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Note

Thermal behaviour of chromium (III) perchlorate hexahydrate

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Thermal behaviour of intimate mixtures of chromium(III) oxide and lithium[1], potassium[2], rubidium[3], cesium[3] and thallium(I)[4] perchlorates revealed that chromium(III) oxide not only catalyses the decomposition by lowering the decomposition temperatures of the pure metal perchlorates but also chemically interacts resulting in the formation of metal dichromate. The oxidation of chromium(III) into the hexavalent state is attributed to the abstraction of oxygen from the perchlorate moiety during the decomposition. In this context, it was thought interesting to study the thermal behaviour of chromium(III) perchlorate and to identify the decomposition products in order to find out whether chromium(III) is oxidized into chromium(VI) by the perchlorate group. Except for a report[5] on the preparation of chromium(III) perchlorate with different molecules of water of hydration no work seems to have been carried out on the thermal decomposition of this compound. In the present study, the decomposition characteristics are followed by TG and DTA techniques and the decomposition products have been examined by chemical analysis, X-ray powder diffraction patterns and infrared spectral measurements.

EXPERIMENTAL

Materials

All the chemicals used were of analytically pure grade. Chromium(III) perchlorate, $Cr(ClO_4)_3 \cdot 6H_2O$ was prepared[5] by the dissolution of $Cr(OH)_3$, obtained by precipitating $Cr(NO_3)_3$ solution with excess ammonia and washing the precipitate until it is free of ammonium and nitrate ions, with a minimum amount of 20% perchloric acid. The resulting solution was concentrated on a water-bath and the separated crystals were collected, dried under reduced pressure and preserved in a dry atmosphere.

Methods

The thermogravimetric analysis was carried out in air using a recording Stanton thermobalance at a linear heating rate of 6°C per min. About 200-mg samples were taken in a platinum crucible container for each run. Differential thermal

analysis was done in air on a Netszch differential thermoanalyzer at a heating rate of 10°C per min using standard alumina as reference material.

The X-ray powder patterns were taken with a Debye-Scherrer camera of 114.6 mm diam. using X-rays of wavelength 1.542 Å. The infrared spectra were recorded in Nujol on a Beckman IR 12 spectrophotometer.

Analytical

Chromium(III) in $Cr(ClO_4)_3 \cdot 6H_2O$ was oxidized to Cr(VI) with sodium peroxide and was determined iodometrically[6]. Chromium(III) in Cr_2O_3 was also determined iodometrically after oxidizing the oxide to $K_2Cr_2O_7$ by fusing with excess potassium perchlorate.

RESULTS AND DISCUSSION

Chromium(III) perchlorate hexahydrate is highly hygroscopic and dissolves in water with the evolution of heat. The infrared spectrum of the compound showed absorptions (cm^{-1}) at 3300 s,b and 1650 m due to stretching and bending modes, respectively, of water[7], 1090 s,b 940 w and 625 m characteristic of Cl–O stretching[7] and a broad medium intensity band at 320 (?).

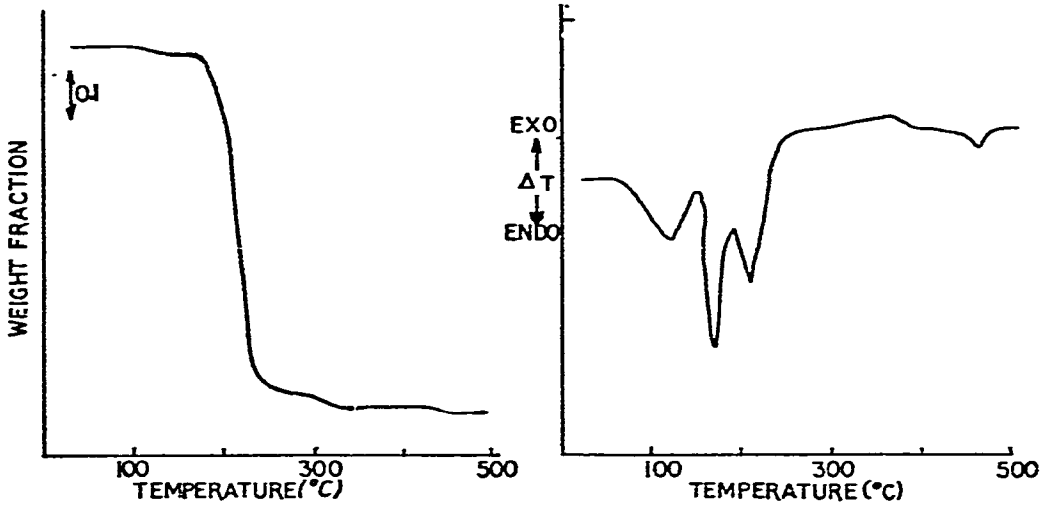

Fig. 1. TG and DTA plots of chromium(III) perchlorate hexahydrate.

The TG and DTA plots of $Cr(ClO_4)_3 \cdot 6H_2O$ are given in Fig. 1. As seen from Fig. 1, it is clear that the decomposition initiated at about 180°C and was rapid up to 230°C. Constancy in the weight loss curve was noticed in the temperature range 260–300°C. Gradual weight loss occurred from 300 to 470°C beyond which no change in weight took place. An initial weight loss of less than 1% around 100°C is due to the removal of absorbed water by the sample.

Separate experiments were performed by heating the sample up to 280 and 480°C. The residues obtained were examined by X-ray and i.r. techniques. The most intense d_{hkl} values observed for the products obtained at 280°C (Å) are 4.24 s, 3.40 s and 3.34 s which agreed[8] with those of pure CrO_3, and the d-spacings of the residue obtained at 480°C (Å) are 2.62 s, 2.44 s and 1.68 s which are characteristic of Cr_2O_3. The i.r. spectrum of the product at 280°C was similar to that of pure CrO_3 and had the absorptions (cm^{-1}) 975 s, 850 w,b and 305 m whereas the spectrum of the residue at 480°C had the absorption frequencies (cm^{-1}) at 625 s, 560 s, 435 w and 405 w which agreed[9] with those of pure Cr_2O_3.

Further confirmation of the residues at 280°C as CrO_3 and at 480°C as Cr_2O_3 was obtained by chemical analysis. The product obtained at 280°C is red in colour, slightly hygroscopic and is easily soluble in water. On the other hand the residue obtained at 480°C is green and is insoluble in water. The chromium contents in the two residues are given in Table 1. The TG curve indicates that weight loss at 280°C was 86% and that at 480°C it was 90%. The corresponding calculated values on the basis of CrO_3 and Cr_2O_3 formation are 78.2 and 83.4%, respectively. This suggests that a part of chromium has volatilized presumably in the form of chromyl chloride, CrO_2Cl_2. In a separate experiment a known amount of $Cr(ClO_4)_3 \cdot 6H_2O$ was taken in a specially designed all-glass apparatus and was slowly heated from room temperature to 480°C. The evolved gases are cought in a flask containing water. The liberated chromyl chloride is hydrolyzed and the solution is boiled to remove any dissolved chlorine and Cr(VI) is determined iodometrically. The mean values of the several experiments are given in Table 1.

TABLE 1
ANALYSIS OF CHROMIUM (%)

	$Cr(ClO_4)_3 \cdot 6H_2O$	CrO_2Cl_2	CrO_3	Cr_2O_3
Found	11.01	3.88	6.99	7.19
Calculated	11.34	3.78*	7.56*	7.56*

*As per reaction scheme 1.

The analytical values suggest that two-thirds of chromium(III) in $Cr(ClO_4)_3 \cdot 6H_2O$ is oxidized into chromium(VI) oxide and the remaining one-third to chromyl chloride. The decomposition scheme is

$$3Cr(ClO_4)_3 \xrightarrow{280\,^\circ C} CrO_2Cl_2 + 2CrO_3 + 7/2Cl_2 + 14O_2$$
$$\downarrow 480\,^\circ C$$
$$Cr_2O_3 + 3/2O_2 \qquad (1)$$

The broad endothermic DTA peak observed at 130°C is attributed to the melting of $Cr(ClO_4)_3 \cdot 6H_2O$. The endothermic peaks at 180 and 220°C are due to the dehydration followed by the decomposition of the perchlorate. The 220 peak may also be associated[10] with the melting of CrO_3 formed. Both the TG and DTA curves in the temperature range 300–480°C are similar[10] to those of pure CrO_3. The small exothermic hump around 350°C is due to the expulsion of oxygen from CrO_3 and the endotherm at 470°C is due to the formation of Cr_2O_3.

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