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THE THERMAL TRANSFORMATIONS IN $Zn(NO_3)_2$–H_2O (1:6) SYSTEM

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Abstract

Using thermal analysis as well as isothermal gravimetric measurements, the thermal stability of the zinc nitrate(V) hexahydrate has been determined. Some intermediate products are the results of melting, evaporation, hydrolysis, polycondensation and decomposition processes occurring in the salt – water system up to 300°C. Solid phases were characterized by means of chemical analyses and X-ray powder diffraction method.

Keywords: decomposition, dehydration, hydrates, hydrolysis, isothermal gravimetry, melting, polycondensation, thermal analysis, zinc nitrate(V)

Introduction

Crystalline hydrated salts are a numerous group of inorganic compounds. Knowledge of their thermal stability is the essential phenomenon in the field of solid-state chemistry. There is a strong connection between the thermal stability and the reactivity of a given substance, e.g. [1–3].

Visual observations of the crystallohydrates during their heating can provide us with valuable information. Knowledge of solubility of anhydrous salts is also important for proper interpretation of the results of thermal decomposition of hydrated salts while the results of the analysis of gaseous products of the decomposition using e.g. TG-MS, TG-FTIR methods are always very useful.

This paper presents an attempt of a more complete interpretation of the phenomena occurring during heating of inorganic crystallohydrates exemplified by the zinc nitrate(V) hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$.

The thermal stability of hydrated zinc nitrate has aroused interest of many researchers not excluding ourselves [4–9]. Although there are a lot of papers concerning thermal changes of the hydrates, the results are usually fragmentary, incoherent and even false. This probably results from different types of water bound in salt structure (from weak adsorption of water molecules to molecules which are strongly bound chemically) and the

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reversible character of dehydration process and thereby there is a considerable influence of external conditions on the course of the process. Generally, for the same salts different effects such as presence/absence of intermediate hydrates, melting or not melting of the initial salt with/without simultaneous decomposition, pseudomelting of the initial salt in its own crystallisation water with creation of aqueous solution can be observed. Then during heating typical processes for solution chemistry, for example evaporation, salt hydrolysis, crystallisation of solid intermediate products, their thermal decomposition into the final products can occur.

For example, Noshida [5] and Wendtland [6] noticed that $Zn(NO_3)_2{\cdot}6H_2O$ losses nitric oxides at 350°C. Duval [1], studying the decomposition at different heating rates, observed a mass loss at low temperatures and continues until 350°C. The dehydration process in the case of zinc nitrate(V) is noticeable from 40°C and occurs without creating intermediate hydrates. In the Atlas of Thermoanalytical Curves [4] the interpretation of the thermal decomposition of $Zn(NO_3)_2{\cdot}6H_2O$ is limited to indicating that the salt melts and crystallisation water is lost with a partial decomposition of $Zn(NO_3)_2$ and finally $Zn(NO_3)_2$ is decomposed into ZnO. Małecki and co-workers [8] deal with the decomposition of zinc nitrate(V) hexahydrate in comparison with other nitrates of transition metals. They do not consider the salt as its aqueous solution in which physical and chemical processes occur simultaneously during heating.

Experimental

Materials

Zinc nitrate(V) hexahydrate used in the present study was of analytical grade (POCh, Gliwice, Poland). Its composition was verified both by the chemical analysis and the X-ray powder diffraction method.

Methods, procedure and apparatus

The thermal decomposition of the salts was carried out in air:

a) isothermally and *b*) under dynamic heating conditions.

Ad *a*) Thermal decomposition degrees were determined gravimetrically on the basis of sample masses determined after heating in a dryer at different fixed temperatures of 75, 105, 150 and 200°C for different lengths of time (from several days to several weeks).

Ad *b*) Typical thermoanalytical curves (TG/DTG-DTA) were obtained for mass samples of 10 mg using an Universal V2.3C TA Instruments. Heating rate was of $10°C\ min^{-1}$.

Chemical analyses of Zn^{2+} and OH^- were made. The amount of zinc of the compounds obtained was determined by complexometric titration using EDTA agent and eriochrome black as indicator. The amount of OH^- was determined by indirect method. 0.1M HCl was added in excess and then titrated with 0.1M NaOH in the presence of methyl orange. Sum of ions (cations and anions) was balanced by ion exchange method.

Results and discussion

Visual observations of the heated zinc nitrate(V) hexahydrate indicate that a homogenous liquid phase at temperature about 50°C is created. It is a confirmation of a well-known process consisting in melting some hydrated salts in their water of crystallisation. Further isothermal heating of the solution e.g. at 75°C connected with the evaporation of volatile constituents of the system causes crystallisation of solid phase, which can be isolated. The results of chemical and X-ray powder diffraction analyses as well as the determination of the amount of the formed solid compound show the formation the salt of the formula – $Zn(OH)NO_3{\cdot}H_2O$ (Fig. 1). It appears that this monohydrate is a result of the hydrolysis in the aqueous solution of zinc nitrate (1:6), which can be expressed by the following equation:

$$\underset{\text{solution (1:6)}}{3[Zn(NO_3)_2\text{–}H_2O]} \rightarrow \underset{\text{solid phase}}{3Zn(OH)NO_3{\cdot}H_2O}+\underset{\text{solution (1:4)}}{3[HNO_3\text{–}H_2O]} \quad (1)$$

In parenthesis the molar ratios of solution components are given.

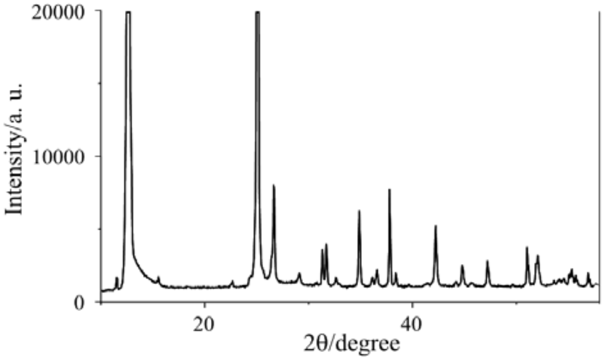

Fig. 1 X-ray diffraction pattern for $Zn(OH)NO_3{\cdot}H_2O$

When $Zn(OH)NO_3{\cdot}H_2O$ is exposed to higher temperature (till 105°C) for a period of a few days the compound undergoes a phase change (without melting). Molar ratio of Zn:OH:NO_3, based on the results of chemical analyses, is equal to 3:4:3 which can correspond to the compound $Zn_3(OH)_4(NO_2)_3$ (Fig. 2). One can assume that the thermal decomposition of $Zn(OH)NO_3{\cdot}H_2O$ is as follows:

$$\underset{\text{solid phase}}{3Zn(OH)NO_3{\cdot}H_2O} \rightarrow \underset{\text{solid phase}}{Zn_3(OH)_4(NO_3)_2}+\underset{\text{solution (1:2)}}{HNO_3\text{–}H_2O} \quad (2)$$

The crystalline $Zn_3(OH)_4(NO_3)_2$ can also be isolated by the direct isothermal (105°C) evaporation of the volatile constituents from the heated system (4–5 days) of the melted salt $Zn(NO_3)_2{\cdot}6H_2O$ (reaction 3). At this temperature $Zn_3(OH)_4(NO_3)_2$ is stable for a period of about 4 weeks. In this case no intermediate product has been noticed.

$$\underset{\text{solution (1:6)}}{3Zn(NO_3)_2\text{–}H_2O} \rightarrow \underset{\text{solid phase}}{Zn_3(OH)_4(NO_3)_2}+\underset{\text{solution (2:7)}}{HNO_3\text{–}H_2O} \quad (3)$$

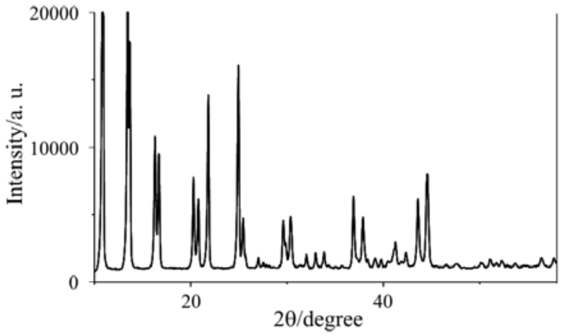

Fig. 2 X-ray diffraction pattern for $Zn_3(OH)_4(NO_3)_2$

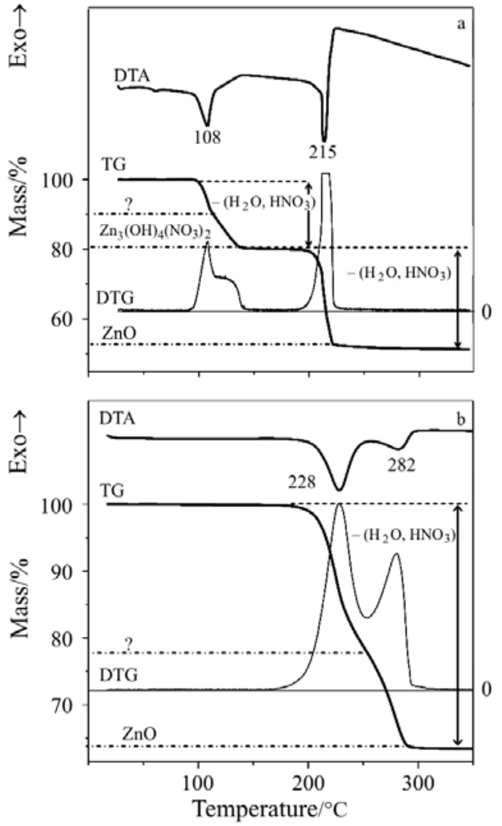

Fig. 3 TG/DTG-DTA curves of thermal decomposition of solid products.
a – reaction (1) – $Zn(OH)NO_3{\cdot}H_2O$; b – reaction (3) – $Zn_3(OH)_4(NO_3)_2$

It has been found that at temperatures higher than 105°C (for instance 150, 200°C) the decomposition of $Zn(NO_3)_2{\cdot}6H_2O$ to ZnO as the ultimate solid product takes place so quickly that the insulation of the products of zinc nitrate hydrolysis is nearly impossible.

It is worth noticing that both insulated solid phases are very hygroscopic. It is obvious that the rate and degree of re-hydration of the salts depend on temperature and partial pressure of water like in cases other hydrates ($CuCl_2{\cdot}2H_2O$, $NiCl_2{\cdot}6H_2O$) [10].

In order to identify the solid products from reactions (1) and (3), the thermal analyses of $Zn(OH)NO_3{\cdot}H_2O$ and $Zn_3(OH)_4(NO_3)_2$, respectively, were made. TG/DTG-DTA curves are presented in Figs 3a and b. In both cases the presence of chemically analysed compounds has been confirmed as well as the possibility of reaction (2) taking place.

Figure 4 shows the TG/DTG-DTA curves of the initial salt, $Zn(NO_3)_2{\cdot}6H_2O$. One can see the effect of melting of the salt at about 40°C and then the four stages of mass loss along with the corresponding endothermic effects. The first effect of the mass loss is the ‘stoppage’ of evaporation process at temperature about 150°C. This ‘stoppage’ still remains to be unexplained. Then the crystallisation of monohydrate zinc hydroxonitrate, $Zn(OH)NO_3{\cdot}H_2O$, takes place. $Zn(OH)NO_3{\cdot}H_2O$ undergoes the polycondensation process creating the solid phase $Zn_3(OH)_4(NO_3)_2$. The latter decomposes below 300°C to ZnO.

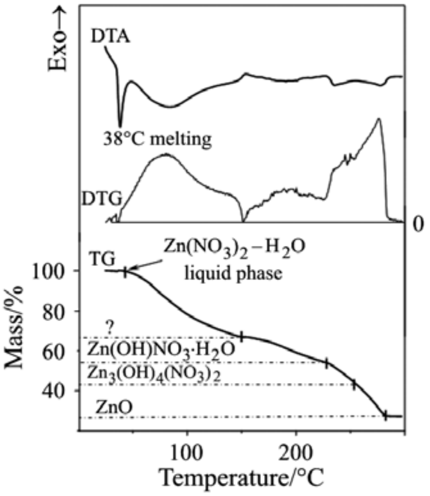

Fig. 4 TG/DTG-DTA curves of thermal decomposition of $Zn(NO_3)_2{\cdot}6H_2O$

Based on the identified and insulated intermediate products of the thermal decomposition of $Zn(NO_3)_2{\cdot}6H_2O$ thermal changes occurring in the system $Zn(NO_3)_2$–H_2O (1:6) can be expressed as follows:

$Zn(NO_3)_2{\cdot}6H_2O$ (solid phase) $\rightarrow$ pseudo-melting $\rightarrow$ HNO_3–H_2O (solution 1:6)$\rightarrow$
evaporation (H_2O, HNO_3), hydrolysis, crystallisation$\rightarrow Zn(OH)NO_3{\cdot}H_2O$ (solid
phase)$\rightarrow$polycondensation, evaporation (H_2O, HNO_3)$\rightarrow Zn_3(OH)_4(NO_3)_2 \rightarrow$
$\rightarrow$dehydroxylation, thermal decomposition$\rightarrow$ZnO (solid phase)

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