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Note

MASS SPECTRAL AND THERMAL DECOMPOSITION STUDIES OF PIPERZINIUM DIPERCHLORATE

M.R. UDUPA

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

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Extensive studies have been made on thermal decomposition studies of perchlorates, in particular ammonium perchlorate, due to their importance as oxidizers in explosives, pyrotechnics and rocket propellants [1]. We have been interested in the thermal stabilities of amine-onium perchlorates such as morpholinium [2], ethylenediammonium [3], cetyl trimethylammonium [4] and diphenylammonium perchlorates [5]. Reported in this note are the results of thermogravimetric, differential thermal analysis and mass spectral studies of hydrated piperzinium diperchlorate.

EXPERIMENTAL

Piperzinium (diethylenediammonium) diperchlorate dihydrate $[H_2N(C_2H_4)_2NH_2](ClO_4)_2 \cdot 2\,H_2O$ was prepared by adding dropwise 40% perchloric acid to an aqueous solution of piperzine, kept on a magnetic stirrer till the whole solution was just acidic to litmus. The resultant solution was heated on a water bath for 15 min and cooled. The separated crystalline product was filtered through suction, washed with a small amount of acetone and dried. Analysis: C, 15.2; H, 4.4; N, 8.9%. Calculated for $C_4H_{16}N_2O_6Cl$: C, 14.87; H, 4.99; N, 8.67%.

The X-ray powder diffraction patterns obtained with a Philips diffractometer using Cu K_α radiation. The IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer using KBr pellet technique. Simultaneous TG and DTA runs were made in an argon atmosphere using a Mettler thermal analyzer at a continuous heating rate of 2°C min^{-1}. Mass spectral analyses were carried out using a Varian mass spectrometer and quartz crucibles with the filament operating at 70 eV and 300 μA.

RESULTS AND DISCUSSION

Piperzinium diperchlorate dihydrate crystals are colourless, non-hygroscopic and stable in air. The X-ray powder patterns gave the following d_{hkl}

TABLE 1

Mass spectral fragments of piperzinium diperchlorate dihydrate

m/e	m^+	Intensity (%)
16	O	4
17	OH	33
18	OH_2	98
26	NC	18
27	NCH	9
28	CO, NCH_2	61
29	$HNCH_2$	23
30	NO, H_2NCH_2	23
32	O_2	6
35	Cl	23
36	HCl	62
39	NCCH	3
40	$NCCH_2$	3
41	$HNCH_2$	9
42	$N(CH_2)_2$	18
43	$HN(CH_2)_2$	8
44	CO_2, N_2O	46
51	ClO	38
52	HCO	8
53	NCC_2H_3	15
54	$NC(CH_2)_2$	3
55	$HNC(CH_2)_2$	3
56	$HNCH(CH_2)_2$	23
57	$HN(CH_2)_2N$	15
67	ClO_2	100
68	$HClO_2$	3
69	$HN(CH_2)_2NCH$	27
80	$N(CH)_2N(CH)_2$	24
81	$HN(CH)_2N(CH)_2$	25
83	$H_2N(CH)_2NH(CH)_2$	83
85	$HN(CH_2)_2N(CH_2)_2$	27
86	$HN(CH_2)_2NH(CH_2)_2$	12
93	$N(CH)_2N(CH)_2 \cdot N$	6
100	$HClO_4$	42
107	$HN(CH)_4NNC$	3
108	$HN(CH)_4N \cdot NCH$	19
109	$HN(CH)_4N \cdot NCH_2$	7
110	$HN(CH)_4N \cdot NCH_3$	4
114	$HN(CH_2)_4N \cdot NCH_3$	13
119	$N(CH)_4N \cdot N \cdot C_2H$	13
120	$N(CH)_4N \cdot N \cdot (CH)_2$	10
121	$N(CH)_4NNH(CH)_2$	6
122	$HN(CH)_4N \cdot NH(CH)_2$	25
133	$(CH)_4N \cdot N(CH)_3CH_2$	6
134	$(CH(_4N \cdot N(CH)_2(CH_2)_2$	5
136	$(CH)_4N \cdot N(CH_2)_4$	3
164	$H_2N(CH)_4N \cdot N(CH)_4NH_2$	4
170	$HN(CH_2)_4N \cdot N(CH_2)_4NH$	2

(Å) values: 6.91w, 6.15m, 4.98m, 4.77s, 4.13m, 3.74s, 3.65s, 3.37m, 3.21s, 3.06w, 3.01m, 2.67m, 2.56m, 2.25w, 1.78w. The IR spectrum of the compound exhibited characteristic absorptions (cm^{-1}) at 1100s, 970m, and 620s due to Cl–O stretching vibrations of ClO_4 with T_d symmetry [6]. The broad absorption band at 3480 and a medium intensity band at 1630 cm^{-1} are the characteristics of lattice water. The absorption frequencies at 3180s and 1595s are attributed to the $-NH_2$ groups of the piperzinium cation.

The TG and DTA curves of piperzinium diperchlorate are reproduced in Fig. 1. It is quite evident that the compound loses weight in two stages. The first stage, registering a loss of 9.5%, occurs in the temperature range 55–170°C. The weight loss observed is attributed to the dehydration process as it corresponds to the calculated weight loss of 11% for the removal of two molecules of water from the parent compound. This inference is supported by the appearance of an endothermic peak around 75°C in the DTA curve. The anhydrous material is found to be stable up to 240°C and does not seem to rehydrate on exposure to cooled atmosphere. In the second stage, between 240 and 280°C, the compound decomposes with a mild explosion and the reaction is found to be highly exothermic. No residue was left behind at 280°C, thereby all the organic moiety was oxidized into gaseous products. The DTA plot exhibits a sharp exothermic peak at 270°C.

The mass spectral results of the salt obtained at 280°C along with the probable assignment of the peaks are given in Table 1. There is no molecular peak of the salt (m/e 187), which supports the theory that -onium type salts cannot be volatilized as such but they undergo decomposition into neutral particles which subsequently ionize and vaporize [7]. Thus, the major fragmentation routes are perchloric acid and its decomposition products and, piperzine and its decomposition products. In addition, there are peaks attributed to CO, NO, CO_2 and N_2O resulting from the oxidation of the

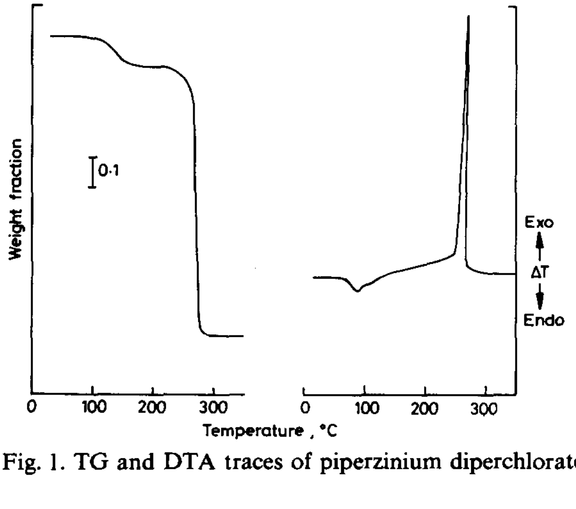
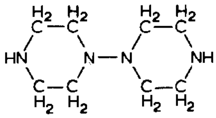


Fig. 1. TG and DTA traces of piperzinium diperchlorate dihydrate in argon.

organic moiety by the perchlorate. Further, there are several peaks in the spectrum with mass number higher than 100. These peaks are attributed to the decomposition products of



(m/e 170) which result from the dimerization of the piperzine radical obtained under the experimental conditions.

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