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BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1142—1144 (1969)

Studies on Photo-polarography. II. Photo-polarographic Behavior of Dissolved Oxygen under Ultraviolet Irradiation

Hideo IMAI and Kazuo YAMASHITA

Department of Chemistry, Faculty of General Education, Hiroshima University, Hiroshima

(Received June 24, 1968)

In the past five years the photocurrents produced by the ultraviolet irradiation of the mercury electrode have been investigated and developed by several workers.[1–6]

Heyrovsky[1] has found a rapid current increase in a magnitude of about 1 microA at the irradiated dropping mercury electrode (DME) in solutions of sulfuric acid. He interpreted the experimental finding in terms of the photosensitized decomposition of water molecules adsorbed on the electrode surface. On the other hand, Barker and his co-workers[2] and Delahay and Srinivasan[3] have explained the same phenomenon by assuming a simplified model in which all the hydrated electrons[*1] are deposited on a plane at a distance, δ, away from the electrode surface.

According to the radiolysis study, it is assumed that, in oxygenated aqueous solutions, the hydrated electron reacts immediately with dissolved oxygen to form the hydroperoxy radical;

$$e^-_{aq} + H^+ \rightarrow H \qquad (1)^{*2}$$

$$H + O_2 \rightarrow HO_2 \qquad (2)$$

$$e^-_{aq} + O_2 \rightarrow O_2^- \qquad (3)^{*2}$$

The relative importance of these relevant reactions depends upon the pH and the oxygen concentration. The kinetics of the hydroperoxy radical there formed have been investigated by fast reaction techniques.[8–11]

Our present investigation is primarily concerned with anomalies of the second reduction wave of dissolved oxygen under polychromatic ultraviolet irradiation on the DME. Observations were carried out on the field dependence of the photocurrents and on the effects of surface-active substances, hydrated electron scavengers, and radical scavengers on the photocurrent. A possible reaction mechanism is proposed for the reaction of dissolved oxygen under ultraviolet irradiation.

Experimental

Reagent-grade methanol, ethanol, and acetone were redistilled. Special-grade sodium sulfate from Wako Pure Chemicals Ind., Ltd., was used without further purification. The water used was distilled twice. All the other chemicals and the apparatus used were the same as those reported in a previous paper.[12] The solutions contained 0.5 M Na_2SO_4 as the supporting electrolyte. The solutions were equilibrated with atmospheric oxygen at room temperature.

Results and Discussion

Polarograms of Dissolved Oxygen under Ultraviolet Irradiation. Oxygen develops two polarographic reduction waves in neutral aqueous salt solutions, the first wave corresponding to the two-electron reduction of oxygen to hydrogen peroxide, and the second, to the two-electron reduction of hydrogen peroxide to hydroxyl ions.

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1) M. Heyrovsky, *Nature*, **200**, 880 (1963).

2) G. C. Barker, A. W. Gardner and D. C. Sammon, *J. Electrochem. Soc.*, **113**, 1132 (1966).

3) P. Delahay and V. S. Srinivasan, *J. Phys. Chem.*, **70**, 420 (1966).

4) H. Berg, *Rev. Polarog.* (Kyoto). **11**, 29 (1963).

5) For a review, see T. Kuwana in "Electroanalytical Chemistry," Vol. I, A. J. Bard ed., Marcel Dekker, New York (1966), p. 210.

6) For a review, see H. Berg, H. Schweiss, W. Stutter and K. Weller, *J. Electroanal. Chem.*, **15**, 415 (1967).

[*1] Walker[7] has recently confirmed the existence of hydrated electrons at the electrode-solution interface by observing the absorption spectra during the electrolysis of water.

7) D. C. Walker, *Can. J. Chem.*, **45**, 807 (1967).

[*2] The rate constants for reactions (1) and (3) are given as $2.36\times10^{10}\text{M}^{-1}\cdot\text{sec}^{-1}$ and $(1.88\pm0.2)\times10^{10}\text{M}^{-1}\cdot\text{sec}^{-1}$ respectively.[11]

8) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *J. Am. Chem. Soc.*, **85**, 1375 (1963).

9) E. Saito and B. H. J. Bielksi, *ibid.*, **83**, 4467 (1961).

10) J. H. Baxendale, *Radiation Res.*, **17**, 312 (1962).

11) G. Czapski and B. H. J. Bielsky, *J. Phys. Chem.*, **67**, 2180 (1963).

12) K. Yamashita and H. Imai, This Bulletin, **41**, 1339 (1968).

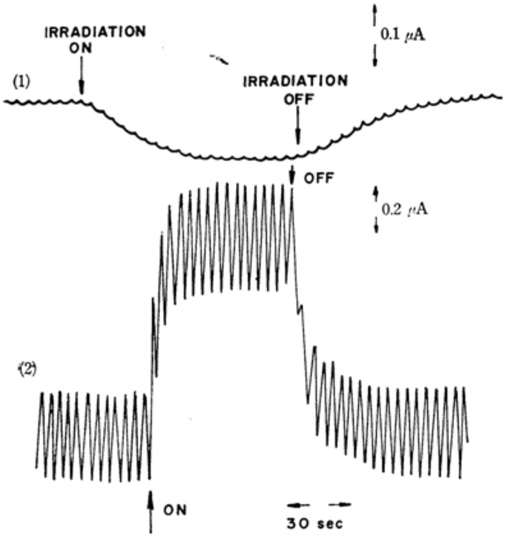

Fig. 1. Photocurrents.

(1) The negative photocurrent observed at -1.3 V *vs.* SCE in deaerated solutions of 0.5M Na_2SO_4.

(2) The positive photocurrent of the dissolved oxygen observed at -1.3 V in solutions of 0.5M Na_2SO_4.

(The photocurrent represents the difference between the currents measured with and without irradiation.)

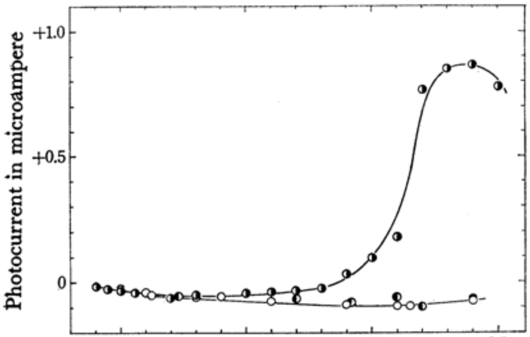

Fig. 2. Dependence of photocurrents on the electrode potentials in aqueous solutions of 0.5 M Na_2SO_4.

○ deaerated 0.5M Na_2SO_2 solutions

◑ 0.5M Na_2SO_4 solutions containing 0.25 mM oxygen

◐ 0.5M Na_2SO_4 solutions containing 0.25 mM oxygen and 0.005% gelatine

In a deaerated 0.5 M Na_2SO_4 solution, a small negative photocurrent was observed under the continuous ultraviolet irradiation of the DME. This residual photocurrent is shown in Figs. 1 and 2. The surface tension and the differential capacity of the DME and the effect of the carbon dioxide dissolved in the solution on the anodic residual photocurrent were measured with and without ultraviolet irradiation. The results, however, showed no appreciable irradiation effect. The mechanism of this negative residual photocurrent may be attributed to the presence of impurities in the solution, but the details are still unknown.

In the presence of oxygen the polarographic reduction under ultraviolet irradiation showed a different pattern from the normal wave; *i. e.*, the first wave did not show any appreciable change, while the height of the second wave was markedly increased. Figure 1 shows the positive photocurrent measured at -1.3 V *vs.* SCE. Figure 2 shows the dependence of the photocurrent on the electrode potential. The marked positive photocurrent begins to appear from the potentials at about -0.9 V when hydrogen peroxide is reduced. In this connection Silvestroni and Carelli[13] have observed anomalies in the oscillograph polarographic wave of oxygen at an irradiated mercury drop; they explain the anomalies as the effect of streaming caused by the heat absorption at the electrode-solution interface. It is noteworthy that, in our experiment, the positive photocurrent are observed at potentials more negative than -0.9 V, while the effect of irradiation was scarcely observed at potentials less negative than -0.9 V. Moreover, it was confirmed that the surface tension and differential capacity of the DME were little influenced by irradiation. Thus, the variation on the reduction wave upon exposure to light can not be interpreted in terms of a mere physical effect such as streaming. The apparent quadratic field dependence of the photocurrent (charge) has been pointed out for the scavenging of e_{aq}^- with H^+ by Delahay and Srinivasan.[3] They have cited Fowler's theory[14] on photoemission by a metal under a vacuum and monochromatic irradiation. No interpretation has, however, been worked out for their particular case, *i. e.*, emission in an aqueous electrolyte and polychromatic irradiation. In our experiment the square root of the photocurrent *versus* the potential plot was far from a linear relationship. The concave curvilinear plot seems to suggest the regeneration of H_2O_2 by a subsequent homogeneous chemical reaction, probably the bimolecular decay of O_2^- to yield H_2O_2.

Effect of Surface-active Substances on Photocurrent. The positive photocurrent was conspicuously affected by very small amounts of such surface-active substances as gelatin (*cf.* Fig. 2) and methylcellulose, and it completely disappeared in the presence of about 2×10^{-4}% gelatin or 4×10^{-4}% methylcellulose. The negative photocurrent was more pronounced with any increase in the methyl-

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13) P. Silvestroni and I. Carelli, *J. Electroanal. Chem.*, **15**, 317 (1967).

14) R. H. Fowler, *Phys. Rev.*, **38**, 45 (1931).

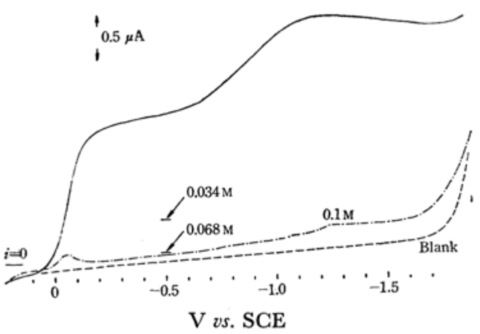

Fig. 3. Effect of acetone on the polarograms of the dissolved oxygen with the continuous irradiation in solutions of $0.5\,\mathrm{M}$ Na_2SO_4.

cellulose concentration higher than $4\times10^{-4}\%$. Anodic photocurrents similar to those in the case of methylcellulose have been observed in solutions of glyoxal, diacetyl, sodium oxalate, *etc.* by Heyrovsky,[15] who explained these findings by assuming that the light-absorbing species responsible for the anodic photocurrents are the complexes between the adsorbed organic molecules and the mercury electrode. In view of the photoemission of electrons and the formation of hydrated electrons, it seems that the effect of surface-active substances on the photocurrents can be interpreted on the basis of the variation in the work function due to the adsorbed molecules or/and to the scavenging of hydrated electrons by the adsorbed molecules.

Effect of Hydrated Electron Scavenger and OH Radical Scavenger on Photocurrent. The effect of acetone as a scavenger for hydrated electrons on the photocurrents was investigated. When the concentration of acetone was increased, the height of the reduction wave of the dissolved oxygen under ultraviolet irradiation was markedly decreased, and it completely disappeared upon the addition of 0.2 M acetone, as is shown in Fig. 3. This indicates that the amount of dissolved oxygen is reduced by the reduced form of acetone.*3 Reaction (3) may be followed by a slow reaction;

$$O_2^- + H_2O_2 \rightarrow O_2 + OH + OH^- \qquad (4)$$

The OH radical thus formed will pertain to the electrode process through several reaction paths such as the dimerization of OH to form H_2O_2, and the reaction of OH with H_2O_2 to form O_2^- and H^+. Methanol and ethanol are known to be effective OH radical scavengers. It was confirmed that these scavengers slightly affected the photocurrent. It may be concluded that contribution of reaction (4) to the photocurrent is negligibly small.

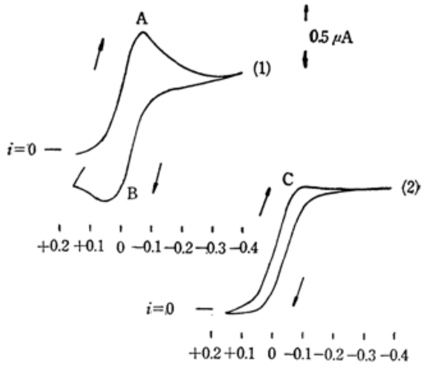

Fig. 4. Cyclic voltammetric curves of the first reduction of oxygen in aqueous solutions of 0.5 M Na_2SO_4 and 0.30 mM oxygen.
(1) without irradiation
(2) with irradiation

Reaction Mechanism and Cyclic Voltammetry. From the above-mentioned results, we assumed the following reaction scheme;

$$(e^-)_{\mathrm{metal}} + h\nu \rightarrow (e^-)^*_{\mathrm{metal}} \qquad (5)$$

$$(e^-)^*_{\mathrm{metal}} \xrightarrow{\text{(transfer reaction)}} e^- \qquad (6)$$

$$e^- + H_2O \rightarrow e^-_{aq} \qquad (7)$$

$$e^-_{aq} + O_2 \rightarrow O_2^- \qquad (8)$$

$$O_2^- + O_2^- + H_2O \rightarrow O_2 + H_2O_2 + 2OH^- \qquad (9)^{*4}$$

The concentration of hydrogen peroxide in the vicinity of the irradiated DME is increased through reaction (9). It is noteworthy that the cyclic regeneration of O_2 through reactions (8) and (9) results in the formation of H_2O_2. This assumption agrees well with the positive photocurrents observed in relation to the second reduction wave of dissolved oxygen.

The *i-E* curves recorded in the cyclic voltammetry of the first reduction of oxygen are shown in Fig. 4. Under continuous irradiation the anodic wave disappeared, as is shown in Fig. 4, curve (2). It seems that this results also supports the assumption of the coupled chemical reaction (possibly by reactions (8) and (9)) through which the irreversible behavior of the $O_2-H_2O_2$ redox couple is favored.

The authors wish to express their hearty gratitude to Professor Niro Matsuura of the University of Tokyo for his kind suggestions regarding this investigation.

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[15] M. Heyrovsky, *Nature*, **209**, 708 (1966).

*3 The reduction of methylene blue by ultraviolet irradiation was more pronounced in the presence of acetone. This inherently suggests that the reduced form of acetone was formed in the bulk of the solution.

*4 The validity of reaction (9) was confirmed by radiation chemistry reaction.