Electron-transfer Reactions of Multidentate Ligand Cobalt(III) Complexes. IV. The Reductions of Cobalt(III) Complexes of Amino Acids by Iron(II) in Aqueous and Water-methanol Solutions

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The kinetics of the Fe(II) reductions of *trans*(O,Cl)-Co(dien)(am)Cl^+ (am=glycine, α-alanine, β-alanine, leucine, and proline) and *trans*(N)-Co$(am)_2(ox)^-$ (am=glycine, α-alanine, β-alanine, ox=oxalate, and dien=diethylenetriamine) have been made spectrophotometrically in an aqueous solution. Except for the β-alanine complex, the reactivities of the Co(III) complexes are not very different when the amino acid is replaced by the other one. The greater reactivities of the β-alanine complexes may be due to the steric strain on the six-membered β-alanine chelate ring. The rates of the reductions of *cis*(N)-Co$(\alpha\text{-ala})_2(ox)^-$ and *cis*(N)-Co$(\beta\text{-ala})_2(ox)^-$ by Fe(II) are greatly affected by the addition of methanol to the aqueous solutions; the rate increases with an increase in the mol fraction of methanol. The replacement of water molecules in the solvation sphere of the reductant by the methanol molecules is considered to be one of the reasons for the greater rate in water-methanol solutions.

In the electron-transfer reactions of Co(III) complexes which proceed *via* the inner-sphere and outer-sphere activated states, the nonbridging ligand can appreciably affect the reaction rates.[1,6,7,9,10] The nonbridging ligand effect has been investigated mostly on the metal complexes with a uni-dentate bridging ligand.[1-10] Kinetic studies of the Fe(II) rdeuctions of Co(III) complexes, with oxalate ions as the bridging ligand, are very few, and the effects of amino acids as the nonbridging ligand in the Fe(II) reductions of Co(III) complexes have not been examined. In this connection, the Fe(II) reductions of *trans*(N)-Co$(am)_2(ox)^-$, and *trans*(O,Cl)-Co(dien)(am)Cl^+ were investigated.

The effect of organic solvents on the reduction rate of *cis*-Co$(en)_2NH_2CH_2CH_2OHCl^{2+}$ by Fe(II) was also examined previously.[11] In this study, we observed the increase in the rate upon the addition of such organic solvents as ethanol, acetone, dimethylformamide, and dimethylsulfoxide to the aqueous solutions. The reactivity of the Co(III) complex in an ethanol-water (0.5 mol fraction of ethanol) is about 10 times grater than that in an aqueous solution at $[H^+]=0.080$M. The reason for this grater reactivity is, however, yet uncertain. A further investigation of the Fe(II) reduction of Co(III) complexes in methanol-water was carried out using anionic Co(III) complexes such as *cis*(N)-Co$(\alpha\text{-ala})_2(ox)^-$ and *cis*(N)-Co$(\beta\text{-ala})_2(ox)^-$ in a methanol-water medium; those results will be also reported in this paper.

Experimental

Preparation of Complexes. The *trans*(O,Cl)-[Co(dien)-(gly)Cl]ClO_4, *trans*(O,Cl)-[Co(dien)(α-ala)Cl]$ClO_4\cdot H_2O$, *trans*(O,Cl)-[Co(dien)(β-ala)Cl]ClO_4, *trans*(O,Cl)-[Co(dien)-(leu)Cl]ClO_4, and *trans*(O,Cl)-[Co(dien)(pro)Cl]ClO_4[12] used as the oxidants were prepared by a method established by Ohkawa.[13] The configurations of these complexes with respect to diethylenetriamine were ascertained by means of the NMR spectra.[14] The coordinated chlorine atom in the *trans*(O,Cl)-Co(dien)(am)Cl^+ is located at the *trans*-positions to the coordinated oxygen atom of amino acid, and the diethylenetriamine occupies the *cis-trans* (mer) position in these complexes (Fig. 1).

The *trans*(N)-K[Co$(gly)_2$(ox)],[15] *cis*(N)-,[16] and *trans*(N)-

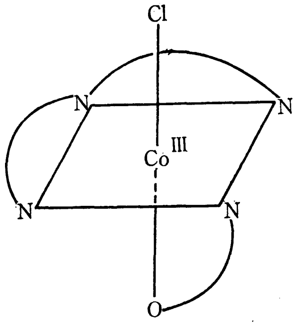

Fig. 1. The configuration of the *trans*(O,Cl)-[Co(dien)(am)-Cl]ClO_4.

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[1] P. Benson and A. Haim, *J. Amer. Chem. Soc.*, **87**, 3826 (1965).

[2] H. Taube, *Adv. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[3] H. Taube, *Can. J. Chem.*, **37**, 129 (1959).

[4] R. T. M. Fraser, *Proc. Chem. Soc.*, **1963**, 262.

[5] T. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).

[6] Y. Kurimura, K. Ohashi, T. Ohtsuki, and K. Yamamoto, This Bulletin, **44**, 1293 (1971).

[7] Y. Kurimura and K. Ohashi, *ibid.*, **44**, 1797 (1971).

[8] Y. Kurimura, I. Meguro, and K. Ohashi, *ibid.*, **44**, 3367 (1971).

[9] K. Ohashi, *ibid.*, **45**, 947 (1972).

[10] R. C. Patel and J. F. Endicott, *J. Amer. Chem. Soc.*, **90**, 6364 (1968).

[11] K. Ohashi, K. Yamamoto, T. Suzuki, and Y. Kurimura, This Bulletin, **44**, 3363 (1971).

[12] The gly, ala, leu, pro, and dien abbreviation represent glycinate, alaninate, leucinate, prolinate ions, and diethylenetriamine respectively.

[13] K. Ohkawa, Ph. D. Thesis, Osaka University, Japan, 1969.

[14] K. Ohkawa, S. Yano, and J. Fujita, This Bulletin, **41**, 2224 (1968).

[15] M. Matsuoka, J. Hidaka, and Y. Shimura, *ibid.*, **40**, 1868 (1967).

[16] This complex has two geometrical isomers. The linear behavior of the log $(A_t - A_\infty)$ *vs.* time plot for the Fe(II) reductions of this complex in aqueous solution indicates that the reactivities of the two isomers with Fe(II) are of almost the same degree or that the content of one isomer is relatively small as compared with that of the other one.

TABLE 1. THE MICROANALYSIS FOR *trans*(O,Cl)-[Co(dien)(am)Cl]ClO_4 AND *trans*(N)-K[Co(am)$_2$ox]

Complex	Obsd. (%)			Calcd. (%)		
	C	H	N	C	H	N
trans(O,Cl)-[Co(dien)(gly)Cl]ClO_4	19.6	4.62	15.06	19.42	4.62	15.10
trans(O,Cl)-[Co(dien)(α-ala)Cl]$ClO_4 \cdot H_2O$	20.8	5.32	13.77	20.86	5.25	13.90
trans(O,Cl)-[Co(dien)(β-ala)Cl]ClO_4	22.31	5.32	14.63	22.81	4.98	14.55
trans(O,Cl)-[Co(dien)(leu)Cl]ClO_4	28.45	6.26	13.27	28.10	5.90	13.10
trans(O,Cl)-[Co(dien)(pro)Cl]ClO_4	26.37	5.20	13.77	26.29	5.17	13.63
trans(N)-K[Co(gly)$_2$(ox)]	21.37	2.20	8.21	21.67	2.49	8.41
trans(N)-K[Co(α-ala)$_2$(ox)]	26.24	3.18	7.58	26.52	3.33	7.73
trans(N)-K]Co(β-ala)$_2$(ox)]·$2H_2O$	26.90	3.40	7.68	26.86	3.35	7.77

a) gly=$CH_2(NH_2)COO^-$, α-ala=$CH_3CH(NH_2)COO^-$, β-ala=$CH_2(NH_2)CH_2COO^-$, leu=$(CH_3)_2CHCH_2CH(NH_2)COO^-$, pro=$NHCH_2CH_2CH_2CHCOO^-$, dien=$NH_2CH_2CH_2NHCH_2CH_2NH_2$, ox=$^-OOCCOO^-$

K[Co(α-ala)$_2$(ox)],[15] and *cis*(N)-,[16] and *trans*(N)-K[Co(β-ala)$_2$(ox)][17] compounds were prepared by the methods cited in the references. The purities and identities of the complexes were ascertained by microanalysis for carbon, hydrogen, and nitrogen and by comparing the absorption spectra with those reported in the literature.

The results of the microanalysis of carbon, hydrogen, and nitrogen for the complexes are presented in Table 1.

Materials. The preparation of the iron(II) solution and the determinations of the concentrations of the iron(II), hydrogen, and perchlorate ions in this solution were carried out by methods similar to those described in a previous paper.[6] Methanol of Tokyo Kasei, spectroscopic-grade, was distilled before use. The other chemicals used were G. R.-grade reagents. The concentration of the perchlorate anion in the reaction mixture was adjusted to 1.0M by the addition of sodium perchlorate.

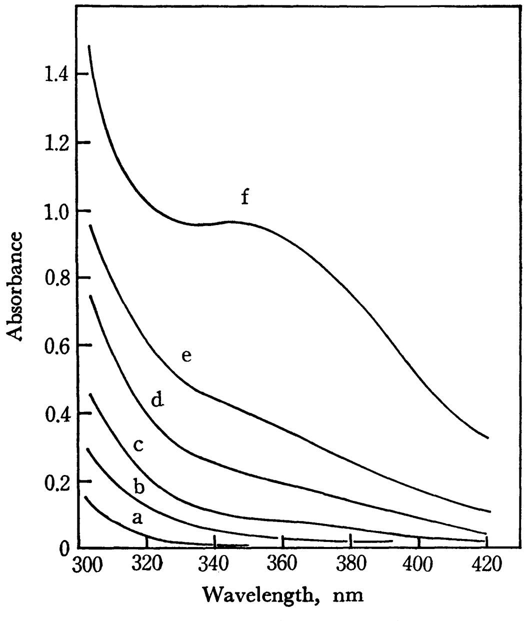

Fig. 2. Absorption spectra of ferric perchlorate in aqueous solution of methanol.
[Fe(III)]=1.09×10^{-3}M, $\sum[ClO_4^-]$=0.24M, [$HClO_4$]=0.24M.
a: aqueous solution
b: 0.16 mole fraction of methanol
c: 0.32 mole fraction of methanol
d: 0.52 mole fraction of methanol
e: 0.64 mole fraction of methanol
f: 0.80 mole fraction of methanol

Measurement of Reaction Rate in Aqueous Solutions. The reduction rate was followed by the usual spectrophotometric method. The wavelengths used were the first absorption maxima of the complexes. For all the complexes, the kinetic runs were carried out under pseudo-first-order conditions.

Measurement of the Reaction Rate in Water-methanol Mixtures. The kinetic runs for *cis*(N)-Co(α-ala)$_2$(ox)$^-$ and *cis*(N)-Co(β-ala)$_2$(ox)$^-$ were carried out under pseudo-first-order and second order conditions respectively. The wavelengths used for the determinations of the rate constants were 535 nm for *cis*(N)-Co(α-ala)$_2$(ox)$^-$ and 550 nm for *cis*(N)-Co(β-ala)$_2$(ox)$^-$.

Absorption Spectra of Ferric Perchlorate in Methanol-water Mixtures. The absorption spectra of ferric perchlorate in aqueous solutions of methanol are represented in Fig. 2. The absorbances of the solutions in the near-ultraviolet region increase with an increase in the mol fraction of methanol. Such increases in absorbance were also observed previously by the addition of ethanol, acetone, dimethylsulfoxide, and dimethylformamide to an aqueous solution of ferric perchlorate.[11]

Results and Discussion

Reductions in Aqueous Solutions. The rate data obtained with Co(dien)(am)Cl$^+$ and Co(am)$_2$(ox)$^-$ listed in Table 2 show that; a) the β-alanine complexes have greater effectiveness than other complexes in the Co(dien)(am)Cl$^+$ and Co(am)$_2$(ox)$^-$ series; for example, the rate constants of the β-alanine complexes are greater than those of the corresponding α-alanine complexes by 114—140 times; b) the patterns of reactivity with respect to the amino acids are very similar in the two series; the ratios of the rate constant of the Co(III) complexes to the corresponding glycine complex (represented) by R values for α-alanine and glycine complex are in the ranges of 0.24—0.41 and 33—42 respectively; c) except for the β-alanine complexes, the reactivities of the amino acid complexes are not very different within the same series. The activation parameters for the reductions which were obtained from the temperature dependence of the rate constant are also listed in Table 2.

Since an oxalate-bridged mechanism has been demonstrated for the Fe(II) reductions of Co(ox)$_3^{3-}$ and

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[17] J. Hidaka and Y. Shimura, This Bulletin, **40**, 2312 (1967).

TABLE 2. SECOND-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE IRON(II) REDUCTIONS OF Co(III) COMPLEXES AT 25°C

Complex ion	Rate constant $\text{M}^{-1}\text{sec}^{-1}$	R_1	R_2	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ eu
trans(N)-Co(gly)$_2$(ox)$^-$	4.13×10^{-3} [a]	1		14	−21
trans(N)-Co(α-ala)$_2$(ox)$^-$	1.01×10^{-3} [a]	0.24		16	−24
trans(N)-Co(β-ala)$_2$(ox)$^-$	1.42×10^{-1} [a]	33		12	−23
Co(dien)(gly)Cl$^+$	2.68×10^{-5} [b]		1	17	−24
Co(dien)(α-ala)Cl$^+$	1.09×10^{-5} [b]		0.41	18	−20
Co(dien)(β-ala)Cl$^+$	1.24×10^{-3} [b]		42	16	−17
Co(dien)(leu)Cl$^+$	1.01×10^{-5} [b]		0.38	20	−16
Co(dien)(pro)Cl$^+$	5.33×10^{-6} [b]		0.20	22	−10

a) $[\text{H}^+]=0.20\text{M}$, $\sum[\text{ClO}_4^-]=1.0\text{M}$. b) *trans*(O,Cl)-Co(III) complex, $[\text{H}^+]=0.26\text{M}$, $\sum[\text{ClO}_4^-]=1.0\text{M}$.
c) R_1 and R_2 represent the ratios of the rate constants to the corresponding glycine complexes.

Co(NH$_3$)$_3$(H$_2$O)(ox)$^+$ by observing the spectrum of Fe(III) product and by determining its rate of formation and decay,[18] and since the reactivity of Co(NH)$_4$(gly)$^{2+}$ with Fe(II) is negligibly small as compared with that Co(NH$_3$)$_4$(ox)$^+$,[19] it is reasonable to assume that the Fe(II) reductions of the Co(am)$_2$(ox)$^-$ proceed *via* oxalate-bridged activated states. For Co(dien)(am)-Cl$^+$, since the rate of the Co(NH$_3$)$_4$(am)$^{2+}$ with Fe(II) can be again ignored as compared with that of Co-(NH$_3$)$_5$Cl^{2+} ($k=1.6\times10^{-3}\text{M}^{-1}\text{sec}^{-1}$, 25°C, $\mu=1.7$),[20] there is little doubt that the Cl$^-$ is the bridging ligand.

These results, (a)—(c), seem to indicate the effect of the nonbridging ligand on the electron-transfer reaction. It is interesting to note here that the reactivity of the β-alanine complex is remarkably greater than that of the corresponding glycine and α-alanine complexes. The greater reactivity of the Co(III) complex with a six-membered chelate ring as compared with that of a five-membered one may be due to strain on the six-membered ring. Such a steric strain on the six-membered ring would reduce the energy needed for the reorganization of the nonbridging ligand in the Co(III) complex for the electron-transfer. The smaller enthalpies of the activation for the β-alanine complexes relative to those for other amino acid complexes seem to be responsible for the smaller reorganization energy for the β-alanine complexes. A part of the energy may consist of the energy for stretching the nonbridging β-alanine ligand away from the Co(III) center.[1,6]

Reduction in an Aqueous Solution of Methanol. The reductions of *cis*(N)-Co(α-ala)$_2$(ox)$^-$ and *cis*(N)-Co(β-ala)$_2$(ox)$^-$ by Fe(II) in a methanol-water mixture obey the first order dependence of the Fe(II) and Co(III) concentrations respectively. In an aqueous solution of methanol, the reactivities of these complexes increase sharply upon the addition of methanol to the aqueous solution (Fig. 3). In the previous work, it was found that the reduction rates of the cationic Co(III) complex, *cis*-Co(en)$_2$NH$_2$CH$_2$CH$_2$OHCl^{2+}, with Fe(II) in aqueous solution is accelerated in the presence of such organic solvents as dimethylformamide, dimethylsulfoxide, ethanol, and acetone.[11] Such an increase in the rate in a mixed solvent medium is contrary to the trend of electron-transfer reactions, such as Co(phen)$_3^{2+}$–Co(phen)$_3^{3+}$[21] and Fe^{2+}–Fe^{3+}.[22,23] The ratio of the rate constants in water ($k_{\text{H}_2\text{O}}$) and isopropanol (k_{alc}) for the Fe^{2+}–Fe^{3+} reaction was calculated by Sutin by assuming that the iron species are not changed in the two solvents. The obtained values of $k_{\text{alc}}/k_{\text{H}_2\text{O}}$ are about 10^{-9} for the Fe^{2+}–Fe^{3+} reaction and about 10^{-6} for the Fe^{2+}–FeOH^{2+} reaction.[22a] These values agree satisfactorily with that experimentally obtained when $[\text{H}^+]=0.01\text{M}$. However, Sutin pointed out that the predominat species may be quite different in the two solvents, as was suggested by the spectrophotometric measurements. If the reactants have larger differences in configuration in isopropanol than in water, the reorganization energy may be much greater in alcohol.[22a]

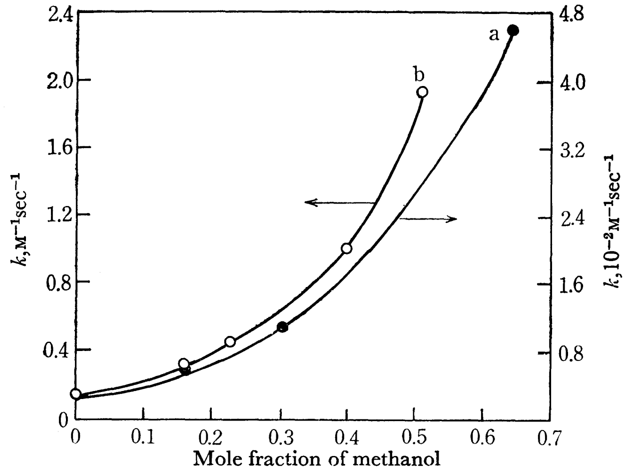

Fig. 3. The plots of the second-order rate constant *vs.* mole fraction of methanol.
$\sum[\text{ClO}_4^-]=0.43\text{M}$, $[\text{H}^+]=0.080\text{M}$, 25 ± 0.1°C.
a) $[cis\text{(N)-Co}(\alpha\text{-ala})_2(\text{ox})^-]=7.43\times10^{-3}\text{M}$, $[\text{Fe(II)}]=0.173\text{M}$.
b) $[cis\text{(N)-Co}(\beta\text{-ala})_2(\text{ox})^-]=1.29\times10^{-2}\text{M}$, $[\text{Fe(II)}]=2.07\times10^{-2}\text{M}$.

Though the formation of the mixed-ligand Fe(II), Fe(H$_2$O)$_{6-n}$(CH$_3$OH)$_n^{2+}$, has not been ascertained, the

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[18] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

[19] C. Hwang and A. Haim, *Inorg. Chem.*, **9**, 500 (1970).

[20] H. Diebler and H. Taube, *ibid.*, **4**, 1029 (1965).

[21] B. R. Baker, F. Basolo, and H. M. Neuman, *J. Phys. Chem.*, **63**, 371 (1959).

[22] a) N. Sutin, *ibid.*, **64**, 1766 (1960); b) R. A. Horne, Ph. D. Thesis, Columbia University, New York, 1955.

[23] L. Menashi, W. L. Reynolds, and G. Van Auken, *Inorg. Chem.*, **4**, 299 (1965).

progressive change in the absorption spectra of the Fe(III) perchlorate solution upon the addition of methanol to an aqueous solution (Fig. 2) would suggest the formation of a mixed-ligand complex such as $Fe(H_2O)_{6-n}(CH_3OH)_n^{2+}$.

The results of the present and of previous studies suggest that the rate increase with an increase in the concentration of organic solvents in the Fe(II) reductions of the cationic Co(III) complex, *cis*-$Co(en)_2NH_2CH_2CH_2OHCl^{2+}$, and anionic Co(III) complexes, *cis*(N)-$Co(\alpha\text{-ala})_2(ox)^-$ and *cis*(N)-$Co(\beta\text{-ala})_2(ox)^-$ proceed *via* the bridged activated states. In the organic substance-water media, the first coordination sphere of the ferrous ion may be changed from that in water; on the other hand, the replacement of the ligands in the Co(III) complex ions by the organic substance need hardly be considered because of the inertness of the complexes.

Consequently, the replacement of the water molecules in only the first coordination sphere of the reductant by organic solvent molecules is considered to be one of the most important reasons for the acceleration of the rate. However, no further discussion about the increase in the rate of electron-transfer reactions between the Co(III)-oxalate complexes and Fe(II) with an increase in the concentration of methanol in an aqueous solution could be made because of the present lack of much kinetic data on these effects.