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Note

THERMAL DECOMPOSITION OF TRIETHYLENEDIAMMONIUMDIPERCHLORATE

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Perchlorates find extensive use [1] in propellants, explosives and pyrotechnics mixtures. Extensive studies have been made of the thermal decomposition of ammonium perchlorate [2]. We are interested in finding out the thermal stability and the precise decomposition temperatures of onium-type perchlorates [3–7]. Reported in this note are findings of the decomposition of triethylenediammonium diperchlorate following thermogravimetry, differential thermal analysis and mass spectrometry.

EXPERIMENTAL

Triethylenediammoniumperchlorate, TED, was prepared by the neutralization of an aqueous solution of triethylenediamine with 40% perchloric acid. The solution containing slight excess of $HClO_4$ was concentrated on a water bath, to reduce the volume, and cooled. The crystallized perchlorate was collected on a filter and recrystallized from hot water.

Anal. Calc. for $C_6H_{14}N_2O_4Cl_2$: C, 23.01; H, 4.51; N, 8.95; Cl, 22.65. Found: C, 23.4; H, 4.9; N, 8.6; Cl, 22.1.

The X-ray diffraction patterns were taken with a Philips diffractometer using Cu K_α radiation. The i.r. spectrum of the compound was recorded on a Perkin–Elmer 257 spectrometer employing the KBr pellet technique The simultaneous TG and DTA studies were made in an argon atmosphere using Mettler thermal analyzer. The heating rate of the furnace was maintained at 4°C per min. A Stanton thermobalance was employed for the thermogravimetric study in air. 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 crystals of TED are colourless, non-hygroscopic and air-stable. The melting point of the compound is 285°C (dec.) The i.r. spectrum of the

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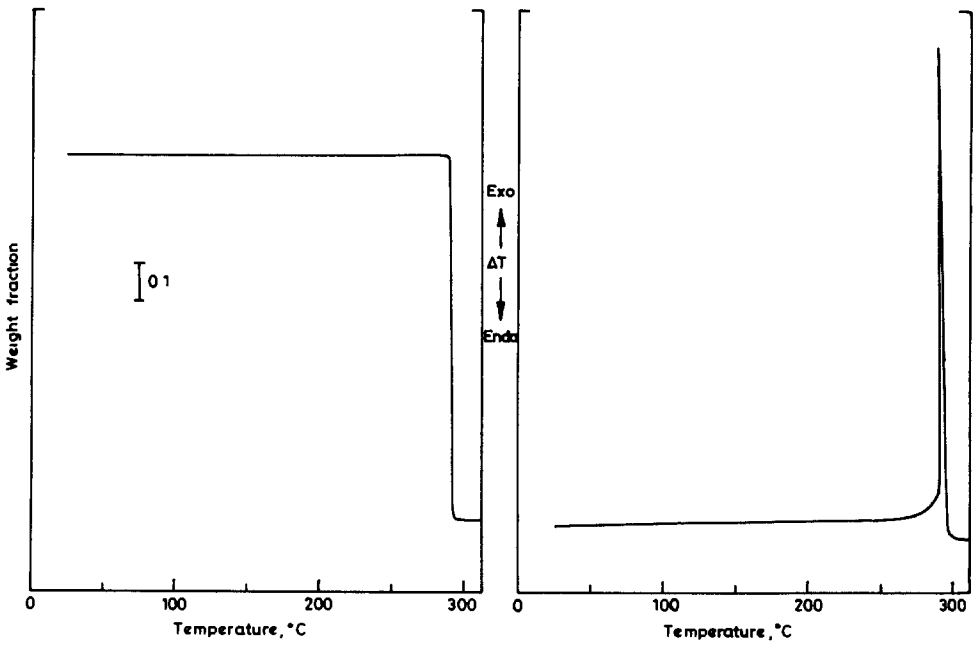


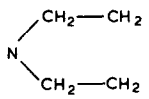
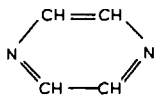
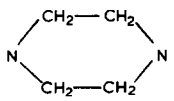
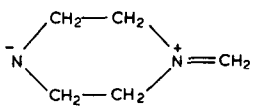
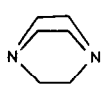
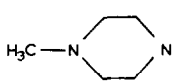
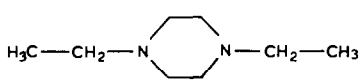
Fig 1 TG and DTA plots of triethylenediammoniumdiperchlorate

TABLE 1

Mass spectral data of triethylenediammoniumdiperchlorate

m/z	Ion(m^+)	Intensity(%)
15	NH	4
16	O	2
17	OH	21
18	OH_2	100
26	CN	9
27	HCN	12
28	C_2H_4, CO	95
29	H_2CNH	20
30	H_2CNH_2	12
35	Cl	14
36	HCl	87
41	H_3CCN	14
42	H_2CCH_2N	73
43	H_2CCH_2NH	9
44	CO_2	97
51	ClO	17
52	HClO	4
54	H_2CCH_2NC	7
55	H_2CCH_2NCH	76
56	$H_2CCH_2NCH_2$	37
57	NCH_2CH_2NH	37

TABLE 1 (continued)

m/z	Ion(m^+)	Intensity(%)
58	$HNCH_2CH_2NH$	19
67	ClO_2	72
68	$HClO_2$	2
70		11
80		20
83	ClO_3	67
84		6
98		2
100	$HClO_4$	35
112		26
128		2
142		24

sample exhibited characteristic bands due to the NH group at 3010 cm^{-1}. The strong intensity of the multiple bands around 1100 cm^{-1} are the characteristic absorption for the perchlorate group [8]. The X-ray powder patterns gave the following d_{hkl} values (Å): 8.26s, 6.11w, 4.62w, 4.50w, 4.07s, 3.92w, 3.35s, 2.71s, 1.98s, 1.92m, 1.31m.

The TG and DTA plots in argon atmosphere are given in Fig. 1. The thermal behaviour in air and argon is found to be alike which suggests that air does not influence the oxidative decomposition of TED. The TG curve suggests that TED decomposes in a single step in the temperature range 270–290°C. No residue is left behind at 290°C which indicates the conversion of the entire mass into gaseous products.

The DTA curve exhibits an exothermic effect with the peak temperature

at 290°C, which is attributed to the oxidative decomposition of TED.

The mass spectral data of TED obtained at 300°C are given in Table 1. As seen from the observed peaks, there is no molecular peak corresponding to TED, which suggests that the decomposition takes place through a proton transfer mechanism. As seen in the case of the onium-type perchlorate [3,4,9,10] this compound also cannot be volatilized as such, but decomposes into neutral particles which are then vaporized and ionized. Apparently, there are three main routes by which fragmentation occurs, namely, perchlorate anion and its disintegration products, triethylenediammonium cation and its fragmentation products and the oxidation products of the organic group by the perchlorate. Further, it is interesting to note that there are two peaks corresponding to m/z values 128 and 142 which are assigned to N-methyl N'-ethylpiperzine and N,N'-diethyl piperzine respectively. The formation of these two products are explained as follows. Triethylene diamine (m/z 112) may disintegrate to give cation radicals, N-ethylene piperzine and N,N'-dimethylene piperazine. These radicals may combine independently with triethylenediammonium cation and to give piperazine radical and N,N'-diethylpiperazine, and N-methylene piperazine radical and N-methyl N'-ethyl piperazine.

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