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AMMONIUM NITRATE CHANGES DURING THERMAL ANALYSIS

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A study was made of the difference occurring in ammonium nitrate during investigation by DTA and by DSC. The results show that the DTA of ammonium nitrate (p.a.) is accompanied by the crystal transformation IV → III → II → I and melting. During DSC investigation of the same ammonium nitrate samples, the salt undergoes the transformations IV → III and IV → II in parallel; then follow the crystal transformations III → II → I and melting. The investigation conditions and the history of the samples do not essentially influence the crystal transformations during thermal analysis.

The crystal transformations of ammonium nitrate have been the subject of examination by numerous investigators with different methods and techniques. In the past ten years the significance of differential thermal analysis and differential scanning calorimetry in the determination of the temperatures and energies of crystal transformations has been increasing.

However, during examinations of ammonium nitrate, with the application of different commercial equipment and under different examination conditions, differences in behaviour have been observed during DTA relative to those during DSC.

The intention of this paper was to register and explain the differences occurring in ammonium nitrate during its examination by means of DTA and DSC, in one laboratory, on the sample and under examination conditions as similar as possible.

Ammonium nitrate is the most widely used nitrogenous fertilizer. It is applied as the nitrogenous component in the majority of mixed and complex fertilizers, and accordingly is an important product of the chemical industry. Many negative features of this salt are attributed to its crystal transformations, in the temperature interval from 20° to 169°. Reliable values of the specific heat of ammonium nitrate, and the energies and temperatures of its crystal transformations, are necessary for control and optimization of the production process [1, 2]. However, the enthalpy of melting has still not been exactly determined, while the processes occurring during its cooling and the behaviour of ammonium nitrate in the temperature interval from 25° to 85°, which is certainly of the greatest technical significance, have not been exactly defined [3].

The calorimetrically measured energy of the crystal transformation IV → III is 21.00–21.24 J/g [4, 5], while that determined by means of DSC is 16.7 J/g [6].

The temperature of the crystal transformation IV → III, determined by means of X-ray diffraction, has been reported as 32±10° [7] and 43–51° [8]. On DTA and

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DSC, the temperature of this transformation was found to be between 31° [9] and 55° [10–12]. The DTA and DSC curves show the good accordance of the melting temperatures, that is the temperatures of solidification, with the temperatures of the crystal transformations I → II and II → III measured by other techniques [13].

The greatest differences between the DTA and DSC techniques appear for the temperature and energy of the crystal transformation IV → III. DSC examinations either register the transformation IV → II, or point to transformation of phase IV to metastable phase III, accompanied by the appearance of exothermic peaks [14]. Because of the difference in the results obtained with the thermal method compared with those of other methods used, special attention has been called to the influence of the experimental conditions on the temperatures and energies of crystal transformations determined by means of DTA and DSC [15, 16].

Experimental

The examinations were carried out with ammonium nitrate of p.a. quality, products of the firms Merck, Chemapol, Kemika, Zorka–Šabac and Laphoma.

The samples contained 0.12–0.30% (by mass) of water, the concentration of which was determined by Karl–Fischer titration.

DTA was carried out on a MOM derivatograph, from ambient temperature up to 250°, with heating rates of 1, 2.5, 5 and 10 deg/min, in a static atmosphere of air, in platinium crucibles of different sizes and forms, with covers and without them, and in a ceramic crucible. Depending on the size of the crucible, the weight of sample ranged from 150 to 1500 mg.

DSC examinations were carried out on a Perkin–Elmer DSC-1 differential scanning calorimeter in the interval from ambient temperature up to 160°, at heating rates of 4 and 8 deg/min, in a dynamic atmosphere of nitrogen and helium. The weight of samples was between 11 and 22 mg.

The derivatograph was calibrated by means of the dehydration of barium chloride dihydrate, the crystal transformation of sodium nitrate, the dehydration of magnesium sulphate heptahydrate, the dehydration of calcium sulphate dihydrate, the crystal transformation and melting of silver nitrate and the melting of tin, while the DSC was calibrated by means of the melting of indium and the boiling of benzene.

The samples for examination, previously ground in an agate mortar, were kept before examination in double polyethylene bags and in a desiccator at ambient temperature and at 5° and 32°.

Results and discussion

All DTA curves of ammonium nitrate reveal peaks for the transformations IV → III, III → II, II → I, and melting. However, the temperature of the beginnings and the maxima of the transformations do not correspond to the literature data determined by means of dilatometry or optical methods.

The termperatures of the beginning and the maxima of the peaks relating to the crystal transformations and ammonium nitrate melting in the various crucibles are shown in Table 1.

As expected, at low heating rates, lower temperatures of beginning of crystal transformation were obtained, the differences being 2–6° for an increase in heating rate from 1 to 10 deg/min. With the increase in mass of the sample, or with the use of a cover at the same mass, we obtained temperatures higher by 1–4°. However, in our opinion none of the investigation conditions could cause an increase of 17--24° in the temperature of the crystal transformation IV → III relative to the values obtained by other techniques [7].

The temperature differences for other crystal transformations and ammonium nitrate melting are within the limits of the measurement errors for the wide range of heating rates and sample masses used. Under definite conditions, the temperatures of the crystal transformations III → II and II → I and melting, obtained by means of DTA analysis with a derivatograph, correspond to the results obtained with other techniques.

The energies of the crystal transformations and of ammonium nitrate melting, determined by DTA analysis, are shown in Table 2.

Comparison of the found energies of the crystal transformations with the literature values reveals that, during DTA analysis in platinum crucibles, regardless of the heating rate, ammonium nitrate undergoes to crystal transformations IV → III → II → I melting. The metastable transformation IV → III is not registered as a peak, but considering the energy changes, it is observed at higher sample weight and higher heating rate (10 deg/min).

DTA gives a reliable value for the energy of the crystal transformation II → I, which agrees with the literature values. The energies of the transformations IV → III and III → II are influenced by the conditions of determination, and probably by the

Table 1 Temperatures of beginning and maximum of crystal transformation peaks and ammonium nitrate melting

Crucible	Temperature of crystal transformations and ammonium nitrate melting (°C)							
	IV → III		III → II		II → I		melting	
	beginn.	max	beginn.	max	beginn.	max	beginn.	max
small platinum	49–52	54–57	83–88	92–96	120–126	128–134	163–168	169–177
small platinum with cover	50–53	55–57	84–87	91--95	124–126	128–132	164--166	170–175
large platinum	52–54	55–62	86–89	92–105	124–125	129–143	163–170	170–180
large platinum with cover	54–56	57–64	86–90	92–100	124–130	129–138	165–171	170–179
platinum plate	50–54	63–90	84–129	93–138	117–169	150–180	168–219	175–295
ceramic	45–50	50–58	84–90	94–103	124–132	135–143	164–173	175–184

Table 2 Energies of crystal transformations and ammonium nitrate melting, determined by DTA

Crucible	Energies of crystal transformations and ammonium nitrate melting, J/g small platinum crucible				small platinum crucible with cover				large platinum crucible				large platinum crucible with cover			
heating rate deg/min \ cryst. transf.	IV→III	III→II	II→I	melt.	IV→III	III→II	II→I	melt.	IV→III	III→II	II→I	melt.	IV→III	III→II	II→I	melt.
1.0	16.459	16.28	53.42	66.96	13.90	15.63	53.11	75.25	14.39	17.06	52.93	76.72	15.25	19.38	53.31	65.82
2.5	13.117	16.15	53.57	73.89	12.67	15.16	52.98	82.86	10.59	13.79	54.79	49.69	13.46	16.54	52.94	87.63
5.0	13.481	13.33	53.07	79.30	12.99	12.62	53.39	67.98	19.91	16.45	53.46	80.40	21.10	13.08	52.22	76.38
10.0	13.551	12.28	53.06	47.78	18.38	10.57	52.92	76.60	22.02	12.89	52.86	92.49	–	–	–	–
literature values	19.89	16.75	52.83	68.03	19.89	16.75	52.83	68.03	19.89	16.75	52.83	68.03	19.89	16.75	52.83	68.03

mode of sample preparation and its moisture content. The melting energy of ammonium nitrate found with this technique is higher than the values obtained with other methods. The cause of this deviation lies in the process of thermal decomposition of ammonium nitrate, which occurs with melting during thermal analysis.

The DSC curves of the given samples of ammonium nitrate, looked completely different. A small, not clearly shaped peak was observed between 26° and 34° only for some samples. This corresponded to the crystal transformation IV → III. The second very clear peak appears in the temperature interval 43–50°, i.e. practically the same interval as for the transformation IV → III in the DTA curve.

The third peak appears at 80–90°, with a considerably smaller area than expected; this corresponds to the crystal transformation III → II. Finally, the fourth, very clear peak appears at 123–131°, the temperature interval of the crystal transformation II → I (Fig. 1).

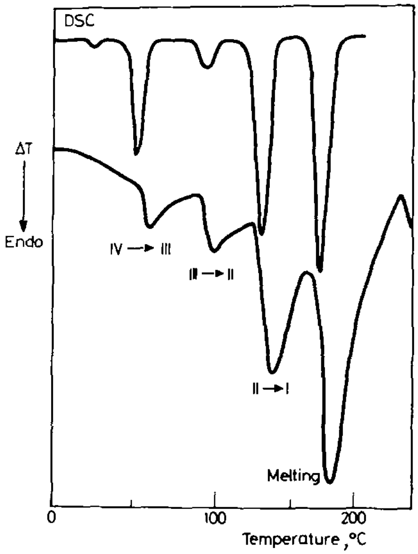

Fig. 1 Thermal curves of the same sample of ammonium nitrate investigated by DSC and DTA

The differences observed between the DTA and DSC curves led us to carry out preliminary examinations on the influence of the sample size, the crucible type, the heating rate, the sensitivity of the instruments, and different inert gas atmospheres.

However, with only minor exceptions, all the thermal curves showed the same changes for ammonium nitrate.

30 samples of p.a. ammonium nitrate from different products were examined by DSC in an attempt to explain the observed phenomenon; the energies of all the registered transformations are shown in Table 3. The energies of the crystal transformations of ammonium nitrate show that, except in traces, none of the examined samples underwent the crystal transformation IV → III at 26–36°.

Table 3 Energies of crystal transformations of ammonium nitrate, determined on differential scanning calorimeter (samples from original packaging)

Sample no.	Weight, mg	Energy of crystal transformation, J/g				Producer
		26–34 °C	43–50 °C	80–90 °C	123–131 °C	
1.	20.40	–	–	8.597	49.045	1–18 Merck
2.	19.31	–	–	9.082	51.087	
3.	21.27	–	1.113	7.256	23.581	
4.	14.07	1.184	17.139	4.799	54.065	
5.	20.90	–	21.649	5.370	–	
6.	14.62	–	23.451	2.699	56.919	
7.	14.24	–	22.538	–	61.455	
8.	14.76	–	19.961	3.565	57.033	
9.	16.35	–	20.756	1.073	55.133	
10.	14.81	–	21.966	–	54.768	
11.	13.82	–	21.324	1.269	57.942	
12.	12.58	–	21.681	1.394	56.957	
13.	13.29	–	21.767	–	56.726	
14.	16.51	–	21.245	0.744	54.971	
15.	16.02	–	18.993	3.832	54.911	
16.	14.77	–	20.982	2.374	64.273	
17.	13.97	–	20.836	1.255	61.442	
18.	18.25	–	21.045	1.0922	56.649	
19.	17.33	–	2.277	14.775	66.234	12–21 Kemika
20.	14.76	0.832	13.961	9.565	62.142	
21.	17.48	0.702	16.755	9.632	58.693	
22.	15.96	–	6.483	12.692	56.536	22–24 Zorka
23.	17.24	–	16.836	10.579	58.187	
24.	14.81	–	22.973	5.980	64.123	
25.	11.82	–	23.294	2.226	59.497	25–27 Laphoma
26.	12.00	–	22.289	0.950	56.271	
27.	11.50	–	18.980	2.287	57.168	
28.	14.25	–	21.357	3.693	65.487	28–30 Chemapol
29.	13.88	–	23.062	1.896	–	
30.	12.84	–	21.437	–	60.2116	

The crystal transformation at 43–50° could be either IV → III or IV → II [12]. The energy of transformation that we determined in this interval is nearer to the energy of the transformation IV → II, but the two transformations have fairly similar energies.

In all curves, the transformation III → II is clearly expressed by a small peak at 80–90°. However, the energy of this crystal transformation was by four times smaller than the literature value. This suggested that only 1/4 of the sample of ammonium nitrate underwent the transformation III → II.

The crystal transformation II → I at 123–131° is accompanied by an energy change of 56.947±7.528 J/g. This result is in good accordance with literature data [11].

On the basis of these results we can assert with resonable confidence that p.a. ammonium nitrate with a water content of 0.12–0.30% (by mass) undergoes the transformations IV → III and IV → II at the same time during DSC examination; the latter is the faster, and the contribution of modification II of ammonium nitrate is three times larger than that of modification III at 50°. This is followed by the crystal transformation III → II at 80–90°, and by II → I at 123--131°, for the entire sample.

The grinding of samples in a laboratory mortar immediately before determination of the crystal transformations of ammonium nitrate by DSC might influence the crystal transformation IV → III or IV → II. Accordingly, examinations were carried out on samples kept for 14 days at + 5° or + 30° after grinding. The results showed that the thermal history of the samples did not have an essential influence on the energies of the crystal transformations. The averages of 10 determinations of the energies of the crystal transformations are given in Table 4.

Table 4 Average values of energies of crystal transformations of ammonium nitrate kept for 14 days at different temperatures

Temperature, °C	Crystal transformations, J/g 37–45 °C	 77–82 °C	 122–123 °C
+ 5	20.08	1.71	49.38
+ 30	20.06	1.86	48.41

These results show that the energies of the crystal transformations IV → II and II → I are lower than the energies of the same transformations of samples prepared for examination by grinding immediately before investigation.

Conclusions

Studies of the changes in ammonium nitrate by means of thermal analysis show that:

1. During differential thermal analysis, ammonium nitrate undergoes the crystal tranformations IV → III → II → I → melting.

2. During differential scanning calorimetry, the crystal transformations IV → II → → I → melting occur.

3. The investigation conditions and the history of the samples do not have an essential influence on the crystal transformations of ammonium nitrate.

References

1 S. Jovanović, G. Rasulić and Lj. Milanović, Determination of specific heats of KAN and AN as a function of temperature, IV. Technical Conference, Herceg Novi, May 1979.

2 G. Rasulić, Influence of the crystal structure of ammonium nitrate on the mechanical characteristics of calcium ammonium nitrate, XXV. Conference of Serbian Technical Society, Beograd, January 1983.

3 I. Dellien, Thermochim. Acta, 55 (1982) 181.

4 Gmelin's Handbuch der Anorganischen Chemie, System N° 23, Band 8, Verlag Chemie, Berlin, 1936.

5 M. Nagatani, T. Seiyama, M. Sakiyama, H. Suga and S. Seki, Bull. Chem. Soc. Japan, 40 (1967) 1833.

6 E. S. Watson, M. J. O'Neill, J. Justin and N. Brenner, Anal. Chem., 36 (1964) 1233.

7 R. N. Brown and A. C. McLarsen, Proc. Roy. Soc., London, Ser. A, 226 (1962) 329.

8 R. R. Sowell, M. M. Karnowsky and L. C. Walters, J. Thermal Anal., 3 (1971) 119.

9 K. Heide, Z. Anorg. Allg. Chem., 344 (1966) 241.

10 E. J. Griffith, J. Chem. Eng. Data, 8 (1963) 22.

11 H. Langfelderovä and P. Ambrović, Thermochim. Acta, 56 (1982) 385.

12 G. Rasulić, Influence of the physical and chemical features of calcium ammonium nitrate on its becoming lumpy, Doctoral dissertation, Faculty of Chemical and Metallurgical Engineering, Beograd, 1982.

13 M. E. Ivanov, V. M. Olevskii, N. M. Poljakov, I. I. Otričevskii, M. L. Ferd and Yu. V. Cehanskaja, Tehnologija ammiačnoi selitri, izdatj Khimija, 1978 str. 10.

14 I. Konkoly-Thege, J. Thermal Anal., 12 (1977) 197.

15 T. Flóra, Acta Chim. Acad. Sci. Hung., 69 (I) (1971) 1.

16 E. Jóna, I. Šramko and D. Nagy, J. Thermal Anal., 27 (1983) 37.

Zusammenfassung — Bei DTA und DSC von Ammoniumnitrat zu beobachtende Unterschiede wurden untersucht. Bei der DTA von p.a. Ammoniumnitrat verlaufen die Kristallumwandlungen IV → III → II → I sowie der Schmelzvorgang. Während der DSC der gleichen Ammoniumnitratproben verlaufen die Übergänge IV → III und IV → II parallel, worauf die Kristallumwandlungen III → II → I und der Schmelzvorgang folgen. Die experimentellen Bedingungen und die Vorgeschichte der Proben hat keinen wesentlichen Einfluß auf die während der thermischen Analyse verlaufenden Kristallumwandlungen.

Резюме — Методами ДТА и ДСК проведено исследование превращений в нитрате аммония. Результаты ДТА исследований образца нитрата аммония (квалификации ч.д.а) показали наличие кристаллических превращений типа IV → III → II → I и плавление. ДСК исследования того же самого образца показали, что превращения типа IV → III и IV → II протекают параллельно, за которыми следует превращение типа III → II → I и плавление. Экспериментальные условия и происхождение образцов влияния на кристаллические превращения.