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The Absorption Spectra of the Electrochemically-generated Unstable Species of Tris(2,2′-bipyridine)cobalt(II) by Reflectivity Measurements at the Silver Electrode in Propylene Carbonate

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Synopsis. Tris(2,2′-bipyridine)cobalt(II) perchlorate gave a two-step reduction wave ascribed to $[Co(bipy)_3]^{2+} \xrightarrow{e} [Co(bipy)_3]^{+} \xrightarrow{2e} [Co(bipy)_3]^{-}$ at the Ag electrode in a propylene carbonate solution. The simultaneously-recorded reflectivity-potential curve showed a reflectivity decrease corresponding to each wave on the *i-E* curve. The absorption spectra due to the unstable reduction products, $[Co(bipy)_3]^{+}$ and $[Co(bipy)_3]^{-}$, were obtained by plotting the reflectivity change *vs.* the wavelengths.

In a previous paper,[1] we showed that the reflectivity measurement enabled one to obtain the spectra of unstable species generated during electrolysis, and that the method has successfully been used to detect the reduction products of the tris(2,2′-bipyridine)chromium(III) complex.

The present communication will extend the method to support the previous conclusion[2] that lower-valence complexes can be generated by the reduction of tris(2,2′-bipyridine)cobalt(II).

Experimental

The current-potential (*i-E*) and reflectivity-potential (R/R_0-*E*) curves were obtained in propylene carbonate (PC) by the same apparatus and method as were reported in the previous paper.[1] Tris(2,2′-bipyridine)cobalt(II) perchlorate, $[Co(bipy)_3](ClO_4)_2$, was prepared according to the literature.[3]

Results and Discussion

Figure 1 shows the *i-E* and R/R_0-*E* curves simultaneously obtained in a solution containing $[Co(bipy)_3](ClO_4)_2$. This complex gave a two-step reduction wave in the potential range between 0 and −2.0 V and the corresponding anodic wave. Upon the addition of free 2,2′-bipyridine to a solution containing the complex, the peak heights of the first and the second step were not affected; this shows that two steps may be concluded to be due to the reduction of the cobalt(II) complex itself and not to the reduction of the free bipyridine liberated from the complex. The peak potential of the first step is not affected, whereas that of the second one is shifted to more negative potentials with an increase in the concentrations of free bipyridine. This seems to be attributable to the substitution labile nature of the product—*viz.*, a dissociation of the ligand from the reduction product.[2] Such an instability could be avoided by the addition of a large excess of free ligands to the solution.

With the aid of the results obtained in an acetonitrile solution,[2] the first step in the cathodic scan seems to be ascribable to the one-electron reduction of;

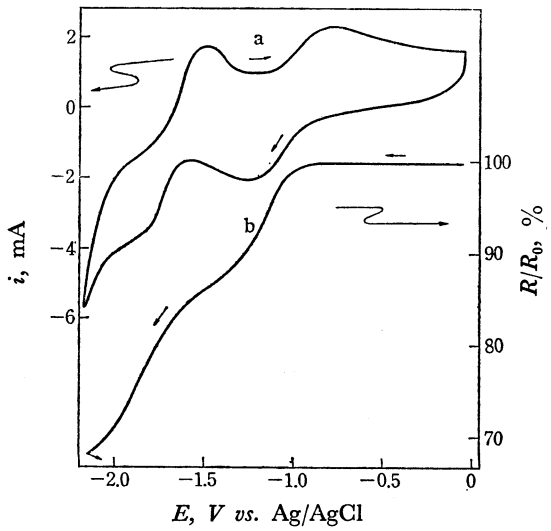

Fig. 1. The *i-E* (a) and R/R_0-*E* (b) curves of 0.5 mM $[Co(bipy)_3](ClO_4)_2$ at silver electrode in the presence of 20 mM 2,2′-bipyridine in 0.05 M $(C_2H_5)_4NClO_4$ of PC solution. Potential sweep rate was 440 mV/s and R/R_0 was measured at 630 nm.

$$[Co(bipy)_3]^{2+} + e \longrightarrow [Co(bipy)_3]^{+} \quad (1)$$

The peak potential difference between the first and the second cathodic peaks in a PC solution is about 0.65 V, nearly equal to the difference between the half-wave potentials of the first and the second reduction waves (0.66 V) obtained in an acetonitrile solution.[2] This fact suggests that the same electrode process as that in an acetonitrile solution occurs in the PC solution in the second process; namely:

$$[Co(bipy)_3]^{+} + 2e \longrightarrow [Co(bipy)_3]^{-} \quad (2)$$

Tanaka and Ogata[4] also pointed out that $[Fe(bipy)_3]^{2+}$ and $[Ni(bipy)_3]^{2+}$ in the PC solution showed almost the same polarographic waves due to the reduction into the low-valence states as those observed in the acetonitrile solution.

The simultaneously-recorded R/R_0-*E* curve is shown in Fig. 1 as Curve (b); only the cathodic process is shown. The correspondence between the *i-E* and R/R_0-*E* curves is very good; *i.e.*, the starting potentials of all the steps on the *i-E* and R/R_0-*E* curves are almost the same, and the first (−1.25 V) and the second peak potentials (−1.90 V) on the *i-E* curve correspond to the potentials where the reflectivity changes most dramatically, implying the formation of the reduced states at these potentials.

The reflectivity decrease is associated with the successive formation of two different types of reduction

products formed at each corresponding potential. The reflectivity decrease at the first wave is considered to be due to the formation of $[Co(bipy)_3]^+$. If this is true, and if Reaction (1) is reversible, the recovery of the reflectivity will be observed upon the oxidation of the reduction product. This was confirmed by measuring the R/R_0-t curve shown in Fig. 2. At first the potential was set at -1.35 V to produce $[Co(bipy)_3]^+$; then the potential was stepped to -0.70 V to oxidize the reduction product. During these operations, the recovery of the reflectivity at -0.70 V was clearly seen on the R/R_0-t curve, seeming to indicate the re-formation of $[Co(bipy)_3]^{2+}$ by the electro-oxidation.

The formation of $[Co(bipy)_3]^+$ is further supported by the absorption spectrum obtained. The reflectivity decrease observed at -1.35 V was plotted *vs.* the wavelength; it is shown in Fig. 3 as Curve (a). The observed reflectivity change is mainly due to the entities formed in the solution and not to the change in the optical properties of the silver electrode*; accordingly, plotting gives the absorption spectrum.

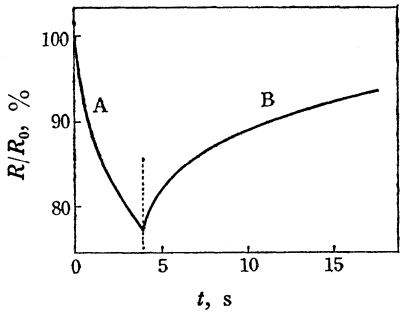

Fig. 2. The R/R_c-t curve of 0.5 mM $[Co(bipy)_3](ClO_4)_2$ in the presence of 20 mM 2,2′-bipyridine and 0.05 M $(C_2H_5)_4NClO_4$ in PC obtained at 630 nm.
Electrode potential was set at -1.35 V in region A and then stepped to -0.70 V in region B.

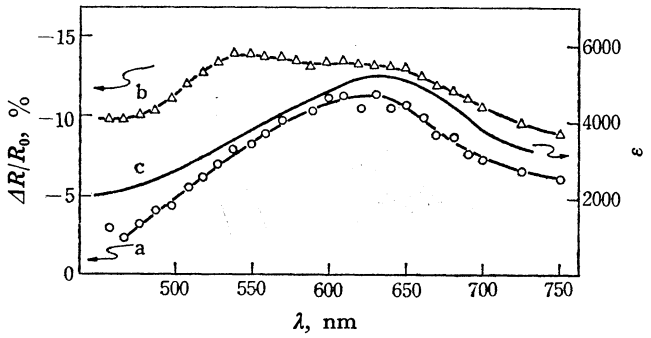

Fig. 3. Wavelength dependence of reflectivity decreases due to electrochemically generated species (a, b) and the absorption spectrum of $[Co(bipy)_3]^+$ in aqueous solution (c).[5] $\Delta R/R_0$ was obtained at varied wavelengths from R/R_0-E curve of the same solution as Fig. 1. $\Delta R/R_0$ of curve (a) was read at -1.35 V and curve (b), at -1.90 V.

* Even during the electrolysis, the decreased reflectivity was eliminated when the solution was stirred vigorously to remove the reduction product from the optical path.

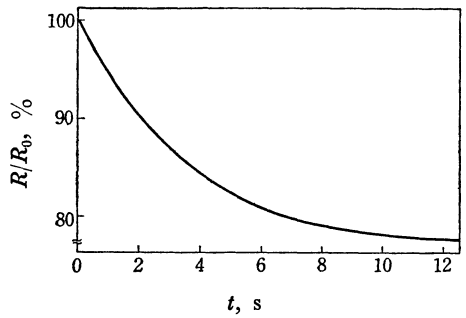

Fig. 4. The $\Delta R/R_0$-t curve measured at 630 nm at open circuit after electrolysis was carried out for 5 s at -1.90 V. Electrolytic solution contained 0.5 mM $[Co(bipy)_3](ClO_4)_2$, 20 mM 2,2′-bipyridine and 0.05 M $(C_2H_5)_4NClO_4$ in PC.

Curve (c) in Fig. 3 is the absorption spectrum of $[Co(bipy)_3]^+$ in an aqueous solution.[5] The curve obtained from the reflectivity measurement fairly well coincides with the reported curve.[5] The small difference in the position of the absorption maximum may be due to the difference in the medium used. Therefore, the reduction product at the first wave on the i-E curve may be concluded to be $[Co(bipy)_3]^+$, and the reflectivity measurement is proved to be a useful method for obtaining the absorption spectrum of the unstable species generated by the electrochemical method.

The absorption spectrum of the species formed at the potential of the second wave, which may be $[Co(bipy)_3]^-$, is given in Fig. 3 as Curve (b), where the difference in R/R_0 between the first and second steps in Fig. 1, (b) is plotted against the wavelength.[1] The bipyridine complex of Co(-I) has not yet been prepared, according to the author's knowledge, so this may be the first spectrum due to $[Co(bipy)_3]^-$.

The $\Delta R/R_0$-t curve was recorded at 630 nm at an open circuit after the electrolysis had been carried out at second wave for 5 s to produce $[Co(bipy)_3]^-$; then the electrolysis was turned off. The curve thus obtained is shown in Fig. 4. The $\Delta R/R_0$ at 630 nm decreased with the lapse of time. This means that $[Co(bipy)_3]^-$ was changed to a substance with an absorption at 630 nm; it may be $[Co(bipy)_3]^+$. That is, a proportionation reaction such as:

$$[Co(bipy)_3]^- + 2[Co(bipy)_3]^{2+} \longrightarrow 3[Co(bipy)_3]^+ \quad (3)$$

seems to occur, where $[Co(bipy)_3]^-$ is formed at -1.90 V and $[Co(bipy)_3]^{2+}$ is supplied from the bulk solution. For the confirmation of such a reaction, however, further detailed study will be required.

References

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