—Communication—

One- and Two-Electron Reduction of Molecular Oxygen Based on Electrode Surface Modification in Alkaline Aqueous Media

Takeo OHSAKA*, Futoshi MATSUMOTO, Fusao KITAMURA
and Koichi TOKUDA

Received February 19, 1993; Accepted April 5, 1993

1. INTRODUCTION

Our current interest has concentrated on the electrochemical behavior of molecular oxygen (O_2) and so-called reactive oxygen species (ROS; superoxide ion (O_2^-), hydroxyl radical ($\cdot OH$), hydrogen peroxide (H_2O_2), etc.) in both aqueous and aprotic media for several reasons, prominent among which is their role in various biological processes.¹⁻⁵ This communication reports on the preliminary results concerning the electrochemical one- and two-electron reduction of O_2 based on the molecular modification of Hg electrode surface by hydrophobic surfactants in alkaline aqueous media.

In aqueous media two-electron reduction of O_2 to hydroperoxide (H_2O_2 or HO_2^-) or four-electron reduction of O_2 to H_2O or OH^- is ordinarily observed, while one-electron reduction of O_2 to O_2^- can be directly observed only in special cases, e.g., by using Hg electrode and making aqueous medium strongly alkaline and providing it with a hydrophobic surfactant.⁶⁻⁸ In the latter case, the Hg electrode surface is coated with a hydrophobic monolayer in contact with aqueous medium, resulting in the chemically modified electrode system with a hydrophobic/hydrophilic interface. Such an interface, which is considered as a model biological one, will be thus used to study the molecular reactivity of O_2 and ROS in biological processes from an electrochemical point of view.

2. EXPERIMENTAL

All electrochemical experiments were done at laboratory temperature ($20 \pm 2^\circ C$) by using a standard three-electrode, one compartment configuration with a

hanging mercury drop electrode (HMDE; PAR 303, EG & G Princeton Applied Research, area: 0.011 cm^2) as the working electrode, a spiral platinum counter electrode and a KCl saturated Ag/AgCl reference electrode. Cyclic voltammetric and double potential-step chronoamperometric measurements and the analysis of the results were conducted as described previously.^{1,9,10} NaOH solutions of various concentrations ($0.001 \sim 1 \text{ M}$, $M = \text{mol dm}^{-3}$) were used as supporting electrolytes, together with phosphate or carbonate buffers or KCl when necessary. α -Quinoline (Wako Pure Chemical Industries, Ltd.) and triphenylphosphine oxide (TPPO, Aldrich) of reagent grade were used as hydrophobic surfactants. Water was purified by a Millipore Milli-Q system.

α -Quinoline

TPPO

3. RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms for $0.1 \text{ M NaOH} + 0.5 \text{ M KCl}$ aqueous solutions saturated with O_2 in the absence (A) and the presence (B) of α -quinoline of 17 mM (close to its saturated concentration). The voltammograms obtained around -0.14 V vs. Ag/AgCl in the absence of α -quinoline correspond to the two-electron reduction of O_2 ^{6,8}:

This reaction is substantially reversible on the experimental time scale used here as can be seen from the following facts: (i) the separation (ΔE_p) of anodic and

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology (Nagatsuta, Midori-ku, Yokohama 227, Japan)

Key Words: Molecular Oxygen, Superoxide Ion, Disproportionation, Electrode Surface Modification, α -Quinoline, Hydrophobic Surfactants

cathodic peak potentials (E_p^a and E_p^c) is ca. 30 ~ 35 mV irrespective of potential scan rate (ν), (ii) the ratios of anodic peak current to cathodic one (i_p^a/i_p^c) are

Fig. 1. Typical cyclic voltammograms obtained with HMDE (area: 0.011 cm²) in O₂-saturated aqueous solutions containing 0.1M NaOH and 0.5 M KCl in the absence (A) and the presence (B) of 17 mM α -quinoline.

almost unity, (iii) i_p^c is proportional to $\nu^{1/2}$ and (iv) the shift of the formal potential ($E^{\circ'}$), estimated as the average of E_p^a and E_p^c , is about -30 mV/ unit pH (Table 1), which is in agreement with that to be expected theoretically for a typical two-electron Nernstian process. These are consistent with the previous data.^{6,8)}

Addition of α -quinoline surfactant into the solution displaces the reduction potential of O₂ toward more negative direction by ca. 200 ~ 250 mV (see voltammograms B). In this case, $E^{\circ'}$ could be regarded as actually independent of pH (or concentration of NaOH) and was ca. -0.31 V vs. Ag/AgCl in agreement with literature values.⁶⁻⁸⁾ i_p^c is about one-half that for the two-electron reduction of O₂ (Table 1).¹¹⁾ Thus, this process corresponds to one-electron reduction of O₂ to O₂⁻ (6-8):

Recently the adsorption of isoquinoline, which is a structural isomer of α -quinoline, on Hg surfaces has been confirmed by in situ FT-IR spectroscopy,^{12,13)} electrocapillary methods,¹⁴⁾ ellipsometry,¹⁵⁾ potential-step techniques,¹⁶⁾ etc. Thus, it can be thought that α -quinoline adsorbs strongly to HMDE surface and displaces the water molecules from the surface, rendering

Table 1. Cyclic voltammetric data for one- and two-electron reduction of O₂ at HMDE in the absence and the presence of α -quinoline^{a)}

Supporting Electrolytes	$i_p^c(\text{O}_2/\text{HO}_2^-)^{\text{b)}}$ $\mu\text{A cm}^{-2}$	$i_p^c(\text{O}_2/\text{O}_2^-)^{\text{c)}}$ $\mu\text{A cm}^{-2}$	$E^{\circ'}(\text{O}_2/\text{HO}_2^-)^{\text{b)}}$ V vs. Ag/AgCl
0.001 M NaOH 0.5 M KCl, pH ca.11	786	500	-0.080
0.01 M NaOH 0.5 M KCl, pH ca.12	773	389	-0.107
0.1 M NaOH 0.5 M KCl, pH ca.13	845	395	-0.140

a) Concentration of α -quinoline: 17 mM, potential scan rate: 0.1 Vs⁻¹.

b) For two-electron process (Eq.(1)).

c) For one-electron process (Eq.(2)).

the access of the solvent to O_2^- formed in the hydrophobic layer difficult. Consequently, one can actually realize one-electron redox process of the O_2/O_2^- redox couple, which has usually been observed in aprotic solvents⁴⁾, even in aqueous media. The similar results were also obtained using TPPO in place of α -quinoline as a hydrophobic surfactant, except that in the former case the i_p^a/i_p^c value at a given ν is a little smaller than that in the latter case.

In contrast to the O_2/HO_2^- process (Eq.(1)), i_p^a/i_p^c is much smaller than unity and strongly depends on ν : it increases with increasing ν . This fact together with the previous results⁶⁻⁸⁾ demonstrates the regeneration of O_2 via the homogeneous disproportionation of O_2^- .⁶⁻⁸⁾

Double potential-step chronoamperometry (DPSCA)⁹⁾ was applied to estimate the rate constant (k_{disp}) of disproportionation by assuming that the adsorption of α -quinoline on the HMDE surface simply results in

Fig. 2. Typical DPSCA responses obtained with HMDE (area: 0.011 cm²) in O_2 -saturated (solid line) and deaerated (dashed line) aqueous solutions containing 0.01 M NaOH, 0.5 M KCl and 17 mM α -quinoline. The inset represents the potential-step mode used in the DPSCA measurement. $E_1 = -0.03$ V, $E_2 = -0.55$ V and $E_3 = -0.02$ V vs. Ag/AgCl. Potential-step width (τ): 100 ms.

the shift of O_2 reduction from two-electron process to one-electron process. A typical example of such measurements is shown in Fig.2. The value of k_{disp} was estimated to be $(4 \pm 1) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ in 0.01 M NaOH + 0.5 M KCl solution (pH 12, concentration of O_2 : $1.25 \times 10^{-3} \text{ M}$ ⁶⁾). Our value is significantly larger than that ($(6 \pm 1) \text{ M}^{-1}\text{s}^{-1}$) obtained by polarography at pH>12,⁶⁾ probably suggesting that in the present case the disproportionation of O_2^- could also be catalyzed by trace amounts of impurities. A detailed study concerning the mechanism is currently under way.

The rates of the disproportionation of O_2^- have been well-known to strongly depend on the properties (e.g., pH, ionic strength) of aqueous media in which

(A) two-electron process

(B) one-electron process

Scheme 1 Schematic depiction of the electrochemical reduction of O_2 on (A) bare Hg electrode and (B) Hg electrode coated with a hydrophobic surfactant layer in alkaline aqueous media. k_{disp} represents the rate constant of homogeneous disproportionation of O_2^- .

its kinetics is investigated.⁸⁾ Further we can see that the k_{disp} values obtained in the present and previous studies⁶⁾ in aqueous media are significantly larger than those (typically $10^{-4} \sim 10^{-2} \text{ M}^{-1}\text{s}^{-1}$) in aprotic media such as acetonitrile and dimethylformamide.¹⁷⁾ This makes us speculate that the effective rates for the disproportionation of O_2^- , which might occur in the aprotic, hydrophobic region, e.g., of cell membranes delimited by the two phospholipid layers, would be much smaller than those in the hydrophilic region composed of bulk water and that the length of the diffusion path of O_2^- is thus longer in the former case. These may be closely associated with the more compelling need for superoxide dismutases (SODs), which catalyze the disproportionation of O_2^- , under biological environments.

In conclusion, the one- and two-electron reduction of O_2 in alkaline aqueous media can be controlled based on the molecular modification of HMDE surface by hydrophobic surfactants such as α -quinoline and TPPO (Scheme 1). The present study reconfirms the previous ones^{6,7)} and further suggests that the present electrode system involving a hydrophobic/hydrophilic interface might provide a model biological interface to examine the biomolecular reactivity of O_2 and ROS in aqueous media.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan, the Nissan Science Foundation and the Nakatani Electric Measuring Technology Foundation.

REFERENCES

- 1) T. Ohsaka, T. Watanabe, F. Kitamura, N. Oyama and K. Tokuda, *J.Chem.Soc.,Chem. Commun.*, 487(1991).
- 2) T. Ohsaka, T. Watanabe, F. Kitamura, N. Oyama and K. Tokuda, *J.Chem.Soc.,Chem. Commun.*, 1072(1991).
- 3) N. Oyama, S. Ikeda, M. Suzuki and T. Ohsaka, *Electroanalysis*, **3**, 665(1991)
- 4) T. Ohsaka, M. Tushima and K. Tokuda, *Bioelectrochem. & Bioenerg.*, in press.
- 5) T. Watanabe, K. Tokuda and T. Ohsaka, *Denki Kagaku*, **60**, 455(1992).
- 6) J. Divisek and B. Kastening, *J.Electroanal.Chem.*, **65**, 603((1975).
- 7) J. Chevalet, F. Rouelle, L. Gierst and J.P. Lambert, *J.Electroanal.Chem.*, **39**, 201(1972).
- 8) D.T. Sawyer and E.T. Seo, *Inorg.Chem.*, **16**, 499(1977).
- 9) M.K. Hanafey and C.N. Reilley, *Anal.Chem.*, **50**, 116(1978).
- 10) T. Ohsaka, T. Sotomura, H. Matsuda and N. Oyama, *Bull. Chem. Soc. Jpn.*, **56**, 3065(1983).
- 11) It should be noted that i_p^c is not exactly one-half that for the two-electron process, reflecting the possible follow-up chemical reactions of O_2^- (e.g., disproportionation (Eg.(3))).
- 12) D.J. Blackwood and S. Pons, *J.Electroanal.Chem.*, **247**, 277(1988).
- 13) F. Matsumoto, F. Kitamura, K. Tokuda and T. Ohsaka, manuscript in preparation.
- 14) C. Buess-Herman, N. Vanlaethem-Meurce, G. Quarin and L. Gierst, *J.Electroanal.Chem.*, **123**, 21(1981).
- 15) M.W. Humphreys and R.J. Parsons, *J.Electroanal. Chem.*, **82**, 369(1977).
- 16) C. Buess-Herman, C. Frank, C. Gierst and L. Gierst, *Electrochim. Acta*, **31**, 965(1986)
- 17) M. Tsushima, K. Tokuda and T. Ohsaka, *J.Chem.Soc, Perkin Trans. 2*, submitted.