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Note

THERMAL DECOMPOSITION OF -ONIUM TYPE OXALATES

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Temperature programmed thermal decomposition of inorganic salts results in the production of new compounds at moderate temperatures provided the thermal stabilities of daughters are always higher than the parent compounds. Thus, ammonium amidosulphonate on thermolysis gives ammonium sulphate through an intermediate stable phase, imidodisulphonate [1]. Likewise, ammonium oxalate dehydrates [2,3] around 200°C to give oxamide. We are interested in the thermal stabilities of -onium type salts and in finding out if any intermediate organic compound resulted during pyrolysis. Reported in this communication are the preparation, characterization and thermal decomposition following thermogravimetry, differential thermogravimetry and differential thermal analysis of hydrazinium oxalate, $(N_2H_5)_2C_2O_4$, HOX, ethylenediammonium oxalate, $(H_3N \cdot C_2H_4 \cdot NH_3)C_2O_4 \cdot H_2O$, EOX and morpholinium oxalate $(C_4H_{10}ON)_2C_2O_4$, MOX.

EXPERIMENTAL

The oxalates of hydrazinium, ethylendiammonium and morpholinium are prepared by neutralizing the respective bases with aqueous oxalic acid solution. The resultant neutral solutions are concentrated on a water bath and kept aside for crystallization. The products are filtered, washed with ether and dried. The analytical results are given in Table 1.

The infrared spectra of the compounds are taken on a Perkin Elmer infrared spectrophotometer. The X-ray diffraction patterns are recorded using CuKα radiation. A Stanton thermobalance and a Stanton Redcroft STA thermal analyzer were employed to record the TG, DTG and DTA plots.

TABLE 1

Analytical data of the oxalates

	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
	Found	Calcd	Found	Calcd	Found	Calcd
HOX	15.24	15 58	6.35	6 54	37 12	36 36
EOX	18 12	28 57	7 83	7 19	17 01	16 66
MOX	45 86	45.44	7 39	7.63	10.45	10 60

RESULTS AND DISCUSSION

All the oxalates are colourless crystalline substances and exhibited characteristic X-ray diffraction patterns. The infrared spectra of the compounds exhibited bands in the region 3100–3400 cm^{-1} due to NH. The absorptions observed around 1600 and 1400 cm^{-1} are characteristic of the symmetric and asymmetric carboxyl stretching frequencies [4]. A strong intensity band at 960 cm^{-1} in the spectrum of HOX is due to the ν_{N-N} group.

The TG, DTG and DTA plots of HOX, EOX and MOX in air are given in Figs. 1–3. HOX is stable up to 180°C and apparently decomposes in two stages. The first stage occurs in the temperature range 180–280°C with a loss of 43% and the second stage takes place from 280–600°C. No residue was left behind at 600°C. In a separate experiment, a known amount of HOX was heated up to 250°C and kept at that temperature till no more weight loss was observed. The product was found to be colourless and insoluble in common solvents. The chemical analysis showed C, 27.81; H, 4.23; N, 32.34% which corresponded to that of oxamide (calcd. C, 27.27; H, 4.58; N, 31.81%). The infrared spectrum of the product exhibited bands (in cm^{-1}) at 3400m, 3200s, 1620s, 1390s, 1180m and 760m which agree with those of free oxamide [5,6]. Further the X-ray powder patterns gave d_{hkl} values (in Å) 5.25m, 4.78s, 3.35w, 3.21w, 3.12s, 2.59s, 2.58w, 2.38w corresponding [7] to the triclinic form of the oxamide. Thus EOX decomposes quantitatively to the oxamide according to the reaction

$$(N_2H_5)_2C_2O_4 \rightarrow H_2N\cdot CO\cdot CO\cdot NH_2 + N_2 + H_2 + 2\,H_2O$$

The calculated weight loss (43%) for the removal of gaseous products agreed very well with the observed weight loss.

The rate of weight loss curve showed a maximum at 200°C which corresponded to the endothermic peak in the DTA and is assigned to the decomposition process of HOX. The oxamide formed decomposes exothermally, exhibiting peak maxima at 420 and 500°C.

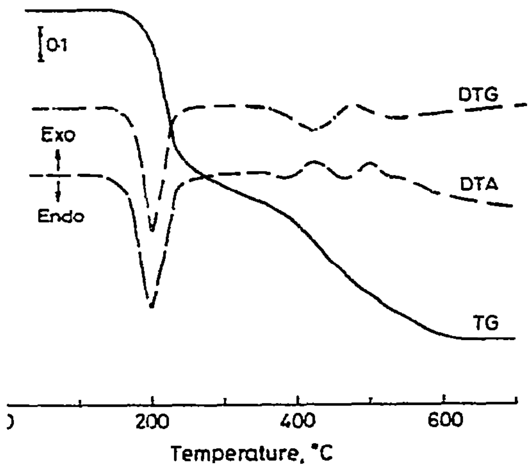

Fig 1 TG, DTG and DTA plots of HOX.

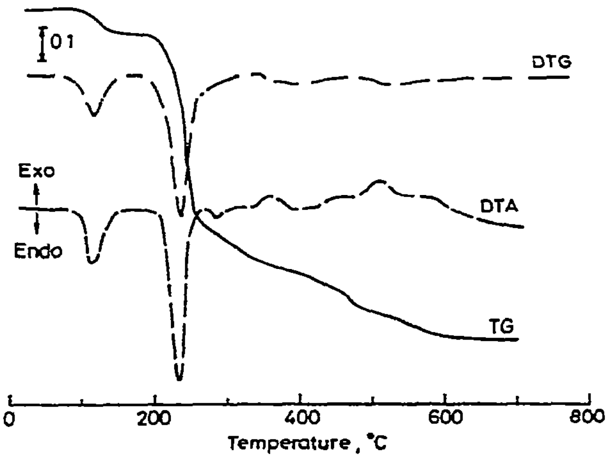

Fig 2. TG, DTG and DTA plots of EOX

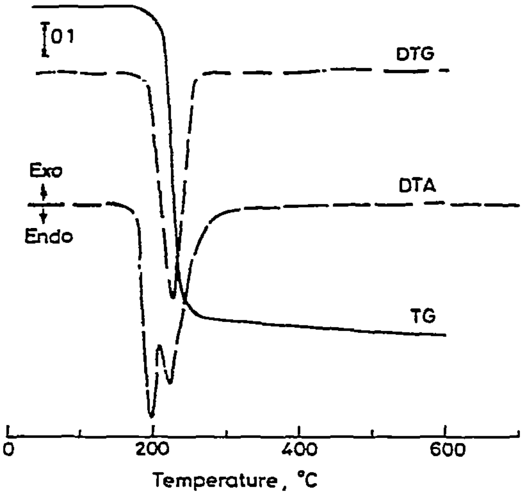

Fig 3 TG. DTG and DTA plots of MOX

The TG curve of EOX suggests that it dehydrates in the temperature range 100–150°C which is confirmed by the DTG peak and endothermic peak at 120°C. The anhydrous product starts decomposing at 200°C. Initially the decomposition was fast but after 300°C the process seems to be very sluggish. The complete oxidation occurred at 600°C with no residue remaining in the crucible. A known amount of EOX was heated at 250°C till constancy in the weight loss curve was obtained. The residue found was black and contained 20% of the initial weight. The wet chemical analysis confirmed the presence of N_2 in addition to C and H_2 but no exact formulation could be derived. However, the infrared spectrum exhibited characteristic bands, most of them corresponding to those of oxamide. Further, the X-ray powder patterns gave d_{hkl} values most of which agreed with those of oxamide. Thus, EOX after dehydration decomposed partly to give oxamide. This might have taken place due to the self condensation of the ethylene diamine moiety to give partly ammonia which on interacting with the oxalate group gives oxamide.

The endotherm at 230°C is due to the decomposition of EOX. The product found around 300°C is a mixture of oxamide and carbonaceous matter which decomposed exothermally as visualized by the DTA peaks at 360 and 510°C.

MOX, on the other hand decomposes in a single step in the temperature range 175–260°C. The carbonaceous residue at 260°C is found to be negligible. The DTA curve shows two endothermic maxima at 200 and 225°C due to the decomposition process. No oxamide or its derivative is formed in this case, probably no ammonia could be formed during the decomposition.

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