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THERMAL AND X-RAY DIFFRACTION INVESTIGATIONS OF THE BINARY SYSTEM CHROMIUM(III) OXIDE – BARIUM PERCHLORATE TRIHYDRATE

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Chromium(III) oxide reverses the sequence of dehydration of barium perchlorate trihydrate (BP). Between 223 and 310° the oxide reacts with anhydrous BP in a 1:1 molar ratio to give the yellow barium dichromite $BaCr_2O_4$. Between 350 and 430° this material reacts in 1:1 stoichiometry with BP, to give barium chromate $BaCrO_4$. The products have been identified by X-ray diffraction analysis. The formation of an unkown phase is also reported.

Chromium(III) oxide has been shown to catalyse the thermal decomposition of the perchlorates and the chlorates of the alkali metals [1–3], and to interact chemically to give the metal dichromates [2,3]. The oxide also catalyses the decomposition of alkali metal pyrosulphates to the sulphates through the formation of chromium sulphate or the double sulphates with the alkali metals [4]. Udupa and Srinivasan [5] recently reported that the oxide reacts with barium chlorate via complex stoichiometry to give barium chromate $BaCrO_4$ and barium chloride. On the other hand, the thermal decomposition of barium perchlorate (BP) is catalysed by manganese(IV) oxide and europium(III) oxide and the initial decomposition temperature can be lowered from 460° down to 310° by the action of these oxides [6].

It is the purpose of the present work, therefore, to study the effects of Cr_2O_3 on the thermal decomposition of barium perchlorate.

Experimental

A MOM-photorecording derivatograph was employed for recording TG, DTG and DTA curves under static air atmosphere; a pair of MOM-platinum crucibles was used for sample and reference material (α-Al_2O_3); sample size: 100 mg; heating rate: 10 deg/min.

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The rest of the procedure was as described earlier [7].

The chemicals were of analytical grade: $Ba(ClO_4)_2.3H_2O$ was a product of Hopkin and Williams, while Cr_2O_3 was prepared by the thermal decomposition of ammonium chromate from BDH.

Results and discussion

Figure 1 shows the TG and DTG curves for mixtures of Cr_2O_3 with BP in molar ratios of 1:4, 1:2 and 1:1. The corresponding DTA curves are shown in Fig. 2. The dehydration of BP occurs in two steps; two molecules are lost first and thereafter another one. This sequence differs from that observed in the dehydration of the individual salt [6]. Similar effects were found with MnO_2 and Eu_2O_3 [6]. A mechanism can be proposed for the role of the oxide in reversing the order of the dehydration process as follows. Two of the water molecules must occupy adjacent sites and are linked similarly to the crystal of BP, while the third one occupies a remote site. The action of the oxide is to stabilize the monohydrate rather than the dihydrate form, and therefore in the presence of the oxide two molecules are expelled first.

The TG curves indicate a multi-step decomposition reaction. For the 1:4 molar mixture, three weight-loss processes are observed, in the temperature ranges 223–302°, 350–429° and 454–531°. The last step typically corresponds to the decomposition of the excess BP [6], which is exactly half of the amount of the BP previously present in the sample. The first and the second steps correspond to weight losses of 7% and 9% respectively. The DTA curve (Fig. 2) for the 1:4 molar mixture clearly shows the phase-change endotherms of anhydrous BP at 280° and 350° [8], although partially overlapping with the decomposition exotherms. The third step of the decomposition is missing from the thermal curves of the 1:2 molar mixture, and the first two steps involve larger weight losses, but still in the same ratio to each other (7:9). The temperature ranges of these two reactions remain unchanged. For the 1:1 molar mixture the main feature that appears in the curves is the first decomposition reaction. The reaction involves a weight loss of 20.5% and occurs in three partially overlapping steps, as seen in the corresponding DTG curve. The reaction is followed by three minor steps, that involve weight losses of 4%, 1.5% and 2%. The following conclusions can be drawn from the thermal curves. The first reaction is of the first order with respect to both Cr_2O_3 and BP, because the largest weight loss was recorded for the 1:1 molar mixture. The second reaction is also of the first order for BP and the products of the first reaction.This is evident from the curves of the 1:2 molar mixture, where half of the BP was consumed in the first reaction and half in the second. Furthermore, the curves of the 1:2 molar mixture indicate no excess of BP. An attempt was made to derive a practical proof regarding the stoichiometry of the second reaction. A sample of the 1:1 molar mixture was cooled from 360° (the final temperature of the first reaction), mixed with fresh BP in a molar ratio of 1:1 and

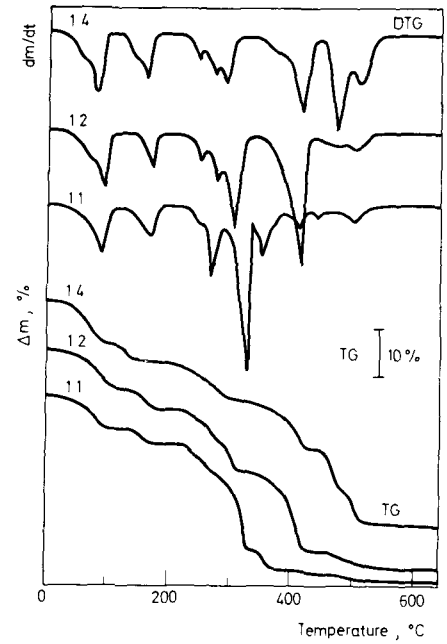

Figure 1 TG and DTG curves for the effects of various ratios of Cr_2O_3 on the decomposition of $BP.3H_2O$

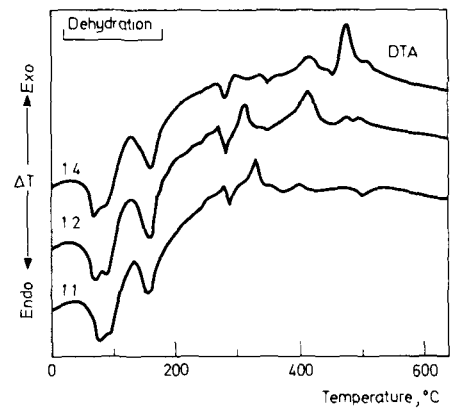

Figure 2 DTA curves for various Cr_2O_3 + $BP.3H_2O$ molar ratios

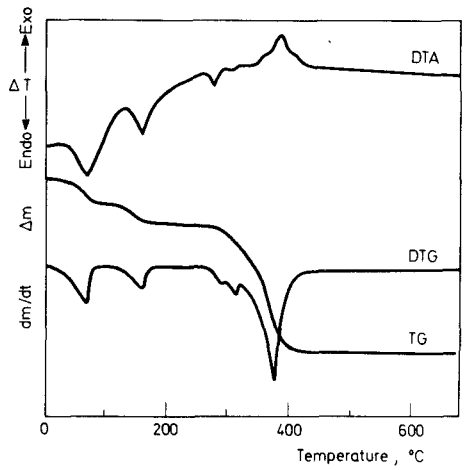

Figure 3 Practical proof of the stoichiometry of the second reaction

heated to record the thermal curves (Fig. 3). The results typically fit with the calculated weight loss from the second reaction, in the same temperature range as for the 1:2 molar mixture. The reactions are well resolved from each other and easily allow examination of the intermediates. The following samples have been sintered at the indicated temperatures for X-ray diffraction analysis: 1:4 at 330°, 1:2 at 330°, 1:1 at 360°, 1:4 at 430°, 1:2 at 435°, 1:1 at 415°, and 1:4 at 580°. The following compounds could be identified in these samples:

Sample	Composition
1:4 at 330°	BP, $BaCr_2O_4$, traces of unkown phase;
1:2 at 330°	BP, $BaCr_2O_4$, unkown phase;
1:1 at 360°	$BaCr_2O_4$, traces of BP, unkown phase;
1:4 at 430°	BP, $BaCrO_4$, unknown phase;
1:2 at 435°	$BaCrO_4$, unknown phase;
1:1 at 415°	$BaCr_2O_4$, traces of $BaCrO_4$;
1:4 at 580°	$BaCrO_4$ and $BaCl_2$.

From the X-ray diffraction it is obvious the BP reacts with Cr_2O_3 in a molar ratio of 1:1 to give barium dichromite, $BaCr_2O_4$. The dichromite was identified by the *d*-spacing lines 351, 315, 215, 394, 437, 452 and 528 pm. The reaction can therefore be described as follows:

$$Cr_2O_3 + Ba(ClO_4)_2 \rightarrow BaCr_2O_4 + 2ClO_2 + \frac{3}{2}O_2 \quad (1)$$

Barium dichromite belongs to the group of compounds of general formula $M^{II}O.Cr_2O_3$ which may be prepared as crystalline compounds from the fusion of Cr_2O_3 with bivalent metal oxides [9]. Such compounds have spinel structure, with the Cr(III) ions occupying the octahedral interstices [9]. This suggests the formation of barium oxide, BaO, as intermediate. The oxide readily reacts with Cr_2O_3 to give $BaO.Cr_2O_3$ or $BaCr_2O_4$. The weight loss predicted from eq. (1) is significantly greater than the recorded weight loss. Furthermore, the X-ray diffraction patterns of the reaction products indicated the presence of a compound (specified above as the unknown phase) for which no formula could be found in the A.S.T.M. card index. The unknown phase gave the following *d*-spacing lines: 435, 361, 274, 251, 234, 223, 213 (the most intense line), 209, 195, 189, 178, 169, 165, 161 and 156 pm.

Barium dichromite reacts with BP in the molar ratio 1:1 to give barium chromate, which was identified by the *d*-spacinglines 217, 290, 317, 340, 352 and 397 pm, with the 317 pm line as the most intense line. The reaction can be expressed by the equation:

$$BaCr_2O_4 + Ba(ClO_4)_2 \xrightarrow{\Delta} 2BaCrO_4 + 2ClO_2 \qquad (2)$$

The predicted weight loss is identical with the practical values obtained from the thermal curves in Figs 1 and 3.

Barium chromate and the unkown phase were found to be thermally stable at temperatures as high as 800°.

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Zusammenfassung – Chrom(III)-oxid kehrt die Reihenfolge der Dehydratisierung von Bariumperchlorat-Trihydrat (BP) um. Das Oxid reagiert zwischen 223 und 310 ° mit wasserfreiem BP im Molverhältnis 1:1 unter Bildung von gelbem Bariumdichromit $BaCr_2O_4$. Diese Verbindung reagiert von 350–430 ° mit BP im stöchiometrischen Verhältnis von 1:1 zu Bariumchromat $BaCrO_4$. Die Produkte wurden durch Röntgendiffraktionsanalyse identifiziert. Eine unbekannte Phase wird ebenfalls gebildet.

Разюме — Окись трехвалентного хрома изменяет ход дегидратации трехгидратированного перхлората бария. В области температур 223—310° окись хрома реагирует с безводным перхлоратом бария в молярном соотношении 1 : 1, давая дихромит бария $BaCr_2O_4$, который затем при температуре 350—430° реагирует дальше с перхлоратом бария в соотношении 1 : 1 с образованием хромата бария. Эти вещества идентифицированы рентгеновским диффракционным анализом. Сообщается также об образовании соединения неизвестного состава.