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Thermoanalytical investigations on the melting and decomposition behaviour of some magnesium halogenide hydrates

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ABSTRACT

The thermal stability of the solid magnesium halogenide hydrates increases in the sequence $MgCl_2 \cdot 6H_2O$, $MgBr_2 \cdot 6H_2O$ and $MgI_2 \cdot 6H_2O$. The degree of hydrolysis of the compounds which were formed in the course of the thermal decomposition rises in the same manner. The number of the intermediate compounds is reduced, however.

INTRODUCTION

$MgCl_2 \cdot 6H_2O$, $MgBr_2 \cdot 6H_2O$ and $MgI_2 \cdot 8H_2O$ are the magnesium halogenide hydrates which are stable at room temperature. The melting and decomposition behaviour of $MgCl_2 \cdot 6H_2O$ was studied so far in detail /1-2/. The salt hydrate melts incongruently at 116 °C. During the decomposition under quasi-isothermal and quasi-isobaric conditions $MgCl_2 \cdot 2H_2O$, a weakly basic monohydrate $MgCl_{1,9}(OH)_{0,1} \cdot 0,8\ H_2O$ and the basic compound $Mg(OH)_{0,65}Cl_{1,35}$ which has the same structure as magnesium hydroxide chloride are formed in the labyrinth crucible. After the decomposition an equimolar mixture consisting of MgO and $MgCl_2$ exists at 690 °C. In this paper further investigations of $MgBr_2 \cdot 6H_2O$ and $MgI_2 \cdot 8H_2O$ are presented and the results are discussed in comparison with $MgCl_2 \cdot 6H_2O$.

MEASURING METHODS

The investigations of the decomposition behaviour of the magnesium halogenide hydrates were performed under quasi-isothermal and quasi-isobaric conditions in the labyrinth crucible by means of a derivatograph Q (MOM, Budapest). A gas titrimeter was used simultaneously to determine the released HBr and HI, respectively. The following parameters were applied: TG = 100 mg, Q-TG = 0,3 mg/min, E = 100-300 mg, program = II, titration with 0,1 n HCl at pH = 9.

The melting behaviour of the compounds was measured in gastight crucibles by means of the DTA equipment (Setaram, Lyon) using

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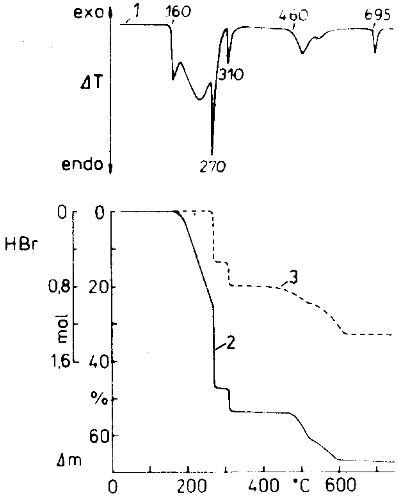
the cryostat at q = 2 K/min. Visual observations of sealed samples under isothermal conditions were applied for the interpretation of the DTA peaks. Moreover, the chemical and X-ray photographic characterization of stable phases which were formed during the thermal decomposition was carried out.

RESULTS AND DISCUSSION

Fig. 1 shows the ΔT, Q-TG and EGA curves of the thermal decomposition of $MgBr_2 \cdot 6H_2O$. The first peak in the T curve at T_{ON} = 160 °C can be explained by the incongruent melting of the compound. In comparison with the above-mentioned values a temperature range between 159 and 160 °C is observed in the closed system (152 - 170 °C /3/). The solid phase is completely dissolved in the melt at 164 °C. During further heating the melt reaches a water vapour pressure of 0,12 MPa /4/ at 175 °C and then the evaporation of H_2O starts from the unsaturated $MgBr_2$ melt. The saturation point is attained at 270 °C and a basic magnesium hydroxide bromide composed of $MgBr_{1,42}(OH)_{0,58}(H_2O)_{0,27}$ is formed. At 310 °C this compound is further decomposed to $Mg(OH)_{0,81}Br_{1,19}$ from which MgO and $MgBr_2$ in the molar ratio of 0,67 : 0,33 are formed in the temperature range between 460 and 600 °C. The formation of the waterfree $MgBr_2$ is shown in the T curve (Fig. 1) by the melting effect at T_{ON} = 695 (711 °C /5/).

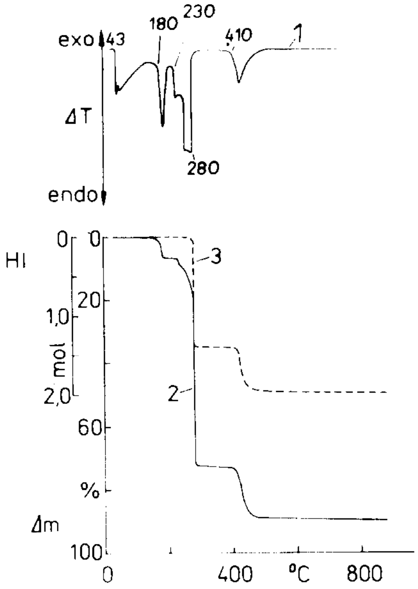


ΔT(1), Q-TG(2) and EGA(3) curves of the thermal decomposition of $MgBr_2 \cdot 6H_2O$ Fig. 1

The thermal decomposition of $MgI_2 \cdot 8H_2O$ (Fig. 2) begins with the incongruent melting at 43 °C (ΔT curve) and the formation of $MgI_2 \cdot 6H_2O$ /6/ followed by the endothermic dissolution of the solid phase in the melt. At a temperature of nearly 180 °C 2 moles of H_2O are evaporated with formation of solid $MgI_2 \cdot 6H_2O$ which melts at 230 °C. In the beginning of the next decomposition step only water is evaporated and then the strongly basic product $Mg(OH)_{1,44}I_{0,56}$ is formed at 280 °C.

Between 410° and 475 °C this compound is almost completely decomposed to MgO.

The following statements can be derived from the results:



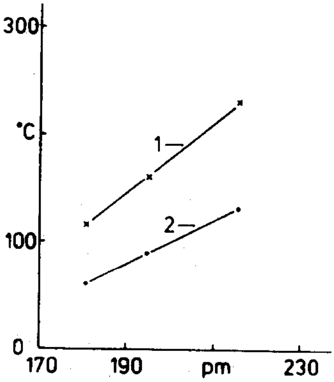
$\Delta T(1)$, Q-TG(2) and EGA(3) curves of the thermal decomposition of $MgI_2 \cdot 8H_2O$ Fig. 2

- During the thermal decomposition the number of the resulting intermediate compounds decreases in the sequence $MgCl_2 \cdot 6H_2O$, $MgBr_2 \cdot 6H_2O$ and $MgI_2 \cdot 8H_2O$. The degree of hydrolysis of the compounds is inversely increased.
- The compounds Mg(OH)Br /7/ and Mg(OH)I /8/ which are known from the literature and which were found during the thermal decomposition are a simplification of the proceeding reactions. From the results of this paper and the literature concerning the thermal decomposition of $MgCl_2 \cdot 6H_2O$ the conclusion can be drawn that the found basic intermediate products are hydroxide halogenides with a high range of existence relating to halogenide and hydroxide ions, by analogy with Mg(OH)Cl /2/.
- The thermal stability of the magnesium halogenide hydrates $MgX_2 \cdot 6H_2O$ is increased with growing radius of the halogenide ions X^- ($I^- > Br^- > Cl^-$). The melting temperature (curve 1) and the beginning of the decomposition at $p \approx 5$ kPa without for-

mation of a melt (curve 2) show approximately linear dependences (Fig. 3).

Dependence of the thermal stability on the radius of the anion X^- (Pauling) in $MgX_2 \cdot 6H_2O$ solid
1 - melting point
2 - beginning of the decomposition

Fig. 3



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