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LIBERATION OF AMMONIA FROM α-CIS-ETHYLENEDIAMINE-N,N'-DIACETATO(DIAMMINE)COBALT(III) ION IN CARBONATE BUFFER SOLUTIONS

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Reaction of the α-cis isomer of ethylenediamine-N,N'-diacetato-(diammine)cobalt(III) ion, α-cis-$[Co(EDDA)(NH_3)_2]^+$, has been examined kinetically in aqueous carbonate buffer solutions. It has been found that the complex releases the coordinated ammonia with first order in concentration of both the complex and hydroxyl ion. It has also been found that the activation energies of the cobalt-nitrogen bond breaking reactions are abnormally large amounting to around 40 kcal.

It is well-known that cobalt(III)-ammine complexes, such as $[CoX(NH_3)_5]^{2+}$ and $[CoX_2(NH_3)_4]^+$, are unstable and decompose to the insoluble hydroxide in basic solutions. This decomposition reaction is the largest trouble encountered in the study on the base hydrolyses of the complexes. Although it is a well-known and important reaction, no quantitative study on the ammonia-liberation from the cobalt(III)-ammine complexes has been carried out as yet, and the kinetic feature of the reaction is not clear. In the preceding report,[1] we indicated that the β-cis isomer of ethylenediamine-N,N'-diacetato(diammine)cobalt(III) ion, β-cis-$[Co(EDDA)(NH_3)_2]^+$, released ammonia to produce a hydroxo complex in basic aqueous solutions. It was also noticed that the Co(III)-EDDA entity was quite stable enough to yield a clean solution. As was described in the report, however, the reaction was somewhat complicated to analyze the process. Therefore, the α-cis isomer, with a presumption of its reaction to be simpler, was examined under the similar conditions as in the previous study.

The kinetic runs were performed spectrophotometrically in the usual manner. Fig. 1 illustrates a variation of the absorption curve of the complex. As may be seen in the figure, three isosbestic points occurred at 466, 443, and 368 nm. (The point at

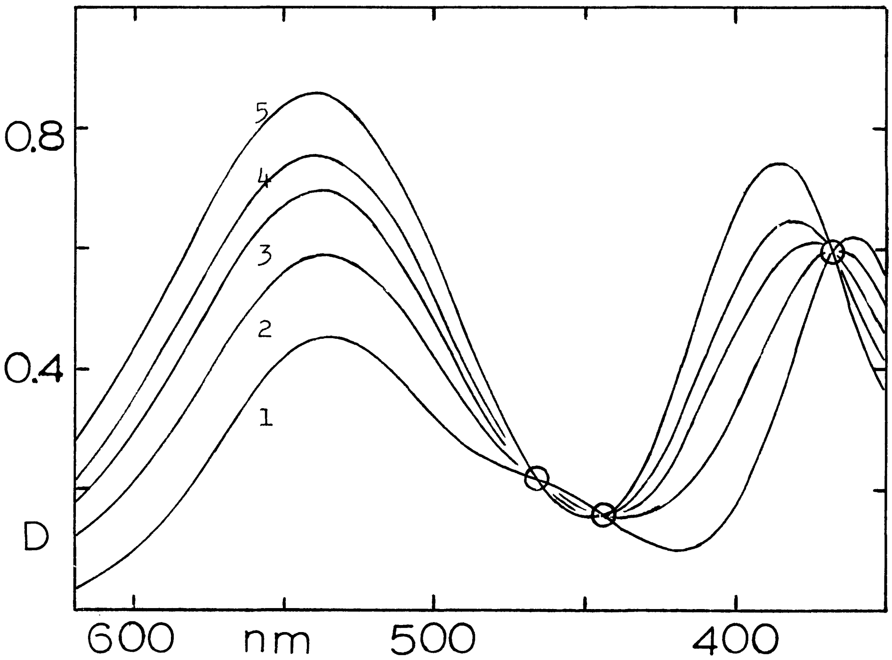

Fig. 1. Change of the absorption curve of α-cis-$[Co(EDDA)(NH_3)_2]^+$ at 65°C in 0.2M $NaHCO_3$-0.2M Na_2CO_3 solution.
1, the α-cis isomer;
2, after 20 min;
3, after 40 min;
4, after 60 min;
5, at equilibrium.

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368 nm is not strict.) Fig. 2 shows the spectra of α-cis-$[Co(EDDA)(NH_3)(H_2O)]^+$[2] in a basic solution, in which the complex exists as the hydroxoammine species. From the comparison of the spectra in the figures, a few characteristics are noticed on the reaction. First, the reaction of the diammine complex proceeds more slowly than that of the hydroxoammine complex. Second, the spectra of the two complexes at equilibrium are almost identical, indicating the identity of products. Third, the shoulder-type absorption curve in the region of the second band (around 370 nm), which is observed at the spectrum of the aquoammine complex immediately after the dissolution, does not appear during the reaction of the diammine complex. Since the ammonia liberation from the complex is certain from the detection of ammonia odor and from the agreement of the final spectra of the two complexes, it may be considered that the α-cis diammine complex hydrolyzes slowly to the α-cis hydroxoammine species and then undergoes carbonation with comparative rapidness:

$$\alpha\text{-cis-}[Co(EDDA)(NH_3)_2]^+ \xrightarrow{\text{slow}} \alpha\text{-cis-}[Co(EDDA)(OH)(NH_3)]$$

$$\alpha\text{-cis-}[Co(EDDA)(OH)(NH_3)] \xrightarrow{\text{fast}} \alpha\text{-cis-}[Co(EDDA)CO_3]^-$$

$$\text{or } \alpha\text{-cis-}[Co(EDDA)(CO_3)(NH_3)]^-$$

Thus, the hydroxoammine species may be regarded as a short-lived intermediate, and the rate constants of the hydrolysis (the first step of the reaction) can be obtained from the optical densities at 540 nm of the aliquots (D_t) and those of the reactant (D_α) and of the solution at equilibrium (D_∞):

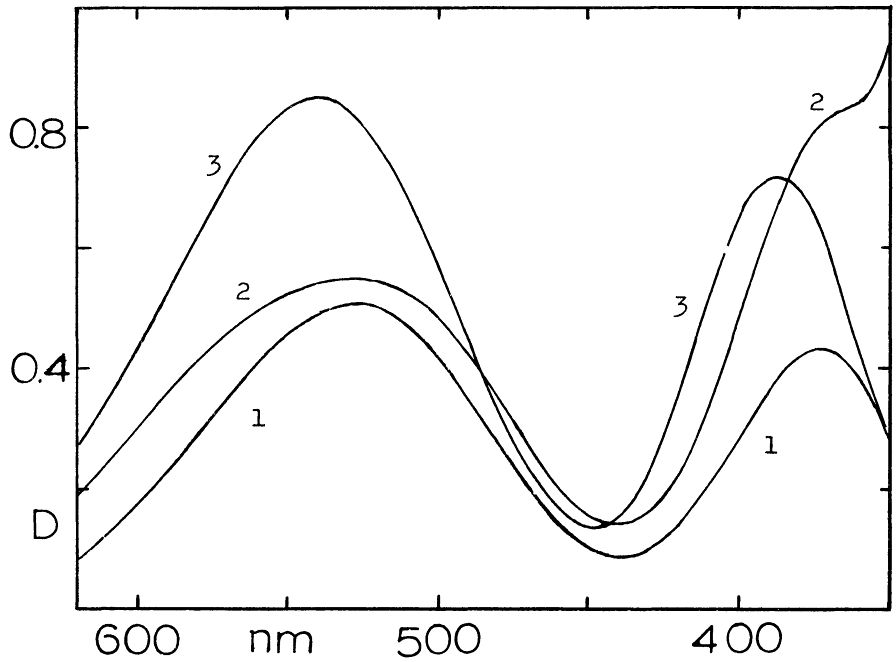

Fig. 2. Absorption spectra of 0.005 molar solutions of α-cis-[Co(EDDA)(NH_3)(H_2O)]ClO_4.
1, in neutral solution;
2, immediately after the dissolution in 0.2M $NaHCO_3$-0.2M Na_2CO_3 at room temperature;
3, after 30 and 60 min after the dissolution in 0.2M $NaHCO_3$-0.2M Na_2CO_3 at 60°C.

$$k = \frac{1}{t}\ln\frac{a}{a - x} = \frac{2.303}{t}\log\frac{D_\infty - D_\alpha}{D_\infty - D_t}$$

where

a = initial concentration of the reactant (0.005 mole/l)

or

$$\log(a - x) = \log a - \frac{k}{2.303} \times t$$

The plots of log(a − x) vs. t are shown in Fig. 3. It may be seen that the plots are linear but the intersections with the ordinate are not at log a. It is clear from these results that the reaction is first order with respect to the complex ion and there is an apparent induction period at the beginning of the reaction. The induction period, however, may be due to the neglect of the accumulation (the assumption of the infinitely large rate) of the intermediate hydroxoammine species. The first order rate constants were obtained from the slopes of the linear plots, and the values are summarized in Table 1. It may be seen in the table that the rate of the hydrolysis is highly dependent on the temperature and the hydroxyl ion concentration. As the ratio of the hydroxyl ion concentrations of the buffer solutions is approximately 1 : 2 : 4, the reaction is also first order with respect to the concentration:

$$k = k'[OH^-], \quad k' = 16\ \text{min}^{-1}\text{mole}^{-1}\,\text{l} \ \text{at}\ 60^\circ\text{C}$$

In the preceding report[1] on the isomerization of β-cis-[Co(EDDA)(en)]$^+$, we noted the similar character as in this case. Both reactions are supposed to start with bond-breaking between cobalt and nitrogen (of en or NH_3) by the action of hydroxyl ion. The

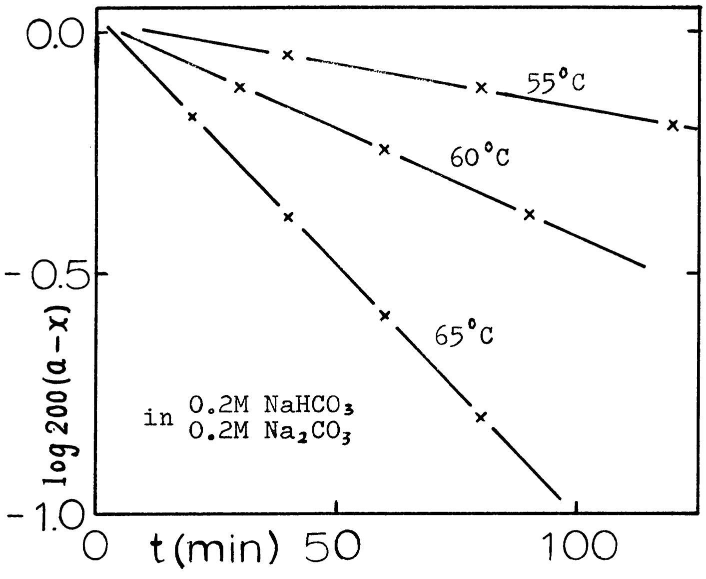

Fig. 3. log(a − x) vs. time plots.

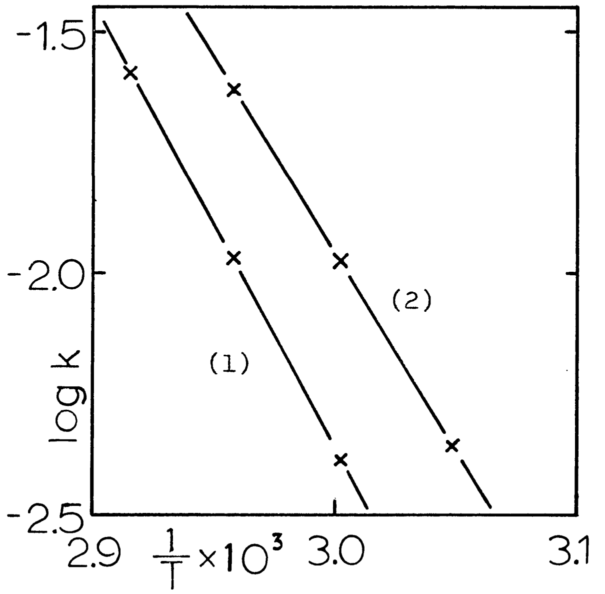

Fig. 4. Arrhenius plots for the reaction of β-cis-$[Co(EDDA)(en)]^+$ [1] (1), and α-cis-$[Co(EDDA)(NH_3)_2]^+$ (2).

Table 1. Rate Constants, $k \times 10^3 (min^{-1})$, of the Hydrolysis of α-cis-$[Co(EDDA)(NH_3)_2]^+$.

Condition	pH at 60°C	55°C	60°C	65°C
0.3M $NaHCO_3$ 0.1M Na_2CO_3	9.48		5.30	
0.2M $NaHCO_3$ 0.2M Na_2CO_3	9.81	4.37	10.6	23.9
0.1M $NaHCO_3$ 0.3M Na_2CO_3	10.18		22.6	

activation energy calculated from the Arrhenius plots (Fig. 4) is 42.1 kcal for the isomerization of the ethylenediamine complex and 37.5 kcal for the hydrolysis of the diammine complex.

On the substitution reactions of anionic ligands in cobalt(III) complexes, a large number of activation energies are available in the literatures,[3] and they are mostly between 20 and 35 kcal. Only in a few cases, such as in the base hydrolyses of nitro and isothiocyanato complexes,[4] have been found the energies slightly over 35 kcal. Abnormally high activation energies seem to be a remarkable characteristics for the reactions which involve the cobalt-nitrogen (of ammonia or amines) bond rupture as the activation process.

References:
1) K. Kuroda and F. Mohri, This Letters, 1972, 719.
2) K. Kuroda, Bull. Chem. Soc. Japan, 45, 2176 (1972).
3) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd Ed., John Wiley and Sons, Inc., New York, (1967), pp. 127 – 246.
4) G. C. Lalor and J. Long, J. Chem. Soc., 1963, 5620; S. C. Chan et al., ibid., 1965, 3207; D. L. Gay and G. C. Lalor, ibid., 1966A, 1179.

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