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THERMAL BEHAVIOUR OF THALLOUS PERCHLORATE

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Thermal decomposition characteristics of thallous perchlorate are investigated in nitrogen and in air using TG and DTA techniques. Isothermal studies at 380°, 400°, 420° and 440° in air and in nitrogen showed that the relative amounts of the decomposition products, namely, thallic oxide and thallous chloride, depend upon both the temperature and the atmosphere around the sample. At low pressures (5×10^{-1} mm/Hg) there is volatilization of thallous perchlorate even at 200°.

Thermal decomposition studies on metal perchlorates are interesting in that either the metal chloride or the metal oxide is formed as product depending on which one has higher free energy of formation under the standard state [1]. If the free energies are of comparable magnitude, both the chloride and the oxide are formed [1]. Thus for alkali metal and silver perchlorates the metal chlorides are the end-products of decomposition [2]. Lanthanide perchlorates give the corresponding oxychlorides [3]. Zirconyl, uranyl and thorium perchlorates yield the highest valent oxides on thermal decomposition [4]. Molybdenyl and hafnyl perchlorates give rise to the corresponding dioxides through the intermediate, oxychlorides [5]. Lead perchlorate gives the oxide, PbO, and lead chloride [6] and magnesium perchlorate also gives magnesium oxide and magnesium chloride [7, 8]. In the case of thallous perchlorates other possibilities, namely, the tendency for the thallous ion to get oxidized either aerially or by the perchlorate group during decomposition, has also to be considered. This paper deals with the results obtained on studies of the thermal behaviour of thallous perchlorate in air, in nitrogen atmosphere and at low pressures (5×10^{-1} mm/Hg). The compound has been reported [9–11] to undergo a phase transition at 266° but its decomposition characteristics have not been studied earlier.

Experimental

Anhydrous thallous perchlorate was prepared by the treatment of an aqueous solution of thallous carbonate with slight excess of perchloric acid and evaporation of the solution. The colourless crystals were filtered and washed with acetone and dried at 100°. Thallium was determined iodometrically by oxidising Tl(I) to

Tl(III) by bromine water in acidic medium and destroying the excess bromine with DMSO [12] and perchlorate by the nitron method [13].

(Found: Tl = 67.20%; ClO_4^- = 32.70%. Calculated: for $TlClO_4$ Tl = 67.25%; ClO_4^- = 32.75%.)

Thermogravimetric studies in air were made in pyrex, platinum and mullite crucibles using a recording Stanton (HT-SM model) thermobalance. 200 mg of powdered (~200 mesh) thallous perchlorate were used in each experiment. A linear rate of heating of 6°/min was employed. Isothermal studies in air were made at 380°, 400°, 420° and 440° by heating the furnace to the required temperature and then lowering the furnace over the sample contained in the crucible. Platinum crucibles were found to be attacked at 460°. There was no effect of crucible material (pyrex, platinum and mullite) on thermal decomposition of thallous perchlorate up to 440°. Hence cylindrical pyrex crucibles of uniform dimension (15 mm diameter and 16 mm height) were used as containers. Studies in low pressure (5×10^{-1} mm/Hg) and in flowing nitrogen (760 mm/Hg) were made in all-glass system. In these experiments 200 mg of powdered (~200 mesh) thallous perchlorate was placed in cylindrical containers (15 mm dia and 16 mm height).

Differential thermal analysis (DTA) experiments were carried out in a Netzsch recording DTA unit. Ignited alumina was used as the reference material. X-ray powder patterns of the solid phases formed during the various stages of decomposition were taken in a 114.6 mm diameter camera employing CuK_α radiation. X-ray examinations of thallous perchlorate at room temperature and at 300° were made using a Rikagu—Denki high-temperature powder camera to confirm a reversible phase transformation indicated at 260° in the DTA run. Infrared spectral examinations (using a Perkin Elmer 257) were made use of to detect the presence of undecomposed thallous perchlorate in various experiments. Thallous

Table 1

Decomposition of thallous perchlorate in air and in nitrogen (760 mm/Hg) at different temperatures

Amount of thallous perchlorate taken = 200 mg.
Amount of thallic oxide expected for the complete decomposition of 200 mg of $TlClO_4$ to Tl_2O_3 = 159.3 mg.

Temperature (°C)	Conditions	Time taken for complete decomposition	Amount of thallic oxide (mg)
380	air	8 hours	126.50
	nitrogen	12 hours	73.50
400	air	60 minutes	112.00
	nitrogen	120 minutes	75.50
420	air	30 minutes	106.50
	nitrogen	60 minutes	86.50
440	air	10 minutes	96.00
	nitrogen	20 minutes	90.00

chloride and thallic oxide, the two products of perchlorate decomposition, do not show any absorption in the region 625–1200 cm^{-1} which is characteristic of perchlorate vibrations.

Results and discussion

Exploratory experiments were carried out in air on the thermal decomposition of thallous perchlorate. It was indicated that the decomposition was initiated at about 375–400° and there was a rapid weight loss at about 440°. Thallic oxide and thallous chloride were both found to be formed. They were identified by their characteristic X-ray patterns [14, 15]. No oxychlorides of thallium(III) are known to exist [16] and there was no evidence for their formation in the present work also. The TG runs were stopped at 500° by which time decomposition was found to be completed. Separate studies on pure thallic oxide and thallous chloride samples showed that thallic oxide was stable up to 600°, whereas thallous chloride began to volatilize in air at an appreciable rate even before it melted at 430°. The rates of volatilization of thallous chloride in glass crucibles at different temperatures were: 5 mg/5 mins at 440° and 4 mg/20 mins at 380°. In mullite crucibles, presumably because of the porous texture of the container, the rate of volatilization was higher. Heating 200 mg of thallous chloride (~200 mesh) in the temperature range 350°–440° caused no aerial oxidation to the thallic state. Thus the thallic oxide formed during the decomposition of thallous perchlorate is not due to the aerial oxidation of the thallous chloride formed. It was also found that thallic oxide and thallous chloride do not mutually affect their thermal behaviour in air. Heating of an intimate mixture of thallic oxide and thallous chloride at temperatures 350°–440° in air resulted in the volatilization of all thallous chloride leaving behind the thallic oxide taken.

To understand the nature of decomposition of thallous perchlorate in detail, isothermal studies were made at 380°, 400°, 420° and 440° recording the weight loss vs. time curves. The amount of thallic oxide formed in each case was quantitatively determined by treating the residue with 2N HCl and determining the thallium(III) iodometrically. The total thallium (thallium as thallic oxide, thallous chloride and undecomposed thallous perchlorate) in the crucible at any stage was determined by bromine-DMSO method. The presence of undecomposed thallous perchlorate was made evident very easily by the characteristic IR bands of perchlorate. Due to the volatilization of thallous chloride, the total thallium determined during the different stages of decomposition was invariably less than that taken as thallous perchlorate.

Decomposition studies were also made under isothermal conditions in nitrogen environment (760 mm/Hg) and the amount of thallic oxide formed under these circumstances was determined and checked with the amount formed during the decomposition in air at the same temperatures. This gave an idea as to the contribution of aerial oxidation of thallous perchlorate towards the formation of thallic oxide. Instead of air or nitrogen (760 mm/Hg), when decomposition of thallous perchlorate was attempted at low pressure (5×10^{-1} mm/Hg) it was observed that the thallous perchlorate samples volatilized under these conditions even at temperatures for below 380°, the temperature at which the decomposition was easily noticed under the same conditions in air or in nitrogen (760 mm/Hg). Working at 5×10^{-1} mm/Hg, it was observed that the following weight losses were sustained

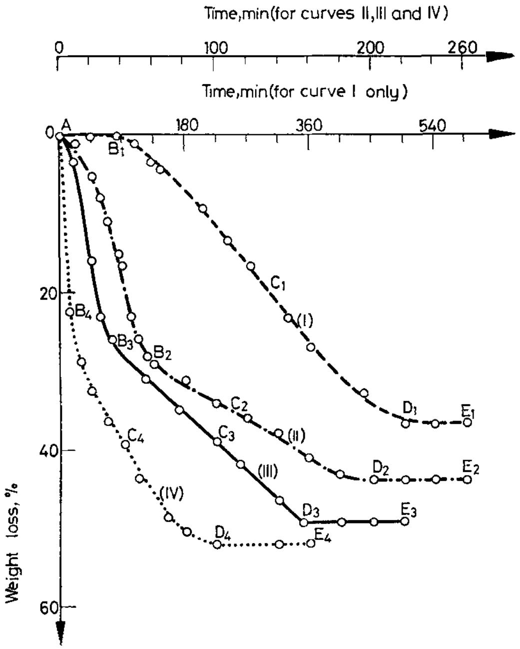

Fig. 1. TG of Thallous Perchlorate in air at (I) 380°, (II) 400°, (III) 420° and (IV) 440°. Sample size: 200 mg. Sample container: pyrex. Heating rate: 6°/min

when 200 mg of thallous perchlorate (~200 mesh), taken in 15 mm diameter and 16 mm height containers, were heated to the temperatures indicated: 0.40 mg (after 90 minutes) and 1.44 mg (after 300 minutes) at 200°; 9.0 mg (after 90 minutes) at 250°; 150.0 mg (after 90 minutes) at 300° and 200.0 mg (after 90 minutes) at 350°. The material left in the crucible and the sublimate were both found to be only pure thallous perchlorate as evidenced by chemical analysis, and X-ray and IR spectral examinations. Therefore, no tangible information could be collected on the decomposition of thallous perchlorate at low ambient pressures. It is intended to take up further investigations on the nature of species present in the vapours of thallous perchlorate.

In Fig. 1 are presented the weight loss vs. time curves obtained for experiments made under isothermal conditions in air. Table 1 gives the amount of thallic oxide formed after complete decomposition of thallous perchlorate and the time required for this under isothermal conditions at different temperatures in air and in nitrogen (760 mm/Hg). The values for thallic oxide cited are the main results of these experiments under each condition and are reproducible to ±2.00 mg of thallic oxide. Working in these two different environments enabled us to find out the extent of involvement of oxygen of the air in the decomposition of thallous perchlorate. Thallous perchlorate was found to be stable in air and in nitrogen (760 mm/Hg), without the slightest decomposition even after 24 hours at 350°; at that temperature there was no weight loss and no evidence of formation of thallic oxide or thallous chloride. At 380° slow decomposition sets in (portion $B_1C_1D_1$ in Fig. 1) after an induction period of about 60 minutes (portion AB_1). Complete decomposition in air was achieved only after 9 hours (portion D_1E_1). The material in the crucible finally was found to be only pure thallic oxide. During the intermediate stages ($B_1C_1D_1$) the crucible was found to contain mixtures of thallous perchlorate, thallic oxide and very little thallous chloride. Visual examination of the material during the intermediate stages showed that no melting had occurred. The thallic oxide was formed as a black coating over the undecomposed thallous perchlorate crystals. Isothermal decompositions at 400° ($AB_2C_2D_2E_2$), 420° ($AB_3C_3D_3E_3$) and at 440° ($AB_4C_4D_4E_4$) showed no induction period and were increasingly very fast. The two parts in the weight loss vs. time curve (AB_n and $B_nC_nD_n$ where $n = 2-4$) showed that first thallous perchlorate decomposed fast (in the region AB_n; $n = 2 - 4$) to thallic oxide and thallous chloride and then the thallous chloride volatilized ($B_nC_nD_n$ where $n = 2 - 4$) leaving behind thallic oxide (D_nE_n where $n = 2 - 4$). The decomposition of thallous perchlorate at 440° was so fast that it was completed within 20 minutes. In the temperature range 380° – 440° the examination of the volatile thallium compounds from the decomposition of thallous perchlorate under 760 mm/Hg in air or in nitrogen showed complete absence of thallous perchlorate. Therefore one can easily conclude that under ambient pressure (760 mm/Hg) there is no volatilization of thallous perchlorate even at 380° – 440°.

An examination of the results presented in Table 1, on the amount of thallic oxide formed after complete decomposition of thallous perchlorate at different temperatures in air and in nitrogen atmosphere (760 mm/Hg) reveals that thallous perchlorate decomposes mainly according to the following three types of processes:

a) $TlClO_4 \xrightarrow{\text{Self decomposition}} TlCl + 2O_2$

b) $TlClO_4 \xrightarrow{\text{Self decomposition}} Tl_2O_3$ + gaseous products (chlorine and oxides of chlorine)

c) $TlClO_4 \xrightarrow{\text{Aerial oxidation}} Tl_2O_3$ + gaseous products (chlorine and oxides of chlorine)

At low temperatures (380°) the aerial oxidation of thallous perchlorate contributes equally to the formation of thallic oxide as does process (b). In absence of air and in nitrogen (at 380°), it takes a longer time for the complete decomposition of thallous perchlorate and this trend is also shown, though less markedly, at higher temperatures. At higher temperatures (440°) the amount of thallic oxide in air is much the same as in nitrogen atmosphere. This is attributed to the faster rate of self decomposition of thallous perchlorate (process (a)) at higher temperatures, giving little scope for aerial oxidation. The observed formation of a greater amount of thallic oxide with increase in temperature during the decomposition of thallous perchlorate in nitrogen atmosphere indicates that with increase in temperature, process (b) becomes progressively more pronounced than process (a). It is most likely that process (a) concerning the formation of thallous chloride is straightforward. However, what is broadly classified as process (b) concerning the formation of thallic oxide in absence of air may not be a simple one-step process. Thus, results on the decomposition of thallous perchlorate show that in contrast to most other perchlorates, the products can be more than one and their relative amounts are dependent on the temperatures of the decomposition and the ambient conditions.

The DTA curves obtained in air and in nitrogen (760 mm/Hg) were similar. There was one endotherm at about 260° ascribed to the orthorhombic to cubic phase transformation [9 – 11]. This was checked by X-ray work on thallous perchlorate taken at 250° and 300° using a high-temperature camera. The transition at 260° was reversible and was shown up as an endotherm while heating, and an exotherm on cooling in DTA runs in the temperature range 250 – 300°. There were many exotherms centering around 440° and were associated with the various decomposition steps leading to the formation of thallic oxide and thallous chloride. The individual assignments in this region are obviously difficult and it is to be pointed out that at temperatures in the region 440° the exothermic decomposition steps of thallous perchlorate are also accompanied by endothermic processes of smaller magnitude such as melting and volatilization of thallous chloride formed.

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Résumé — On a étudié par TG et ATD les caractéristiques de la décomposition thermique du perchlorate de thallium(I) dans l'azote et dans l'air. Des études isothermes à 380, 400, 420 et 440°C dans l'air et dans l'azote ont montré que les taux relatifs de produits de décomposition, c'est-à-dire l'oxyde de thallium(III) et le chlorure de thallium(I), dépendent de la température ainsi que de l'atmosphère autour de l'échantillon. Sous faible pression ($5 \cdot 10^{-1}$ torr) le perchlorure de thallium(I) se volatilise même à 200°.

Zusammenfassung — Die thermischen Zersetzungscharakteristika von Thallium(I)-perchlorate wurden in Stickstoff und in Luft unter Anwendung der TG- und DTA-Techniken untersucht. Isotherme Studien bei 380°, 400°, 420° und 440° in Luft und in Stickstoff zeigten, daß die relativen Mengen der Zersetzungsprodukte, Thallium(III)oxid und Thallium(I) chlorid, sowohl von der Temperatur als auch von der das Muster umgebenden Atmosphäre abhängen. Bei niedrigen Drücken (5×10^{-1} mm/Hg) verflüchtigt sich Thallium(I)perchlorat bei 200°.

Резюме — Исследован термораспад перклората таллия в азоте и в воздухе с использованием ТГ и ДТА. Изотермический нагрев, при 380°, 400°, 420°, 440° в воздухе и в азоте показал, что относительные количества продуктов распада, а именно, окиси хлорида и таллия, зависят как от температуры, так и от окружающей образец атмосферы. При низких давлениях ($5 \cdot 10^{-1}$ мм рт.ст.) перхлорат таллия является летучим уже при 200°.