Thermochimica Acta, 92 (1985) 731-734
Elsevier Science Publishers B.V., Amsterdam

THERMAL PROPERTIES OF AMMONIUM NITRATE
II. Study of modification transformations and their completeness by the change of heating mode

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ABSTRACT

Using DTA method and powder diffractograms the modification transformations of ammonium nitrate (AN) and their completeness were investigated. In heating AN for a certain time at a constant temperature (over a thermodynamic temperature assigned to the modification transition IV ⟶ III) a good reproducibility and, as a rule, also the completeness of these transformations were achieved.

INTRODUCTION

The study of modification transformations of ammonium nitrate (AN) using DTA method, is a problem frequently investigated[1]. Recently[2] we studied the reproducibility of the DTA curves measured for AN as a function of both the grain size of the samples (ground, unground, and lump AN) and the atmosphere during measurements. The temperatures and the areas of the peaks assigned to the modification transitions IV → III (peaks 1), III → II (peak 2), and II → I (peak 3) were evaluated. The changes in the areas were observed in particular for the first and the second peak, and moreover, they were mutually dependent. The possible explanation for it may be connected with various factors, such as formation of an amorphous product, recrystallization processes, and especially incompleteness of the modification transition IV → III[2]. This paper has the aim to investigate the modification transformations of AN influenced by the changes of heating mode.

EXPERIMENTAL

Ammonium nitrate of analytical grade (Lachema) containing 0,15 % of water was used in measurements. In order to eliminate the thermal history of studied samples[2], it was kept in a closed vessel in an exsiccator at a constant temperature (25 °C). The DTA curves of AN were measured with an OD-102 derivatograph

Proceedings of ICTA 85, Bratislava

(MOM, Budapest) at the following conditions: sample mass 100 mg, DTA sensitivity 1/1, rate of temperature increase 1.5 degree per minute. Powder diffractograms were obtained with a powder diffractograph GON-3 (Chirana).

RESULTS AND DISCUSSION

For thermal analysis of AN the following procedure was chosen:

- heating at a linear increase of temperature to $t_1 \approx 40$ °C and $t_2 \approx 36$ °C for samples 1 and 2, respectively,
- interruption of heating for 10 minutes,
- further heating at a linear temperature increase to 150 °C.

Each sample (1,2) was measured six times. The results were statistically evaluated and they are given in Table 1 and 2.

Two sets of measurements were made with interruption of heating at i) 40 °C when usually the first endothermic peak begins in our conditions of measurements[1], ii) at ca. 36 °C, i.e. before the modification transformation IV → III of AN is registered on DTA curves at a linear temperature increase equal to 1.5 °C per minute. Under these conditions, the shape of the first peak is changing (it is broadening and several minima are observed as shown in Table 1 and 2).

This paper had the aim to create such experimental conditions which would make it possible to perform a complete transformation IV → III of AN. The method of X-ray powder diffraction was used for indentification of the individual modifications. The powder diffractograms were measured at 22 °C (Fig. 1a), 35 °C (Fig. 1b), 50 °C (Fig. 1c), and 50 °C after the sample had been 60 minutes heated (Fig. 1d). As shown in Fig. 1a and 1b, there are maxima in the characteristic region of diffraction angles 2Θ (from 25 to 35 °) which correspond to the pure phase IV of AN. It means that a short lasting heating (5 minutes) up to a temperature of 35 °C (i.e. to a greater value than that of the thermodynamic temperature of the modification transformation) is not sufficient enough for the formation of such an amount of modification III which could be registered. The further heating up to 50 °C (Fig. 1c and 1d) gives a compound with diffraction maxima corresponding to the pure phase III.

The above results show that AN when heated for a certain

Table 1 Data of DTA curves of sample 1 ammonium nitrate

No. of measurement	Endotermic peak 1		2		3	
	t, °C	area, mm^2	t, °C	area, mm^2	t, °C	area, mm^2
1.	39-41	316	84	160	119	574
2.	39,41	262	85	140	122	562
3.	37,40	225	81	146	120	557
4.	38,41	337	84	163	118	598
5.	39,43	312	83	162	118	606
6.	39,48	293	85	159	119	578
$\bar{x}$	-	290,8	83,7	155,0	119,3	579,2

Table 2 Data of DTA curves of sample 2 ammonium nitrate

No. of measurement	Endotermic peak 1		2		3	
	t, °C	area, mm^2	t, °C	area, mm^2	t, °C	area, mm^2
1.	36,43	384	84	188	119	595
2.	36	325	84	163	118	563
3.	37,44	304	82	183	116	600
4.	37,40	350	83	161	118	587
5.	37	391	86	183	120	594
6.	39	324	84	142	117	569
$\bar{x}$	-	346,3	83,8	170,0	118,0	584,7

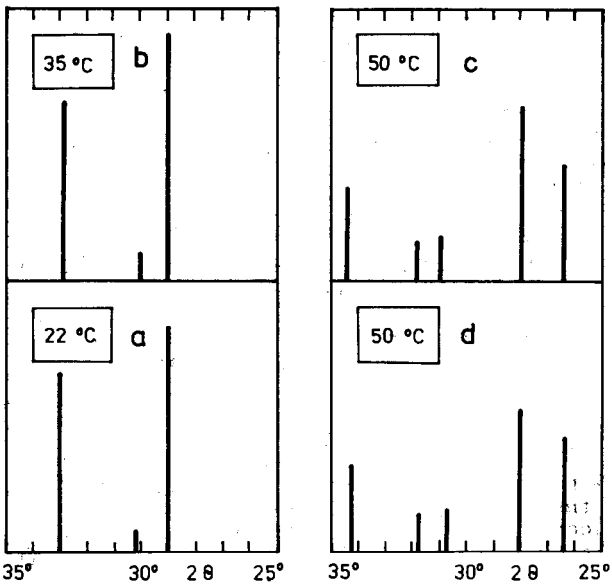

Fig. 1: Powder - diffractograms at various conditions

time at a constant temperature (over the thermodynamic temperature of modification transformation IV → III) is quantitatively changed to a pure modification III.

The complicatedness of the modification transformation IV → III of AN registered previously[1,2], is manifested by changes of temperatures and areas of peaks on DTA curves (sometimes the second peak even disappears). These anomalies may be connected before all with incompleteness of the modification transformation IV → III caused by unsuitable experimental conditions which are realized at linear temperature increase when common thermal derivatographic method is used[3].

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