Thermochimica Acta, 77 (1984) 251–257
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A POSSIBLE MECHANISM FOR THE REACTION BETWEEN HEXAAMMINECHROMIUM(III) NITRATE AND L-ALANINE IN THE SOLID STATE

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(Received 13 January 1984)

ABSTRACT

A possible mechanism for the solid-state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-alanine is given. The overall reaction, on the basis of this mechanism, is

$$[Cr(NH_3)_6](NO_3)_3 + 3\ \text{alanine} \rightarrow [Cr(ala)_3] + 3\ NH_4NO_3 + 3\ NH_3$$

The thermal behaviour of the solid-state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-leucine is also discussed, which is different from the above reaction; however, a possible mechanism for the leucine system is similar to the alanine one.

INTRODUCTION

Many solid-state reactions have been utilized for the preparation of chromium(III) complexes. However, a possible mechanism for the preparation of these complexes by a thermal reaction in the solid state is rarely proposed, except for *cis*-$[CrX_2(en)_2]X$ ($X^- =$ F, Cl, Br and NCS) which has been reported by Wendlandt and Sveum [1].

In a previous communication [2], the solid-state reaction between $[Cr(NH_3)_6]X_3$ ($X^- =$ Cl, I, NCS and NO_3) and L-alanine has been reported. For the synthesis of $[Cr(ala)_3]$ the most desirable starting complex was $[Cr(NH_3)_6](NO_3)_3$.

In this communication, a possible mechanism for the solid-state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-alanine is discussed. The thermal behaviour of the solid-state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-leucine is shown to be different from that of the above reaction.

EXPERIMENTAL

Preparation of the complexes

Hexaamminechromium(III) nitrate, $[Cr(NH_3)_6](NO_3)_3$, was prepared by the usual method given in the literature [3].

$[Cr(NH_3)_6](NO_3)_3$ (0.001 M) and L-alanine (0.003 M) were mixed in a mortar in order to allow the solid-state reaction to proceed. In the case of L-leucine, a similar method to the above was used.

Continuous temperature-rise measurement

The measurement of the rise in temperature was carried out with a Metripex derivatograph (model OD-102) and a Yamato Scientific Instrument FCN 3 electric furnace. Derivatographic measurement was made in a nitrogen stream at a heating rate of 1°C min^{-1}. The samples were removed from the electric furnace at various temperatures at a heating rate of > 1.4°C min^{-1}.

Apparatus

The electronic absorption spectra were measured with a Hitachi 139 spectrophotometer. The IR spectra were measured in a KBr disk with a Hitachi EPI-G3 infrared spectrophotometer. The CD spectra were recorded with a JASCO spectrophotometer (model ORD/UV-5) with a CD attachment.

RESULTS AND DISCUSSION

The derivatogram of the mixture of hexaamminechromium(III) nitrate and L-alanine is given in Fig. 1. The TG curve gives a rapid weight loss at 130–150°C and a slow one at 150–190°C. These correspond to the liberation of 8–9% and 4–5% ammonia, respectively. The DTA curve gives three endothermic and two exothermic peaks. The first endothermic peak corresponds to the melting of the mixture, the second and third correspond to the liberation of ammonia. However, the reaction corresponding to the first exothermic peak at 130°C is not clear in the present work. The second exothermic peak corresponds to the burning of the mixture.

In order to follow the sequence of the reaction, the reaction mixtures were removed from the electric furnace at 113, 130 and 170°C, on the basis of the characteristics of the derivatogram in Fig. 1. The reaction products were added to acetone. After filtration, the filtrate was evaporated to dryness. When the reaction mixtures were removed at temperatures lower than 113°C, the crystals obtained after evaporation were alanine nitrate. In the case of a reaction temperature of 130–170°C, only ammonium nitrate was obtained. At 113–130°C, the products were a mixture of alanine nitrate and ammonium nitrate. It should be noted that the formation of ammonium nitrate occurred in preference to the liberation of ammonia. Alanine nitrate was confirmed by elemental analysis and the IR spectrum. Found (%): C,

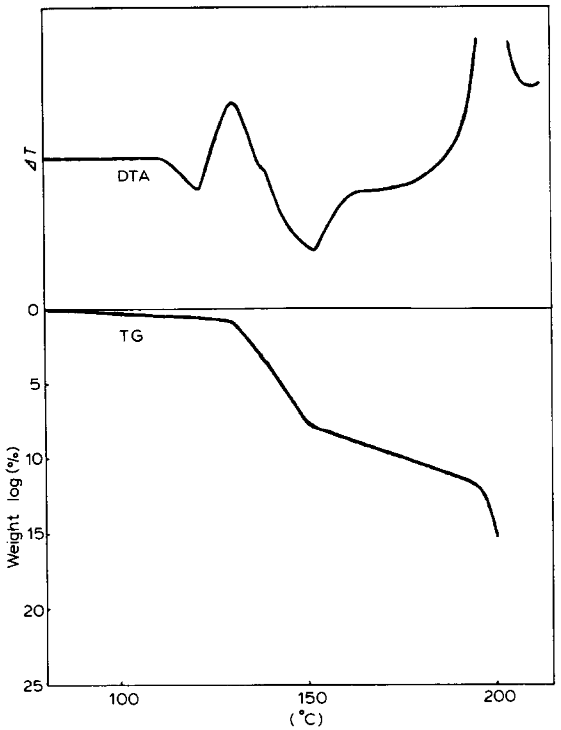

Fig. 1. The derivatogram of the mixture of $[Cr(NH_3)_6](NO_3)_3$ and L-alanine.

23.74; H, 5.29; N, 18.48. Calcd. for $C_3H_8N_2O_5$ (alanine nitrate, %): C, 23.69; H, 5.30; N, 18.42. Ammonium nitrate was confirmed by the IR spectrum.

The colour of the reaction mixture at 113, 130 and 170°C was yellowish brown, brown and reddish purple, respectively. Ramasami et al. [4] reported that pentaammineglycinatochromium(III) perchlorate was orange and soluble in methanol. The yellowish brown and brown products were dissolved in water and when perchloric acid was added to the solution, yellow crystals were instantly deposited. The crystals consisted entirely of $[Cr(NH_3)_6](ClO_4)_3$ and the solution, on filtration, was reddish purple. Therefore, the colours of reaction products at 113 and 130°C are those of a mixture of the starting material, and the other product which is reddish purple, respectively. The formation of the (alaninato-*O*)pentaamminechromium(III) complex has not been confirmed.

To analyse the components of the solution, the reddish purple product (170°C) was placed on an ion-exchange column (Dowex 50W X2, Na^+ type). First, the reddish purple material was eluted with water (elution No. 1), the second elution was with 0.5 N NaCl (elution No. 2). A reddish brown material remained at the top of the column at this stage. This material was eluted with 2 N NaCl. The reddish brown material might be a mixture of the starting material with another product obtained by aquation.

The complex of elution No. 1 must be a neutral one, because this complex was eluted with water. Therefore, the ratio of alanine to chromium was 3 : 1. The determination of ammine nitrogen/chromium ratio using JIS G 1228-1968 (ammine) and colorimetric analysis (chromium) gave a ratio of 1.2 : 1. This solution gave a UV spectrum with peaks at 514 and 389 nm. The final product by the matrix method was only a fac-isomer of the tris-type. It can be assumed that the coordinating structure of the complex is *cis*(O)–*cis*(N)-$[Cr(ala)_2(ala\text{-}O)NH_3]$. This type of complex was also obtained by the thermal matrix method between hexaamminechromium(III) nitrate and L-valine or L-isoleucine [5]. Therefore, it seems reasonable to assume that the structure of the complex of elution No. 1 is the above structure.

The solution of elution No. 2 must contain a +1 type complex, because this was eluted together with the NH_4^+ ion-containing ammine nitrate. Therefore, the determination of the nitrogen/chromium ratio has not been performed. However, the determination of the total carbon/chromium ratio using elemental (carbon) and colorimetric (chromium) analysis gave the ratio 6.6 : 1, i.e., the alanine/chromium ratio was 2 : 1. The CD spectrum of this solution was measured to determine whether the alaninato ligand was coordinated as a monodentate or bidentate ligand. The $\Delta_{(ext)}$ was -0.57 (460 nm). This value was consistent with that of the component of elution No. 1 [$\Delta_{(ext)} = -0.59$ (480 nm)]. Therefore, it seems reasonable to assume that two alaninato molecules are coordinated to chromium as a bidentate ligand. The solution of elution No. 2 gave a spectrum with peaks at 512 and 369 nm. The peak showed a blue shift with a lapse of time. The shift might be due to aquation. With reference to the structure of elution No. 1, it can be assumed that the coordinating structure of elution No. 2 is the *cis*(O)–*cis*(N)–*cis*(NH_3)-$[Cr(ala)_2(NH_3)_2]^+$ ion.

Alanine nitrate was obtained on mixing $[Cr(NH_3)_6](NO_3)_3$ with alanine in a mortar at room temperature. Therefore, it can be presumed that the NO_3^- ion, which is weakly bonded to ammonia by a hydrogen bond, is transformed to NH_3^+ in alanine.

The possible mechanism for this reaction, on the basis of the above discussion, is shown in Fig. 2. In the first step of the reaction, the alanine nitrate anion is formed. The alanine nitrate anion dissociates into an alanine anion and hydrogen nitrate (Fig. 2a). The next step of the reaction might be the protonation of an ammonia nitrogen followed by the production of NH_4NO_3 and the formation of the bond of the alanine anion to the hexaamminechromium(III) complex. This mechanism is similar to that of the solid-state reaction between $[Cr(en)_3]X_3$ and NH_4Y, except that alanine nitrate dissociates instead of NH_4Y [1].

The pentaammine(alaninato-*O*)chromium(III) complex was not observed as described above. However, the probability of the formation of the tetraammine-bis(alaninato-*O*) complex (**I**), as intermediate substance is undoubtedly high and probably plays a role in the postulated step. Therefore,

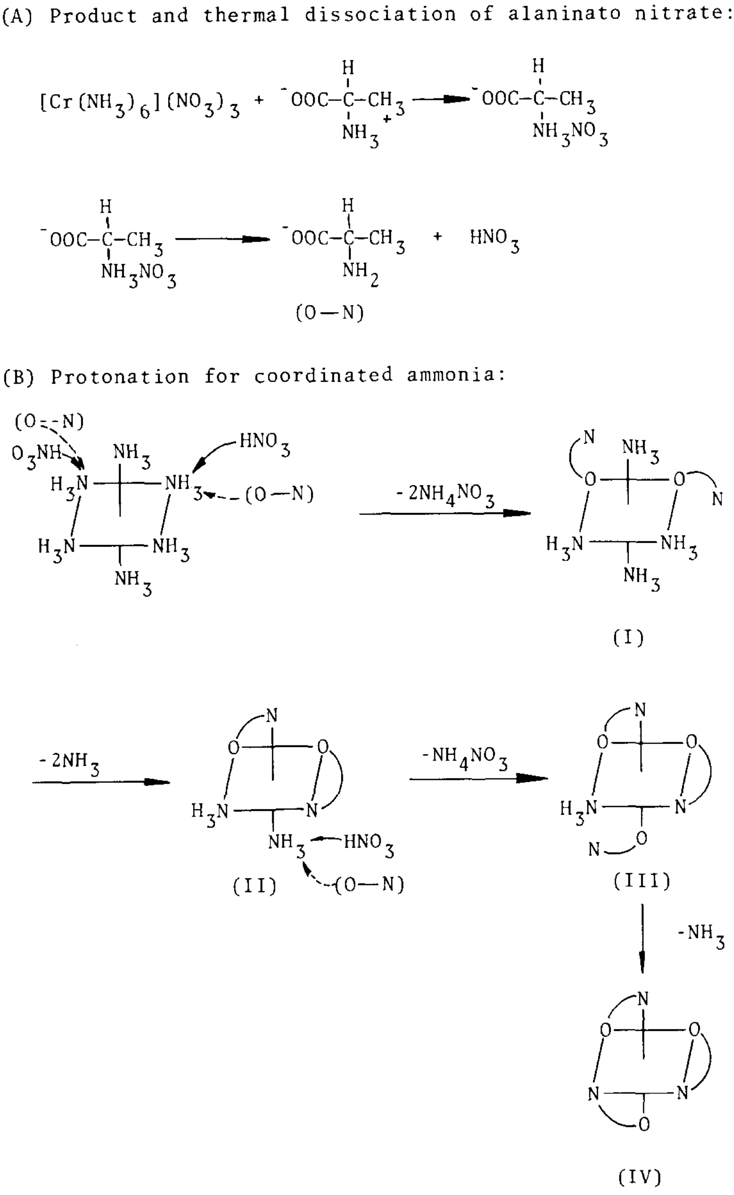

Fig. 2. A possible mechanism for the solid-state reaction between $[Cr(NH_3)_6](NO_3)_3$ and L-alanine.

the formation of NH_4NO_3 occurred in preference to the liberation of 2 NH_3 as described above.

The next step of the reaction might be the liberation of 2 NH_3 followed by the production of the diamminebis(alaninato)chromium(III) complex (**III**). Parallel to this reaction, the reaction which produced NH_4NO_3 and $[Cr(ala)_2(ala\text{-}O)NH_3]$ (**III**), probably occurred. The final step of the reaction might be the liberation of NH_3 followed by the production of $[Cr(ala)_3]$ (**IV**). The tris(alaninato)chromium(III) complex obtained in this reaction had Λ-configuration [5]. However, complexes (**II**) and (**III**) in the intermediate step of the reaction consist of a mixture of diastereoisomers as described above. The reason why only fac-Λ-$[Cr(ala)_3]$ was produced is not clear in the present work.

The overall reaction, on the basis of this mechanism, is

$$[Cr(NH_3)_6](NO_3)_3 + 3\ \text{L-alanine} \rightarrow [Cr(\text{L-ala})_3] + 3\ NH_4NO_3 + 3\ NH_3$$

In the case of L-leucine, the derivatogram of $[Cr(NH_3)_6](NO_3)_3$ and L-leucine is shown in Fig. 3. The DTA curve of the mixture is similar to that of $[Cr(NH_3)_6](NO_3)_3$ [2]. No peak due to the melting is found and the sample burns at 170°C. The TG curve of the mixture shows a distinct plateau up to 170°C. Therefore, it is evident that this reaction consists only of decomposition. A pale pink product was obtained at 150°C, which was not, however, a tris-type complex. This pale pink product was soluble in water or alcohol. The yield of this product was low and the majority of the starting material remained. However, the reaction product was dissolved in acetone. After removal of the residue by filtration, the filtrate was evaporated to dryness, and leucine nitrate and ammonium nitrate were obtained. There-

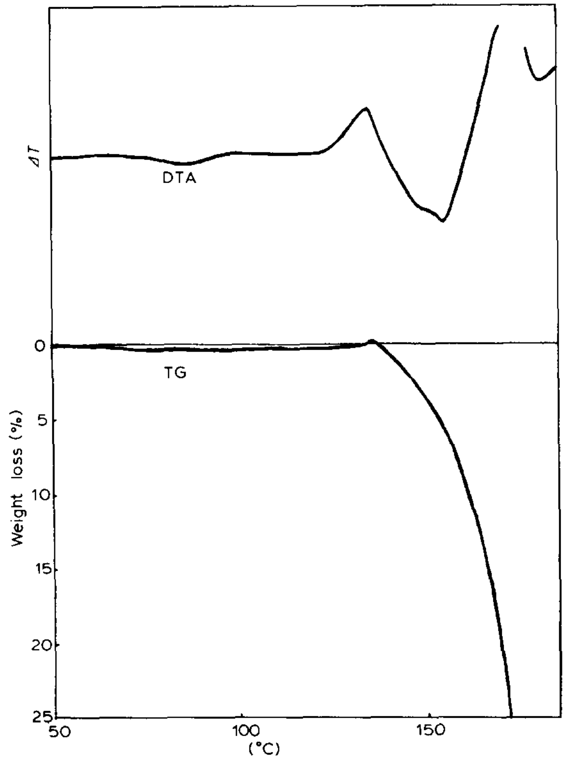

Fig. 3. The derivatogram of the mixture of $[Cr(NH_3)_6](NO_3)_3$ and L-leucine.

fore, the reaction mechanism of L-leucine is similar to that of L-alanine. The structure of the pale pink product, which dissolves in alcohol, may correspond to (**I**) in Fig. 2, that is, $[Cr(leu\text{-}O)_2(NH_3)_4]^+$, as the endothermic peak and the weight loss correspond to the liberation of ammonia in Fig. 3. The tris-type complexes with L-leucine were obtained when the reaction products of the isothermal reaction (heating time, 15 min; 150°C) were extracted in ethanol and the solution was kept at room temperature for 1 week [5]. Leucine nitrate was also dissolved in ethanol and the reaction of $[Cr(leu\text{-}O)_2(NH_3)_4]^+$ and leucine nitrate was carried out in ethanol solution. However, the reason why only the fac-Δ-$[Cr(leu)_3]$ was produced is not clear in the present work.

The reason why the thermal behaviour of leucine is different from that of alanine is probably because the side chain of alanine is smaller than that of leucine. The voluminous leucine molecules do not move smoothly in the solid state and the reaction was stopped at an intermediate step. However, in the case of alanine, the solid-state reaction proceeds smoothly, and a tris-type complex is obtained.

ACKNOWLEDGEMENTS

The authors thank Dr. Akira Urhara of Kanazawa University for derivatogram measurements and Professor Ryokichi Tsuchiya of Kanazawa University for valuable discussion and suggestions.

REFERENCES

1 W.W. Wendlandt and L.K. Sveum, J. Inorg. Nucl. Chem., 28 (1966) 575.
2 H. Oki, Thermochim. Acta, 31 (1979) 55.
3 M. Mori, Nippon Kagaku Zasshi, 74 (1953) 253.
4 T. Ramasami, K.K. Wharton and A.G. Sykes, Inorg. Chem., 14 (1975) 359.
5 H. Oki, Bull. Chem. Soc. Jpn., 50 (1977) 680.