

## Electrochemical Studies on the Reaction of Superoxide Ion with Halocarbons in Aprotic Media

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**Abstract :** The reactivity of superoxide ion ( $O_2^{\cdot-}$ ) with halogenated substrates is investigated by cyclic voltammetry and rotated ring-disk electrode method in aprotic solvents. The more positive the reduction potential of the substituted nitrile, the more facile is nucleophilic displacement by  $O_2^{\cdot-}$ . The reaction rates of halogenonitriles with  $O_2^{\cdot-}$  vary according to the leaving-group propensity of halide ( $Br > Cl > F$ ). The relative reaction rates of other substituted nitriles are in the order of electron-withdrawing propensity of the substituent group ( $CN > C(O)NH_2 > Ph, CH_2CN$ ). The reaction of  $O_2^{\cdot-}$  with dihalocarbons indicates that five-membered rings can be rapidly formed by the cyclization of substrate and  $O_2^{\cdot-}$ , and the relative rates of cyclization depend on the number of methylenic carbons ( $\{Br(CH_2)_nBr, [n=1 < 2 < 3 > 4 > 5]\}$ ). Mechanisms are proposed for the reaction of  $O_2^{\cdot-}$  with halogenated substrates.

**Keywords :** Cyclic voltammetry, Rotating ring-disk electrode, Dioxygen reduction, Superoxide ion, Halogenonitriles, Dihalocarbons

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### 1. Introduction

Although superoxide ion ( $O_2^{\cdot-}$ ) is a powerful nucleophile in aprotic media[1-3], it is deactivated in water because of its large hydration energy (~100 kcal) and rapid hydrolysis and disproportionation[4,5]. In aprotic media stable solutions of  $O_2^{\cdot-}$  can be prepared

by electrochemical[6-10] and chemical[11-14] reduction of dioxygen. The reactivity of  $O_2^{\cdot-}$  with alkyl halides via nucleophilic substitution in aprotic solvents was first reported in 1970[15,16]. These and subsequent kinetic studies confirm that the reaction is first order in substrate in aprotic media[17-19], that the

attack by  $O_2^{\cdot-}$  results in inversion of configuration[20-25]. Polyhalogenated aromatic hydrocarbons [e.g., hexachlorobenzene ( $C_6Cl_6$ ) and polychlorobiphenyls (PCB's)] are rapidly degraded by superoxide ion to bicarbonate and halide ions in aprotic solvents[3,26-28]. Vicinal dibromoalkanes react with  $O_2^{\cdot-}$  to produce products of carbon-carbon bond cleavage[29]. It has been proposed that superoxide ion reacts with nitriles by proton abstraction[30] and by nucleophilic addition[31,32], and that nitrile reacts with hydroperoxide ion ( $HOO^-$ ) or  $HO^-$  that is generated from the disproportionation of superoxide ion by water[33,34]. The possibility of a nitrile reaction via the addition of superoxide ion to its triple bond cannot be fully excluded. In fact,  $NaO_2$  converts aliphatic and aromatic nitriles into the corresponding amides[20]. The rate for the ( $HOO^- + CH_3CN$ ) reaction is faster than that for the ( $HO^- + CH_3CN$ ) reaction[33];  $ROO^-$  can also convert nitriles to amides[35]. The present study has been directed to the evaluation of the reactivity of electrogenerated  $O_2^{\cdot-}$  with halogenonitriles and dihalocarbons [ $X(CH_2)_nX$ ,  $X=Br$  or  $Cl$ ,  $n=2-6$ ].

## 2. Experimental

Tetraethylammonium perchlorate [TEAP( $Et_4NClO_4$ )] from G. F. Smith Chemicals was vacuum-dried over  $P_2O_5$  for 24 hours prior to use as the supporting electrolyte (0.1 M TEAP). Bromoacetonitrile ( $BrCH_2CN$ ), 2-bromopropionitrile [ $BrCHMeCN$ ], and malononitrile ( $CNCH_2CN$ ) were used without further purification. All other solvents and chemicals were analytical grade or highest purity available and were used as received.

The cyclic voltammetric measurements were accomplished with a three electrode potentiostat (EG & G PAR 273). The electrochemical measurements were made with a microcell assembly (10-mL capacity) that

was adapted to use a platinum (area,  $0.023\text{ cm}^2$ ) or a glassy-carbon (area,  $0.06\text{ cm}^2$ ) inlay working electrode, a platinum-wire auxiliary electrode (contained in a glass tube with a medium-porosity glass-frit and filled with a concentrated solution of supporting electrolyte), and a  $Hg/Hg_2SO_4$  (sat'd  $K_2SO_4$ ) (+0.40V vs SCE) was used as the reference electrode. Rotating ring-disk experiments were conducted with a bipotentiostat (EG & G PAR 366A). A glassy carbon disk/platinum ring electrode was used. The electrochemical cell assembly was treated with  $HNO_3$  overnight and repeatedly soaked in a distilled water bath, and oven-dried at  $140^\circ C$  for several hours. The electrode surfaces were polished with alumina and Buehler finest quality microcloth immediately prior to each experiment.

The apparent reaction rates for superoxide ion with the various substrates were determined from cyclic voltammetric peak-current measurements[36] and rotating ring-disk electrode method[37]. The reaction stoichiometry of superoxide ion per substrate ( $O_2^{\cdot-}/S$ ) was determined by adding a known amount of substrate to a known excess of  $O_2^{\cdot-}$  in aprotic solvents. The unreacted  $O_2^{\cdot-}$  was assayed by anodic voltammetry. The reaction products from the stoichiometric combination of  $O_2^{\cdot-}$  and substrates were characterized by cyclic voltammetry, UV-VIS spectroscopy, GC, and GC-MS. Halide-ion products were assayed by  $AgNO_3$  titration. For the potentiometric titration of halide ion, 10 mL of distilled water and 0.5 mL of 98% of  $H_2SO_4$  were added to the 10-mL aprotic solution. Argon gas was introduced continuously into the solution during the titration. Cyanate ion in the reaction mixture was quantitatively assayed by a spectrophotometric method [based on the  $(py)_2(NCO)_2Cu^{II}$  complex][38].

## 3. Results and Discussion

Halogenonitriles exhibit a single irreversible two-electron reduction in aprotic solvents (Table I). Their effect on the electrochemical reduction of  $O_2$  is illustrated in Figure 1. The cathodic peak current ( $i_{p,c}$ ) for  $O_2$  increases and the anodic peak current ( $i_{p,a}$ ) for the reverse scan decreases. This is consistent with the effect of alkylhalides in general and is the result of a reaction between  $O_2^{\cdot-}$  and halogenonitriles. The anodic peaks at +0.75 V and +1.00 V vs SCE after a negative scan to -2.5 V indicate that  $Br^-$  and  $Cl^-$ , respectively, are produced from the  $O_2^{\cdot-}$ /substrate reaction. In MeCN, the halogenonitriles give a single cathodic peak at almost the same potential as in DMF. Controlled-potential reductive electrolysis of  $O_2$  in the presence of excess  $Br(R)CHCN$  ( $R=H$  or  $Me$ ) yields  $Br^-$ ,  $NCO^-$ , and aldehyde  $[RCH(O)]$ . The apparent reaction rates for  $O_2^{\cdot-}$  with halogenonitriles are determined from cyclic voltammetric peak-current measurements[36]. The reaction stoichiometry of superoxide ion per substrate ( $O_2^{\cdot-}/S$ ) was determined by adding a known amount of substrate to a known excess of  $O_2^{\cdot-}$  in aprotic solvents.

Table I. Voltammetric Reduction Potentials ( $E_{p,c}$ ) for Substituted Acetonitriles, and the Stoichiometries and Kinetics for Their Reactions with  $O_2^{\cdot-}$  in aprotic solvents [0.1 M (Et<sub>4</sub>N)ClO<sub>4</sub>].

substrate (S)	$E_{p,c}$ <sup>a</sup> V vs SCE	$O_2^{\cdot-}$ <sup>b</sup>	$k/[S]$ <sup>c</sup> , M <sup>-1</sup> s <sup>-1</sup> DMF
FCH <sub>2</sub> CN	-2.6	2±0.5	$1.3±0.3 \times 10^1$
ClCH <sub>2</sub> CN	-1.9	2±0.5	$1.3±0.3 \times 10^3$
BrCH <sub>2</sub> CN	-1.4	2±0.3	$1.5±0.3 \times 10^3$
Br(Me)CHCN	-1.5	2±0.3	$1.4±0.3 \times 10^3$
NOCH <sub>2</sub> CN	-2.5	2±0.4	$3.5±0.5 \times 10^2$
NOCH <sub>2</sub> C(O)NH <sub>2</sub>	<-3.0	2±0.5	$1.0±0.3 \times 10^2$
NOCH <sub>2</sub> CH <sub>2</sub> CN	-3.0	2±0.5	$5.0±1.0 \times 10^1$
PhCH <sub>2</sub> CN	-2.9	2±0.5	$4.9±1.0 \times 10^1$
C <sub>6</sub> H <sub>5</sub> CN	-2.4 <sup>d</sup>		

<sup>a</sup>GC electrode; scan rate 0.1 V s<sup>-1</sup>.

<sup>b</sup> $O_2^{\cdot-}$  consumed per S

<sup>c</sup>Pseudo first-order rate constant,  $k$  (normalized to unit substrate concentration  $[S]$ ;  $[O_2] = 1$  mM).

<sup>d</sup>Reversible one-electron couple ( $E_{p,a}$ , -2.3 V vs SCE).

The unreacted  $O_2^{\cdot-}$  was assayed by anodic voltammetry. Meanwhile, the apparent pseudo-first order rate constants for  $O_2^{\cdot-}$  with the halogenonitriles are confirmed by the rotating ring-disk electrode technique;  $O_2$  is reduced at the disk to  $O_2^{\cdot-}$  which reacts with substrate, and the unreacted  $O_2^{\cdot-}$  is oxidized at the ring electrode. The reaction stoichiometry is two electrons ( $2 O_2^{\cdot-}$ ) per substrate molecule of  $Br(R)CHCN$  ( $R=H$  or  $Me$ ). The stoichiometries and kinetics for the reactions between  $O_2^{\cdot-}$  and substituted nitriles (RCN) are summarized in Table I. The reactivity of  $O_2^{\cdot-}$  with halogenonitriles in MeCN is about one-fourth of that in DMF. The overall reaction stoichiometry and products from the combination of  $O_2^{\cdot-}$  and the bromonitriles  $[Br(R)CHCN]$ .

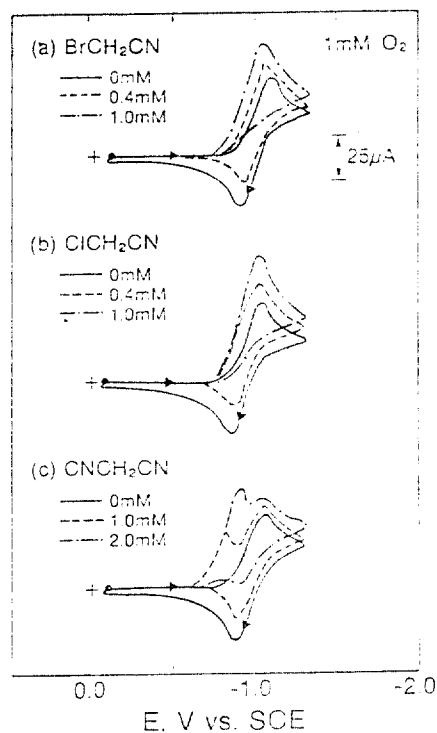
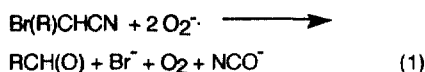


Fig. 1. Effect of halogenoacetonitriles on the cyclic voltammograms of 1 mM  $O_2$  at a GC electrode in DMF. (a)  $BrCH_2CN$ , (b)  $ClCH_2CN$ , and (c)  $NCCH_2CN$ . 0.1 M  $Et_4NClO_4$ , scan rate 0.1 V s<sup>-1</sup>.

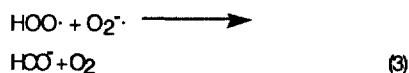
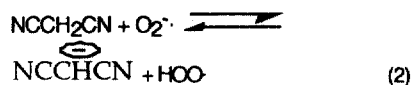
R = H or Me] in aprotic solvents are represented by Eq. 1 (Table I).



Because half of the Br(R)CHCN remains unreacted from a 1:1 Br(R)CHCN/O<sub>2</sub><sup>·-</sup> combination, the primary step must be rate limiting and followed by a rapid step that consumes a second O<sub>2</sub><sup>·-</sup>. A reasonable reaction sequence is nucleophilic attack of the halocarbon by O<sub>2</sub><sup>·-</sup> with displacement of halide ion as the rate-limiting step. The resulting peroxy radical is reduced by a second O<sub>2</sub><sup>·-</sup> to peroxide ion. The resulting peroxide ion attacks the adjacent cyano group to give a dioxetanimine intermediate via intramolecular ring formation, which homolytically dissociates to an aldehyde and a cyanate ion. Neighboring group participations are well known and the related intramolecular four-membered ring formation is 10<sup>2</sup> ~ 10<sup>3</sup> times as fast as the intermolecular reaction[39].

The electrochemical reduction of O<sub>2</sub> in the presence of NCCH<sub>2</sub>CN exhibits a unique prewave in addition to the regular quasi-reversible couple (Figure 1). The new peak increases in height and shifts to more negative potentials with increasing concentrations of NCCH<sub>2</sub>CN, and finally merges with the regular O<sub>2</sub>/O<sub>2</sub><sup>·-</sup> couple. Because the reaction rate between CNCH<sub>2</sub>CN and O<sub>2</sub><sup>·-</sup> is faster than that of PhCH<sub>2</sub>CN, the primary path must be a Brønsted acid-base reaction to give  $\overset{\ominus}{\text{N}}\text{CCHCN}$ , which is stable in the presence of O<sub>2</sub> and reacts with water to regenerate CNCH<sub>2</sub>CN. NCCH<sub>2</sub>CN also reacts with HOO<sup>-</sup> (generated by the disproportionation of O<sub>2</sub><sup>·-</sup> with water) to give NCCH<sub>2</sub>C(O)NH<sub>2</sub> (E<sub>p,a.</sub> +0.14 V vs SCE; ε<sub>251</sub> nm = 15 mM<sup>-1</sup>s<sup>-1</sup> for its anion). The new prepeak for O<sub>2</sub> reduction in the presence of NCCH<sub>2</sub>CN (Figure 1) probably is due to the latter's Brønsted acidity towards O<sub>2</sub><sup>·-</sup>. An analogous prepeak for O<sub>2</sub> reduction is observed in acidified dimethylformamide[40]. Malononitrile (pK<sub>a</sub>' = 15.6 in DMF) reacts with O<sub>2</sub><sup>·-</sup> to

give  $\overset{\ominus}{\text{N}}\text{CCHCN}$  (E<sub>p,a.</sub> = +0.40 V vs SCE, ε<sub>226</sub> nm = 21 mM<sup>-1</sup>cm<sup>-1</sup>), which is stable in the presence of O<sub>2</sub>



However, the resultant HOO<sup>-</sup> reacts with NCCH<sub>2</sub>CN via nucleophilic addition followed by internal proton transfer to produce NCCH<sub>2</sub>C(OO<sup>-</sup>)NH. In turn the product hydrolyzes to give NCCH<sub>2</sub>C(O)NH<sub>2</sub> and O<sub>2</sub>.

The reactivity of O<sub>2</sub><sup>·-</sup> with substituted acetonitriles is affected by the electron-withdrawing and leaving propensities of the substituent group. The more positive the reduction potential of the substituted nitrile, the more facile is nucleophilic displacement by O<sub>2</sub><sup>·-</sup>. Likewise, the greater the electron-withdrawing by the substituents the smaller the pK<sub>a</sub> of the methylenic hydrogens. The results of Table I indicate that the reaction rates of halogenonitriles with O<sub>2</sub><sup>·-</sup> vary according to the leaving-group propensity of halide (Br>Cl>F). On the other hand, the relative reaction rates of other substituted nitriles are in the order of electron-withdrawing propensity of the substituent group (CN>C(O)NH<sub>2</sub>>Ph,CH<sub>2</sub>CN) vis-a-vis the Brønsted basicity of O<sub>2</sub><sup>·-</sup>. The slight decrease of the reaction rate of BrCH(Me)CN compared to BrCH<sub>2</sub>CN is due to weak electron-donation by the methyl group.

Superoxide ion readily reacts with substrates that have dihalide groups in aprotic solvents. The reaction stoichiometries and kinetics for the reaction of O<sub>2</sub><sup>·-</sup> with dihalocarbons, and voltammetric reduction potentials (E<sub>p,c</sub>) for dihalocarbons [X(CH<sub>2</sub>)<sub>n</sub>X, n=1-6, X= Br, Cl] in DMF are determined. There is a rough correlation between the apparent second order rate constants for the reaction of O<sub>2</sub><sup>·-</sup> with dihalocarbons and the number of methylene in substrates (Figure 2). The apparent reaction rates for O<sub>2</sub><sup>·-</sup> with the dihalocarbons are determined from cyclic voltammetric peak-current

measurements and rotating ring-disk electrode technique. The reaction stoichiometry of superoxide ion per substrate ( $O_2^{\cdot-}/S$ ) was determined by adding a known amount of substrate to a known excess of  $O_2^{\cdot-}$  in aprotic solvents. The results of Figure 3 indicate that five-membered rings can be rapidly formed by the cyclization of substrate and  $O_2^{\cdot-}$ , and the relative rates of cyclization depend on the number of methylenic carbons  $Br(CH_2)_nBr$  [ $n=1<2<3>4>5$ ]. Vicinal dibromoalkanes react with  $O_2^{\cdot-}$  to produce products of carbon-carbon bond cleavage. The mechanism proposed for these reactions is a nucleophilic attack on carbon followed by a one-electron reduction of the peroxy radical and nucleophilic displacement on the adjacent carbon to form a dioxetane that subsequently cleaves to form two molecules of aldehyde.

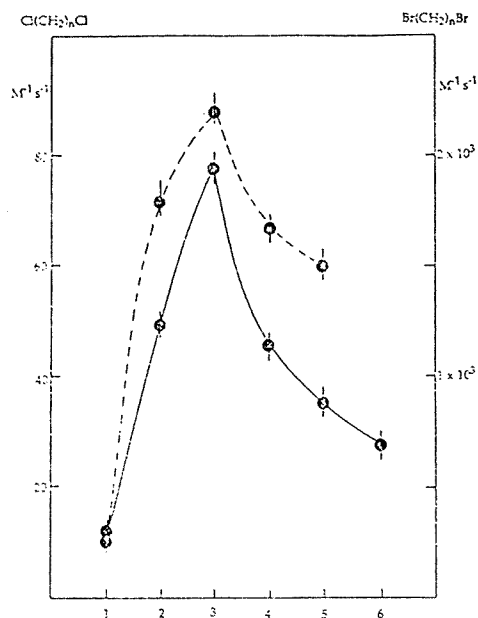


Fig. 2. Reaction rates of dihalohydrocarbons with  $O_2^{\cdot-}$  in relation to their carbon number in DMF. (—),  $Cl(CH_2)_nCl$ ; (---),  $Br(CH_2)_nBr$ .

Therefore, the reaction of  $O_2^{\cdot-}$  with  $Br(CH_2)_2Br$  as a kind of vicinal dibromo groups yields bromide ion, dioxygen, and two equivalents of formaldehyde. A reasonable mechanism for this cyclization is an initial nucleophilic attack of a bromo carbon by  $O_2^{\cdot-}$  as a rate limiting step, followed by displacement of a bromide ion. A second  $O_2^{\cdot-}$  reduces the peroxy radical to a peroxide ion, which attacks another bromo carbon to displace the second bromide ion to produce a ring intermediate.

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