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SHORT COMMUNICATION

Studies on oxidation of arene by superoxide ions electrocatalysed by metallo-porphyrins

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1. Introduction

The superoxide ion, O_2^-, is a potential toxic oxygen-derived species for aerobic organisms, and it can react with various organic compounds, owing to its anionic, radical and redox nature. This makes it important in biochemistry [1, 2] but also it may find application as a new organic synthetic reagent [3–6]. Of particular concern are the redox reactions of O_2^- with organic compounds.

The superoxide ion can be generated by one-electron reduction of O_2 in aprotic media. The electrochemical method of generating O_2^- is experimentally more convenient because the continuous generation of O_2^- is possible on the electrode and the solubility of O_2^-, in the presence of the tetraethylammonium cation as supporting electrolyte, is sufficiently high [7]. However, the electrochemical method is often restricted by the reduction potential of the organic compounds. If the organic compound possesses less negative reduction potential than that of O_2, it undergoes undesirable electroreduction before the generation of O_2^-.

It has previously been reported that metallo-porphyrins, FeTTP and MnTTP, possess higher electrocatalytic activity for the nucleophilic substitutions of haloarenes with O_2^- from electroreduction of O_2 in DMF [8].

In this paper we report on the catalytic activity of metallo-porphyrins in the oxidation of nitrotoluene with O_2^- from the electroreduction of O_2. Advantages of oxidation by electrogenerated superoxide ion in the presence of metallo-porphyrins are threefold. The oxidation can proceed under mild conditions, it does not require any oxidizing chemicals and it can be more widely used in organic synthesis.

2. Experimental details

2.1. *Materials*

The metallo-porphyrins, manganese tetraphenylporphyrin (MnTTP), iron tetraphenylporphyrin (FeTTP) and cobalt tetraphenylporphyrin (CoTTP) were synthesized and purified by the reported methods [9]. The supporting electrolyte, tetraethylammonium perchlorate (TEAP) was prepared and purified in the usual manner [10]. The aprotic solvent DMF was dried over anhydrous $MgSO_4$ for 24 h then $CaSO_4$ for 24 h and then distilled under reduced pressure in condition protected by nitrogen. Finally, DMF was dried over a 0.4 nm molecular sieve previously regenerated at 400° C for further dehydration. The *p*-nitrotoluene, *p*-nitrobenzoic acid, *p*-nitrobenzaldehyde, trans-stilbene and trans-stilbene oxide were purified by recrystallization from AR grade reagents.

2.2. *Cyclic voltammetry*

Cyclic voltammetry was carried out in a three-compartment cell equipped with a cover, and gas inlet and outlet. A small platinum ball of area 0.21 cm^2 was used as working electrode and a saturated calomel electrode (SCE) as reference electrode.

2.3. *Controlled potential electrolysis*

Controlled potential electrolysis was carried out at -0.4 V vs SCE. The electrolyte solution was 10 ml 0.2 M TEAP in DMF. The concentration of nitrotoluene was 0.02 M with or without 10^{-3} M metallo-porphyrins. Gaseous oxygen was bubbled into the solution at a rate of 19 ml min^{-1}. A platinum plate of area 5.19 cm^2 was used as working electrode and a saturated calomel electrode (SCE) as reference electrode.

2.4. *Analysis and identification*

The electrolyte solution was acidified with H_2SO_4, then product *p*-nitrobenzoic acid, *p*-nitrobenzaldehyde, and unreactive *p*-nitrotoluene, trans-stilbene and trans-stilbene oxide were determined by high pressure liquid chromatography. I.r. and u.v. also were used for the identification of compounds.

3. Results and discussion

The reduction peak potentials (E_{pc}) of metallo-porphyrins FeTTP, MnTTP, CoTTP and that of main product *p*-nitrobenzoic acid, and substrate *p*-nitrotoluene and that of oxygen were determined by cyclic voltammetry.

It may be seen from Table 1 that E_{pc}^1 of O_2 is -0.95 V vs SCE. It is obvious that if metallo-porphyrins are not in the system, in order for the controlled potential electrolysis of oxygen in the presence of *p*-nitrotoluene to be carried out, the electrolysis potential must be controlled at -0.95 V vs SCE or more negative. However, the E_{pc}^1 of the main product, *p*-nitrobenzoic acid, is -0.85 V vs SCE. It is thus more positive than the E_{pc}^1 of O_2. This will result in electrolysis of *p*-nitrobenzoic acid and a decrease in the yield of *p*-nitrobenzoic acid.

Table 1. Reduction peak potentials of various compounds investigated

Compound	E^1_{pc}	E^2_{pc}	E^c_{pc}
FeTPP	−0.29	−1.08	
MnTPP	−0.31	−1.26	
CoTPP	+0.24	−0.85	
p-nitrotoluene	−1.05(−1.10)*	−1.85	
p-nitrobenzoic acid	−0.85(−0.80)*	−1.20(−1.16)*	−1.75(−1.70)*
O_2	−0.95(−0.85)*		

E/V vs SCE; solvent: DMF; supporting electrolyte: 0.2 M TEAP/DMF; electrode, platinum ball; temperature: 25° C.
* Data in brackets taken from [11].

To avoid undesirable electrolysis of main product *p*-nitrobenzoic acid, the potential must be moved in the positive direction. Metallo-porphyrins have this function. The controlled potential electrolysis experiments were carried out in the presence and absence of metallo-porphyrins FeTPP, MnTPP and CoTPP in DMF. The potentials were controlled at −0.4 V vs SCE, a little more negative than the E^1_{pc} of FeTPP, MnTPP and CoTPP. The results are shown in Table 2.

The results in Table 2 indicate that the metallo-porphyrins, FeTPP, MnTPP and CoTPP catalyse the oxidation of *p*-nitrotoluene with electrogenerated superoxide ion. The yield of *p*-nitrobenzoic acid amounted to 63.5–43.6% and selectivity of generated acid achieve to 31.4–56.6% in the presence of FeTPP, MnTPP and CoTPP. While in the absence of metallo-porphyrins yields and selectivity are all zero. A yield of 56% and a selectivity of 44% were reported in the absence of metallo-porphyrins in [11], but the potential was controlled at −0.9 V/Ag/AgCl, which is 0.5 V more cathodic than that in the presence of metallo-porphyrins.

In the presence of metallo-porphyrins, higher yields and selectivities may be closely related to the smaller negative potential of electrolysis, because the main produce *p*-nitrobenzoic acid is not electrolyzed under −0.4 V vs SCE.

There was a smaller quantity of *p*-nitrobenzaldehyde in the products as shown in Table 2 and yields achieved were 7.4–1.5%.

It has been reported in [11] that when the electrolysis potential was controlled at −0.9 V/Ag/AgCl, *p*-nitrobenzaldehyde, as an intermediate product, cannot be determined. This suggests that *p*-nitrobenzaldehyde is electrolysed rapidly at higher negative potential.

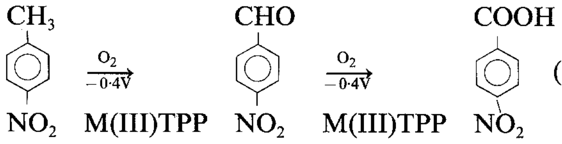
The first reversible reduction wave of metallo-porphyrins corresponds to one electron reduction of M(III) TPP to M(II) TPP [12]. Here the electrolysis potential in the presence of metallo-porphyrins was controlled at −0.4 V vs SCE, so the electrocatalysis of metallo-porphyrins may be explained by the following equations.

$$\mathrm{M(III)\ TPP} \underset{-0.4\,\mathrm{V}}{\overset{e^-}{\rightleftharpoons}} \mathrm{M(II)\ TPP} \qquad (1)$$

$$\mathrm{M(II)\ TPP} \xrightarrow{O_2} [\mathrm{M(III)\ TPP} \cdot O_2^-] \qquad (2)$$

$$[\mathrm{M(III)\ TPP} \cdot O_2^-] \xrightarrow{\text{substrate}} \mathrm{M(III)\ TPP} + \text{products (or intermediates)} \qquad (3)$$

The complex $(\mathrm{M(III)TPP} \cdot O_2^-)$ is a donor of superoxide ion. When it reacts with the substrate, molecules of the substrate abstract superoxide ion from the complex, and then release M(III)TPP, which can be reduced to M(II)TPP on the electrode. Because *p*-nitrobenzaldehyde is an intermediate product, *p*-nitrobenzoic acid can be formed by the processes shown in Equation 4.



(4)

When trans-stilbene (0.02 M) was added to the oxidation system of *p*-nitrotoluene with O_2^- in the presence of Fe(III)TPP, stilbene oxide was obtained. The production of epoxide suggests that the peroxide may be produced in the presence of M(III)TPP. The reaction may proceed via a radical mechanism [13]. But the reaction mechanism is to be proven by further experiments.

From the data of yields and selectivities in Table 2,

Table 2. The oxidation of p-nitrotoluene with electrogenerated superoxide ion in the presence and absence of metallo-porphyrins (MTPP)

MTPP	*Yields of p-nitrobenzoic acid /%*	*Selectivities /%*	*Yields of p-nitrobenzaldehyde /%*	*Selectivities /%*
FeTPP	63.5	81.4	7.4	9.5
MnTPP	48.3	66.1	5.0	6.9
CoTPP	43.6	56.6	1.5	2.0
None	0		0	

Electrolyte: 0.2 M TEAP/DMF. [MTPP]: 10^{-3} M. [*p*-nitrotoluene]: 10^{-2} M.
Electrode: Pt plate; reference electrode: SCE.
Temperature: 25° C; electrolysis time: 20 h.

it may be seen that the order of catalytic activity of the metallo-porphyrins is FeTPP > MnTPP > CoTPP. Studies on the relation between catalytic activities and the structure of metallo-porphyrins are in progress.

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