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SHORT COMMUNICATION

Nucleophilic substitution of halogeno-nitrobenzenes by superoxide ions electrocatalyzed by metallo-porphyrins

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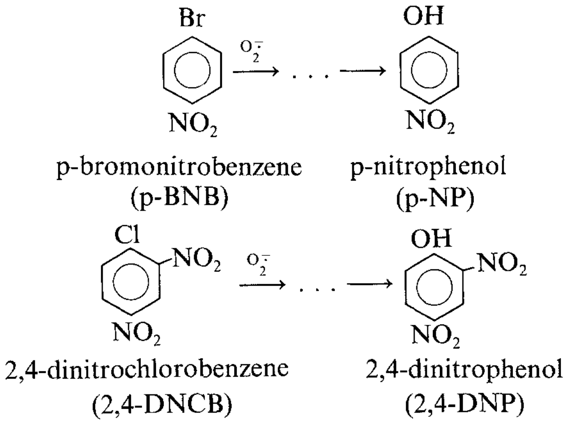
1. Introduction

The chemistry and reactivity of the superoxide ion ($O_2^{\cdot -}$) has received much attention from chemists and biochemists during the past two decades [1, 2]. The $O_2^{\cdot -}$ ion, usually generated from oxygen reduction, is being investigated as a new reagent for organic synthesis [3–7]. Of particular concern is the nucleophilic substitution of halohydrocarbon by $O_2^{\cdot -}$. Under suitable conditions, such nucleophilic substitution reactions may proceed via electroreduction of O_2. However, they are often restricted by two factors: 1. the electrogenerated $O_2^{\cdot -}$ is unstable in aqueous media because of its rapid spontaneous disproportionation with the participation of protons [8]; and 2. the aromatic nitro-compound may itself undergo undesirable electroreduction before the generation of $O_2^{\cdot -}$ if the reduction potential of the compound is less negative than that of oxygen. To bring about the desired substitution reaction, effective measures must be taken to overcome these restrictions, i.e. one must make the $O_2^{\cdot -}$ more stable and, more importantly, catalyze the reaction. It has been reported that iron-porphyrin is effective as a catalyst for the selective oxidation of saturated hydrocarbons in which the key oxidant is superoxide formed by one-electron reduction of triplet oxygen [9]. In this paper we report the use of metallo-porphyrins in aprotic media for electrocatalyzing the nucleophilic substitution of halogeno-nitrobenzenes with $O_2^{\cdot -}$. Studies are focused on the following typical reactions, one involving a mono nitro-ring, the other involving a dinitro-ring.



The metallo-porphyrins are considered to possess electrocatalytic activities toward oxygen reduction and may thus act as good $O_2^{\cdot -}$ donors [10]. Instead of using aqueous solutions as reaction media, aprotic solutions were used in which the $O_2^{\cdot -}$ is relatively stable and exhibits significant reactivity [1].

2. Experimental details

2.1. *Reagents*

The aprotic solvent dimethylformamide (DMF) was first dried over anhydrous $MgSO_4$ and then $CaSO_4$ for 24 h and then distilled under reduced pressure. Further dehydration was done over a 0.4 nm molecular sieve which had been pretreated by heating at 400° C.

The supporting electrolyte tetraethylammonium-perchlorate (TEAP) was synthesized and purified according to the method described in [11].

The two organic reactants p-BNB and 2,4-DNCB were both recrystallized twice from C.P. grade reagents.

The metallo-porphyrins, specifically manganese tetraphenylporphyrin (MnTPP) and iron tetraphenylporphyrin (FeTPP) were synthesized and purified according to the method given in [12].

2.2. *Cyclic voltammetry*

The base electrolyte for cyclic voltammetry was 0.1 M TEAP in DMF. Controlled by a potentiostat with incorporated sweep signal generator, the potential of the platinum disc working electrode was scanned linearly at a rate of $100\,mV\,s^{-1}$. A saturated calomel electrode (SCE) was used for reference to which all the potential values given in this paper are referred.

2.3. *Constant potential electrolysis*

For constant potential electrolysis, the electrolyte solution was 25 ml 0.2 M TEAP in DMF containing 0.02 M organic reactant with or without 10^{-3} M metallo-porphyrin. Oxygen was bubbled through the solution at a rate of $19\,ml\,min^{-1}$. A platinum foil of $4.59\,cm^2$ surface area was used as the working cathode. Using a potentiostat for potential control, the electrolysis was carried out in a single compartment cell with a SCE reference and another platinum foil as counter electrode. Each electrolysis lasted 12 h 20 min.

2.4. *Determination of the yield*

After electrolysis, the electrolyte solutions were analysed by high pressure liquid chromatography with standard samples of reactant and product for qualitative identification and quantitative determination.

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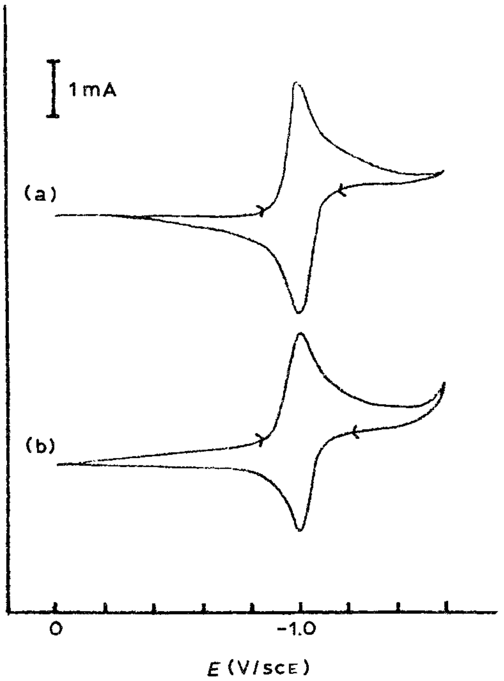


Fig. 1. Cyclic voltammogram of (a) 0.02 M p-BNB and (b) 0.02 M p-BNB + 0.02 M p-NP. Electrode: Pt. Sweep rate: 100 mV s^{-1}. Electrolyte: 0.1 M TEAP/DMF.

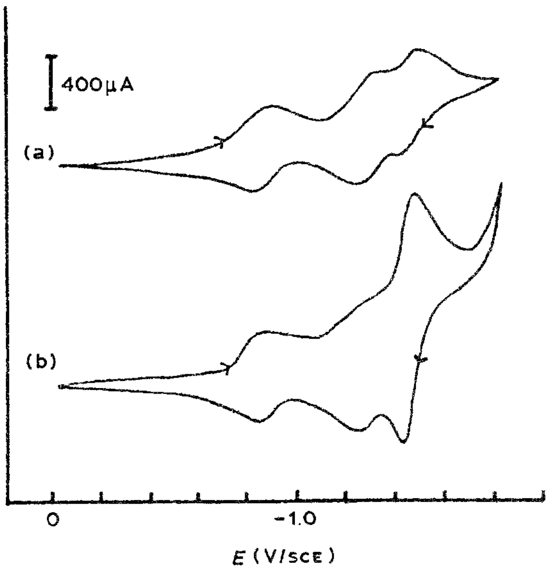


Fig. 2. Cyclic voltammogram of (a) 0.02 M 2,4-DNCB and (b) 0.02 M 2,4-DNCB + 0.02 M 2,4-DNP. Electrode: Pt. Sweep rate: 100 mV s^{-1}. Electrolyte: 0.1 M TEAP/DMF.

3. Results and discussion

The potential of the cathodic peak, E_{pc}, of O_2 in DMF solution according to [13] appears at around −0.95 V.

Figures 1 and 2 show the cyclic voltammograms of the two organic reactants p-BNB and 2,4-DNCB (Curves 1a and 2a), respectively, together with that in the presence of their respective substitution products p-NP and 2,4-DNP (Curves 1b and 2b). Cathodic peak potentials of p-BNB and 2,4-DNCB are at −1.02 V and −0.80 V respectively, the latter is less cathodic than that of O_2, indicating that, during electrolysis, the 2,4-DNCB itself undergoes preferential reduction before the generation of $O_2^{\cdot-}$ and hence renders the direct nucleophilic substitution reaction impossible. It is also seen that the electrochemical behaviour of the reactants is not significantly affected by their substitution products, implying no chemical interactions between the nitrophenols and the corresponding halogenonitrobenzenes.

Cathodic peak potentials of MnTPP(III) to Mn(II)-TPP and Fe(III)TPP to Fe(II)TPP in DMF solution are located at −0.30 V and −0.24 V [14], respectively. They are considerably (0.65 to 0.71 V) more positive compared with the E_{pc} of O_2. Since, quite probably $O_2^{\cdot-}$ can be furnished from the reduction product of MnTPP or FeTPP, the shift of E_{pc} to more positive potentials means that the MnTPP or FeTPP may be effective in catalyzing the nucleophilic substitution reactions of organic compounds with $O_2^{\cdot-}$, particularly those which would be impossible because of the preferential reduction of the organic reactants in the absence of catalysts.

Figure 3 shows the cyclic voltammograms of MnTPP, O_2 and 2,4-DNCB in DMF solution alone or in combination. It is seen that, when the three species are present at the same time in the solution, the current for 2,4-DNCB reduction increases and the relevant potential shifts in the positive direction. This means that MnTPP may catalyze the nucleophilic substitution reaction.

Constant potential electrolysis experiments were then carried out to verify the effectiveness of the electrocatalytic action of MnTPP and FeTPP. The potential of the working cathode was controlled at −0.40 V, a little more negative than the E_{pc} of MnTPP or FeTPP. The results are summarized in Table 1.

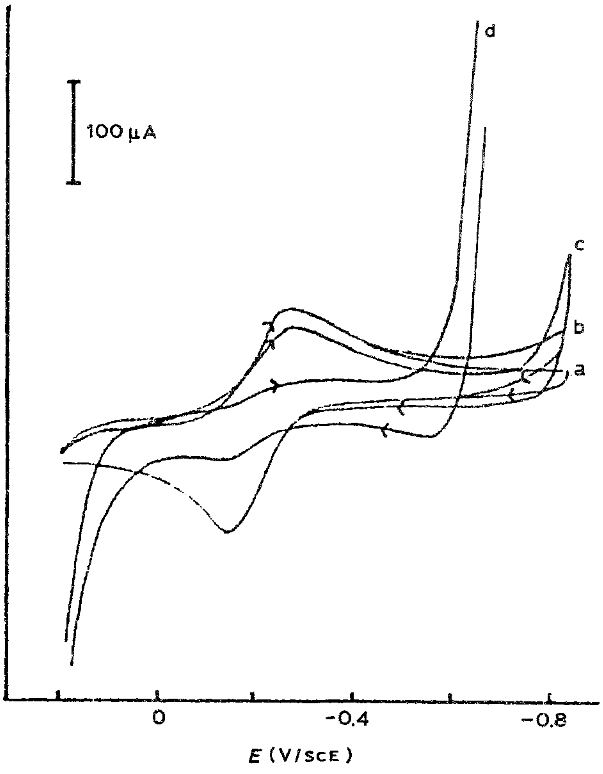


Fig. 3. Cyclic voltammogram of (a) MnTPP + Ar, (b) MnTPP + O_2, (c) MnTPP + Ar + 2,4-DNCB, and (d) MnTPP + O_2 + 2,4-DNCB. Electrode: Pt. Sweep rate: 100 mV s^{-1}. Electrolyte: 0.1 M TEAP/DMF.

Table 1. Nucleophilic substitution of halogeno-nitrobenzenes by constant potential electrolysis

Electrocatalyst	*Reactant*	*Product*	*Conversion* (%)	*Yield* (%)
MnTPP	p-BNB	p-NP	31.1	21.2
FeTPP	p-BNB	p-NP	33.3	25.8
none	p-BNB	p-NP	0	0
MnTPP	2,4-DNCB	2,4-DNP	59.8	50.0
FeTPP	2,4-DNCB	2,4-DNP	89.5	67.5
none	2,4-DNCB	2,4-DNP	0	0

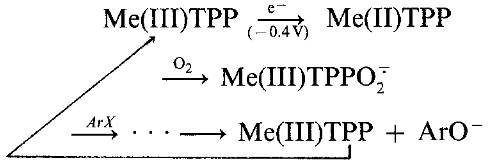
Electrolyte: 0.2 M TEAP in DMF with O_2 bubbling at 19 ml min^{-1}.
Concentration: 10^{-3} M for MeTPP, 0.02 M for halogenonitrobenzene.
Working electrode: Pt Potential, -0.40 V; reference electrode, SCE.
Temperature: 25° C. Duration of each electrolysis: 12 h 20 min.

It can be seen that, in sharp contrast to the zero yield for electrolysis in the absence of catalyst, the yields in the presence of metallo-porphyrins are quite good, especially for 2,4-DNP, amounting to 50.0 and 67.5%. The yields for p-NP are lower, 21.2% and 25.8%, respectively, in the presence of MnTPP and FeTPP. We note that in [7] a yield of 52% was reported for p-NP. However, the controlled potential was -0.9 V (against SCE), that is 0.5 V more cathodic than here.

The catalytic activity of FeTPP is seen to be somewhat higher than that of MnTPP. This is in conformity with the fact that the reduction of FeTPP commences at more positive potentials than the reduction of MnTPP, as can be seen from the difference in their E_{pc} values.

The higher yield of 2,4-DNP than p-NP may probably be attributed to the fact that the dinitro-ring is more readily attacked by nucleophiles than the mono nitro-ring.

In conclusion, our experiments have shown that both MnTPP and FeTPP are effective in electrocatalyzing the nucleophilic substitution reaction of halogenonitrobenzenes with $O_2^{\cdot -}$. The electrocatalytic process, according to our thin layer spectroelectrochemical studies [15], may involve the formation of certain metallo-prophyrin-$O_2^{\cdot -}$ complexes and the subsequent abstraction of the $O_2^{\cdot -}$ from the complex by the halogenonitrobenzene according to the following scheme:



Acknowledgement

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