CHEMISTRY LETTERS, pp. 1027-1030, 1973. Published by the Chemical Society of Japan

OPTICAL DETECTION OF ELECTROCHEMICALLY GENERATED UNSTABLE REDUCTION INTERMEDIATES OF TRIS(2,2'-BIPYRIDINE)CHROMIUM(III) BY REFLECTIVITY MEASUREMENT AT SILVER ELECTRODE IN PROPYLENE CARBONATE

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Tris(2,2'-bipyridine)chromium(III) perchlorate gave three step reduction waves ascribed to $[Cr(bipy)_3]^{3+} \xrightarrow{e} [Cr(bipy)_3]^{2+} \xrightarrow{e} [Cr(bipy)_3]^{+} \xrightarrow{e} [Cr(bipy)_3]^{0}$ on Ag electrode in propylene carbonate. Simultaneously recorded reflectivity-potential curve shows three steps of reflectivity decrease corresponding to the each wave on i-E curve. Absorption spectra due to the unstable low valence state of the complex produced during the electrolysis have successfully been obtained by the plotting of the reflectivity change at each step vs. wavelength.

It is known that tris(2,2'-bipyridine)chromium(III) complex shows three electro-reduction steps in aqueous solution[1], and six steps in acetonitrile solution[2] at the dropping mercury electrode, and the first three steps from positive to negative potentials are ascribed to the reduction processes of

$$[Cr(bipy)_3]^{3+} \xrightarrow{e} [Cr(bipy)_3]^{2+} \xrightarrow{e} [Cr(bipy)_3]^{+} \xrightarrow{e} [Cr(bipy)_3]^{0} \qquad (1)$$

These complexes of low valence state can be prepared only under the very drastic conditions[3], but no measurements of absorption spectra of these species seem to have been carried out during the electrolysis because of their instability.

Reflectivity measurement[4] has been undertaken in an attempt to provide a method of obtaining the absorption spectra of such unstable species generated during the electrolysis. In the present communication, we will report on the low valence states of tris(2,2'-bipyridine)-chromium complex in propylene carbonate (PC) solution to support the previous conclusion.

EXPERIMENTAL Silver plate of 99.99 % purity and 0.5 mm thickness was cut into two rectangular plates of areas 45 x 15 mm and 35 x 15 mm as working electrode (surface area = 12 cm^2). The pre-treatment and the arrangement of the electrode is the same as described in the previous paper[5]. The angle of incidence of light is 57.5° and the number of reflection is 3. The electrode potential was referred to a Ag/AgCl electrode.

Electrolysis and optical systems are the same as those described in the previous paper[5].

The electrolysis was carried out mainly by the potential sweep method where current-potential (i-E) and reflectivity-potential (R/R_0-E) curves were recorded simultaneously.

The water content of distilled PC was about 100 ppm. Tris(2, 2'-bipyridine)chromium(III) perchlorate was prepared according to the literature⁶⁾ and identified by elementary analysis. All the measurements were carried out in an atmosphere of dried nitrogen gas at 26 ± 1 °C.

RESULTS AND DISCUSSION Typical i-E and R/R_0-E curves obtained in solution containing 0.5 mM $[Cr(bipy)_3](ClO_4)_3$ and 0.05 M $(C_2H_5)_4NClO_4$ are reproduced in Fig. 1.

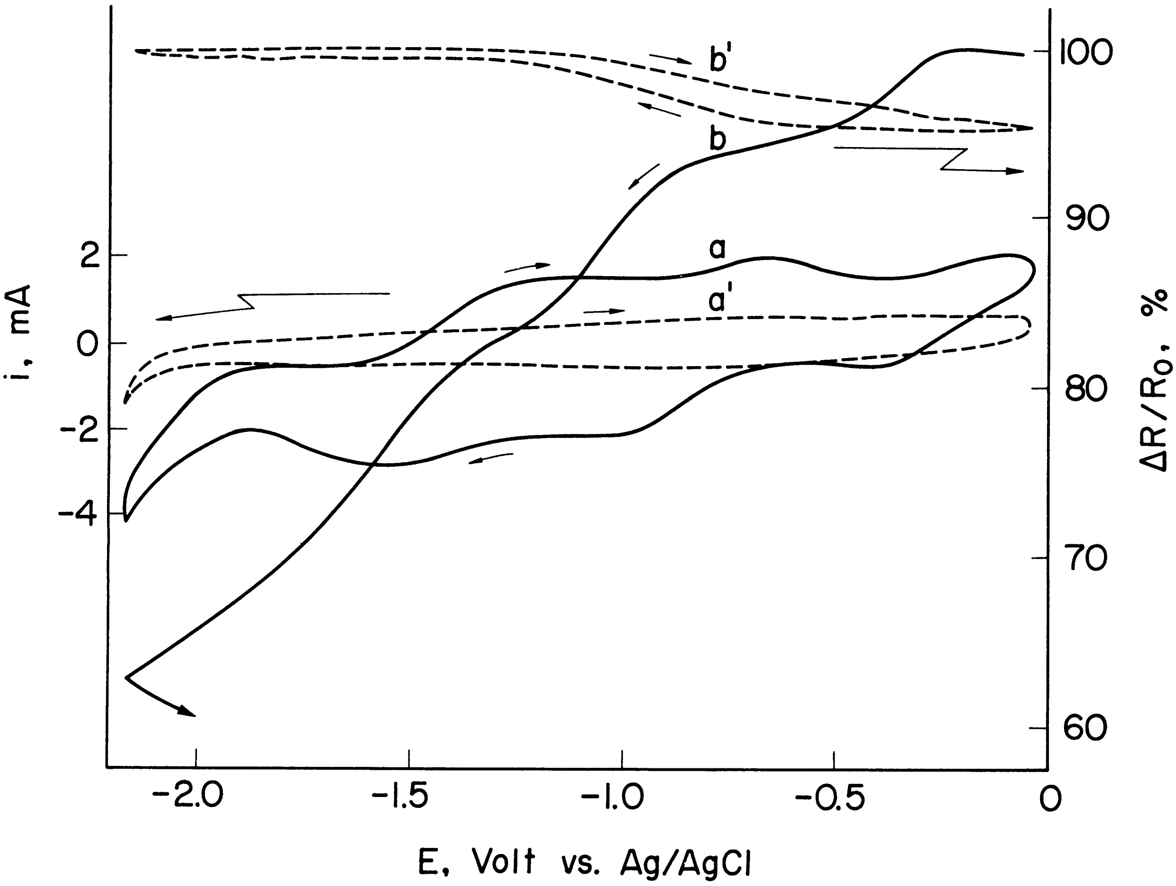

Fig. 1 Current-potential (a, a') and reflectivity-potential (b, b') curves at silver electrode in the absence (a', b') and the presence (a, b) of 0.5 mM $[Cr(bipy)_3](ClO_4)_3$ in 0.05 M $(C_2H_5)_4NClO_4$ of PC solution. Potential sweep rate was 424 mV/s and R/R_0 was measured at 560 nm.

Three clear waves at about -0.4 V, -1.05 V and -1.5 V were observed accompanying the corresponding anodic waves on the anodic sweep i-E curve. Each step is considered to correspond to the one-electron reduction step given in equation (1) as those obtained at DME¹˒ ²⁾. Simultaneously recorded R/R_0-E curve (curve b in Fig. 1) shows clearly three steps of reflectivity decrease, each of which corresponds to each wave on the cathodic sweep i-E curve, respectively. This shows three types of reduction products were formed on the electrode surface at each potential. The solution containing only supporting electrolyte shows no remarkable change in reflectivity as seen in Fig. 1 as dashed line (b'). From R/R_0-E curves at varied wavelengths, we obtained the absorption spectra of species which were electrochemically generated at -0.6 V,

-1.2 V and -1.85 V respectively: The difference in R/R_0 ($\Delta R/R$) between successive steps in Fig. 1, (b) was plotted against wavelength, and this will give the absorption spectra since the reflectivity decrease in the present case is only caused by the entities formed during the electrolysis. The results are shown in Fig. 2.

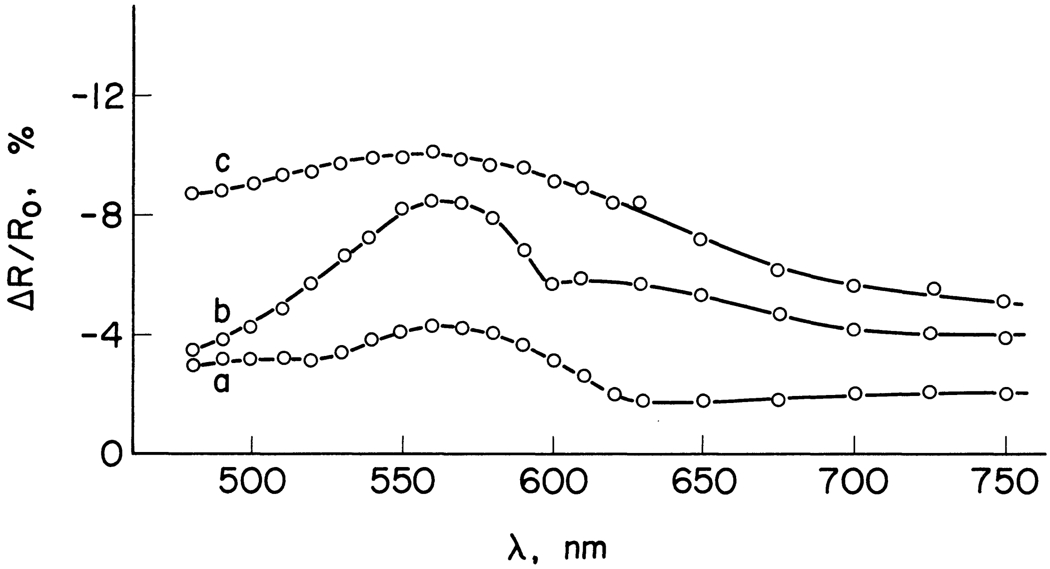

Fig. 2 Wavelength dependences of reflectivity decreases due to electrochemically generated species. $\Delta R/R_0$ was obtained from R/R_0-E curve (see curve b in Fig. 1) at varied wavelengths. $\Delta R/R_0$ of curve a was read at -0.6 V, curve b, at -1.2 V, and curve c, at -1.85 V.

Curve a in Fig. 2 obtained at -0.6 V is considered to be due to $[Cr(bipy)_3]^{2+}$, curve b to $[Cr(bipy)_3]^{+}$, and curve c to $[Cr(bipy)_3]^{0}$. König and Herzog[7] reported the electronic spectra of $[Cr(bipy)_3]^{2+}$, $[Cr(bipy)_3]^{+}$ in methanol, and $[Cr(bipy)_3]^{0}$ in tetrahydrofurane. According to the paper[7], $[Cr(bipy)_3]^{2+}$ has absorption maximum at 555 nm, $[Cr(bipy)_3]^{+}$ 555 nm with a shoulder at about 620 nm, and $[Cr(bipy)_3]^{0}$ at 555 nm. In view of the peak position and the intensity, each spectrum obtained in the present study is in fair agreement with that reported by König and Herzog[7]. Therefore, the species formed at the potential region of the first wave of the i-E curve is concluded to be $[Cr(bipy)_3]^{2+}$, at the second wave to be $[Cr(bipy)_3]^{+}$, and at the third wave to be $[Cr(bipy)_3]^{0}$.

The $\Delta R/R_0$-time curve was recorded at 560 nm and 650 nm at open circuit after the electrolysis was carried out at -1.17 V (second wave) for 5 sec to produce $[Cr(bipy)_3]^{+}$, then the electrolysis was turned off. The reflectivity at 560 nm decreased slightly (about 0.2%), while that at 650 nm increased by about 5% for 10 sec after the electrolysis was turned off. A similar $\Delta R/R_0$-t curve was also measured after the electrolysis at -0.54 V where $[Cr(bipy)_3]^{2+}$ was formed, but it was unchanged both at 560 nm and 650 nm. These results will suggest the reduction product formed at -1.17 V having absorption at 650 nm was changed to a substance having absorption at 560 nm, which may be $[Cr(bipy)_3]^{2+}$. The fact that the reflectivity change at

560 nm is small may be attributed to the absorption peak of $[Cr(bipy)_3]^{2+}$ whose absorption coefficient is about the half that of $[Cr(bipy)_3]^{+}$ 7). When the cyclic i-E curve of the second step was measured at different potential scan speed, the ratio of anodic peak height to cathodic one was far less than unity at slower scan speed (4.3 mV/s), while it tends to unity at faster scan speed, suggesting the consumption of $[Cr(bipy)_3]^{+}$ during slower scan. These results may be explained on the basis of the proportionation reaction such as

$$[Cr(bipy)_3]^{+} + [Cr(bipy)_3]^{3+} \longrightarrow 2[Cr(bipy)_3]^{2+} \qquad (2)$$

where $[Cr(bipy)_3]^{+}$ is formed at the second step of electrochemical reduction and $[Cr(bipy)_3]^{3+}$ is supplied from the bulk solution. For the confirmation of such reaction, further detailed study will be required. In the absorption spectrum shown in Fig. 2 as curve b, however, the contribution of such reaction as (2) will be negligibly small, because curve b was obtained from the rapid scanning R/R_0-E curve (see Fig. 1). Time consumed from the starting potential of the second wave to its plateau where $\Delta R/R_0$ was read is about 1 sec, while for 10 sec the reflectivity change is about 5% as described above. Thus, the reflectivity measurement is proved to be one of usefull method to obtain the absorption spectrum of the unstable species generated by electrochemical method.

ACKNOWLEDGEMENT The author wishes to thank Dr. T. Takamura of this laboratory for his kind advice and encouragement in this study.

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(Received July 12, 1973)