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Note

THERMAL AND MASS SPECTRAL STUDIES OF UREA OXALIC ACID

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It is known that temperature-programmed thermal decomposition of materials would result in the formation of new products. Thus, ammonium [1] and related [2] oxalates decompose to give oxamide at moderate temperatures. Our interest is to follow the thermal behaviour of amine-onium type salts and to evolve a condition for the isolation of the intermediates formed. In this communication, the results of the thermal decomposition of the urea–oxalic acid addition compound are reported. The study has been made by thermogravimetry, differential thermal analysis and mass spectral analysis.

EXPERIMENTAL

Urea oxalic acid (UOX), $OC(NH_2)_2 \cdot H_2C_2O_4$, was prepared by the interaction of an aqueous solution of a 1 : 1 mole ratio of urea and oxalic acid. The colourless crystalline precipitate was filtered, washed with acetone, and dried. The infrared spectrum of the addition compound gave the characteristic bands (cm^{-1}) of urea [3] at 3440 and 3240 (ν_{NH_2}), 1700 ($\nu_{C=O}$) and 1505 (ν_{CN}) and of oxalic acid at 1640 and 1250 (ν_{COO}). The appearance of carboxylic frequencies in the same region as that of free oxalic acid suggests that a proton is attached to the COO group and not to the urea oxygen or NH_2 group, as evidenced by the crystal structure analysis of the compound [4]. The X-ray powder diffraction patterns of UOX gave d_{hkl} values (Å), 6.13s, 4.58s, 3.59s, 3.08s, 2.74m, 2.64m, 2.31w, 2.23w, 2.06m and 1.54m.

The thermogravimetric and differential thermal analyses were carried out using a DuPont thermal analyzer in both oxidative and inert atmospheres. The furnace was heated linearly at the rate of 10°C min^{-1} and samples of about 5 mg were taken for each run. The mass spectra were taken on a VG Micromass 70-70FF double focussing spectrometer with a VG 2235 data system. The X-ray powder patterns were recorded using Cu K_α radiation on a

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Philips X-ray diffractometer and the infrared spectra were recorded using Perkin Elmer 257 spectrophotometer.

RESULTS AND DISCUSSION

The thermal behaviour of UOX in an atmosphere of nitrogen is similar to that in air, which suggests that an oxidative atmosphere does not influence the decomposition pattern of the compound. The TG and DTA curves in air are given in Fig. 1. As seen from the TG plot, it is clear that UOX starts decomposing at 150°C and the decomposition is fast up to 250°C. The compound loses nearly 90% of the initial mass between 150 and 250°C. The loss in weight is sluggish above 250°C. No residue is left behind at 400°C.

The DTA curve exhibits a sharp endotherm at 162°C, which is immediately followed by an exotherm at 174°C. These two effects are attributed to the initiation of the decomposition process. The endotherms at 220, 240 and 375°C are probably due to the secondary reactions occurring. The gaseous products liberated around 200°C consist mainly of cyanamide and CO_2.

The mass spectral fragments with the probable assignment of the peaks are listed in Table 1. There is not molecular peak at *m/z* 148 corresponding to $OC(NH_2)_2 \cdot H_2C_2O_4$ present. The fragments are grouped into two cate-

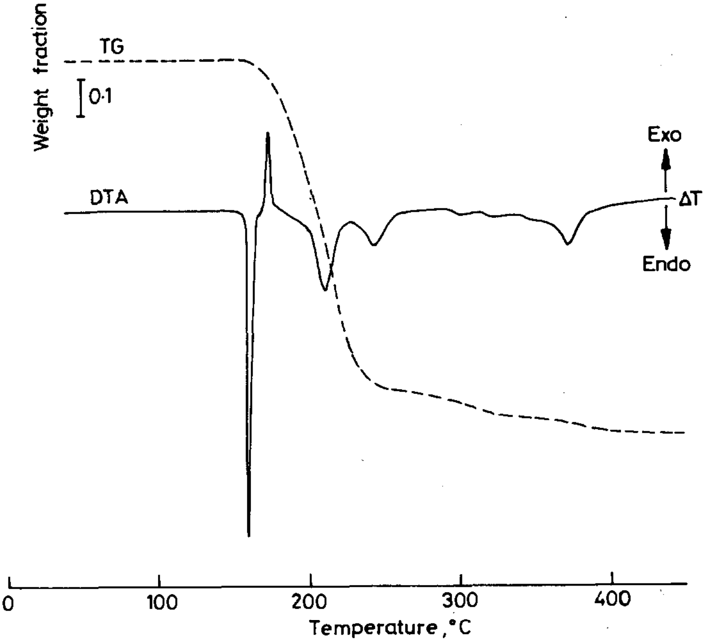

Fig. 1. TG and DTA plot of urea oxalic acid in air.

TABLE 1

Mass spectral fragments of urea oxalic acid

m/z	Ion (m^+)
60	$OC(NH_2)_2$
46	HCOOH
45	COOH
44	CO_2, $OC(NH_2)$, $C(NH_2)_2$
43	HOCN, H_2NCNH
42	H_2NCN
41	HNCN
31	H_2COH
30	H_2CO
29	HCO, H_2CNH
28	CO
27	HCN

gories; the one derived from urea consists mainly of cyanamide and its disintegration products and that from oxalic acid consists chiefly of CO_2 and HCOOH.

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