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Derivatographic Studies on Transition Metal Complexes. III.*1 The Thermal *trans-cis* Isomerization of $[CoCl_2pn_2](H_5O_2)Cl_2$ in Solid-Phase*2

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The thermal decomposition of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ in solid-phase was measured by derivatography and the isothermal method with a thermobalance. It was found by the latter that dehydration and dehydrochlorination took place with partial isomerization below 170°C. The rate of isomerization gradually increased with temperature until it became equal to the rate of dehydration and dehydrochlorination above 170°C. The activation energies for dehydration and dehydrochlorination and for isomerization were calculated from the isothermal measurement below 170°C to be 10 kcal/mol and 23 kcal/mol, respectively. The activation energy obtained from DTA curve analysis at about 144°C in the derivatogram was 33 kcal/mol. The reaction was explained in terms of "aquation-anation" mechanism. Since the *trans-cis* isomerization in anhydrous state at 180°C gave a larger activation energy in DTA analysis, the "twisting" mechanism might be preferable to "aquation-anation" for the reaction.

Several examples of *cis* ↔ *trans* isomerization on transition metal complexes in solution[1] are known. However, the situation is different in solid-phase.[2] The complex, *trans*-$[CoCl_2(NH_3)_4]IO_3\cdot2H_2O$, undergoes a distinct color change on being heated in solid state.[3] A detailed study was reported.[4] A complicated *trans-cis* isomerization involving both the thermal dehydration and the dehydrochlorination was also found for the complex, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$.[5,6] It has been proposed that the *trans-cis* isomerization in the two complexes, *trans*-$[CoCl_2(NH_3)_4]IO_3\cdot2H_2O$ and *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, occurred *via* an "aquation-anation" pathway on crystal surface when the water molecules are set free from the crystalline hydrates.[4,6]

It is of interest to note that the dehydration and dehydrochlorination of *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$ are accompanied by no isomerization as in the corresponding pn-complex.[7]

A recent study on the dehydration and dehydrochlorination of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and of the corresponding en-complex indicates that both chlorides exhibit the closely equal activation energies of 16.1 kcal/mol *in vacuo* regardless of the occurrence of *trans-cis* isomerization.[6,7] The activation energies in the thermal reaction of analogous bromo-complex bromides, *trans*-$[CoBr_2(A\text{–}A)_2](H_5O_2)Br_2$ (A–A: en or pn), were 24—29 kcal/mol. Only the corresponding pn-complex was found to undergo *trans-cis* isomerization such as the chloride.[8] The above difference of activation energies between the chloro- and the bromo-complexes is understood to be due to a somewhat more difficult diffusion of HBr and H_2O in the latter complex. In the present work, thermochemical and kinetic analysis of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ was carried out from derivatograms. They were also done by means of isothermal measurements. The mechanism is discussed in detail.

Experimental

Preparation of Complexes. Both *trans*-$[CoCl_2pn_2]$-

[*1] Part II in this series: see R. Tsuchiya, A. Uehara and E. Kyuno, This Bulletin, **42**, 1886 (1969).

[*2] Presented at the 18th Symposium on Coordination Chemistry, Kyoto, October, 1968.

1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd Ed., John Wiley & Sons, Inc., New York, N. Y. (1967), pp. 274—291.

2) *Ibid.*, pp. 327—328.

3) N. I. Lobanov, *Zhur. Neorg. Khim.*, **4**, 151 (1959).

4) H. E. LeMay, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 5577 (1967).

5) This compound is frequently formulated as *trans*-$[CoCl_2pn_2]Cl\cdot HCl\cdot2H_2O$. However, recent X-ray studies indicated that it contains $H_5O_2^+$ and Cl^- ions; Y. Saito and H. Iwasaki, This Bulletin, **35**, 1131 (1962). The same is true of *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$; A. Nakahara, Y. Saito and H. Kuroya, *ibid.*, **25**, 331 (1952).

6) H. E. LeMay, Jr., *Inorg. Chem.*, **7**, 2531 (1968).

7) J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 222 (1946).

8) H. E. LeMay, Jr., University of Nevada, Reno, Nevada, U. S. A., private communication (1969).

$(H_5O_2)Cl_2$[9] and *cis*-$[CoCl_2pn_2]Cl$[10] were prepared by the known method partly modified.*3 The corresponding *trans*-en-complex was prepared by the method in literature.[7] These compounds were confirmed by elemental analysis and spectrophotometric measurements.

Derivatographic Measurements. The derivatograms (the chart involves TGA, DTA and DTG curves) for these complexes were obtained with a MOM Derivatograph Typ-OD-102.[11,12] The activation energies (E^*) in the desired reaction steps were calculated by analysis of DTA curves in the derivatograms.[12,13] The enthalpy changes (ΔH) in the corresponding steps were estimated from the same DTA curves.[12,14] 0.5 g finely powdered samples were used in each run (100—200 mesh/inch) under a constant flow of nitrogen stream with the heating rate of 1°C min^{-1}.

Isothermal Measurements using a Thermobalance. Direct and isothermal determination of the dehydration and dehydrochlorination accompanied by isomerization were made by using a Shimadzu TM-1A Thermanobalance. Samples of 0.5 g in each run placed in a small platinum basket hung from one arm of the balance were heated at desired temperatures. The mass loss of each sample in a constant time interval at each temperature was recorded as a TGA curve, and the rates of dehydration and dehydrochlorination were determined. In the same experiment, a part of the products in the basket was dissolved in methanol and the *trans-cis* ratio was determined spectrophotometrically as follows. The visible and UV absorption spectra of the starting complex, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, and the final product, *cis*-$[CoCl_2pn_2]Cl$, were measured in methanol with a Hitachi R-3 Spectrophotometer, because the complexes are fairly soluble in methanol and the solutions do not undergo further isomerization within 20 min at room temperature. Their spectra are shown in Fig. 1. Since the pure *trans*- and *cis*-compounds have the absorption coefficients, 6.8 and 62.7, at 530 mμ, and, 40.8 and 51.6, at 600 mμ in methanol, respectively, the *trans*/*cis* ratios in the product in each step can be determined spectrophotometrically by means of the equations:

$$6.8X + 62.7Y = D_{530}$$

$$40.8X + 51.6Y = D_{600}$$

where X and Y are the concentrations (in mol^{-1}) of *trans*- and *cis*-compounds, and D_{530} and D_{600} are the absorbancies at 530 and 600 mμ with 1.0 cm cell, respectively. Thus, *trans*/*cis* ratios are given by X/Y.

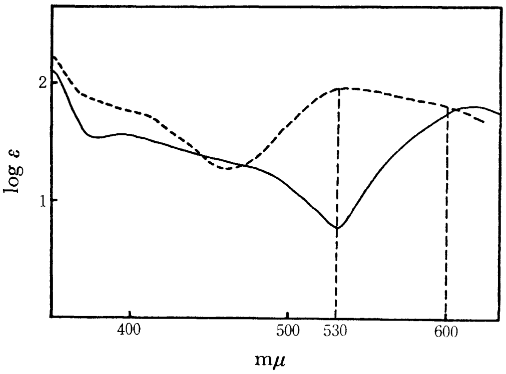

Fig. 1. The electronic absorption spectra of *trans*-$[CoCl_2pn_2](H_5O_2)Cl$ (————) and *cis*-$[CoCl_2pn_2]Cl$ (------) in methanol.

Results and Discussion

The derivatogram obtained for the thermal decomposition of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ is shown in Fig. 2, together with that of the corresponding en-complex.

In the case of the former pn-complex, as seen in Fig. 2, one molecule of hydrogen chloride and two molecules of water are simultaneously lost with partial isomerization at 144°C, where both DTA and DTG curves show a single peak. An apparently analogous decomposition reaction was observed for the corresponding en-complex by the appearance of a single endothermic peak in DTA due to the dehydration and dehydrochlorination as in the above pn-complex, but no isomerization occurred.

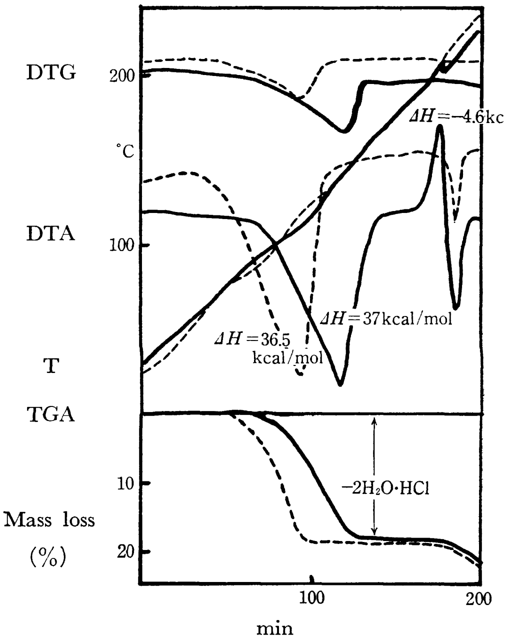

Fig. 2. The derivatograms for *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ (————) and *trans*-$[CoCl_2en_2](H_5O_2)Cl_2$ (------).

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9) A. Werner and A. Frohlich, *Ber.*, **40**, 2228 (1907).

10) J. C. Bailar, Jr., C. A. Stiegmen, J. H. Balthis and E. H. Huffman, *J. Amer. Chem. Soc.*, **61**, 2402 (1939).

*3 The details will be published elsewhere.

11) F. Paulik, J. Paulik and L. Erdey, *Talanta*, **13**, 1405 (1966).

12) R. Tsuchiya, Y. Kaji, A. Uehara and E. Kyuno, This Bulletin, **42**, 1881 (1969).

13) N. G. Dave and S. K. Chopra, *Z. Phys. Chem.*, **48**, 257 (1966).

14) H. G. Borchardt and F. Daniels, *J. Amer. Chem. Soc.*, **79**, 41 (1957).

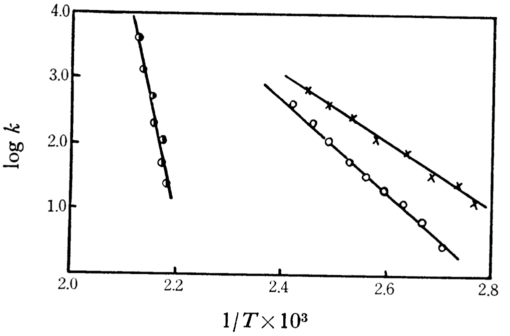


Fig. 3. The "Arrhenius plots" of the rate constants of the dehydration and dehydrochlorination and of the exothermic reaction without mass loss on *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$.
◑—◑: isomerization $E_i^{\neq}=120\pm3$ kcalM^{-1}
○—○: $-HCl\cdot2H_2O$ reaction $E_{d}^{\neq}{}_{(i)}=33\pm2$ kcal·M^{-1} (DTA)
×—×: $-HCl\cdot2H_2O$ reaction $E_{d}^{\neq}{}_{(i)}=31\pm2$ kcal·M^{-1} (DTG)

Dehydration and dehydrochlorination of the pn-complex begin to take place at a lower temperature than that of the corresponding en-complex as shown in Fig. 2.

Analysis of DTA curve for *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ gave 36.5 kcal/mol as ΔH. The Arrhenius plots for the pn-complex, *viz.*, the relationships between the rate constants derived from the analysis of DTA and DTG curves and reciprocal absolute temperatures are shown in Fig. 3. The activation energies, $E^{\neq}$, are obtained to be 33 ± 2 and 31 ± 2 kcal/mol, respectively.

The values are larger than that for the dehydration and dehydrochlorination of the complex, *i. e.*, 16.1 kcal/mol given in literature.[6]

The second peak in DTA curve was found only for the pn-complex without any mass change in TGA, probably due to the occurrence of a small exothermic reaction at 180°C before complete decomposition. Since the corresponding en-complex did not show a similar peak, appearance of such a peak in the former complex is believed to be due to a certain constitutional change; *i e.*, *trans-cis* isomerization *trans*-$[CoCl_2pn_2]Cl$ in an anhydrous state partly remained after complete dehydration and dehydrochlorination. From the analysis of DTA curve, the enthalpy change was estimated to be -4.6 kcal/mol, and the activation energy in this step was calculated to be about 120 kcal/mol.

The relationship between mass losses and *trans*/*cis* ratios at various heating temperatures, obtained from the isothermal measurements with a thermobalance, are shown in Fig. 4.

From this figure, the *trans*/*cis* ratio at 140°C corresponding to the temperature of the first peak in the derivatogram of *trans*-complex is found to be 70 : 30. With stepwise elevation of temperature, the *trans*/*cis* ratio gradually increased. It should be emphasized that, in other words, isomerization proceeds more slowly than dehydration and dehydrochlorination below 170°C, but it is completed as soon as dehydration and dehydrochlorination are finished above 170°C.

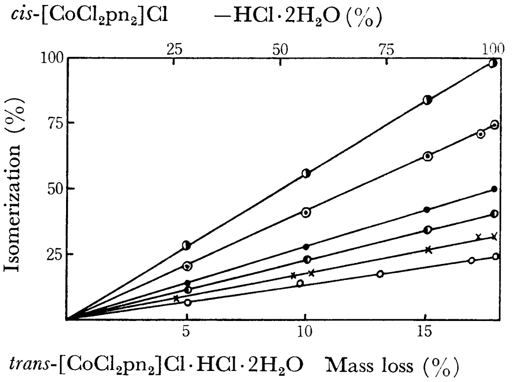


Fig. 4. The relationships between mass loss and *trans-cis* mixture ratio of various constant temperatures on *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$.
○—○: 110°C, ×—×: 130°C, ◐—◐: 140°C,
●—●: 150°C, ⊙—⊙: 160°C, ◑—◑: 170°C

From the results, the rate constants for the mass loss (dehydration and dehydrochlorination), k_d, and those for the *trans-cis* isomerization, k_i, of the *trans* complex were calculated. They are listed in Table 1. At 110°C, the rate constant, k_d, is almost six times larger than that of isomerization, k_i. However, with the rise of temperature, the value of k_d gradually increases and approaches the value of k_i above 170°C.

The Arrhenius plots of the rate constants are shown in Fig. 5. The activation energies were obtained from these plots as 10 ± 2 and 23 ± 3 kcal/mol for the mass loss reaction and for isomerization, respectively. The activation energies for thermal dehydration and dehydrochlorination in this case may be considerably smaller than those in literature.[6] However, it can be accepted that the sum of the values of the activation energies for the mass loss reaction and isomerization is equal to the value 33 kcal/mol obtained from TDA analysis of the derivatogram.

Table 1. Rate constants for the mass loss k_d and isomerization k_i of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$

Temp., °C	k_d, sec^{-1}	k_i, sec^{-1}
110	$(2.6\pm0.4)\times10^{-4}$	$(4.4\pm0.4)\times10^{-5}$
120	$(4.3\pm0.4)\times10^{-4}$	$(1.2\pm0.4)\times10^{-4}$
130	$(8.2\pm0.4)\times10^{-4}$	$(1.8\pm0.4)\times10^{-4}$
140	$(1.2\pm0.2)\times10^{-3}$	$(3.8\pm0.4)\times10^{-4}$
150	$(1.6\pm0.2)\times10^{-3}$	$(7.3\pm0.2)\times10^{-4}$
160	$(1.9\pm0.2)\times10^{-3}$	$(1.3\pm0.2)\times10^{-3}$
170	$(2.4\pm0.2)\times10^{-3}$	$(2.4\pm0.2)\times10^{-3}$
180	$(3.3\pm0.2)\times10^{-3}$	$(3.3\pm0.2)\times10^{-3}$
190	$(4.1\pm0.2)\times10^{-3}$	$(4.1\pm0.2)\times10^{-3}$

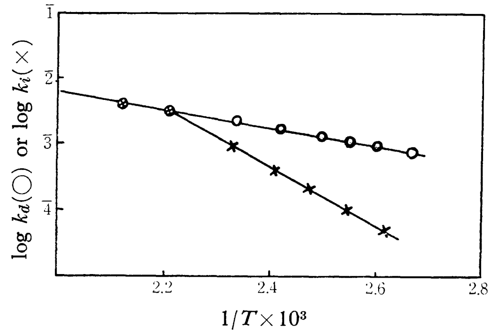
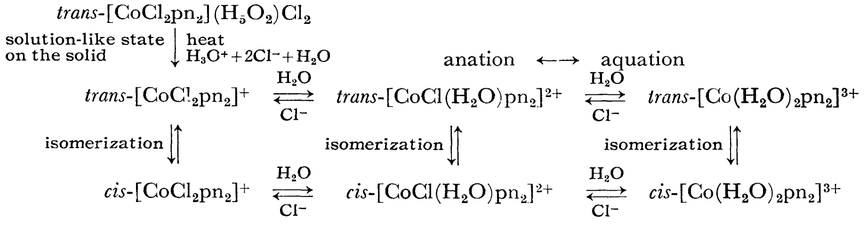


Fig. 5. The "Arrhenius plots" of k_d and k_i on *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ in isothermal conditions by using a Shimadzu Thermobalance.
○—○: $-HCl\cdot2H_2O$ reaction $E_d^{\ddagger}=(10\pm2)$ kcal M^{-1}
×—×: Isomerization $E_i^{\ddagger}=(23\pm3)$ kcal M^{-1}.

The mechanism in the *trans*↔*cis* isomerization of the complex, $[CoCl_2en_2]Cl$, in polar solvents has been interpreted by solvation-anation reaction.[15,16] In a neutral solution, *trans*-isomer clearly changes to *cis*-isomer upon heating.[17] However, in an acidic solution, the inversed reaction occurs even at room temperature.[18] A similr isomerization has also been found with $[CoCl_2pn_2]^+$ in aqueous solution,[10] but the *trans*-complex undergoes more rapid acid hydrolysis than the corresponding en-complex under similar conditions.[8]

Isomerization with dehydration and dehydrochlorination in *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ in the solid-phase is believed to occur by aquation-anation mechanism like that in aqueous solutions as follows:



LeMay, Jr., has found that the pn-complex shows a greater resistance to the loss of hydrogen chloride and water from the prominent (100) faces of the crystals than the corresponding en-complex.[6] Radioactive chloride-exchange studies[8] have indicated that the dehydration and dehydrochlorination of the pn-complex are accompanied by the almost complete scrambling of chloride ions in both inner and outer coordination spheres, but this is not the case for the corresponding en-complex under the same conditions. Considerable amounts of chloride ion were exchanged when the pn-complex was heated in solid phase at 120°C for 90 min in air.[8] However, in the corresponding en-complex only 1% exchange could be found upon heating at 125°C for 90 min.

Although the lack of examples for isomerization in solid-phase makes clarification of mechanism difficult, isomerization of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ to the *cis*-complex below 170°C might proceed through the aquation-anation pathway accelerated by the dehydration and dehydrochlorination on the faces except for (100).

All the pathways in the thermal decomposition of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and the values of the thermochemical functions, ΔH and $E^{\ddagger}$, in each process are schematically summarized in Fig. 6.

The derivatogram for *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ in Fig. 2 shows that the anhydrous *trans*-pn-complex remaining after dehydration and dehydrochlorination still undergoes *trans-cis* isomerization over 180°C. This indicates that the anhydrous *trans*-

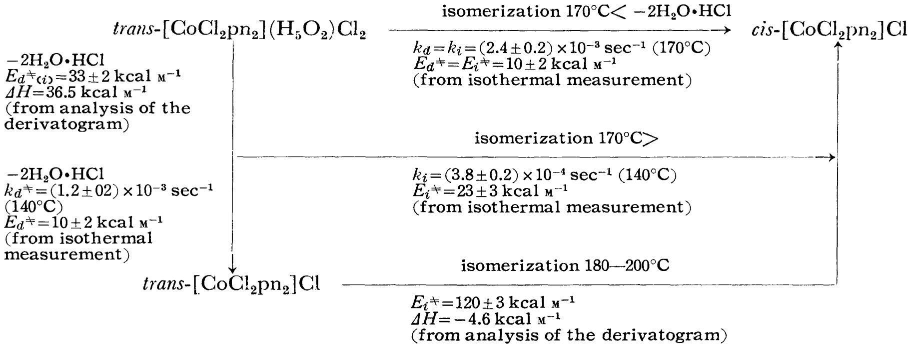


Fig. 6. Summary of results.

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[15] W. R. Fitzgerald and D. W. Watts, *J. Amer. Chem. Soc.*, **89**, 821 (1967).

[16] M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, **1964**, 2991.

[17] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[18] S. M. Jφrgensen, *J. Prakt. Chem.*, **39**, 16 (1889).

complex is unstable and is changed to *cis*-complex. The mechanism may be explained by means of intramolecular isomerization, *e. g.*, "twisting"[17,19] or "chelate ring opening-closing"[20] because of a relatively large activation energy such as 120 kcal/mol. Although examples of activation energies calculated derivatographically on thermal *trans*↔*cis* isomerization are rare, the large value described above might be accepted as reasonable.

It should be noted that the activation energies calculated in a similar way by authors were 51.4 and 87 kcal/mol for the complexes, *cis*,*trans*-$[CoCl_2(NH_3)_2en]ClO_4$ and *trans*-$[CrBr(H_2O)(NH_3)_4]Br_2$, respectively. The details will be published elsewhere.

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19) P. Pay and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

20) H. D. K. Drew and N. H. Pratt, *J. Chem. Soc.*, **1937**, 506.