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DERIVATOGRAPHIC STUDIES ON TRANSITION METAL COMPLEXES

XV. THERMAL ISOMERIZATION OF *trans*-$[CrBr_2pn_2]Br \cdot H_2O$ IN SOLID PHASE

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ABSTRACT

The thermal *trans*-to-*cis* isomerization of $[CrBr_2pn_2]Br \cdot H_2O$ in a solid phase was studied by means of both derivatography and isothermal measurement. It was found that *trans*-$[CrBr_2pn_2]Br \cdot H_2O$ undergoes isomerization to the *cis*-complex by about 10% with complete dehydration followed by isomerization of the residual *trans* complex in the anhydrous state. It was characteristic of the complex, *trans*-$[CrBr_2pn_2]Br \cdot H_2O$, that the thermal dehydration was remarkably rapid in comparison with that of the *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and the isomerization of the *cis* complex occurred even in the anhydrous state though it did not in the corresponding cobalt(III) complex *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ in an analogous state.

INTRODUCTION

In a previous paper[1], the isomerization of the *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ to the *cis* complex was studied and compared with that of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$. In the former complex, the rate of *trans*-to-*cis* isomerization was greater than that of dehydration and dehydrobromination in an earlier thermal reaction step different from the case of the latter complex[2]. However, in the later step, the isomerization of the former complex was inferior to that of the latter complex in an inverse rate until it gave a certain constant isomerization ratio. In addition, after dehydration and dehydrobromination were completed, no further isomerization proceeded in the former complex, differing from the latter complex which isomerized even in the anhydrous state. As mentioned above, a slight variation of ligand materials involved in coordination sphere and of counter ions without change of the framework of the starting complexes gives, in general, a delicately different feature for their thermochemical reactions[1–6].

Inferring to the above results, when the central cobalt(III) ion is replaced by chromium(III) ion, some differences should also be observed in the thermochemical change. The present study deals with the *trans*-to-*cis* isomerization of $[CrBr_2pn_2]$-$Br \cdot H_2O$ and the comparison of its reaction features with that of $[CoBr_2pn_2](H_5O_2)$-Br_2.

EXPERIMENTAL

Preparation of complexes

trans-[$CrBr_2pn_2$]$Br \cdot H_2O$. When 24 g of anhydrous 1,3-propanediamine were added drop by drop to 26 g of chromium(III) chloride hexahydrate with grinding in a mortar, the mixture gave violet product under exotherm. By heating it in an air-bath at 140°C for 4 h while crushing the aggregates, dry yellow lumps containing tris-propylenediaminechromium(III) chloride as a main product were obtained. After the lumps were dissolved into 200 ml of water and filtered, the filtrate to which 30 ml of concentrated hydrobromic acid were added with stirring was kept in a refrigerator. The precipitate produced was filtered, washed with ethanol and air-dried. By recrystallizing in an ethanol–water mixture, the purified tris-propylenediaminechromium(III) bromide was obtained.

The mixture obtained by grinding 4.6 g of the above complex together with 6.5 g of mercury bromide in a mortar was heated under reduced pressure for 2 h in an egg-plant shaped flask dipped in an oil-bath at 210°C. The product formed was washed with 0.6 N hydrobromic acid until the washing solution became green and then it was air-dried. Four grams of *trans*-[$CrBr_2pn_2$]$Br \cdot HgBr_2$ were obtained by the above procedure. When this complex was suspended in 20 ml of cold water and hydrogen sulfide was passed through the solution while cooling with cold water, mercury sulfide was precipitated. After this black precipitate was sedimented by centrifugation, the supernatant solution was saturated with hydrogen bromide while cooling with cold water or an equal volume of concentrated hydrobromic acid was added to the solution, and the resulting solution was evaporated under reduced pressure at 40°C. Green crystals formed were filtered, washed with acetone and dried. At recrystallization with ethanol, green scale-like crystals were obtained as the desired product. *Anal.* Found: C, 16.04; H, 5.03; N, 12.02%. Calc. for [$CrBr_2pn_2$]$Br \cdot H_2O$; C, 15.73; H, 4.48; N, 12.23%.

cis-[$CrBr_2pn_2$]Br and cis-[$CrBr_2pn_2$]ClO_4. When 4.5 g of anhydrous 1,3-propanediamine were added drop by drop to 12 g of chromium(III) bromide hexahydrate while grinding the latter in a mortar, the mixture became bluish violet and then turned to the violet lumps by heating in an air-bath at 190°C for 10 h. By dissolving these lumps into 300 ml of acetone in a dark place, and adding 200 ml of ether to the solution, violet powdered crystals separated. These crystals were filtered, washed with ether and dried at 50°C under reduced pressure. When they were dissolved in boiling nitromethane and were kept in a refrigerator, *cis*-[$CrBr_2pn_2$]Br was obtained as violet needle crystals. When this bromide was dissolved in 2 N perchloric acid at room temperature and, after the undissolved residue was filtered off, the filtrate was cooled, *cis*-[$CrBr_2pn_2$]ClO_4 was obtained as violet needle crystals. *Anal.* Found: C, 15.40; H, 4.89; N, 10.20%. Calc. for [$CrBr_2pn_2$]ClO_4: C, 15.67; H, 4.39; N, 12.27%.

Derivatographic measurements

The derivatogram for the complex, *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ was obtained with a MOM Type-OD-102 derivatograph. 0.5 g of sample was used in each run under a constant flow of nitrogen with a heating rate of 2 °C min^{-1}. The enthalpy change was estimated from the DTA peak area.

Isothermal measurements

The rate of dehydration of *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ was measured at 122, 127, 138 and 146 °C with a Shimadzu TM-1A thermobalance.

The rate of isomerization was obtained by measuring the absorbancy of the samples heated at various time intervals in an Ikemoto Rika Kogyo air-bath at 160, 170, 180, 190 and 200 °C, respectively. 50 ~ 60 mg of sample were taken out from the air-bath in each run. The isomerization ratio was calculated by the following equations:

$$6.1x + 83.6y = D_{530}$$

$$26.4x + 29.1y = D_{460},$$

where x and y are the molar concentrations of *trans* and *cis* complexes contained in the sample, respectively, after heating it for some time, and D_{530} and D_{460} are the molar extinction coefficients of the sample measured at 530 nm and 460 nm, respectively. 6.1 and 26.4 are those of the *trans* complex and 83.6 and 29.1 are those of the corresponding *cis* complex at 530 nm and 460 nm, respectively. The electronic spectra of the *trans* and *cis* complexes which give basic data for the above calculation are shown in Fig. 1. The isomerization ratio is given by $y/(x+y)$.

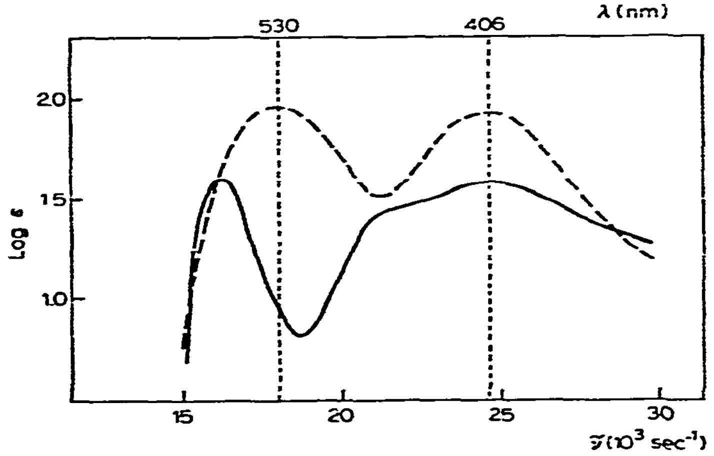


Fig. 1. Electronic spectra of *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ (———) and the corresponding *cis* complex (– – –).

RESULTS AND DISCUSSION

Derivatography

The derivatogram of *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ is shown in Fig. 2, together with that of the corresponding cobalt(III) complex, *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2, for comparison. The feature of the DTA curves of these two complexes due to dehydration and dehydrobromination (the latter cannot be taken into account in the case of the chromium(III) complex) is similar. The values of the enthalpy change, however, were quite different from each other in the two complexes: the value for dehydration of *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ was calculated from the DTA endothermic peak to be 3.0 kcal mol^{-1}, whereas the corresponding value of *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2 was calculated to be 37.3 kcal mol^{-1}, which is larger than the former value due to dehydrobromination. And the peak temperature of dehydration and dehydrobromination is 145°C in the cobalt(III) complex, while that of dehydration is 225°C in the chromium(III) complex. It shows that this chromium(III) complex can be more difficult to be dehydrated than the corresponding cobalt (III) complex.

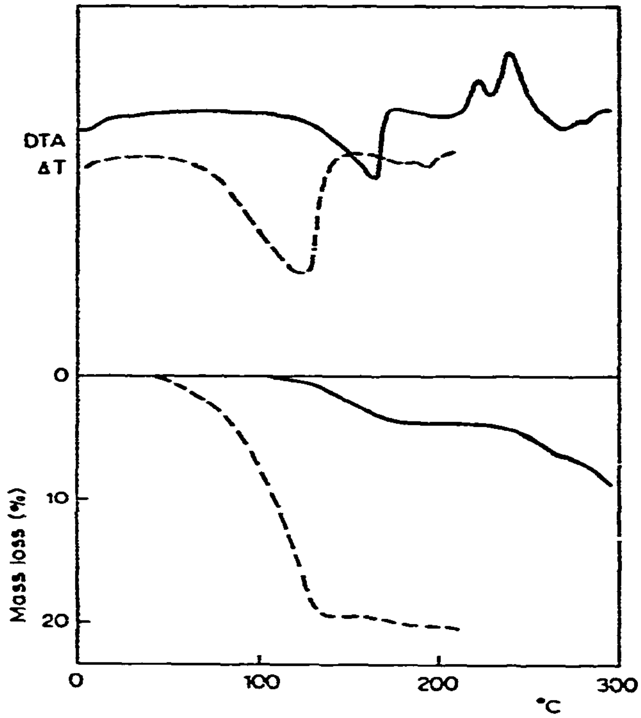


Fig. 2. Derivatograms of *trans*-[$CrBr_2pn_2$]$Br \cdot H_2O$ (——) and *trans*-[$CoBr_2pn_2$](H_2O_5)Br_2 (– – –).

Another more distinct difference in these two DTA curves is seen in the anhydrous state: in the cobalt(III) complex, no appreciable DTA peak could be observed, whereas in the chromium(III) complex, a distinct exothermic peak appeared at 220 ~ 235 °C due to isomerization followed by the larger exothermic peak due to decomposition. It suggests that the chromium(III) complex [$CrBr_2pn_2$]Br isomerized, but the cobalt(III) complex [$CoBr_2pn_2$]Br did not in the anhydrous state.

Rate of dehydration

If the rate of dehydration at each temperature obeys the first order law, it is given by the following equation,

$$2.303 \log \frac{a}{a-x} = k_d t, \tag{1}$$

where a and x are the initial amount of the starting complex and the amount of anhydrous complex formed during time t, respectively, and k_d is the rate constant of dehydration.

When the values of $\log a/(a-x)$ versus t were plotted at each temperature designated in the Experimental section, approximately straight lines were obtained, which are shown in Fig. 3. The rate constants k_d at each temperature were obtained from the slope of the respective lines. Their values are listed in Table 1, together with those of isomerization obtained in the later section of this paper and the corresponding data for *trans*-[$CoCl_2pn_2$](H_5O_2)Cl_2[2] and *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2[1] already reported. From the Arrhenius plots for the rate constant, the activation energy E_a^d was evaluated to be 23 kcal mol^{-1}.

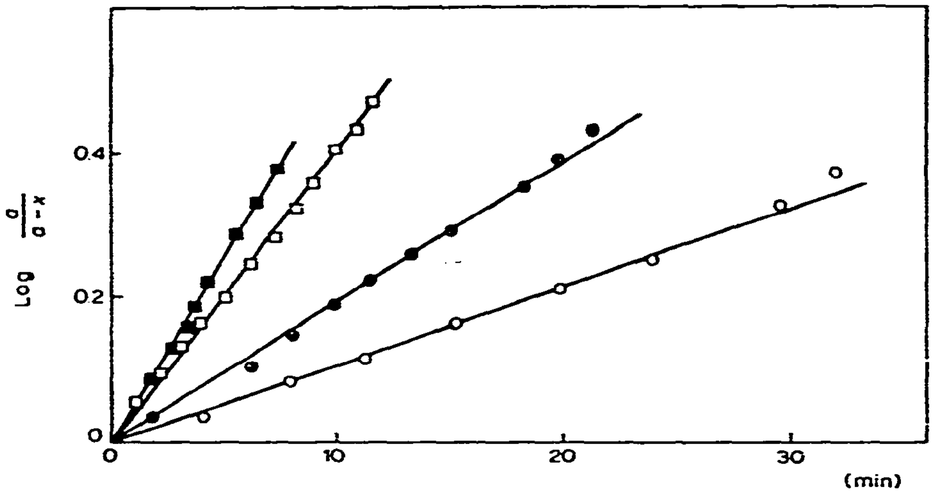


Fig. 3. Relation of $\log a/(a-x)$ vs. time for the dehydration. ○, 122 °C, ●, 127 °C, □, 138 °C; ■, 146 °C.

Rate of isomerization

The isomerization ratio of *trans*-[$CrBr_2pn_2$]Br·H_2O was determined by measuring the change of the absorbancy for the sample after it is heated in the

TABLE 1

RATE CONSTANTS OF DEHYDRATION AND DEHYDROHALOGENATION, k_d, AND ISOMERIZATION, k_i

trans-$[CoCl_2pn_2](H_5O_2)Cl_2$

t (°C)	*110*	*130*	*150*	*170*
$k_d \times 10^4$ sec^{-1}	2.6	8.2	16	24
$k_i \times 10^4$ sec^{-1}	0.44	1.8	7.3	24

trans-$[CoBr_2pn_2](H_5O_2)Br_2$

t (°C)	*90*	*98*	*100*	*110*	*111*	*117*	*130*
$k_d \times 10^4$ sec^{-1}			0.28		0.78	1.7	5.5
$k_i \times 10^4$ sec^{-1}	0.36	0.60		2.5		40	

trans-$[CrBr_2pn_2]Br \cdot H_2O$

t (°C)	*122*	*127*	*138*	*146*	*160*	*170*	*180*	*190*	*200*
$k_d \times 10^4$ sec^{-1}	7.3	8.8	23	35					
$k_i \times 10^5$ sec^{-1}					0.31	1.4	2.9	8.8	23

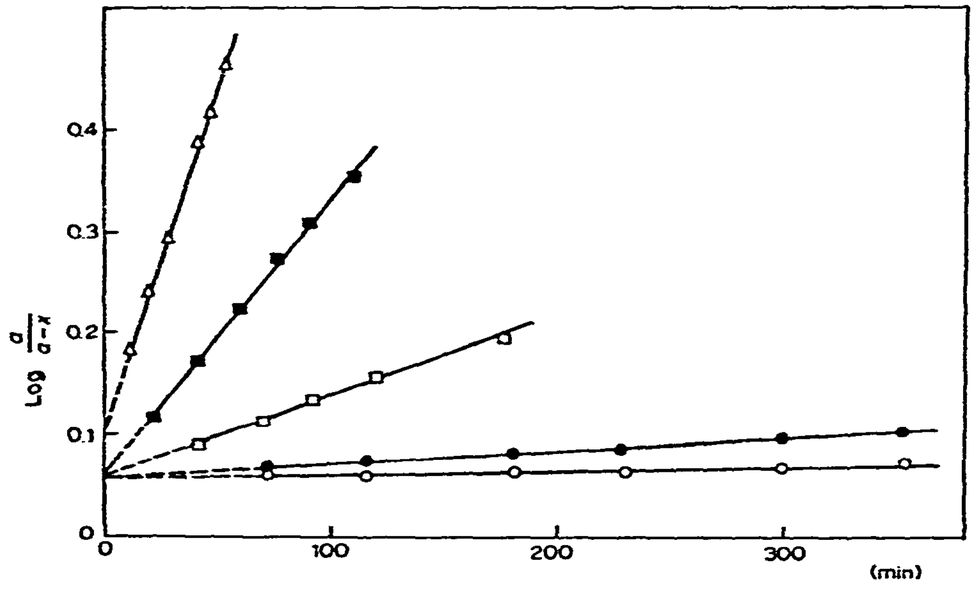


Fig. 4. Relation of log $a/(a-x)$ vs. time for the isomerization. ○, 160 °C; ●, 170 °C; □, 180 °C; ■, 190 °C; △, 200 °C.

air-bath at each constant temperature for various time intervals on the basis of the absorbancies of the starting complex, *trans*-$[CrBr_2pn_2]Br \cdot H_2O$, and the completely isomerized complex, *cis*-$[CrBr_2pn_2]Br$, shown in Fig. 1. If the rate of isomerization obtained from the change of isomerization ratio also obeys the first order law, it should be expressed by the following equation analogous to eqn (1),

$$2.303 \log \frac{a}{a-x} = k_i t, \tag{2}$$

where a and x are the initial amount of the starting complex, *trans*-$[CrBr_2pn_2]$-$Br \cdot H_2O$, and the amount of *cis* complex produced during t, and k_i is the rate constant of isomerization.

When the values of $\log a/(a-x)$ versus t were plotted at each temperature, the approximately straight lines were obtained in a similar manner to that in the case of dehydration, which are shown in Fig. 4. These extrapolated lines are found, however, not to pass through an origin, but they all pass through the point indicating about 10% of isomerization ratio in the abscissa at time zero except that at 20°C. This shows that about 10% of isomerization is completed within fairly short time via a different mechanism contributed by dehydration from that of isomerization in the anhydrous state; on the other hand, the dehydration at 130°C and at 140°C was found to be finished within 50 min and 16 min, respectively, and the hydration at 160°C was almost instantly finished. From these results, it was concluded that dehydration is very rapid in comparison with isomerization, and therefore, a greater part of isomerization occurs in the anhydrous state.

The rate constants obtained from Fig. 4 and eqn (2) are listed in Table 1. From the Arrhenius plots of the rate constant, the activation energy, E_a^i, was calculated to be 43 kcal mol^{-1}.

When the correlation between isomerization and dehydration in *trans*-$[CrBr_2pn_2]Br \cdot H_2O$ and compared with those in *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ and in the corresponding complex *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, referring to the summarized data collected in Table 1, the following information can be deduced.

(1) In *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, the rate of dehydration is always larger than that of isomerization and, therefore, the dehydration accompanies a partial isomerization, and the isomerization of the residual *trans* complex in the anhydrous state proceeds at a higher temperature range via a different mechanism from that of the hydrated form.

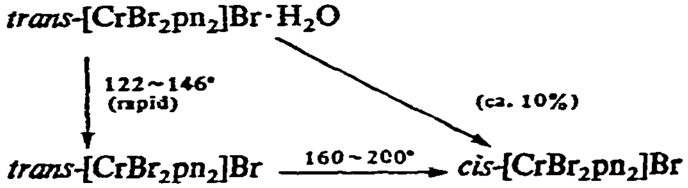
(2) In *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$, the isomerization is more rapid than the dehydration in the earlier thermal step, but it becomes slower in the later step until the rate of dehydration exceeds that of isomerization which remains almost constant. And, therefore, the isomerization occurs only simultaneously with the dehydration, but it does not proceed further in the anhydrous state.

(3) In *trans*-$[CrBr_2pn_2]Br \cdot H_2O$, however, the dehydration is sufficiently rapid to be completed before the isomerization proceeds by about 10%, and, therefore, a greater part of isomerization occurs in the anhydrous state. This is a striking charac-

teristic of this complex different from the former two complexes, *trans*-[$CoCl_2pn_2$](H_5O_2)Cl_2 and *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2.

Thermochemical reaction scheme

On the basis of the experimental results described above, the thermochemical reaction scheme for the path-way of the *trans*-to-*cis* isomerization of [$CrBr_2pn_2$]Br·H_2O can be expressed by the following:



By comparing this scheme with those for *trans*-[$CoCl_2pn_2$](H_5O_2)Cl_2 and *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2 depicted in the previous paper[1], the information about the correlations between isomerization and dehydration enumerated above will be well understood.

In addition, the activation energies of dehydration and isomerization of *trans*-[$CoBr_2pn_2$](H_5O_2)Br_2 were the same value of 28 kcal mol^{-1}, whereas those of *trans*-[$CrBr_2pn_2$]Br·H_2O were 23 kcal mol^{-1} and 43 kcal mol^{-1}, respectively. The last, relatively larger value than the former two, suggests that the isomerization of the latter complex proceeds by a different mechanism from "aquation–anation" which may be considered in the isomerization of the hydrated complexes[2–4], e.g., twisting.

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