Thermochimica Acta, 16 (1976) 128–131

Note

Thermal behaviour of thallium(I) chlorate

M. R. UDUPA

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

(Received 10 December 1975)

Thermal decomposition studies on alkali metal chlorates revealed[1–3] that they are congruently melting and decompose to metal chlorides. It is also observed that during the decomposition, a part of the chlorates disproportionates to perchlorates and chlorides. In an earlier paper[4] we made a detailed investigation on the thermal behaviour of thallium(I) perchlorate which decomposes to thallium(I) chloride and thallium(III) oxide. Solymosi and Bánsági[5] have studied the thermal stability of $TlClO_3$ and according to them, the decomposition occurs according to $7TlClO_3 \rightarrow TlCl+3Tl_2O_3+6ClO_2$. The authors failed to detect the formation of $TlClO_4$ during the decomposition. Thallium(I) resembles alkali metals in its crystallochemical behaviour and it was thought interesting to examine again, its thermal behaviour and to compare it with that of alkali metal chlorates. The decomposition studies are followed by thermogravimetry, differential thermal analysis, chemical analysis, infrared spectral measurements and X-ray powder diffraction patterns.

EXPERIMENTAL

Materials

Thallium(I) chlorate was prepared by mixing equal volumes of aqueous solutions containing equimolar ratios of thallium(I) sulphate and barium chlorate. The precipitated $BaSO_4$ was filtered and the clear solution was evaporated on a water-bath. $TlClO_3$ thus obtained had d_{hkl} values (Å) 4.41s, 3.20s, 3.00s, 2.72w, 2.52m, 2.24w, 1.95w which agreed with the reported values[6]. All other chemicals used were of analytically pure grade.

Methods

The thermogravimetric analysis was made using a Stanton recording thermobalance at a linear heating rate of 6°C min^{-1}. About 100-mg samples were taken for each run in a platinum crucible container of dimension, ht. 20 mm, bottom diam. 12 mm and top diam. 20 mm. Differential thermal analysis was done in air on a Netzsch differential thermoanalyzer at a heating rate of 10°C min^{-1} using standard alumina as reference material.

The infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer in Nujol mull. The X-ray powder patterns were taken with a Debye–Scherrer camera of 11.46 cm diam. using Cu$K\alpha$ radiation.

Analytical

Thallium(III) in the decomposition products was analysed iodometrically. Thallium(I) or total thallium in the decomposition residues was determined by the bromine–DMSO method[7].

RESULTS AND DISCUSSION

The thermogravimetric plot of $TlClO_3$ is given in Fig. 1 and it indicates that there are three stages in the decomposition process. The first stage of decomposition set in at 200°C with a mild explosion and a loss of 28% of initial weight. There was splashing of the sample along the walls and outside the crucible. The loss in weight at this stage is due to the liberation of gaseous products and the loss of a part of the sample due to splashing. The second stage of weight loss begins around 300°C and

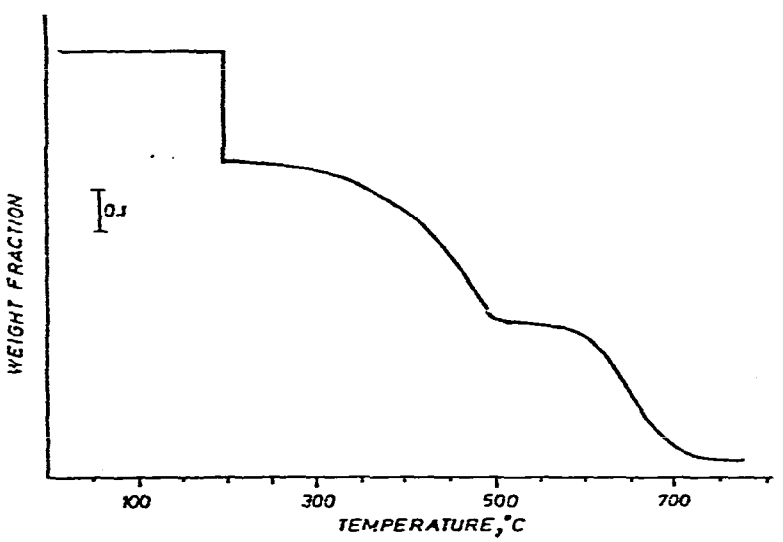

Fig. 1. TG plot of $TlClO_3$.

continues upto 520°C accounting for a total loss of 65% of weight. The final stage of decomposition begins at 600°C and is complete at 750°C. No residue is found at this temperature.

Separate experiments were carried out with 100 mg of $TlClO_3$ in a glass crucible (ht. 40 mm, bottom diam. 12 mm and top diam. 30 mm) by heating gently with a flame. When the decomposition starts the flame was withdrawn and the sample was examined by X-ray and IR techniques. The IR spectra of $TlClO_3$, $TlClO_4$ and the residues of partly decomposed and completely decomposed $TlClO_3$ around 200°C

are given in Fig. 2. The IR spectrum of the partly decomposed $TlClO_3$ had absorptions (cm^{-1}) 1100 and 605 characteristic[8] of Cl–O stretching of perchlorate and 988, 950 and 925 due to Cl–O stretching of chlorate[8]. The IR spectrum of the splashed out residue also had bands due to both ClO_4 and ClO_3 moieties. A weak absorption around 1100 cm^{-1} observed for the completely decomposed $TlClO_3$ indicates the

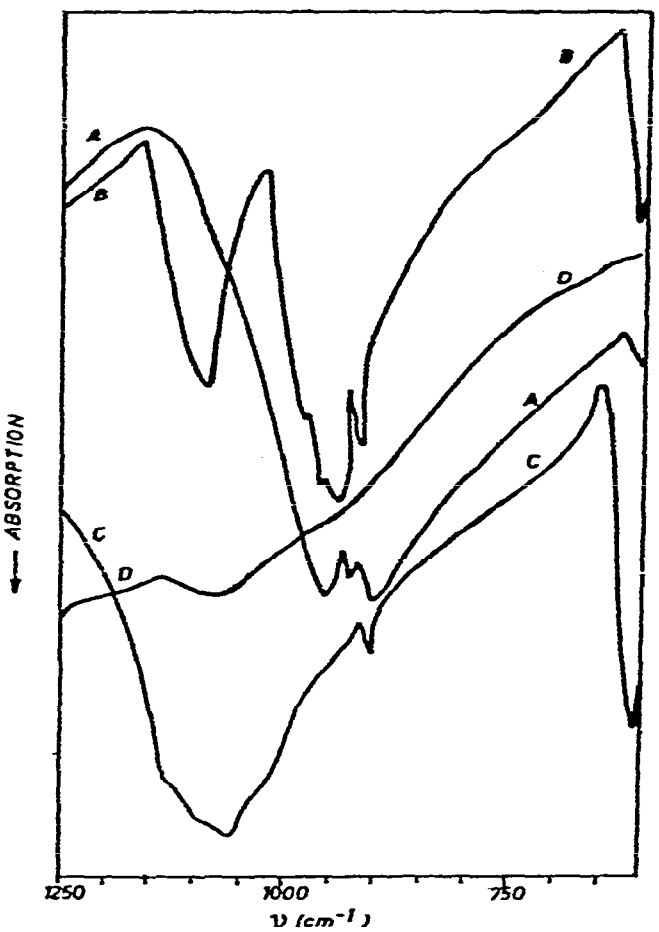

Fig. 2. Infrared spectra of $TlClO_3$ (A), partly decomposed $TlClO_3$ (B), $TlClO_4$ (C) and completely decomposed $TlClO_3$ (D).

presence of a small amount of $TlClO_4$ in the residue. The X-ray powder patterns of partially decomposed $TlClO_3$ had d_{hkl} values corresponding to $TlClO_3$, TlCl, Tl_2O_3 and additional lines 3.51 and 2.19 Å due to $TlClO_4$[9]. The X-ray patterns of the splashed out residue indicate that it consists of mainly $TlClO_3$. The completely decomposed $TlClO_3$ showed characteristic X-ray patterns of TlCl[10] and Tl_2O_3[11] suggesting only a very small amount of $TlClO_4$ left undecomposed.

Taking care that no splashing out of the sample occurred during the decomposition, by controlled heating, the weight loss observed around 200°C was 18%.

The residue was analyzed for thallium content and found to have 42% TlCl and 39% Tl_2O_3. Separate studies on TlCl and Tl_2O_3 suggest that TlCl volatilizes in the temperature range 400–550°C and Tl_2O_3 decomposes above 600°C. The residue at 200°C consists of TlCl, Tl_2O_3 and a trace amount of $TlClO_4$. The volatilization of TlCl and the decomposition of $TlClO_4$ take place in the temperature range 300–520°C and the decomposition of Tl_2O_3 occurs in the temperature range 600–750°C. Though the thermogravimetric analysis does not give the exact amount of TlCl and Tl_2O_3 due to the splashing out of the sample around 200°C, the mole ratio of TlCl to Tl_2O_3 is calculated to be 2:1 attributing the weight losses in the temperature range 300–550°C to TlCl and that in the range 600–750°C to Tl_2O_3. This is also in agreement with the weight loss observed and the analytical data of the residues obtained by controlled heating at 200°C. These results suggest an overall reaction for the decomposition as

$$4TlClO_3 \rightarrow 2TlCl + Tl_2O_3 + Cl_2 + 9/2O_2$$

The DTA of $TlClO_3$ is similar to that reported by Solymosi and Bánsági[5]. It exhibits an exotherm at 200°C due to the decomposition of $TlClO_3$ and an endotherm at 460°C attributed to the volatilization of TlCl. Two more endotherms observed at 670 and 750°C are assigned to the decomposition of Tl_2O_3.

REFERENCES

1 M. M. Markowitz, D. A. Boryta and H. Stewart, *J. Phys. Chem.*, 68 (1964) 2282.
2 E. S. Freeman and W. K. Rudloff, in R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Vol. I, Academic Press, London and New York, 1970, p. 364.
3 F. Solymosi and T. Bánsági, *Acta Chim. Acad. Sci. Hung.*, 56 (1968) 337.
4 A. S. Giridharan, M. R. Udupa and G. Aravamudan, *J. Therm. Anal.*, 7 (1975) 65.
5 F. Solymosi and T. Bánsági, *Thermal Analysis*, Vol. 2, Proc. Third ICTA, Davos, Birkhäuser Verlag, Basel, 1971, p. 289.
6 *ASTM Index* No. 9-406.
7 M. Chandrasekharan, V. R. S. Rao and G. Aravamudan, *Talanta*, 19 (1972) 383.
8 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 2nd ed., 1969.
9 *Inorganic Index to the Powder Diffraction File*, JCPDS, 1971.
10 *ASTM Index* No. 6-0486.
11 *ASTM Index* No. 5-0584.