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Note

THERMAL BEHAVIOUR OF ETHYLENEDIAMMONIUM PERCHLORATE

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Perchlorates are powerful oxidizing agents [1] and are used as oxidants in explosives, pyrotechnics and solid state rocket propellants. Extensive studies have been made on the thermal stability of ammonium and related perchlorates due to their technological importance as oxidants [2,3]. This note reports the preparation, characterization and thermal behaviour of ethylenediammonium perchlorate. The study has been followed by XRD, IR, TG, DTA and MS techniques.

EXPERIMENTAL

Ethylenediammonium perchlorate, $[H_3NC_2H_4NH_3](ClO_4)_2$, EDP, was prepared by neutralizing 20 ml 1 : 1 aqueous ethylenediamine by the addition of 20% perchloric acid. The resultant very weakly acidic solution was concentrated over a water bath and the separated crystals were filtered, washed with an acetone—ether mixture and recrystallized from alcohol. Analysis: C, 9.4; H, 4.1; N, 10.9%. Calculated for $C_2H_{10}N_2O_8Cl_2$: C, 9.2; H, 3.9; N, 10.7%.

The X-ray powder diffraction patterns were taken on a Philips diffractometer using CuK_α radiation. The IR spectra were obtained on a Perkin-Elmer 257 spectrometer using Kbr pellet technique. TG and DTA studies were made in air using a Stanton thermobalance and Netzsch differential thermal analyzer, respectively. A Netzsch STA 429 thermal analyzer was employed for the studies in flowing nitrogen. Mass spectral analyses were made using a Varian mass spectrometer in a quartz crucible with the filament operating at 70 eV and 300 μA.

RESULTS AND DISCUSSION

The EDP crystals are colourless, non-hygroscopic and stable in air. The X-ray powder patterns of the compounds gave the following d_{hkl} values (Å): 6.28s, 5.09m, 4.82m, 4.14s, 4.04m, 3.95w, 3.86m, 3.63s, 3.44m, 3.13s, 3.02m, 2.52w, 2.39w, 1.63m. The IR spectrum of the compound exhibited [4] characteristic bands due to the NH_3 group at 3400s, 3180s (ν_{NH_3}) and 1588 cm^{-1} (δ_{NH_3}). The absorptions at 1065s, 942w and 620s are characteristic of the ClO_4 group [4].

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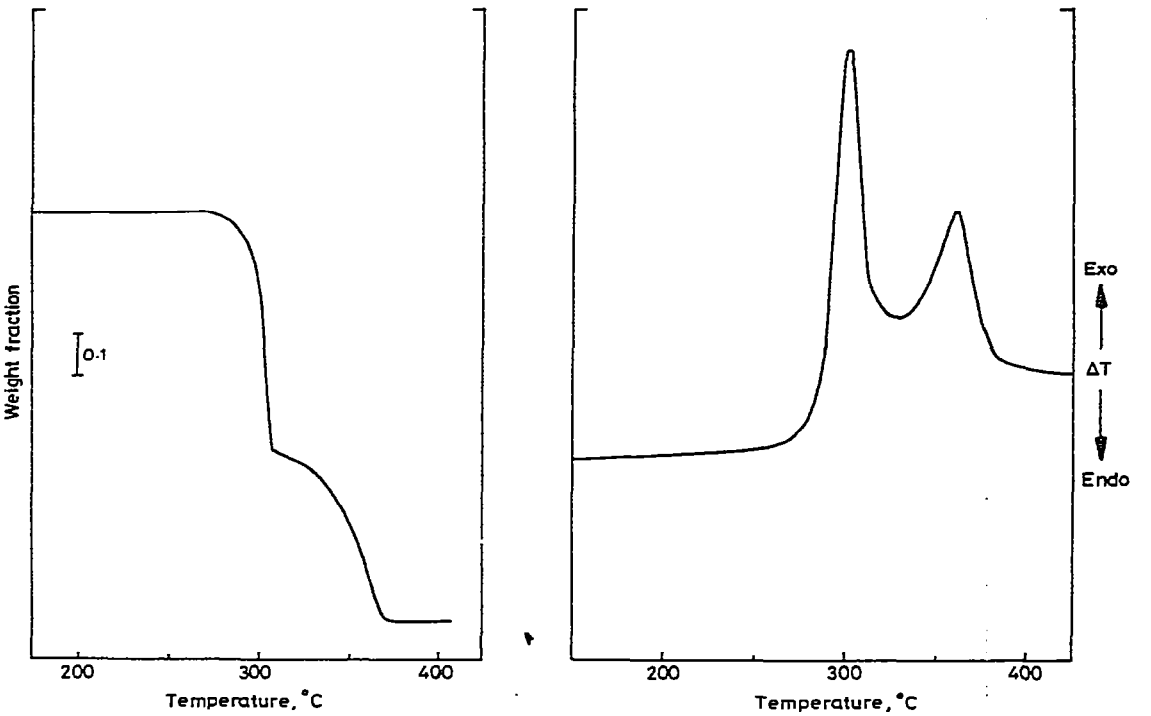

Fig. 1. TG and DTA plots of ethylenediammonium perchlorate.

TABLE 1

Mass spectral results of ethylenediammonium perchlorate at 100 and 230°C

m/e	Ion (M^+)	Intensity (%)	
		100°C	230°C
16	NH_2	28	13
17	OH_2NH_3	77	27
18	H_2O, NH_4	100	70
28	CO, N_2	46	59
29	H_2NCH		10
30	H_2CO, NO		52
32	O_2	17	21
35	Cl	6	23
36	HCl	25	70
41	H_2NCCH		20
42	$H_2N \cdot C \cdot CH_2$		16
43	$H_2NCH \cdot CH_2$		13
44	CO_2, N_2O	65	68
51	ClO	13	65
67	ClO_2	30	100
68	$HClO_2$		15
83	ClO_3	13	88
100	$HClO_4$	26	87

The thermal behaviour of EDP in an atmosphere of nitrogen is similar to that in air, which suggests that air does not influence the oxidative decomposition of EDP. The TG and DTA curves in air are given in Fig. 1. The TG plot indicates that the decomposition takes place in two stages in the temperature ranges 275—310 and 320—365°C. No residue remained at 365°C, thereby the whole material was oxidized to gaseous products. The weight loss observed at the end of the first stage of decomposition is found to be 61%, which corresponds to the loss of a molecule each of ethylenediamine and $HClO_4$ from EDP (calculated weight loss 61.5%). In a separate experiment a known weight of EDP was heated to 310°C and the remaining residue was examined. It was a liquid phase and acidic to litmus. The IR spectrum of the residue gave a strong absorption around 1080 cm^{-1} due to ClO_4, in addition to peaks around 3400 and 1650 cm^{-1} due to absorbed water. No bands characteristic of ethylenediamine were found. The DTA runs showed two exothermic effects peaking at 300 and 358°C ascribed, respectively, to the oxidative reaction of perchlorate with the organic moiety and the decomposition of $HClO_4$.

The mass spectral data obtained at 100 and 230°C are given in Table 1 with the probable assignment of the observed peaks. As seen from the results, there is no indication of a molecular peak of EDP, suggesting that the decomposition takes place by proton transfer as in the case of onium type perchlorates [5,6]. It is found that the spectral fragments HCl, ClO, ClO_2, ClO_3 and $HClO_4$ are more predominant at higher temperatures.

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