Thermochimica Acta, 52 (1982) 363–366
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

THERMAL BEHAVIOUR OF CETYL TRIMETHYLAMMONIUM PERCHLORATE

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(Received 21 July 1981)

Thermal decomposition studies of ammonium and related perchlorates [1,2] have been made extensively due to their technological use as oxidants in explosives, pyrotechnics and solid state rocket propellants. We have been interested in the study of thermal stabilities of the -onium type perchlorates [3,4] and reported in this note are the preparation, characterization and thermal behaviour of cetyl trimethylammonium perchlorate, following XRD, IR, TG, DTA and MS techniques.

EXPERIMENTAL

Cetyl trimethylammonium perchlorate, $[CH_3(CH_2)_{15}N(CH_3)_3]ClO_4$, CTAP was prepared by adding dropwise 40% perchloric acid to an aqueous solution of cetyl trimethylammonium bromide kept on a magnetic stirrer till the precipitation was complete. The precipitated perchlorate salt was collected on a filter, washed with acetone and dried. Analysis: C, 59.2; H, 10.8; N, 3 6%. Calculated for $C_{19}H_{42}NO_4Cl$: C, 59.4; H, 11.0; N, 3.7%; m.p. 112°C.

The X-ray powder patterns were recorded with Philips diffractometer using CuKα radiation. The IR spectra were taken with a Perkin Elmer 257 spectrophotometer using the KBr pellet technique. Simultaneous TG and DTA curves were recorded in an argon atmosphere using a Mettler thermal analyzer at a continuous heating rate of 4°C per min. A Stanton thermobalance was employed for the thermal studies in air. 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

The crystals of CTAP are colourless, non-hygroscopic and stable in air. The X-ray patterns gave the following interplanar spacings (Å) when the incident angle 2θ was scanned from 5 to 70°: 11.33s, 5.72s, 5.28w, 4.60s, 4.23m, 4.06m, 3.93m, 3.85s, 3.30m, 2.36w, 2.02w, 1.44w. The infrared spectrum of CTAP gave characteristic absorptions (cm^{-1}) at 1110s, b, 985m, and 625s due to the ClO_4 group and at 2930s,

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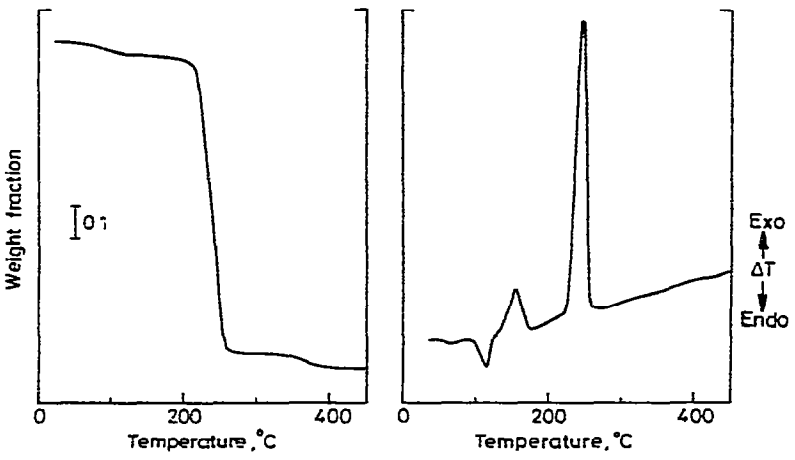

Fig 1 TG and DTA plots of cetyl trimethylammonium perchlorate

2860, 1445s, 915m, 725m due to the cetyl trimethylammonium cation [5].

The TG and DTA plots obtained in argon atmosphere are given in Fig. 1. As seen from the TG curve, CTAP loses about 4% weight in the temperature range 70–160°C and about 95% is lost between 215–260°C. The DTA curve showed an endotherm at 115° and two exothermic peaks at 155 and 250°C. In a separate experiment, a simultaneous TG-DTA run was made up to 200°C and the sample was cooled at the same rate as that of heating. There was an exothermic effect at 85°C which supports the theory that the endotherm in the heating curve at 115°C is due to the melting of the sample. The sample was found to be pale brown in colour and when reheated exhibited the endotherm at 115° and a sharp exotherm at 250°C due to the oxidative decomposition. There was no weight change up to 215°C and the exotherm at 155°C was absent. The 155° exotherm is probably due to the characteristic property of the compound, in the sense that it decomposes to a slight extent during the initial melting. Similar observations were made by Wendlandt and Zief [6,7] that certain organic compounds lose some weight below their melting points. The thermal behaviour in air is found to be not significantly different from that in an argon atmosphere.

The mass spectral peaks obtained at 280°C are tabulated with the probable assignments. The spectral results suggest that there is no indication of molecular peak of CTAP, $[C_{19}H_{42}NO_4Cl]$ and there are three routes by which the fragmentation occurs, namely, perchlorate anion and its disintegration, cetyl trimethylammonium cation and its disintegration following the Hofmann dealkylation mechanism [8] and the oxidation of the organic group by the perchlorate. This confirms the assumption [9] that quaternary ammonium salts cannot be volatilized as such but they undergo decomposition into neutral particles which subsequently ionize and vaporize. It is interesting to note from the spectral peaks that the intensities of perchlorate and its disintegration products are comparatively very weak, which may be due to the limited oxygen availability for the oxidation of a long chain cetyl group.

TABLE 1

Mass spectral data of cetyl trimethylammonium perchlorate

m/e	Ion (m^+)	Intensity (%)
15	CH_3	12
17	OH	6
18	OH_2	37
27	NCH	17
28	CO, H_2CN, C_2H_4	12
30	NO, CH_2O	6
35	Cl	2
36	HCl	5
39	NC CH	14
41	CH_3CN	17
42	$(CH_2)_2N$	43
43	CH_3CH_2N	78
44	CO_2, N_2O,$(CH_3)_3N$	42
45	$(CH_3)_2NH$	6
50	CH_3Cl	17
52	HClO	5
53	C_2H_3CN	5
54	$(CH_2)_2CN$	10
55	CH_3CH_2CN	75
56	$(CH_2)_3N$	44
57	$CH_3(CH_2)_2N$	72
58	$(CH_3)_2CH_2N$	100
59	$(CH_3)_3N$	25
67	ClO_2	11
68	$(CH_2)_3CN$, $HClO_2$	9
69	$CH_3(CH_2)_2CN$	49
70	$(CH_2)_4N$	37
71	$CH_3(CH_2)_3N$	31
72	$CH_3(CH_2)_3NH$	31
73	$(CH_3)_2CH_2$ NH	18
81	$(CH_2)_3CHCN$	5
82	$(CH_2)_4CN$	11
83	$CH_3(CH_2)_3CN$, ClO_3	44
84	$(CH_2)_5N$, $HClO_3$	25
85	$CH_3(CH_2)_4N$	13
96	$(CH_2)_5CN$	5
97	$CH_3(CH_2)_4CN$	32
98	$(CH_2)_6N$	11
111	$CH_3(CH_2)_5CN$	12
112	$(CH_2)_7N$	5
126	$(CH_2)_8N$	5
138	$(CH_2)_8CN$	7
139	$CH_3(CH_2)_7CN$	21
140	$(CH_2)_9N$	32
141	$CH_3(CH_2)_8N$	6
142	$CH_3(CH_2)_8NH$	17

TABLE 1 (continued)

m/e	Ion (m^+)	Intensity (%)
152	$(CH_2)_9CN$	5
153	$CH_3(CH_2)_8CN$	9
154	$(CH_2)_{10}N$	22
155	$CH_3(CH_2)_9N$	16
168	$(CH_2)_{11}N$	12
170	$CH_3(CH_2)_{10}NH$	12
182	$(CH_2)_{12}N$	10
184	$CH_3(CH_2)_{11}NH$	10
196	$(CH_2)_{13}N$	16
198	$CH_3(CH_2)_{12}NH$	10
210	$(CH_2)_{14}N$	2
212	$CH_3(CH_2)_{13}NH$	11
224	$(CH_2)_{15}N$	46
225	$CH_3(CH_2)_{14}N$	12
226	$CH_3(CH_2)_{14}NH$	9
238	$(CH_2)_{16}N$	2
240	$CH_3(CH_2)_{15}NH$	9
254	$CH_3(CH_2)_{15}N\ CH_3$	15
255	$CH_3(CH_2)_{15}NH\ CH_3$	5
266	$CH_3(CH_2)_{15}NC\ CH_3$	13
267	$CH_3(CH_2)_{15}NCH\ CH_3$	5
268	$CH_3(CH_2)_{15}N{\cdot}CH_3CH_2$	65
269	$CH_3(CH_2)_{15}N(CH_3)_2$	77
270	$CH_3(CH_2)_{15}NH(CH_3)_2$	18
283	$CH_3(CH_2)_{15}N(CH_3)_2{\cdot}CH_2$	27
284	$CH_3(CH_2)_{15}N(CH_3)_3$	37

ACKNOWLEDGEMENT

The author wishes to thank Professor Dr. B. Krebs, Münster, F.R.G., for his interest in the work.

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