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Note

THERMAL BEHAVIOUR OF UREA NITRATE

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Oxidants such as nitrates and perchlorates react violently in the presence of reducing agents with exothermic effects. Due to the powerful oxidation property, they are extensively used in pyrotechnic and explosive mixtures [1]. Detailed studies have been made on the thermal decomposition of perchlorates [1,2] but not much information is available on nitrate decomposition, especially that of amine-onium nitrates. Certain ammonium [3] and -onium type [4] salts rearrange with the liberation of gaseous products to give new compounds at moderate temperatures. Recently we have studied the thermal behaviour of guanidinium nitrate [5]. In this communication the results of thermogravimetry, differential thermal analysis and mass spectral studies of urea nitrate are reported.

EXPERIMENTAL

Urea nitrate, $(H_2N)_2CO \cdot HNO_3$ (UN), was prepared by the addition of concentrated nitric acid to an aqueous solution of urea. The precipitated colourless crystalline product was filtered, washed with acetone and dried. The compound gave satisfactory analytical results for the composition $CH_5N_3O_4$. The X-ray powder diffraction patterns of the compound gave d_{hkl} values (in Å) of 4.12 m, 3.92 m, 3.65 w, 3.41 s, 3.10 s, 2.38 m and 1.55 m, in agreement with literature values [6].

The thermogravimetric and differential thermal analyses were carried out both in air and an atmosphere of nitrogen using a DuPont thermal analyzer. About 5 mg samples were employed at a linear heating rate of 10°C min^{-1}. The mass spectrum of the compound was recorded on a VG micromass 70–70F double focussing mass spectrometer with a VG 2235 data system. The ionization was achieved by bombardment with 70 eV electrons.

The X-ray powder diffraction patterns were recorded on a Philips X-ray diffractometer using CuK_α radiation and the IR spectra were recorded on a Perkin-Elmer 257 spectrometer.

RESULTS AND DISCUSSION

The TG and DTA plots in air and nitrogen are given in Figs. 1 and 2, respectively. The decomposition patterns were almost alike in the two atmospheres. UN starts to decompose at 125°C and there is a break in the weight loss curve at 155°C, showing about 40% weight loss. The decomposition is rapid up to 275°C and about 95% of the initial mass volatilizes by 275°C. No residue remains at 325°C.

In a separate experiment, a known amount of UN was heated at 140°C and the residue obtained was examined. It was found to be a melt at a higher temperature and on cooling absorbed moisture. Wet chemical analysis showed the presence of NH_4^+ and NO_3^-. The weight loss observed was 35%, corresponding to the calculated weight loss of 35% for the formation of NH_4NO_3 from UN. Further, the IR spectrum of the residue exhibited strong bands around 3100, 1620 and 1400 cm^{-1}, characteristic of NH_4^+, and at 820 cm^{-1}, attributed to NO_3^- [7], and resembled that of NH_4NO_3.

The DTA plots exhibited exothermic peaks at 155, 175 and 285°C and an endotherm at 160°C. The initial exotherm, attributed to the expulsion of HOCN from UN, was more pronounced in air than in nitrogen. The removal

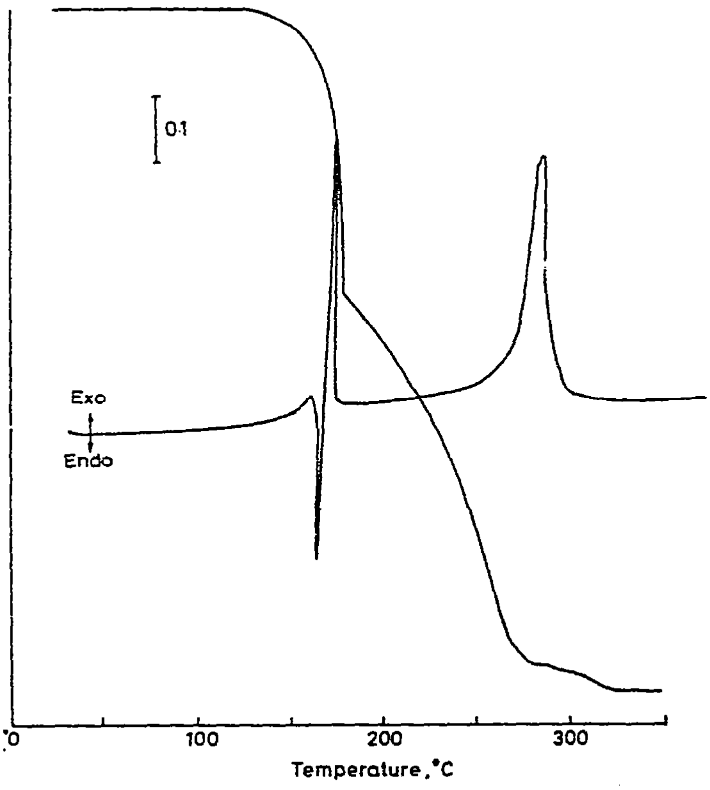

Fig. 1. TG and DTA plots of UN in air.

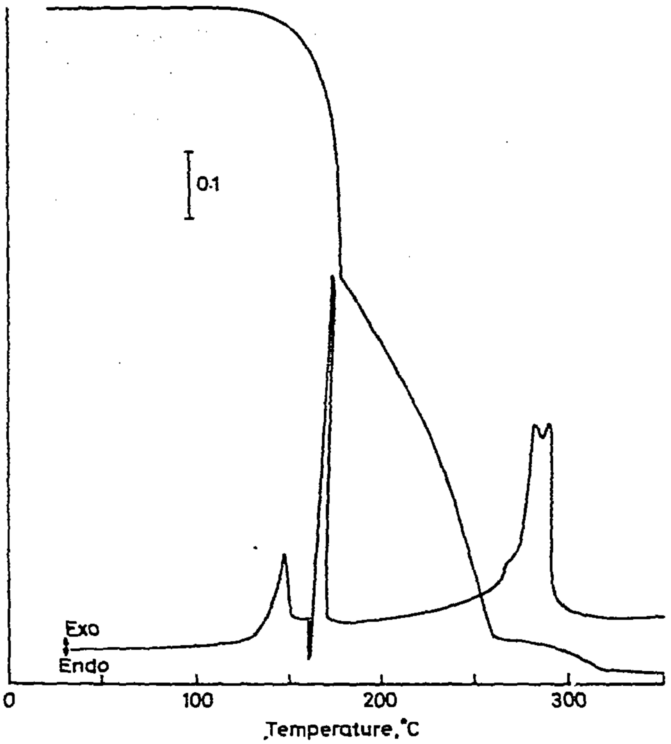

Fig. 2. TG and DTA plots of UN in nitrogen.

of HOCN is probably explained as follows. At higher temperature UN may exist in equilibrium with $NH_4NCO \cdot HNO_3$ from which the weaker acid, HOCN, is expelled. NH_4NO_3 thus formed melts [8,9] at 160°C as visualized by the endothermic effect. Increase in temperature causes the exothermic decomposition of NH_4NO_3 to give N_2O and H_2O.

The mass spectral data are given in Table 1 with the probable assignment

TABLE 1

Mass spectral data of urea nitrate

m/e	Ion (m^+)	Intensity(%)
30	NO	32
42	H_2NCN,OCN	5
43	HNCO	19
44	N_2O	81
46	NO_2	44
60	$OC(NH_2)_2$	100
61	$HOC(NH_2)_2$	5

of the fragments. There is no molecular peak corresponding to UN, *m/e* 123, and no mass peaks above *m/e* 61, $[(CH_2N)_2COH]^+$, are observed. This suggests that the fragmentation takes place through a proton transfer mechanism [10–12]. The major fragmentations are NO, N_2O and NO_2 derived primarily from nitrate, and H_2NCN, HNCO, NCO and $OC(NH_2)_2$ obtained from the cation moiety.

REFERENCES

1 J.C. Schumacher, Perchlorates, Reinhold, New York, 1960.
2 E.S. Freeman and W.K. Rudloff, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Academic Press, London, New York, 1970, p. 363.
3 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 2nd edn. 1963.
4 M.R. Udupa, Thermochim. Acta, 52 (1982) 367.
5 M.R. Udupa, Thermochim. Acta, 53 (1982) 383.
6 ASTM Index (Organic) No. 6.0332.
7 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination compounds, Wiley, Interscience, New York, 3rd edn., 1978.
8 S. Gordon and C. Campbell, Anal. Chem., 27 (1955) 1102.
9 L.G. Berg, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 1, Academic Press, London and New York, 1970, p. 343.
10 C.A. Heath and J.R. Majer, Trans. Faraday Soc., 60 (1964) 1783.
11 M.R. Udupa, Thermochim. Acta, 38 (1980) 241.
12 M.R. Udupa, Thermochim. Acta, 42 (1980) 383.