

# The Effects of Pressure and Oxalate on the Rate of Anation of $\text{cis-}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$ with Oxalate in Acidic Aqueous Solution

Jong-Chul Byun\*

酸性水溶液中에서  $\text{cis-}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$ 와 Oxalate間的  
Anation 反應速度에 미치는 壓力과 Oxalate 影響

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## Summary

The effects of oxalate ion and pressure up to 1,600 bar on the anation reaction of  $\text{cis-}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$  with oxalate in aqueous solution of 0.5M nitric acid have been studied by utilizing spectrophotometric method at 60°C. The rate law was obtained from the oxalate ion effect on the pseudo first-order rate constant ( $k_{\text{obs}}$ ), and then the equilibrium quotients ( $Q_{\text{IP}}$ ) for ion-pairing process and the interchange rate constants ( $k_a$ ) at given pressures were determined.

The volume of activation ( $\Delta V_{\text{obs}}^*$ ) corresponding to the over-all reaction was about  $+9.2\text{cm}^3\text{M}^{-1}$ , nearly pressure-independent and similar to the change of volume ( $\Delta V_a^* = +9.6\text{cm}^3\text{M}^{-1}$ ) for an interchange step, which also was pressure-independent. Since  $\Delta V_{\text{obs}}^*$  primarily consists of  $\Delta V_a^*$  for  $k_a$  and  $\Delta V_{\text{QIP}}$  representing the change of volume for  $Q_{\text{IP}}$ , it might be concluded that the contribution of  $\Delta V_{\text{QIP}}$  toward  $\Delta V_{\text{obs}}^*$  is ignored. The analysis of volume changes for each steps during the reaction further supported that the mechanism is a dissociative interchange.

## Introduction

$$\left(\frac{\partial \log k}{\partial P}\right)_T = -\frac{\Delta V^*}{2.303RT} \quad (1)$$

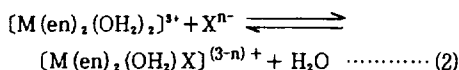
The effect of pressure  $P$  on the rate constant  $k$  for a reaction is summarized in the following expression

and is now a well accepted approach in elucidating reaction mechanisms (Kelm, 1977). The activation volume ( $\Delta V^*$ ) in eq(1) represents

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the partial molar volume change when the reactants are converted to the activated complex. Eq(1) shows that the rate constant increases with increasing pressure if  $\Delta V^*$  is negative, which is also predictable simply from Le Chatelier's principle. When the compressibilities of reactants and transition state are different, usually  $\Delta V^*$  is pressure dependent.

$\Delta V^*$  primarily consists of two contributions: i. e., the intrinsic part,  $\Delta V_{int}^*$  and the electrostrictive part,  $\Delta V_{el}^* \cdot \Delta V_{int}^*$  represents the intrinsic difference in the molecular size between reactants and transition state due to the effects of bond making, breaking and stretching.  $\Delta V_{el}^*$  represents the accompanying change of volume of the surrounding solvents resulting from changes in electrostriction for charged or polar species. The clear-cut point to  $\Delta V_{int}^*$  predicts that for the reaction(2) a dissociative mechanism will result in a positive  $\Delta V_{int}^*$  value due to stretching of the M-OH<sub>2</sub>, while for an associative mechanism the formation of the M-X bond should give rise to a negative  $\Delta V_{int}^*$  value.



The high positive charges on the reactant demand that  $\Delta V_{el}^*$  due to the neutralization during the reaction is strongly positive and the dominant term for an associative or an interchange mechanisms (Billo, 1984).

Until recently, the reaction of aquometal cations with anionic nucleophiles is frequently explained in terms of an ion-pair interchange processes (Fairbank, 1986). The interchange mechanism (I) is labeled I<sub>a</sub> in an associative, in which bond making is apparently more important than bond breaking in the transition state. The opposite situation in which bond breaking is more important than bond making is labeled I<sub>d</sub> in a dissociative. The structural changes of reactants

arising from the interchange mechanism during reaction could be analyzed by the determination of activation volumes and the consideration of their pressure dependence (Swaddle, 1976). Then the parameter could be used as a criterion to distinguish between an associative and a dissociative interchange reaction.

In this paper, diaquobis(ethylenediamine) cobalt(III) complex ion of which proton dissociation (Coates, 1981), water-exchange (Dwyer and Sagenon, 1963) and isomerization reactions (Stranks and Vanderhoek, 1976), already investigated was selected to consider the effects of pressure and oxalate ion on the reaction mechanism. This complex is an appropriate substrate for the evaluation of activation volume for anation proceeding by ion-pair interchange mechanism. This result will be compared with that reported in literature (Fleisher, 1968), in which the oxalate ion effect is established in low concentration of oxalate and at a atmospheric pressure.

## Experiments

### 1. Preparation of sample

At first cis-[Co(en)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> was synthesized according to the procedure of Dwyer, Sargeson and Reid. Cis-[Co(en)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> obtained finally by adding 3N HNO<sub>3</sub> to [Co(en)<sub>2</sub>-CO<sub>3</sub>]<sub>2</sub>NO<sub>3</sub> was filtered, then recrystallized from methanol, washed with acetone and dried in vacuo over P<sub>2</sub>O<sub>5</sub> at room temperature for at least 24 hours. The chemical analyses and uv-visible spectra ( $\epsilon=81 \text{ M}^{-1} \text{ cm}^{-1}$  at 495 nm and pH=0.5-4.0) were in good agreement with the theoretical values and with the result reported in literature, respectively (Dwyer and Sagenon, 1963). The recrystallizations for purification were repeated until no further effect on the analytical and

spectral data. Other materials were analytical commercial reagents (methanol, acetone, sodium nitrate, perchloric acid, etc.,).

The stock solution of nitric acid was standardized by sodium carbonate solution which was prepared by weighing correctly. The standard solution of sodium nitrate used to control an ionic strength was determined by gravimetric method. Ionic strength was maintained at 1.4 throughout all experiments. All solutions were prepared with triply distilled water.

## 2. Measurement of pseudo first order rate constants

The rate of anation of complex ion with oxalate was followed by observing the decrease in absorbance at 495nm and 60°C. The changes of spectra were obtained using Shimadzu uv-visible 210A & Beckmann 25 spectrophotometers. In all measurements of absorbance the same width of slit was used, although it was shown that the absorbance does nearly not depend upon a slit width. The pseudo first order rate constants fulfilled by adding in at least 15-fold excess the concentration of oxalate than that of complex ion were obtained from plots of logarithms of  $(A_\infty - A_t)$  against time.  $A_t$  and  $A_\infty$  are absorbances at time  $t$  and infinity, respectively. These plots proved to be linear until at least two or three times the half-life.

All measurements were carried out in a high pressure vessel (Fig.1) with two sapphire windows, which is called Lentz cell. This cell was a part of high pressure apparatus consisting of a pressure generator (Nova Co.), a manometer (Heise Co.) and a column separating the oil branch of system from the part of sample solution. The setting is already described in literatures. The vessel was maintained at  $60 \pm 0.5$  °C using Haake F4391 circulator and Lande Model

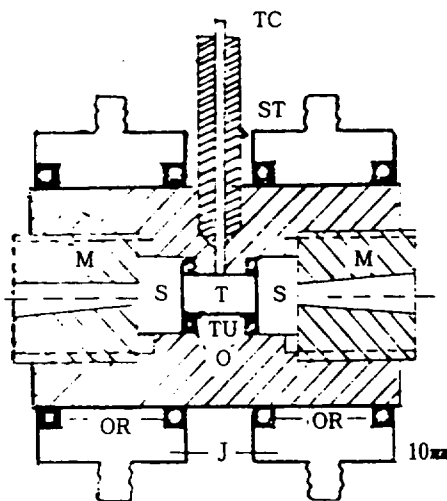


Fig. 1. Optical high pressure cell. J : temperature jacket, M : steel mountings, O : O-rings sealing the sapphire windows, OR : O-rings sealing the temperature jacket, S : sapphire windows, ST : steel tubing, T : teflon cylinder, TC : Teflon capillary, TU : U-shaped teflon rings.

-T2 thermostat. A sample solution was drawn into a syringe (20ml) equipped with teflon plunger and Pt-Ir outlet tube, and then moved into the high pressure vessel. The rate constants were measured in the range of pressures up to 1,600 bar.

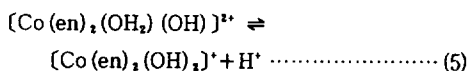
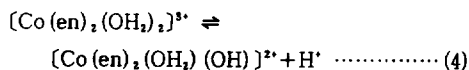
## Results and Discussion

For the reaction (3), the total concentration of oxalate ion was varied in the range of 0.025-0.300M, while that of complex ion was kept constantly in  $1.5 \times 10^{-3}$ M, in which pseudo first order condition was fulfilled.



Co(III) and Ox indicate Co(III) species ( $\text{cis}-(\text{Co}(\text{en})_2(\text{OH})_2)^{3+}$ ,  $\text{cis}-(\text{Co}(\text{en})_2(\text{OH})_2(\text{OH}))^{3+}$ , and  $\text{cis}-(\text{Co}(\text{en})_2(\text{OH})_2)^{3+}$ ) and oxalate species ( $\text{H}_2\text{C}_2\text{O}_4$ ,

$\text{HC}_2\text{O}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ , respectively. The equilibria of both chemical species are represented as in eq (4) and (5), and eq (6) and (7)



The rate law of reaction (3) becomes eq (8),

$$\text{Rate} = k[\text{Co}(\text{III})]_{\text{T}} [\text{Ox}]_{\text{T}} \quad \dots\dots\dots (8)$$

When  $[\text{Ox}]_{\text{T}} \gg [\text{Co}(\text{III})]_{\text{T}}$ , eq (8) becomes eq (9),

Table 1. The Pseudo First Order Rate Constants ( $k_{\text{obs}} \times 10^4$ ) as a Functions of Pressure and Oxalate Concentration at 1.4 of Ionic Strength and 60°C.

Pressure (bar) \n [Ox] (M)	Pressure (bar)					
	1	300	600	1,000	1,300	1,600
0.025	1.39	1.25	1.15	1.02	0.88	0.80
0.033	1.57	1.48	1.35	1.13	1.08	0.99
0.040	1.78	1.72	1.50	1.27	1.18	1.08
0.050	2.04	1.97	1.75	1.49	1.40	1.25
0.100	2.83	2.68	2.50	2.04	1.81	1.80
0.200	4.06	3.64	3.23	2.90	2.60	2.25
0.300	4.48	4.07	3.64	3.33	2.79	2.47

$$\text{Rate} = k_{\text{obs}}[\text{Co}(\text{III})]_{\text{T}} \quad \dots\dots\dots (9)$$

Where  $k_{\text{obs}}$  is  $k[\text{Ox}]_{\text{T}}$ . The pressure effect on  $k_{\text{obs}}$  was followed by running experiments at 1, 300, 600, 1,000, 1,300 and 1,600 bars. Pseudo first order rate constants observed were collected in Table 1. The value at atmospheric pressure was agreed with that of other investigator ( $1.1 \times 10^{-4} \text{ sec}^{-1}$  at 2.0 of ionic strength and  $[\text{Ox}]_{\text{T}} = 0.02\text{M}$ ). The plots of logarithms of  $k_{\text{obs}}$  against pressure at a given concentration of oxalate ion were nearly linear within experimental uncertainty (Fig.2). The volume of activation ( $\Delta V_{\text{obs}}^*$ ) obtained from Fig.2 was about  $+9.2 \text{ cm}^3 \text{ M}^{-1}$  and pressure-independent irrespective to the concentration of oxalate ion. Such an effect on  $\Delta V_{\text{obs}}^*$  supports that the change of solvation on

going to transition state in this reaction is not so important. In general, a significant change of solvation shows themselves in a pressure-dependence of the volume of activation (Guldi, 1992; Palmer, 1979). Thus the pressure effect on  $k_{\text{obs}}$  can be reasonably considered when the reaction (3) is assumed as a dissociative interchange mechanism.

As shown in Fig.3, the values of  $k_{\text{obs}}$  in low concentration of oxalate were invariably proportional to  $[\text{Ox}]_{\text{T}}$  so that  $k_{\text{obs}}/[\text{Ox}]_{\text{T}}$  could be a second order rate constant. At higher concentration, however, a deviation from constancy for  $k_{\text{obs}}/[\text{Ox}]_{\text{T}}$  were observed and eventually the oxalate effect on  $k_{\text{obs}}$  was nearly disappeared, in which the reaction (3) turned over to first order in complex ion alone. In such a

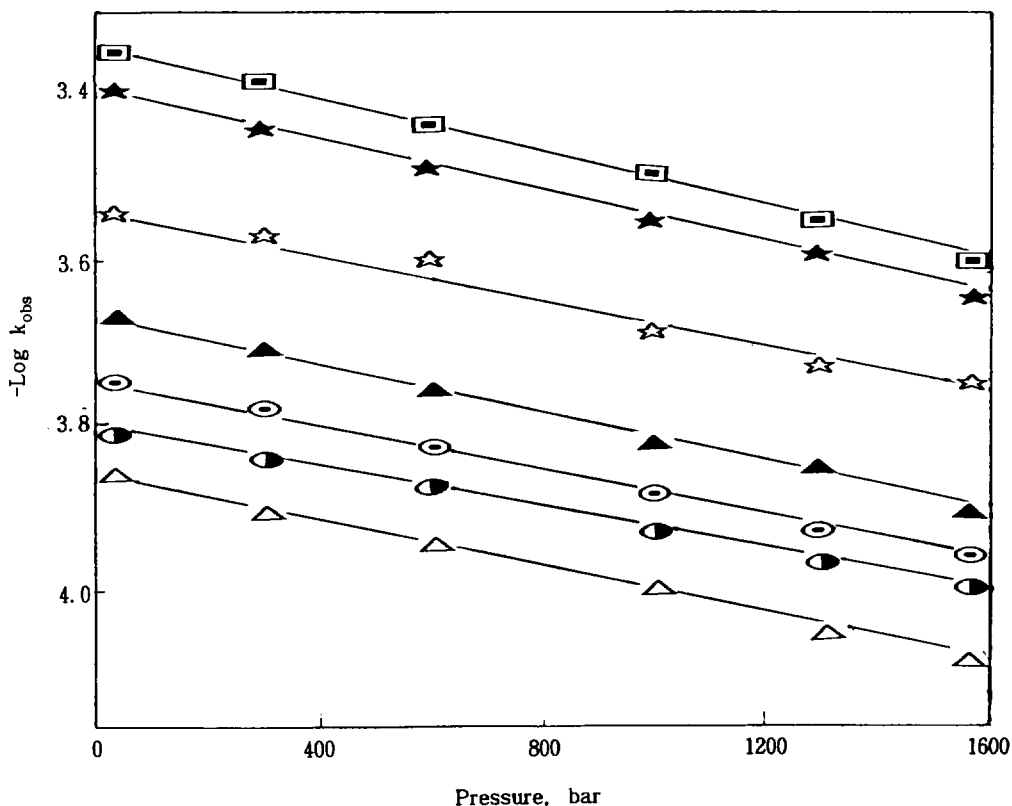


Fig. 2. The plots of logarithms of  $k_{\text{obs}}$  against pressure at 60°C and various concentrations of oxalate ion : 0.025M ( $\Delta$ ), 0.033M ( $\bullet$ ), 0.040M ( $\odot$ ), 0.050M ( $\blacktriangle$ ), 0.100M ( $\star$ ), 0.200M ( $\blackstar$ ) and 0.300M ( $\square$ ).

situation, the rate law is generally represented as in eq(10) (Kodama, 1980; Stranks and Vanderhoek 1976).

$$k_{\text{obs}} = \frac{a[\text{Co(III)}]_{\text{T}}[\text{Ox}]_{\text{T}}}{1 + [\text{Ox}]_{\text{T}}b} \dots\dots\dots (10)$$

There are several reasonable mechanisms for this type of kinetics expression. One of them is  $S_{\text{N}}1$  or D type in which a five coordinated intermediate is generated with a sufficient lifetime. The other is ion-pair (SNIP) or  $I_{\text{d}}$  type in which a dissociative interchange between leaving and entering groups within an outer-sphere or ion

-pair is occurred. Since the reaction (3) is already accepted to proceed according to a dissociative interchange mechanism, the pressure and oxalate ion effects on  $k_{\text{obs}}$  listed in table 1 might be interpreted as due to interchange process. Kinetics studies on Co(III) complex systems have firmly established as  $I_{\text{d}}$  mechanism (Swisher, 1986). If a proton dissociation constants of both oxalate and complex ions which reported by our laboratory and other investigator are together considered the process of reaction(3) can be represented as in scheme ( $\star$ ).

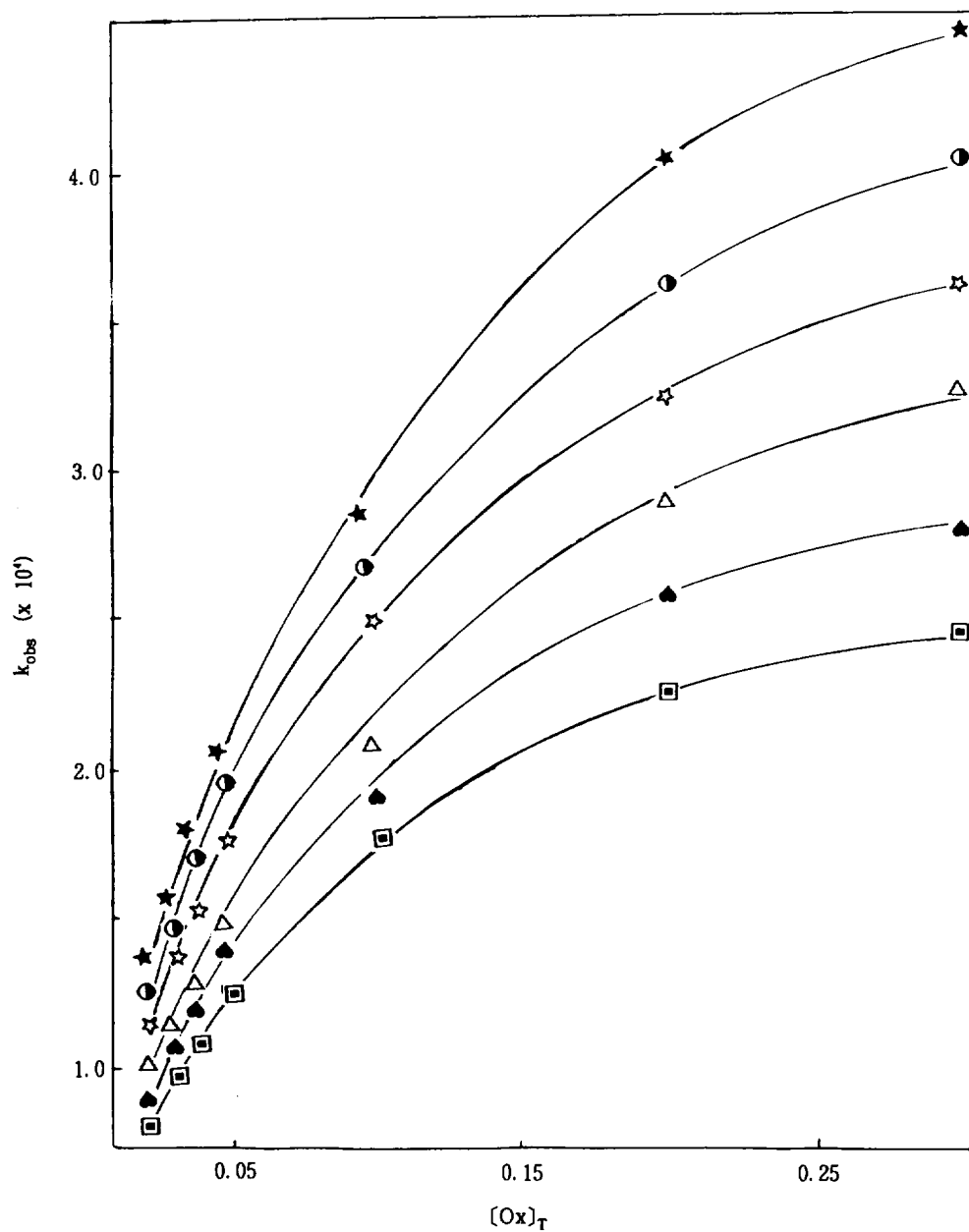
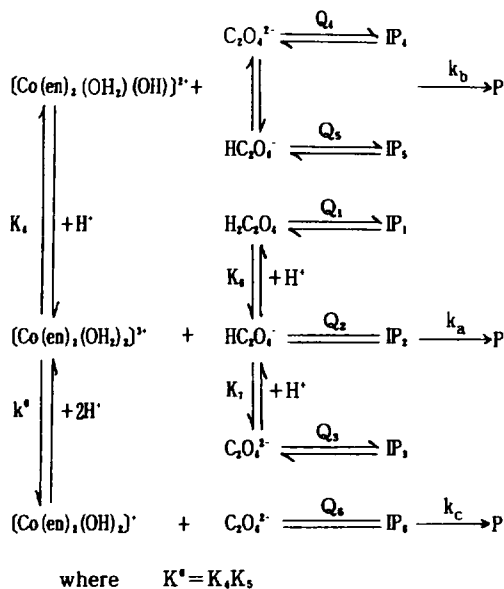


Fig. 3. The plots of  $k_{obs}$  against total concentration of oxalate ion ( $[Ox]_T$ ) at various pressures : common (★), 300bar (●), 600bar (☆), 1,000bar (△), 1,300bar (▲) and 1,600bar (◻).



SCHEME (☆)

One can usually apply the stationary state approximation to obtain the rate law for such an interchange mechanism, and then  $k_{\text{obs}}$  must be deduced to eq (11).

$$k_{\text{obs}} = \frac{(k_a G_1 + k_b G_2 + k_c G_3) (\text{H}_2\text{C}_2\text{O}_4)}{[(\text{H}^+)^2 + K_4(\text{H}^+)^3 + K_4 K_5 (\text{H}^+)^4 + (G_1 + G_2 + G_3) (\text{H}_2\text{C}_2\text{O}_4)]} \quad (11)$$

Where  $G_1 = Q_1(\text{H}^+)^4 + K_6 Q_2(\text{H}^+)^3 + K_6 K_7 Q_3(\text{H}^+)^2$   
 $G_2 = K_4 K_5 Q_4(\text{H}^+)^3 + K_4 K_6 K_7 Q_5(\text{H}^+)^2$   
 $G_3 = K_4 K_5 K_6 K_7 Q_6$

Substituting the total concentration of oxalate,  $(\text{Ox})_T$ , leads to eq (12).

$$k_{\text{obs}} = \frac{(k_a G_1 + k_b G_2 + k_c G_3) (\text{Ox})_T}{W ((\text{H}^+)^2 + K_4(\text{H}^+)^3 + K_4 K_5) + (G_1 + G_2 + G_3) (\text{Ox})_T} \quad (12)$$

Where  $W = ((\text{H}^+)^2 + K_4(\text{H}^+)^3 + K_4 K_5)$

Using the values of  $K_4$ ,  $K_5$ ,  $K_6$  and  $K_7$  in literatures (Kruse, 1961), the distribution curves

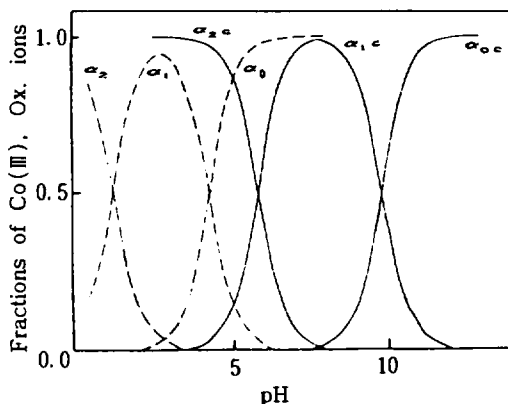


Fig. 4. The fraction,  $\alpha_n^o$  (—) and  $\alpha_n$  (-----) of cobalt (III) species and oxalate species as a function of pH using  $K_4 = 1.5 \times 10^{-4}$  and  $K_5 = 1.5 \times 10^{10}$  for cobalt (III) species, and  $K_6 = 5.4 \times 10^2$  and  $K_7 = 5.3 \times 10^{-5}$  for oxalate species.

for all chemical species of both Co(III) and oxalate could be obtained. The curves in Fig. 4 shows that the predominant species of oxalate and Co(III) ions in the solution of 0.5M HNO<sub>3</sub> are  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{HC}_2\text{O}_4^-$ , and  $(\text{Co}(\text{en})_2(\text{OH})_2)^{2+}$ , respectively. Since  $(\text{H}^+) \gg K_4$  and  $K_5$  under such a condition,  $k_{\text{obs}}$  should be simplified to eq (13).

$$k_{\text{obs}} = \frac{k_a G_1 (\text{Ox})_T / (\text{H}^+)^2}{((\text{H}^+)^2 + K_6(\text{H}^+) + K_6 K_7) + G_1 (\text{Ox})_T / (\text{H}^+)^2} \quad (13)$$

Inverting eq (13),

$$\frac{1}{K_{\text{obs}}} = \frac{1}{Q_{\text{IP}} k_a (\text{Ox})_T} + \frac{1}{k_a} \quad (14)$$

where  $Q_{\text{IP}}^{-1}$  indicates  $((\text{H}^+)^4 + K_6(\text{H}^+)^3 + K_6 K_7 (\text{H}^+)^2) / G_1$ . If one plots  $k_{\text{obs}}^{-1}$  against  $(\text{Ox})_T^{-1}$  at a given  $(\text{H}^+)$ , a straight line should be obtained with a slope of  $(Q_{\text{IP}} k_a)^{-1}$  and an intercept of  $k_a^{-1}$ . Therefore the determination of  $k_{\text{obs}}$  against the concentration of oxalate makes possible the calculation of ion-pairing term ( $Q_{\text{IP}}$ ) and interchange rate constant ( $k_a$ ). The values of  $Q_{\text{IP}}$

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〈國文抄錄〉

## 酸性水溶液中 $\text{cis}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$ 와 Oxalate 間的 Anation 反應速度에 미치는 壓力과 Oxalate 影響

0.5M  $\text{HNO}_3$  水溶液 (60°C) 에서  $\text{cis}[\text{Co}(\text{en})_2(\text{OH}_2)_2]^{3+}$  과 oxalate 이온間的 anation 反應에 미치는 oxalate 이온과 壓力 影響을 分光光度法으로 研究하였다. 類似一次 反應速度常數( $k_{\text{obs}}$ )에 미치는 oxalate 이온의 影響으로 부터 速度法則을 얻은 후, 주어진 壓力에서 이온쌍에 대한 equilibrium quotient( $Q_{\text{IP}}$ )와 交換速度常數( $k_a$ )를 決定하였다.

總括反應에 相當하는 活性化부피( $\Delta V_{\text{obs}}^*$ )는 약  $+9.2\text{cm}^3\text{M}^{-1}$ 로서 거의 壓力에 無關하였으며, 이 값은 亦是 壓力에 無關한 交換反應의 부피變化( $\Delta V_a^* = +9.6\text{cm}^3\text{M}^{-1}$ )와 類似하였다.  $\Delta V_{\text{obs}}^*$ 는 주로  $k_a$ 에 대한  $\Delta V_a^*$ 와  $Q_{\text{IP}}$ 에 의한 부피變化를 나타내는  $\Delta V_{\text{QIP}}$ 로 構成되어 있지만,  $\Delta V_{\text{QIP}}$ 의 寄與度는 無視할 수 있었다. 反應동안 各 段階에 대한 부피變化를 分析하므로써 反應은 解離交換메카니즘으로 進行됨을 알 수 있었다.