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Note

THERMAL DECOMPOSITION OF GUANIDINIUM NITRATE

M.R. UDUPA

Department of Chemistry, Indian Institute of Technology, Madras-600 036 (India)

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The onium type perchlorates are powerful oxidizing agents and are employed extensively in propellant mixtures, pyrotechnics and explosives [1]. The corresponding nitrates are also supposed to be good oxidizers and the studies on these systems are sparse. Guanidinium nitrate on thermolysis is reported [2] to start decomposing around 100°C, however, the precise temperature of decomposition is not known. Reported in this communication are the results of thermogravimetry, differential thermal analysis and mass spectral studies of guanidinium nitrate.

EXPERIMENTAL

Commercially available guanidinium nitrate was recrystallized from hot water and used. The thermogravimetric studies were carried out in air on a Stanton thermobalance at a heating rate of 6°C per min, and the simultaneous TG-DTA studies were made in an argon atmosphere on a Mettler thermal analyzer at a heating rate of 4°C per min. Mass spectral analyses were made using a Varian mass spectrometer in quartz crucibles with the filament operating at 70 eV and 300 μA.

RESULTS AND DISCUSSION

The thermal behaviour of guanidinium nitrate in an atmosphere of argon is similar to that in air, which suggests that air does not influence the oxidative decomposition of guanidinium nitrate. The TG and DTA curves in argon atmosphere are given in Fig. 1. As seen from the TG plot, it is clear that guanidinium nitrate starts losing weight at 230°C and the decomposition is fast between 275–325°C. The weight loss is found to be sluggish in the temperature range 325–500°C. No residue was left behind at 500°C which suggests that the entire mass has been converted into gaseous products. The activation energy calculated by analyzing the TG curve based on the Coats and Redfern equation [3] is found to be 46 kcal mole^{-1}.

The DTA plot shows an endotherm at 210°C and an exotherm at 305°C. The exothermic effect is attributed to the oxidative decompositon of guanidinium nitrate. As the compound melts at 210°C and since there is no weight change around this

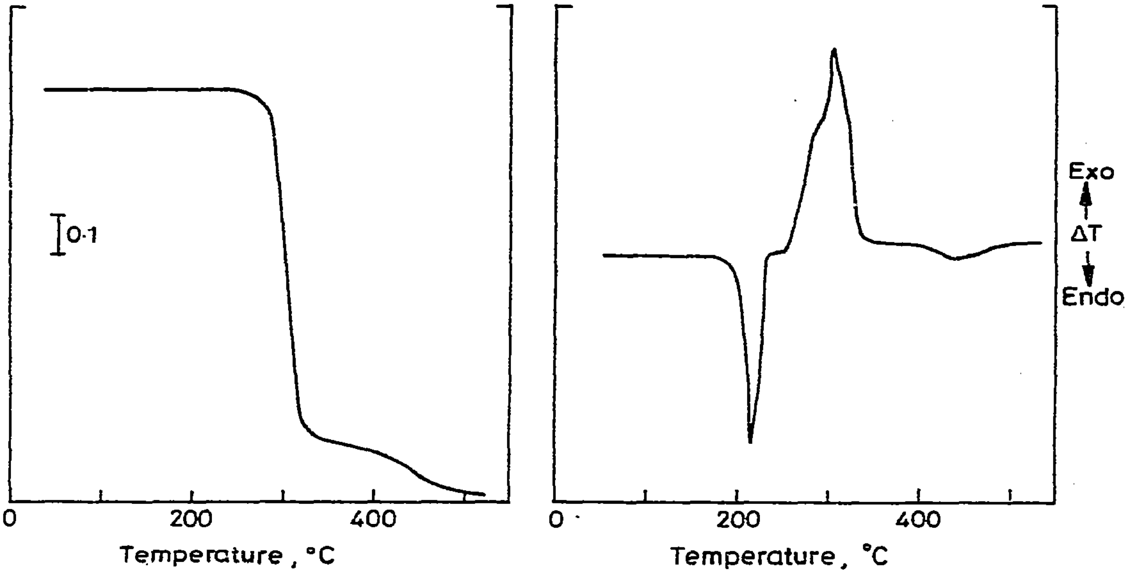

Fig. 1. TG and DTA plots of guanidinium nitrate.

TABLE 1

Mass spectral data of guanidinium nitrate

m/e	Ion (m^+)	Intensity
16	NH_2	16
17	NH_3, OH	27
18	NH_4^+, H_2O	58
27	HCN	9
28	CNH_2, CO	44
29	$HCNH_2$	10
30	NO	98
31	H_3CNH_2	19
41	HNCN	15
42	H_2NCN	85
43	H_3NCN	100
44	CO_2	5
46	NO_2	99
59	$HNC(NH_2)_2$	93
84	$H_2N \cdot CNH \cdot NH \cdot CN$	44
85	$H_2N \cdot CNH_2 \cdot NH \cdot CN$	19
126	$(H_2N)\overline{CNC(NH_2)NC(NH_2)N}$	45

temperature, the endothermic peak is assigned to the melting effect of guanidinium nitrate. This has been further confirmed by the appearance of an exothermic peak at 190°C in the DTA curve when the sample is cooled from 250°C to room temperature.

The mass spectral results obtained at 230°C are shown in Table 1. There is no indication of a molecular peak corresponding to guanidinium nitrate, ($C_4H_6N_4O_3$), which suggests that the decomposition process occurs through a proton transfer mechanism as observed in similar onium type salts [4–6]. The compound apparently undergoes decompostion into neutral particles which are then vapourized and ionized. There seem to be primarily three major routes of fragmentation, namely, the guanidinium cation and its disintegration products, the nitrate anion and its fragmentation and the oxidation products of the organic moiety by the nitrate. It is interesting to note that the fragmentation product, cyanamide ($m/e = 42$) undergoes dimerization to cyanoguanidine ($m/e = 84$) and trimerization to melamine ($m/e = 126$).

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