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INVESTIGATIONS ON THERMAL STABILITY OF ADDUCT ALUMINIUM NITRATE(V)-UREA (1/6)

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Abstract

The adduct of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ has been prepared and characterized by means of chemical analysis, IR spectroscopy, X-ray patterns and microscopy.

A thermoanalytical study of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ as well as urea, for comparison purposes, under conventional dynamic and quasi-isothermal – quasi-isobaric conditions in air has been carried out.

It has been found that the adduct is thermally stable up to about 200°C, i.e. up to higher temperature than the decomposition temperature of the constituent compounds. The thermal decomposition mechanism of the adduct is complex, thus infrared spectroscopy and X-ray diffraction techniques have been used to determine the intermediate products. Aluminium oxide(III) is the final decomposition product.

Keywords: adduct, aluminium nitrate(V), crystallization, thermal analyses, urea

Introduction

Many crystalline compounds of urea with both inorganic and organic compounds are known. Some of these are good fertilizers (e.g. $Ca(NO_3)_2 \cdot CO(NH_2)_2 \cdot 3H_2O$ [1]) or can be used as additives to animal fodder and to crop and animal protection preparations, or for introducing trace elements. They can also be employed for pharmaceutical purposes and in analytical procedures [2]. Recently a study of equilibria in the aluminium nitrate(V) – urea –water system at 25°C has been made. The position of the solubility isotherms has been determined and the areas of crystallization of the solid phases found. One of solid phases corresponds to a new compound with an empirical formula $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ [3], which has not been described in the literature. Therefore, this adduct should correspond to well-defined phases in the $Al(NO_3)_3$–$CO(NH_2)_2$–H_2O system and an investigation of all aspect of its stability is of practical importance.

The results of a thermoanalytical study of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ as well as $CO(NH_2)_2$ for comparison purposes, under dynamic and quasi-isothermal –

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quasi-isobaric conditions supplemented by X-ray diffraction and IR absorption measurements are presented below.

Experimental

The synthesis of the adduct $Al(NO_3)_3 \cdot 6CO(NH_2)_2$

In the synthesis of the adduct, p.a. grade chemicals were used: $Al(NO_3)_3 \cdot 9H_2O$ and $CO(NH_2)_2$ /POCh Gliwice/. Crystals were grown from aqueous solution of aluminium nitrate(V) and urea at molar ratios between 1:0.5 and 1:50, by isothermal evaporation at 25.0±0.1°C [3].

Instrumentation and experimental conditions

X-ray powder diffraction patterns were obtained using a Siemens Diffractometer D5000. The IR spectra in the region of 4000–400 cm^{-1} were recorded by means of UR-20 (Zeiss-Jena) Spectrometer using KBr pellets.

Thermal analysis under conventional dynamic heating conditions was carried out using Derivatograph-C (Hungarian Optical Works, Budapest) with platinum crucibles, sample mass 7 mg, in air. The heating rate was 5 $deg \cdot min^{-1}$. For thermal analysis using the quasi-isothermal – quasi-isobaric technique, transformation rate of 0.15 $mg \cdot min^{-1}$ was selected, sample size was about 50 mg and a labyrinth sample holder was used [4].

Results and discussion

Characteristics of the compound synthesized

The adduct is crystalline, colourless. Figure 1a shows crystals at a magnification of 100× and Fig. 1b – a single crystal at a magnification of 800×.

Chemical analysis results are summarized in Table 1. The amount of aluminium nitrate in the adduct aluminium nitrate(V)-urea (1/6) was determined gravimetrically as an Al_2O_3. Urea was determined by hypobromite method [5]. The results agree well with the theoretical content corresponding to the chemical composition of the adduct.

Table 1 Chemical analysis of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$, wt.%

Compound	Calculated	Found
$Al(NO_3)_3$	37.12	37.2±0.50*
$CO(NH_2)_2$	62.88	60.7±1.80*

*standard diviation for $\alpha = 0.05$ and $n = 6$

The melting point of the adduct determined by the Boetius method is 214±2°C. This is in agreement with the temperature indicated by the Q-DTA curve (Fig. 2).

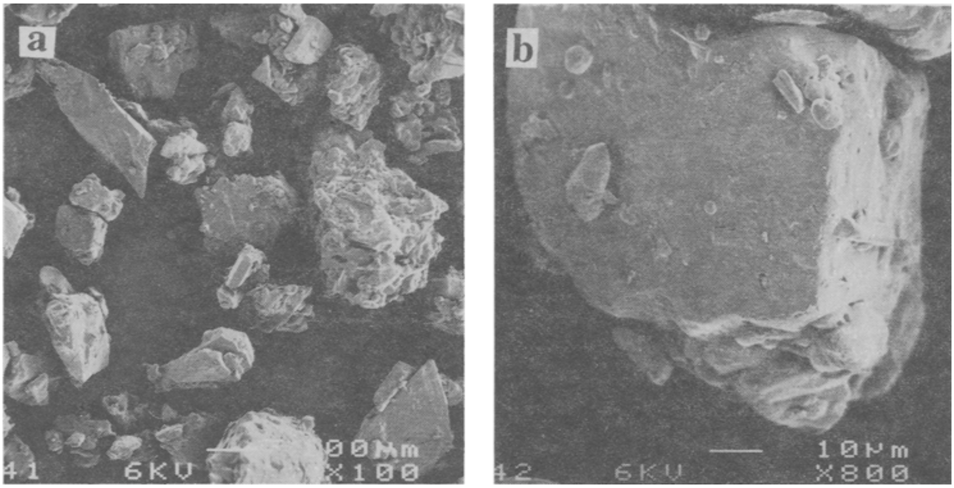

Fig. 1 SEM micrographs of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$; a) crystals at magnification of 100×; b) view of crystal at a magnification of 800×

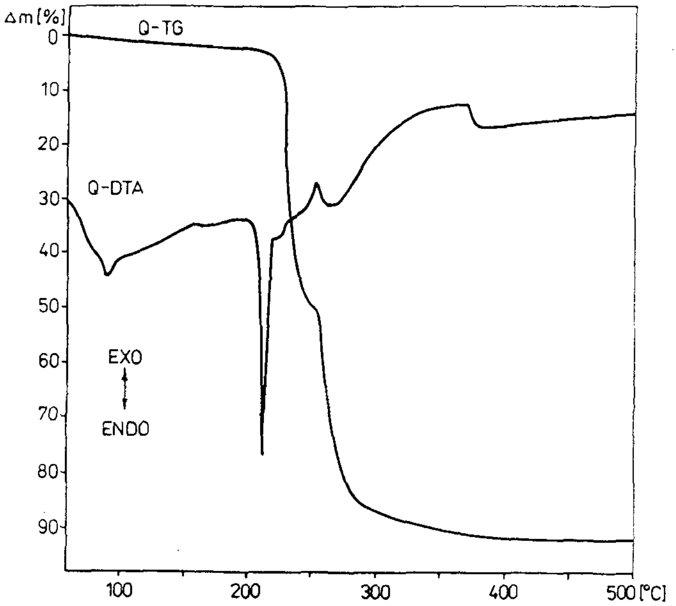

Fig. 2 Q-TG–Q-DTA curves of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ as a function of temperature; dynamic conditions

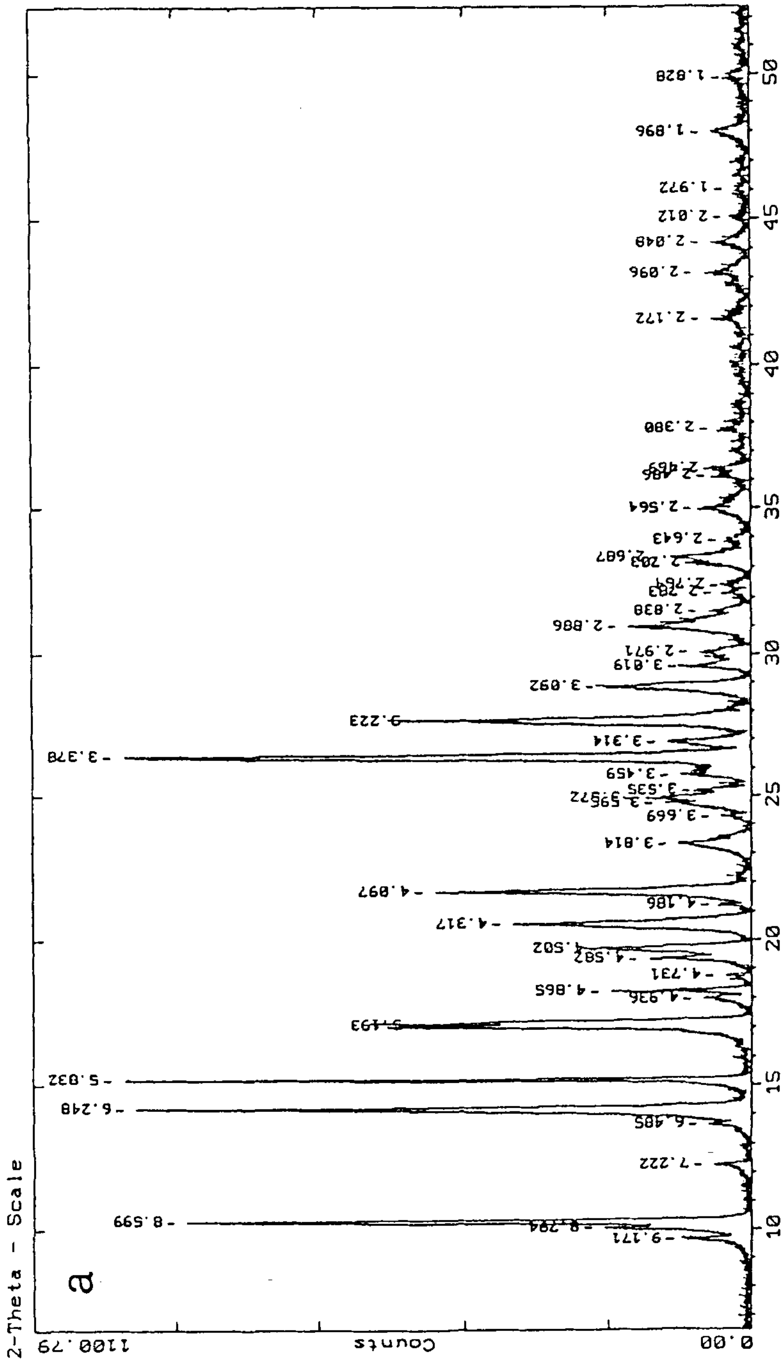

Fig. 3a X-ray diffractogram of $Al(NO_3)_3.6CO(NH_2)_2$

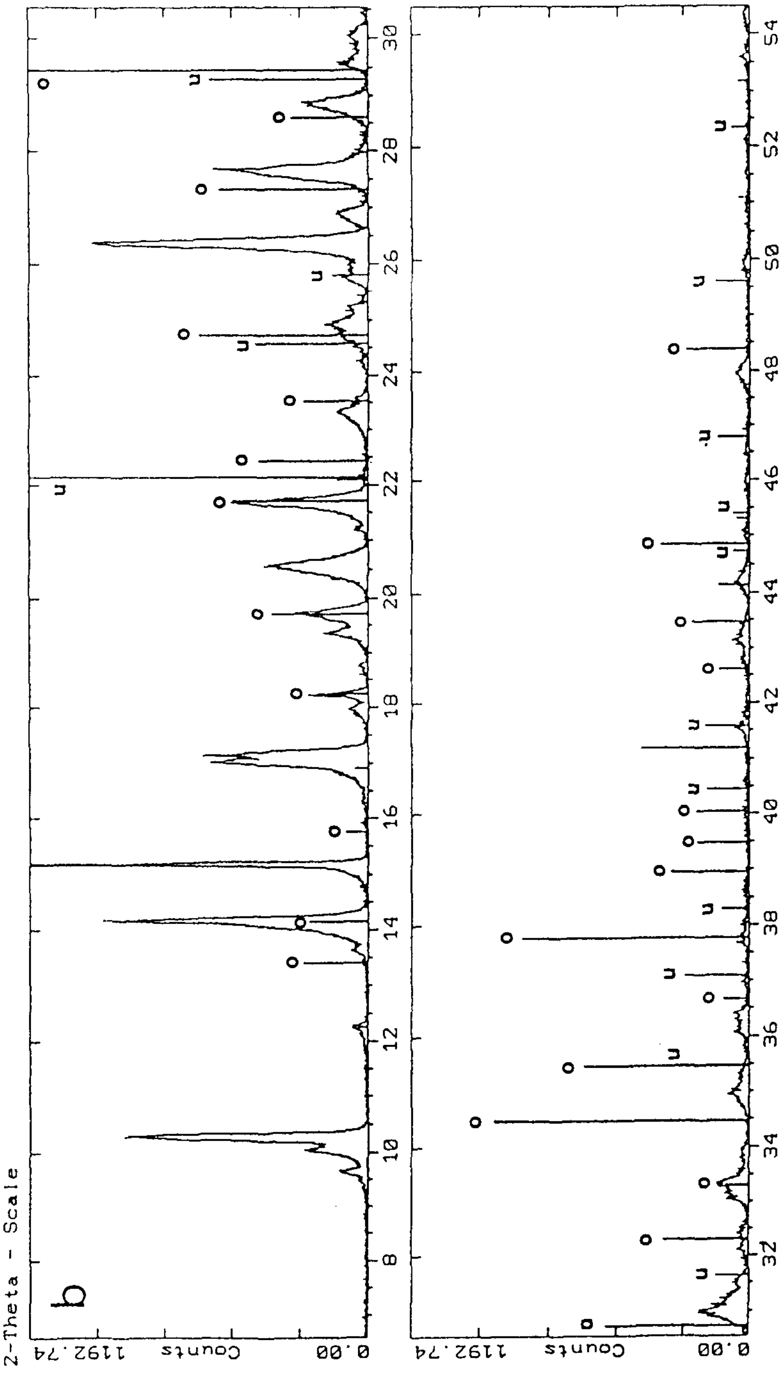

Fig. 3b X-ray diffractogram of $Al(NO_3)_3.6CO(NH_2)_2$ with marked the position lines for $Al(NO_3)_3.9H_2O$ (o), and $CO(NH_2)_2$ (u)

Because X-ray diffraction lines for $Al(NO_3)_3{\cdot}6CO(NH_2)_2$ are not given in ASTM cards and no data could be found in the literature, the diffraction 'pattern' for this compound is shown in Fig. 3a. Unfortunately, the adduct is sensitive towards the operating conditions of the X-ray diffractometer. Some of the peaks changed their intensity and their positions could be shifted (e.g. d=6.248Å and d=3.378Å) without any apparent reason. In view of the above, it is obvious that X-ray powder diffraction is not sufficient to characterize the adduct, but it allowed us to prove that the adduct is not a physical mixture of aluminium nitrate(III) and urea, what is demonstrated in Fig. 3b, where the diffraction lines for $Al(NO_3)_3{\cdot}9H_2O$ and $CO(NH_2)_2$ are also marked.

IR spectra have provided useful information about the adduct and also its decomposition intermediate products after heating. Characteristic absorption bands in the infrared spectra of the adduct, urea and aluminium nitrate(V) hydrate (1/9) are summarized in Table 2. They may be used for the identification of $Al(NO_3)_3{\cdot}6CO(NH_2)_2$ compound. The influence of the presence of urea on aluminium nitrate(V) characteristic bands was found for the adduct $Al(NO_3)_3{\cdot}6CO(NH_2)_2$. The position of the nitrate group band (1390 cm^{-1}) was shifted 20 cm^{-1} towards higher wavelengths.

Table 2 Characteristic absorption bands in infrared spectra (cm^{-1})

Compounds		
$Al(NO_3)_3{\cdot}6CO(NH_2)_2$	$CO(NH_2)_2$	$Al(NO_3)_3{\cdot}9H_2O$
565 w	565 w	
640 w	580 w	630 w
790 w	790 w	
855 w		840, 880 w
1060 w		1060 w
1200 w	1155 w	
1380–1410 vs	1465 s	1390 vs
1530 m	1605–1630 s	1650 s
1620–1700 vs	1682 s	3130–3420 w
3220 w	3355, 3455 w	
3370–3480 w		

Key: vs very strong; m medium; s strong; w weak

The thermal stability and behaviour of the adduct heated in air is described on the basis of thermal analysis under dynamic and quasi-isothermal – quasi-isobaric conditions.

It is clear from the TG/DTG and DTA curves in Fig. 4 that the adduct is stable in air up to about 200°C. The DTA endoeffect (maximum at 220°C) corresponds to the melting of the adduct, together with its decomposition, in two or

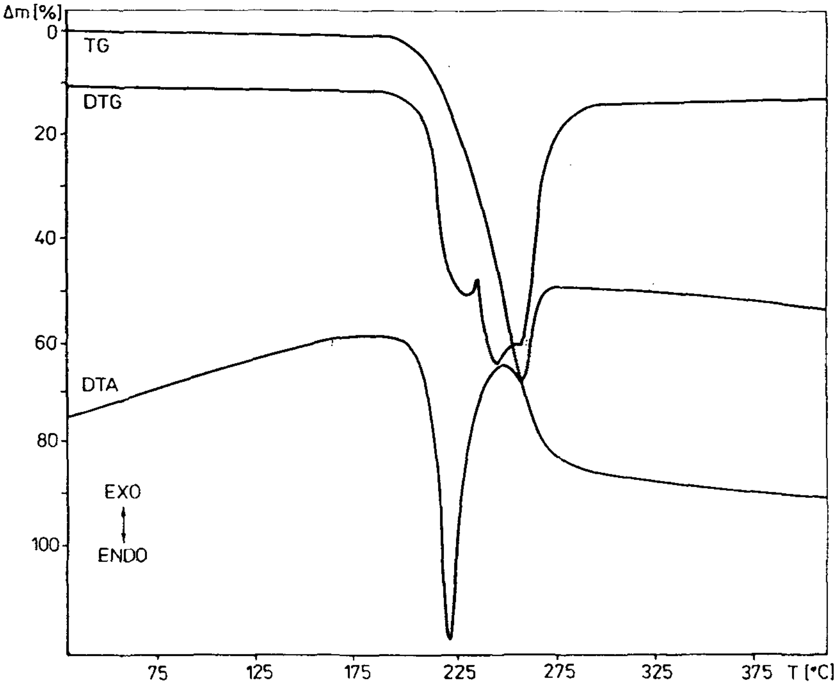

Fig. 4 TG/DTG–DTA curves of $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ under dynamic conditions

three overlapping steps, (curve DTG), up to 400°C as indicated by mass loss on the TG curve (ca. 90 wt%) and DTA second endothermal effect with a peak at 255°C. Aluminium oxide(V) is the final decomposition product.

It was of interest to investigate the difference between the thermal behaviour of pure urea and urea combined with aluminium nitrate(V) in the adduct using the same experimental conditions. TG/DTG and DTA characterization of the thermal behaviour of urea during heating in air is given in Fig. 5. The course of urea decomposition appears to be similar to that described earlier [3, 6] probably because the experimental conditions were comparable (viz. low heating rate). It was known that the thermal decomposition of urea proceeds differently in dependence on measurement circumstances. It should not be excluded the formation of a series of compounds:

$$H_2NCONH_2 \rightarrow HCNO + NH_3$$

$$H_2NCONH_2 \rightarrow HCNO + H_2O$$

$$H_2NCONH_2 \rightarrow HCNO + H_2NCONHCONH_2 \text{ (biuret)}$$

$$H_2NCONHCONH_2 + HCNO \rightarrow H_2NCONHCONHCONH_2 \text{ (triuret)}$$

TG-DTA curves for thermal decomposition of adduct measured by the Q-isothermal – Q-isobaric technique is shown in Fig. 2. Note that by this technique it is possible to resolve reactions even with closely lying reaction temperatures in contrast to the conventional measurements (Fig. 4), when the decomposition of adduct started together with the melting process.

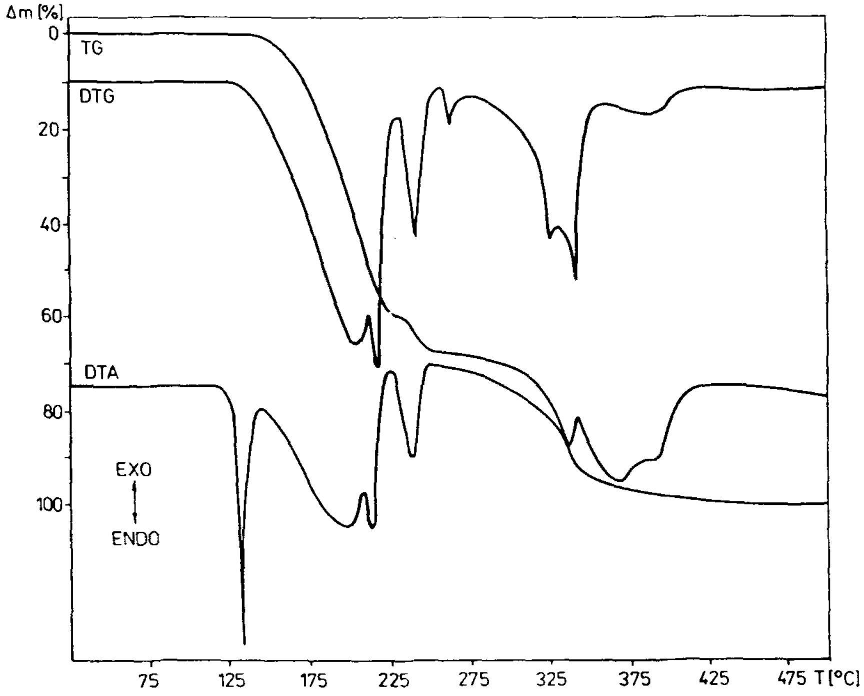

Fig. 5 TG/DTG curves of $CO(NH_2)_2$ under dynamic heating conditions

Analysis of the results allows to distinguish three stages of the thermal decomposition. On the Q-DTA curve, first – very sharp and intensed endothermic peak appeared due to melting. Under these conditions, the process is not accompanied by mass loss. The second small endothermal effect is connected with decomposition of adduct influenced by chemical structure of the adduct. In this stage one or more intermediate products of the decomposition are formed. Taking into account multidirectional course of the decomposition/transformation of organic structure (e.g. urea) it is very difficult to establish the composition of intermediate products. The analyses of solid products after interruption of the decomposition at different temperatures by IR spectroscopy are not sufficient. The described thermal measurements must be complemented using e.g. FTIR method for the evolved gases analyses during the decomposition. The study is to be continued.

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Zusammenfassung — Das Addukt $Al(NO_3)_3 \cdot 6CO(NH_2)_2$ wurde hergestellt und mittels chemischer Analyse, IR-Spektroskopie, Röntgenaufnahmen und Mikroskopie charakterisiert.
Unter konventionellen dynamischen und quasi-isothermen – quasi-isobaren Bedingungen in Luft wurde eine thermoanalytische Untersuchung von $Al(NO_3)_3 6CO(NH_2)_2$ und – zu Vergleichszwecken – auch von Harnstoff durchgeführt.
Man fand, daß das Addukt bis 200°C stabil ist, d.h. bis zu einer Temperatur, die oberhalb der Zersetzungstemperatur der Bestandteile liegt. Der Mechanismus der thermischen Zersetzung des Adduktes ist komplexer Art, weshalb Infrarotspektroskopie und Röntgendiffraktionstechniken zur Ermittlung der Zwischenprodukte eingesetzt wurden. Das Endprodukt der Zersetzung ist Aluminiumoxid(III).