Thermochimica Acta, 12 (1975) 147–153
© Elsevier Scientific Publishing Company, Amsterdam – Printed in Belgium

DERIVATOGRAPHIC STUDIES ON TRANSITION METAL COMPLEXES

XIV. THERMAL ISOMERIZATION OF *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ IN SOLID PHASE

R. TSUCHIYA, Y. NATSUME, A. UEHARA AND E. KYUNO
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920 (Japan)
(Received 30 December 1974)

ABSTRACT

Thermal isomerization of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ to the *cis*-form complex in the solid phase was studied by means of derivatographic and isothermal measurements. It was found that the rate constant of isomerization is larger than that of dehydration and dehydrobromination in the initial step of the reaction, different from the case of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$. Another distinction was that anhydrous *trans*-$[CoBr_2pn_2]Br$ does not isomerize to the *cis*-form.

INTRODUCTION

There have been several studies on the geometrical isomerization of cobalt(III) complexes in the solid phase: e.g., *trans*-$[CoCl_2(NH_3)_4IO_3]\cdot 2H_2O$[1], *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$[2,3], *cis,trans*-$[CoCl_2(NH_3)_2en]ClO_4$[4], *cis,trans*-$[CoCl_2(NH_3)_2en]SCN\cdot H_2O$[5] and *cis, trans*-$[CoCl_2(NH_3)_2en]Br\cdot H_2O$[6].

Above all, in the previous studies on *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, the isomerization was found to proceed in two steps. The first step consisted of the partial isomerization of the *trans*-form complex to the *cis*-form accompanying both dehydration and dehydrochlorination. For this reaction step, the "aquation–anation" mechanism was considered to be applied on the basis of the activation energy of 33 kcal mol^{-1} evaluated by the authors[2]. The second was characterized by the isomerization of the *trans*-form complex in anhydrous state produced by dehydration and dehydrochlorination to the *cis*-form. This reaction might be considered to proceed through an intramolecular reaction mechanism like twisting with due regard to the activation energy of 120 kcal mol^{-1} (ref. 3).

It has been pointed out, in general, that a slight difference in ligand material and counter ion contained in cobalt(III) complexes often shows an appreciable distinction in the thermal behavior in the solid phase. From this standpoint, it may be of special interest to us to investigate the difference of the feature in the isomerization which will be seen between *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ and the complex in which chloride ions coordinated and contained as counter ion are both replaced by bromide ions in the former complex. This paper deals with the thermal *trans*-to-*cis* isomerization of $[CoBr_2pn_2](H_5O_2)Br_2$ in the solid phase and comparison of its behavior with that of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$.

EXPERIMENTAL

Preparation of complexes

trans-$[CoBr_2pn_2](H_5O_2)Br_2$. Fifty grams of cobalt(II) acetate tetrahydrate were dissolved into 600 ml of the aqueous solution containing 12.5 g of propylenediamine (pn). Air was passed through the above solution for 16 h in order to oxidize Co(II) to Co(III): the passing of air was done gently during the first few hours to prevent liberation of propylenediamine. After the oxidation by air was completed, 200 ml of concentrated hydrobromic acid were added to the above solution which was then concentrated to about 150 ml under reduced pressure below 70°C. When the solution was kept at room temperature overnight, light-green plate crystals precipitated. The recrystallization was carried out from the solution of diluted hydrobromic acid. Yield, 50%. *Anal.* Found: C, 13.14; H, 4.64; N, 9.65%. Calc. for $[CoBr_2pn_2](H_5O_2)Br_2$: C, 12.78; H, 4.47; N, 9.94%.

cis-$[CoBr_2pn_2]Br$. The complex, *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$, prepared by the manner described in the preceding section was dissolved into an amount of methanol as small as possible. When ether was added to the solution while scratching the glass wall of the vessel with a glass rod under cooling, *trans*-$[CoBr_2pn_2]Br\cdot H_2O$ precipitated as the powdered state. After the precipitate was dried, it was dissolved into an amount of water as small as possible and after an appropriate amount of ammonia ($NH_3:H_2O = 1:4$) was added to adjust the solution to pH 7~8, the solution was evaporated to dryness. Since the residue was considered to contain a small amount of *trans*-$[CoBr(H_2O)pn_2]Br_2$ and *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ as impurities, the recrystallization was carried out with distilled ethanol, making use of the difference of the solubilities between the complexes described above. After the crystals were heated at about 120°C to eliminate the aquo complexes, the recrystallization was repeated with distilled ethanol. *Anal.* Found: C, 15.22; H, 5.31; N, 12.83%. Calc. for $[CoBr_2pn_2]Br$: C, 16.12; H, 4.52; N, 12.54%.

Derivatographic measurements

TG, DTA and DTG curves for the complexes, *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$, are obtained with a MOM Typ-OD-120 derivatograph. 0.4~0.5 g of sample was used in each run under a constant flow of nitrogen with a heating rate of $1\,°C\,min^{-1}$. The enthalpy change was estimated from the DTA peak area and the activation energy was obtained by analyzing the DTA or DTG curve.

Isothermal measurements

The rate of dehydration and dehydrobromination of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ was measured at 100, 108, 111, 117, 130 and 139°C with a Shimadzu TM-1A thermobalance. 0.3~0.4 g of sample was used in each run.

The rate of isomerization was obtained by measuring the absorbancy of the sample taken from the Abderhalden apparatus after various time intervals of heating at 90, 98, 110, 117, 124 and 130°C, respectively. 50~60 mg of sample were taken out in each run. The isomerization ratio was calculated by the following equations,

$$56.5x+16.1y = A$$

$$5.3x+70.5y = B$$

where x and y are the molar concentrations of *trans-* and *cis-*form complexes in the sample, respectively, after heating *trans-*$[CoBr_2pn_2](H_5O_2)Br_2$; and A and B are the molar extinction coefficients of the sample measured at 650 and 550 nm, respectively. 56.5 and 5.3 are the molar extinction coefficients of the *trans-*form complex at 650 and 550 nm, respectively, and 16.1 and 70.5 are those of the corresponding *cis-*form complex. The electronic spectra of the *trans-* and *cis-*form complexes which give the basic data for the above calculation are shown in Fig. 1. The isomerization ratio is given by $y/(x+y)$.

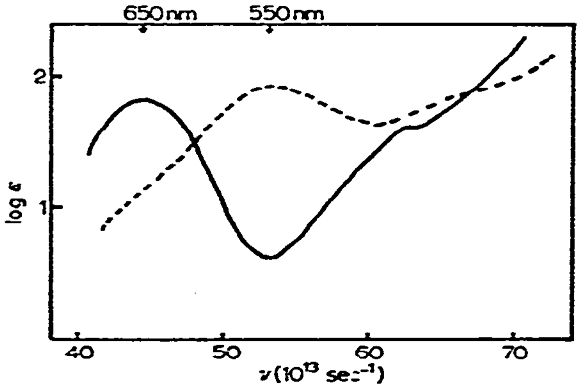


Fig. 1. Electronic spectra of *trans-*$[CoBr_2pn_2](H_5O_2)Br_2$ (———) and the corresponding *cis-*form complex (– – –).

RESULTS AND DISCUSSION

Derivatography

The derivatogram of *trans-*$[CoBr_2pn_2](H_5O_2)Br_2$ is shown in Fig. 2, together with that of *trans-*$[CoCl_2pn_2](H_5O_2)Cl_2$ for comparison. The feature of DTA curves of complexes due to dehydration and dehydrohalogenation is similar in that the enthalpy changes were calculated to be 37.3 and 36.5 kcal mol^{-1}, respectively. The distinct difference of DTA curves is seen in that an exothermic peak appeared at 170°C in *trans-*$[CoCl_2pn_2](H_5O_2)Cl_2$, whereas such a peak could not be found in the corresponding dibromo complex. This indicates that the isomerization of anhydrous *trans-*$[CoCl_2pn_2]Cl$ produced by dehydration and dehydrochlorination to the

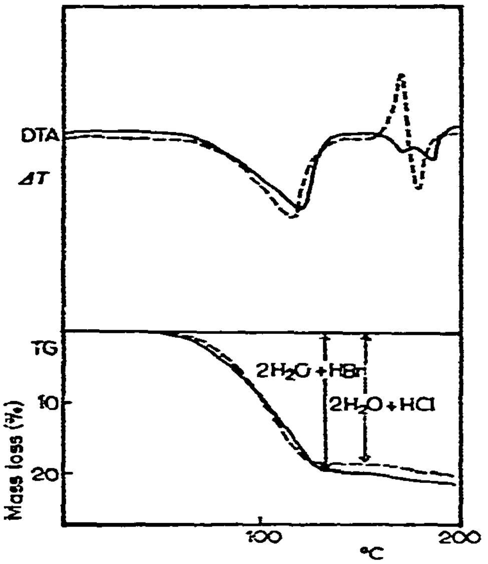


Fig. 2. Derivatograms of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ (———) and *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$ (– – –).

cis-form complex does occur, while *trans*-$[CoBr_2pn_2]Br$ does not undergo isomerization in the anhydrous state.

Rate of isomerization

If the rate of isomerization of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ determined by measuring the change of the absorbancy for the samples after they are heated in the Abderhalden apparatus for various time intervals obeys the first order law, it is given by the following equation.

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

where a and x are the initial amount of the starting complex and the amount of *cis*-form complex produced during t irrespective of whether it is a hydrate or an anhydride, respectively, and k_i is the rate constant of isomerization.

When the values of $\log(a-x)$ calculated for *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ versus t were plotted at each constant temperature described in the experimental section, the approximately linear relationships were obtained, which are shown in Fig. 3. The rate constants k_i at each temperature were obtained from the slope of the respective lines. Their values are listed in Table 1, together with those of dehydration and dehydrobromination obtained in the later section. From the Arrhenius plots for the rate constant, the activation energy E_a^i was evaluated to be 28 kcal mol^{-1}.

Rate of dehydration and dehydrobromination

If the dehydration and dehydrobromination proceed also in the first order, the

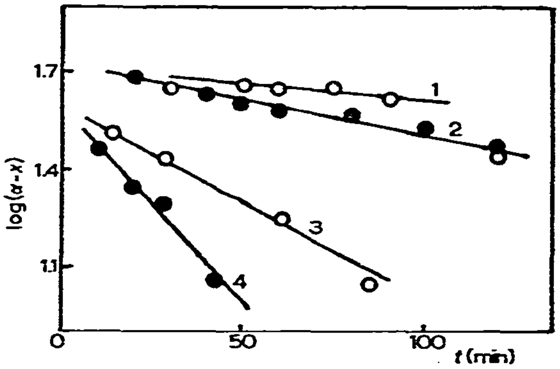


Fig. 3. Relation of log $(a-x)$ vs. time for the isomerization. 1 = 90 °C; 2 = 98 °C; 3 = 110 °C; 4 = 117 °C.

TABLE 1

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

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

rate should be expressed by the following equation analogous to eqn (1),

$$2.303 \log \frac{a}{a-x} = k_d t \qquad (2)$$

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

When the values of $\log a/(a-x)$ versus t were plotted at each temperature desired in the Experimental section, the approximately straight lines, which are shown in Fig. 4, were obtained. The rate constants k_d obtained from the slope of these lines are also listed in Table 1 together with those of isomerization. The activation energy E_a^d was calculated to be 28 kcal mol^{-1} from the Arrhenius plots.

Change of chemical composition with time

The isomerization ratios are plotted against the dehydration and dehydrobromination ratios in Fig. 5. Two characteristic features are found in this figure. The first is that the rate of isomerization remarkably exceeds that of dehydration and dehydrohalogenation in the earlier step of reaction, differing from the case of *trans*-

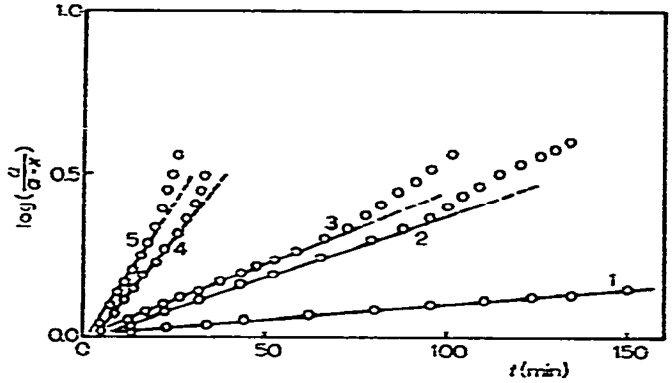


Fig. 4. Relation of log $a/(a-x)$ vs. time for the dehydration and dehydrobromination. 1 = 100 °C; 2 = 111 °C; 3 = 117 °C; 4 = 130 °C; 5 = 139 °C.

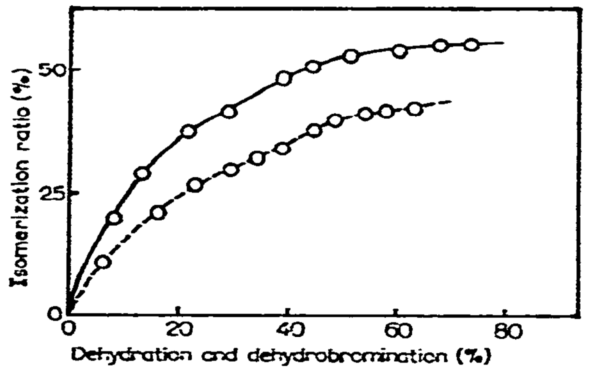


Fig. 5. Relation of isomerization ratio vs. dehydration and dehydrobromination ratio at 110 °C (— — —) and 117 °C (———).

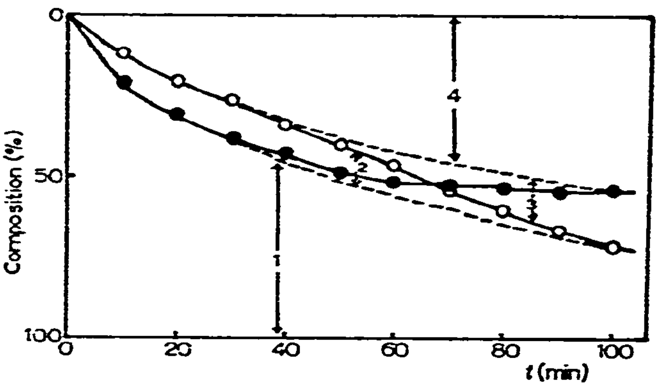


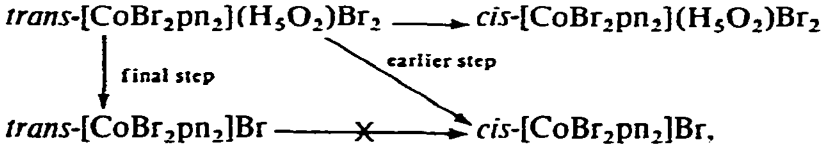
Fig. 6. Change of chemical composition in percentage in the thermochemical reaction of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ at 117 °C. (○——○), rate of dehydration and dehydrobromination; (●——●), rate of isomerization. 1 = presence ratio of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$; 2 = that of the corresponding *cis*-form complex; 3 = that of *trans*-$[CoBr_2pn_2]Br$; 4 = that of the corresponding *cis*-form complex.

$[CoCl_2pn_2](H_5O_2)Cl_2$ where the rate of isomerization is smaller than or is equal at most to that of dehydration and dehydrohalogenation. The second is that the isomerization becomes slower as the reaction proceeds and, as a result, it is not completed even upon heating at 130°C, although, in *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, the degree of isomerization increased with temperature until it goes up to 100% at 180°C.

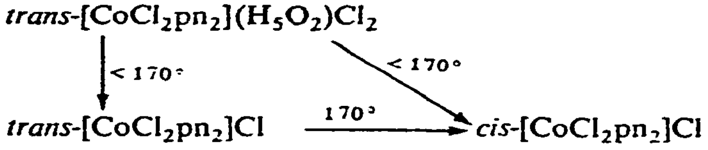
Although the rate of isomerization obeys the first order law in the earlier step, it gradually deviates from the law with time. This deviation is considered to arise from the fact that, as the reaction proceeds, it does not only contain the isomerization of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ to the corresponding hydrated *cis*-form complex but also the isomerization of the anhydrous *trans*-form complex to the *cis*-form.

On the basis of the inspection described above, the change of the chemical compositions in the thermal reaction product with time can be evaluated. The change in percentage at 117°C is depicted diagrammatically in Fig. 6.

The pathway of the *trans*-to-*cis* isomerization of $[CoBr_2pn_2](H_5O_2)Br_2$ can be deduced from Fig. 6. The reaction scheme is as follows:



being compared with that of *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$.



The striking features in the isomerization of *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ differing from that of the corresponding chloro complex, *trans*-$[CoCl_2pn_2](H_5O_2)Cl_2$, are, as seen in the scheme, that the hydrated *cis*-form complex is formed from *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ without dehydration and dehydrobromination and the anhydrous *trans*-form complex, once produced, can never be isomerized to the corresponding *cis*-form, *trans*-$[CoBr_2pn_2](H_5O_2)Br_2$ being, therefore, not isomerized completely as a final result.

REFERENCES

1 H. E. LeMay, Jr. and L. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 89 (1967) 5577.
2 H. E. LeMay, Jr., *Inorg. Chem.*, 10 (1971) 1990.
3 R. Tsuchiya, K. Murai, A. Uehara and E. Kyuno, *Bull. Chem. Soc. Japan*, 43 (1970) 1383.
4 R. Tsuchiya, Y. Nakata and E. Kyuno, *Bull. Chem. Soc. Japan*, 44 (1971) 705.
5 R. Tsuchiya, M. Suzuki and E. Kyuno, *Bull. Chem. Soc. Japan*, 44 (1971) 709.
6 R. Tsuchiya, M. Suzuki and E. Kyuno, *Bull. Chem. Soc. Japan*, 45 (1972) 1065.