The Thermal Decomposition of Ammonium Chloride Tetrachlorozincate and the Formation of Tetrachlorozincate Complexes of Alkali Metal by Means of Solid Reactions with Alkali Chlorides

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(Received April 14, 1980)

Ammonium chloride tetrachlorozincate, $(NH_4)_3Cl[ZnCl_4]$, decomposes to $ZnCl_2$ in two stages through an intermediate phase $(NH_4)_2[ZnCl_4]$. In the first stage, 1 mol of NH_4Cl is lost by one-dimensional diffusion mechanisms with the activation energy of 138 kJ mol^{-1}, and in the second stage the release of two moles of NH_4Cl is controlled by a random nucleation reaction with the activation energy of 126 kJ mol^{-1}, corresponding to the bond-breaking. Anhydrous alkali metal tetrachlorozincate complexes, $M_2[ZnCl_4]$(M=Na, K, Rb, Cs), are obtained by solid reactions with alkali chlorides when $(NH_4)_3Cl[ZnCl_4]$ decomposes. A dry chemical method using $(NH_4)_3Cl[ZnCl_4]$ as a starting material is proposed for the preparation of the anhydrous chlorozincate complexes, which have thus far been difficult to synthesize.

Ammonium chloride tetrachlorozincate, $(NH_4)_3Cl[ZnCl_4]$, is known to decompose to zinc chloride upon heating.[1] However, the mechanisms and kinetics of the thermal decomposition are not well understood. In this study, the mechanisms and kinetics of the decomposition were examined by thermogravimetry (TG), differential scanning calorimetry (DSC), and X-ray diffraction.

The solid reaction which took place in the mixtures of $(NH_4)_3Cl[ZnCl_4]$ and MCl (M=Na, K, Rb, Cs) simultaneously when $(NH_4)_3Cl[ZnCl_4]$ decomposed was also studied by TG, DSC, and X-ray diffraction. The products are interesting because the preparation of the anhydrous chlorozincate complexes is difficult on account of the deliquescence of $ZnCl_2$ and hydrolysis in water, and the anhydrous complexes have yet to be examined. That is, the stereochemistry of the chlorozincate complexes is not obvious other than that of the tetrahedral anion $[ZnCl_4]^{2-}$, though a number of other halogenozincate complexes, such as fluorozincate complexes, $M^{I}ZnX_3$, $M^{I}_2ZnX_4$, $M^{I}_3ZnX_5$, and $M^{I}_4ZnX_6$, have been reported.[2]

Experimental

Materials. Ammonium chloride tetrachlorozincate was prepared by a published method.[3] Commercial alkali chlorides were used without further purification. The samples for the solid reaction were prepared by mixing alkali chloride and $(NH_4)_3Cl[ZnCl_4]$ in a 2 : 1 molar ratio in an agate mortar in a nitrogen atomosphere. For the X-ray diffraction measurements, the samples were prepared by heating pure $(NH_4)_3Cl[ZnCl_4]$ or the mixture powder in a furnace with a nitrogen gas flow for two hours at the temperature where the reaction occurs in the DSC curve.

Measurements. The TG and DSC curves were recorded simultaneously using a Rigaku Thermoflex TG–DSC M8085 by heating the sample in flowing nitrogen gas at a rate of 2 K min^{-1}. About a 10-mg of the sample was placed in a platinum crucible, and α-alumina was used as the reference material. The TG curves were analysed by the method of Šatava and Škvára[4] to obtain the parameters of the reaction mechanisms and kinetics.

Results and Discussion

Thermal Decomposition of $(NH_4)_3Cl[ZnCl_4]$. The TG-DSC curves of $(NH_4)_3Cl[ZnCl_4]$ are shown in Fig. 1. $(NH_4)_3Cl[ZnCl_4]$ decomposed to $ZnCl_2$ in two stages. From the weight loss, the stages are confirmed as:

$$(NH_4)_3Cl[ZnCl_4](s) \longrightarrow (NH_4)_2[ZnCl_4](s) + NH_4Cl(g) \quad (1)$$

$$(NH_4)_2[ZnCl_4](s) \longrightarrow ZnCl_2(s) + 2NH_4Cl(g). \quad (2)$$

The existence of $(NH_4)_2[ZnCl_4]$ as an intermediate phase was also confirmed by X-ray diffraction. The endothermic peak at 313 °C corresponded to the

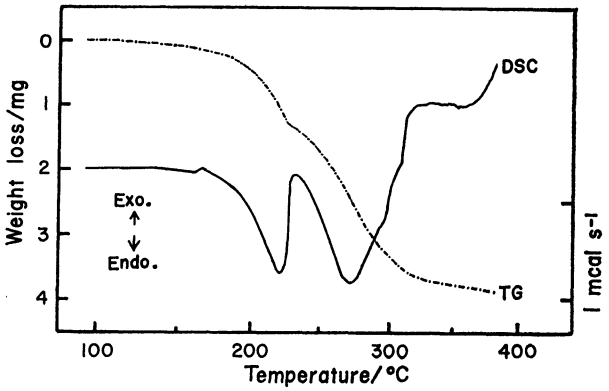

Fig. 1. TG–DSC curves of $(NH_4)_3Cl[ZnCl_4]$. Sample weight: 6.38 mg.

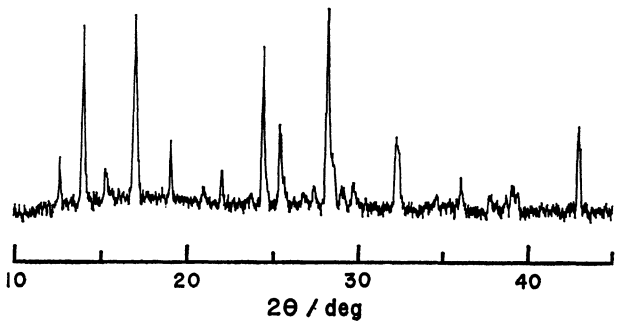

Fig. 2. X-Ray diffraction pattern of $ZnCl_2$ produced by thermal decomposition of $(NH_4)_3Cl[ZnCl_4]$.

melting point of $ZnCl_2$. The $ZnCl_2$ produced was mainly in the β-form, but containing a small amount of α-form, as determined by X-ray diffraction (Fig. 2). The compositions of the two forms changed according to the cooling conditions: the α-form is obtained by the rapid cooling of the melt, and the β-form, by the slow cooling.

The decomposition reaction mechanisms and kinetic parameters are deduced from the TG curve by the method of Šatava and Škvára. This method was used because it allows a fairely quick estimation of the parameters.

The thermogravimetric curve of a decomposition reaction can be expressed by this equation: $\log g(\alpha) - \log p(x) = B$. In this equation, the $g(\alpha)$ function requires a knowledge of the reaction mechanism and can be calculated from the experimental data of α, the fraction of the initial compound reacted. Šatava and Škvára gave data for $\log g(\alpha)$ which cover nine common reaction models.[4] Graphs of $\log p(x)$ can be computed for various activation energies, E, over a given range of temperature. The B values depend only upon the nature of the compound studied and upon the heating rate, not upon the temperature. A graphical comparison of the curves of both $\log g(\alpha)$ and $\log p(x)$ over the known experimental temperature range allows the reaction mechanisms and reaction parameters to be determined. The evaluation of the TG curve of the decomposition of $(NH_4)_3Cl[ZnCl_4]$ by the method of Šatava and Škvára is shown in Fig. 3 as an example. The enthalpy change for the reaction was obtained from the DSC curve.

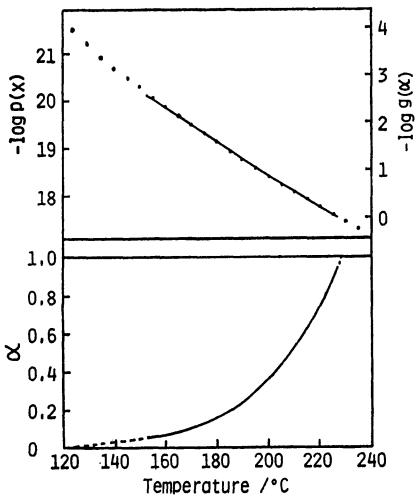

Fig. 3. The evaluation of the TG curve of the first decomposition stage of $(NH_4)_3Cl[ZnCl_4]$. The upper solid line is a plot of $-\log g(\alpha)$ *vs.* T calculated from TG curve (lower curve) for the reaction kinetic equation of one-dimensional diffusion. The dotted line is a plot of $\log p(x)$ *vs.* T for $E = 138$ kJ mol^{-1}.

The best fits between experimental and calculated thermogravimetric curves and ΔH for each stage are as follows:

The First Stage: The loss of one mole of NH_4Cl occurs through a one-dimensional diffusion process following the parabolic law ($\alpha^2 = kt$). The activation energy of the diffusion process, E, is 138 kJ mol^{-1}, the frequency factor, Z, 4.8×10^{13} s^{-1} mol$^{1/2}$, and ΔH, 85 kJ mol^{-1}.

The Second Stage: The loss of two moles of NH_4Cl is controlled by a random nucleation of one nucleus on each particle, with the activation energy of 126 kJ mol^{-1} corresponding to a bond breaking. The value of Z is 1.2×10^{11} s^{-1} mol$^{1/2}$, and that of ΔH, 134 kJ mol^{-1}.

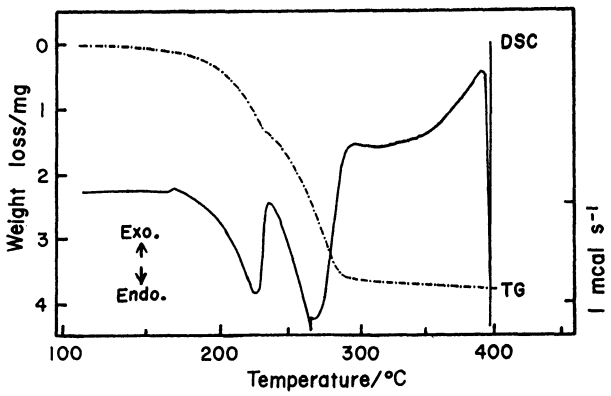

Fig. 4. TG–DSC curves of the mixture powder of $(NH_4)_3Cl[ZnCl_4]$ and NaCl with a 1 : 2 molar ratio. Sample weight: 9.31 mg.

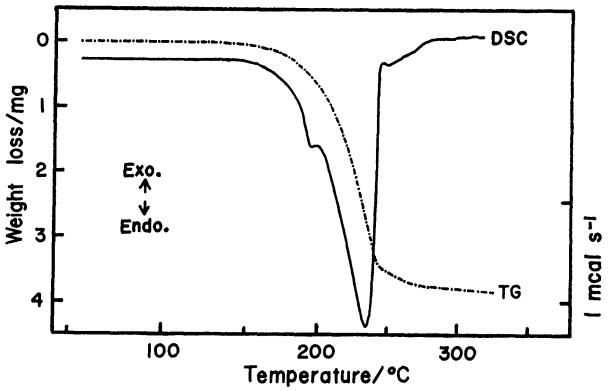

Fig. 5. TG–DSC curves of the mixture powder of $(NH_4)_3Cl[ZnCl_4]$ and CsCl with a 1 : 2 molar ratio. Sample weight: 14.36 mg.

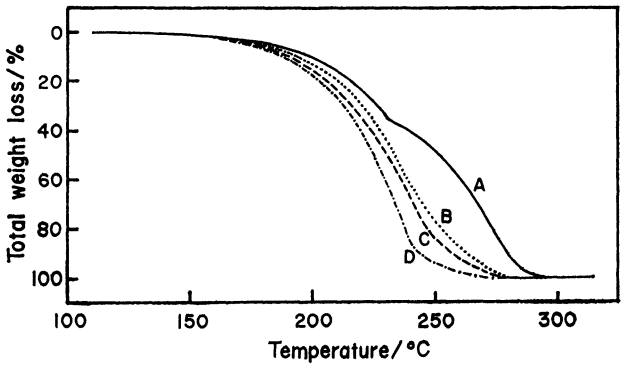

Fig. 6. Weight loss curves of the mixtures of $(NH_4)_3Cl[ZnCl_4]$ and MCl (M=Na, K, Rb, Cs) with a 1 : 2 molar ratio.
A: NaCl, B: KCl, C: RbCl, D: CsCl.

Those results are not inconsistent with the structure of $(NH_4)_3Cl[ZnCl_4]$, in which tetrahedral $[ZnCl_4]^{2-}$ ions are contained.

Solid Reaction between $(NH_4)_3Cl[ZnCl_4]$ and Alkali Chloride. A solid reaction took place between $(NH_4)_3Cl[ZnCl_4]$ and alkali chloride simultaneously when $(NH_4)_3Cl[ZnCl_4]$ decomposed upon the heating of the mixture in a 1 : 2 molar ratio. The mechanisms and kinetics of this reactions were followed in the usual way. The TG-DSC curves of the mixtures of 2NaCl–$(NH_4)_3Cl[ZnCl_4]$ and 2CsCl–$(NH_4)_3Cl[ZnCl_4]$ are shown in Figs. 4 and 5 respectively. The weight-loss curves of the mixtures of MCl (M=Na, K, Rb, Cs) and $(NH_4)_3Cl[ZnCl_4]$ with a 2 : 1 molar ratio are arranged in Fig. 6. The tail parts of the curves were sensitive to the sample properties, such as the paritcle-size distribution, and the contact condition of the reactants.

2NaCl–$(NH_4)_3Cl[ZnCl_4]$: Figure 4 shows that the reaction proceeds in two stages, in the same way as the decomposition reaction of pure $(NH_4)_3Cl[ZnCl_4]$. When the TG-DSC curves in Fig. 4 are compared with the curves in Fig. 1, the first stages of the reactions coincided with each other well, but in the second stage the loss of two moles of NH_4Cl occurs well below the temperature of the pure compound. In Fig. 1 the melting point of $ZnCl_2$ is observed at 313 °C, in accordance with the literature value, whereas in Fig. 4 a large peak is observed at 390 °C, which corresponds to the melting point of the product compound of $Na_2[ZnCl_4]$. Thus, the reaction pattern of the 2NaCl–$(NH_4)_3Cl$-$[ZnCl_4]$ mixture is as follows:

$$(NH_4)_3Cl[ZnCl_4](s) + 2NaCl(s) \longrightarrow (NH_4)_2[ZnCl_4](s) + 2NaCl(s) + NH_4Cl(g) \longrightarrow Na_2[ZnCl_4](s) + 2NH_4Cl(g) \xrightarrow{390°C} Na_2[ZnCl_4](l). \quad (3)$$

$(NH_4)_3Cl[ZnCl_4]$–2MCl (M=K, Rb, Cs): In these mixtures three moles of NH_4Cl were lost at one stage of the reaction, as is shown in Fig. 5. The reaction temperatures at which the loss of NH_4Cl occurs in these mixtures are well below the temperature of the pure compound of $(NH_4)_3Cl[ZnCl_4]$, as is shown in Fig. 6. The product of $Cs_2[ZnCl_4]$ was identified by means of X-ray diffraction. The other products were also confirmed to be $K_2[ZnCl_4]$ and $Rb_2[ZnCl_4]$, though the X-ray data were not available. The melting point of $K_2[ZnCl_4]$ was observed at 450 °C in the DSC curve.

Table 1. Mechanisms and kinetic parameters for the solid reactions between $(NH_4)_3Cl[ZnCl_4]$ and alkali chlorides

MCl	Mechanisms	E / kJ mol^{-1}	Z / s^{-1} mol$^{1/2}$	ΔH / kJ mol^{-1}	Products
KCl	One-dimensional diffusion	159	1.0×10^{15}	226	$K_2[ZnCl_4]$
RbCl	One-dimensional diffusion	159	1.7×10^{15}	231	$Rb_2[ZnCl_4]$
CsCl	One-dimensional diffusion	159	1.8×10^{15}	263	$Cs_2[ZnCl_4]$

The reaction mechanisms and kinetic parameters derived from the TG curves are shown in Table 1, along with the values of ΔH. These results show that the reaction pattern in these mixtures is as follows:

$$(NH_4)_3Cl[ZnCl_4](s) + 2MCl(s) \longrightarrow M_2[ZnCl_4](s) + 3NH_4Cl(g). \quad (4)$$

The mechanisms exhibit one-dimensional diffusion, so that the alkali chloride diffuses over the surface of the $(NH_4)_3Cl[ZnCl_4]$ particles prior to the formation of alkali metal tetrachlorozincate. No difference in the values of the activation energy was distinguished in those mixtures, but the reaction temperatures fall in accordance with the lattice energy of the alkali chlorides, as is shown in Fig. 6. The values of ΔH, as estimated from the DSC curves, changed considerably with the ending part of the curves. However, the values of ΔH were much larger than the values of the activation energy. This disagreement between ΔH and E seems to be ascribable to the contributions to ΔH from the fast reaction stages other than the rate-controlling diffusion process.

A solid reaction which occurs simultaneously when $(NH_4)_3Cl[ZnCl_4]$ decomposes is proposed for the synthesis of the other chlorozincate complexes.

References

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