Electron-Transfer Reactions between Cobalt(III) Complexes and Polymer-Bound Ferrous Chelate

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Synopsis. The reductions of some cobalt(III) complexes having overall charges of −1 to +3 by the polymer-bound ferrous chelate, Fe(II)-PBDA (PBDA=vinylbenzylamine-*N*,*N*-diacetate-co-4-styrenesulfonate), and the effect of sodium chloride on the reduction rate have been investigated. The specific rate increases sharply with the positive charge on the Co(III) complexes by electrostatic interactions between reactant species.

In previous papers,[1-4] the reductions of macromolecular cobalt(III) complexes by some low-molecular-weight ferrous chelates have been reported. The results of kinetic studies, i.e., the acceleration and retardation of the rates of electron-transfer reactions relative to the corresponding low-molecular-weight systems, have been interpreted, essentially, by the effects of the electrostatic, steric, and hydrophobic interactions between the reactant species in the macromolecular domains.

Experimental

The preparation of (vinylbenzyl)amine-*N*,*N*-diacetic acid (VBDA) and a method for the copolymerization of VBDA with sodium 4-styrenesulfonate (NaSS) have been described elsewhere.[5,6] To the reaction mixture after copolymerization, dilute sodium hydoxide solution was added. The mixture was dialyzed in water for 3 d with cellulose dialyzer tubing (Nakarai Chemicals Co., MW cutoff 8,000), evapolated to dryness, grained with a mortar, and dried in vacuo at 80 °C. The sodium salt of VBDA-co-NaSS (PBDA) was obtained as a white powder. The intrinsic viscosity of an aqueous solution of PBDA was 1.3 dl g^{-1} at 25 °C. (Ethylbenzyl)amine-*N*,*N*-diacetic acid (EBDA) was prepared according to a similar method described elsewhere.[5] Sodium chloro[ethylenediaminetetraacetato(3−)]-cobaltate(III) (Na[CoCl(Hedta)]),[7] bis(ethylenediamine)oxalatocobalt(III) chloride ($[Co(ox)(en)_2]Cl$),[8] pentaamminechlorocobalt(III) chloride ($[CoCl(NH_3)_5]Cl_2$),[9] hexaamminecobalt(III) chloride ($[Co(NH_3)_6]Cl_3$),[10] and tris(ethylenediamine)cobalt(III) chloride ($[Co(en)_3]Cl_3$)[11] were prepared by the reported methods. The concentration of PBDA is represented by the monomer unit of the VBDA in the copolymer and the unit of the concentration is expressed by mol dm^{-3}. Solutions of Fe(II)-PBDA and Fe(II)-EBDA were prepared by mixing a deoxygenated buffer solution of the chelating agent with equivalent amounts of deoxygenated ammonium iron(II) sulfate solution under an atmosphere of argon. The viscosities were measured in aqueous solutions, using Ubbelohde-type viscometer at 25±0.1 °C.

The kinetic experiments were undertaken at pH 7.5—8.5 (phosphate buffer), I=0.03 (I; ionic strength), and 25±0.2 °C. The reactions were followed under pseudo-first-order conditions with a large excess of the ferrous chelate by observing the decay of the absorbances of the cobalt(III) complexes at 350—600 nm using a Yanagimoto Model SPS-1 stopped-flow spectrophotometer. The concentrations of Co(III) and Fe(II) in the reaction solutions were 1.0×10^{-4} and 1.0×10^{-3} mol dm^{-3}, respectively. The rate constants were determined from the slopes of the log (A_t-A_∞) vs time. Absorption spectra were recorded on a Hithachi Model 320 recording spectrophotometer.

Results and Discussion

The chemical structure and composition of the sodium salt of PBDA prepared is illustrated in Fig. 1. The content of the VBDA moieties on the polymer chain was also ascertained spectrometrically: e.g., examinations of the method of continuous variation and the absorption spectra for a VBDA-co-NaSS-Ni^{2+} solution were carried out. The molecular weight of this polymer-bound chelating agent was estimated to be at least 8000 since a dialysis of the copolymer solution was carried out using cellulose dialyzer tubing of MW cutoff through 8000. This molecular weight corresponds to about 4 monomer units of the chelating agent and about 33 units of the sulfonate groups on a polymer chain. This indicates that this polymer has a great number of negatively charged sulfonato groups on the polymer backbone.

In all cases for the polymer and the low-molecular-weight systems, plots of log (A_t-A_∞) vs time gave

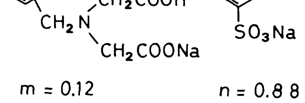

Fig. 1. Chemical structure of PBDA.

Table Pseudo-First-Order Rate Constants for the Reductions of Co(III) Complexes with the Ferrous Chelates at pH 8.0, I=0.03, and 25 °C[a)]

Co(III) complex ion	Reductant	
	Fe(II)-PBDA k_p/s^{-1}	Fe(II)-EBDA k_m/s^{-1}
$[CoCl(Hedta)]^-$	1.75±0.04	1.40±0.30
$[Co(ox)(en)_2]^+$	42.7±2.2	17.6±0.6
$[CoCl(NH_3)_5]^{2+}$	7.6±0.4	2.1±0.04
	7.4±0.4[b)]	2.2±0.1[b)]
	7.6±0.8[c)]	2.0±0.07[c)]
$[Co(en)_3]^{3+}$	41.9±0.5	3.5±0.1
$[Co(NH_3)_6]^{3+}$	60.4±0.5	8.8±0.1

a) Initial concentrations are 1.0×10^{-4} mol dm^{-3} Co(III) and 1.0×10^{-3} mol dm^{-3} Fe(II). b) pH 7.5. c) pH 8.5.

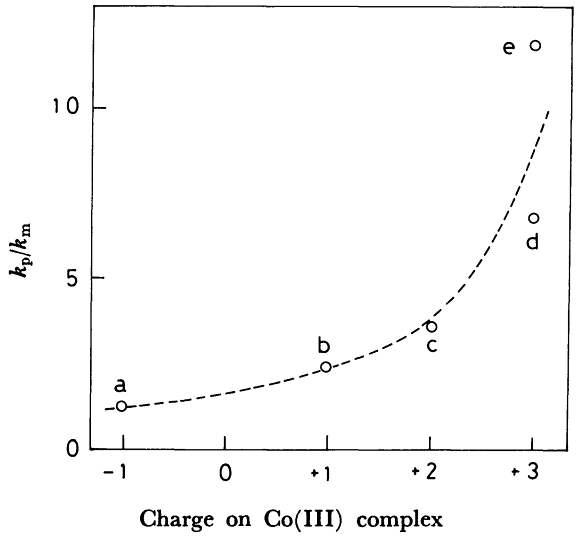

Fig. 2. Relationship between acceleration factor and the charges on the Co(III) complexes.
a: $[CoCl(Hedta)]^-$, b: $[Co(ox)(en)_2]^+$, c: $[CoCl(NH_3)_5]^{2+}$, d: $[Co(en)_3]^{3+}$, e: $[Co(NH_3)_6]^{3+}$.

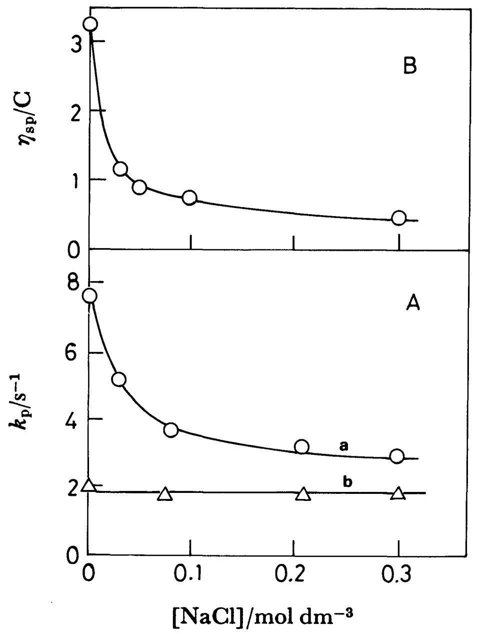

Fig. 3. Dependences of k_p on [NaCl] (A) and η_{sp}/C on [NaCl] (B).
(A): 1.0×10^{-4} mol dm^{-3} $[CoCl(NH_3)_5]^{2+}$, $I=0.03$, pH 8.0, and 25 °C. (a) 1.0×10^{-3} mol dm^{-3} Fe(II)–PBDA. (b) 1.0×10^{-3} mol dm^{-3} Fe(II)–EBDA (B): 1.0×10^{-3} mol dm^{-3} Ni(II)–PBDA, $I=0.03$, pH 8.0, and 25 °C.

straight lines for at least two-times the half-life of the reactions, indicating a first-order dependency of the rates with respect to Co(III). The pseudo-first-order rate constant for the reductions of the Co(III) complexes with a polymer-bound Fe(II)-chelate and those with a low-molecular-weight Fe(II)-chelate, k_p and k_m, respectively, are summerized in the Table. The rate constant for the reduction of $[CoCl(NH_3)_5]^{2+}$ was independent on pH in the region of pH 7.5—8.5. This suggests that no appreciable change in the chemical species of the polymer and the low-molecular-weight Fe(II)-chelates occur in this pH region. The results show explicitly that the overall charges of the Co(III) complexes are of great importance in controling the rate of the electron-transfer reactions in the polymer system; the rate constant for the negatively charged Co(III) complex with Fe(II)–PBDA was of the same order as that with Fe(II)–EBDA, whereas the rate constants for the positively-charged Co(III) complexes with Fe(II)–PBDA were greater than that of the corresponding Co(III) with Fe(II)–EBDA. The ratio of the rate constants, k_p/k_m (represented by acceleration factor) where k_p is the pseudo-first-order rate constant for a given Co(III) complex for the polymer system and k_m is that for the corresponding low-molecular-weight system, is introduced as a measure of the degree of the acceleration. The relationship between the acceleration factor and the overall charge of the Co(III) complex is represented in Fig. 2. The results show that the acceleration factor increases sharply with the positive charges on the Co(III) complexes, i.e., in the domains of the polymeric metal complex anions, a great enhancement of the specific reduction rate occurs with an increase in the positive charge on the low-molecular-weight metal complex ions. Such a charge effect might be ascribed to a large negative charge density in the domains of the Fe(II)–PBDA polymers. Namely, positively-charged inorganic Co(III) complex ions tend to concentrate within the polymer domain with an increase in their positive charge due to an electrostatic attraction between these, leading to an enhancement of the collision frequency between the reactant species. However, no appreciable decrease in the enhancement factor was observed for a reduction of the negatively charged species of $[CoCl(Hedta)]^-$ by a polymeric ferrous chelate relative to that of the monopositively charged species, $[Co(ox)(en)_2]^+$. This seems to indicate that the effect of the coulombic repulsion between the negatively charged polymer domain and a mono-negatively charged Co(III) complex is quite small or can be ignored.

The pseudo-first-order rate constant for the reduction of $[CoCl(NH_3)_5]^{2+}$ by Fe(II)–PBDA decreased rapidly with the addition of NaCl in the concentration region below 0.1 mol dm^{-3}. However, the rate constant for the low-molecular-weight system was little affected by the presence of 0—0.3 mol dm^{-3} NaCl (Fig. 3A). It is known that the local charge density in the polyion domains is greatly affected by the presence of inorganic salts.[12] For example, an addition of sodium chloride to a dilute solution of sodium 4-styrenesulfonate containing $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine), which was concentrated in the domains of the poly(4-styrenesulfonate), tended to replace by the sodium ions with an increase in the concentration of sodium chloride.[6] The results of the salt effect on the reduced viscosity of the polymer-bound Ni(II) chelate solution (Fig. 3B) also seems to account for the salt effect on the rate. For a lower salt concentration than 0.1 mol dm^{-3}, a sharp decrease in the viscosity of the Ni(II)–PBDA solution was observed along with an increase in the salt concentration, indicating a shrinkage of the polymer chain by the shielding of the negative charge in the domains by counter ions. The explanation for the acceleration of the rate is quite similar to that for the reduction of the polymeric Co(III) complexes with low-molecular-weight Fe(II) species.

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