Derivatographic Studies on Transition Metal Complexes. XIX.[1] Thermal Isomerization of *trans*-$[CrCl_2(en)_2](H_5O_2)Cl_2$ and *trans*-$[CrCl_2(pn)_2]Cl \cdot 1.5H_2O$ in Solid Phase[2]

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Thermal *trans*-to-*cis* isomerization of $[CrCl_2(en)_2](H_5O_2)Cl_2$ and $[CrCl_2(pn)_2]Cl \cdot 1.5H_2O$ was studied in the solid phase by derivatographic and isothermal measurements. The former complex was found to isomerize in anhydrous state after the complete elimination of hydrogen chloride and water, the latter in the temperature range for dehydration. The activation energies for the isomerization of these two complexes were isothermally estimated to be 202 and 193 kJ mol^{-1}, respectively. The same type of isomerization mechanism is suggested for these complexes, differing from that for the corresponding cobalt(III) complexes in which lattice waters participate.

Few papers have been given on the *cis*↔*trans* isomerization of $[MX_2(a\text{-}a)_2]X$ in solid phase, where M= Co(III) or Cr(III), X=halide ion and a-a=diamine. The *trans*-to-*cis* isomerization is known to take place in *trans*-$[CoCl_2(pn)_2](H_5O_2)Cl_2$[3,4] and *trans*-$[CoBr_2(pn)_2](H_5O_2)Br_2$,[5] but not in *trans*-$[CoCl_2(en)_2](H_5O_2)Cl_2$. The isomerization of the former two always proceeds at the elimination step of hydrogen halide and water, for which "aquation-anation mechanism" has been proposed.[3,4] In contrast, *trans*-$[CrBr_2(pn)_2]Br \cdot H_2O$ isomerizes in the anhydrous state; the presence of lattice waters has no effect on the isomerization.[6] Thus, another mechanism seems to play an important role in the isomerization of the chromium(III) complexes.

The present study was undertaken (1) to investigate derivatographically and isothermally the *trans*-to-*cis* isomerization of $[CrCl_2(en)_2](H_5O_2)Cl_2$ and $[CrCl_2(pn)_2]Cl \cdot 1.5H_2O$, and (2) to find what differences can be produced by changing ethylenediamine with propylenediamine.

Experimental

Preparation of Complexes. *trans*-$[CrCl_2(en)_2](H_5O_2)Cl_2$ (I),[7] *cis*-$[CrCl_2(en)_2]Cl$(II),[8] *trans*-$[CrCl_2(pn)_2]Cl \cdot 1.5H_2O$ (III),[9] and *cis*-$[CrCl_2(pn)_2]Cl$ (IV)[10] were prepared by modification of the usual methods.

The chemical formulas of these complexes were confirmed by elemental analyses, spectrophotometric measurements and Karl Fischer's method of water determination.

Derivatography. The derivatograms for the complexes were obtained with a MOM Typ-OD-102 Derivatograph. The operating conditions are the same as those reported previously.[1]

Isothermal Measurements. The rates of hydrogen chloride elimination and dehydration were measured with a CHYO 100L thermobalance at 92, 105, 119, and 126 °C for complex I and at 160, 172, 178, and 184 °C for complex III. The rates of isomerization were followed by measuring the change in the absorbancies of a 0.1 M $HClO_4$ solution of each sample heated in an Abderhalden apparatus at 249, 260, 269, 279, or 288 °C for complex I, and at 154, 160, 166, or 172 °C for complex III, and by the use of the following simultaneous equations:

$$\left.\begin{aligned} D_{400} &= 32.3X + 71.1Y \\ D_{520} &= 7.6X + 73.1Y \end{aligned}\right\} \quad \text{for complex I}$$

$$\left.\begin{aligned} D_{400} &= 35.8X + 74.6Y \\ D_{530} &= 10.4X + 74.4Y \end{aligned}\right\} \quad \text{for complex III}$$

where X and Y are the molar concentrations of *trans*- and *cis*-isomers, respectively, contained in a 0.1 M $HClO_4$ solution of each sample, the numerical factors are the molar extinction coefficients of pure *trans*- and *cis*-isomers at two wavelengths 400 and 520 or 530 nm for each complex and D is the absorbancy measured. Figure 1 shows the electronic spectra of *trans*- and *cis*-complexes. The isomerization ratios are, therefore, given by $Y/(X+Y)$.

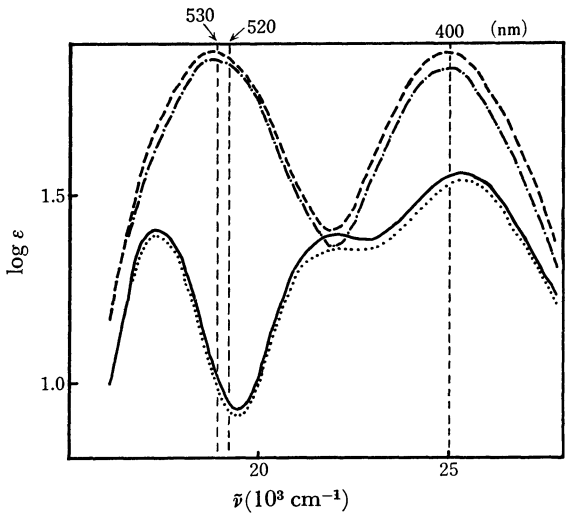

Fig. 1. Electronic spectra of complexes I (·····), II (—·—), III(——) and IV(----).

Results and Discussion

Derivatography. Figure 2 shows the derivatograms of *trans*-$[CrCl_2(en)_2](H_5O_2)Cl_2$ (I) and *trans*-$[CrCl_2(pn)_2]Cl \cdot 1.5H_2O$(III). The TG curve of complex I shows that the complex evolves one mole of hydrogen chloride and two moles of water at 25—120 °C (step I) and then remains unchanged up to 290 °C, above which the decomposition begins. In the DTA curve, an endothermic peak appears at step I and another endothermic peak at 250 °C; a small but clear exothermic peak can be seen just before the second endothermic peak. This is due to the *trans*-to-*cis* isomerization, which was visually confirmed by the color change of the sample from

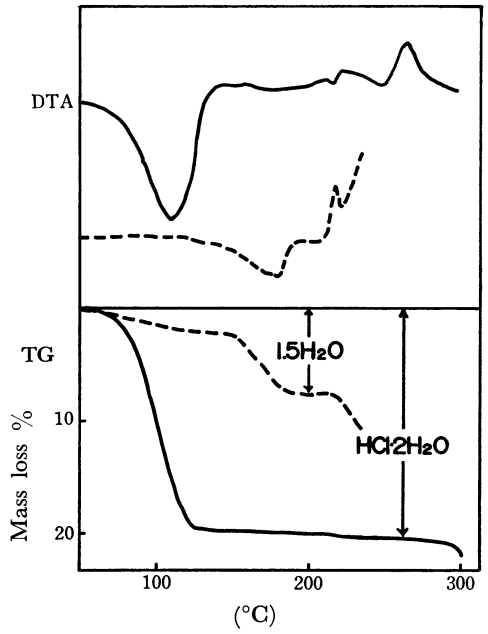

Fig. 2. Derivatograms of complexes I (——) and III (----).

green to violet. The enthalpy change, ΔH, for step I was estimated to be 55 kJ mol^{-1} from analysis of the endothermic curve in the derivatogram.

On the other hand, as seen from the TG curve of complex III, the complex loses 1.5 mol of water at 45—180 °C and decomposes above 215 °C. In the DTA curve, an endothermic peak appears at the dehydration step, and then a clear exothermic peak appears at 210 °C just before the decomposition starts. The complete *trans*-to-*cis* isomerization was also visually confirmed at the end of dehydration.

The isomerization of complex I takes place in an anhydrous state in a manner similar to that of *trans*-[$CrBr_2(pn)_2$]Br·H_2O[6] and *cis*-[$CrCl_2(tn)_2$]Cl·0.5H_2O.[1] On the other hand, complex III undergoes isomerization with dehydration as mentioned above.

It seems, however, that the presence of lattice water is not always required for the isomerization to occur, if the value of the activation energy obtained by the isothermal measurements is taken into account.

Rate of Step I. The rate of step I was measured with a thermobalance from the weight loss with time. The results for complex I are shown in Fig. 3 in the same way as that reported,[1,6] *viz.*, $\log\{a/(a-x)\}$ is plotted against time, assuming the reaction to proceed in the first order, where a is the initial amount of the starting complex, and x the amount of the hydrated complex which has lost hydrogen chloride or of the anhydrous complex. A curve having a point of inflection was obtained at each temperature. The part below the point of inflection is due to the evolution of hydrogen chloride, and the part above it to dehydration. This was confirmed by chemical analysis of the evolved gas.

The rate constants of step I are given in Table 1 together with those of isomerization. The activation energies for the loss of hydrogen chloride and the dehydration were calculated to be 118 kJ mol^{-1} and 42 kJ mol^{-1}, respectively, from the Arrhenius plots.

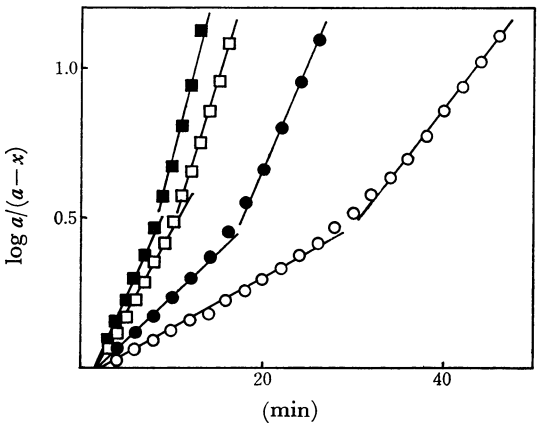

Fig. 3. Plots of $\log\{a/(a-x)\}$ *vs.* time for the hydrogen chloride elimination and dehydration of complex I.
○ 92, ● 105, □ 119, ■ 126 °C.

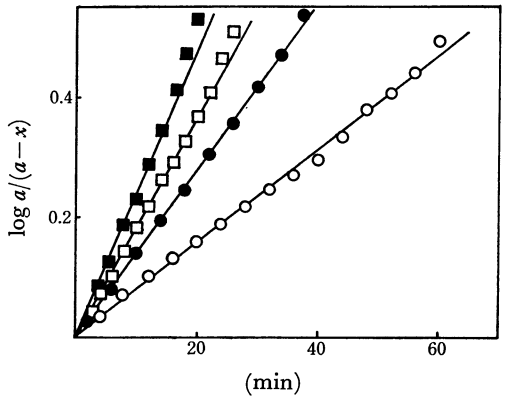

Fig. 4. Plots of $\log\{a/(a-x)\}$ *vs.* time for the dehydration of complex III.
○ 160, ● 172, □ 178, ■ 184 °C.

The relationship of $\log\{a/(a-x)\}$ *vs.* time for the dehydration of complex III is shown in Fig. 4. The rate constants of dehydration are given in Table 2 together with those of isomerization. The activation energy was estimated to be 76 kJ mol^{-1} from the Arrhenius plots of the rate constant.

Rate of Isomerization. The rate of isomerization of complex I measured spectrophotometrically is shown in Fig. 5. It is assumed that the reaction proceeds in

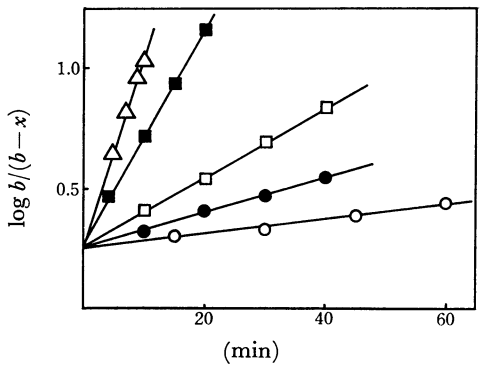

Fig. 5. Plots of $\log\{b/(b-y)\}$ *vs.* time for the isomerization of complex I.
○ 249, ● 260, □ 269, ■ 279, △ 288 °C.

Table 1. Rate constants of hydrogen chloride elimination, dehydration and isomerization of complex I

Temp/°C	92.0	105.0	119.3	125.5	249	260	269	279	288
$k_d(HCl)\times 10^{-3}/s^{-1}$	0.642	1.075	2.084	2.572					
$k_d(H_2O)\times 10^{-3}/s^{-1}$	1.574	2.764	3.964	4.798					
$k_i\times 10^{-4}/s^{-1}$					1.151	2.955	5.245	16.79	29.17

Table 2. Rate constants of dehyration and isomerization of complex III

Temp/°C	154	160	166	172	178	184
$k_d\times 10^{-4}/s^{-1}$		3.009		5.322	7.043	9.135
$k_i\times 10^{-2}/s^{-1}$	1.490	3.133	6.821	13.083		

the first order. The plots converge to *ca.* 0.26 in the coordinate $\log\{b/(b-y)\}$, where b is the initial amount of the complex I and y that of the *cis*-complex formed during time t. The point to which the plots converge corresponds to 45% isomerization of the complex. Taking the dehydration temperature range under the isothermal heating into account (Fig. 3), the point suggests that 45% of the complex isomerizes very rapidly accompanied by dehydration at least above 249 °C, the residual 55% isomerizing in anhydrous state in the first order.

The rate constants of isomerization for complex I in anhydrous state are summarized in Table 1. From the Arrhenius plots of the rate constants, the activation energy for the isomerization was evaluated to be 202 kJ mol^{-1}.

The rate of isomerization of complex III is shown in Fig. 6 by plotting the isomerization ratio (%) *versus* time. All the plotted lines are linear, indicating that the reaction proceeds in the zeroth order. The rate constants of isomerization for complex III are given in Table 2. The activation energy for the isomerization is calculated to be 193 kJ mol^{-1}.

Complex I isomerizes similarly to *trans*-$[CrBr_2(pn)_2]Br\cdot H_2O$ and *cis*-$[CrCl_2(tn)_2]Cl\cdot 0.5H_2O$, though the last complex undergoes *cis*-to-*trans* isomerization, indicating that the reaction occurs in an anhydrous state with a remarkably large activation energy as compared with cobalt(III) complexes.[4,5] In these complexes, a mechanism differing from "aquation-anation" in the cobalt(III) complexes should be considered.

On the other hand, in complex III, the *trans*-to-*cis* isomerization is completed before dehydration is over. The activation energy is, however, relatively large as compared with the values for the isomerization in cobalt(III) complexes. This suggests that the process of isomerization is independent of the presence of lattice water in these chromium(III) complexes.

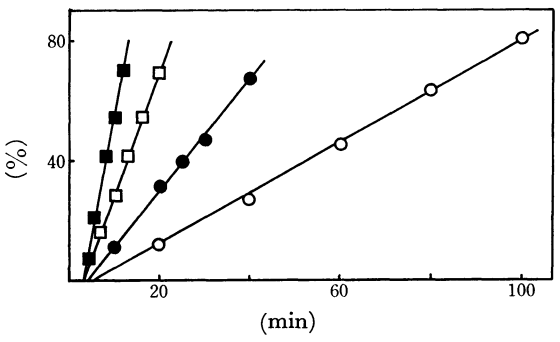

Fig. 6. Plots of isomerization ratio (%) *vs.* time for the isomerization of complex III.
○ 154, ● 160, □ 166, ■ 172 °C.

Thermochemical Reaction Scheme. On the basis of the data presented, the thermochemical reaction schemes for the isomerization of the complexes I and III are illustrated as follows:

In the temperature range 92—126 °C:

trans-$[CrCl_2(en)_2](H_5O_2)Cl_2$

↓ $E_d(HCl)=118$ kJ mol^{-1} (28 kcal mol^{-1})
↓ $E_d(H_2O)=42$ kJ mol^{-1} (10 kcal mol^{-1})

trans-$[CrCl_2(en)_2]Cl$

At 249—288 °C:

trans-$[CrCl_2(en)_2](H_5O_2)Cl_2$ $\xrightarrow{45\%}$ *cis*-$[CrCl_2(en)_2]Cl$

↓ 55%

trans-$[CrCl_2(en)_2]Cl$ ⟶ *cis*-$[CrCl_2(en)_2]Cl$ ($E_i=202$ kJ mol^{-1} (48 kcal mol^{-1}))

At 154—184 °C:

trans-$[CrCl_2(pn)_2]Cl\cdot 1.5H_2O$: ⟶ *cis*-$[CrCl_2(pn)_2]Cl$ ($E_i=193$ kJ mol^{-1} (46 kcal mol^{-1}))

↓ $E_d=76$ kJ mol^{-1} (18 kcal mo^{-1})

$[CrCl_2(pn)_2]Cl$

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