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Stereoselectivity in the Polarographic Reduction of Chromium(Ⅲ) Complexes with L-α-Amino Acids

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Polarographic reduction behaviors of fac-[Cr(AA)$_3$] complexes, where AA is an L-α-amino acidato ligand, have been studied in Me$_2$SO. These complexes showed two reduction waves at mercury electrode and the first corresponded to Cr(Ⅲ)→Cr(Ⅱ). This reduction potential was found to be more positive for the (+)$_{546}$-isomer than for the corresponding (-)$_{546}$-isomer in the presence of Et$_4$N$^+$.

Stereoselectivity effects in redox reactions of the transition metal complexes have been studied to obtain informations about their mechanistic details. Several authors have reported that there was a rate difference for the reaction of enantiomers with a chiral reagent and the favorable stereochemical situation for the contact paring was necessarily suitable for the electron transfer.1) Also, in the electrode reactions, which involve electron transfer steps, some papers have been published on stereoselectivity in the electrochemical reduction of transition-metal complexes.2) For example, in the reduction of singly charged cobalt(Ⅲ) complexes such as a [Co(NCS)(NO$_2$)(en)$_2$]$^+$, it was found to lead to faster specific rate constants for the cis-isomer than the symmetrical trans-isomer, indicating an easier reduction. But, there have been little reports on selectivity in the electrochemical behaviors of diastereoisomers of tris-bidentate complexes. Recently, Ueyama et al. reported that in one-electron reduction of mononuclear oxomolybdenum(Ⅴ) complex of cysteine-containing tetrapeptide as analogues of molybdoenzymes the potential difference (0.28 V) had been found between isomers and it might be due that their electrochemical properties were largely controlled with the structural changes by steric congestion in their chelations.3)

This report deals with the stereoselectivity observed in the polarographic reduction of diastereoisomers of fac-[Cr(AA)$_3$].

The fac-[Cr(AA)$_3$] complexes (AA is an L-norvaline, L-isoleucine, L-leucine or L-methionine) used here were prepared by applying the same methods as described in Ref. 4. Me$_2$SO as a solvent was distilled over

CaH_2 under reduced pressure in a stream of nitrogen. Polarographic measurements were carried out with a Yanaco voltammetric analyzer model P-1000. The sample solution containing 0.05 M (1 M = 1 mol dm^{-3}) Et_4NClO_4 as a supporting electrolyte and 0.1–1 mM Cr(III) complex in Me_2SO was deoxygenated by nitrogen gas before measurements. The working electrode was a dropping mercury electrode, and counter electrode was a Pt wire. All potentials were measured against a 0.01 M Ag/Ag^+ electrode in Me_2SO. Potential of this reference electrode was -0.12 V versus ferricinium/ ferrocene couple. All measurements were made at 25 ℃.

Regardless of its importance, it is rather difficult to obtain optically pure isomers separately in the preparation of diastereoisomers of fac-$[Cr(AA)_3]$ complexes, and both of isomers were isolated as optically pure compounds, only when L-isoleucine was used as AA. In the preparation or separation processes of these isomers, it is quite of importance for kinetic studies to determine the ratio of diastereoisomers mixture quantitatively in situ. But, in many cases, if both of optically pure isomers could not be obtained, it is difficult to determine the mixing ratio, e.g., by comparing the circular dichroism (CD) spectra.

At first, in the polarographic measurements for fac-$[Cr(isoleu)_3]$, we have found that there was a significant potential difference (ca. 0.14 V) between $(+)_{546}$- and $(-)_{546}$-isomer in the presence of Et_4NClO_4. Dc and differential pulse (DP) polarograms for pure $(+)_{546}$- and $(-)_{546}$-isomer are shown in Fig. 1. For each isomer, two-step polarographic waves were observed and the ratio of those wave-heights was ca. 1 : 2. Half-wave potential ($E_{1/2}$) for the first wave of $(+)_{546}$-isomer was more positive than $E_{1/2}$ for the corresponding $(-)_{546}$-isomer, while $E_{1/2}$'s for the second waves agreed with less than 30 mV. The log-plot analysis for the first waves revealed that the first reduction step was irreversible, one-electron process to the corresponding Cr(II) species and the limiting currents for the first waves were

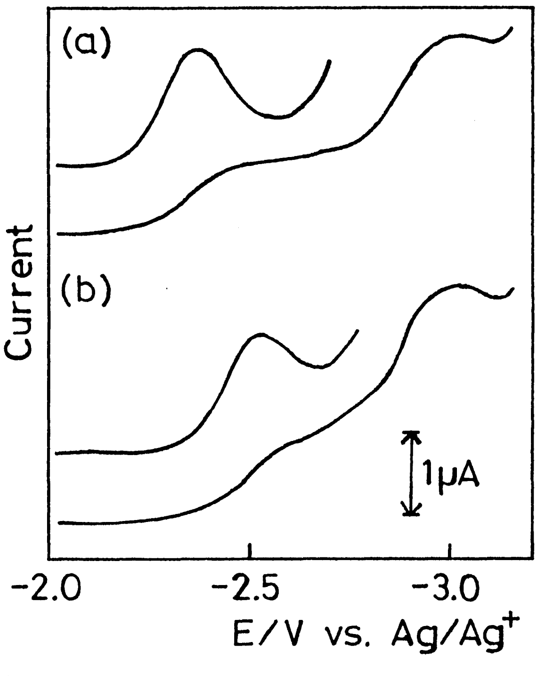

Fig. 1. Dc and DP polarograms of 7.2 x 10^{-4} M fac-$[Cr(isoleu)_3]$ observed in 0.05 M Et_4NClO_4-Me_2SO-soln. ; (a) $(+)_{546}$-isomer, (b) $(-)_{546}$-isomer.

proportional to the concentration of complex and to the square root of the height of a mercury reservoir.

On the complexes with other amino acids, optical purities for diastereoisomers were presumed to be less than about 90% from their CD spectra. But, polarographic measurements of isomers mixture have allowed the estimation of mixing ratio in situ, since the potential differences ($\Delta E = E_{1/2}{}^{+} - E_{1/2}{}^{-}$) were ca. 0.24 V for L-met, 0.14 V for L-leu and 0.16 V for L-norval, respectively. For example, Fig. 2 shows polarograms of diastereoisomers of fac-[Cr(met)$_3$], which had the most ΔE value, and the content of (+)$_{546}$-isomer could be easily estimated from their limiting currents or peak ones.

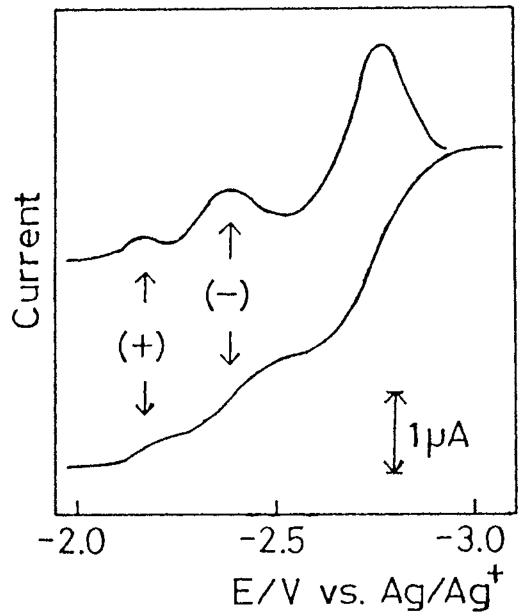

Fig. 2. Dc and DP polarograms of 1.0×10^{-3} M diastereoisomers of fac-[Cr(met)$_3$] observed in 0.05 M Et_4NClO_4-Me_2SO-soln.

These stereoselective behaviors have not been observed clearly in the presence of (n-But)$_4$N$^+$, and so they should be discussed considering to the interaction between each isomer and cations of supporting electrolytes. Construction of ball and stick models, a part of which are

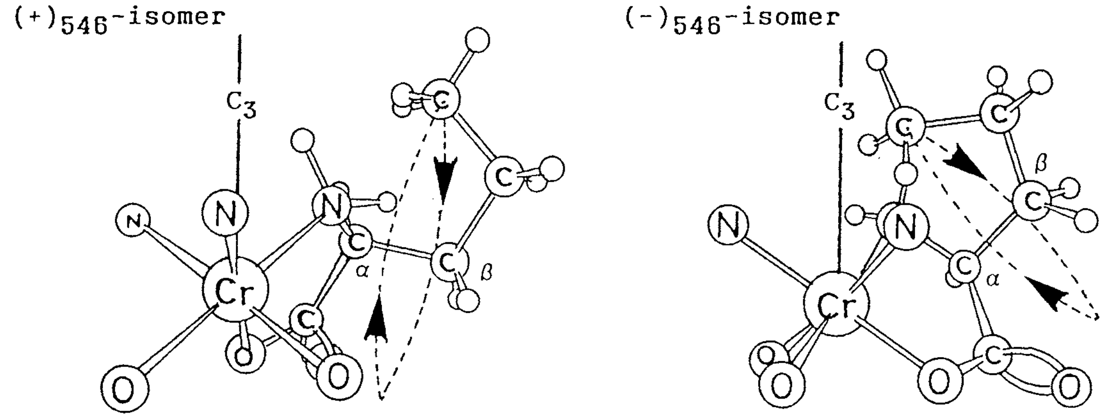

Fig. 3. Schematic geometry of (+)$_{546}$- and (−)$_{546}$-fac-[Cr(norval)$_3$]. Only nitrogen, oxygen atoms bonded to chromium atom and one amino acid molecule, which has an ethyl-group in the β-position, are illustrated. The arrows show the rotational direction of an ethyl-group around C_α-C_β bonding.

shown in Fig. 3, revealed a significant difference in molecular crowding on the site of nitrogen atoms around the three fold axis (C_3). That is, in the case of the $(-)_{546}$-isomer, nitrogen atoms are surrounded by the hydrophobic side chains of amino acids residues bonded to carbon atom (β-position) and shielded from the solvent or cation, while the $(+)_{546}$-isomer is exposed to them. The fact that the electrode reactions of these complexes with amino acids were influenced by such steric differences as implied here, is very interesting for us to investigate the direct electron transfer process between the electrode surface and metallo enzymes such as an oxido-reductase.

In addition, we have observed that the reduction potentials of the $[Cr(AA)_2(AA-N)X]$ type complexes, where AA-N was a monodentate amino acidato ligand which was coordinated through the nitrogen atom and X was a solvent molecule, were more negative than ones of corresponding fac-type complexes, and a little difference was also found in the reduction potential of their diastereoisomers. These phenomena have been utilized to do an "in situ" quantitative or qualitative analysis for Cr(Ⅲ) complexes with L-α-amino acids. Not only further discussions on the electrochemical behaviors of these Cr(Ⅲ) complexes but also studies on cobalt(Ⅲ) complexes are now undergoing in our laboratory.

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