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A CYCLIC VOLTAMMETRIC STUDY OF THE MESO-CHLORINATION OF ZINC OCTAETHYLPORPHYRIN VIA ANODIC OXIDATION[1]

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A detailed study of the cyclic voltammetry of ZnOEP-Et_4NCl system in different concentration of chloride ion and different scan rate reveals that complexation between chloride ion and ZnOEP and $ZnOEP^{\dagger}$ occur and the complexes are active species in electrode and chemical reactions. We infer that in the synthetic experiments carried out under constant anodic potential between 0.60-0.65V, meso-chlorination occurs via an ECE mechanism.

The classical way of introducing substituents into the methine positions of porphyrins involves electrophilic substitution on the porphyrin nucleus.[2] Smith and co-workers[3] introduced a new approach to this synthesis by treating the chemically generated cation radical of porphyrin with nucleophiles such as nitrite, chloride, pyridine imidazole, cyanide, triphenylphosphine, thiocyanate, acetate and azide to give the corresponding meso-substituted porphyrins.

There are three possible mechanisms for this reaction, as suggested by Smith and coworkers[3]. The first mechanism involves a chemical reaction taking place in between two electron transfer processes (ECE). In the second one, two electron transfer processes occur consecutively to generate a porphyrin dication and then followed by a chemical rection (EEC). In the third one, oxidation of the nucleophile occurs also to give a radical and the chemical reaction involved is a radical combination process (EE'C). Smith and coworkers proposed that the reaction took place via the ECE mechanism. Dolphin and coworker studied the nitration of MgOEP cation radical with respectively nitrite and nitrogen dioxide and arrived at the conclusion that even at the nitrite reaction the reaction proceeds through the EE'C mechanism.[4]

Callot and coworkers generated the π cation radical electrochemically and developed an efficient synthesis of meso-mono- to tetra-cyanooctaethylporphyrin [OEP(CN)$_n$].[5] Similarly, we have reported the mono- and di-nitration, mono- and di-chlorination and mono-acetoxylation of ZnOEP.[6] Because oxidation of ZnOEP was carried out under controlled anodic potential, EEC mechanism can be eliminated from this electrolytic process. In the nitration and acetoxylation reaction, oxidation of the nucleophiles was observed to take place under the applied potential, generating the appropriate radicals necessary for the EE'C mechanism. Therefore, we suggest that EE'C mechanism is operative if not exclusively. In the chlorination reaction, EE'C mechanism is unlikely as anodic oxidation of chloride ion to a significant extent at +0.60-0.65V is unlikely at a low chloride concentration. In this paper, we would like to report our recent findings on a cyclic voltammetric study of meso-chlorination of ZnOEP via anodic oxidation. We believe this is an example of ECE mechanism.

RESULTS AND DISCUSSION

The electrode reaction of ZnOEP in the presence of free chloride ion was studied by cyclic voltammetry.

The first set of experiment was on the effect of concentration of Et_4NCl on redox properties of ZnOEP. The cyclic voltammograms were recorded at a normal scan rate of 100 mV/s (Figure 1). Voltammogram 1.a is that of ZnOEP in the absence of Et_4NCl. In between 0 - +1.3V, there are two reversible single electron oxidation processes occuring, corresponding to the following electrode reactions:

$$\mathrm{ZnOEP} \rightleftharpoons \mathrm{ZnOEP}^{\dagger} + e \quad E_{1/2}(1) = +0.75\mathrm{V} \quad (1)$$

$$\mathrm{ZnOEP}^{\dagger} \rightleftharpoons \mathrm{ZnOEP}^{++} + e \quad E_{1/2}(2) = +1.06\mathrm{V} \quad (2)$$

with the difference in half-wave potential $\Delta E_{1/2} = E_{1/2}(2) - E_{1/2}(1) = 0.31V$; and the difference in anodic peak potentials $\Delta E_p^a = E_p^a(2) - E_p^a(1) = 0.32V$.

Voltammogram 1.c is that of ZnOEP in the presence of 0.01 Molar concentration of Et_4NCl. The first oxidation reaction is a reversible one with the half-wave potential $E_{1/2}(1) = +0.53V$, a negative shift of 0.22V relative to that of ZnOEP in the absence of Et_4NCl. The second oxidation reaction is an irreversible one. The oxidation wave has a peak potential $E_p^a = +0.84V$, with a negative shift of 0.22V relative to that of 1.a. No significant change has been observed by having the concentration of Et_4NCl increased to 0.02 Molar.

From the red shift of the absorption spectrum of ZnOEP in the presence of chloride ion, it has been realized that chloride ion forms ground state complex with ZnOEP,[8] and the ratio was determined to be 1:1:[9]

$$\mathrm{ZnOEP} + \mathrm{Cl^-} \xrightleftharpoons{\beta_1} \mathrm{ZnOEP(Cl^-)} \qquad (3)$$

Assumming the coordination number for $\mathrm{ZnOEP^{\dagger}}$ to be the same as that of ZnOEP:

$$\mathrm{ZnOEP^{\dagger}} + \mathrm{Cl^-} \xrightleftharpoons{\beta_2} \mathrm{ZnOEP^{\dagger}(Cl^-)} \qquad (4)$$

the ratio of the two complexation constants, β_2/β_1 can be related to the first oxidation potential of ZnOEP in the presence (equation 5)

$$\mathrm{ZnOEP(Cl^-)} \xrightleftharpoons{\beta_3} \mathrm{ZnOEP^{\dagger}(Cl^-)} + e \qquad E_{1/2} = +0.57\mathrm{V} \qquad (5)$$

or absence (equation 1) of chloride ion by the following equation:[10]

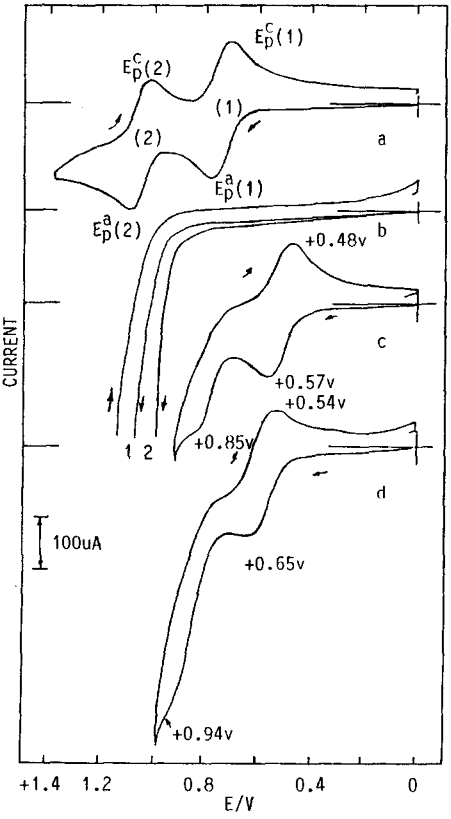


Figure 1. Cyclic voltammograms of ZnOEP in CH_2Cl_2 at different chloride concentration: a) 0 M Cl^-, c) 0.01 M Cl^-, d) 0.1 M Cl^-; b) Cyclic voltammograms of (1) 0.01 M and (2) 0.1 M Cl^- in CH_2Cl_2; scan rate 100mv/s.

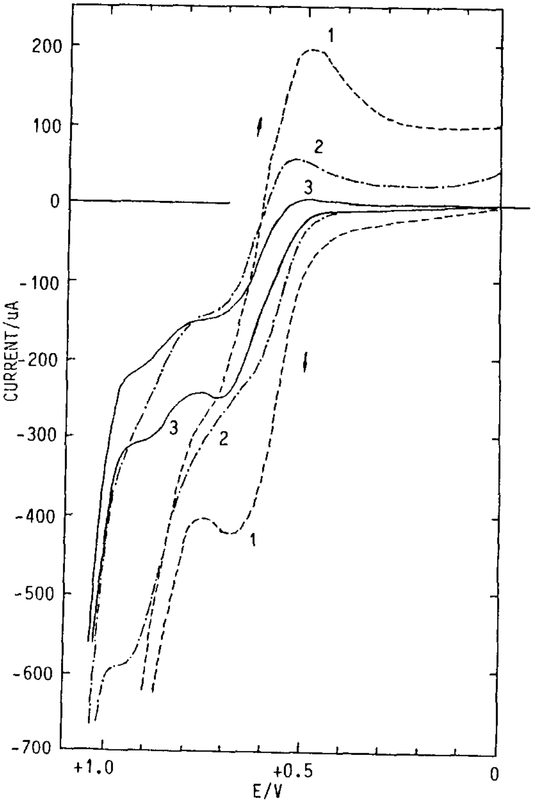


Figure 2. Cyclic voltammograms of ZnOEP/Cl^-(0.1M) system at different scan rate: 1) ----,250mv/s; 2) —·—·, 50mv/s; 3) ——, 10mv/s; for 100mv/s,see figure 1d; solvent, CH_2Cl_2.

$$-\frac{RT}{nF}\ln\frac{\beta_2}{\beta_1} = E^c_{\frac{1}{2}}(1) - E_{\frac{1}{2}}(1)$$

At 25^o, with $[Et_4NCl]$ = 0.01 Molar, $E_{1/2}(1)$ = +0.53V, $\beta_2/\beta_1 = 7 \times 10^3$, indicating a much stronger interaction occurs between $ZnOEP^{+\cdot}$ and Cl^- than ZnOEP and Cl^-.[9]

From voltammogram 1.b, it is demonstrated that below +0.90V, oxidation of chloride ion does not take place, implying that no chloro-radical can be formed. Therefore, radical combination between $Cl\cdot$ and $ZnOEP^{+\cdot}$ is not important for an anodic potential between 0 and +0.90V. Absence of cathodic current for the second oxidation process (voltammogram 1.c) when $[Cl^-]$ = 0.01 Molar indicates that a rather fast chemical reaction occurs between Cl^- and the dication, $ZnOEP^{2+}$. Voltammogram 1.d is that of ZnOEP at $[Et_4NCl]$ = 0.1 Molar, the reversibility of the first oxidation decreases. The first oxidation wave becomes a broad wave with $E_{1/2}$ = +0.60V, shifted to the positive by 0.07V relative to that of ZnOEP with $[Et_4NCl]$ = 0.01 Molar. The second oxidation peak is an ill-defined one with a current intensity much larger than that of the first oxidation. This is an indication that some kind of chemical process is taking place at a high concentration of chloride ion following the first oxidation process.

In order to have a closer look at the possible chemical processes occurring at the first oxidized states of ZnOEP, we investigated on the cyclic voltammetry of ZnOEP ($[Et_4NCl]$ = 0.1 Molar) at different scan rates. The results are shown in Figure 2. At 250 mV/s, the first oxidation process is still reversible, with the oxidation peak potential $[E^a_p(1)]$ at +0.67V. Lowering of the scan rate decreases the reversibility of the process. At 10 mV/s, the process becomes entirely irreversible, as the reduction wave is missing. The oxidation peak potential $[E^a_p(1)]$ appears at +0.72V, with a positive shift of 50 mV relative to that at 250 mV/s. This implies that some slow chemical and/or electrode reactions are occurring other than that described by equation 5.

From the previous study, we have demonstrated that complexation causes a negative shift of the second oxidation wave $[E^a_p(2)$ = +1.11V for ZnOEP vs $E^a_p(2)$ = +0.85V for $ZnOEP(Cl^-)]$ and that chloro-radical cannot be formed at this potential. We postulate that apart from reaction 5, the following processes are taking place too:

$$ZnOEP^{+\cdot}(Cl^-) + Cl^- \rightleftharpoons ZnOEP^{+\cdot}(Cl^-)_2 \quad (6)$$

$$ZnOEP^{+\cdot}(Cl^-)_2 \rightleftharpoons ZnOEP^{2+}(Cl^-)_2 + e \quad E^a_p \leqslant +0.72 \quad (7)$$

$$ZnOEP^{2+}(Cl^-)_2 \longrightarrow Zn\text{-}\alpha\text{-}Cl\text{-}OEP(Cl^-) \quad (Fast) \quad (8)$$

$$ZnOEP\text{-}\alpha\text{-}Cl\text{-}OEP(Cl^-) \rightleftharpoons Zn\text{-}\alpha\text{-}Cl\text{-}OEP^{+\cdot}(Cl^-) + e \quad E^a_p \approx +0.7V \quad (9)$$

As demonstrated by Dolphin and coworkers[11] and us in this work, the reaction of dication with nucleophile is efficient at a high enough potential. But at a low anodic potential (~ 0.7V), loss of the second electron by the porphyrin cation radical (equation 7) can only take place after a chemical reaction (equation 6).

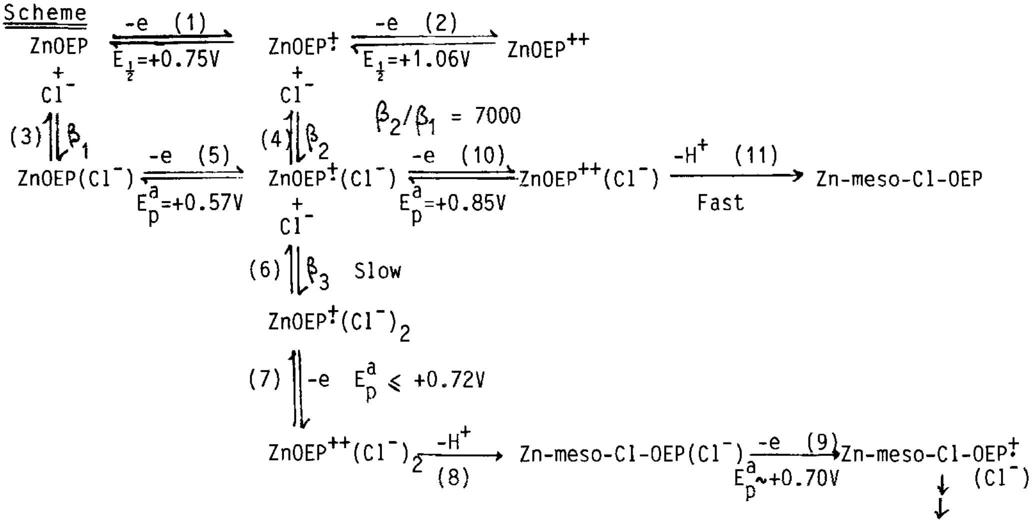
Dolphin and coworkers[12] suggested that a dication can be generated by dimerization of the mono-cation radical,

$$2\ \mathrm{ZnOEP}^{+\cdot} \rightleftharpoons (\mathrm{ZnOEP})_2^{2+}$$

which means the increase of the probability of the EEC process at a considerably low anodic potential. This is ruled out in our case since in the absence of a high concentration of chloride ion, the above described phenomenon in cyclic voltammetry was not observed and it was reported that the chance of a dimer formation in dichloromethane at room temperature is negligible.[13]

Listed in Scheme is a summary of the processes taking place studied by cyclic voltammetry. In low concentration of chloride ion, process (3), (5), (10) and (11) are taking place sequentially. All of them are rather fast processes, detected by cyclic voltammetry at fast scan rate. At high concentration of chloride ion and slow scan rate, process (5), (6), (7), (8) and (9) are picked up by cyclic voltammetry. We note also that at slow scan rate, the current intensity around 0.9V is much lower than that at fast scan rate, indicating that at slow scan rate, a lot is happening at a lower potential, while at fast scan rate, all the above processes are occurring at the high potential region.

Scheme



In the synthetic experiments, the anodic potential is controlled between 0.60 - 0.65V and at a chloride concentration of 0.1 Molar, the sequence of processes taking place should be (3), (5), (6), (7), (8), an example of ECE mechanism.

EXPERIMENTAL

The cyclic voltammetric studies were performed on a Jinan No. 4 Factory, Model 79-1 instrument. A closed cell with a three electrode system was used. The working electrode was platinum button. The counter electrode was a platinum wire coiled around the working electrode. The reference electrode was Ag/AgCl, KCl (sat.), isolated from the sample solution with a Luggin capillary salt bridge. Concentration of the porphyrin was maintained at 2×10^{-3} Molar. The supporting electrolyte used was tetra-n-butylammonium perchlorate (0.1 Molar). The solvent used was dichloromethane pretreated with anhydrous potassium carbonate and redistilled. Temperature of the system was maintained at 25±1°C. The solution was deaerated by bubbling nitrogen through for 15 min before experiment. The voltammogram was taken with the instrument scanning between +1.7V and 0V. All data reported were in volts vs Ag/AgCl, KCl (saturated).

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