH 11, −0.02 V at pH 7 and 0.15 V at pH 3) and above the oxidation potential (0.6 V at pH 11, 0.75 V at pH 7 and 1.1 V at pH 3). However, both anodic and cathodic emissions were inhibited significantly by the addition of alkene (cyclopent-2-ene-1-acetic acid) solutions downstream of the working electrode. Further, the spectra at both anodic and cathodic sides shifted to the longer wavelength (>424 nm) compared to the original spectrum of Fe[III]TMPyP (422 nm), which was not observed with the addition of alkene solution. Therefore, the results suggest that the electrochemically generated oxo-ferryl species have been engaged in catalytic oxidation of alkene before the flow reaches the observation cell.
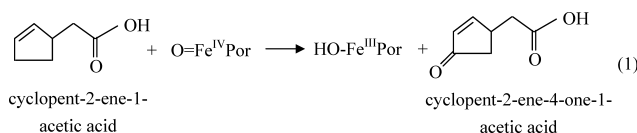
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Electrochemical formation and characterization of high-valent metalloporphyrins have been of interest for a long time because of their central roles in a number of important biological processes.[1,2] Formation of a high-valent oxo-metal complex is essential in these catalytic reactions. It can be achieved either by a reduction in the presence of molecular oxygen or by applying a strong oxidant for metalloporphyrins. Many such metalloporphyrin complexes have been synthesized for mimicking these biological reactions, but most were studied in non-aqueous systems.[3,4] The generation of oxo-ferryl porphyrins in aqueous solutions by a number of chemical methods has been reported.[5,6] Recently, it was also reported that ferryl porphyrin can be produced by the reduction of ferric porphyrin to ferrous porphyrin by dithionite followed by autoxidation of ferrous porphyrin in the presence of molecular oxygen.[7]

We have been working on electrochemical formation of ferryl porphyrin in aqueous solution to avoid possible interference due to excess reactants or secondary products in the chemical system. A number of electrochemical methods have been reported for the generation of oxo-ferryl porphyrins in aqueous[8] and non-aqueous[9] solutions. However, all of these methods were limited to the direct electrochemical oxidation of iron(III) porphyrin by applying higher anodic potentials. In this work, using a flow-injection method, we detected the formation of ferryl porphyrin by electrochemical reduction of iron(III) porphyrin in aqueous solution. In order to estimate the electrochemical formation of oxo-ferryl porphyrin, the measurement of luminol chemiluminescence was employed[7,10] as it was demonstrated to have relatively higher production of light and greater sensitivity.[11] Detection of ferryl porphyrin was also achieved by measuring its absorption spectrum.

High-valent iron porphyrins exhibit different activities towards alkene oxidations in aqueous media. The catalytic oxidation of a series of water-soluble carboxylic alkenes *via* a pathway of allylic hydrogen abstraction in the presence of molecular oxygen has been reported.[12] By this process the oxo-ferryl porphyrins returned into their original form, ferric porphyrins (Eq. 1). We attempted to monitor the electro-chemical formation of oxo-ferryl porphyrin by supplying alkene solutions downstream to the working electrode under aerated conditions. Alkene oxidation catalyzed by oxo-ferryl porphyrin was interpreted by the quenching rate of luminol chemiluminescence.

$$\text{cyclopent-2-ene-1-acetic acid} + \text{O=Fe}^{IV}\text{Por} \longrightarrow \text{HO-Fe}^{III}\text{Por} + \text{cyclopent-2-ene-4-one-1-acetic acid} \quad (1)$$

We have selected alkene, cyclopent-2-ene-1-acetic acid in this experiment for its higher reaction rate with oxo-ferryl porphyrin. It has been reported that electrochemically generated O=Fe[IV]TMPyP reacts readily with cyclopent-2-ene-1-acetic acid and is then reduced back to HO–Fe[III]TMPyP.[12]

Experimental

Materials Synthesis   The solution of Fe[III]TMPyP (Mid-Century Laboratories) was prepared in the appropriate buffer or in an un-buffered acid/base at desired pH. 0.2 mM luminol solutions were prepared in 0.1 M Na_2CO_3 aqueous buffer to keep the pH of the observation cell favorable for emission. Buffer solutions (20 mM) were prepared from $HClO_4$, phosphate, carbonate and NaOH for the pH range of 0—14. Supporting electrolytes include 0.1 M Na_2SO_4 or $NaClO_4$. The pH values were measured with a TOA HM-20S pH meter. Luminol (Ishizu Seiyaku Ltd.) and cyclopent-2-ene-1-acetic acid (Aldrich Chemical Co.) were used as received. The other reagents used were of the highest purity available. Deoxygenation was achieved by purging with highly pure N_2 gas.

Experimental Methods   Chemiluminescence and spectrophotometric experiments were performed with a laboratory constructed flow-injection apparatus (Fig. 1).

Iron(III) porphyrin and buffer solutions were passed through channel 1 (ch1) and channel 2 (ch2) respectively, which were then mixed in a ratio of 1:1 by volume before undergoing electrochemical reaction at the working electrode. The electrochemically generated species were mixed within 1 s with aerated luminol solution, supplied through channel 3 (ch3) to give emission. All experiments were carried out at a continuous flow rate of 2.7 ml/min, controlled by a 4-channel Ismatec® Reglo-Digital pump (Model ISM-834).

Electrochemistry and Chemiluminescence   Luminol chemiluminescence was measured with a photomultiplier *via* an optical fiber mounted with an observation cell and amplified by changing the sensitivity of the Jasco photometer. A cyclic voltammogram along with the emission intensity were measured with a laboratory-constructed potentiostat and were recorded simultaneously by a computer-controlled instrument. Cyclic voltammetry
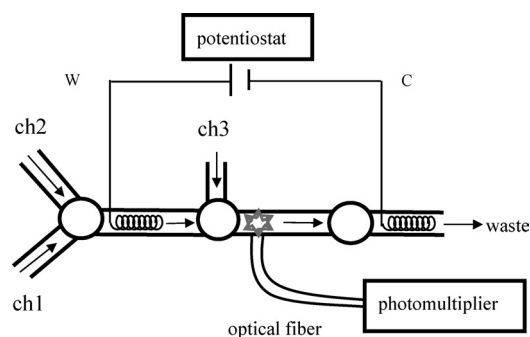

Fig. 1. Schematic Diagram of the Flow-Injection Apparatus

was conducted using a three-electrode cell in which a glassy carbon rod was used as the working electrode. A platinum wire was used as the counter electrode and a home-made Ag/AgCl/KCl(sat) electrode as the reference electrode.

Absorption Spectroscopy Absorption spectra, as a function of potentials, were measured with a Hewlett Packard Model 8450A diode array spectrophotometer. The sample was introduced into the spectrophotometric cell within 1—2 s through a narrow tube downstream to the working electrode of the flow-injection apparatus (Fig. 1). The sets of spectra were analyzed using software DPR, developed in our laboratory.

Results and Discussion

The electrochemical behavior of the $Fe^{III}TMPyP$ complexes in aqueous solutions has been extensively studied.[13,14] We report here the generation and characterization of high-valent iron porphyrins induced by electrochemical reduction of $Fe^{III}TMPyP$ using luminol chemiluminescence and absorption spectrum. A laboratory constructed flow-injection system operated by a 4-channel digital pump was used in this study to obtain a uniform and continuous supply of reagent solutions.

Electrochemical reduction of $Fe^{III}TMPyP$ was conducted in 0.1 M Na_2SO_4 aqueous solutions on a carbon electrode. Figure 2 shows the emission intensity of 10 μM $Fe^{III}TMPyP$ as a function of potential in three different acidic conditions.

It can be clearly seen that emissions were observed both below the reduction potential of $Fe^{III}TMPyP$ (-0.08 V at pH 11, -0.02 V at pH 7 and 0.15 V at pH 3) and above the oxidation potential (0.6 V at pH 11, 0.75 V at pH 7 and 1.1 V at pH 3) where Fe^{II} and Fe^{IV} species were expected to be the first electrochemical products. The onset of emission shifted to a more negative potential as the pH increased. According to an earlier report,[15] the actual product formed at the anodic region was ferryl or $O=Fe^{IV}TMPyP$. In our laboratory, the formation of $O=Fe^{IV}TMPyP$ induced by electrochemical reduction of $Fe^{III}TMPyP$ has been confirmed in aqueous solutions. $Fe^{II}TMPyP$, electro-generated by one-electron ($1e^-$) reduction of $Fe^{III}TMPyP$, was autoxidized in the presence of molecular oxygen to form $O=Fe^{IV}TMPyP$. Ferryl is widely accepted to be the species responsible for stimulating emission in the hydrogen peroxide+iron porphyrin+luminol system.[7] So it is expected that the luminol chemiluminescence observed under both reductive and oxidative conditions resulted due to ferryl formation.

However, the luminol chemiluminescence produced by the electrochemical reaction of $Fe^{III}TMPyP$ was significantly quenched when the alkene solutions were added by making another channel between the working electrode and luminol
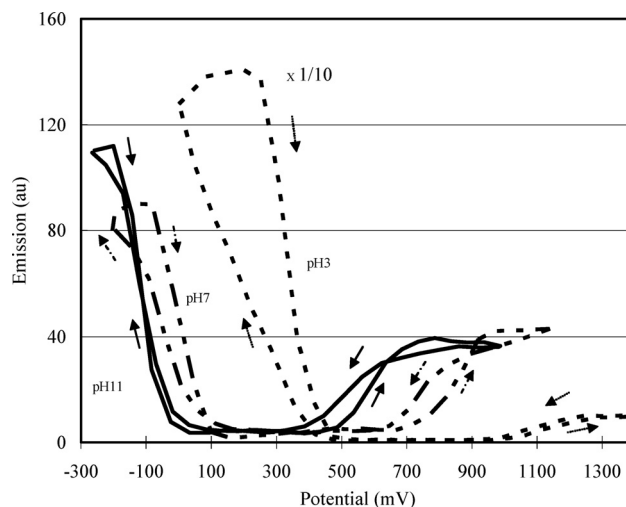

Fig. 2. Emission Intensity of 10 μM $Fe^{III}TMPyP$ as a Function of Applied Potential at Working Electrode in the pH 3 (······), pH 7 (−·−) and pH 11 (—) Buffer Solutions
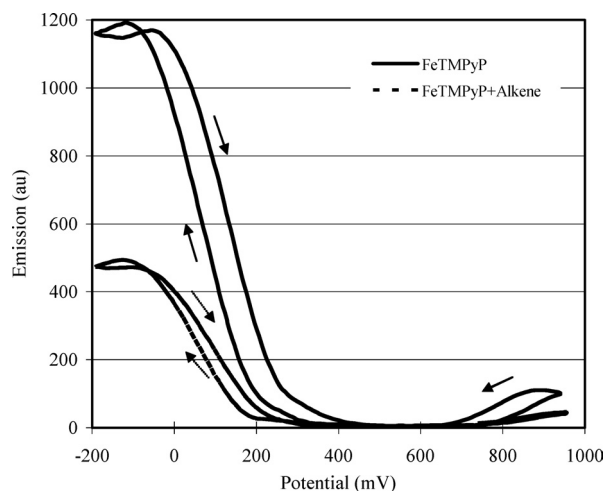
Scan rate 1 mV/s.

Fig. 3. Emission Intensity Observed as a Function of Potential for 10 μM $Fe^{III}TMPyP$ with and without 10 μM Alkene Solutions under Aerated Condition at pH 4

Scan rate 1 mV/s. Sample flow rate 2.7 ml/min.

inlet (Fig. 1). Figure 3 shows the emission intensity of 10 μM $Fe^{III}TMPyP$ solution produced as a function of potentials and the effect of alkene in quenching that emission intensity in the buffer solutions of pH 4.

Since the electrochemical response of $Fe^{III}TMPyP$ depends on the acidity of the supporting solutions,[16] the emission intensity was also found to be pH dependent (as shown in Fig. 2). Keeping all the conditions as above, the emission observed at both the cathodic and anodic sides with and without alkene in different pH solutions are presented in the Table 1.

From Fig. 3, it can be seen that the emission intensity at both cathodic and anodic conditions has been quenched by about 65% with the addition of alkene. The results observed are almost the same over the entire pH range (Table 1), except under strong alkaline conditions (pH 12) where the intensity decreased about 80%. This can be explained by the earlier report[12] that the reaction rate of $O=Fe^{IV}TMPyP(OH)$

Table 1. Emission Observed (au) with and without Alkene Solution of 10 μM in Different pH

		pH 2	pH 4	pH 7	pH 9	pH 12
Cathodic	Fe^{III}TMPyP	2100	1150	55	90	160
	Fe^{III}TMPyP+alkene	650	450	20	25	35
Anodic	Fe^{III}TMPyP	40	80	120	140	90
	Fe^{III}TMPyP+alkene	0	25	30	35	25
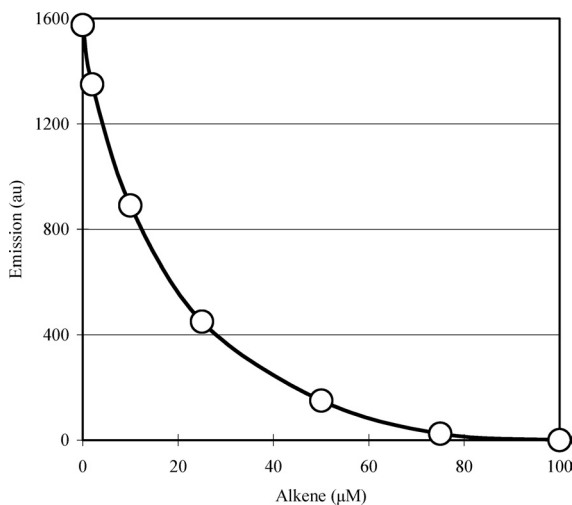
Fig. 4. Emission Intensity with Different Concentrations of Alkene at pH 12.0

Fig. 5. Shift of Wavelength as a Function of Potential for 5 μM Fe^{III}-TMPyP with and without Alkene under Aerated Condition at pH 11

Scan rate 1 mV/s. Measuring interval 60 s.

with alkene is higher than that of O=Fe^{IV}TMPyP. Although the emission was not quenched completely with alkene, perhaps due to an inadequate concentration of alkene or an insufficient reaction time, it can be considered as evidence of the formation of oxo-ferryl species in this system.

Meanwhile, the effect of alkenes in diminishing the luminol chemiluminescence was found to be concentration-dependent. Experimental results with different concentrations of alkene in the buffer solutions of pH 12 are shown in Fig. 4.

It can be clearly observed that emission decreased in accordance with the increase in alkene concentrations. Similar results were obtained for all other pH examined, but as reported[9] the activity was found to be maximum at higher pH (data not shown).

This is justified further by the observations of the spectrophotometric analysis carried out under the same conditions. Figure 5 shows the spectral change in Fe^{III}TMPyP solution as a function of potentials with and without alkene at pH 11.

The shift of absorption spectra towards a longer wavelength under aerated conditions was not observed when alkene solution was added downstream to the working electrode (data presented in Fig. 5). Hence, the results suggest that the electrochemically-generated oxo-ferryl species are engaged in catalytic oxidation of alkene. In the process, oxoferryl species returned into ferric form before it reaches at the observation cell.

The chemiluminescence pattern was also checked by using other water-soluble carboxylic acids like 2,3-dimethylacrylic acid, 3-methylacrylic acid and methacrylic acid, and all were found to be positive in quenching emission. On the other
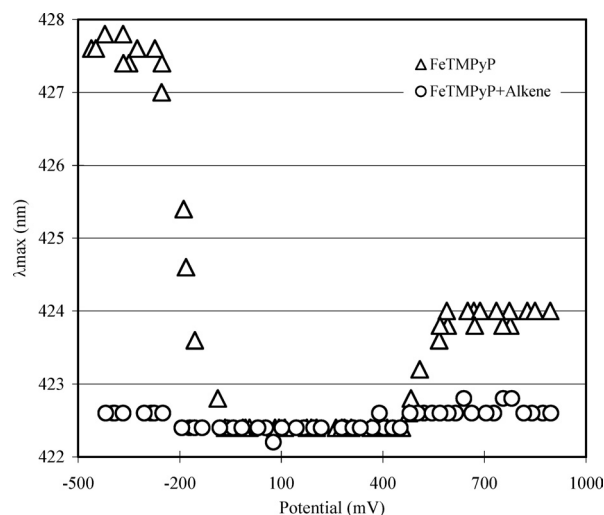
hand, cyclopentyl acetic acid, which is inactive in electrocatalytic oxidation, showed no effect on chemiluminescence.

Concluding Remarks O=Fe^{IV}TMPyP formation induced by electrochemical reduction of Fe^{III}TMPyP has been confirmed by electrocatalytic oxidation of alkene. Chemiluminescence were observed at both the anodic and cathodic potentials as a function of the potentials over the wide range of pH inhibited by the addition of alkene solutions. Absorption spectrum of O=Fe^{IV}TMPyP at 436 nm in the pH 11 aqueous buffer solution was not observed in the presence of alkene. Therefore, the results were considered to be evidence of O=Fe^{IV}TMPyP formation. Conversely, the method of luminol chemiluminescence is expected to be useful for monitoring high-valent metalloporphyrin-induced electrocatalytic oxidations of alkene or other substrates.

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