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SOLID-PHASE THERMAL S_E REACTION OF METAL COMPLEXES

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A new type of solid-phase thermal reaction of metal complexes was found with $[Cr(NH_3)_6][Al(ox)_3]$ and $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ by means of derivatography. Both the complexes were found to convert finally into $Al[Cr(ox)_3]$. The reaction is differentiated from prior thermal S_N reaction of metal complexes in respect to the involvement of metal substitution.

There have been many studies on the thermal reactions of metal complexes in a solid-phase. Thermal reactions which appeared in past publications can be conventionally classified into Dissociation,[1] Substitution,[2] Polymerization,[3] Configurational Transformation,[4] Isomerization,[5] and Racemization.[6] These belong to the type of S_N reaction.

We have been seeking the metal complexes which display a new thermal reaction as formulated in the following scheme.

$$M'[M\ Ln] \xrightarrow[\Delta]{} M[M'\ Ln]$$

In the scheme, M' and M denote different metal ions, and Ln means n coordinated ligands. The reaction may be called "Thermal S_E Reaction" since it involves the substitution of metal ions upon heating.

The discovery of such a reaction in a solid-phase would develop a new field not only in the area of the solid-phase thermal reactions of metal complexes but also in the coordination chemistry. Recently, we succeeded in discovering the first examples which exhibit a reaction similar to that described above.

Preparation of Model Complexes. The complexes which fulfill our purpose have to satisfy at least the following requirements; first of all there must be indicators (e. g., distinct color change or other changes in properties) which verify the occurrence of the new thermal reaction under consideration, secondly the stability of ligands toward both metal ions is adequately fitted from preparative standpoint, and thirdly other complicated reactions such as electron transfer are not involved in the reaction. The following two complexes were found to satisfy these requirements.

1) Hexaamminechromium(III) Tri(oxalato)aluminum(III), $[Cr(NH_3)_6][Al(ox)_3]$ (yellow). Three and four tenth grams (0.01 mol) of $[Cr(NH_3)_6](NO_3)_3$ and 4.6 g (0.01 mol) of $K_3[Al(ox)_3]\cdot 3H_2O$ were dissolved separately in about 200 ml of water and then these two solutions were mixed. In this step, care should be taken to avoid the rapid formation of precipitate, or otherwise undesirable components such as $K_3[Al(ox)_3]\cdot 3H_2O$ frequently coprecipitate. After the wall of the container had been scratched with a glass rod, the resulting solution was allowed to stand in a refrigerator for 1 or 2 days. Yellow rectangular crystals were obtained, and could not be recrystallized because no optimum solvent was found. However, if the starting materials were recrystallized prior to the preparation of the desired complex, the complex obtained was of high purity as evidenced from the analytical results. Found: C, 17.2; H, 4.5; N, 20.2 %. Calcd for $[Cr(NH_3)_6][Al(ox)_3]$: C, 17.3; H, 4.3; N, 20.2 %.

2) Aquopentaamminechromium(III) Tri(oxalato)aluminum(III), $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ (orange). The complex was prepared by a procedure similar to that for the above complex except that 3.4 g (0.01 mol) of $[Cr(H_2O)(NH_3)_5](NO_3)_3$ was used in place of $[Cr(NH_3)_6](NO_3)_3$. Orange crystals were obtained and could not be recrystallized too, but the crystals were satisfactorily pure. Found: C, 17.6; H, 4.3; N, 16.5 %. Calcd for $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$: C, 17.3; H, 4.1; N, 16.8 %.

Observation on Thermal Reaction Processes. The thermal reaction processes of the complexes were measured by means of derivatography under the heating rate of 2°C/min in a nitrogen stream. Four hundred milligrams of sample was used in each run. As seen from the TG curves in Fig. 1, $[Cr(NH_3)_6][Al(ox)_3]$ evolves 6 moles of NH_3 at 110——150°C, at which stage the original yellow complex changes to green product. In contrast to the simplicity of the TG curve, both the DTA and DTG curves show split peaks. This implys that all of the coordinated ammonia molecules are not liberated in a single step, but in a few separate steps.7)

On the other hand, $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ evolves first 4 moles of NH_3 at 50——100°C, and then H_2O and NH_3 at 140——150°C. The color of the complex successively changes from orange to pink and finally to green.

The green products obtained in the thermal reaction processes of both the complexes were dissolved in water, and recrystallized. Analyses showed that the green products contain 19.5 % of carbon, 0.8 % of hydrogen and none of nitrogen, whereas the calculated values of carbon and hydrogen for $Al[Cr(ox)_3]\cdot H_2O$ are 20.0 and 0.5 %, respectively.

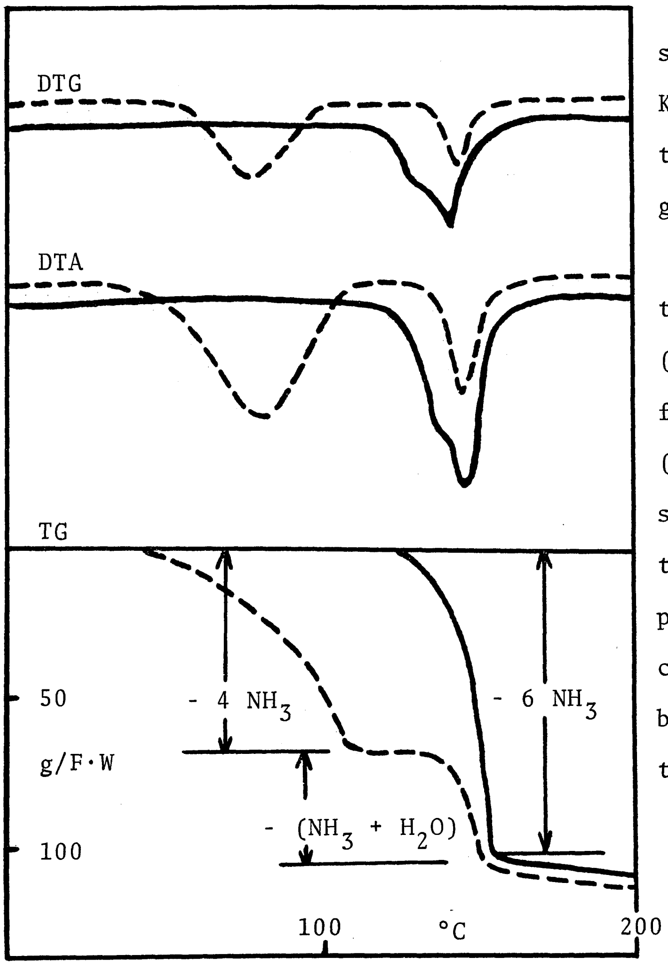


Fig. 1 Derivatograms of $[Cr(NH_3)_6][Al(ox)_3]$ (———) and $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ (— — —).

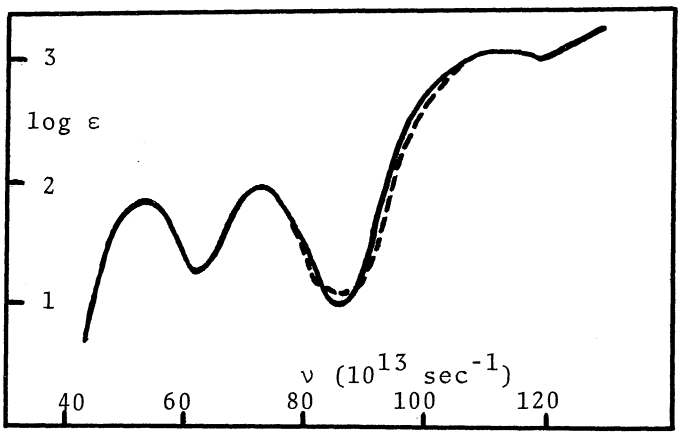


Fig. 2 Electronic spectra of $K_3[Cr(ox)_3]\cdot3H_2O$ (———) and both the green products (------).

Figure 2 shows the electronic spectra of both the green products and $K_3[Cr(ox)_3]\cdot3H_2O$. Resemblance among these spectra suggests that both the green products consist of $[Cr(ox)_3]^{3-}$.

The pink product obtained in the thermal reaction process of $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ was recrystallized from a mixture of 60% $HClO_4$ and DMF (1 : 1). Figure 3 contains the IR spectra of the original orange complex, the pink product and both the green products in the region of 3600——2800 cm^{-1}. As seen from the figure, the band due to the -NH stretching vibration (3500——3100 cm^{-1}) can be detected

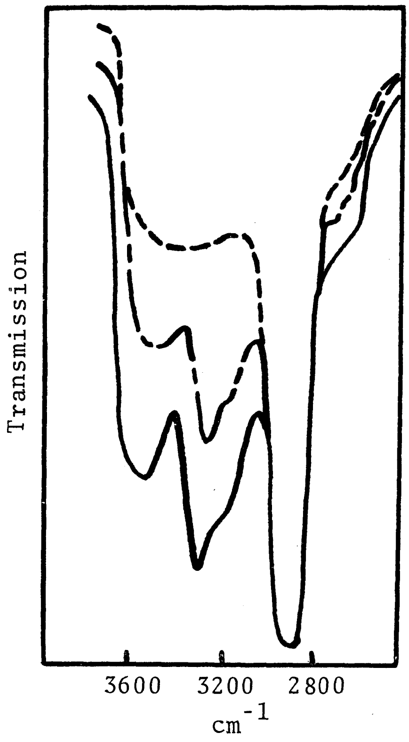


Fig. 3 IR spectra of $[Cr(H_2O)(NH_3)_5][Al(ox)_3]$ (———), the pink product (— — —), and both the green product (------).

in the original yellow complex and the pink product, but not in the green products. This indicates that the pink product contains NH_3, but the green product does not. The analytical results of the pink product were 18.9 (19.0) % of carbon, 1.1 (1.3) % of hydrogen and 3.8 (3.7) % of nitrogen, where the numerical values in each parenthesis are those calculated for $[(H_2O)(NH_3)\ Cr(ox)_2Al\ (ox)]$.

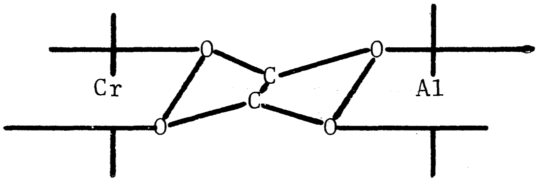
Proposed Thermal Reaction Process. On the basis of the above results, the thermal reaction processes of both the complexes can be expressed in the following equations.

$$[Cr(NH_3)_6][Al(ox)_3] \xrightarrow[-\ 6\ NH_3]{} Al[Cr(ox)_3] \qquad (\ I\ )$$

$$[Cr(H_2O)(NH_3)_5][Al(ox)_3] \xrightarrow[-\ 4\ NH_3]{} (\ [(H_2O)(NH_3)\ Cr(ox)_2Al\ (ox)]\ )$$

$$\xrightarrow[-(H_2O\ +\ NH_3)]{} Al[Cr(ox)_3] \qquad (\ II\ )$$

Since there still remains the questions whether or not the pink product may be polymers such as dimer, trimer and so on, $[(H_2O)(NH_3)\ Cr(ox)_2Al\ (ox)]$ in equation II is parenthesized. The reaction expressed as above is quite different from prior thermal reactions of metal complexes in respect to the involvement of metal substitution. Such substitution is probably due to the fact that the oxalate ions originally coordinated to Al(III) ion move to Cr(III) ion via the formation-step of transient tetradentate oxalate bridge as shown below.



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