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THERMAL DECOMPOSITION OF THALLIUM(I) PERCHLORATE IN PRESENCE OF CHROMIUM(III) OXIDE

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ABSTRACT

Thermal decomposition of an intimate mixture of thallium(I) perchlorate and chromium(III) oxide revealed that chromium(III) oxide lowers the decomposition temperature of thallium(I) perchlorate and is oxidized into hexavalent state to give thallium(I) dichromate. The thermal decomposition was followed by constant temperature heating, thermogravimetry and differential thermal analysis. The reaction products were characterized by chemical analysis, X-ray diffraction and infrared spectral measurements.

INTRODUCTION

Burcat and Steinberg[1] have studied the influence of transition metal oxides on the thermal decomposition of lithium perchlorate. Chromium(III) oxide was found to lower the decomposition temperature of lithium perchlorate and chromium(III) was oxidized into hexavalent state to give lithium dichromate[2]. Thallium(I) resembles alkali metal ions as regards its crystallochemical behaviour and it was thought interesting to study the influence of chromium(III) oxide on the decomposition of thallium(I) perchlorate. Recently, we reported[3] in detail the thermal behaviour of thallium(I) perchlorate and found that the decomposition of pure thallium(I) perchlorate set in at 380 °C and the decomposition products depended on the ambient conditions. The decomposition studies in the present work were followed by thermogravimetry (TG), differential thermal analysis (DTA) and isothermogravimetry and the products are characterized by chemical analysis, X-ray powder diffraction patterns and infrared spectral data.

EXPERIMENTAL

Anhydrous thallium(I) perchlorate was prepared by the reaction of thallium(I) carbonate with required amount of 20% perchloric acid. The resultant clear solution was concentrated on a water-bath and the crystals separated were recrystallized from hot water.

Chromium(III) oxide was obtained by heating reagent grade $Cr(NO_3)_3 \cdot 9H_2O$ at 300 °C until the decomposition was complete.

Mixtures of thallium(I) perchlorate and chromium(III) oxide were prepared in 1:1, 2:1, 4:1 and 8:1 molar ratios by taking the required amounts and grinding in an agate mortar for 1/2 h.

Thermogravimetric runs were made in air using a Stanton recording thermobalance at a heating rate of 6 °C min^{-1}. In each run about 250 mg of the samples were taken in mullite crucible containers. Differential thermal analyses were made on a Netzch differential thermal analyzer using inert alumina as reference material. About 80–100 mg of the samples were taken for each run.

Constant temperature heating experiments were carried out in air on a muffle furnace whose temperature could be controlled with an accuracy of ±5 °C using vitreosil crucibles as containers.

X-Ray powder diffraction patterns were taken using CuK_α radiation and a 114.6-mm diameter Debye–Scherrer camera.

Infrared spectra were measured in nujol mull on Beckman IR-12 spectrophotometer. Polyethylene plates were employed in the range 200–600 cm^{-1} and sodium chloride cells in the range 600–1600 cm^{-1}.

Thallium(I) in the reaction mixture was precipitated by the addition of sodium peroxide as $Tl(OH)_3$ and was determined by iodometry after dissolving it in dilute acid. Chromium(VI) was determined iodometrically.

RESULTS AND DISCUSSION

Preliminary experiments at different constant temperatures were carried out with thallium(I) perchlorate–chromium(III) oxide (2:1) to ascertain whether Cr(III) was oxidized and at which minimum starting temperature. The mixture was heated at 220, 250, 270 and 280 °C for about 30 min and the products were examined on the presence of Cr(VI); no hexavalent chromium was detected at these runs. However, it was detected in the decomposition products of the mixture heated at 290 °C. Heating of pure thallium(I) perchlorate at this temperature did not indicate decomposition of the perchlorate group as it is stable[3] up to 380 °C, it is reasoned that the reaction of

TABLE 1

DATA ON HEATING MIXTURES OF THALLIUM(I) PERCHLORATE AND CHROMIUM(III) OXIDE AT 295 °C FOR 1 h

Molar ratio $TlClO_4:Cr_2O_3$	*Amount taken* (*mg*)	*Cr(VI) oxidized* (%)	*Extent of Cr(VI) oxidation* (%)
1:1	304.0	11.10	48.7
2:1	253.3	13.42	98.0
4:1	273.5	7.50	98.5
8:1	258.3	3.94	97.8

chromium(III) oxide with thallium(I) perchlorate lowers the decomposition temperature of the latter. Constant temperature experiments were carried out in air at 295 °C for 1 h for 1:1, 2:1, 4:1 and 8:1 molar mixtures of thallium(I) perchlorate and chromium(III) oxide. The products of decomposition were analyzed for Cr(VI) and Tl contents and the results are given in Table 1. The percentage weight losses and the extent of Cr(III) oxidation were reproducible for a particular mixture. The conversion of Cr(III) to Cr(VI) was quantitative in the case of 2:1, 4:1 and 8:1 mixtures. The amount of Cr(VI) obtained could be rationalized assuming that the solid product formed from the 2:1 mixture is thallium(I) dichromate according to the overall reaction,

$$2TlClO_4 + Cr_2O_3 \rightarrow Tl_2Cr_2O_7 + Cl_2\uparrow + 2O_2\uparrow \quad (1)$$

The X-ray powder patterns of this product gave d_{hkl} values 3.54 (s), 3.26 (s), 2.15 (s), 2.08 (w), 1.90 (m), 1.84 (w), 1.65 (w), 1.57 (w). These values are in good agreement with the reported[4] values of pure thallium(I) dichromate. The d-spacings of the solid phases remaining after reaction of 4:1 and of 8:1 mixtures had values corresponding to this new phase and those of the excess unreacted thallium(I) perchlorate. On the other hand the d-spacings of the solid phases after the reaction of 1:1 mixture gave values corresponding to pure thallium(I) dichromate and chromium(III) oxide; in this case the analytical values showed that about 49% of chromium(III) oxide is oxidized and that there was no free thallium(I) perchlorate left, which is in confirmity with the stoichiometry of reaction (1). The infrared spectrum of the product of decomposition of 2:1 thallium(I) perchlorate and chromium(III) oxide gave the following absorptions (in cm^{-1}): 910 (w), 890 (s), 772 (m) and 525 (w). These frequencies are in agreement with those observed[5] for pure thallium(I) dichromate. The absorption frequencies of the decomposition products of 4:1 and 8:1 mixtures had additional absorptions (in cm^{-1}) at 1075 (s, b), 620 (s) and 450 (s) which are assigned to the free ClO_4 group. On the other hand the absorption frequencies of the decomposition products of the 1:1 mixture are observed (in cm^{-1}) at 910 (w), 890 (s), 775 (m) and 620 (m), 560 (m) and 400 (w). The latter set of values correspond[6] to those of Cr_2O_3. Thus the in-

TABLE 2

THERMOGRAVIMETRIC DATA ON HEATING MIXTURES OF THALLIUM(I) PERCHLORATE AND CHROMIUM(III) OXIDE

Molar ratio $TlClO_4:Cr_2O_3$	*Amount taken* (*mg*)	*Weight loss* (%)	
		Found	*Expected*[a]
1:1	248.0	15.0	14.8
2:1	262.4	18.0	17.76
4:1	255.6	10.0	9.80
8:1	271.0	5.0	5.22

[a] As per reaction (1).

frared spectral frequencies are in confirmity with the conclusions drawn from the results of chemical and X-ray analyses.

In conjunction with the heating at constant temperature, TG and DTA studies, were carried out for 1:1, 2:1, 4:1 and 8:1 thallium(I) perchlorate and chromium(III) oxide mixtures. The percentage weight loss observed and the expected weight loss for reaction (1) for different molar mixtures are given in Table 2 and Fig. 1. The TG and DTA curves of 2:1 mixtures shown in Fig. 1 are representative and a similar behaviour was noticed for other mixtures. The TG and DTA runs were made up to 350 °C as

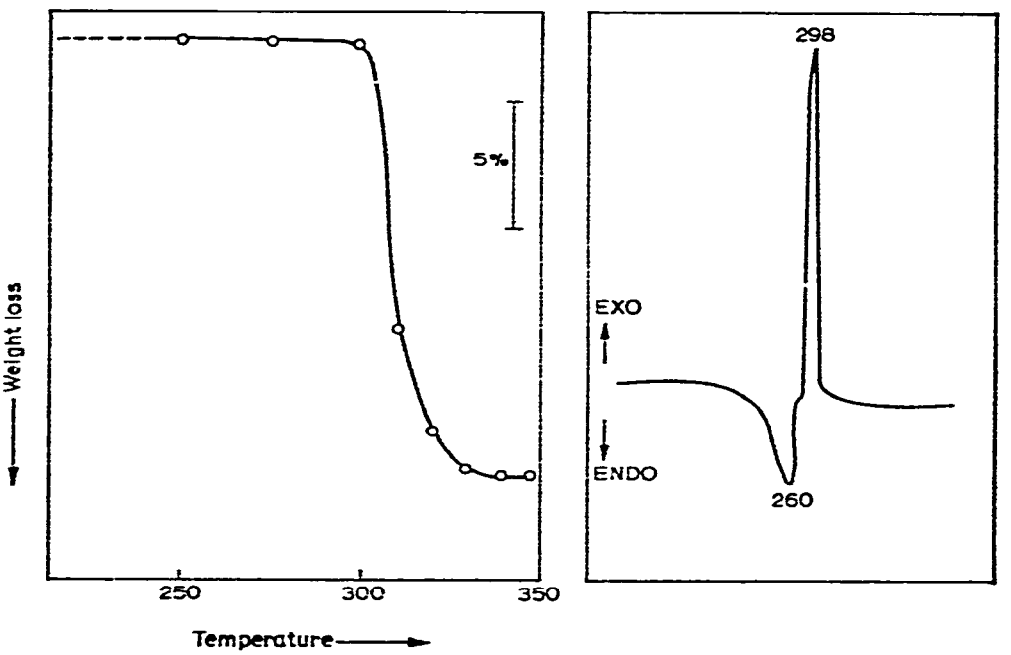

Fig. 1. TG and DTA plots of 1:2 molar ratio of $TlClO_4$ and Cr_2O_3.

thallium(I) dichromate is found to melt[4] around 360 °C. The TG runs for all the mixtures suggest that the decomposition reactions begin in all the cases around 300 °C and are complete by 340 °C. The weight loss (Table 2) observed for the different mixtures is in good agreement with the proposed reaction (1). Further the decomposition products of all the mixtures subjected to chemical, X-ray and spectral analyses, and the results agree well with those of heating experiments at constant temperature. DTA runs of the mixtures gave one endothermic peak around 260 °C due to phase transformation[7] and an exotherm around 300 °C due to the formation of thallium(I) dichromate.

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