CHEMISTRY LETTERS, pp. 99-102, 1973. Published by the Chemical Society of Japan

BASE-CATALYZED AUTOXIDATION OF 9,10-DIHYDROANTHRACENE WITH ELECTRO-GENERATED SUPEROXIDE ION

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The superoxide ion formed by the electrolysis of oxygen molecule dissolved in pyridine was shown to act as a base-catalyst in autoxidation of 9,10-dihydroanthracene. Iron and cobalt phthalocyanine accelerated the reaction. The rate equation of oxygen consumption was given. The effect of metal phthalocyanine was discussed by cyclic voltammetry.

Oxygen molecule dissolved in aprotic solvents such as acetonitrile forms a superoxide ion by a reversible one electron reduction$^{1)}$.

$$O_2 + e \longrightarrow O_2^-$$

The superoxide ion which has basic, nucleophilic and other properties, can be effective in occurrence of the reaction such as a base-catalyzed autoxidation or a nucleophilic substitution to some kinds of organic compounds$^{2)}$.

In this communication, the reactions of the electro-generated superoxide ion with 9,10-dihydroanthracene having labile hydrogens were carried out, and the mechanism was discussed using the results of products and kinetics. Furthermore, the catalytic effect of metal phthalocyanine added in the reaction system was also shown.

In a solvent of pyridine, cyclic voltammogram$^{3)}$ of oxygen was measured using a supporting electrolyte of tetraethylammonium perchlorate and a working electrode of platinum plate. The reversible wave of $E_{1/2}$ = -0.85V(vs.SCE) was obtained. When 9,10-dihydroanthracene was added to the electrolytic solution, some new peaks differed from the reduction wave of oxygen were observed and the re-oxidation peak of reduced oxygen spieces, that is, superoxide ion diminished or disappeared. The cyclic voltammogram is shown in Fig. 1. The new peaks correspond to anthracene and anthraquinone, which are similar to the results of Peover et al. in dimethylformamide$^{2)}$. This reaction can be understood to be base-catalyzed autoxidation.

In order to elucidate the reaction mechanism, the consumption of oxygen in a controlled potential electrolysis of 9,10-dihydroanthracene was measured. A H-type cell separated by glass filter was used in a macro-electrolysis and each 20 ml of the solution was put in the separated chambers. A 0.1M concentration of tetraethylammonium perchlorate and 50 cm^2 surface areas of platinum gauze were used. Guaranteed grade of pyridine was used after ordinary purification of dehydration by solid

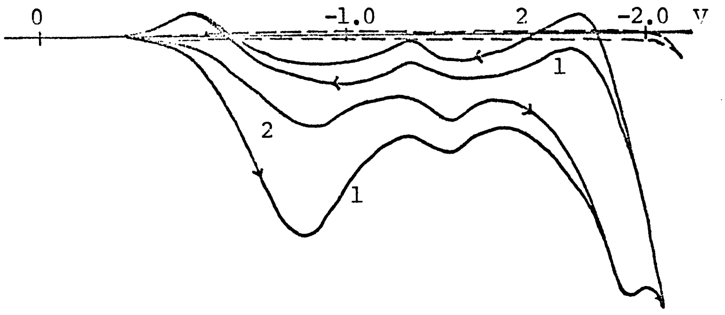

Fig.1. Cyclic voltammogram of 9,10-dihydroanthracene in 0.1M TEAP-Pyridine solution
--- under N_2
—— aerated
scan rate 0.02 V/sec

potassium hydroxide followed by distillation. A controlled potential was set at -0.8V(vs.SCE). The consumed amount of oxygen was obtained from the reduced amount of oxygen gas in the burette connected to the cell. The temperature of the reaction apparatus was kept at 20°C by water bath. When electrolysis started, the consumption of oxygen gas was observed after some induction period, and the solution was gradually deep blood-red color(ca.350nm), which was derived from either the solution of anthraquinone in pyridine or a reaction intermediate$^{4)}$ of 9,10-dihydroanthracene. After long electrolysis, anthraquinone was precipitated. The consumption of oxygen continued for some period after electric current was interrupted as shown in Fig.2. The addition of zinc isopropyl dithioxantate as an autoxidation inhibitor to the solution resulted in the remarkable elongation of the induction period. These results clearly show the radical mechanism of the present reaction.

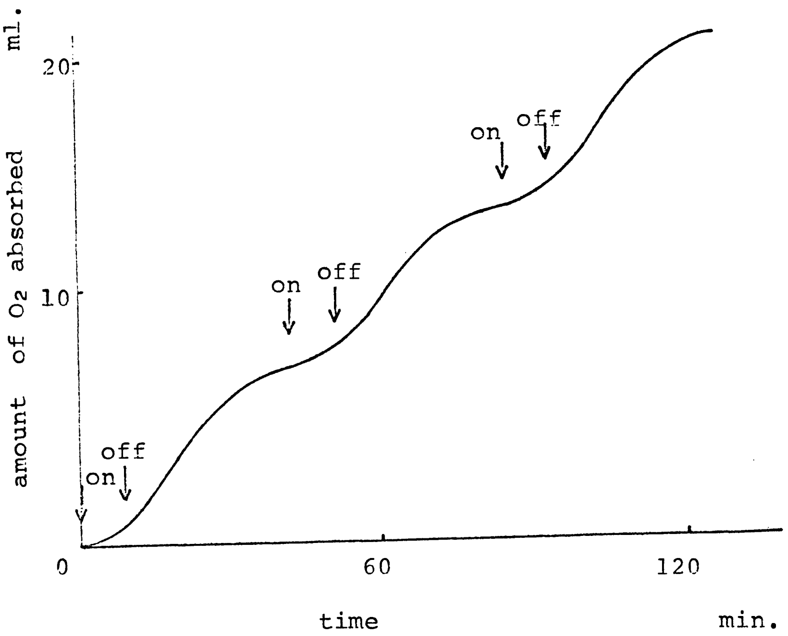

Fig.2. Oxidation of 9,10-dihydroanthracene in 0.1M TEAP-Pyridine solution

on (cathodic potential) ; -0.8 V vs SCE.
concn. of 9,10-DHA ; 50mM
O_2 satd., 20°C

In the condition of a fairly long chain length and a sufficient oxygen partial pressure in the ordinary elementary reactions of autoxidation, the rate of oxygen consumption is expressed as eq.(1):

$$-\frac{d[O_2]}{dt} = k[RH]\sqrt{Ri} \tag{1}$$

The reaction orders of substrate concentration and oxygen pressure were determined experimentally, and the following rate equation was given in a low concentration under 2×10^{-2}M substrate.

$$-\frac{d[O_2]}{dt} = k'[RH]^{3/2}[O_2]^{1/2} \tag{2}$$

Therefore, the rate equation of the initiation was shown in eq.(3) and the mechanism of the initiation is proposed as eqs.(4) and (5).

$$Ri = k''[RH][O_2] \tag{3}$$

$$O_2 + e \longrightarrow O_2^{-} \tag{4}$$

$$RH + O_2^{-} \longrightarrow R\cdot + O_2H^{-} \tag{5}$$

When iron(II) phthalocyanine was added to the solution, the reaction rate increased as shown in Table 1. The rate equations of oxygen consumption and initiation are given in eqs.(6) and (7), respectively.

$$-\frac{d[O_2]}{dt} = k'''[RH]^{3/2}[O_2]^{1/2}[Cat]^{1/2} \tag{6}$$

$$Ri = k''''[RH][O_2][Cat] \tag{7}$$

Table 1. Effect of metal phthalocyanine catalyst

Catalyst	$-d[O_2]/dt$*	Ri**
none	4.46×10^{-6}	1.28×10^{-6}
Fe-Pc	10.2	6.71
Co-Pc	10.4	6.94

O_2 satd.in 0.1M TEAP-pyridine solution
concn. of 9,10-DHA: 50mM, concn, of cat.:1mM, 20°C
* mol/l·sec
** $Ri = \left[\frac{-d[O_2]/dt}{k[RH]}\right]^2, k = 79.0 \times 10^{-3}\,(\text{mol sec/l})^{-1/2}$

This means iron phthalocyanine acts as a positive catalyst in the reaction and is effective in the initiation step of $RH \longrightarrow R\cdot$. Table 2 shows the changes of electric current and potential in both waves of reduction and re-oxidation of oxygen molecule by the addition of iron(II) or cobalt(II) phthalocyanine catalyst. Reduction current increased by 20-30% and re-oxidation current reversely reduced. The ratio of re-oxidation current to reduction one also reduced. The above facts can be explained by a postulated formation of superoxide ion - metal phthalocyanine complex$^{5)}$. This complex would be more reactive to 9,10-dihydroanthracene and therefore, the rate of the initiation reaction increases. In the absence of the substrate,

Table 2. Effect of added M-Pc on oxygen wave

	$E_{1/2}$ (V)	Ep (mV)	Ip_{red} (mA)	Ip_{ox} (mA)	Ip_{ox}/Ip_{red}
None	-0.83	150	0.105 0.104	0.093 0.091	0.886 0.875
Fe-Pc	-0.80	110	0.124 0.116	0.056 0.068	0.451 0.586
Co-Pc	-0.76	130	0.148 0.142	0.082 0.086	0.554 0.605

sweep rate : 0.02V/sec
*the upper row : 1st sweep, the lower row : 2nd sweep

the complex would regenerate oxygen and give a catalytic current as shown in the second stage in eq.(8).

$$O_2^{\overline{\cdot}} + M - Pc \rightleftharpoons [O_2^{\overline{\cdot}} \cdots M - Pc] \longrightarrow O_2 + [M - Pc]^- \qquad (8)$$

However the action of metal phthalocyanine will be more complicated because it influences the deactivation of peroxy radical, decomposition of hydroperoxide, etc. Detailed results will be reported in a future.

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(Received November 25, 1972)