

## ACTIVATION ENERGIES OF THERMAL DECOMPOSITION PROCESSES OF $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$

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### ABSTRACT

The activation energies of thermal decomposition processes of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  were studied by applying Kissinger's method to DTA and DTG curves. The activation energy of dehydration appeared to be higher for the hexahydrate (43 kcal.mole<sup>-1</sup>, or 180 kJ.mole<sup>-1</sup>) than for the dihydrate (31.5 kcal.mole<sup>-1</sup>, or 132 kJ.mole<sup>-1</sup>). This may be attributed to the fact that the large  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  cation is more stable in the  $\text{Br}^-$  sub-lattice than the relatively small  $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$  cation.

### INTRODUCTION

The thermal decompositions of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  were recently studied in our laboratory by combining thermal methods with IR spectroscopy, X-ray diffraction and chemical determination of magnesium and halide [1,2]. The kinetic analysis of DTA and DTG curves of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  revealed activation energies on the order of 30 kcal/mole for the release of the first four water molecules, and about 50 kcal/mole for the release of the last two [1]. Very little has been published on the kinetics of the thermal decomposition of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  despite the fact that the DTA and DTG curves of this salt [2-4] and those of hydrated magnesium chloride have many similarities [1, 4-8]. In the present work we evaluated the activation energies of the DTA and DTG peaks which correspond to thermal decomposition processes of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  (non-dried and partly dried) upon heating from 20° to 800°C. The results are correlated with the reactions which occur during the heating, and compared to those obtained for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . In the present study single crystals were used whereas in our previous study the salt was ground before the thermal analysis. There are small differences between the thermal curves of the powder samples and the single crystals, which may be attributed to the diffusion of gases through the crystal, and are therefore important for the kinetics study.

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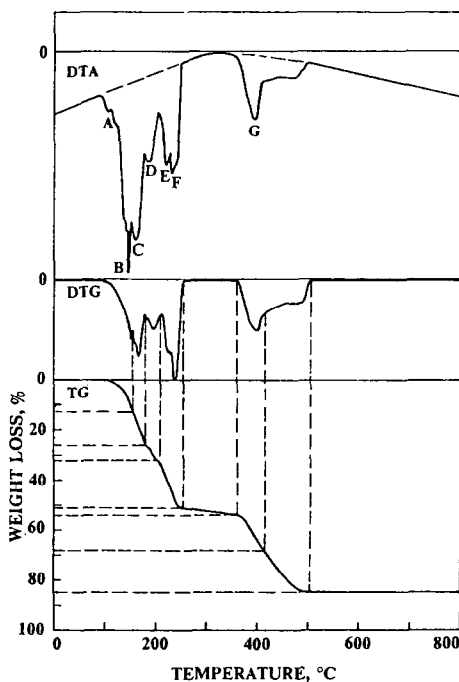
## EXPERIMENTAL

Laboratory reagent  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  supplied by BDH was used for our experiments. Partly dried as well as non-dried samples were studied. The former was obtained by drying the salt for 7 days over 70% sulfuric acid. A single crystal (of 10 mg) was heated in a Stanton Redcroft apparatus (STA 780) which simultaneously recorded the TG, DTG and DTA curves. The crucibles were of quartz and the reference material was calcined alumina. Measurements in static as well as in flowing nitrogen were performed.

## RESULTS

The DTA curve of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  shows six endothermic peaks in the temperature range  $130^\circ\text{--}360^\circ\text{C}$  (designated A-F in Fig. 1) and an additional complex peak at about  $400^\circ\text{C}$  (G). The temperatures of the peaks appeared to be quite close to those obtained with powder samples [2]. Each of the DTA peaks is apparently accompanied by a DTG peak. The curves are similar to the DTA and DTG curves which were obtained for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  [1]. Fig. 1 describes the results for a non-dried sample in flowing nitrogen. Similar results were found for the dried

Fig. 1: DTA, DTG and TG curves of a non-dried  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  single crystal in flowing nitrogen. The heating rate was  $10^\circ\text{min}^{-1}$ .



samples. However, the heating rate and the change of the atmosphere from dynamic to static, were found to affect the shapes of the DTA peaks and the temperatures of the peak maxima. In some of the measurements peaks C, F and G split into two or three small peaks. This is typical of peaks which involve reactions comprising several stages.

The activation energies of the various peaks were evaluated by Kissinger's "various heating rates" method [9] which is one of the few techniques applicable to highly overlapping peaks. This method is based on the relation:

$$\beta = (ZR/E)T^2 \exp(-E/RT) , \quad (1)$$

where T is the temperature of the peak (in K), E its activation energy, Z the frequency factor, R the gas constant and  $\beta$  the heating rate ( $^{\circ}\text{C}/\text{sec}$ ). The graph of  $\ln(\beta/T^2)$  vs.  $1/T$  should be a straight line of the slope  $-E/R$ . Several authors have discussed the validity of this method for DTA peaks [10-12]. It can be shown [13] that when the temperature reading is reasonably accurate (a negligible lag between the temperatures of the sample and the thermocouple) and when the sample is small (several mg) this method gives reliable results for both DTG and DTA curves, provided that  $\beta$  is taken as the instantaneous rather than the average heating rate. Equation (1) was developed for peaks of first order kinetics but it is a very good approximation for n-th order kinetics as well.

Heating rates of 2, 10 and 25  $^{\circ}\text{C min}^{-1}$  were used for evaluating the activation energies of the DTA and DTG peaks. Table 1 shows the temperatures of the DTA peaks for these nominal heating rates. The instantaneous heating rate, which usually differs from the nominal one, is also shown. The curves of  $\ln(\beta/T^2)$  vs.  $1/T$  for measurements in flowing air are depicted in Fig. 2, which is based on the temperatures appearing in Table 1. The computed activation energies for the dried samples are presented in Table 2. The frequency factors, Z, were calculated using the equation

$$Z = (\beta E/T^2 R) \exp(E/RT) . \quad (2)$$

Equation (2) is accurate for first order kinetics and gives a very good approximation for n-th order kinetics [13]. Table 2 also presents the kinetics parameters which were computed for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  [1], in order to compare them with the present results.

Peak A is in the initial temperature range where the heating is still slow and independent of the heating programme. Peaks B and D appear at approximately constant temperatures, independently of the heating rate, which is typical of phase transitions. Consequently, these peaks were not accessible to this sort of analysis. The experimental error in the computed activation energies is estimated to be up to  $\pm 10\%$ . The exceptionally high value of  $63.14 \text{ kcal.mole}^{-1}$  for the  $F_2$  DTA peak in static atmosphere is probably due to strong overlapping which distorted the results. This value was not taken into account for computing the average activation energy.

Table 1: Temperatures (in  $^{\circ}\text{C}$ ) of several DTA peaks in flowing nitrogen, for various heating rates ( $2^{\circ}$ ,  $10^{\circ}$  and  $25^{\circ}\text{C min}^{-1}$ ). The numbers in brackets indicate the instantaneous heating rate,  $\beta$  (deg/sec) which usually differs from the nominal value.

| peak  | $2^{\circ}/\text{min}$ | $10^{\circ}/\text{min}$ | $25^{\circ}/\text{min}$ |
|-------|------------------------|-------------------------|-------------------------|
| B     | 146 (0.0278)           | 146 (0.1722)            | 146 (0.4639)            |
| C     | 133 (0.0278)           | 149 (0.1722)            | 152 (0.4639)            |
| E     | 173 (0.0312)           | 190 (0.1722)            | 206 (0.4667)            |
| $F_1$ | 212 (0.0354)           | 225 (0.1806)            | 240 (0.4639)            |
| $F_3$ | 223 (0.0355)           | 239 (0.1819)            | 255 (0.5306)            |
| G     | 372 (0.0372)           | 389 (0.1875)            | 401 (0.4750)            |

Table 2: Activation energies,  $E$  ( $\text{kcal.mole}^{-1}$ ), and frequency factors,  $Z$ , of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  (partly dried) in flowing and static atmospheres. The kinetic parameters of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (from [1]) are also given, for comparison.

| peak  | Flowing atm. |       | Static atm. |       | Average values |                      | $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ |                      |
|-------|--------------|-------|-------------|-------|----------------|----------------------|---|----------------------|
|       | DTA          | DTG   | DTA         | DTG   | E              | $Z(\text{sec}^{-1})$ | E   | $Z(\text{sec}^{-1})$ |
| C     | 45.85        | 42.79 | 41.29       | 41.93 | 43.0           | $5.9 \times 10^{20}$ | 30.6                                      | $6.5 \times 10^{13}$ |
| E     | 34.00        | 25.93 | 32.53       | 33.46 | 31.5           | $1.2 \times 10^{13}$ | 48.0                                      | $1.8 \times 10^{21}$ |
| $F_1$ | 43.83        | 48.04 | 41.77       | ---   | 44.5           | $9.7 \times 10^{17}$ | 50.3                                      | $3.9 \times 10^{19}$ |
| $F_2$ | ---          | 47.80 | (63.14)     | 40.14 | 44.0           | $2.7 \times 10^{17}$ |   |                      |
| $F_3$ | 42.69        | 47.20 | 46.26       | 44.44 | 45.1           | $3.6 \times 10^{17}$ |   |                      |
| G     | 71.87        | 66.87 | 73.88       | 65.55 | 69.5           | $5.8 \times 10^{20}$ | 72.4                                      | $1.1 \times 10^{19}$ |

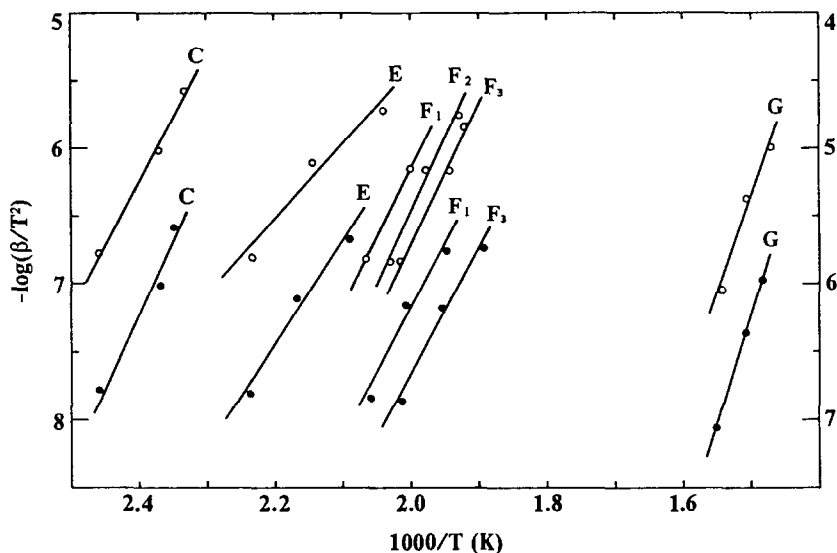


Fig. 2: Curves of  $-\log(\beta/T^2)$  versus  $1000/T$  for the DTA peaks (full circles, right scale) and DTG peaks (empty circles, left scale) of dried samples in flowing nitrogen.  $\beta$  is the instantaneous heating rate (deg/sec) and  $T$  is the peak temperature (in K).

## DISCUSSION

The thermal decomposition of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  is a complex process which consists in dehydration, melting of the hydrous salts, thermal hydrolysis and dehydrobromidization [2]. It has been shown that although several reactions may occur simultaneously, each peak in the DTA curve is due mainly to one specific thermal reaction [2].

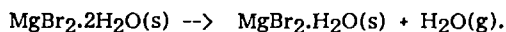
Comparison of the activation energies of the corresponding DTA and DTG peaks shows that they usually match within the error limit. This is consistent with the assumption that the parallel DTA and DTG peaks are associated with the same reaction and can be characterized by the average activation energy appearing in column 6 of Table 2.

Peak A corresponds mainly to the drying of the salt, though dehydration starts at that region too. Peak B is ascribed mainly to the melting of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  and peak D to the melting of  $\text{MgBr}_2 \cdot 4\text{H}_2\text{O}$ . Both peaks also involve

weight losses which are clearly seen in the DTG curve, indicating that the phase transitions occur simultaneously with dehydration [2].

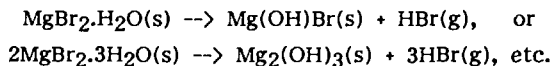
Dehydration of  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{MgBr}_2 \cdot 4\text{H}_2\text{O}$  are the main reactions involved in peak C. The activation energy of this peak was found to be  $43.0 \text{ kcal.mole}^{-1}$  compared to  $30.6$  in  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (see Table 2). This may be explained by the assumption that the large magnesium-hexahydrate cation is more stable in the  $\text{Br}^-$  sub-lattice than in the  $\text{Cl}^-$  one, due to the larger size of the bromine ion [16].

Peak E represents dehydration of the dihydrate to form the monohydrate:



The dehydration is accompanied by a small amount of hydrolysis which contributes only little to the weight loss at this stage. For this peak the activation energy is lower for  $\text{MgBr}_2 \cdot 2\text{H}_2\text{O}$  ( $31.5$ ) than for  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$  ( $48.0$ ), indicating that the  $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$  cation (which is much smaller than  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ ) is more stable in the  $\text{Cl}^-$  sub-lattice. The fact that in hydrated  $\text{MgBr}_2$  less energy is required for the release of the fifth molecule of water, than for the first 4 molecules is remarkable; usually the activation energy of dehydration increases with the decreasing hydration number [1]. This is probably associated with the smaller size of  $[\text{Mg}(\text{H}_2\text{O})_2]^{2+}$  compared to  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ , the latter being more stable in the  $\text{Br}^-$  sub-lattice. It should be remembered, however, that the activation energy is meaningful only if the peak is related mainly to a single reaction, and is not affected greatly by other reactions. Otherwise, the evaluated activation energies and other kinetic parameters describe a specific combination of experimental conditions and have no universal importance. Further work is needed, in order to find out whether the activation energies which are evaluated here can be assigned to pure dehydration, or if they are considerably affected by other processes such as hydrolysis.

The principal reaction associated with peak F is thermal hydrolysis:



In some of the measurements, especially in static atmosphere, this peak was found to split into several peaks, indicating a complicated multi-stage reaction. Activation energies of about  $45 \text{ kcal.mole}^{-1}$  were found for all these peaks, compared to  $\sim 50$  for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

Peak G represents processes of dehydroxylation by dehydrobromidization of the magnesium hydroxy bromide and the formation of  $\text{MgO}$ . The activation energy is quite high ( $\sim 70 \text{ kcal.mole}^{-1}$ ) and may reflect complicated processes, including

recrystallization and crystal growth [1,2]. As in peak F, the activation energy is somewhat lower for  $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$  than for  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ .

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