May, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *62*, *1405—1409 (1989)* 1405

# Continuous Electrochemiluminescence of $[Ru(2,2'\text{-bipyridine})_3]^{2+}$ in Solution

Ryuji Igarashi, Yoshio Nosaka,* Nobuyuki Fujii, and Hajime Miyama
Department of Chemistry, Nagaoka University of Technology,[1] Nagaoka 940-21

(Received September 28, 1988)

Electrochemiluminescence (ECL) of tris(2,2′-bipyridine)ruthenium(2+) ($[Ru(bpy)_3]^{2+}$) was observed in a propylene carbonate–dimethylacetamide–water mixed solvent by applying direct current (dc) voltage to a cell which consists of a sheet cathode of metals such as Al and Pt and a wire anode of Pt. The intensity of the dc ECL increased with the water concentration (up to 30 vol%) and the applied voltage. Besides water, oxygen was found to be necessary for observing the dc ECL. A plausible mechanism is the formation of $[Ru(bpy)_3]^{2+*}$ from the reaction of $[Ru(bpy)_3]^+$ and $HO_2$, those species are both produced at the cathode. This mechanism was supported by a separate experiment in which the chemiluminescence was observed by the reactions with a reducing agent.

The continuous electrochemiluminescence (ECL) of tris(2,2′-bipyridine)ruthenium(2+) ($[Ru(bpy)_3]^{2+}$) in acetonitrile solution with a small amount of water was observed recently by the authors.[2] Some unique characteristics of the dc-ECL observation were (i) a quick response to the direct current (dc) application, (ii) the restriction to Al for cathode materials when the applied voltage was 10 V, and (iii) a special arrangement for the electrodes in which the area of the anode was much smaller than that of the cathode. On the application of ac voltage to the same cell, these characteristics did not appear, although the ECL intensity was significantly large. Accordingly the reaction mechanism of the dc ECL should be different from the conventional ac ECL in which a diffusion process is involved. Although the emitting species was considered to be $[Ru(bpy)_3]^{2+*}$, its formation mechanism was not clarified in the previous study, where a two-electrode cell was used in connection with its application to ECL devices.[2] In the present study, however, a three-electrode cell was also used to explain the unique characteristics of the dc-ECL. For comparison with the previous study, the cathode potential in the two-electrode cell was measured against the concentration of the supporting electrolyte and by changing the cathode materials. A mechanism of the dc ECL will be proposed based on the influence of oxygen on the emission intensity and the observation of chemical luminescence by using a reducing agent.

## Experimental

**Materials.** Tris(2,2′-bipyridine)ruthenium(2+) complex ($[Ru(bpy)_3]Cl_2\cdot 6H_2O$), obtained from Aldrich Chemical Co., was purified by recrystallizing three times from distilled water followed by drying in vacuum. Propylene carbonate (PC, extra pure reagent) and *N*,*N*-dimethylacetamide (DMA, guaranteed reagent) obtained from Nakarai Chemicals, Ltd. were dried with molecular sieve followed by vacuum distillation. A mixture of PC, DMA, and $H_2O$ was used as a solvent, unless otherwise stated. Tetrabutylammonium perchlorate (TBAP, polarographic grade of Nakarai Chemicals) was used without further purification. Aluminum sheet (0.08 mm in thickness) obtained from Tokai Kinzoku Co., Ltd., was used as received. A copper sheet (0.3-mm thick), a titanium sheet (0.05 mm thick), and a molybdenum sheet (0.1-mm thick) from the Japan Lamp Industrial Co., Ltd., and a Pt sheet (0.023-mm thick), from Itimura Metal Co., Ltd., were rinsed with a 1.2-M HCl solution (1 M=1 mol dm$^{-3}$) and subsequently with distilled water before use.

**Method.** The two-electrode cell consists of a metal sheet of 8-mm width and 2-cm effective height and a wire of Pt of 0.5-mm diameter and 1-cm effective length. The sheet was used as a working electrode (WE) while the wire was used as a counter electrode (CE). The three-electrode cell consists of an Al or a Pt sheet WE, a Pt wire CE, and an $Ag/Ag^+$ reference electrode (RE) which are placed in a H-shaped glass vessel having a sintered-glass filter separator. The WE and CE were the electrodes as used in the two-electrode cell, respectively. The ECL intensity was measured for a 0.2-mM $[Ru(bpy)_3]^{2+}$ solution under controlled polarization with a potentiostat (Toho Technical Research, Type 2090). The potential was usually supplied by a function generator (Leader, LFG-1300). The ECL light after passing through a grating monochromator (Ritsu, MC-25N) was detected by a photomultiplier (Hamamatsu Photonics, R928). The experimental setup for the two-electrode cell was similar to that in the previous report.[2]

Effective potentials of the metal sheet WE against the $Ag/Ag^+$ RE were measured by using the Pt wire CE, which were the same as for the two-electrode cell. Cyclic voltammograms were measured by using a square Pt WE (0.5 cm×0.5 cm), and a Pt coil CE, and the $Ag/Ag^+$ RE in the H-shaped vessel.

The measurement of chemiluminescence of $[Ru(bpy)_3]^{2+}$ was performed by adding 1 M HCl to the mixture of PC, DMA, and $H_2O$ containing 1-mM $[Ru(bpy)_3]^{2+}$ and a piece of Mg ribbon.

## Results

In our previous study on the dc ECL,[2] acetonitrile was used as a solvent. Since acetonitrile is a volatile and virulent substance, propylene carbonate (PC) was used as a solvent in the present study. In order to observe the dc ECL, a small amount of water had been required in the previous study. Since water is poorly soluble in the PC solution, DMA was added to the mixture to increasing the water solubility. DMA is

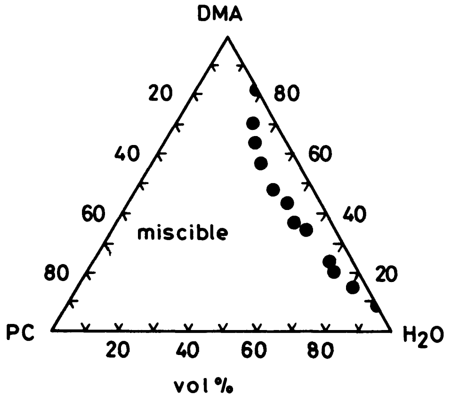

Fig. 1. Limits of miscibility in the ternary system of PC, DMA, and $H_2O$.

also an aprotic nonvolatile substance used commonly as a solvent. Figure 1 shows the limit of miscibility for the three-component system consisting of PC, DMA, and $H_2O$. On this basis a DMA concentration of 20 vol% was chosen for this study. The three compositions are completely miscible at this concentration.

The dc-ECL intensity was measured by changing the water concentration. When the water was absent from the solution no emission was observed. The intensity of the emission increased with the water concentration which became saturated at 30 vol%. Therefore, in the following experiments, the contents of the mixed solvent were fixed to be 50 vol% of PC, 30 vol% of $H_2O$, and 20 vol% of DMA. The dc ECL was observed without delay (less than 0.2 s) and continued for several hours similarly to the case of the acetonitrile–$H_2O$ solution.[2] However, the emission intensity is higher and more stable than that observed in the previous study,[2] although no quantitative comparison was performed.

Redox potentials of $[Ru(bpy)_3]^{2+}$ in the mixture were examined to investigate the mechanism of the dc ECL. The cyclicvoltammetric behavior at the Pt electrode was measured for the PC–DMA–$H_2O$ solution containing 1-mM $[Ru(bpy)_3]^{2+}$ and a supporting electrolyte of 0.1 M TBAP. The potential for each peak obtained from the voltammogram is given in Table 1. These electrode reactions are one-electron reversible processes, because the potential differences between the reduction and oxidation peaks, $E_{pa}-E_{pc}$, were approximately equal to 59 mV.[3] This observation indicates that the mixed solvent does not participate in the electrode reaction over the potential range. For the following discussion, note that $[Ru(bpy)_3]^{2+}$ was reduced to $[Ru(bpy)_3]^{+}$ at −1.52 V vs. $Ag/Ag^+$ in this solvent.

The emission intensity was measured under the controlled potential using the three-electrode cell. Figure 2 shows the relationship between the dc-ECL intensity and the electrode potential of the Al and Pt sheet cathodes in the PC–DMA–$H_2O$ solution containing 0.2-mM $[Ru(bpy)_3]^{2+}$ and 0.1-M TBAP. For the Al electrode, emission was observed at −1.9 V vs. $Ag/Ag^+$ and the intensity increased with the potential. For the Pt sheet cathode, the dc ECL was observed above −1.6 V vs. $Ag/Ag^+$. This onset potential roughly agrees with the reduction potential for $[Ru(bpy)_3]^{2+}$ mentioned above.

Table 1. Peak Potentials at Cathodic ($E_{pc}$) and Anodic ($E_{pa}$) Sweeps of the Cyclic Voltammogram for $Ru(bpy)_3Cl_2$ in PC–DMA–$H_2O$ Mixed Solvent[a)]

| Oxidation state | I | II | III | IV |
|---|---|---|---|---|
| $E_{pc}$ | 0.96 | −1.52 | −1.70 | −1.91 |
| $E_{pa}$ | 1.02 | −1.47 | −1.64 | −1.85 |

a) In V vs. $Ag/Ag^+$ reference electrode. Sweep rate; 200 mV $s^{-1}$.

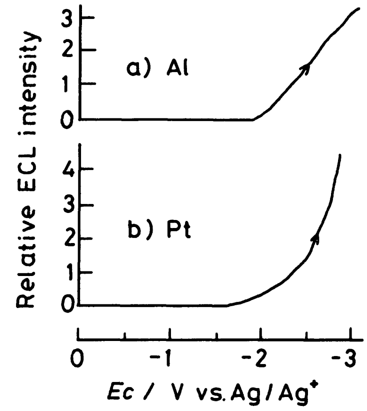

Fig. 2. ECL intensity-potential ($E_c$) curves at (a) Al and (b) Pt sheet cathodes in PC–DMA–$H_2O$ solution containing 0.2-mM $[Ru(bpy)_3]^{2+}$ and 0.1-M TBAP.

In the experiments using the two-electrode cell with 10-V application, the dc ECL was not observed at the Pt cathode similarly to the case in the previous study. Therefore, the actual potential of the cathode in the two-electrode cell against RE was measured. Table 2 shows the observed potential for various metal sheets to $Ag/Ag^+$ RE when −10 V was applied against the Pt-wire electrode. The values of the redox potential of the metals and whether the dc-ECL was observed or not are also shown in the table. The dc ECL was observed at the Al and Ti sheet cathodes whose actual potentials were lower than the reduction potential of $[Ru(bpy)_3]^{2+}$. At the Mo, Cu, and Pt sheet cathodes the dc ECL was not observed because the potential was not high enough to reduce the ruthenium complex. The cathode potential appears to correlate with the standard electrode potential.

The actual potential at the Al and Pt sheet cathodes was measured by adding various amount of TBAP as shown in Fig. 3. For both electrodes, the negative

Table 2. Cathode Potential ($E_c$) and the Standard Electrode Potential ($E_s$) with dc-ECL[a)]

| Sheet cathode | $E_c$ V vs. Ag/Ag$^+$ | $E_s$ V vs. NHE | dc-ECL emission |
|---|---|---|---|
| Aluminum | −2.00 | −1.66[b)] | ○ |
| Titanium | −1.74 | −1.63[b)] | ○ |
| Molybdenum | −1.31 | −0.2[c)] | × |
| Copper | −1.18 | 0.34[b)] | × |
| Platinum | −0.93 | 1.12[b)] | × |

a) Applied voltage is 10 V without TBAP. $E_c$=cathode potential, $E_s$=standard electrode potential. b) "CRC Handbook of Chemistry and Physics" 66th ed, ed by R. C. Weast, CRC Press, D151-D155 (1985). c) "Electrochemical Data," D. Dobos, Elsevier Scientific Publishing Company, (1975), p. 255.

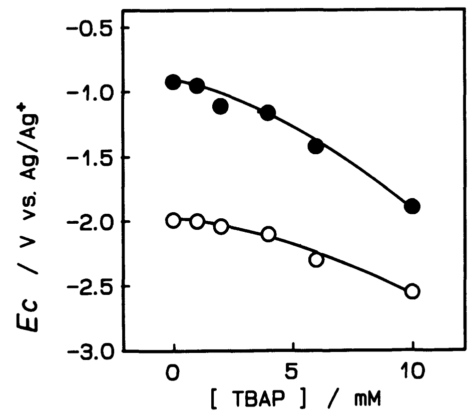

Fig. 3. Observed potentials ($E_c$) at the Pt (●) and Al (○) cathodes for various concentration of TBAP. At the cathode, −10 V was applied against the Pt wire. PC–DMA–$H_2$ solution containing 0.2-mM $[Ru(bpy)_3]^{2+}$ was used.

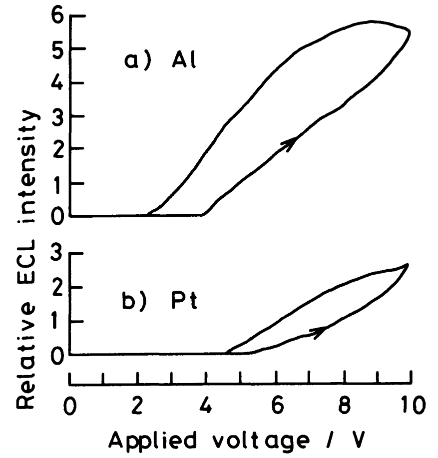

Fig. 4. ECL intensity-applied voltage curves at (a) Al and (b) Pt sheet cathodes in PC–DMA–$H_2O$ solution containing 0.2-mM $[Ru(bpy)_3]^{2+}$ and 0.1-M TBAP.

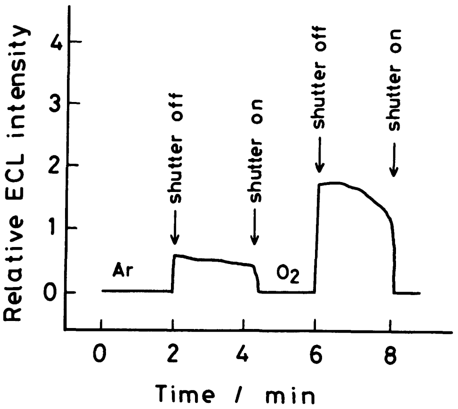

Fig. 5. Effect of oxygen on ECL intensity at Al sheet cathode in PC–DMA–$H_2O$ solution containing 0.2-mM $[Ru(bpy)_3]^{2+}$. Both $O_2$ and Ar gases were purged alternatively when the shutter for the photomultiplier was on.

potential increased with the TBAP concentration. In the presence of 10-mM TBAP, the cathode potential at the Pt sheet became more negative than −1.52 V which is the reduction potential of $[Ru(bpy)_3]^{2+}$. Consequently, in the presence of TBAP, the dc ECL may be observed for the Pt cathode in the two-electrode cell at a lower applied voltage. Figure 4 shows the dc-ECL intensity in the presence of 0.1-M TBAP as a function of the applied voltage at the Al and Pt sheet cathodes. As mentioned previously, in the absence of a supporting electrolyte, no emission was observed at applied voltages ranging from 0 to 10 V at the Pt cathode. However, when TBAP was added in the solution, emission was observed at the Pt cathode as shown in Fig. 4. The thresholds of the applied voltage for the emission at the Al and Pt cathodes were 3.8 V and 5.5 V, respectively. The threshold voltage for emission at the Al sheet cathode was smaller than that at the Pt sheet cathode. This originates from the fact that the potential of the Al sheet cathode was more negative than the Pt cathode at the same applied voltage as shown in Fig. 3. Thus the influence of the cathode materials on the dc ECL in the two-electrode cell is explained by the cathode potential instead of the participation to the emission mechanism as a chemical reactant.

As mentioned above, $H_2O$ is necessary for the dc-ECL. Besides $H_2O$, atmospheric oxygen is considered to contribute to the mechanism of the dc ECL. The dc ECL was next measured by alternating the conditions between those in the presence of oxygen by bubbling oxygen gas and in the absence of oxygen by bubbling argon gas through the solution. As shown in Fig. 5, the ECL intensity was weakened without oxygen and recovered on adding oxygen. These results suggest that oxygen participates in the emission mechanism of the dc ECL.

The emission occurs only at the cathode surface, indicating that some reduction process accounts for

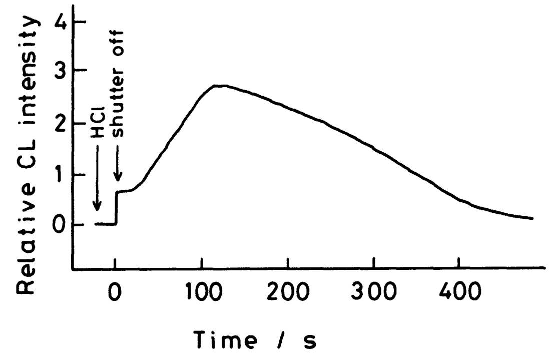

Fig. 6. Emission profile of chemiluminescence (CL) obtained by adding 1-M HCl to the 1-mM $[\mathrm{Ru(bpy)_3}]^{2+}$ solution containing a piece of Mg ribbon.

the dc ECL. The chemiluminescence was next measured in order to confirm that the emission is caused by a reduction process. Figure 6 shows the chemiluminescence obtained by adding 1-M HCl to a 1-mM $[\mathrm{Ru(bpy)_3}]^{2+}$ solution containing a piece of Mg ribbon. This result suggests that the mechanism of the dc ECL involves a process similar to the chemiluminescence.

## Discussion

Although the separation between the anode and the cathode is as large as 8 mm, the dc ECL was observed without delay on the dc application. This phenomenon suggests that the electrochemical reaction proceeds through the short diffusion length at only one electrode. Bard et al. demonstrated that the ECL phenomenon occurred at only one electrode when a sacrificial reagent such as oxalate[4] and peroxodisulfate[5] was employed. In the case of peroxodisulfate, for example, a strong oxidant, $\mathrm{SO_4^{\cdot -}}$, was produced by the reduction of $\mathrm{S_2O_8^{2-}}$ at the cathode. Then $[\mathrm{Ru(bpy)_3}]^{2+*}$ was formed by oxidizing $[\mathrm{Ru(bpy)_3}]^{+}$ with $\mathrm{SO_4^{\cdot -}}$.[5] In the present study, oxygen and water are essential to the appearance of the dc ECL. Therefore, $\mathrm{O_2}$ and $\mathrm{H_2O}$ may be replaced to the peroxodisulfate in the ECL mechanism. For example, Reaction 1 may take place at the cathode.

$$\mathrm{O_2 + e^- \longrightarrow O_2^-} \qquad (1)$$

At the low pH the super oxide ion becomes the $\mathrm{HO_2^{\cdot}}$ radical.

$$\mathrm{O_2^- + H^+ \rightleftharpoons HO_2^{\cdot}} \quad \mathrm{p}K\,4.8^{6)} \qquad (2)$$

The reduction potential of Eq. 1 is $-0.32$ V vs. NHE.[7] The observation of the $\mathrm{HO_2^{\cdot}}$ radical with a UV spectrophotometer failed because of the low estimated concentration and the overlapping of the solvent at the maximum of $\mathrm{HO_2^{\cdot}}$ (225 nm).[8] However, the formation of $\mathrm{HO_2^{\cdot}}$ by the reduction of water has been reported already.[8] Since the product $\mathrm{HO_2^{\cdot}}$ radical is a strong oxidant, it may act in the same role as the $\mathrm{SO_4^{\cdot -}}$ radical. Then, $[\mathrm{Ru(bpy)_3}]^{2+*}$ was produced via electron transfer from $[\mathrm{Ru(bpy)_3}]^{+}$ to $\mathrm{HO_2^{\cdot}}$ as expressed by Eq. 3.

$$\begin{aligned} &[\mathrm{Ru(bpy)_3}]^{+} + \mathrm{HO_2^{\cdot}} + \mathrm{H^+} \\ &\qquad \longrightarrow [\mathrm{Ru(bpy)_3}]^{2+*} + \mathrm{H_2O_2} \end{aligned} \qquad (3)$$

Here, the redox potencials of $\mathrm{HO_2^{\cdot} + H^+/H_2O_2}$ and $[\mathrm{Ru(bpy)_3}]^{2+}$ in aqueous solution are $+1.495$ V[9] and $-1.28$ V[10,11] vs. NHE, respectively. The difference of the potentials, $1.495-(-1.28)$, is 2.775 V. This value is larger than the excitation energy for $[\mathrm{Ru(bpy)_3}]^{2+}$ of 2.7 eV which corresponds to the absorption maximum of 455 nm. Therefore, $[\mathrm{Ru(bpy)_3}]^{2+*}$ is probably produced by the Reaction 3.

At the anode the oxidation of $[\mathrm{Ru(bpy)_3}]^{2+}$ and water may occur. One of the products is likely to be oxygen. This oxygen may be used for the reduction at the cathode. Thus the ECL continued for hours.

The contribution of $\mathrm{HO_2^{\cdot}}$ in the dc-ECL mechanism was supported by the experiment with a reducing reagent. As shown in Fig. 6 the chemiluminescence was observed when a $[\mathrm{Ru(bpy)_3}]^{2+}$ aqueous solution was reduced with the Mg metal in the presence of $\mathrm{O_2}$. In this case the reaction scheme is considered as follows;

$$1/2\mathrm{Mg} + [\mathrm{Ru(bpy)_3}]^{2+} \longrightarrow 1/2\mathrm{Mg^{2+}} + [\mathrm{Ru(bpy)_3}]^{+} \qquad (4)$$

$$1/2\mathrm{Mg} + \mathrm{H^+} + \mathrm{O_2} \longrightarrow 1/2\mathrm{Mg^{2+}} + \mathrm{HO_2^{\cdot}} \qquad (5)$$

Here, the two reactions are highly exothermic as calculated to be $\Delta G = -105.2$ and $-372.9$ kJ mol$^{-1}$ for Eqs. 4 and 5, respectively. The products of these reactions may produce $[\mathrm{Ru(bpy)_3}]^{2+*}$ as shown by Eq. 3, followed by light emission.

The discussion next turns to the third feature of the dc ECL at which the area of the anode is smaller than that of the cathode. In the two-electrode cell, the applied voltage V is represented by

$$V = E_{\mathrm{a}}(i) + (-E_{\mathrm{c}}(i)) + Vr(I) \qquad (6)$$

Here, $E_{\mathrm{a}}(i)$ and $E_{\mathrm{c}}(i)$ are the anode and cathode potentials with the current density $i$, and $Vr(I)$ is the ohmic drop associated with the solution resistance and the current $I$ through the cell. When the area of the cathode is considerably larger than that of the anode, the current density of the cathode is very small and $E_{\mathrm{c}}(i)$ is close to the standard electrode potential of the electrode substance. This explains the fact that the cathode potential correlates with the redox potential of the electrode materials as shown in Table 2. Further-more, by adding TBAP to the solution, the resistance of the solution decreases and consequently *Vr*(*I*) decreases. Thus the cathode potential increases with the TBAP concentration at a constant applied potential as shown in Fig. 3.

In the present study, the current through the cell is limited by the substance transport at a wire CE having a small surface area. Then, at the larger sheet WE the current density is low although the potential is high enough for oxygen and $[Ru(bpy)_3]^{2+}$ to be reduced. This situation may be necessary to produce both $[Ru(bpy)_3]^{+}$ and $HO_2^{\cdot}$ at the cathode. In order to prevent the further reduction of $HO_2^{\cdot}$ and $[Ru(bpy)_3]^{+}$, the species produced must quickly diffuse from the cathode surface to the solution. This may also be achieved by the small current density at the cathode.

## Conclusion

The most plausible mechanism of the dc ECL in the two-electrode cell is the formation of $[Ru(bpy)_3]^{2+*}$ by the reaction between $[Ru(bpy)_3]^{+}$ and $HO_2^{\cdot}$ both of which are produced at the cathode. The potential of the sheet cathode in the two-electrode cell is affected by the standard potential of the electrode material and the concentration of the supporting electrolyte. This observation is used to reveal the emission mechanism and to solve the questions in the previous report.

We are grateful to Professor A. J. Bard for very useful discussions on the dc-ECL mechanism and to Dr. Masao Kaneko for valuable discussions. This work was supported by Nippon Seiki Co., Ltd.

## References

1) Former name is the Technological University of Nagaoka.

2) R. Igarashi, Y. Nosaka, H. Miyama, M. Kaneko, and M. Yokoyama, *J. Electrochem. Soc.*, **135**, 2987 (1988).

3) N. E. Tokel and A. J. Bard, *J. Am. Chem. Soc.*, **94**, 2862 (1972).

4) I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **103**, 512 (1981).

5) H. S. White and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 6891 (1982).

6) D. Meisel and G. Gzapski, *J. Phys. Chem.*, **79**, 1503 (1975).

7) P. George, "Oxidases and Related Redox Systems," ed by T. E. King, H. S. Mason, and M. Morison, Wiley, New York (1965), p. 3.

8) J. Divisek and B. Kastening, *J. Electroanal. Chem.*, **65**, 603 (1975).

9) "CRC Handbook of Chemistry and Physics" 66th ed, ed by R. C. Weast (1985).

10) N. Sutin and C. Creutz, *Adv. Chem. Ser.*, **168**, 1 (1978).

11) F. Bolletta, M. Ciano, V. Balzani, and N. Serpone, *Inorg. Chim. Acta*, **62**, 207 (1982).