Reductions of Cobalt(III) Complexes by Ferrous Chelates. II. The Reductions of Cobalt(III) Complex with Polymeric Ligands by Means of Some Ferrous Chelates

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The effects of polymeric ligands on the electron-transfer reaction of the cobalt(III) complex have been studied for the reductions of the complex ions of *cis*-$Co(en)_2ACl^{2+}$ (A=poly-4-vinylpyridine, PVP, or pyridine, py) by the aquo ferrous ion and some Fe(II)-nitrilopolycarboxylate chelates. The specific rate of the Fe^{2+} reduction of the $Co(en)_2PVPCl^{2+}$ is smaller than that of the $Co(en)_2PyCl^{2+}$. The specific rate of the Fe(II)-chelate reduction increases considerable when the pyridine ligand in the $Co(en)_2$-$PyCl^{2+}$ is replaced by PVP. The effects of the chelating agents, the degree of coordination, the ionic strength, and the concentration of the reductant on the reduction rate of the $Co(en)_2ACl^{2+}$ by the Fe(II)-nitrilopolycarboxylate were also examined. The resulting reactivity patterns of the polymer complex ions could mainly explained by the effect of the higher electrostatic field caused by the positively-charged polymer structure.

Kinetic studies have been made of the $FeEDTA^{2-}$ reduction of $Co(NH_3)_5Y^{2+}$ (Y=halogen ions, NCS^-, NO_3^-, and N_3^-) and of $Fe^{II}Z^{m-}$ (Z=EDTA, CyDTA, EDTAOH, and EDTA)1) reductions of $Co(NH_3)_5Cl^{2+}$: the results were reported in a previous paper.2) The pattern of reactivities for the $FeEDTA^{2-}$ reductions of the $Co(NH_3)_5Y^{2+}$, in which the Y ligand is varied, indicates the inner-sphere natuer of the reactions: furthermore, the variation in the rate of reaction of the $Fe^{II}Z^{m-}$ with $Co(NH_3)_5Cl^{2+}$ were explained in terms of the steric, charge, and stabilization effects. For the reductions of the $Co(NH_3)_5Y^{2+}$ by the $Fe^{II}Z^{m-}$, it is suggested that the stabilization effect, the degree of which is expressed by the values of the logarithmic ratio of the stability constants ($\log K_{Fe^{III}Z}/K_{Fe^{II}Z}$), is the most important factor controlling the reaction rate.

A water-soluble polymer metal complex of *cis*-$[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$ (PVP=poly-4-vinylpyridine) was prepared,3) and the specific rate and activation parameters for the ferrous-sulfate-ion reduction were determined in dilute sulfuric acid solution.4) The rate of the reduction of the polymer complex ions is expected to be sensitive to the charge on the reductant species, since the polymer ion forms a "domain" with a greater charge density in the solution.

In the present study, the effects of the polymer ligand on the rate of the electron-transfer reactions were examined for the reduction of the polymer complex ion by ferrous chelate and aquo-ferrous ions.

Experimental

Materials. The *cis*-$[Co(en)_2Cl_2]Cl$5) and *cis*-$[Co(en)_2pyCl]Cl_2$6) were prepared by the procedures described in the references cited. Poly-4-vinylpyridines with degrees of polymerization (P_n) of 19 and 98 were prepared such as has been reported by Katchalsky *et al.*7)

Preparations of cis-$[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$. $[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$ was prepared by means of substitution reaction between *cis*-$[Co(en)_2Cl_2]Cl$ and PVP in water-ethanol solution.3) The identity and the purity of the *cis*-$[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$ were confirmed by the elementary analysis of C, H, and N, and the infrared and electronic spectra. The absorption peak at 1600 cm^{-1}, based on $\nu_{C=C,C=N}$ of the pyridine ring of the PVP, shifts to a wave number higher by about 20 cm^{-1} in the PVP complex. This indicates the coordination of the pendant pyridine to the Co(III). The absorption peaks due to the $\nu_{C=C}$, δ_{CH} (in plane) and the δ_{CH} (out of plane) also shift to a wave number higher by 2—10 cm^{-1} as a result of coordination. Some examples of the results of the elementary analysis are shown in Table 1. The degree of coordination (x) was determined from carbon content.8) The absorption maximum and the molar extinction coefficient of the first absorption band of the $Co(en)_2$ $PVPCl^{2+}$ in the aqueous solution agree with those in the literature (λ_{max}=518 nm and $\varepsilon_{max}=72\pm2$).3) The configuration of the *cis*-$[Co(en)_2PVPCl]^{2+}$ is shown in Fig. 1. The *cis*-configuration of the $[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$ we prepared was ascertained from the sharp splitting of the $-CH_2$ rocking band (870—900

Table 1. Elementary analysis of $[Co(en)_2PVPCl]Cl_2 \cdot nH_2O$

P_na)		C, %	H, %	N, %	x	n
98	Found	43.51	6.13	14.19		
	Calcd	43.5	6.74	14.6	0.36	2
98	Found	42.49	6.77	15.86		
	Calcd	42.5	6.45	15.7	0.45	2
98	Found	33.53	5.65	14.97		
	Calcd	33.5	5.96	15.0	0.68	4
19	Found	34.43	6.48	14.95		
	Calcd	34.4	6.75	14.9	0.64	4
19	Found	34.11	6.27	14.77		
	Calcd	34.1	5.97	14.9	0.65	4

a) Degree of polymerization of the PVP.

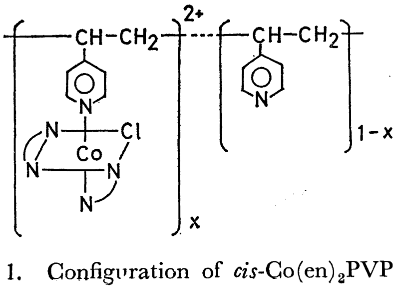

Fig. 1. Configuration of *cis*-$Co(en)_2PVPCl^{2+}$.

cm^{-1})⁹⁾ of the ethylenediamines in the complex.

Kinetic Measurements. The solution of the ferrous perchlorate was prepared by dissolving a known amount of analytical-grade iron wire, (Mallincroft Co.) in an excess of perchloric acid solution. The methods of determinations the ferrous, hydrogen and perchlorate ions in the ferrous perchlorate solution and the method of preparation for the ferrous chelate solutions were identical with those used in a previous work.²⁾

The solution of the Co(III) complex was prepared by dissolving weighed amounts of the Co(III) complex into an acetate-buffered solution. The ionic strength of the reaction mixture was maintained at a constant value by the addition of sodium perchlorate. The reaction was followed spectrophotometrically at the wave-lengths in the vicinity of the first absorption maximum (—520 nm) of the Co(III) complex for higher concentrations of the complex and at the charge-transfer absorption maximum (~230 nm) of the Co(III) complex for lower Co(III) concentrations. The rate constants were calculated from the data which were obtained under pseudo-first-order conditions in which, in most cases, the concentration of the Fe(II) was in great excess over that of the Co(III). In some cases, the concentration of the Fe(II) was in not so great an excess over that of the Co(III): in such cases, then, the value of [Fe(II)] used for the calculation of the rate constant was an average value of the Fe(II) concentrations between the initial time and the half-life of the reaction. The values of k_{py} and k_{PVP} were obtained by means of this equation: $2.3\times m/[Fe(II)]$, where m is the slope of the straight line which was obtained from the slopes of the $\log(A_t-A_\infty)$ vs. time plots, where A_t is the absorbance at time t, and A_∞, the absorbance after all the Co(III) has been reduced to Co(II).

Results

The rate equations for the reduction of $Co(en)_2pyCl^{2+}$ by Fe^{2+} and $Fe^{II}Z^{m-}$ and that of the $Co(en)_2PVPCl^{2+}$ by Fe^{2+} almost fit the second-order kinetics: $-d[Co(III)]/dt=k[Co(III)][Fe(II)]$ ($k=k_{py}$ or k_{PVP}), under the experimental conditions employed. The apparent second-order rate constant of k_{PVP} for the $Fe^{II}Z^{m-}$ reductions was calculated from the initial slopes of the $\log(A_t-A_\infty)$ vs. time plots. In most cases, such plots give straight lines for about a half-life of the reaction.

Table 2 shows that the rate constant for the Fe^{2+} reduction of the polymer complex with $P_n=98$ is almost identical with that of the polymer complex with $P_n=19$ within the limits of experimental errors when the values of x are equal to each other ($x=0.68$ for $P_n=98$ and $x=0.65$ $P_n=19$). This indicates that the value of k_{PVP} for Fe^{2+} reduction is not so much affected by the chain length of the polymer ligand when the P_n value ranges between 19 and 98 under the experimental conditions given in Table 2. For the Fe^{2+} reduction, the reactivity of the polymer complex is lower than that of the monomeric one by about one-third.

Table 2. Rate constants for the Fe^{2+} reduction of $Co(en)_2ACl^{2+}$

A	P_n	x	kᵃ⁾, $M^{-1}s^{-1}$
Py			1.1×10^{-3}
PVP	98	0.68	3.7×10^{-4}
PVP	19	0.65	3.7×10^{-4}

a) $[Co(III)]=4.0\times10^{-3}$ M, $[Fe(II)]=3.4\times10^{-2}$ M, $[Fe(II)]=3.4\times10^{-2}$ M, $[H^+]=2.0\times10^{-2}$ M, $\mu=0.12$, 40 °C.

Ferrous Chelate Reduction. All the reductions of the $Co(en)_2pyCl^{2+}$ and $Co(en)_2PVPCl^{2+}$ by $Fe^{II}Z^{m-}$ except for the $Fe^{II}DTPA$ were followed in the solution of pH=5 in which the predominant species of Fe(II) are normal ferrous chelates. For the $Fe^{II}DTPA$ reduction, the rate constants of Reactions (1) and (2) could be obtained separately from the pH dependence of the rate constant:

$$Co(en)_2ACl^{2+} + FeHDTPA^{2-} \rightarrow Co(II) + Fe(III) \quad (1)$$

$$Co(en)_2ACl^{2+} + FeDTPA^{3-} \rightarrow Co(II) + Fe(III) \quad (2)$$

where A=py or PVP. From Reactions (1) and (2), we obtaine:

$$k_a(1+K_{FeHZ}[H^+]) = k_1 + k_2K_{FeHZ}[H^+] \quad (3)$$

In this equation, k_1 and k_2 are the rate constants of Reactions (1) and (2) respectively, while K_{FeHZ} is the formation constant of the protonated chelate, $FeHDTPA^{2-}$, and k_a is k_{py} or k_{PVP}. The value of K_{FeHZ} was $10^{5.4}$ ($\mu=0.1$ and at 25 °C).¹⁰⁾ As is shown in Fig. 2, the plots of $k_a(1+K_{FeHZ}[H^+])$ vs. $[H^+]$ become linear in both cases. The slopes and intercepts of these lines give the values of k_2K_{FeHZ} and k_1 respectively.

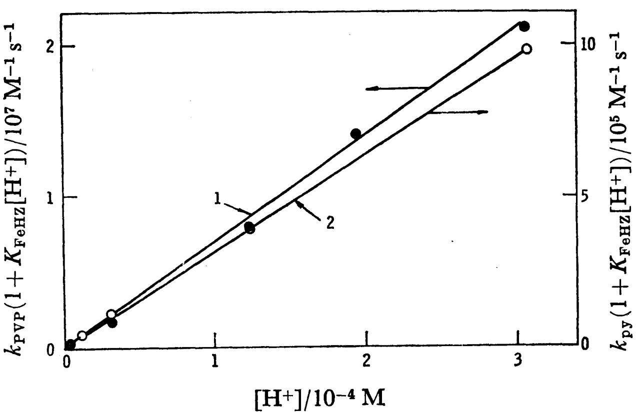

Fig. 2. Plots of $k_a(1+K_{FeHZ}[H^+])$ vs. $[H^+]$.
$[Co(III)]=1.0\times10^{-5}$ M, $[Fe^{II}DTPA]=5.1\times10^{-5}$ M, $\mu=0.02$, 25 °C,
1, $Co(en)_2PVPCl^{2+}$, 2, $Co(en)_2pyCl^{2+}$.

Unfortunately, the intercepts of such plots were too small for us to determine the values of k_1 for the $Co(en)_2pyCl^{2+}$ and the $Co(en)_2PVPCl^{2+}$. The values of k_1 were, however, estimated to be smaller than corresponding k_2 values by at least one-tenth in both cases. The rate constants for the reductions of $Co(en)_2pyCl^{2+}$ and $Co(en)_2PVPCl^{2+}$ by several ferrous chelates are summarized in Table 3.

The effects of the conentration of the ferrous chelate and the degree of the coordination and that of the polymerization on the rate of the reduction of the polymer complex are represented in Fig. 3 and Table 4 respectively. For the $Fe^{II}Z^{m-}$ reduction, The apparent rate constant is affected by the degree of coordination, x, in

TABLE 3. RATE CONSTANTS FOR THE REDUCTIONS OF $Co(en)_2pyCl^{2+}$ AND $Co(en)_2PVPCl^{2+}$ BY Fe(II)-CHELATES ($\mu=0.02$, 25 °C)

Reductant	Rate constant, $M^{-1} s^{-1}$	
	k_{py}	k_{PVP}[a]
$FeEDTA^{2-}$	1.4×10^4	2.8×10^5
$FeCyDTA^{2-}$	1.2×10^4	1.9×10^5
$FeEDTAOH^-$	2.4×10^4	8.8×10^4
$FeHDTPA^{2-}$	1.3×10^4	2.8×10^5

a) Apparent rate constants for the $Co(en)_2PVPCl^{2+}$ with $P_n=19$ and $x=0.64$.
$[Co(III)]=1.0\times10^{-5}$ M, $[Fe(II)]=5.1\times10^{-4}$ M.

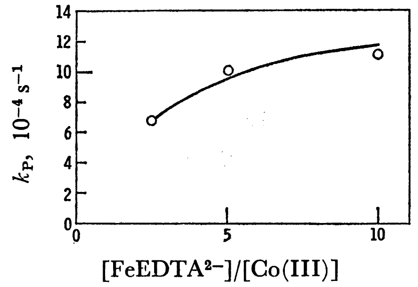

Fig. 3. Plots of the pseudo-first-order rate constant *vs.* $[FeEDTA^{2-}]/[Co(III)]$.
$[Co(en)_2PVPCl^{2+}]=1.0\times10^{-5}$ M ($P_n=19$, $x=0.65$), $\mu=0.02$, pH=5.0, 25 °C.

TABLE 4. EFFECTS OF THE DEGREE OF COORDINATION AND THE DEGREE OF POLYMERIZATION ON THE RATE CONSTANT

P_n	x	$x/10^5 M^{-1} s^{-1}$
98	0.32	2.2
	0.36	3.6
	0.45	3.4
	0.69	4.5
19	0.65	2.8

$[Co(en)_2PVPCl^{2+}]=1.0\times10^{-5}$ M, $[FeEDTA^{2-}]=5.0\times10^{-5}$ M, pH=5.0, $\mu=0.02$, 25 °C.

TABLE 5. EFFECT OF IONIC STRENGTH ON THE RATE CONSTANTS FOR THE REDUCTIONS OF $Co(en)_2pyCl^{2+}$ AND $Co(en)_2PVPCl^{2+}$ BY $FeEDTA^{2-}$ [a]

	Rate constant/$M^- s^{-1}$	
	k_{py}	k_{PVP}[b]
0.02	1.4×10^4	2.8×10^5
0.10	7.3×10^3	2.3×10^4

a) $[Co(III)]=1.0\times10^{-5}$ M, $[FeEDTA^{2-}]=5.0\times10^{-5}$ M, pH=5.0, 25 °C. b) Apparent rate constants, $P_n=19$, $x=0.65$.

the polymer complex and by the degree of polymerization of the polymer ligand: the rate constant increases with an increase in the value of x and the rate constant in the complex of PVP with $P_n=98$ is greater than that for $P_n=19$ when the values of x are almost the same. A comparison the rate constants for the $Co(en)_2pyCl^{2+}$ and $Co(en)_2PVPCl^{2+}$ complexes at different ionic strengths is also shown in Table 5.

Discussion

It may be reasonable to assume that the reductions of the $Co(en)_2PVPCl^{2+}$ and $Co(en)_2pyCl^{2+}$ complexes by Fe^{2+}, $FeSO_4$,[11] and $Fe^{II}Z^{m-}$ proceed through a chloride-bridged mechanism, since it has been suggested that $Co(NH_3)_5Cl^{2+}$ reacts with Fe^{2+},[12] $FeEDTA^{2-}$,[12] and $FePDTA^{2-}$[13] *via* the chloride-bridged activated state.

The rate of reaction between two cationic species in an aqueous solution, for example, the reaction of $Co(NH_3)_5Cl^{2+}$ with Fe^{2+}, is markedly accelerated in the presence of small amounts of polyions, such as polyvinylsulfonate or polymethacryloxyethylsulfonate anions.[14-17] In dilute solution of a polyelectrolyte, the damains occupied by the polyions contain very high density of the ionized group, while the space between the domains has only a very low concentration of ionic species.[14] It was also demonstrated by means of several experimental techniques, such as electronic mobility,[18,19] osmotic pressure,[20] and potentiometric titration,[21,22] that appreciable amounts of the counter ions are fixed near the polyion structure in an aqueous solution of polyelectrolytes due to Coulombic attraction between the polyion and the counter ion. The polycation domain consisting of the $Co(en)_2PVPCl^{2+}$ also tends to concentrate the opposite-charged $Fe^{II}Z^{m-}$ species. This causes an increase in the local concentration of the $Fe^{II}Z^{m-}$ species, thus promotes the reduction rate. The results listed in Table 6 qualitatively support this electrostatic explanation: the results show that the acceleration factor depends essentially on the charges of the reductant. The reduction of the activity coefficient of the multiplycharged activated complex in the strong field of the polyion domain[23] is considered to be another factor controlling the rates of polyion catalyzed reactions. Among the reactions investigated, the latter factor, however, seems to be less important than the former, since the acceleration factor for the Fe^{2+} reduction of the $Co(en)_2PVPCl^{2+}$, in which the reaction takes place through the multiply positive-charged activated complex, is not so far from unity. The specific rate for the $FeEDTA^{2-}$ reduction of the $Co(en)_2PVPCl^{2+}$ complex increases as the degree of coordination increases (Table 5). This could also be explained in terms of the accumulation of the $FeEDTA^{2-}$ in the polycation doamin as the degree of

TABLE 6. ACCELERATION FACTORS FOR THE Fe(II) REDUCTION OF $Co(en)_2PVPCl^{2+}$

Reductant	Acceleration factor k_{PVP}/k_{py}
Fe^{2+}	0.33[a]
$FeSO_4$	0.59[b]
$FeEDTAOH^-$	3.7[c]
$FeEDTA^{2-}$	21[c]
$FeCyDTA^{2-}$	16[c]
$FeHDTPA^{2-}$	22[c]

a) $\mu=0.12$, 40 °C, $P_n=98$, $x=0.45$, in 0.1 M $HClO_4$.
b) $\sum[SO_4^{2-}]=1.25$, $[H^+]=1.0$ M, $P_n=98$, $x=0.45$.[4]
c) $\mu=0.02$, $P_n=19$, $x=0.64$.

coordination increases, since it is considered that the charge density of the polymer domain becomes larger with the degree of coordination. For a $FeEDTA^{2-}$ reduction, the pseudo-first order rate constant, k_p, increases with the concentration of the reductant, but the relationship between the rate constant and the $[FeEDTA^{2-}]/[Co(III)]$ is not linear as is shown in Fig. 3. This seems to suggest the existence of an equilibrium between the $FeEDTA^{2-}$ in the bulk and that in the domain in the polyion-$FeEDTA^{2-}$ system.

The greater influence of the ionic strength or the concentration of the nonparticipating salts on the specific rate of the $FeEDTA^{2-}$ reduction of the $Co(en)_2PVPCl^{2+}$ than the influence of the $Co(en)_2pyCl^{2+}$ (Table 5) also indicates greater effect of the Coulombic force between the polycations and the nonparticipating anions. As the amounts of the nonparticipating anions in the solution increase, their concentrations in the domain would increase also, this causing a partial neutralizing of the positive charges carring on the polyion domain. Therefore, the amounts of the $FeEDTA^{2-}$ will tend to be diluted in the polyion domains, resulting in a lower collision frequency.

References

1) The abbreviations of the chelating agents used here are: EDTA, ethylenediaminetetraacetic acid: CyDTA, cyclohexanediaminetetraacetic acid: EDTAOH, hydroxyethylethylenediaminetriacetic acid: DTPA, diethylenetriaminepentaacetic acid, and PDTA, propylenediaminetetraacetic acid.

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