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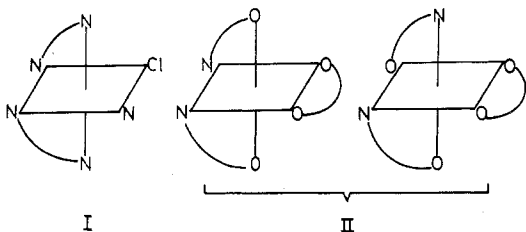Faculty of Science, Ibaraki University, Mito 310, Japan

Solvent Effects on Rates of Reductions of Some Cobalt(III) Complexes by Iron(II), Vanadium(II), and Chromium(II) in Acidic Aqueous Solutions of N,N-Dimethylformamide and Alcohols

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Previous kinetic studies[1,2] of the effect of organic solvents such as *N,N*-dimethylformamide (HCONMe$_2$), dimethyl sulfoxide, ethanol, and acetone on the rates of reductions of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2$$^{2+}$ (I) , *cis*(*N*)-Co(ox)-

I   II

(α-ala)$_2$$^-$ (II),[3] and *cis*(*N*)-Co(ox)(β-ala)$_2$$^-$ (II)[3] by iron(II) have shown that the rates of the reductions increased with increase in the mole fraction of organic solvents.

Recently, Watts et al.[4] investigated reductions of Co(X)-(NH$_3$)$_5$$^{2+}$ (X = F$^-$, Cl$^-$, and Br$^-$) by iron(II) in pure *N,N*-dimethylformamide, dimethyl sulfoxide, and aqueous solutions of dimethyl sulfoxide. They presented evidence suggesting that the coordination sphere of the iron(II) in the inner-sphere-bridged intermediate changes from octahedral structure in water to tetrahedral structure with the increase in the content of dimethyl sulfoxide in the case of Co(X)(NH$_3$)$_5$$^{2+}$ (X = Cl$^-$ and Br$^-$) and that iron(II) maintains octahedral coordination in the inner-sphere-bridged intermediate for the reduction of Co(F)(NH$_3$)$_5$$^{2+}$ by iron(II).

A lot of data about the organic solvent effect on redox reactions should be accumulated to discuss the mechanism of redox reactions in detail. In this work, the kinetic study of reactions of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2$$^{2+}$ and *cis*-(*N*)-Co(ox)(β-ala)$_2$$^-$ by iron(II), Co(en)$_3$$^{3+}$, Co(Cl)(NH$_3$)$_5$$^{2+}$, and Co(N$_3$)(NH$_3$)$_5$$^{2+}$ by vanadium(II), and Co(en)$_3$$^{3+}$ by chromium(II) was carried out to obtain further information

about the effect of *N,N*-dimethylformamide and alcohols such as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol on the reductions of these cobalt(III) complexes.

Furthermore, the effect of ionic strength on the rates of reductions of Co(en)$_3$$^{3+}$ and Co(Cl)(NH$_3$)$_5$$^{2+}$ by vanadium(II) and Co(en)$_3$$^{3+}$ by chromium(II) in nonaqueous systems was investigated.

Experimental Section

Materials. *cis*(*N*)-K[Co(ox)(β-ala)$_2$],[5] *cis*-[Co(Cl)-(NH$_2$CH$_2$CH$_2$OH)(en)$_2$]Cl$_2$,[6] [Co(N$_3$)(NH$_3$)$_5$](ClO$_4$)$_2$,[7] [Co(Cl)(NH$_3$)$_5$](ClO$_4$)$_2$,[8] and [Co(en)$_3$](ClO$_4$)$_3$,[9] used as the oxidants, were prepared by methods similar to those described in the references cited. The identity and purity of the complexes were confirmed by microanalyses for carbon, hydrogen, and nitrogen and by comparing the molar extinction coefficients at the low-energy absorption maximum with those reported.

The preparation of the iron(II) stock solution and the determinations of the concentrations of the iron(II), hydrogen, and perchlorate ions in this solution were carried out by the method reported in the previous paper.[10] In all cases, the hydrogen and perchlorate ion concentrations of the solution were adjusted by the addition of perchloric acid and sodium perchlorate solutions.

The acidic solution of chromium(III) perchlorate was prepared by the reduction of sodium dichromate in perchloric acid by hydrogen peroxide. Solutions of chromium(II) perchlorate were prepared by the reduction of chromium(III) perchlorate with zinc amalgam. The concentrations of chromium(II) ion and hydrogen ion in chromium(II) solution were determined by the method reported in the literature.[11,12]

The acidic solution of vanadium(IV) perchlorate was prepared by dissolving vanadium metal, 99.99% purity, into excess perchloric acid. Solutions of vanadium(II) perchlorate were obtained by the reduction of vanadium(IV) perchlorate solution with zinc amalgam. The concentrations of vanadium(II) ion and hydrogen ion in vanadium(II) solution were analyzed by a method similar to that described in the reference cited.[13]

N,N-Dimethylformamide of spectroscopic grade (Tokyo Kasei) was used without further purification. Methanol, ethanol, 2-propanol, and 2-methyl-2-propanol of reagent grade (Tokyo Kasei) were distilled before use.

Kinetic Measurements. The kinetic measurements of the reductions of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2$$^{2+}$ and *cis*(*N*)-Co(ox)(β-ala)$_2$$^-$ by iron(II) at below 0.30 mol fraction of methanol were followed spectrophotometrically using a Hitachi EPS-3 type spectrophotometer.

The kinetic measurements of the reductions of Co(en)$_3$$^{3+}$ by vanadium(II) and chromium(II) were carried out under nitrogen gas atmosphere by a method similar to that for the reduction of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2$$^{2+}$ by iron(II).[1]

The kinetic measurements of reductions of *cis*(*N*)-Co(ox)(β-ala)$_2$$^-$ by iron(II) above 0.30 mol fraction of methanol and the reduction of Co(X)(NH$_3$)$_5$$^{2+}$ (X = Cl$^-$ and N$_3$$^-$) by vanadium(II) in aqueous solutions and in aqueous solutions of *N,N*-dimethylformamide or alcohols were carried out by the stopped-flow method, using a Hitachi EPS-1 rapid-scan spectrophotometer.

All the kinetic experiments were carried out using a large excess of reductant. Temperatures were kept at 25.0 ± 0.2 °C during the series of experiments.

For all systems the concentration of perchlorate ion of the solution was adjusted by the addition of sodium perchlorate and perchloric acid. The concentration of perchloric acid was maintained over a range of 0.03–0.80 M.

Results and Discussion

The Effect of Organic Solvent on the Reduction Rates. The rate of reduction of cobalt(III) complexes by reductants such as iron(II), vanadium(II), and chromium(II) is first order dependent on the concentrations of reductants and cobalt(III) complexes, respectively, in aqueous solutions of organic solvent. The second-order rate constant of the reduction of *cis*-Co-(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2$$^{2+}$ by iron(II) in aqueous solutions of such alcohols as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol gradually increases with the mole fraction of alcohols up to ca. 0.53 mol fraction of the alcohols (Table I). The rate of reduction increases with the increase in the number of carbon atoms of the alcohols: 2-methyl-2-propanol

Table I. Rate Constants for the Reduction of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2^{2+}$ by Iron(II) in Aqueous Solutions of Alcohols[a]

Alcohol	Mol fraction	Rate constant,[b] M^{-1} s^{-1}
Methanol	0	4.8 × 10^{-5}
	0.16	5.6 × 10^{-5}
	0.32	8.4 × 10^{-5}
	0.44	1.3 × 10^{-4}
	0.56	1.8 × 10^{-4}
Ethanol	0.21	1.1 × 10^{-4}
	0.32	1.7 × 10^{-4}
	0.56	3.7 × 10^{-4}
2-Propanol	0.07	7.2 × 10^{-5}
	0.20	1.6 × 10^{-4}
	0.33	2.6 × 10^{-4}
	0.45	4.2 × 10^{-4}
	0.53	6.0 × 10^{-4}
2-Methyl-2-propanol	0.16	1.6 × 10^{-4}
	0.31	4.0 × 10^{-4}
	0.36	5.1 × 10^{-4}
	0.40	6.1 × 10^{-4}

[a] Σ[ClO$_4^-$] 0.60 M, [H$^+$] 0.16 M, [Fe^{2+}] 0.16 M; 25.0 ± 0.2 °C. [b] Each value is the average of at least two determinations.

Table II. Rate Constants for Reduction of *cis*(N)-Co(ox)(β-ala)$_2^-$ by Iron(II) at Various Mole Fractions of Methanol[a]

Methanol, mol fraction	Rate constant,[b] M^{-1} s^{-1}	Methanol, mol fraction	Rate constant,[b] M^{-1} s^{-1}
0	8.0 × 10^{-2}	0.68	5.7
0.17	2.8 × 10^{-1}	0.79	9.4
0.30	8.0 × 10^{-1}	0.90	2.5 × 10
0.41	1.4	0.95	4.0 × 10
0.58	3.2	0.99	6.4 × 10

[a] Σ[ClO$_4^-$] 0.60 M, [H$^+$] 0.03 M, [Fe^{2+}] 0.025 M–0.10 M; 25.0 ± 0.2 °C. [b] Each value is the average of at least three determinations.

> 2-propanol > ethanol > methanol.

Table II shows the second-order rate constant for the reduction of *cis*(N)-Co(ox)(β-ala)$_2^-$ by iron(II) in an aqueous solution of methanol. The rate constant at 0.99 mol fraction of methanol is ca. 800 times larger than that in pure aqueous solution. The degree of the acceleration effect of the methanol for the reduction of *cis*(N)-Co(ox)(β-ala)$_2^-$ by iron(II) is larger than that of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2^{2+}$.

The second-order rate constants for the reduction of Co(en)$_3^{3+}$ (Table III) and Co(Cl)(NH$_3$)$_5^{2+}$ (Table IV) by vanadium(II) increase with the increase in the content of *N,N*-dimethylformamide. The similar effect of *N,N*-dimethylformamide on the rate of reduction of Co(en)$_3^{3+}$ by chromium(II) was observed (Table III). However, the rate of reduction of Co(N$_3$)(NH$_3$)$_5^{2+}$ by vanadium(II) is indifferent to the addition of *N,N*-dimethylformamide up to 0.13 mol fraction.

The free energy due to the coulombic repulsion for the electron-transfer reaction between metal complexes with the same sign for the charge would increase with the decrease in the macroscopic dielectric constant; the macroscopic dielectric constant decreases with the increase in the content of organic solvent.[14] Therefore, it may be supposed that the rates of the electron-transfer reactions between metal complexes with the same charge are in general slower in organic solvents than in water, assuming that the same ionic species are present in both media. In the present system, the anomalous increase in the rate of reductions of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2^{2+}$ and

Table III. Rate Constants for Reduction of Co(en)$_3^{3+}$ by Vanadium(II) and Chromium(II) at Various Mole Fractions of *N,N*-Dimethylformamide and Ethanol[a]

Organic solvent	Mol fraction	Rate constant,[b] M^{-1} s^{-1}
N,N-Dimethylformamide	0	4.9 × 10^{-4} [c]
	0.04	5.5 × 10^{-3} [c]
	0.15	1.6 × 10^{-2} [c]
	0.29	2.9 × 10^{-2} [c]
	0.37	7.4 × 10^{-2} [c]
Ethanol	0.09	2.5 × 10^{-3} [c]
	0.16	1.1 × 10^{-2} [c]
	0.24	4.0 × 10^{-2} [c]
	0.29	6.3 × 10^{-2} [c]
	0.40	7.0 × 10^{-2} [c]
N,N-Dimethylformamide	0	3.9 × 10^{-5} [d]
	0.06	3.5 × 10^{-4} [d]
	0.20	2.3 × 10^{-3} [d]
	0.32	4.7 × 10^{-3} [d]
	0.42	6.5 × 10^{-3} [d]

[a] Σ[ClO$_4^-$] 0.52 M, [H$^+$] 0.40 M; 25.0 ± 0.2 °C. [b] Each value is the average of at least three determinations. [c] Vanadium(II) reduction, [V^{2+}] 6.0 × 10^{-2} M. [d] Chromium(II) reduction, [Cr^{2+}] 6.0 × 10^{-2} M.

Table IV. Rate Constants for Reduction of Co(Cl)(NH$_3$)$_5^{2+}$ by Vanadium(II) at Various Mole Fractions of *N,N*-Dimethylformamide[a]

HCONMe$_2$, mol fraction	Rate constant,[b] M^{-1} s^{-1}
0	7.4
0.06	1.8 × 10
0.13	5.3 × 10

[a] Σ[ClO$_4^-$] 0.92 M, [H$^+$] 0.80 M, [V^{2+}] 6.0 × 10^{-2} M; 25.0 ± 0.2 °C. [b] Each value is the average of at least three determinations.

cis(N)-Co(ox)(β-ala)$_2^-$ by iron(II), Co(Cl)(NH$_3$)$_5^{2+}$ and Co(en)$_3^{3+}$ by vanadium(II), and Co(en)$_3^{3+}$ by chromium(II) upon the addition of *N,N*-dimethylformamide or the alcohols to the aqueous solution can not be explained by the change in the dielectric constant of the medium.

Though the absorption peaks of vanadium(II) and chromium(II) undergo no significant change upon addition of *N,N*-dimethylformamide, the fact that the molar extinction coefficients increase with the addition of *N,N*-dimethylformamide suggests that *N,N*-dimethylformamide coordinates to vanadium(II) and chromium(II). The coordination of the organic solvent molecules to iron(II) was suggested in a previous paper.[1] In acidified aqueous solutions of *N,N*-dimethylformamide or the alcohols, the main species of iron(II), vanadium(II), and chromium(II) ions may be Fe(H$_2$O)$_{6-n}$(OS)$_n^{2+}$, V(H$_2$O)$_{6-n}$(OS)$_n^{2+}$, and Cr(H$_2$O)$_{6-n}$(OS)$_n^{2+}$, where OS represents molecules of *N,N*-dimethylformamide or the alcohols.

The change of the first coordination sphere of reductants would be one of reasons for the increase in the rate upon addition of *N,N*-dimethylformamide or the alcohols.

The rate of reduction of Co(N$_3$)(NH$_3$)$_5^{2+}$ by vanadium(II) is not affected by the addition of *N,N*-dimethylformamide, in spite of the change in the coordination sphere of the vanadium(II) ion, and the rate of reduction of *cis*-Co(Cl)-(NH$_2$CH$_2$CH$_2$OH)(en)$_2^{2+}$ by iron(II) increases with the number of the carbon atoms of the alcohols (Table I). We offer no explanation for these phenomena.

The Salt Effect. The effects of the concentration of perchlorate on the rates of reductions of Co(en)$_3^{3+}$ (Table V) and Co(Cl)(NH$_3$)$_5^{2+}$ (Table VI) by vanadium(II) and the reduction of Co(en)$_3^{3+}$ by chromium(II) (Table V) were also examined in pure aqueous solution and in aqueous solutions

Table V. Effect of Concentration of Perchlorate Ions on the Rate Constant for the Reduction of $Co(en)_3^{3+}$ by Vanadium(II) and Chromium(II) in Aqueous *N,N*-Dimethylformamide

HCONMe$_2$, mol fraction	[ClO$_4^-$], M	Rate constant,^{a} M^{-1} s^{-1}
0^b	0.50	4.9×10^{-4}
	1.00	5.6×10^{-4}
	1.50	6.7×10^{-4}
0.26^b	0.50	2.6×10^{-2}
	1.00	6.2×10^{-2}
	1.50	1.1×10^{-1}
0^c	0.50	3.9×10^{-5}
	1.00	4.4×10^{-5}
	1.50	5.3×10^{-5}
0.35^c	0.50	8.4×10^{-3}
	1.00	3.5×10^{-2}
	1.50	4.7×10^{-2}

^{a} Each value is the average of at least two determinations. ^{b} Vanadium(II) reductions, [H$^+$] 0.38 M, [V^{2+}] 6.0×10^{-2} M; 25.0 ± 0.2 °C. ^{c} Chromium(II) reductions, [H$^+$] 0.38 M, [Cr^{2+}] 6.0×10^{-2} M; 25.0 ± 0.2 °C.

Table VI. Effect of Concentration of Perchlorate Ions on the Rate Constant for the Reduction of $Co(Cl)(NH_3)_5^{2+}$ by Vanadium(II) in Aqueous *N,N*-Dimethylformamide

[ClO$_4^-$], M	Rate constant,^{a} M^{-1} s^{-1}
0.92	7.2^b
1.42	8.1^b
1.90	9.8^b
0.92	5.3×10^c
1.42	8.0×10^c
1.90	9.2×10^c

^{a} Each value is the average of at least three determinations. ^{b} In aqueous solution. ^{c} *N,N*-Dimethylformamide 0.13 mol fraction, [V^{2+}] 6.0×10^{-2} M, [H$^+$] 0.60 M; 25.0 ± 0.2 °C.

of *N,N*-dimethylformamide. The rates of reduction increase with the increase in the concentration of perchlorate in both media, but the enhancement by perchlorate of the reduction in aqueous *N,N*-dimethylformamide solution is larger than that in a pure aqueous solution.

Though Tanaka demonstrated that the ion-pair formation constant between $Co(en)_3^{3+}$ and perchlorate ions in *N,N*-dimethylformamide is larger than that in a pure aqueous solution,[15] it is not clear whether the effect of perchlorate on the reduction rates is attributed to the simple salt effect or the ion-pair formation between $Co(en)_3^{3+}$ and perchlorate.

Mechanism. The reduction of $Co(en)_3^{3+}$ by vanadium(II) in aqueous solutions of *N,N*-dimethylformamide must proceed via an outer-sphere mechanism as well as in the case of in aqueous solution.[16] It is noteworthy that the outer-sphere electron-transfer reaction between $Co(en)_3^{3+}$ and vanadium(II) is accelerated upon addition of *N,N*-dimethylformamide, whereas the rate of electron-transfer between $Co(phen)_3^{2+}$ and $Co(phen)_3^{3+}$ in aqueous acetone decreases with the increase in the content of acetone.[17]

For the reduction of $Co(Cl)(NH_3)_5^{2+}$ by vanadium(II), an outer-sphere mechanism was proposed by Taube,[18] Linck,[13] and Sykes.[19] It was found that the rate of reduction of $Co(Cl)(NH_3)_5^{2+}$ by vanadium(II) increases with the increase in the mole fraction of *N,N*-dimethylformamide (Table IV). The difference between the effect of *N,N*-dimethylformamide in the reductions of $Co(Cl)(NH_3)_5^{2+}$ and $Co(N_3)(NH_3)_5^{2+}$ may be related to a difference of mechanism. The inner-sphere electron-transfer mechanism and the formation of the precursor complex as the rate-determining step have been proposed for the reduction of $Co(N_3)(NH_3)_5^{2+}$ by vanadium(II) in aqueous solution.[20]

Watts et al.[4] suggested that the reductions of Co(X)-$(NH_3)_5^{2+}$ (X = F$^-$, Cl$^-$, and Br$^-$) by iron(II) in dimethyl sulfoxide and *N,N*-dimethylformamide proceed through the inner-sphere mechanism, as is the case in a pure aqueous solution. We favor the inner-sphere mechanism for the reduction of *cis*-Co(Cl)(NH$_2$CH$_2$CH$_2$OH)(en)$_2^{2+}$ by iron(II) based on the effect of the alcohols such as methanol, ethanol, 2-propanol, and 2-methyl-2-propanol (Table I).

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Chemically Catalyzed Disproportionation of Ru(bpy)$_3^{2+}$*

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The complex Ru(bpy)$_3^{2+}$ (bpy is 2,2'-bipyridine) absorbs light strongly in the visible region to give the relatively long-lived charge-transfer excited state Ru(bpy)$_3^{2+}$*.[1] The excited state is known to undergo oxidative quenching to give Ru(bpy)$_3^{3+}$ and reductive quenching to give Ru(bpy)$_3^+$.[2-15] The formal reduction potential for the excited-state couple Ru(bpy)$_3^{3+/2+}$* has been estimated in a quenching study using a series of nitroaromatics as quenchers.[14] The value obtained in the quenching study and the potentials for the ground-state couples Ru(bpy)$_3^{3+/2+}$ and Ru(bpy)$_3^{2+/+}$ [16] have been used to construct the reduction potential diagram in Scheme I (DMA = dimethylaniline). In the reduced ion Ru(bpy)$_3^+$, the added electron appears to be in a π*(bpy) level, as expected.[11,12]