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DERIVATOGRAPHIC STUDIES ON TRANSITION METAL COMPLEXES. XXI*. THERMAL ISOMERIZATION OF *TRANS*-$[CrBr_2en_2]Br \cdot H_2O$ AND *CIS*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ IN THE SOLID PHASE **

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ABSTRACT

The thermal *trans*-to-*cis* isomerization of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ and *cis*-to-*trans* isomerization of *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ were studied by means of derivatographic and isothermal measurements. In both cases isomerization took place in anhydrous state after the complete dehydration. The activation energies for dehydration of the above two complexes were evaluated isothermally to be 61 and 38 kJ $mole^{-1}$, respectively, and for their isomerization to be 420 and 275 kJ $mole^{-1}$, respectively. These data were compared with those for the corresponding chloro complexes and the ease of isomerization between them was discussed.

INTRODUCTION

Few papers have been published on the *trans* → *cis* isomerization of chromium(III) complexes of the type $[CrCl_2(a\text{-}a)_2]Cl \cdot n\ H_2O$, where a-a is one of diamines such as ethylenediamine (en), propylenediamine (pn), butylenediamine (bn) and trimethylenediamine (tn) [2—4]. It has been found as one of the striking experimental facts that complexes containing the diamine which forms the five-membered chelate ring with chromium(III) ion undergo isomerization from the *trans*- to *cis*-form in contrast to the isomerization of the *cis*- to *trans*-form in the complexes containing the diamine which forms the six-membered chelate ring. In both cases, the isomerization generally proceeded in anhydrous state except for the case of *trans*-$[CrCl_2en_2](H_5O_2)Cl_2$, where 45% of isomerization took place during dehydration and the remaining 55% occurred in anhydrous state.

The present study was undertaken to investigate the isomerization of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ and *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ non-isothermally (derivatographically) and isothermally, and to compare the ease of isomerization between these complexes and the corresponding dichloro complexes.

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* For part XX, see ref. 1.

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EXPERIMENTAL

Preparation of complexes

trans-Dibromobis(ethylenediamine)chromium(III) bromide monohydrate, trans-$[CrBr_2en_2]Br \cdot H_2O$ *and trans-dibromobis(trimethylenediamine)chromium(III) bromide dihydrate, trans-*$[CrBr_2tn_2]Br \cdot 2\,H_2O$. These were prepared by the known methods [5,6] partially modified.

cis-Dibromobis(ethylenediamine)chromium(III) bromide monohydrate, cis-$[CrBr_2en_2]Br \cdot H_2O$. This was prepared by slight modification of the method reported earlier [7].

cis-Dibromobis(trimethylenediamine)chromium(III) bromide dihydrate, cis-$[CrBr_2tn_2]Br \cdot 2\,H_2O$. 10 g (25 mmole) of chromium(III) bromide hexahydrate was dissolved in 30 ml of dimethylformamide (DMF). A certain amount of liquid was then distilled off until the vapor temperature of 148°C was reached (b.p. of DMF: 153°C). The solution was allowed to cool to 100°C with stirring and thereto 4.2 ml of trimethylenediamine (50 mmole) was added (the temperature had to be kept below 130°C). After half an hour at 100°C, the crystalline mush was filtered, washed with ethanol and air dried. The product was recrystallized from 0.5 mole dm^{-3} HBr at room temperature. Yield, 65%; anal. found: C, 15.21; H, 5.01; N, 11.07%; calc. for $[CrBr_2tn_2]Br \cdot 2\,H_2O$: C, 15.14; H, 5.08; N, 11.77%.

Derivatography

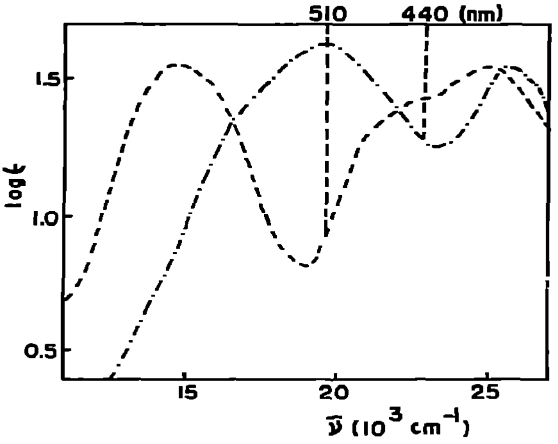
The derivatograms for the complexes were obtained with a MOM Typ-OD-102 Derivatograph under a constant flow of nitrogen with a heating rate of 1°C min^{-1} in order to decide the temperature ranges in the isothermal measurements. In each case 300 mg sample was taken.

Isothermal measurements

The rates of dehydration of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ were measured at 75, 81, 90, 98 and 107°C, and those of *cis*-$[CrBr_2tn_2]Br \cdot 2\,H_2O$ at 67, 76, 85 and 94°C with a CHYO thermobalance. The rates of isomerization of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ at 220, 225, 230, 235 and 240°C and of *cis*-$[CrBr_2tn_2]Br \cdot 2\,H_2O$ at 200, 209, 218 and 225°C were followed by measuring the changes in absorbancy and by calculating the molar amounts of *cis*- and *trans*-complexes, x and y, respectively, on the basis of the following equations

$$\left.\begin{array}{l} 18.0\,x + 26.4\,y = D_{440} \\ 38.4\,x + 8.6\,y = D_{510} \end{array}\right\} \begin{array}{l} \text{for } trans\text{-}[CrBr_2en_2]Br \cdot H_2O \text{ and} \\ \quad cis\text{-}[CrBr_2en_2]Br \cdot H_2O \end{array}$$

$$\left.\begin{array}{l} 13.9\,x + 29.2\,y = D_{640} \\ 62.1\,x + 8.3\,y = D_{540} \end{array}\right\} \begin{array}{l} \text{for } trans\text{-}[CrBr_2tn_2]Br \cdot 2\,H_2O \text{ and} \\ \quad cis\text{-}[CrBr_2tn_2]Br \cdot 2\,H_2O \end{array}$$



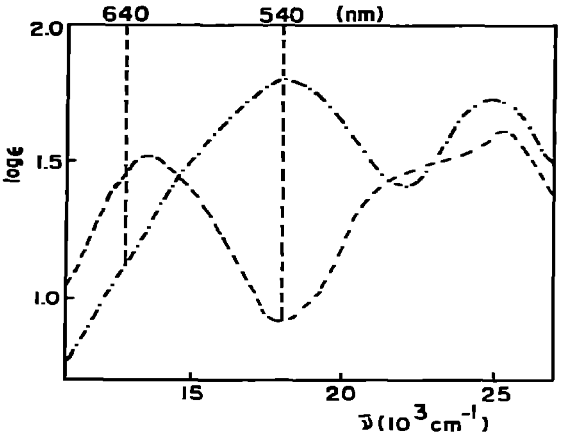


Fig. 1. Electronic spectra of *trans*- (- - - - - -) and *cis*-$[CrBr_2en_2]Br \cdot H_2O$ (· — · — ·).

Fig. 2. Electronic spectra of *trans*- (- - - - - -) and *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ (· — · — ·).

where the numerical factors are the molar extinction coefficients of pure *cis*- and *trans*-isomers and *D* represents the absorbancies at the wavelengths specified by the subscripts. The electronic spectra of the complexes are shown in Figs. 1 and 2.

RESULTS AND DISCUSSION

Derivatography

Figure 3 shows the derivatograms of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ and *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$. The TG curve of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ shows that the complex evolves 1 mole of water at 75—113°C and remains unchanged up to 220°C, above which isomerization and then decomposition begin. In the DTA curve, a small but clear exothermic peak can be seen just before the large exothermic peak starts to appear. This small exothermic peak is due to the *trans*-to-*cis* isomerization which was visually confirmed by the color change of the sample from green to violet. The enthalpy change for dehydration was found to be 35 kJ $mole^{-1}$. The previous work on *trans*-$[CrCl_2en_2](H_5O_2)Cl_2$ showed that about 45% of isomerization took place during dehydration and the remaining 55% occurred in anhydrous state. But such an observation was not noticed in the case of *trans*-$[CrBr_2en_2]Br \cdot H_2O$.

On the other hand, the TG curve of *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ shows that it loses 2 moles of water at 35—135°C and decomposes above 225°C. In the DTA curve an endothermic peak appears at the dehydration step and then an exothermic peak begins to appear at 200°C. The *cis*-to-*trans* isomerization was also visually confirmed at this stage. The enthalpy change for dehydration was 37 kJ $mole^{-1}$. The isomerization of *cis*-$[CrBr_2tn_2]Br \cdot 2\ H_2O$ takes place in anhydrous state in a manner similar to that of *cis*-$[CrCl_2tn_2]Cl \cdot$

0.5 H_2O, as reported earlier [2]. In the latter case, the enthalpy change for dehydration was 9.2 kJ $mole^{-1}$, which is lower than that of the dibromo complex obtained here. This suggests that the dibromo complex is dehydrated with more difficulty than the dichloro complex.

Rate of dehydration

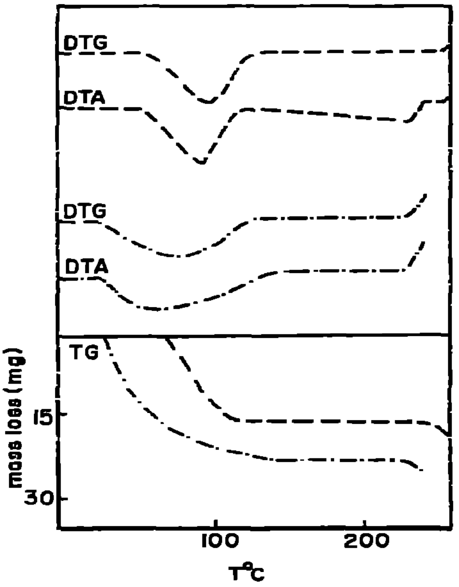
If the rate of dehydration at each temperature obeys the first order law, the following equation holds

$$2.303 \log a/(a - x) = k_d t$$

where a and x are the initial amounts of the starting complex and the amount of the anhydrous complex formed during time t. Approximately linear relationships were obtained and are shown in Figs. 4 and 5, in which $\log a/(a - x)$ is plotted against time t. The rate constants of dehydration are given in Table 1. The activation energy for dehydration of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ was evaluated to be 61 kJ $mole^{-1}$, which is higher than the value for the corresponding dichloro complex (42 kJ $mole^{-1}$). The energy of activation for dehydration of *cis*-$[CrBr_2tn_2]Br \cdot 2\,H_2O$ was 38 kJ $mole^{-1}$ which is more or less the same as the value for *cis*-$[CrCl_2tn_2]Cl \cdot 0.5\,H_2O$.

Rate of isomerization

For the isomerization, $\log b/(b - y)$ were similarly plotted vs. t at each temperature (Figs. 6 and 7), where b is the initial amount of the starting



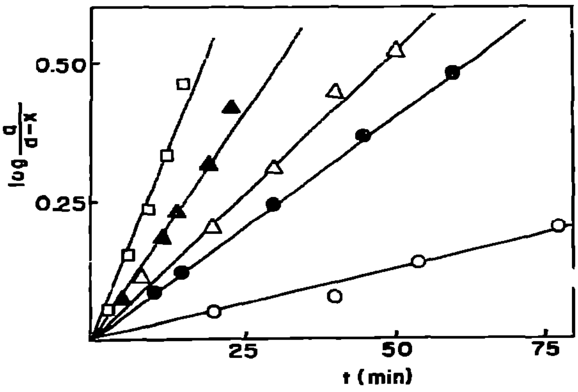


Fig. 3. Derivatograms of *trans*-$[CrBr_2en_2]Br \cdot H_2O$ (- - - - - -) and *cis*-$[CrBr_2tn_2]Br \cdot 2\,H_2O$ (· — · — ·).

Fig. 4. Relation of $\log a/(a - x)$ vs. time for the dehydration of *trans*-$[CrBr_2en_2]Br \cdot H_2O$. ○, 75°C; ●, 81°C; △, 90°C; ▲, 98°C; □, 107°C.

TABLE 1

Rate constants of dehydration (k_d) and isomerization (k_i)

trans-$[CrBr_2en_2]Br \cdot H_2O$											
T (°C)	75	81	90	98	107	220		225	230	235	240
$k_d \times 10^4$ (sec^{-1})	0.96	3.07	3.95	6.20	9.74						
$k_i \times 10^4$ (sec^{-1})						0.10		0.26	0.94	2.29	6.12
cis-$[CrBr_2tn_2]Br \cdot 2\ H_2O$											
T (°C)	67	76	85	94		200	209	218	225		
$k_d \times 10^4$ (sec^{-1})	8.53	10.87	18.05	28.99							
$k_i \times 10^4$ (sec^{-1})						0.27	0.53	1.78	5.02		

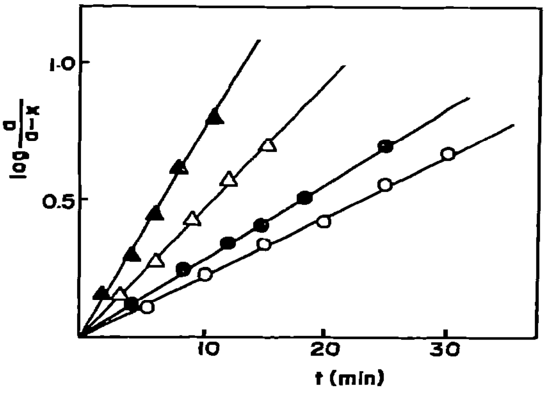


Fig. 5. Relation of log $a/(a-x)$ vs. time for the dehydration of *cis*-[$CrBr_2tn_2$]Br · 2 H_2O. ○, 67°C; ●, 76°C; △, 85°C; ▲, 94°C.

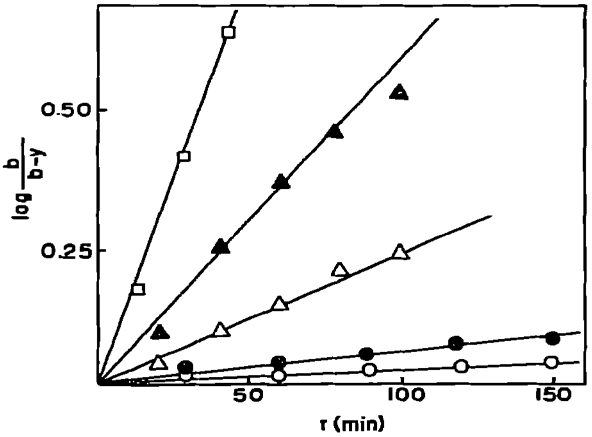


Fig. 6. Relation of log $b/(b-y)$ vs. time for the isomerization of *trans*-[$CrBr_2en_2$]Br · H_2O. ○, 220°C; ●, 225°C; △, 230°C; ▲, 235°C; □, 240°C.

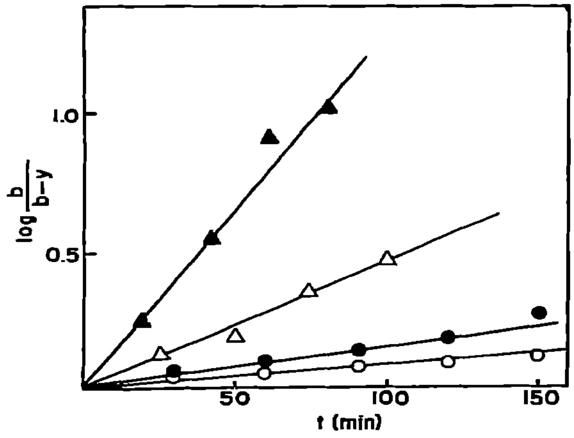


Fig. 7. Relation of log $b/(b-y)$ vs. time for the isomerization of *cis*-[$CrBr_2tn_2$]Br · 2 H_2O. ○, 200°C; ●, 209°C; △, 218°C; ▲, 225°C.

complex and *y* is the amount of the complex formed by isomerization during time *t*. Approximately linear relationships were obtained, supporting that the rate of isomerization obeys the first order law. The rate constants for isomerization are summarized in Table 1. The activation energy for isomerization (E_i) of *trans*-[$CrBr_2en_2$]Br · H_2O was estimated to be 420 kJ mole^{-1}, which is about twice the value for the corresponding dichloro complex (202 kJ mole^{-1}). The value for *cis*-[$CrBr_2tn_2$]Br · 2 H_2O was 215 kJ mole^{-1} which is also higher than that of the corresponding dichloro complex (163 kJ mole^{-1}). As far as these complexes in the present work are concerned, the dibromo complexes give generally higher values of activation energy than the corresponding dichloro complexes. This suggests that the dibromo complexes isomerize with difficulty as compared with the dichloro complexes.

Thermochemical reaction schemes

The thermochemical reaction schemes for the pathway of *cis* ↔ *trans* isomerization can be expressed as follows

trans-[$CrBr_2en_2$]Br · H_2O

Dehydration | E_d = 61 kJ mole^{-1}
75—113°C ↓ ΔH = 35 kJ mole^{-1}

trans-[$CrBr_2en_2$]Br $\xrightarrow[\text{Isomerization 220—242°C}]{}$ *cis*-[$CrBr_2en_2$]Br
E_i = 420 kJ mole^{-1}

cis-[$CrBr_2tn_2$]Br · 2 H_2O

Dehydration | E_d = 38 kJ mole^{-1}
35—135°C ↓ ΔH = 37 kJ mole^{-1}

cis-[$CrBr_2tn_2$]Br $\xrightarrow[\text{Isomerization 200—225°C}]{}$ *trans*-[$CrBr_2tn_2$]Br
E_i = 275 kJ mole^{-1}

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