The Effect of H^+ on Reduction of $[Co(NH_3)_4(C_2O_4)]^+$ with $[Fe(H_2O)_6]^{2+}$

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Kinetic studies were carried out for the redox reaction of $[Co(NH_3)_4(C_2O_4)]^+$ with aqueous $[Fe(H_2O)_6]^{2+}$ solution in the present of H^+ by UV/VIS-spectrophotometric method. It was found that the order of H^+ for the reaction is first one in the higher H^+ concentration range of $1.67 \times 10^{-1}M \sim 1.00M$, while second order in the lower range of $6.30 \times 10^{-2}M \sim 1.67 \times 10^{-1}M$. Reaction order of the substrates was found to be first order with respect to each of them. Accordingly overall reactions are third or fourth order. The results of calculation for the Extended Huckel Molecular Orbital theory contribute to estimate the preferred intermediates, bridging form of binuclear complex. On the basis of these results, we propose that this redox reaction proceed *via* inner-sphere reaction mechanism.

Introduction

Dominating current work on oxidiation-reduction (redox) reactions of transition metal complexes in solution is the question of the mechanism by which the overall electronic change occurs. Such systems involving electron transfer have been studied extensively in the past.[1] The mechanisms for redox reactions fall into two classifications. An inner-sphere electron transfer is accompanied by makred changes in the coordination sphere of the transition state, usually with a ligand bridging the two metal centers. In an outer-sphere electron transfer mechanism the coordination spheres of the reactants remain intact. The question of whether electron transfer proceeds through an inner- or outer-sphere mechanism has constituted a central theme in recent studies of electron transfer reactions of metal ions.[2] But differentiating between the two mechanistic types is in general not easy. Taube and Ogard[3] reported that redox reaction of metal ions is the specific influence exerted on the rates of reaction by ligands in complex, and the mechanisms by which these influence are exerted. And Ellerhorst[4] has described that the way of electron transfer depends on characteristic of the ligand. Haim[5] and Wieghrdt[6] have shown that the many results of studies on inner- and outer-sphere mechanim.

An important problem in the field of mechanisms of "electron transfer" reactions is concerned with the changes taking place in the coordination spheres of the oxidant and the reductant on electron transfer. This problem has been but little elucidated for the reaction which involves catalyst.

The present studies have been made spectrophotometrically for the following redox reaction in acidic solution.

$$[Co(NH_3)_4(C_2O_4)]^+ + [Fe(H_2O)_6]^{2+} \xrightarrow{H^+}$$

$$[Co(H_2O)_6]^{2+} + [Fe(C_2O_4)(H_2O)_2]^{+2} + 4NH_4^+$$
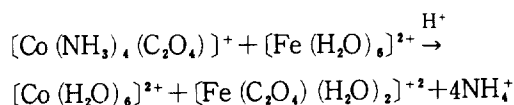
We obtained the experimental rate equation from activation parameters and reaction orders of reactants and catalyst H^+. On the basis of experimental kinetic data and the result of Extended Huckel Molecular Orbital calculation, which is necessary for the decision of the adequate intermediate, we will propose the plausible mechanism.

Theory

Treatment of Rate Equation. This system dealt with pseudo first-order for $[Co(NH_3)_4(C_2O_4)]^+$ in an excess concentration of the $[Fe(H_2O)_6]^{2+}$ compared to that of $[Co(NH_3)_4 (C_2O_4)]^+$. The rate constant was obtained from the rate of $[Fe(C_2O_4)(H_2O)_2]^+$ formation in stead of the rate for decrease of $[Co(NH_3)_4(C_2O_4)]^+$ by the UV/VIS-spectrophotometer. Therefore observed rate constant, k_{obs}, was obtained from the slope of plot of $-\ln(A_t - A_\infty)$ against time, where A_t and A_∞ correspond to the absorbance at anytime and at equilibrium point, respectively. The overall reaction involving H^+ ion can be expressed as equation (1).

$$v = k_H^+ \{[H^+]\}^l \{[Fe^{2+}]\}^m \{[Co(NH_3)_4(C_2O_4)]^+\}^n \quad (1)$$

A plot of $\ln k_{obs}$ against $\ln[Fe^{2+}]$ is linear with slope equal to m as the reaction order of $[Fe^{2+}]$ because the k_{obs} is equal to $k_{H^+}\{[H^+]\}^l\{[Fe^{2+}]\}^m$ in the eq. (1). As the $k_{obs}/\{Fe(II)\}^m$ is $k_{H^+}\{[H^+]\}^l$, the present reaction system is represented by eq. (2).

$$\ln(k_{obs}/\{[Fe^{2+}]\}^m) = \ln[H^+] + \ln k_H^+ \quad (2)$$

The reaction order n of $[Co(NH_3)_4(C_2O_4)]^+$ is determined from the linear slope of a graph of the logalithm of initial rate against the logalithm of the initial concentration of $[Co(NH_3)_4(C_2O_4)]^+$.

Activation Parameters. Activation energy ΔE_a^* is calculated Arrhenius equation, and activation enthalpy ΔH^* and activation entropy ΔS^* were determined from previously derived equation:[7]

$$\Delta H^* = R \frac{T_i T_j}{T_i - T_j} (k_i T_j / k_j T_i) \quad (3)$$

$$\Delta S^* = R \ln \left\{ \frac{(k_i/T_i)^{|T_i/T_i - T_j|}}{(k_j/T_j)^{|T_i/T_i - T_j|}} \frac{h}{K} \right\} \quad (4)$$

Molecular Orbital Theory for Transition Metal Complex[8]. The net charge of atoms and Reduced Overlap Population between orbitals are necessary for the estimation of an intermediate in elementary reactions. The net charge and Reduced Overlap Population are expressed as:

$$Q_{i\alpha} = \sum_{\alpha}^{occ} 2C_i\alpha \sum_j C_i\alpha S_{ij} \quad (5)$$

$$P_{ij} = 2 \sum_\alpha n\alpha C_i\alpha C_j\alpha S_{ij} \quad (6)$$

Table 1. Observed Rate Constants, k_{obs}, for Various Constants of Reactants ([Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ and [Fe(H$_2$O)$_6$]$^{2+}$) in Serval Constants of [H$^+$]

[Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ ($\times 10^4$ mol/l)	[Fe(H$_2$O)$_6$]$^{2+}$ ($\times 10^2$ mol/l)	HClO$_4$ ($\times 10$ mol/l)	$k_{obs}(\times 10^4$ sec)
10.00			7.32(0.50)
8.00			7.28(0.48)
5.00	2.50	7.00(0.85)	7.33(0.43)
4.00			7.30(0.47)
2.50			7.27(0.48)
2.00			7.28(0.45)
			7.30(0.47)
	10.00		30.85(2.01)
	8.00		23.53(1.67)
4.00	5.00	7.00(0.85)	13.92(1.10)
	4.00		10.45(0.79)
	2.50		7.30(0.47)
	2.00		5.81(0.38)
		10.00	9.35
		7.00	7.30
		5.00	5.27
		2.50	2.92
4.00	2.50	1.67	1.83
		1.25	1.28
		1.00	0.65
		0.85	0.47
		0.63	0.27

Condition: I = 2.2 (NaClO$_4$), 25 °C, ( ): lower range of concentration for H$^+$.

Experimental

The complex of [Co(NH$_3$)$_4$(C$_2$O$_4$)]ClO$_4$ was prepared according to the previous method.[9] The aqueous solution of FeCl$_2$.nH$_2$O and HClO$_4$ was used as reductant and catalyst, respectively. The concentration of reductant was determined by redox titration method.[10] The progress of reaction was followed spectrophotometrically, using the absorption peak of the Fe^{3+} complex in the vicinity of 336 nm at 2.2 ionic strength with NaClO$_4$. The cell was brought to reaction temperature in a regulated bath of 25.0 ± 0.1 °C. Either continuous or intermittent absorbance reading were made with a Hitachi Model 320 UV/VIS–spectrophotometer.

Results and Discussion

The observed rate constant, k_{obs}, was obtained from the plot of $-\ln(A_t-A_\infty)$ against time at the various amount of reactants. These rate constants are listed in Table 1.

In Table 1, k_{obs} can be seen to have constant value in fixed concentration of [Fe^{2+}] and [H$^+$] irrespective of the concentration of [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$. As a result, the electron transfer between [Fe^2]$^+$ and [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ can be though of as pseudo first order for [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$. Initial rates are given in Table 2. As shown in Table 2 and Figure 1, reaction order for [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ also can be confirmed to be first order.

Since the reaction rate depend on concentration of [Fe^{2+}],

Table 2. Values of Initial Rate for Various Amounts of [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ at 0.1M [Fe(H$_2$O)$_6$]$^{2+}$ in 0.8M H$^+$

[Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ ($\times 10^4$ mol/l)	10.00	8.00	5.00	4.00	2.50	2.00
v_i ($\times 10^3$ mol/l·sec)	5.10	4.00	3.03	2.05	1.46	1.02
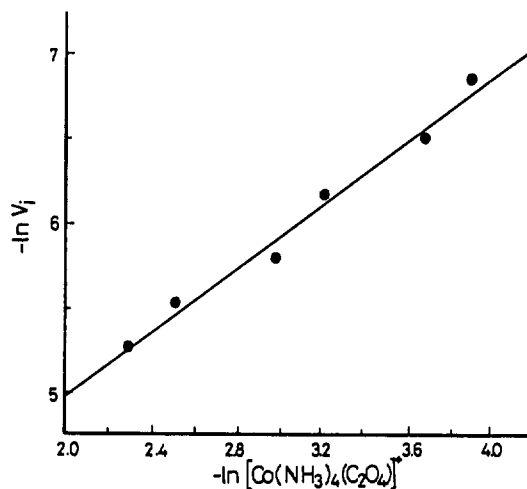
Figure 1. Plot of $-\ln v_i$ versus $-\ln\{[Co(NH_3)_4(C_2O_4)]^+\}$ at 25 °C, ([Fe(H$_2$O)$_6$]$^{2+}$: 0.1M, HClO$_4$: 0.8M).
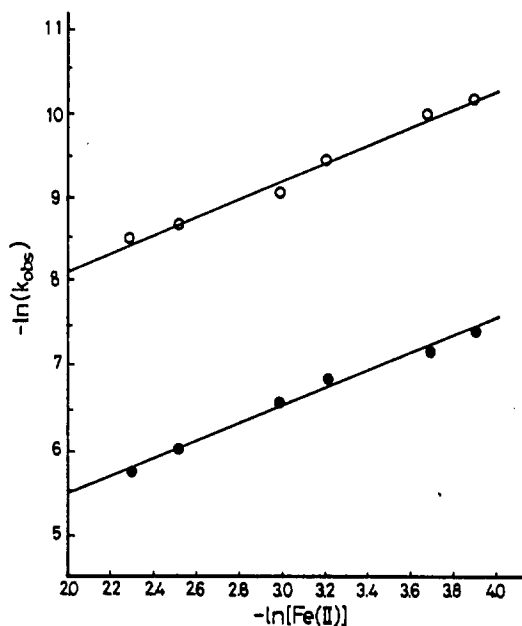
Figure 2. Plot of $-\ln k_{obs}$ versus $-\ln\{Fe(H_2O)_6]^{2+}\}$ at 25 °C, ([Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$: 4 × 10^{-4}M, ●: 7.0 × 10^{-1}M [H$^+$], ○: 8.5 × 10^{-2}M [H$^+$]).

reaction order for [Fe^{2+}] must be obtained from the plot of ln k_{obs} against ln [Fe^{2+}] as shown in Figure 2. From the slope of the graph, it is or was found to be unit.

Reaction order for H$^+$ and the rate constant for this system was obtained from the slope and intercept in Figure 3 by using eq. (2).

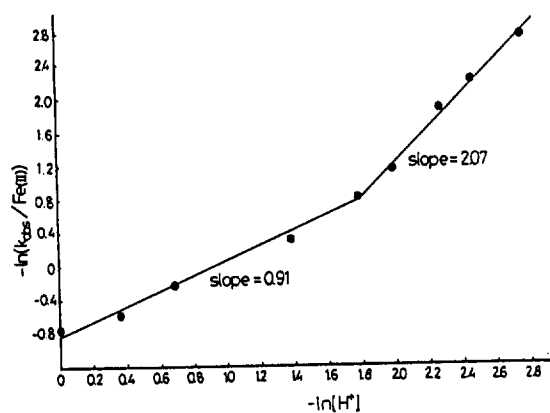It was found that the reaction order for H$^+$ is first order in

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Figure 3. Plot of $-\ln(k_{obs}/\text{Fe(II)})$ versus $-\ln\{[H^+]\}$ at 25 °C. ([Co (NH$_3$)$_4$(C$_2$O$_4$)]$^+$: 4×10^{-4}M, [Fe(H$_2$O)$_6$]$^{2+}$: 2.5×10^{-2}M).

Table 3. Activation Parameters for Redox Reaction of [Co(NH$_3$)$_4$ (C$_2$O$_4$)]$^+$ with [Fe(H$_2$O)$_6$]$^{2+}$ in acidic solution

T(K)	E_a(kcal/mol)	ΔH^*(kcal/mol)	ΔS^*(e.u.)
298.15		16.55 (15.39)	−11.86 (−20.70)
303.15		16.93 (15.38)	−10.59 (−20.57)
308.15	17.39^a (15.94)^b	16.76 (15.40)	−11.04 (−20.55)
313.15		16.79 (15.39)	−11.04 (−20.56)
		16.76^a (15.39)^b	−11.16^a (−20.59)^b

Conditions: I = 2.2 (NaClO$_4$)

^{a}The third order for overall reactions. ^{b}The fourth order for overall reactions.

the higher H$^+$ concentration range of 1.67×10^{-1}M ~ 1.00M, while that for H$^+$ is second order in the lower range of 6.30×10^{-2}M $\sim 1.67 \times 10^{-1}$M. The rate constants were 3.91×10^{-2} l^2mol^{-2}sec^{-1} and 3.10×10^{-1} l^3mol^{-3}sec^{-1} in higher and lower H$^+$ concentration, respectively. From the above results the rate equation for overall reaction is given in eqs. (7) and (8).

$$v = (3.91 \times 10^{-2})\{[\text{Fe}^{2+}]\}\{(\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_4]^+\}\{[\text{H}^+]\}$$
(higher range) (7)

$$v = (3.10 \times 10^{-1})\{[\text{Fe}^{2+}]\}\{[\text{Co}(\text{C}_2\text{O}_4)(\text{NH}_3)_4\}^+\}\{[\text{H}^+]\}^2$$
(lower range) (8)

The activation parameters for the reaction are listed in Table 3.

The change in activation entropy(ΔS^*) is generally over the range of $-10 \sim -20$ e.u. in the inner-sphere reaction and $-30 \sim -40$ e.u. in the outer-sphere reaction, respectively.[11] As shown in Table 3, the value of ΔS^* for this system are over the range of $-11 \sim -21$ e.u., and hence this system would proceed *via* inner-sphere reaction mechanism. We calculated net charge and Reduced Overlap Population (R.O.P.) of reactant and various assumed intermediates by EHMO method as shown in Figure 4, by which determined plausible intermediate structures.

From the results of EHMO calculation, it can be expected that [Fe^{2+}] attack two oxygen atoms of the [Co(NH$_3$)$_4$(C$_2$O$_4$)]$^+$ which have the largest electron density as (II) in Figure 4. Either of the two oxygen atoms is attacked by H$^+$, and activated complex is formed as (III) in Figure 4. And so Co-O* bond for the activated complex is weakened as can be seen
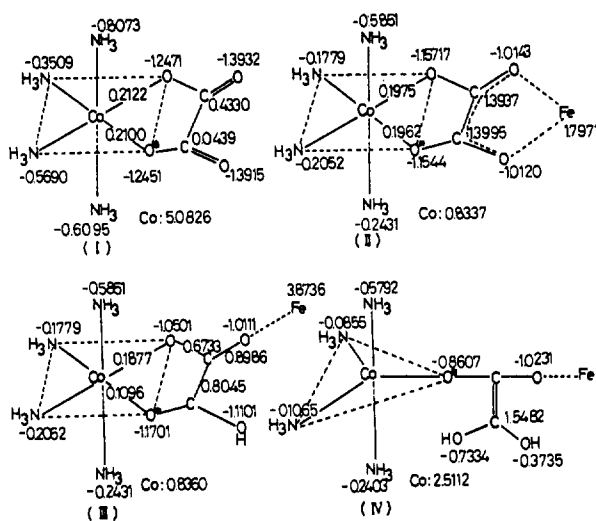

Figure 4. Net charge of atoms and reduced overlap population between oribitals of Co(III) complexes.

(III) in Figure 4, while net charge of Co(III) in the activated complex decreases because electron lean to the Fe(II). Another H$^+$ attack successively the O* of the activated complex (III) in Figure 4, and Co-O* bond has been broken and net charge of the Co(III) increase as seen in (IV) of Figure 4. As such a result, the electron transfer would facilitate from Fe(II) to Co(III). Therefore the role of H$^+$ would make easy electron transfer from Fe(II) to Co(III).

Afterall, [Fe^{2+}] attacks the oxygen atom of [Co(NH$_3$)$_4$ (C$_2$O$_4$)]$^+$ which has the largest electron density, and oxalato act as a bridging ligand as suggested by Crumbliss.[12] Since Co(III) and Fe(II) hold oxalato in common, so that two metals would approach each other, and H$^+$ facilitate electron transfer in the binuclar complex, As a such a result, Co(III) is reduced to Co(II) which is extermely labile, and Fe(II) is oxidized to Fe(III) which is inert complex.

On the basis of these results, the presumed reaction mechanism will be presented as follows.

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(presumed mechanism)
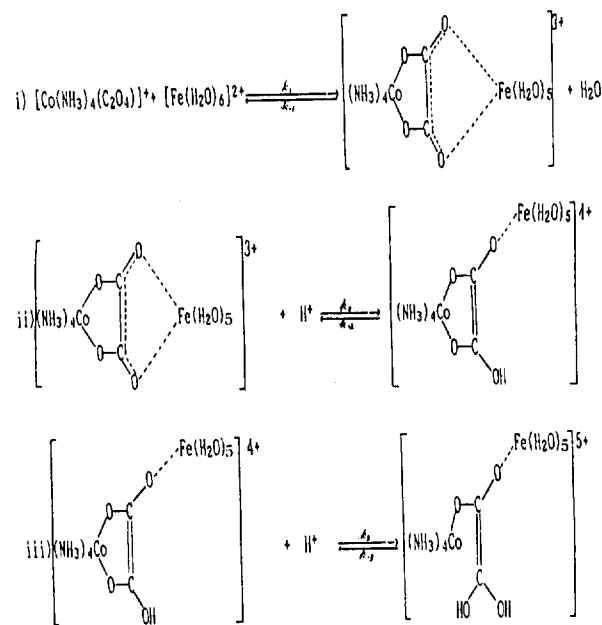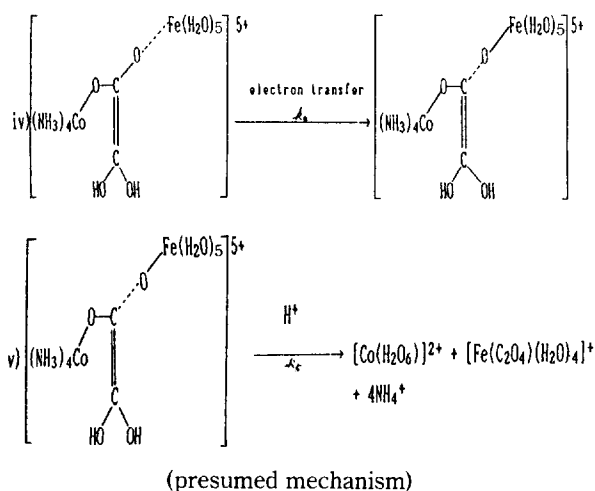
In the presumed mechanism, step (i) is pre–equilibrium state and step (ii) and (iii) are reversible process. The theoretical rate equation has been derived from the above presumed mechanism by using steady state approximation method and equilibrium method.

$$v = -\frac{d\{[Co(NH_3)_4(C_2O_4)]^+\}}{dt} = \frac{\{[Fe^{3+}]\}}{dt}$$

$$\frac{K_1 k_2 k_3 k_4 \{[Co(NH_3)_4(C_2O_4)]^+\}\{[Fe^{2+}]\}\{[H^+]\}^2}{k_{-2}k_{-3} + k_{-2}k_4 + k_3 k_4 \{[H^+]\}}$$

In the case of higher range of H^+ concentration, step (ii) and (iii) preferred forward reaction. Thus, $k_3 k_4\{[H^+]\}$ is very large, and rate equation is reduced to eq. (9).

$$v_{theo} = K_1 k_2 \{[Co(NH_3)_4(C_2O_4)]^+\}\{[Fe^{2+}]\}\{[H^+]\} \quad (11)$$

If k_{H^+} is equal to $K_1 k_2$, it is consistent with the experimental rate equations (7) in the higher range of H^+ concentration. In the case of lower range of H^+ concentration, step (ii) and step (iii) preferred backward reaction. Thus, $k_3 k_4\{[H^+]\}$ is very small.

$$v_{theo} = \frac{K_1 k_2 k_3 k_4}{k_{-2}k_{-3} + k_{-2}k_4}\{[Co(NH_3)_4(C_2O_4)]^+\}$$

$$\{[Fe^{2+}]\}\{[H^+]\}^2 \quad (10)$$

If k_{H^+} is equal to $(K_1 k_2 k_3 k_4/k_{-2}k_{-3} + k_{-2}k_4)$, the theoretical rate equation is consistent with equations (8) in lower range of H^+ concentration.

Since the theoretical rate equation is the same as the experimental rate equations, the proposed mechanism is adequate one. Therefore, this system proceed *via* inner–sphere reaction mechanism, which electron transfer is promoted by H^+ through bridging ligand with oxalato.

Conclusion

Kinetic studies were carried out for the redox reaction of $[Co(NH_3)_4(C_2O_4)]^+$ with $[Fe^{2+}]$ in acidic solution by UV/VIS–spectrophotometric method. It has been found that the reac-

tion order for H^+ catalyst is first order in the higher range of H^+ concentration, while that for H^+ catalyst is second order in the lower range. And the reaction order for each substrates is first order. Accordingly, overall reactions are third or fourth order reaction. The rate constants were 3.91×10^{-2} $l^2mol^{-2}sec^{-1}$ and 3.10×10^{-1} $l^3mol^{-3}sec^{-1}$ when the H^+ react as first and second order, respectively. From the value of activation entropy, we can see that this system would proceed *via* inner–sphere reaction mechanism. And we calculated net charge and R. O. P. of reactants and assumed intermediates by EHMO theory.

On the basis of the kinetic data and results of calculation, we suggest that this system proceed *via* inner–sphere reaction mechanism.

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