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POLAROGRAPHY OF THE CIS-DICYANOBIS(ETHYLENEDIAMINE)CHROMIUM(III) COMPLEX

Nobufumi MAKI
Department of Chemistry, Faculty of Engineering
Shizuoka University, Hamamatsu

The cis-$[Cr^{III}(CN)_2en_2]ClO_4$ complex gave rise to a two-stepped wave responsible for the reductions of Cr(III) to Cr(II) and to Cr(I) state at the dropping mercury electrode(DME) in dimethyl sulfoxide(DMSO). The reduction of the first step is reversible, while that of the second is quasi-reversible. The standard redox potential of the Cr(III)/Cr(II) couple was - 1.586 V (vs. aq. SCE). In aqueous solutions containing 0.5 M Na_2SO_4 or acetate buffer, however, the cis-$[Cr(CN)_2en_2]^+$ ion gave rise to only one irreversible wave for the reduction of Cr(III) to Cr(II) even in the presence of ethylenediamine in a large excess. Unlike the cases of cis-$[Co(CN)_2en_2]^+$ and cis-$[Co(CN)_2dip_2]^+$, the aquation of the resulting Cr(II) complex occurs so fast that a cyanide disproportionation reaction cannot be observed under such conditions.

In 100% dimethyl sulfoxide(DMSO) containing 0.1 M tetraethylammonium perchlorate, the cis-$[Cr^{III}(CN)_2en_2]^+$ ion gave rise to a well-defined wave of two steps at the dropping mercury electrode(DME).[1)] The ratio of the wave-heights was approximately 1 : 1.04, corrected for drop time. The two steps, each corresponding to the stepwise acceptance of one electron, represent the reductions of Cr(III) to Cr(II) and of Cr(II) to Cr(I) state respectively, similar to the polarographic behavior of cis-$[Co(CN)_2en_2]^+$ and cis-$[Co(CN)_2dip_2]^+$ ions in DMSO,[2,3,4)] with the exception of the fact that no further reduction to Cr(0) state occurs over the potential range of 0 ~ - 2.7 V (vs. aq. SCE). The limiting current of both the steps is proportional to the complex concentration in the range between 10^{-4} and 10^{-2} M. No appreciable shift with the concentration of the half-wave potentials was observed in DMSO. Plots of log i versus log t during the life of a single mercury drop exhibit slopes of 0.179 and 0.180 at the first and the second step respectively, the values of which are reasonable for a diffusion-controlled feature. The limiting current of the first step increases linearly with temperature over the wide range of 20 ~ 50°C, while that of the second does within the range of 20 ~ 36°C. Above this temperature, the current of the second step becomes kinetically-controlled, but no deformation of the wave was observed. The temperature coefficients of the current were 1.56 and 1.68 %/degree at 25°C for the first and the second step respectively.

The logarithmic analysis of the current-potential curve shows straight lines with slopes of 0.059 and 0.056 V for the first and the second step respectively, indicating that the reduction of the first step is a one-electron reversible process, while that of the second is also very near to the reversible process. This conclusion is supported by the fact that the cathodic half-wave potential(- 1.586 V vs. aq. SCE) agrees quite well with the anodic one for the first step, but not strictly for the second, using a Kalousek commutator. Namely, the continuous cathodic-anodic wave apparently in one step was recorded at the auxiliary constant potential of - 1.70 V (vs. aq. SCE), but not at - 2.40 V (vs. aq. SCE). The conclusion is further reinforced by the fact that the result inferred from Kalousek polarograms is consistent with that of oscillopolarograms of the Heyrovsky-Forejt type. That is, the clear-cut cathodic indentation agreed in its magnitude and position with the anodic one.

From the results obtained thus far, the electrode reaction responsible for the two-stepped wave may be considered as follows:

$$\underset{\text{inert}}{\text{cis-}[\mathrm{Cr}^{\mathrm{III}}(\mathrm{CN})_2\mathrm{en}_2]^+} \xrightarrow{e} \underset{\text{inert}}{\text{cis-}[\mathrm{Cr}^{\mathrm{II}}(\mathrm{CN})_2\mathrm{en}_2]^0} \xrightarrow{e} \underset{\text{inert}}{\text{cis-}[\mathrm{Cr}^{\mathrm{I}}(\mathrm{CN})_2\mathrm{en}_2]^-}.$$

Thus, the original Cr(III) complex remains structurally intact throughout its degradation in DMSO. Namely, the polarographic reduction in DMSO may be said to be the process of an "inert-inert" type, to which the high reversibility of the two steps would be ascribed.

On the other hand, only one reduction wave was observed at the DME for 10^{-3} to 10^{-2} M of cis-$[Cr(CN)_2en_2]^+$ in aqueous solutions containing 0.5 M Na_2SO_4 or acetate buffer. The acidic buffer solutions were made of sodium acetate and acetic acid, the pH values of which ranged from 3.19 to 6.22. The ionic strength was adjusted to a unity by adding sodium sulfate. No essential difference was found in the polarographic behavior between the unbuffered and the buffered solutions, although the wave form is seen to be improved with the acidic buffer due chiefly to the prevention of the ligandolysis following aquation of the Cr(II) complex, because the release of ethylenediamine permits an increase of the OH^- concentration at the vicinity of the electrode surface. The limiting current of the first step is diffusion-controlled and depends linearly on the complex concentration of 10^{-2} to 10^{-3} M both in buffered and in unbuffered solutions. A small maximum appears on the shoulder portion of the wave with decreasing pH values, but the effect of pH value on the current-potential curve was very small in acidic regions. Therefore, data in buffer solutions will hereafter be referred to a solution with pH = 4.1, unless otherwise stated. In alkaline regions, the ill-defined, enlongated wave of one step, Cr(III) → Cr(II), was obtained due to the formation of aquo-hydroxo mixtures in an equilibrium state. In a 0.5 M Na_2SO_4 solution with an excess of ethylenediamine, the aquation of the resulting Cr(II) complex would be expected to be prevented to some extent. The result, however, did not meet this prediction. The degraded Cr(II) complex aquates so rapidly in aqueous media that even the presence of 2 M ethylenediamine could not prevent the aquation at all. In this respect, the behavior of cis-$[Cr(CN)_2en_2]^+$ is quite different from that of the corresponding cis-$[Co(CN)_2en_2]^+$ and cis-$[Co(CN)_2dip_2]^+$ ions.[2,4)] That is, the Cr(II) complex can no longer retain their ligands within the sphere of coordination in aqueous media. Recently, the one-electron reduction of $[Cr^{III}Cl_2dip_2]^+$ ion was found to be followed by fast ligand disproportionation reaction and water substitution reaction which produce an equimolar mixture of $[Cr^{II}dip_3]^{2+}$ and $[Cr^{II}dip(OH_2)_4]^{2+}$ during its degradation at the DME in aqueous media.[5)] This can be ascribed solely to the difference in the lability of the Cr(II) complex with four nitrogen donors, since the ethylenediamine is a ligand of σ-bonding nature, whereas 2,2'-dipyridyl has π-bonding character.

Table 1. Cathodic half-wave potentials(25°C)

Compound	1st step	2nd step	Supporting electrolyte
	Cr(III) → Cr(II)	Cr(II) → Cr(I)	
cis-$[Cr(CN)_2en_2]ClO_4$	-1.58_6^*	-2.08	DMSO containing 0.1 M TEAP
	-1.37	—	0.5 M Na_2SO_4 aqueous solution
	-1.36_7	—	0.5 M Na_2SO_4 aq.soln.containing 2 M en and 0.012% Triton X 100
	-1.18		$CH_3COONa + CH_3COOH$ buffer soln. (pH = 4.1, 0.0016% Triton X 100)
		Cr(II) → Cr(0)	
$[Cr\ en_3](ClO_4)_3$	-1.38^*	-1.99	DMSO containing 0.1 M TEAP

The data in DMSO involve the liquid junction potential for DMSO containing 0.1 M TEAP/ sat. KCl aq.soln., which is estimated as + 0.05(K^+) by the pilot ion method.[6] * Reversible

Voltage unit: V vs. aq. SCE TEAP is tetraethylammonium perchlorate.

From these results, it would be reasonable to conclude that the irreversible one electron reduction process in aqueous media corresponds to the reversible one of the first step in DMSO except the subsequent chemical reaction following the electron transfer. Table 1 summarizes cathodic half-wave potentials and their electrode processes and those of $[Cr\ en_3]^{3+}$ ion in DMSO for sake of comparison.

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