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Reaction of Halogenonitrobenzenes with Electro-generated Superoxide Ion

Hiromitsu Sagae, Masamichi Fujihira, Katsutaro Komazawa,**
Henning Lund,† and Tetsuo Osa*
Pharmaceutical Institute, Tohoku University, Aobayama, Sendai 980
*** Tokyo Metropolitan College of Aeronautical Engineering, Minamisenju, Arakawa-ku, Tokyo 116*

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The reaction of halogenonitrobenzenes (XNBs) with electrogenerated superoxide ion in *N*,*N*-dimethylformamide was studied electrochemically using cyclic voltammetry (CV) and controlled potential macro-electrolysis. It was shown in the CV that electro-generated superoxide ion reacts with all of the *o*- and *p*-isomers of iodo-, bromo-, and chloronitrobenzene in the dissolved oxygen medium. However the superoxide ion did not react with the other XNBs during CV. Controlled potential macro-electrolysis of oxygen in the presence of *o*- and *p*-bromonitrobenzene yielded the corresponding nitrophenols as the main products. The reaction mechanism *via* nucleophilic attack of the superoxide ion on the XNB, in the preference to an electron-transfer mechanism, is proposed.

Electrochemical reduction of oxygen dissolved in non-aqueous organic solvents,1–4) such as pyridine, acetonitrile, and *N*,*N*-dimethylformamide (DMF), occurs at *ca.* −0.85 V *vs.* silver–silver chloride (Ag/AgCl) and yields, reversibly, superoxide ion as shown in Eq. 1:5–7)

$$O_2 + e \rightleftharpoons O_2^{\cdot-} \qquad (1)$$

Recently, several studies regarding chemical reactions of electro-generated superoxide ion with organic compounds have been reported. Dietz *et al.*8) suggested that superoxide ion in nonaqueous solvents possesses various reactivities, namely characteristics of a strong base, nucleophile, oxidant, reductant, and free radical. During the past several years we have studied the reactivity of electro-generated superoxide ion with alkylbenzenes,9,10) methylpyridines and methylpyridine *N*-oxides.11) Simultaneously we have studied the reaction of electro-generated superoxide ion with halogenonitrobenzenes (XNBs), expecting to observe the electron transfer reaction of superoxide ion. At the almost same time as this work was presented,12) Rosenthal and Frimer also reported that superoxide ion solubilized in benzene by crown ether reacts rapidly with electron acceptors such as nitro substituted hydrocarbons and halides.13)

There are several reports on the electrochemical reaction of XNBs in nonaqueous solvents, using electrochemical methods such as cyclic voltammetry and polarography.14–17) However, electrochemical studies in the presence of oxygen have not previously been published. The cyclic voltammetric behavior of oxygen in the presence of some XNBs seemed to be interpretable in terms of the same mechanism as for catalytic reduction of aromatic halides, *via* electron transfer from the electro-generated radical anion to aromatic halides, as reported Lund *et al.*18)

However, after detailed investigation using macro-electrolysis and cyclic voltammetry in DMF, we have concluded that the reaction mechanism of the system should be considered more in terms of a nucleophilic reaction of electro-generated superoxide ion19–23) with XNBs than in terms of the electron transfer reaction of electro-generated superoxide ion to XNBs followed merely by elimination of halide ion. We report here the reaction of electro-generated superoxide ion with XNBs using macro-electrolysis and cyclic voltammetry in DMF solution, and discuss the results in terms of the nucleophilicity and reductant properties of superoxide ion.

Experimental

Materials. DMF was dried over anhydrous $CuSO_4$ for 24 h and then distilled under reduced pressure. Further purification was achieved by passage through a column of molecular sieve (4A 1/16) and activated alumina (both pretreated by heating at 400 °C). Tetraethylammonium perchlorate (TEAP) was synthesized and purified in the usual manner.24) Iodonitrobenzenes (INBs), bromonitrobenzenes (BNBs), chloronitrobenzenes (CNBs), and fluoronitrobenzenes (FNBs) of E. P. grade were purchased commerically (Wako Pure Chemical Industries) and were recrystallized or distilled before use.

Cyclic Voltammetry. Cyclic voltammetry was carried out in DMF solution containing 0.1 M (1 M = 1 mol dm^{-3}) TEAP as a supporting electrolyte on a hanging mercury drop electrode (HMDE). The cathode potential was referred to Ag/AgCl, aq 1 M KCl. Cyclic potential sweeps were generated by an NF Circuit Desigh Block FG-100AD function generator in connection with a potentionstat which was self-made according to the literature.25)

Controlled Potential Macro-electrolysis. For controlled potential macro-electrolysis, a three compartment cell was employed in which the cathodic and anodic chambers were separated by two porous glass disks and a reference electrode with a Luggin capillary was put near the cathode. A mercury pool with a surface area of 16 cm^2 was used as the cathode, and platinum gauze as the anode. The electrolyte solution (0.1 M TEAP) of 60 cm^3 containing 0.06 M substrate was placed in the cathodic chamber, 40 cm^3 of electrolyte solution in the anodic chamber, and 10 cm^3 of electrolyte solution in the middle chamber. Oxygen was bubbled through the catholyte. The cathode potential was controlled with a Yanagimoto VE-8 controlled potential electrolyzer.

Separation of Products and Determination of the Yields. The main products of the electrolyses, nitrophenols, were separated and identified by the following procedure. The catholyte was poured into 200 cm^3 of 10% aqueous $NaHCO_3$ solution. Starting material and products other than nitrophenols were removed by extraction with CH_2Cl_2. The aqueous layer was evaporated to dryness *in vacuo* to remove DMF. The resulting solid was dissolved in water and acidified with 5% aqueous

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† On leave from Department of Organic Chemistry, University of Aarhus, DK-8000, Aarhus C, Denmark.

HCl. The liberated nitrophenol was extracted with ether and purified by recrystallization from ethanol and weighed. The crystalline nitrophenol was identified by comparing its melting point and infrared spectrum (IR) with those of an authentic sample. The by-products of electrolysis, such as nitrobenzene and dinitrobiphenyls, were detected by using a Shimadzu gas chromatograph Model GC-6A equipped with 2 m×3ϕ SUS column packed with Silicone OV-1, and identified by comparing their retention times with those of authentic samples. Yields of products were also determined by gas chromatographic analysis.

Results and Discussion

Controlled Potential Macro-electrolysis. The reduction peak potentials of cyclic voltammograms of XNBs, together with those for oxygen, nitophenols, and nitrobenzene, are listed in Table 1. The controlled potential macro-electrolysis of oxygen in the presence of *p*-bromonitrobenzene (*p*-BNB) was carried out at −0.9 V in DMF solution. At −0.9 V, oxygen was reduced to superoxide ion while *p*-BNB was not reduced. The results of electrolysis are collected in Table 2. *p*-BNB reacted with electro-generated superoxide ion to yield *p*-nitrophenol as the main product. Trace amounts of nitrobenzene and 4,4′-dinitrobiphenyl were detected as by-prodects. In order to investigate the positional effect of the nitro group attached to the benzene ring, macro-electrolyses of oxygen in the presence of *o*- and *m*-BNB were also carried out. *o*-BNB reacted with electro-generated superoxide ion to yield *o*-nitrophenol as the main product. Trace amounts of nitrobenzene and 2,2′-dinitrobiphenyl were detected as by-products. *m*-BNB did not react with electro-generated superoxide ion and starting material was recovered.

Table 1. Reduction peak potentials of halogeno-nitrobenzenes by cyclic voltammetry

Compound	E_p^1	E_p^2	E_p^3
o-Fluoronitrobenzene	−1.09	−2.01	
m-Fluoronitrobenzene	−1.00	−1.90	
p-Fluoronitrobenzene	−1.12	−2.07	
o-Chloronitrobenzene	−1.10	−1.85	
m-Chloronitrobenzene	−1.00	−1.86	
p-Chloronitrobenzene	−1.04	−1.91	
o-Bromonitrobenzene	−1.12	−1.85	
m-Bromonitrobenzene	−0.94	−1.78	
p-Bromonitrobenzene	−1.02	−1.86	
o-Iodonitrobenzene	−0.96	−1.05	−1.77
m-Iodonitrobenzene	−0.96	−1.05	−1.90
p-Iodonitrobenzene	−1.02	−1.15	−1.92
o-Nitrophenol	−0.89	−1.85	
m-Nitrophenol	−1.19	−1.52	
p-Nitrophenol	−1.30	−1.95	
Nitrobenzene	−1.10	−1.95	
Cf. Oxygen	−0.85	−1.75	

E/V *vs.* Ag/AgCl, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE.

Table 2. Controlled potential macro-electrolysis of oxygen in the presence of bromonitrobenzenes

Starting material	Product	Yield/%
o-Bromonitrobenzene	*o*-Nitrophenol	39
	Nitrobenzene	2—3
	2,2′-Dinitrobiphenyl	1—2
m-Bromonitrobenzene	—	—
p-Bromonitrobenzene	*p*-Nitrophenol	52
	Nitrobenzene	1—2
	4,4′-Dinitrobiphenyl	1

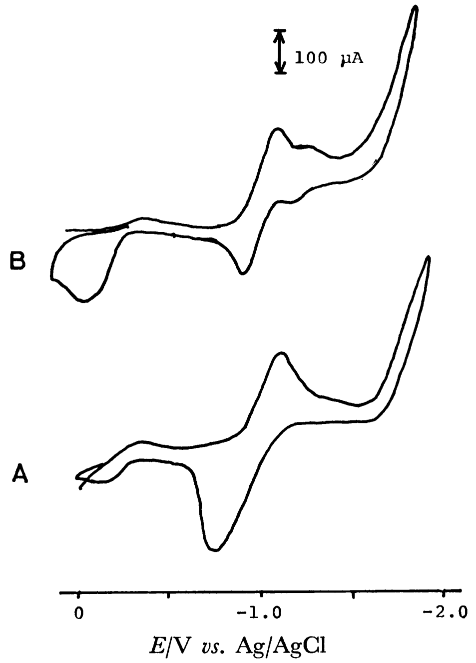


Fig. 1. Cyclic voltammograms of the catholyte in the course of the electrolysis at −0.9 V in the presence of *p*-bromonitrobenzene (oxygen is removed from the solution).
Electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, A: after 1 h, B: after 6 h.

Cyclic Voltammetry of the Catholyte. In the course of macro-electrolysis of oxygen at −0.9 V in the presence of *p*-BNB, cyclic voltammetry of the catholyte was carried out. The result is shown in Fig. 1. A and B are the cyclic voltammograms of the catholyte after 1 h and 6 h respectively from commencement of macro-electrolysis. During these cyclic voltammetric experiments, oxygen was removed by bubbling nitrogen. Since *p*-BNB remained as a major substrate in the solution, two large reduction waves observed at *ca.* −1.1 V and −1.8 V are attributed to *p*-BNB. The oxidation wave at *ca.* −0.13 V results from bromide ion as is described later. While no reduction wave other than that for *p*-BNB is appreciable on curve A, a new reduction wave is apparent at *ca.* −1.3 V on curve B. On curve B, the oxidation peak height of bromide ion is greater in comparison with that on curve A.

Cyclic Voltammetry of Bromonitrobenzenes (BNBs). In order to clarify the reaction mechanism of the reaction of electro-generated superoxide ion with XNBs,

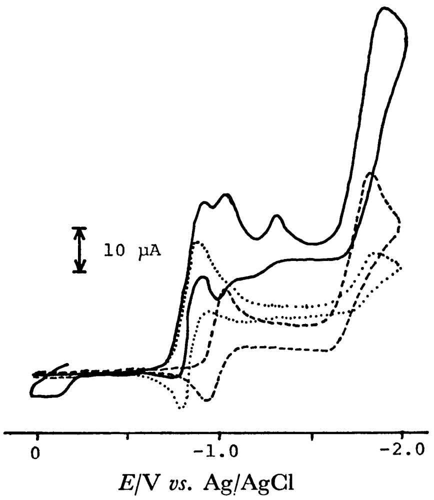


Fig. 2. Cyclic voltammograms of *p*-bromonitrobenzene. Concentration of *p*-bromonitrobenzene: *ca.* 1 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ——: in the presence of air-saturated oxygen, ------: in the absence of oxygen, *cf.* ······: cyclic voltammogram of air-saturated oxygen.

cyclic voltammetry of *o*-, *m*-, and *p*-BNB was carried out under air-saturation and under a nitrogen atmosphere. The cyclic voltammetric behaviors of *p*-BNB are shown in Fig. 2. The broken line represents the cyclic voltammogram of *p*-BNB under a nitrogen atmosphere and the solid line that under air-saturation. The dotted line represents the cyclic voltammogram of air-saturated oxygen. For *p*-BNB under a nitrogen atmosphere, only a reversible reduction wave at −1.0 V and an irreversible reduction wave at *ca.* −1.8 V were observed. On the other hand, under air saturation, a new reduction wave at *ca.* −1.3 V appeared on the first cathodic sweep, and another new wave was seen at *ca.* −0.13 V on the anodic sweep, in addition to the waves observed for oxygen alone and for *p*-BNB under nitrogen. On the subsequent cathodic sweep, a new wave, corresponding to the reduction of the oxidation product at −0.13 V, appeared at *ca.* −0.17 V. The peak potential of the new wave at −1.3 V corresponds accidentally to the first reduction peak potential of *p*-nitrophenol as is shown in Fig. 3. The first reduction wave of *p*-nitrophenol is the phenoxide formation from phenol.[26] Consequently the new reduction wave may not be that of *p*-nitrophenol because *p*-nitrophenol exists as phenoxide in such an aprotic medium as DMF even if *p*-nitrophenol is formed during cyclic voltammetry. The product showing this new reduction wave seemed to be dinitrophenyl peroxide as described later. Since the peak height of the redox wave near −0.15 V increased on addition of NaBr, this redox wave is attributed to the redox reaction of bromide ion at the mercury electrode. Consequently these additional wave of bromide and the product, observed only in the case of the simultaneous electro-reduction of oxygen, suggest the following. (1) The electro-generated superoxide ion reacted with *p*-BNB to release bromide ion and to give the redox wave during cyclic voltammetry. (2) A compound probably assigned dinitrophenyl peroxide was produced during cyclic voltammetry by the reaction of electro-generated superoxide ion with *p*-BNB.

In the cyclic voltammogram of *p*-BNB under air-saturation, the first reduction peak height of oxygen at *ca.* −0.85 V increased, and the reoxidation peak height of superoxide ion at −0.80 V diminished, in comparison with those of air-saturated oxygen in the absence of *p*-BNB (dotted line in Fig. 2). These behaviors depended on the concentration of *p*-BNB. In order to clarify the dependence of the increase of the reduction peak height of oxygen on the concentration of *p*-BNB, cyclic voltammetry of oxygen in the presence of increasing concentrations of *p*-BNB was carried out in the potential region

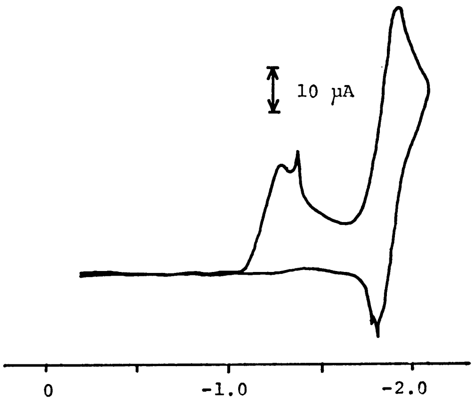


Fig. 3. Cyclic voltammogram of *p*-nitrophenol under nitrogen atmosphere.
Concentration of *p*-nitrophenol: *ca.* 10 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}.

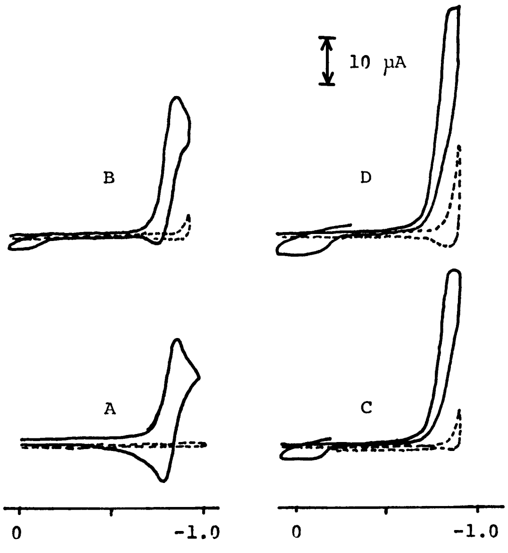


Fig. 4. Cyclic voltammograms of oxygen in the presence of increasing concentration of *p*-bromonitrobenzene. A: 0 mM, B: *ca.* 1 mM, C: *ca.* 4 mM, D: *ca.* 8 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ——: air-saturation, ------: under nitrogen atmosphere.

from 0 to −1.0 V. The results are shown in Fig. 4. A is the cyclic voltammogram of air-saturated oxygen in the absence of *p*-BNB. Cyclic voltammograms of oxygen in the presence of increasing concentrations of *p*-BNB are shown in Figs. 4B, C, and D, in the order of increasing concentrations of *p*-BNB. Increasing concentration of *p*-BNB resulted in a corresponding increase in the reduction peak height of oxygen. This increase in height with increasing concentration of *p*-BNB did not continue infinitely but reached a limit. The maximum value of the ratio, i_c/i_p, for *p*-BNB is *ca.* 2, where i_c is the reduction peak height of oxygen in the presence of XNB and i_p is the peak height in the absence of XNB. Under a nitrogen atmosphere no oxidation wave corresponding to that of bromide ion appeared, as shown in Fig. 4A, while in the presence of air-saturated oxygen the oxidation wave of bromide ion was observed and the peak height increased with increasing concentration of *p*-BNB. Disappearance of the oxidation wave of superoxide ion indicates that the electro-generated superoxide ion was consumed by subsequent chemical reaction during cyclic voltammetry in the presence of a high concentration of *p*-BNB.

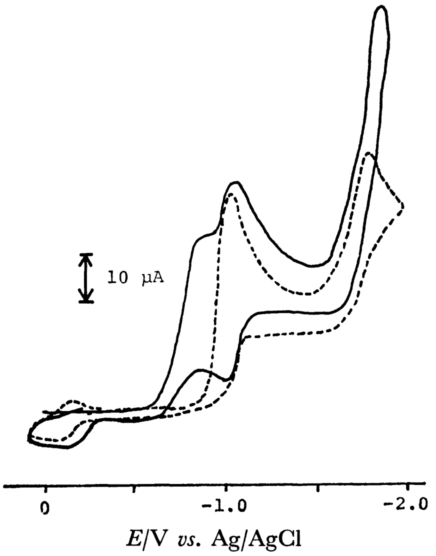


Fig. 5. Cyclic voltammograms of *o*-bromonitrobenzene. Concentration of *o*-bromonitrobenzene: *ca.* 10 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ——: in the presence of air-saturated oxygen, ------: in the absence of oxygen.

In order to investigate the positional effect of the nitro group attached to the benzene ring, cyclic voltammetry of oxygen in the presence of increasing concentrations of *o*- and *m*-BNB was also carried out. The reduction peak height of oxygen increased in the presence of increasing concentration of *o*-BNB. This increase did not continue infinitly and the maximum of the i_c/i_p ratio for *o*-BNB is also *ca.* 2. Cyclic voltammetric behaviors of *o*-BNB in the presence and in the absence of oxygen are shown in Fig. 5. Under nitrogen atmosphere, the first reduction wave of *o*-BNB on the first cathodic sweep is irreversible, while that of *p*-BNB is reversible, and a redox wave corresponding to that of bromide ion appeared on the anodic sweep and on the subsequent cathodic sweep in spite of the absence of oxygen. In the presence of oxygen, the oxidation peak height of bromide ion also increased compared with that observed under a nitrogen atmosphere though the new reduction wave corresponding to the reduction of a product are not recognized. It is concluded from these results that bromide ion is released from *o*-BNB by an electrochemical reaction of *o*-BNB itself, but the reaction of electro-generated superoxide ion with *o*-BNB accelerates this release of bromide ion.

In the cyclic voltammogram of *m*-BNB in the presence of oxygen, no reduction wave appeared other than those for oxygen and *m*-BNB. An increased concentration of *m*-BNB did not results in a corresponding increase in the reduction peak height of oxygen, or in diminution of the reoxidation peak height of superoxide ion, in these cyclic voltammograms of oxygen in the presence of *m*-BNB. These results indicate that the electro-generated superoxide ion does not react with *m*-BNB during their cyclic voltammetry.

In order to investigate the difference in reactivity of electro-generated superoxide ion towards XNBs, dependent on the nature of substituted halogen, cyclic voltammetry of INBs, CNBs, and FNBs in the presence and in the absence of oxygen was carried out and is described in the following sections.

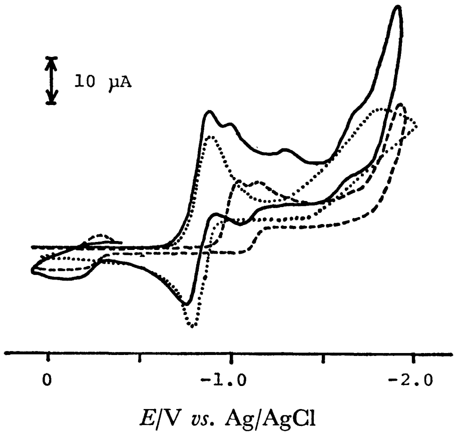


Fig. 6. Cyclic voltammograms of *p*-iodonitrobenzene. Concentration of *p*-iodonitrobenzene: *ca.* 1 mM, electrolyte: 0.1 M TEAP/DMF, electrode: HMDE, sweep rate: 0.1 V s^{-1}, ——: in the presence of air-saturated oxygen, ------: in the absence of oxygen, *cf.* ······: cyclic voltammogram of air-saturated oxygen.

Cyclic Voltammetry of Iodonitrobenzenes (INBs).
The cyclic voltammetric behavior of *p*-INB in the presence and in the absence of air-saturated oxygen is shown in Fig. 6, together with that of oxygen in the absence of *p*-INB. For *p*-INB under nitrogen, there are well-defined reduction waves near −1.0, −1.15, and −1.90 V on the cathodic sweep, and an oxidation wave near −0.2 V on the anodic sweep.[16b)] On the subsequent cathodic sweep, a new reduction wave corresponding to reduction of the oxidation product apperaed at *ca.* −0.25 V. Since the oxidation peak height at −0.2 V increased on addition of NaI as

for the bromide peak described above, this oxidation wave is assigned to that of iodide ion. Under air-saturation, two new reduction waves at *ca.* −1.30 V and −1.75 V appeared as well as those for oxygen and *p*-INB, and the peak height of the oxidation wave at *ca.* −0.2 V was increased in comparison with that under a nitrogen atmosphere. The first reduction peak height of oxygen increased and the reoxidation peak height of superoxide ion diminished as compared with that for air-saturated oxygen in the absence of *p*-INB (dotted line in Fig. 6).

The cyclic voltammetric behavior of *o*-INB in the presence and in the absence of oxygen is almost identical to that of *p*-INB except absence of the new reduction wave of the product in the presence of oxygen corresponding to that appeared at −1.3 V for *p*-INB. An increase in the concentration of *o*- and *p*-INB resulted in a corresponding increase in the reduction peak height of oxygen in the cyclic voltammograms. Maximum values of the ratio, i_c/i_p, for both *o*- and *p*-INB are also *ca.* 2. In the cyclic voltammogram of *m*-INB in the presence of oxygen, no reduction wave appeared other than those for oxygen and *m*-INB as for *m*-BNB. The reduction peak height of oxygen in the presence of *m*-INB did not increase in comparison with that of air-saturated oxygen in the absence of *m*-INB.

Cyclic Voltammetry of Chloronitrobenzenes (CNBs). The cyclic voltammetric behavior of *o*-, *m*-, and *p*-CNB in the presence and in the absence of oxygen are almost identical to those of *o*-, *m*-, and *p*-BNB, respectively. Namely, *o*- and *p*-CNB readily react with electro-generated superoxide ion while *m*-CNB dose not. The ratio, i_c/i_p, for *o*- and *p*-CNB also reached a limit with increase in the concentration of *o*- and *p*-CNB, and their maximum values were *ca.* 2.

Cyclic Voltammetry of Fluoronitrobenzenes (FNBs). Reversible and irreversible reduction waves appeared near −1.1 and −2.0 V in the cyclic voltammograms of *o*-, *m*-, and *p*-FNB under a nitrogen atmosphere. In the cyclic voltammograms of *o*-, *m*-, and *p*-FNB in the presence of oxygen, no reduction waves other than those for oxygen and FNB appeared. The electro-generated superoxide ion did not therefore react with FNBs during their cyclic voltammetry. Although an increase in the reduction peak height of oxygen was observed in the presence of *o*- and *p*-FNB, the maximum values of the ratio, i_c/i_p, are close to unity, *ca.* 1.1, compared with *ca.* 2 in the presence of *o*- and *p*-isomers of other XNBs. In the presence of *m*-FNB, this increase in the reduction peak height of oxygen was not observed.

Reaction Mechanism for the Reaction of Superoxide Ion with Halogenonitrobenzenes (XNBs). A mechanism for the reaction of electro-generated superoxide ion with XNBs can be proposed as shown in Schemes 1 and 2. Scheme 1 represents $S_N 2$ type reaction mechanism. This $S_N 2$ type reaction of superoxide ion is well known with alkyl halides and alkyl sulfonate esters.[22,23] Electrochemically produced superoxide ion at −0.85 V attacks the carbon atom bearing halogen on the XNB to release halide ion (Eq. 2). The resulting peroxyl radical is readily reduced, by superoxide ion or at the electrode, to peroxide anion $ArOO^-$ (Eq. 3). Scheme 2 represents the electron-transfer mechanism. Electron transfer reactions between superoxide ion and aromatic nitro compounds have been reported.[13] An electron is transferred from electro-generated superoxide ion to XNB to give an anion radical $[ArX]^{\cdot-}$ and oxygen is regenerated (Eq. 5). Halide ion is released from the anion radical $[ArX]^{\cdot-}$ to yield phenyl radical $Ar\cdot$ (Eq. 6). Peroxide anion $ArOO^-$ is then produced according to Eqs. 7 and 3. In both mechanisms two electrons per molecule of oxygen are necessary to finally obtain the peroxide anion.

$$O_2 + e \rightleftarrows O_2^{\cdot-} \qquad (1)$$

$$O_2^{\cdot-} + ArX \longrightarrow ArOO\cdot + X^- \qquad (2)$$

$$ArOO\cdot + O_2^{\cdot-} \longrightarrow ArOO^- + O_2 \qquad (3)$$

overall: (1) × 2 + (2) + (3)

$$O_2 + ArX + 2e \longrightarrow ArOO^- + X^- \qquad (4)$$

Scheme 1.

$$O_2 + e \rightleftarrows O_2^{\cdot-} \qquad (1)$$

$$O_2^{\cdot-} + ArX \longrightarrow [ArX]^{\cdot-} + O_2 \qquad (5)$$

$$[ArX]^{\cdot-} \longrightarrow Ar\cdot + X^- \qquad (6)$$

$$Ar\cdot + O_2 \longrightarrow ArOO\cdot \qquad (7)$$

$$ArOO\cdot + O_2^{\cdot-} \longrightarrow ArOO^- + O_2 \qquad (3)$$

overall: (1) × 2 + (5) + (6) + (7) + (3)

$$O_2 + ArX + 2e \longrightarrow ArOO^- + X^- \qquad (4)$$

Scheme 2.

Since in the cyclic voltammograms of *p*-BNB and *p*-CNB under a nitrogen atmosphere the oxidation wave of halide ion did not appear, the formed anion radicals $[ArX]^{\cdot-}$ are stable so that the elimination reaction as described in Eq. 6 could not occur during the period of cyclic voltammetry. In the presence of oxygen as shown in Fig. 2, the oxidation wave of halide ion appeared. These results support nucleophilic attack of superoxide ion on *p*-BNB and *p*-CNB as described in Eq. 2. In the cyclic voltammograms of INBs, *o*-BNB, and *o*-CNB, the oxidation wave of halide ion appeared even under a nitrogen atmosphere, and in the presence of oxygen these halide peaks increased further. These results indicate that these anion radicals $[ArX]^{\cdot-}$ are unstable compared with those of *p*-BNB and *p*-CNB, and that the electron transfer reaction of superoxide ion to XNB (Eq. 5) proceeds forwards to some extent. If the superoxide ion reacts with XNB *via* an electron transfer mechanism, then the yield of nitrobenzene and dinitrobiphenyls should be great because of the production of radical $Ar\cdot$ (Eq. 6). However, as the main products of the macro-electrolysis of oxygen in the presence of *o*- and *p*-BNB were *o*- and *p*-nitrophenol respectively (Table 2), the contribution of the electron transfer reaction mechanism operating in these case is considered to be slight.

The difference in reactivity of electro-generated superoxide ion towards XNBs dependent on the nature of substituted halogen and on the position of the nitro group attached to benzene ring is discussed next. The maximum values of the ratio, i_c/i_p, of the reduction peak heights of oxygen in the presence of *o*- and *p*-

isomers of INB, BNB, and CNB are *ca.* 2. This result corresponds well with the fact that two electrons are necessary to produce peroxide anion $ArOO^-$ from XNB in Scheme 1, but disagrees with usual EC catalytic mechanism.[27] In the cyclic voltammograms of the *m*-isomers of INB, BNB, and CNB, the reduction peak heights of oxygen did not increase in the presence of high concentrations of XNB. In the case of FNBs, the reduction peak heights of oxygen did not increase even in the presence of *o*- and *p*-FNB. It has been reported that potassium superoxide reacted with some nitrophenyl halides[13] as electro-generated superoxide reacted with XNBs in this work but did not react with phenyl halides.[22] The difference in reactivity between nitrophenyl halides and phenyl halides is interpretable in terms of activation by the nitro group on the benzene ring. In the cyclic voltammograms of XNBs in the presence of oxygen, the high reactivities of *o*- and *p*-isomers of XNB, other than FNB, to superoxide ion are manifest, but the reactivity of *m*-isomers of XNB is seen to be very low.

The wave corresponding to the oxidation of peroxide anion $ArOO^-$ did not appear in Figs. 2, 5, and 6. This is probably due to the fact that its oxidation potential may be more positive than the measured potential region, as for alkylperoxide anion,[19] and also due to its reaction with XNB to yield bis(nitrophenyl) peroxides,[19] ArOOAr (Eq. 8). In general, the reduction peaks of dialkylperoxides appear at more negative potentials than −2.0 V *vs.* SCE (Et_2O_2; −2.15 V, Bu_2O_2; −2.19 V, $Bu^t{}_2O_2$; −2.4 V *vs.* SCE).[19] Since the bis(nitrophenyl) peroxides formed in this study have two nitro groups, their reduction peak potential should be more positive than those of dialkyl compounds. The first reduction potentials of organic nitro compounds between −1.0 and −1.2 V *vs.* SCE. The reduction of bis(nitrophenyl) peroxides by electrogenerated superoxide ion cannot occur because the maximum value of the i_c/i_p ratio is not over two. Consequently the reduction potentials of bis(nitrophenyl) peroxides lie at more negative potential than that of oxygen. The reduction wave of the bis(*p*-nitrophenyl) peroxide may correspond to the new reduction wave at *ca.* −1.3 V in Figs. 2 and 6, and that of the bis(*o*-nitrophenyl) peroxide may overlap with those of *o*-XNBs, and thus the new wave are not appreciable in Fig. 5.

As probable mechanisms for formation of phenols, two mechanisms can be proposed in the same manner as

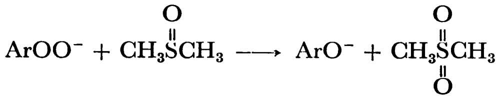
$$ArOO^- + ArX \longrightarrow ArOOAr + X^- \qquad (8)$$

$$\begin{aligned} ArOOAr + O_2^{\bar{\cdot}} &\longrightarrow ArO_3\cdot + ArO^- \\ &\quad \longrightarrow ArOOAr,\ ArO^-,\ O_2 \end{aligned} \qquad (9)$$

$$ArOOAr + O_2^{\bar{\cdot}} \longrightarrow ArO\cdot + ArO^- + O_2 \qquad (10)$$

$$ArO\cdot + O_2^{\bar{\cdot}} \longrightarrow ArO^- + O_2 \qquad (11)$$

Scheme 3.



$$ArOO^- + CH_3\overset{O}{\overset{\|}{S}}CH_3 \longrightarrow ArO^- + CH_3\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}CH_3 \qquad (12)$$

Scheme 4.

for the reaction of superoxide ion with alkyl halides[28,29] as shown in Schemes 3 and 4. If Reaction 9 or 10 and 11 proceed rapidly, the ratio i_c/i_p will exceed two due to the regeneration of oxygen *via* these reactions. Since the observed ratios were *ca.* 2, these reactions might be too slow to occure in the period of cyclic voltammetry.[19] On the other hand, nitrophenols can be formed without further consumption of electron *via* reaction 12 shown in Scheme 4. However this reaction is characteristic of dimethyl sulfoxide, and it is hardly applicable to the reaction in DMF.[29] Thus in the present system nitrophenols may be formed *via* the mechanism shown in Scheme 3 rather than the mechanism in Scheme 4. However, as shown in Fig. 1B, the appearance of the new reduction peak at *ca.* −1.3 V attributed to ArOOAr are clear, while the wave corresponding to the reduction of phenoxide is difficult to appreciate due to overlapping of the expected wave to that of the abundant starting material. From these results, therefore, it is not clear yet whether phenol obtained was produced during the macro-electrolysis according to the mechanism described in Scheme 3 or it was produced during the procedure for separation and purification. However it is difficult to determine the more probable mechanism for formation of nitrophenols between the reaction path of Reaction 9 and that of Reactions 10 and 11 from our present results.

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