

ノート

赤外分光法による $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ の分解過程

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Infrared Study on Decomposition Process of



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Abstract

The decomposition of $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ over a period of 5 months was studied by infrared spectroscopy. The spectrum changed drastically with the disappearance of the bands due to ethylenediamine and the appearance of some new bands. The decomposition process of $\text{en} \longrightarrow 2\text{NH}_3 + \text{HCCH}$ was analyzed using two models regarding the concentration of T_2O . These reveal that about one thousand ethylenediamines decompose due to one β particle in the initial state.

We have reported¹⁾ the infrared spectrum of $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$ over a period of 5 months. The spectrum changes drastically with time: disappearance of bands attributed to ethylenediamine and appearance of some new bands. Because of complex

changes in spectral features we have reported mainly identification of new species and proposed that a decomposition reaction of $\text{en} \longrightarrow 2\text{NH}_3 + \text{HCCH}$ takes place through intermediates such as vinylamine. A species such as NH_4^+ ions has been also identified. In the present study we report the decomposition process on the basis of the identification.

$[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{H}_2\text{O}$ was prepared by means of air oxidation of a mixture of CoCl_2 + ethylenediamine in aqueous solution. The complex was mixed mechanically with excess potassium chloride (1 : 75), which was pressed into a disk. The infrared spectrum was observed in the range of $4000 \sim 330\text{cm}^{-1}$ by use of a JASCO-IRA-302 spectrometer.

The dehydration was carried out at 140°C . After dehydration, about 0.5Ci of T_2O (10 times of the amount of the complex) was admitted into an infrared cell and it was kept at room temperature. The observed spectra in the range of $1750 \sim 700\text{cm}^{-1}$ are shown in Fig. 1.

The absorbance, $\ln(I_0/I)$, was measured for some bands. They are plotted against time, $t(\text{day})$, in Fig. 2. The assignments of the bands¹⁾ are: 2550cm^{-1} , N—H \cdots N stretching in $[\text{en}-\text{H}]^+$; 2100cm^{-1} , O—T stretching in T_2O ; 1620cm^{-1} , NH_3 asymmetric bending in NH_3 ; 1400cm^{-1} , ν_4 in NH_4^+ ; 1065cm^{-1} , C—N stretching in en; 730cm^{-1} , HCCH bending in HCCH.

The new bands, except for 1065cm^{-1} , were, as a whole, broad and overlap with each other. Fortunately, however, since the new bands were intense, the error in an absorbance is expected to be within $\pm 5\%$, except for the band at 730cm^{-1} , which overlapped with another new bands, as seen in Fig. 1.

As seen from Figs. 1 and 2, the spectrum changed rapidly in the initial stage ($t = 0 \sim 13$). Subsequently ($t = 13 \sim 38$) the intensities of new bands, especially of the HCCH bending, decreased gradually, indicating decomposition of these species. At $t \geq 38$ the

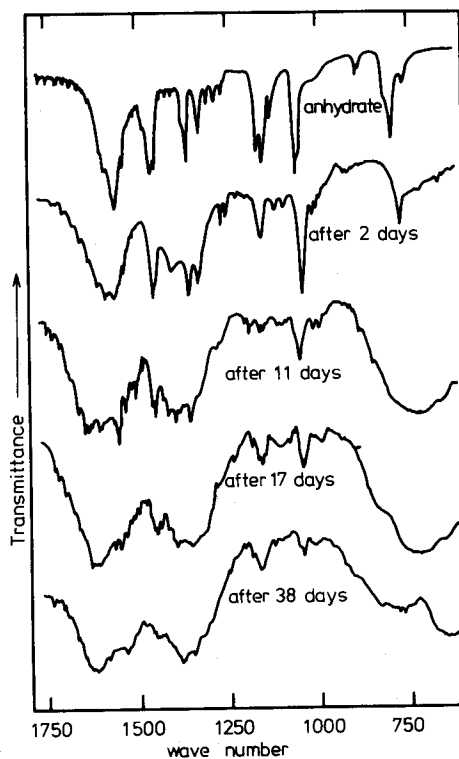


Fig. 1. The change in the spectral features in $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$. The hot runs are shown by day after addition of T_2O to the anhydrate.

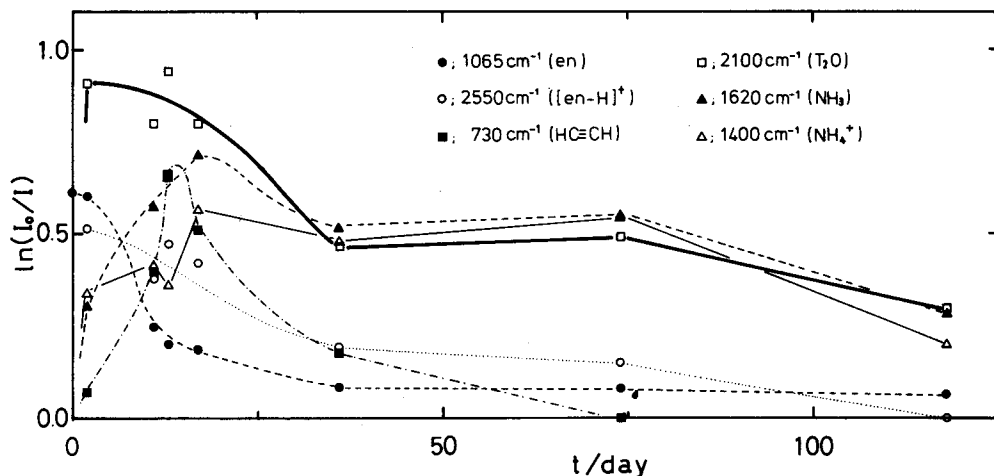


Fig. 2. Variation of absorbance for some species with time.

spectrum changed further with slower rate, even for ethylenediamine.

These are caused clearly by β -rays (5.7 keV in average). That is, the species is excited or ionized by β -rays, decomposing to the other species, which means that the process obeys the first order kinetics with respect to the concentration of T_2O . Hence we can assume that the rate of the change in spectral features or concentrations of species depends linearly on the concentration of T_2O , $[\text{T}_2\text{O}]$; brackets mean concentration, which is represented by absorbance in the present treatment. The decomposition process of ethylenediamine will be examined in details by use of two models.

The decomposition of ethylenediamine may take place as follows :

$$-d[\text{en}]/dt = k_1 [\text{en}] [\text{T}_2\text{O}] \quad (1)$$

Since T_2O was admitted to the anhydrate, $[\text{T}_2\text{O}]$ is zero at $t=0$. At $t>0$, T_2O is absorbed as hydrates in cavities or empty sites. The process may be diffusional, by referring that sites for water is a zeolite type one^{2,3)} in the present system. Thus, we have approximately a relation⁴⁾ :

$$d[\text{T}_2\text{O}]/dt = \frac{8}{\pi^2} [\text{en}] \alpha \exp(-\alpha t) - k_2 [\text{en}] [\text{T}_2\text{O}] \quad (2)$$

where α is a time constant relating to diffusion and k_2 is a rate constant for decomposition of T_2O . The results are given by the solid lines in Fig. 3, where the parameters used were $k_1=0.30$ (1/day), $\alpha=0.25$ (1/day) and $k_2=0.18$ (1/day).

In Fig. 3 the time course of the absorbance of ethylenediamine calculated with Eqs. (1) and (2) fits good with those observed, while that for T_2O fits only partly. The Model-I has the maximum at $t \approx 4.5$, though there is a lack of the data around the

maximum. The discrepancy at $t \geq 13$ in T_2O indicates probably the presence of another type of water, coordinated water, as suggested previously¹⁾.

The infrared spectrum has shown that ethylenediamine at $t=2$ is different in the site symmetry from the parent one. This is also true for water, which is expected to be no zeorite water¹⁾. These suggest that there is no site for water at $t=2$. Namely, the absorption process does not play a role. In this stage, the decomposition of the hydrate predominates over in the absorbance change. This process is expressed as :

$$-d[T_2O]/dt = k_3 [T_2O] \quad (3)$$

That is, both Eqs. (1) and (3), Model-II, are used under the initial condition of $t=2$. The results using $k_1=0.35$ and $k_3=0.056$ (1/day) are also given by the dotted lines in Fig. 3. The line for ethylenediamine fits fairly well with the observations and that for T_2O too, though the discrepancy at $t=13$ is large.

The Model-II was defined at $t \geq 2$. However, the basis of $t \geq 2$ is uncertain. The absorbance of the NH_4^+ ion varies somewhat complexly in Fig. 2, especially at $t=2$. This indicates that the formation process changes at $t \approx 2$, which may be a result from the change in structure. The absorbance of the $[en-H]^+$ ion varies similarly to that of T_2O in Fig. 2. From the Model-I we can expect the maximum at $t \approx 5$, being followed by rapid decay, which does not agree with observation at $t \geq 17$, because there is no source for the $[en-H]^+$ ion. Hence this also indicates the change in the formation and decomposition processes at $t \approx 2$. These support the Model-II.

On the other hand the absorbance of ethylenediamine fits better in the Model-I than -II in Fig. 3. This suggests a modified Model- I, where α decreases at $t \geq 2$. This model could be regarded as an intermediate of the Model- I and -II and be more plausible for the decomposition process. In other words, the Model- I is predominant at $t \leq 2$ and both the Models- I and -II have nearly the same effect at $t \geq 2$.

The value of k_1 is, thus, expected to be ~ 0.32 (1/day). This means that about 30% of ethylenediamine decomposes per one day in the ideal complex of $[Co(en)_3] Cl_3 \cdot 3T_2O$. The coefficient of the decomposition due to the β decay, f , is given as :

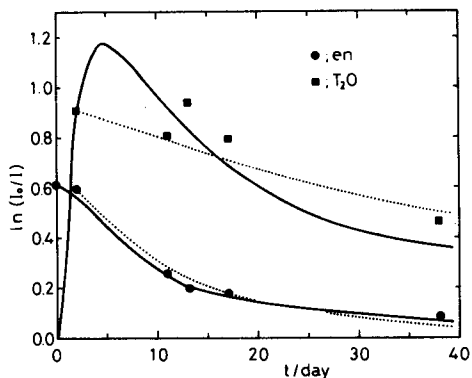


Fig. 3. Variation of analyzed absorbance for ethylenediamine and T_2O with time. Solid and dotted lines are obtained from Model- I and -II, respectively.

Decomposition process of $[\text{Co}(\text{en})_3] \text{Cl}_3 \cdot 3\text{T}_2\text{O}$

$$f = \frac{d[\text{en}]}{d[\text{T}_2\text{O}]_{\beta}} = \frac{d[\text{en}]}{dt} \bigg/ \frac{d[\text{T}_2\text{O}]_{\beta}}{dt} = k_1/2k_{\beta} = 1030 \quad (4)$$

where k_{β} is the rate constant of the β decay, $1/6460$ (1/day). That is, about one thousand molecules decompose by one β particle. This is not surprising, because the reaction of $\text{en} \longrightarrow 2\text{NH}_3 + \text{HCCH}$ could take place with energy about 1.0eV .

References

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