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Note

THERMAL AND MASS SPECTRAL STUDIES OF THIOUREA NITRATE

M.R. UDUPA

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

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Nitrates are powerful oxidizing agents and undergo exothermic oxidation reactions, often explosively, in the presence of reducing agents. The amine-onium type nitrates, in addition to exothermic decomposition during thermolysis, undergo thermal rearrangement to give new reaction products. Recently, we have investigated the thermal decomposition of guanidinium [1] and uronium [2] nitrates. Reported in this note are the results for thiouronium nitrate obtained by thermogravimetry, differential thermal analysis and mass spectral studies.

EXPERIMENTAL

Thiouronium nitrate (TUN), $[(H_2N)_2CSH]NO_3$, was prepared by mixing equimolar amounts of aqueous thiourea and conc. HNO_3. The reaction mixture was cooled to 5°C and the precipitated colourless crystalline product was collected on a filter, washed with acetone, and dried.

The infrared spectrum of the compound exhibited characteristic frequencies (cm^{-1}) at 3300 and 3200 (ν_{NH}), 1650 (δ_{NH_2}), 1380 (ν_{NCN}) and 710 (ν_{CS}). The appearance of the band at 2530 cm^{-1} confirms that a proton is attached to S [3] and not to NH_2 or NO_3 groups, in confirmity with the single crystal X-ray analysis of the compound [4]. The X-ray powder diffraction patterns of the compound gave d_{hkl} values (Å) 6.86m, 5.05m, 4.34m, 3.97w, 3.58s, 3.44s, 3.18s, 2.61w, 2.57m, 2.35w, 2.31s, 2.00w, 1.59w, 1.39w.

The thermogravimetric and differential thermal analyses were carried out both in oxidative (air) and inert (nitrogen) atmospheres using a DuPont thermal analyzer. About 5 mg of sample were employed at a linear heating rate of 10°C min^{-1}. The mass spectrum of the compound was recorded on a VG Micromass 70-70 FF double focussing mass spectrometer with a VG 2235 data system attachment. Ionization was achieved by bombardment with electrons of 70 eV energy. The infrared spectra were recorded on a Perkin Elmer 257 spectrophotometer and the X-ray powder patterns were taken using Philips X-ray unit with CuK_α radiation.

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RESULTS AND DISCUSSION

The thermal plots of TUN in air and nitrogen are reproduced in Fig. 1. The TG curves in the two atmospheres are apparently alike; however, above 200°C, the DTA curves behave differently. The compound starts decomposing at 120°C with a rapid weight loss of 40% up to 155°C. Above this temperature, the rate of weight loss is sluggish. The substance was oxidized and volatilized by 550°C and no residue was left behind. In order to find out the intermediate products formed, known amounts of TUN were heated to 150°C both in air and nitrogen and the residues obtained were examined. The wet chemical analysis of the yellow residues showed the presence of NH_4^+, SCN^- and elemental sulphur. The residue obtained on heating in nitrogen, gave a positive indication of nitrate. Further, the infrared spectra of the residues exhibited bands characteristic of the NH_4 group at 3120, 1630 and 1390 cm^{-1} and of the SCN group at 2050 cm^{-1} [5]. The presence of NH_4SCN is explained by the rearrangement of thiourea at 150°C.

The DTA plots exhibited a sharp exotherm at 150°C in both atmospheres. Above this temperature, another exotherm appeared at 475°C in air, whereas, in nitrogen, an exotherm at 245°C followed by two endothermic effects at 295 and 350°C were observed. The exothermic effect at 475°C is ascribed to the oxidation of the decomposition products in air. The 245°C exotherm is probably due to the complete decomposition of the nitrate moiety. The subsequent endothermic effects are probably due to the volatilization and decomposition of the intermediate products.

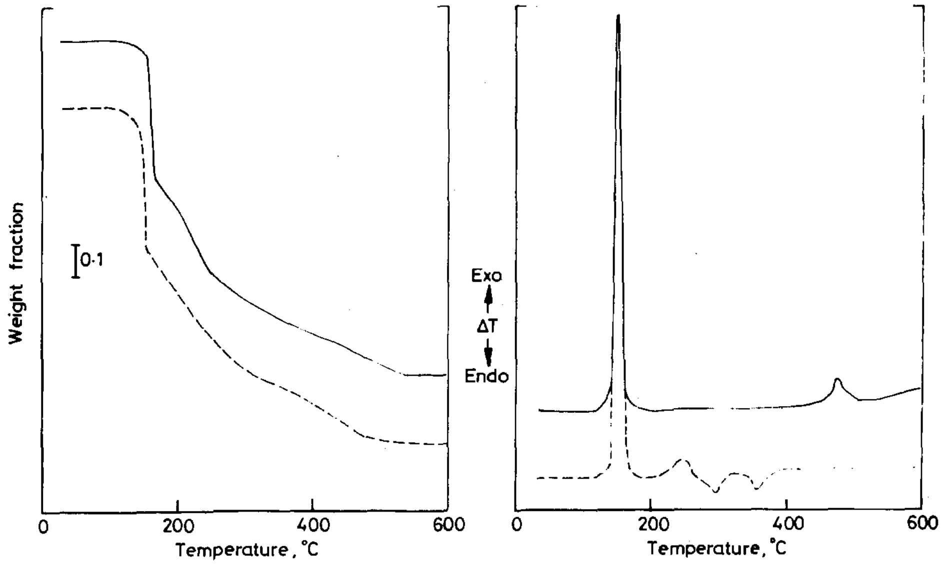

Fig. 1. TG and DTA plots of thiouronium nitrate. ————, In air; - - - - - -, in nitrogen.

TABLE 1

Mass spectral fragments of thiouronium nitrate

m/z	Ion (m^+)
77	$HSC(NH_2)_2$
76	$SC(NH_2)_2$
64	SO_2
60	$SC(NH_2)$
59	HSCN
48	SO
46	SC, $C(NH_2)_2$, N_2O, CO_2
43	H_2NCNH
42	H_2NCN
32	S
30	NO
28	H_2NC, CO
27	HCN

The mass spectral data with the probable assignment of the fragments are given in Table 1. There is no molecular peak corresponding to $[HSC(NH_2)_2]NO_3$ (*m/z* 139). The fragmentation occurs mainly due to the disintegration of the anion, cation and the oxidation of the cation by the nitrate. The major fragments are NO_2, N_2O and NO derived from nitrate and $SC(NH_2)_2$, $SCNH_2$, SCNH, H_2NCNH, H_2NCN, and SO_2 obtained from the thiouronium cation.

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