Reactivity of Electrogenerated Superoxide Ion. I. Autoxidation of 9,10-Dihydroanthracene

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The superoxide ion, which was generated by means of electroreduction of the oxygen molecule dissolved in pyridine, abstracted the labile hydrogen from 9,10-dihydroanthracene and yielded anthraquinone and anthracene as the final products. From the products and their kinetics, the reaction was proposed to be a radical-chain autoxidation. Reactions with some other hydrocarbons were also carried out. The addition of ferrous or cobaltous phthalocyanine to the reaction system resulted in the increase of the reaction rate. A discussion of the effects led to the postulation of the intermediate formation of the superoxide ion-metal phthalocyanine complex.

Electrochemically an oxygen molecule is reduced by a reversible one-electron transfer to form a fairly stable species, namely a superoxide ion in common solvents such as dimethylformamide, dimethylsulfoxide and pyridine.[1-3]

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

The superoxide ion might be a kind of an extreme form of activated oxygen molecule, which is usually observed in the adsorption on metal oxide[4,5] and in the coordination with transition metal complexes, due to the electron transfer from a low-valent metal atom.[6,7] Hence, it is interesting to investigate the reactivity of the superoxide ion, since it leads to a clearer understanding of the chemical nature of the activated oxygen.

The superoxide ion is expected to possess various reactivities to extensive organic compounds, because of its basic, nucleophilic and other properties.[8,9]

In this paper we report on the reactions of the superoxide ion with some hydrocarbons having labile hydrogens. In the case of 9,10-dihydroanthracene as a substrate, the rate equation was determined and the mechanism was proposed to be a radical-chain autoxidation. The catalytic effect of metal phthalocyanine added to this reaction system was also discussed.

Experimental

Materials. Pyridine was dried over potassium hydroxide for several days, then distilled and stored under nitrogen atmosphere. Tetraethylammonium perchlorate (TEAP) was synthesized and purified by the ordinary method.[10] 9,10-Dihydroanthracene, fluorene and diphenylmethane of reagent grade were used without any further purification. Cumene and cyclohexane were used after distillation. Ferrous and cobaltous phthalocyanines were synthesized and purified according to the method given in literature.[11]

Cyclic Voltammetry. In the solvent of pyridine, cyclic voltammograms were recorded using TEAP as a supporting electrolyte on a platinum plate of 0.40 cm^2. Potential was referred to saturated calomel electrode (SCE).

Macro-electrolysis. For controlled potential electrolysis, an H-type cell was employed in which cathodic and anodic chambers were separated from each other by a glass filter and a reference electrode was connected to the cathodic chamber with a double salt bridge. Platinum gauze of 50 cm^2 was used as a cathode. 20 ml each of the electrolytic solution containing 0.1 M TEAP was put in each chamber and vigorously stirred. The cathode potential was controlled with a Yanagimoto Type VE-3 controlled potential electrolyzer.

The consumed amount of oxygen during electrolysis was measured by means of a gas burette connected to the cell in a closed oxidation system. The temperature of the solution was kept at 20±1 °C.

Spectrometry. In the ESR study, the solution was charged into the quartz tube immediately aftet electrolysis, and then the spectra were recorded at room temperature or −196 °C with a JEOL Model JS-3BS-X spectrometer. Otherwise, the spectra were measured while electrolysis was being carried out in the cavity. The *g*-factors were determined in comparison with Mn^{2+} marker. The electronic spectra of the solution after electrolysis were recorded with a Shimadzu MPS-50L spectrophotometer.

Results and Discussion

Electrogenerated Superoxide Ion. An oxygen molecule dissolved in 0.1 M TEAP–pyridine solution was reduced on platinum to form the superoxide ion (Fig. 1). This species was re-oxidized in the reverse sweep of the potential. The peak potentials of reduction and re-oxidation were respectively −0.91 and −0.77 V. The value of 140 mV as ΔE_p shows that the electrode process is quasi-reversible.[12] In addition, the fact that the ratio of anodic current to cathodic one is substantially unity even at slow sweep rate such as 0.02 V/s means that the superoxide ion remains fairly stable in a pyridine solution.[13]

In the ESR measurement, the superoxide ion gave no signal at room temperature, but the spectrum, which possessed marked anisotropy of $g_{//}=2.069$ and $g_{\perp}=2.006$, was obtained at −196 °C (Fig. 2). These

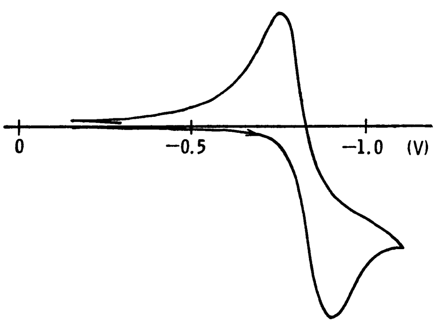


Fig. 1. Cyclic voltammogram of oxygen molecule in 0.1 M TEAP–pyridine solution, scan rate; 0.02 V/s, V *vs.* SCE.

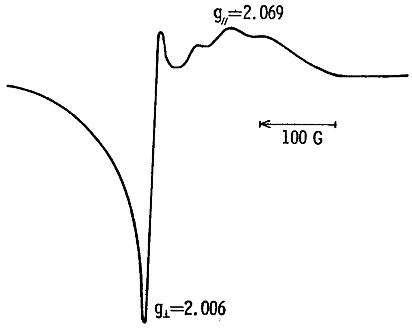


Fig. 2. ESR spectrum of the superoxide ion in 0.1 M TEAP–pyridine solution, measured at −196 °C.

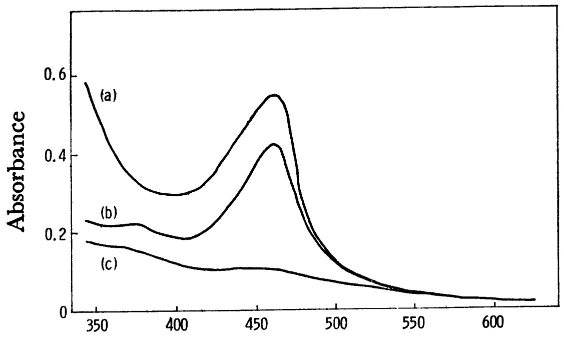


Fig. 3. Electronic spectra of the superoxide ion in 0.1 M TEAP–pyridine solution. After electrolysis, (a); 20 min, (b); 3 hr, (c); 20 hr.

results were identical with those reported previously.[1,3]

The superoxide ion in pyridine gave electronic spectra which had an absorption band of $\lambda_{max}=462$ nm (Fig. 3). This band became reduced in intensity as the anion radical decayed. After 20 hours at room temperature, it almost disappeared and a small absorption band at $\lambda_{max}=375$ nm appeared, due probably to the absorption of the products from the reaction of the superoxide ion with pyridine or other possible substances in the system. The band at 462 nm seems to be due not to the electronic transition in the free superoxide ion but to the charge-transfer complex, where the superoxide ion behaves as a donor and pyridine as an acceptor.[14]

Effect of Metal Phthalocyanine. In the voltammetric study, ferrous or cobaltous phthalocyanine added into the electrolytic solution gave the catalytic current to the reduction wave of oxygen and shifted the reduction potential to the positive direction (Table 1). These results suggest the intermediate formation of superoxide ion-metal phthalocyanine complex (**1**), which was concluded by Beyer *et al.* with respect to a phthalocyanine electrode.[15]

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

$$O_2^- + \text{M-Pc} \rightleftarrows \underset{\textbf{complex 1}}{[O_2^- \cdots \text{M-PC}]} \longrightarrow O_2 + [\text{M-Pc}]^- \quad (1)$$

Table 1. Effect of metal phthalocyanine on voltammetric reduction of oxygen

M–Pc	E_p (V *vs.* SCE)	I_p (mA)
None	−0.90	0.105
Fe–Pc	−0.86	0.124
Co–Pc	−0.82	0.148

M–Pc; metal phthalocyanine, 1 mM in 0.1 M TEAP–pyridine solution. E_p: peak potential. I_p: peak current. potential sweep rate; 0.02 V/s.

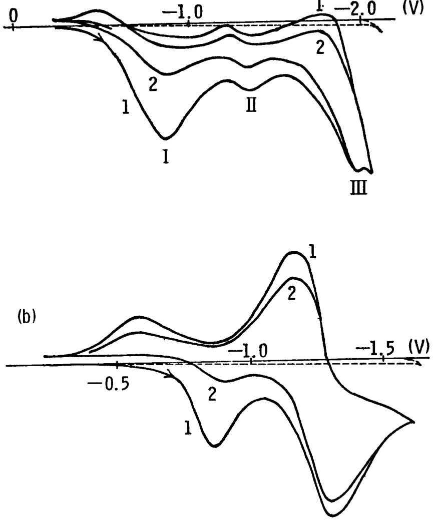


Fig. 4. Cyclic voltammograms of 9,10-dihydroanthracene (a) and fluorene (b), respectively 10 mM in 0.1 M TEAP–pyridine solution. Scan rate; 0.02 V/s. ----; under nitrogen atmosphere, ——; aerated. 1; the first sweep, 2; the second sweep. V *vs.* SCE.

Reactions of Superoxide Ion with Hydrocarbons Having Labile Hydrogens. 9,10-Dihydroanthracene or fluorene were oxidized easily by the seperoxide ion. Figure 4a is the cyclic voltammogram of 9,10-dihydroanthracene in 0.1 M TEAP–pyridine solution with or without oxygen. In the presence of oxygen, some new reduction peaks, which were not observed in the absence of oxygen, appeared. These peaks I, II and III corresponded respectively to the reduction of oxygen, anthraquinone monoanion radical and anthracene. But the re-oxidation peak of the superoxide ion disappeared. In the second sweep the reduction peak of oxygen was remarkably diminished. In the case of fluorene, the similar phenomena were observed (Fig. 4b). The new reduction peak differed from that of oxygen was due to fluorenone. These results show that the electrogenerated superoxide ion reacted easily with 9,10-dihydroanthracene or fluorene, the species resulting from which subsequently took up oxygen molecule in the vicinity of electrode to yield anthraquinone and anthracene or fluorenone.

In order to elucidate the reaction mechanism, the consumption of oxygen during the reaction of the superoxide ion and 9,10-dihydroanthracene was pursued. The reactions were carried out by the controlled potential electrolysis of oxygen-saturated electrolytic sloution containing a certain amount of the substrate at −0.8 V which was approximately the minimum potential for the generation of the superoxide ion and at which the substrate was not reduced. When electrolysis was commenced, the absorption of oxygen

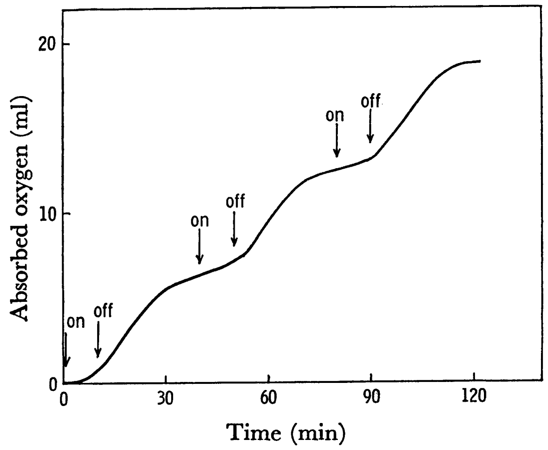


Fig. 5. Oxidation of 9,10-dihydroanthracene in 0.1 M TEAP–pyridine solution, oxygen-saturated at 20 °C, on; cathode (−0.8 V *vs.* SCE), concentration of 9,10-dihydroanthracene; 50 mM.

was observed after several minutes of induction period. Almost simultaneously the electrolytic current increased and the solution gradually became deep wine-red which seemed to be derived from anthraquinone monoanion radical since the ESR spectra of this solution gave the same signal as that of anthraquinone monoanion radical.[16] After long electrolysis, anthraquinone precipitated.

As shown in Fig. 5, when the electric circuit was opened (off) just after the beginning of oxygen absorption, the absorption went on constantly for a while and then gradually ceased. The subsequent closing of the circuit (on) recovered the absorption, preceded by the same induction period as ever.

Zinc isopropyl dithioxantate, which is a peroxy radical-trapping agent in ordinary autoxidations and is reduced at a much more negative potential than −0.8 V,[17] was added to solution, causing a remarkable prolongation of the induction period, followed by the absorption of oxygen at the same rate as that in the absence of the antioxidant. Use of 2,6-di-*tert*-butyl-4-methyphenol as another antioxidant was unsuccess, for the phenol itself was reduced and evolved hydrogen gas.

The reaction orders on substrate and oxygen partial pressure concerning the rate of oxygen absorption were determined experimentally, and the following rate equation was given in lower concentration than 2×10^{-2} M of substrate.

$$-\mathrm{d}[O_2]/\mathrm{d}t = k_1[\mathrm{RH}]^{3/2}[O_2]^{1/2} \qquad (2)$$

When a considerable chain length and sufficient oxygen pressure in the general elementary steps of autoxidation are present, the rate of oxygen absorption is expressed as follows, where R_i represents the rate of initiation reaction.[18]

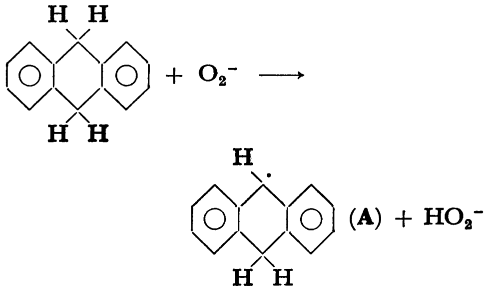
$$-\mathrm{d}[O_2]/\mathrm{d}t = k_2[\mathrm{RH}](R_i)^{1/2} \qquad (3)$$

Comparison of Eqs. (2) and (3) gives the rate equation of the initiation of this reaction as

$$R_i = k_3[\mathrm{RH}][O_2] \qquad (4)$$

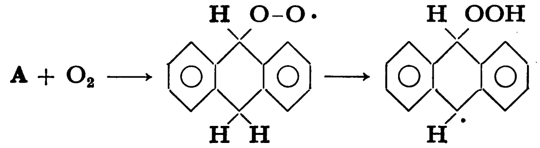
From the products and their kinetics mentioned above, the following mechanism seems to be acceptable for the initiation;

$$O_2 + e \rightleftharpoons O_2^- \qquad (5)$$

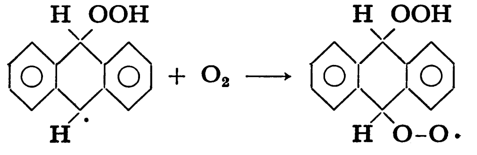


(6)

The electrogenerated superoxide ion abstracts hydrogen from 9,10-dihydroanthracene to yield radical **A**. The subsequent process may be illustrated as follows.



(7)



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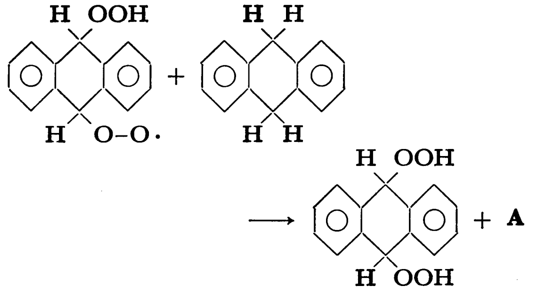
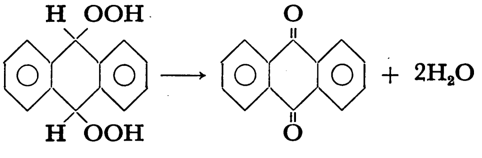


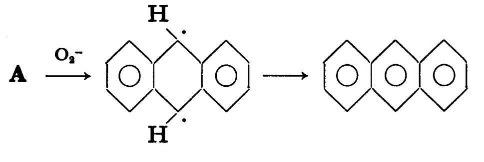
(9)

The addition of oxygen to radical **A** is followed by intramolecular hydrogen abstraction, as proposed by Hawthorne *et al.* in their study of base-catalyzed autoxidation.[19] Dihydroperoxide, one of the products in mechanism (9), is decomposed to give anthraquinone.



(10)

On the other hand, the production mechanism of anthracene seems to be as follows.



(11)

Some other compounds were also used as substrate. The results are shown in Table 2. The superoxide ion oxidized the compounds with the secondary hydrogen such as fluorene or diphenylmethane to yield ketones, that is fluorenone or benzophenone. It also oxidized cumene to yield the hydroperoxide. Moreover,

TABLE 2. OXIDATION BY ELECTROGENERATED SUPEROXIDE ION

Compounds	$-d[O_2]/dt$ ($\times 10^6$ M/s)	Main products
9,10-Dihydroanthracene	4.37	Anthraquinone: Anthracene (3: 1)
Fluorene	1.17	Fluorenone
Diphenylmethane	3.53	Benzophenone
Cumene	3.27	Cumene hydroperoxide
Cyclohexane	0.35	Unidentified

Concentration of hydrocarbons; 50 mM in oxygen-saturated 0.1 M TEAP–pyridine solution, 20 °C.

it could abstract the hydrogen of cyclohexane although its bond energy of C–H is considerably higher than those of the other substrates.[20] However, the final product could not be detected because of the slow rate of oxidation. Differing from the case of 9,10-dihydroanthracene, the oxidations of these compounds do not proceed according to the usual autoxidation, for these chain lengths were very short.

TABLE 3. EFFECT OF METAL PHTHALOCYANINE ON THE OXIDATION RATE OF 9,10-DIHYDROANTHRACENE

M–Pc	$-d[O_2]/dt$ ($\times 10^6$ M/s)
None	4.37
Fe–Pc	10.2
Co–Pc	10.4

Concentrations of M–Pc and 9,10-DHA; repectively, 1 mM and 50 mM in oxygen-saturated 0.1 M TEAP–pyridine solution, 20 °C.

It is well known that metal phthalocyanine activates oxygen molecule to initiate the autoxidation of various organic compounds such as cumene and α-methylstyrene.[21,22] In our study, ferrous or cobaltous phthalocyanine added to the macro-electrolytic solution acted as a positive catalyst and increased the reaction rate (Table 3). In the presence of ferrous phthalocyanine under 0.2 mM concentration, the rate equation was determined as follows.

$$-d[O_2]/dt = k_4[RH]^{3/2}[O_2]^{1/2}[Cat.]^{1/2} \tag{12}$$

The initiation rate is then expressed as

$$R_i = k_5[RH][O_2][Cat.] \tag{13}$$

This means that the catalyst is involved in the initiation step of Eq. 6. Addition of the catalyst gave no substantial change to the macro-electrolytic current. Therefore, it is inferred that the catalyst makes the superoxide ion more powerful in the hydrogen abstraction by the formation of complex **1** described in Eq. (1) and consequently increases the reaction rate. In the absence of a compound having labile hydrogen, complex **1** regenerates oxygen and gives the catalytic current (Table 1). However, the role of metal phthalocyanine might be more complicated, since it will deactivate the peroxy radical and decompose hydroperoxide.[23,24]

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