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Electrochemical Study of Reaction of Hyperoxide with Tris(1,10-phenanthroline)iron(II) in Dimethyl Sulfoxide

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Reaction of hyperoxide with $Fe(phen)_3^{2+}$ in DMSO was studied by polarography, cyclic voltammetry, and spectroscopy. Voltammetric study of oxygen showed that disproportionation of hyperoxide is promoted by $Fe(phen)_3^{2+}$. Controlled potential coulometry exemplified the stoichiometry of the reaction to be 2:1 for hyperoxide to $Fe(phen)_3^{2+}$ in support of the proposed disproportionation mechanism of hyperoxide. Analysis of reaction products proved that $Fe(phen)_3^{2+}$ decomposes on reaction with hyperoxide in DMSO; the reaction products were iron(III) hydroxide and liberated ligands, neither metal hyperoxide nor oxygen bridged metal complexes being detected.

In aprotic media electrochemical reduction of oxygen occurs in two one-electron steps, the first step being well defined as formation of hyperoxide anion.[1-4] Effects of acids,[1-3] metal ions,[4,5] metal complexes,[6] water,[7] and organic materials[8] on oxygen waves have been studied, general characteristics of reactions of hyperoxide being reviewed by several authors.[9-11]

The discovery of metalloenzyme catalyzing hyperoxide dismutation[12,13] has increased interest in reactions of hyperoxide with transition metal complexes, and some low molecular weight metal complexes containing Mn(III), Cu(II), Fe(II), or Co(II) have been found to catalyze disproportionation of hyperoxide.[6,14-17]

Metal complexes of 1,10-phenanthroline are of interest, since they have heterocyclic nitrogen ligands similar to hystidine imidazole sites thought to be present in the enzyme.[13] However, quite few investigations have been performed on reactions of such complexes with hyperoxide.[14] In a preliminary work,[18] the authors presented that 1,10-phenanthroline complexes of Mn(II), Cu(II), or Fe(II) promote the disproportionation of hyperoxide in DMSO. The present paper is concerned with details of reaction of hyperoxide with $Fe(phen_3)^{2+}$ in DMSO.

Experimental

Materials. Dimethyl sulfoxide (DMSO) of Wako GR grade was shaken with dried activated alumina for one day and distilled twice under a nitrogen of reduced pressure. The portion distilled out at 53—54 °C at *ca.* 3 Torr (1 Torr≈133.322 Pa) was collected. Tetraethylammonium perchlorate (TEAP) was prepared as described elsewhere[19] and $Fe(phen)_3(ClO_4)_2 \cdot H_2O$ by literature method.[20] Potassium hyperoxide obtained from Alfa Division and 1,10-phenanthroline from Wako Pure Chemicals were used as received.

Apparatus and Procedure. The cyclic voltammetry and controlled potential electrolysis were performed on a potentiostat constructed according to a circuit configuration similar to the one cited in literature.[21] Modification was made in the current booster so as to supply max. 700 mA. The platinum electrode used for the cyclic voltammetry was soaked in aqua regia for 30 s and heated in a blue flame. The controlled potential electrolysis was carried out with both a platinum plate and a mercury pool cathode. The counter electrode was a spiral platinum electrode. The two compartments of the cell were separated with a fine sintered glass filter. The current through the cell was recorded on a coulometer by integrating the potential drop across a 10 Ω resistor placed in the electrolysis current path. The coulometer was constructed according to a circuit configuration described elsewhere.[22] Modification was made in the input circuit in such a way that it was replaced with an instrumentational amplifier. Correction for blank current was made in the measurement of electrolysis current. Polarograms were recorded on a Shimadzu RP 50 polarograph. Potentials are all referred to SCE as described previously.[19] All electrochemical measurements were thermostated at 25.0±0.2 °C. The UV and visible absorption spectra were measured on a Hitachi Model 100-60 spectrometer.

The solubility of oxygen in DMSO was determined by gas chromatography. Dry oxygen was bubbled through DMSO in a test tube for 30 min at 25.0 °C and the test tube was then sealed with a serum-type rubber stopper. In order to assure that all the oxygen bubbles had got off the solution, gas chromatographic measurements of oxygen were repeated at 30 min intervals until measured values became constant. The concentration of oxygen saturated in DMSO was determined to be 2.36 mmol dm^{-3} at 25.0 °C. The concentration of oxygen in the aerated DMSO was determined to be 0.42 mmol dm^{-3} at 25.0 °C by comparing the first polarographic reduction wave height of oxygen obtained in the aerated DMSO with that obtained in the oxygen-saturated DMSO.

Results and Discussion

Cyclic voltammograms of oxygen and $Fe(phen)_3^{2+}$ are given in Fig. 1. The cathodic and anodic current peaks of oxygen correspond to the well established reversible one-electron redox process:

$$O_2 + e^- \rightleftharpoons O_2^{\cdot-}. \tag{1}$$

The potential separation between the cathodic and anodic current peaks was 0.079 V, a little greater than 0.059 V, the separation for the reversible process, but sufficiently lower than those reported in literature.[1,9] The usual cyclic polarization method for pretreatment of the platinum electrode in DMSO[17] did not improve the potential separation between the cathodic and anodic current peaks lower than 0.11 V, indicating that the method for pretreatment performed in this work is preferred to the usual method and is recommendable as one of the best methods

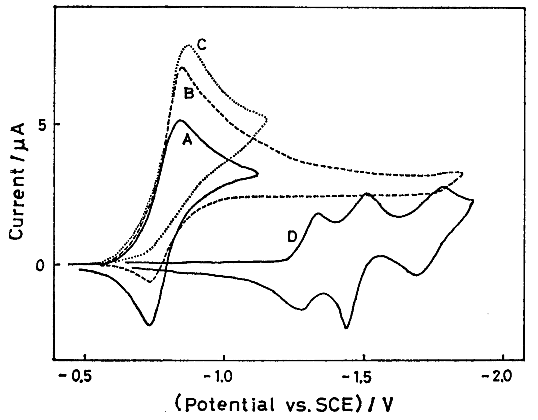


Fig. 1. Cyclic voltammograms of oxygen and Fe(phen)$_3^{2+}$ in DMSO containing 0.1 mol dm^{-3} TEAP. A: 0.42 mmol dm^{-3} O_2, B: 0.42 mmol dm^{-3} O_2+0.50 mmol dm^{-3} Fe(phen)$_3^{2+}$, C: 0.42 mmol dm^{-3} O_2+1.6 mmol dm^{-3} Fe(phen)$_3^{2+}$, D: 0.41 mmol dm^{-3} Fe(phen)$_3^{2+}$. Scan rate: 0.052 V s^{-1}.

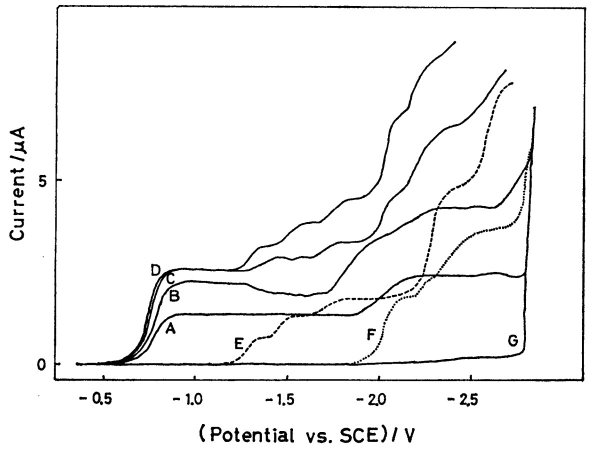


Fig. 2. Polarograms of O_2 and Fe(phen)$_3^{2+}$ in DMSO containing 0.1 mol dm^{-3} TEAP.
A: 0.42 mmol dm^{-3} O_2, B: 0.42 mmol dm^{-3} O_2+0.30 mmol dm^{-3} Fe(phen)$_3^{2+}$, C: 0.42 mmol dm^{-3} O_2+0.80 mmol dm^{-3} Fe(phen)$_3^{2+}$, D: 0.42 mmol dm^{-3} O_2+2.0 mmol dm^{-3} Fe(phen)$_3^{2+}$, E: 1.0 mmol dm^{-3} Fe(phen)$_3^{2+}$, F: electrolyzed solution of 0.41 mmol dm^{-3} Fe(phen)$_3^{2+}$, G: base current.

ever adopted.

Polarograms of oxygen and Fe(phen)$_3^{2+}$ are shown in Fig. 2. The logarithmic analysis of the first wave of oxygen gave a slope of 0.068 V. An ac polarographic current peak was observed at the first wave, showing that the first wave corresponds to the reversible one-electron process as given in Eq. 1.

When Fe(phen)$_3^{2+}$ was added to the solution, the cathodic current peak of the cyclic voltammogram of oxygen increased and the anodic current peak decreased in height as shown in Fig. 1. The first wave of polarogram increased in height with the addition of Fe(phen)$_3^{2+}$ as shown in Fig. 2, approaching asymptotically twice its original height as shown in Fig. 3. The half wave potential slightly shifted to less negative and the slope of the logarithmic analysis was 0.066 V after the first wave attained its maximun height.

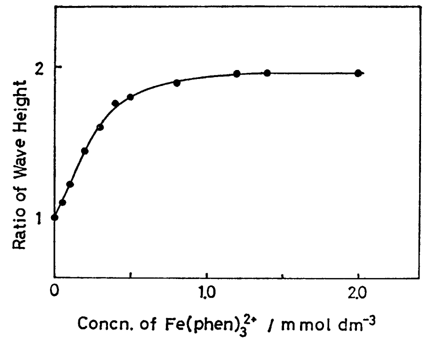


Fig. 3. Effect of Fe(phen)$_3^{2+}$ on the first wave height of the polarogram of O_2 in DMSO containing 0.1 mol dm^{-3} TEAP.
O_2: 0.42 mmol dm^{-3}.

These observations are well explained by the disproportionation mechanism: The regeneration of oxygen is promoted by the reaction of Fe(phen)$_3^{2+}$ on hyperoxide as shown in Eqs. 2—4:

$$\mathrm{Fe(phen)_3^{2+}} + \mathrm{O_2^{\cdot-}} \longrightarrow \mathrm{Fe(phen)_3^{2+}\cdot O_2^{\cdot-}}, \tag{2}$$

$$\mathrm{Fe(phen)_3^{2+}\cdot O_2^{\cdot-}} + \mathrm{O_2^{\cdot-}} \longrightarrow \mathrm{Fe(phen)_2^{2+}(O_2^{\cdot-})_2} + \mathrm{phen}, \tag{3}$$

$$\mathrm{Fe(phen)_2^{2+}(O_2^{\cdot-})_2} \longrightarrow \mathrm{Fe(phen)_2^{2+}O_2^{2-}} + \mathrm{O_2}. \tag{4}$$

This reaction mechanism is similar to that of the dissociation of Fe(phen)$_3^{2+}$ induced by the attack of nucleophilic anions:[27] The close approach of the metal and hyperoxide due to the formation of an ion pair (Eq. 2) causes the interaction between the π-orbital of hyperoxide and the antibonding d-orbital of the metal with resultant destabilization of the metal ligand bond and subsequent dissociation of the complex, the single bonded ligand in the intermediate being replaced with another hyperoxide (Eq. 3). The liberation of oxygen (Eq. 4) is caused by the formation of stronger Fe–O bonds with the bidentate peroxide ion according to a mechanism similar to that given for the liberation of oxygen in the reaction of hydrogen peroxide with triethylenetetramine-di-hydroxo-iron complex.[28]

The irregular minimum observed in the polarogram B in Fig. 2 appeared at a low concentration of Fe(phen)$_3^{2+}$. This minimum may be due to the adsorption of the reaction product inhibiting part of the electrode process. At higher concentrations of Fe(phen)$_3^{2+}$, the reduction waves of the metal complex and the reaction product are clearly seen to be superimposed on the oxygen wave.

In order to establish the stoichiometry for the reaction, a controlled potential reduction of oxygen was accomplished at −1.0 V *vs.* SCE in a DMSO solution containing 0.2 mmol dm^{-3} Fe(phen)$_3^{2+}$ and 0.1 mol dm^{-3} TEAP under continuous bubbling of dry oxygen. As electrolysis proceeds, the color of the solution changed from red to yellow and simultaneously an yellow substance precipitated on the cathode. The change of the UV and visible absorption spectra of the solution is given in Fig. 4.

The autoxidation of Fe(phen)$_3^{2+}$ within the time frame of the present experiment was completely ruled

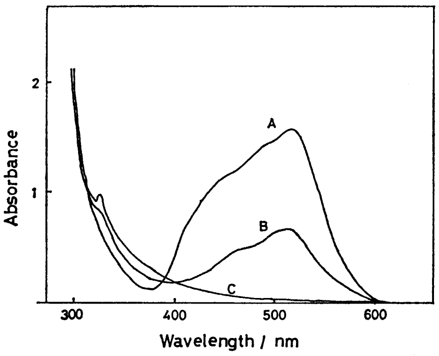


Fig. 4. UV and visible spectra of $Fe(phen)_3^{2+}$ in DMSO containing 0.1 mol dm^{-3} TEAP.
A: 0.20 mmol dm^{-3} $Fe(phen)_3^{2+}$, B: half electrolyzed, C: completely electrolyzed.

out by confirming that the spectrum of a solution with the same composition as that used for the electrolysis showed no substantial change under sunlight as well as in the dark for over 50 h.

By knowing the amount of current used for the electrolysis until the color of the solution turned yellow, 1.93 electrons were found to be required for each $Fe(phen)_3^{2+}$; namely, the stoichiometry of the reaction is 1:2 for $Fe(phen)_3^{2+}:O_2$, in accord with that required for Eqs. 1—4.

The peroxo complex shown in Eq. 4 is not a reaction product with a defined chemical structure but assumed to be a transiently lived reaction intermediate, since no peroxo species could be stable in DMSO.[23] Indeed, the direct mixing of a DMSO solution of KO_2 with one of $Fe(phen)_3^{2+}$ provided a dark violet solution which decayed in a few seconds, yielding an yellow solution and a brown precipitate. Although this transiently lived reaction intermediate has not been identified, it is supposed to be a peroxo complex as shown in Eq. 4. A similar peroxo complex has been found in reaction of Fe^{II}-edta with hyperoxide,[16] where a violet colored reaction intermediate was identified to be a peroxo complex of a formula of Fe^{III}-edta-O_2^{3-}.

Degradation of the peroxo complex may give an oxygen bridged iron complex, since formation of such a complex seems to be favored in aprotic media because it would not require utilization of water or proton donor. Indeed, a stable μ-peroxo-dicobalt(II) complex was obtained in DMSO in reaction of bis(acetylacetonato)Co(II) with hyperoxide.[6] For the autoxidation of iron containing porphyrin, where hyperoxide is considered to play an important role, an oxygen bridged iron dimer was suggested to be formed.[24] In order to check the formation of oxygen bridged iron complex, a μ-oxo complex of iron, $(Fe(phen)_2X)O(ClO_4)_2$, where X is Cl^- or NO_3^-, was prepared by literature method[25] in attempt to use it as a reference.

The cyclic voltammogram of the μ-oxo-diiron(II) complex is shown in Fig. 5. The reversible cathodic and anodic current peaks at −1.3—1.7 V *vs.* SCE are typical for the octahedral 1,10-phenanthroline complex of iron(II) since the lowest vacant molecular orbitals of the complex consist mainly of the π-orbital of the ligand.[26] The yellow colored solutions obtained by the electrolysis and the direct reaction of KO_2 with $Fe(phen)_3^{2+}$ showed no redox current peaks over the potential range shown in Fig. 5. Thus, any oxygen bridged complexes are ruled out as stable reaction products. The presence of hydrogen peroxide also was ruled out since the polarogram of the yellow solution did not give any waves corresponding to hydrogen peroxide.

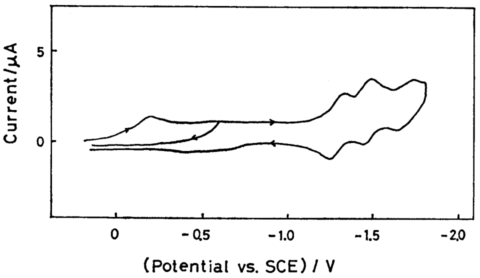


Fig. 5. Cyclic voltammogram of 0.20 mmol dm^{-3} $[\{Fe(phen)_2Cl\}O_2]^{2+}$ in DMSO containing 0.1 mol dm^{-3} TEAP.

The qualitative analysis of the yellow solution exemplified chemical properties quite similar to a DMSO solution containing both 1,10-phenanthroline and a saturated amount of iron(III) hydroxide: Addition of Fe^{2+} regenerated the spectrum of $Fe(phen)_3^{2+}$ but addition of 1,10-phenanthroline did not, indicating the presence of liberated 1,10-phenanthroline as well as the absence of free Fe^{2+}: Exposure to mercury gave no color change, showing the absence of free Fe^{3+} since a DMSO solution containing Fe^{3+} and 1,10-phenanthroline generates the spectrum of $Fe(phen)_3^{2+}$ upon reduction with mercury: Addition of hydrogen peroxide evolved oxygen, the spectrum of $Fe(phen)_3^{2+}$ being regenerated.

The yellow substance precipitated on the cathode turned brown when dried. The qualitative analysis of this as well as the brown precipitate obtained by

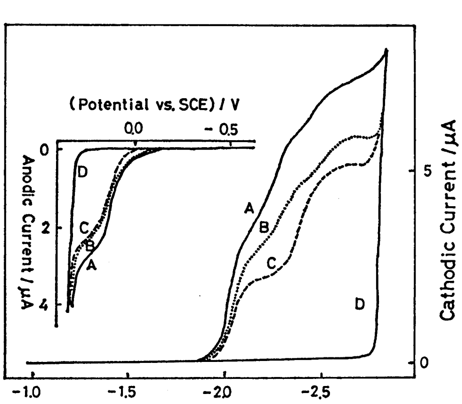
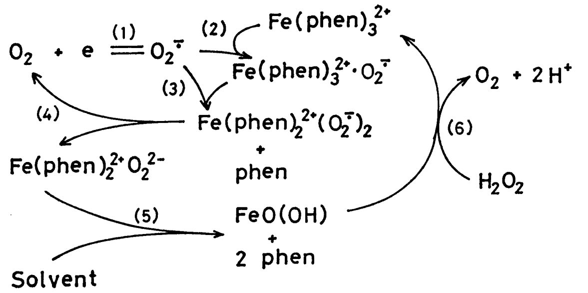


Fig. 6. Polarograms of DMSO solutions containing 0.1 mol dm^{-3} TEAP.
A: Electrolyzed solution of 0.81 mmol dm^{-3} $Fe(phen)_3^{2+}$, B: 1.7 mmol dm^{-3} 1,10-phenanthroline with saturated amount of iron(III) hydroxide, C: 1.9 mmol dm^{-3} 1,10-phenanthroline, D: base current.

direct mixing of KO_2 with $Fe(phen)_3^{2+}$ exhibited chemical properties similar to iron(III) hydroxide: They dissolved in acidic aqueous solution without evolution of gas, ruling out the presence of hyperoxide species in the precipitate; subsequent addition of 1,10-phenanthroline showed no color change, suggesting the absence of free Fe^{2+}; further exposure to mercury generated the spectrum of $Fe(phen)_3^{2+}$ due to the reduction of Fe^{3+}.

The polarographic results shown in Fig. 6 demonstrate that the polarogram of the yellow solution resulting from reaction of 1 mol of $Fe(phen)_3^{2+}$ with $O_2^{\cdot-}$ corresponds quantitatively to that of a solution containing *ca.* 3 mol of 1,10-phenanthroline and a saturated amount of iron(III) hydroxide.

These results indicate that $Fe(phen)_3^{2+}$ decomposes on reaction with hyperoxide. In this sense, $Fe(phen)_3^{2+}$ does not act as a catalyst but acts as a promoter for the disproportionation of hyperoxide, since an alternate reduction and oxidation of Fe^{2+}/Fe^{3+} is not involved in the reaction. The reaction scheme presented in this work is summarized as follows:



The mechanism of the degradation of peroxo complex (Reaction 5) may consist of the combination of the decomposition of peroxide ion in DMSO yielding hydroxide ion[23] and the fission of bis(phen)-iron(II) complex yielding iron(II) hydroxide with release of ligands.[27] The result that the final product was iron(III) hydroxide may be due to the oxidation of iron(II) hydroxide with DMSO, since the former is a strong reducing reagent and the latter an oxidizing one.

Reaction 6 was found to be too slow to expect to restore the catalytic activity of $Fe(phen)_3^{2+}$ during the electrochemical reaction. However, Reaction 6 would be noticeable as a reaction which demonstrates the restoration of the catalytic activity of $Fe(phen)_3^{2+}$ in DMSO.

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