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Electrochemical Kinetic Parameters of Geometric Isomers of Singly Charged Cobalt(III) Complexes

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The kinetic parameters of electrode reactions of several geometric isomers of singly charged cobalt(III) complexes have been determined by means of Tast polarography. The complexes studied are *trans*-$[Co(NCS)(NO_2)(en)_2]Cl\cdot H_2O$, *cis*-$[Co(NCS)(NO_2)(en)_2]Cl\cdot 2H_2O$, *trans*-$[Co(NO_2)_2(en)_2]NO_3$, *cis*-$[Co(NO_2)_2(en)_2]NO_3$, *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3\cdot 0.5H_2O$, *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$, *trans*-$[CoCl(NO_2)(en)_2]NO_3$, and *cis*-$[CoCl(NO_2)(en)_2]NO_3$. These complexes showed two irreversible reduction waves; the first corresponds to $Co^{III}\rightarrow Co^{II}$, and the second, to $Co^{II}\rightarrow Co^0$. The electrochemical kinetic parameters for the one-electron reduction wave were obtained in 0.1 and 1.0 M acetate buffer solutions. The half-wave potentials for the first wave of the complexes were more positive for the *cis* isomers than for the corresponding *trans* isomers. The cathodic rate constants at $E=0$ for the *cis* isomers were also larger than those for the corresponding *trans* isomers. A slight increase in the rate constant with the decrease in ionic strength was observed.

A number of electrochemical studies of cobalt(III) complexes[1] have been carried out. Among these studies, the polarography of geometric isomers of cobalt(III) complexes has been discussed by Holtzclaw and Sheetz,[2] Holtzclaw,[3] Inoue and Imai,[4] and Vlček.[5] However, no systematic work on geometric isomers under the same conditions has yet been done. In this paper, the electrochemical kinetic parameters of geometric isomers of singly charged cobalt(III) complex ions are determined, and the differences in kinetic parameters between isomeric pairs are discussed.

Experimental

Materials. The complexes, *trans*-$[Co(NCS)(NO_2)(en)_2]Cl\cdot H_2O$,[6] *cis*-$[Co(NCS)(NO_2)(en)_2]Cl\cdot 2H_2O$,[7] *trans*-$[Co(NO_2)_2(en)_2]NO_3$,[8] *cis*-$[Co(NO_2)_2(en)_2]NO_3$,[9] *trans*-$[Co(NO_2)_2(NH_3)_4]NO_3\cdot 0.5H_2O$,[10] *cis*-$[Co(NO_2)_2(NH_3)_4]NO_3$,[11] *trans*-$[CoCl(NO_2)(en)_2]NO_3$,[12] and *cis*-$[CoCl(NO_2)(en)_2]NO_3$,[7] were prepared by the literature methods. The ionic strength of the solution was adjusted with a sodium acetate buffer(pH=5.0). A portion of 0.005% gelatin was used as the maximum suppressor. All the other chemicals used were of a guaranteed reagent grade.

Electrochemical Measurements. A three-electrode cell[13] equipped with a saturated calomel electrode (Yanagimoto MR-P2-05-1) and a platinum-wire electrode was employed. A dropping mercury electrode (flow rate, 1.17 mg s^{-1} and drop time, 3.97 s in 0.1 M (1 M=1 mol dm^{-3}) acetate buffer solutions) served as a working electrode. The kinetic parameters of the electrode reactions were determined by means of Tast polarography. The Tast polarograms were recorded by means of a Fuso Model 312 polarograph with a Watanabe Model WX441 X-Y recorder. A Takeda Riken digital multimeter, Model TR-6355, was used, the current and the potential were thus measured precisely. Dissolved oxygen was removed by bubbling purified nitrogen gas through the solution. All the measurements were made at 25 °C.

Results and Discussion

In every complex studied, two polarographic waves were obtained. The height of the second step was about twice that of the first, which suggests that a one-electron reduction is followed by a two-electron reduction. Both steps were found to be proportional to the bulk concentration of the complex and to be diffusion-controlled. The present investigation is concerned only with the reduction of Co^{III} to Co^{II}. Slopes of the log-plots for the Tast polarogram indicate an irreversible reduction throughout. Figure 1 shows a Tast polarogram of the first waves of the *cis* and *trans* isomers obtained in 0.1 M acetate buffer solutions.

The Tast polarograms were analyzed by applying the following relations for a totally irreversible electrode process:[14]

$$(\boldsymbol{RT}/\alpha n\boldsymbol{F})\ln[2x(3-x)/5(1-x)] = E_{1/2}-E, \qquad (1)$$

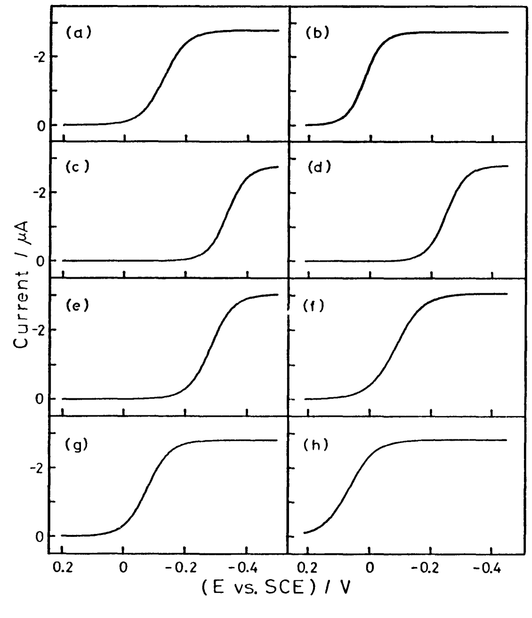

Fig. 1. Tast polarograms for the first wave of several isomeric cobalt(III) complex ions obtained in 0.1 M acetate buffer and 0.005% gelatin at 25 °C.
(a) *trans*-$[Co(NCS)(NO_2)(en)_2]^+$, (b) *cis*-$[Co(NCS)(NO_2)(en)_2]^+$, (c) *trans*-$[Co(NO_2)_2(en)_2]^+$, (d) *cis*-$[Co(NO_2)_2(en)_2]^+$, (e) *trans*-$[Co(NO_2)_2(NH_3)_4]^+$, (f) *cis*-$[Co(NO_2)_2(NH_3)_4]^+$, (g) *trans*-$[CoCl(NO_2)(en)_2]^+$, (h) *cis*-$[CoCl(NO_2)(en)_2]^+$.

with

$$x = I/I_{\mathrm{d}}, \tag{2}$$

and

$$E_{1/2} = (\boldsymbol{RT}/\alpha n\boldsymbol{F})\ln[1.35k_{\mathrm{c}}^{\circ}(t_{\mathrm{d}}/D)^{1/2}], \tag{3}$$

where I is the current at the potential, E; I_{d}, the diffusion-controlled current; D, the diffusion coefficient; t_{d}, the drop time; α, the transfer coefficient; k_{c}°, the cathodic rate constant at $E=0$; n, the number of electrons; $\boldsymbol{R}$, the gas constant; $\boldsymbol{F}$, the Faraday constant, and T, the absolute temperature. According to Eq. 1, a plot of $\ln[2x(3-x)/5(1-x)]$ *vs.* E should be a straight line. The transfer coefficient, α, can be obtained from the slope, and the half-wave potential, $E_{1/2}$, from the intersection. The rate constant, k_{c}°, can be obtained from $E_{1/2}$ by applying Eq. 3.

The kinetic parameters of the electrode reactions thus obtained in 0.1 M acetate buffer solutions are given in Table 1. The kinetic parameters thus obtained were checked by calculating the current according to this relation:

$$2x(3-x)/5(1-x) = 1.35k_{\mathrm{c}}^{\circ}(t_{\mathrm{d}}/D)^{1/2}\exp(-\alpha n\boldsymbol{F}E/\boldsymbol{R}T). \tag{4}$$

The calculated currents were in good agreement with the observed ones.

The diffusion coefficient of the cobalt complexes was measured by means of a method previously reported[15] by using $[\mathrm{Co(NH_3)_6}]^{3+}$ as the reference substance; the results are also given in Table 1. The magnitude of the diffusion coefficients of these isomers decreased in this order; *cis*- and *trans*-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+ >$ *cis*- and *trans*-$[\mathrm{CoCl(NO_2)(en)_2}]^+ >$ *cis*- and *trans*-$[\mathrm{Co(NO_2)_2(en)_2}]^+ >$ *cis*- and *trans*-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+$. According to the Stokes-Einstein equation, a diffusion coefficient increases with a decrease in the ion size. Since the size of the complex depends on that of the ligand, the magnitude of the diffusion coefficient reflects the bulkiness of the ligand.

An examination of Table 1 shows that the half-wave potentials for the first wave of the complex containing negative groups in two of the coordination positions and neutral groups in the other four are more positive for the *cis* isomer than for the corresponding *trans* isomer. This tendency is in good agreement with the earlier polarographic observation which dealt with *cis* and *trans* isomers of cobalt(III).[2] The order of the half-wave potential in the series of isomers is: *cis*- and *trans*-$[\mathrm{CoCl(NO_2)(en)_2}]^+ >$ *cis*- and *trans*-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+ >$ *cis*- and *trans*-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+ >$ *cis*- and *trans*-$[\mathrm{Co(NO_2)_2(en)_2}]^+$. This may be attributed to the electronegativity of the ligand.

The specific rate constant, k_{c}°, of the *cis* complex which contains two negative groups and four neutral groups was found to be larger than that of the symmetrical *trans* isomer. In this type of complex, a dipole exists within the coordination sphere of the *cis* form, but not in that of the symmetrical *trans* isomer. Because of the mutual electrostatic repulsion of these adjacent centers of electronegativity, the *cis* complex may be less stable than the symmetrical *trans* isomers. This may be expected to lead to faster specific rate constants for the *cis* isomer, indicating an easier reduction. The transfer coefficients of the *cis* complex in Table 1 tend to be slightly smaller than those of the corresponding *trans* isomers except for the *cis*- and *trans*-isothiocyanatonitrobis(ethylenediamine)cobalt-

TABLE 1. KINETIC PARAMETERS OF ONE-ELECTRON REDUCTION OF SEVERAL ISOMERIC COBALT(III) COMPLEX IONS OBTAINED IN 0.1 M ACETATE BUFFER (pH=5.0) AT 25 °C

Complex ion	α	$E_{1/2}$ *vs.* SCE / V	k_{c}° / cm s^{-1}	D / 10^{-6} cm^2 s^{-1}
trans-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+$	0.61	−0.129	4.86×10^{-5}	7.96
cis-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+$	0.74	−0.003	9.41×10^{-4}	7.68
trans-$[\mathrm{Co(NO_2)_2(en)_2}]^+$	0.73	−0.335	8.16×10^{-8}	8.00
cis-$[\mathrm{Co(NO_2)_2(en)_2}]^+$	0.68	−0.287	5.10×10^{-7}	8.10
trans-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+$	0.64	−0.283	1.04×10^{-6}	9.51
cis-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+$	0.50	−0.114	1.28×10^{-4}	9.68
trans-$[\mathrm{CoCl(NO_2)(en)_2}]^+$	0.63	−0.079	1.51×10^{-4}	8.10
cis-$[\mathrm{CoCl(NO_2)(en)_2}]^+$	0.52	+0.046	2.72×10^{-3}	8.21

TABLE 2. KINETIC PARAMETERS OF ONE-ELECTRON REDUCTION OF SEVERAL ISOMERIC COBALT(III) COMPLEX IONS OBTAINED IN 1.0 M ACETATE BUFFER (pH=5.0) AT 25 °C

Complex ion	α	$E_{1/2}$ *vs.* SCE / V	k_{c}° / cm s^{-1}
trans-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+$	0.65	−0.143	2.82×10^{-5}
cis-$[\mathrm{Co(NCS)(NO_2)(en)_2}]^+$	0.72	−0.014	7.03×10^{-4}
trans-$[\mathrm{Co(NO_2)_2(en)_2}]^+$	0.72	−0.346	6.46×10^{-8}
cis-$[\mathrm{Co(NO_2)_2(en)_2}]^+$	0.69	−0.317	2.12×10^{-7}
trans-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+$	0.62	−0.293	9.73×10^{-7}
cis-$[\mathrm{Co(NO_2)_2(NH_3)_4}]^+$	0.49	−0.123	1.10×10^{-4}
trans-$[\mathrm{CoCl(NO_2)(en)_2}]^+$	0.61	−0.085	1.40×10^{-4}
cis-$[\mathrm{CoCl(NO_2)(en)_2}]^+$	0.53	+0.038	2.32×10^{-3}

(III) complexes. Since the thiocyanate ion is strongly adsorbed on mercury, the transfer coefficient of *cis*-$[Co(NCS)(NO_2)(en)_2]^+$ is probably larger than that of the corresponding *trans* isomer.

The effect of the ionic strength on the kinetic parameters of the electrode reaction was tested in solutions of a 1 M acetate buffer. The results are shown in Table 2. With the increase in the ionic strength, the half-wave potential shifted toward negative potentials. This would be expected for the reduction of the positive-charge complex ions in this potential region. The specific rate constant decreased slightly with the increase in the ionic strength. The effect of the ionic strength on the rate constant may be estimated by means of Frumkin's equation as a first approximation:[16)]

$$k_c^\circ = (k_c^\circ)_t \exp[(\alpha n - z)\boldsymbol{F}\phi/\boldsymbol{RT}], \tag{5}$$

where $(k_c^\circ)_t$ is a true cathodic rate constant at $E=0$; z, the ionic charge of the reactant, and ϕ, the double-layer potential. In this work, the value of $(\alpha n - z)$ is negative, as may be seen from Table 1. The double-layer potential of acetate salt has a small negative value in this potential region and decreases with the decrease in the ionic strength;[17)] this may cause the slight increase in the rate constant with the decrease in the ionic strength.

It is difficult to compare the electrochemical kinetic parameters obtained in this work with those reported in the literature since the experimental conditions are quite different and only few data have been reported. Inoue and Imai[4)] have determined the kinetic parameters for the reduction of *trans*- and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ at the DME in 1 M $NaNO_2$: the values are $k_c^\circ = 2.9\times10^{-3}$ cm s^{-1}; $\alpha=0.65$ for *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ and $k_c^\circ=7.1\times10^{-2}$ cm s^{-1}; $\alpha=0.58$ for *cis*-$[Co(NO_2)_2(NH_3)_4]^+$ at 25 °C. Vlček[5)] has also reported the kinetic parameters of the same complex in 0.14 M $HClO_4$+1.26 M $NaClO_4$: $k_c^\circ/\sqrt{D}=1.9\times10^{-4}$ s$^{-1/2}$; $\alpha=0.6$ for *trans*-$[Co(NO_2)_2(NH_3)_4]^+$ and $k_c^\circ/\sqrt{D}=2.3\times10^{-2}$ s$^{-1/2}$; $\alpha=0.54$ for *cis*-$[Co(NO_2)_2(NH_3)_4]^+$.

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