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THE STUDY OF THERMAL DEHYDRATION AND HYDROLYSIS OF $MgBr_2.6HOH$ BY DTA AND TG

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ABSTRACT

The thermal decomposition of $MgBr_2.6HOH$ (non- and partly dried) was studied by DTA, TG, DTG, IR, X-ray diffraction and chemical determinations of Mg and Br. The reactions which occurred in the course of the thermal analysis were identified as dehydration, melting of hydrous salts, thermal hydrolysis and dehydrobromidization. Although several reactions may occur simultaneously, each endothermic peak in the DTA curve could be related to a certain thermal reaction. MgO was the end product of the thermal treatment.

INTRODUCTION

The DTA and TG curves of hydrated magnesium chloride have been widely investigated (see e.g., refs. 1-7). On the other hand, very little has been published on the DTA and TG curves of hydrated magnesium bromide. DTA curves of $MgBr_2.6HOH$ were recently described by Naumann, Emons and Pohl [8] and by Shoval et al. [9]. The profiles of both curves are very similar. They differ only in the temperatures of the various peaks, and this is probably due to different calibrations of the furnaces. In the present study we are going to relate the various peaks to the various thermal reactions which occur during the DTA run. For this purpose, TGA was recorded simultaneously with the DTA and samples were taken from the DTA furnace at various stages of the thermal treatment and were examined by IR spectroscopy, X-ray diffraction and chemical analysis of Mg and Br. In addition to the conventional TGA, a stepwise isothermal TGA was carried out. In this technique the sample is heated to

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constant weight at the temperature of the peak [10, 11]. This technique enables to determine the maximum weigtloss associated with each peak. The present interpreation is also based on our previous study of the DTA curve of $MgCl_2.6HOH$ [1].

EXPERIMENTAL

$MgBr_2.6H_2O$ (Laboratory Reagent) was supplied by BDH. Both, non-dried and partly dried salts were used. The latter was obtained by equilibrating the former over 70% sulfuric acid. Water content was determined from the TG curves. The compositions of non-dried and partly dried samples correspond to $MgBr_2.6.3H_2O$ and $MgBr_2.6H_2O$, respectively. The techniques used for the DTA, TG and DTG (Stanton Redcroft, STA 780), X-ray (Philips) and IR spectroscopy (Nicollet ZDX FTIR Spectrometer), as well as the method applied for the chemical analysis of the thermal products, were previously described [1].

In the stepwise isothermal TGA technique, 10 mg of the sample was gradually heated (10^oC per minute) in the DTA-TGA furnace to the temperature of the first peak. At this stage the temperature of the sample was kept constant as long as it lost weight. After that the TGA curve showed constant weight and the DTG curve returned to its original shape, the temperature of the sample was gradually raised by 20^o. Again the temperature was kept constant until the sample lost no further weight .The heating continued in steps up to 300^oC and at each step the temperature of the sample was kept constant as long as it lost weight.

RESULTS

DTA, TG and DTG curves

Fig. 1 shows the DTA, TG and DTG curves of dried $MgBr_2.6HOH$ recorded at a heating rate of $10^oC\ min^{-1}$. Table 1 summarizes the thermal curves of dried and non-dried $MgBr_2.6H_2O$, recorded under a flow of nitrogen, or under static air, at heating rates of 10 and $25^oC\ min^{-1}$. The temperature range for each peak according to the DTG curves and weightloss associated with the various peaks are given in Table 1. For most peaks, the DTA curves of dried and non-dried $MgBr_2.6H_2O$ are very similar. On the other hand, the heating rate and the flow of nitrogen during the thermal run affect the shapes of the DTA curves and the locations of the peak maxima.

Under a flow of nitrogen and at a heating rate of $10^oC\ min^{-1}$ the DTA curves show seven endothermic peaks which are associated with thermal weightloss. At a heating rate of 25°C min^{-1} most peaks shift to higher temperatures. Such shifts are characteristic for reactions in which gases are evolved. Both peaks C and G split into two small peaks. This is characteristic of peaks which describe reactions of several stages. Peak B shows a small shift whereas peak D does not shift at all with the heating rate. These two peaks should be related to phase transitions which are associated with weightloss, such as incongruent melting. The dried sample which was recorded at a heating rate of 25°C per minute shows an additional endothermic sharp peak at 715°C. This peak is not associated with a parallel DTG peak and seems to be due to a phase transition.

The DTA curves which were recorded in static air differed from those which were recorded under the flow of nitrogen. Peaks B and D which are associated with the melting of the salt did not shift. (Peak D shifted slightly when the heating rate was 25°C min^{-1}.) All other peaks, which are associated with gas evolution, shifted to higher temperatures. Peak G was splitted into three peaks. Although the locations of most peaks appear at higher temperatures, in static air the reactions terminate at lower temperatures than under flowing nitrogen.

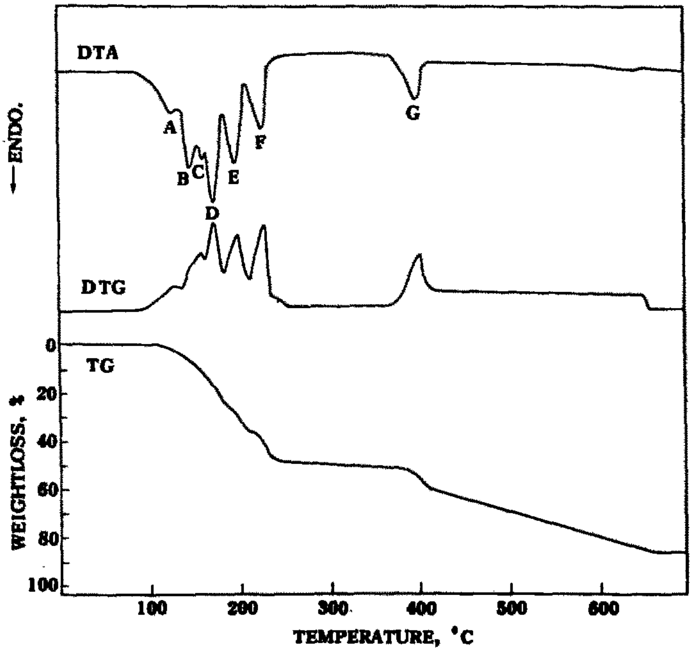

Fig. 1: DTA, TG and DTG curves of dried MgBr$_2$.6HOH under a flow of nitrogen.

TABLE 1

Peak temperatures (°C) of DTA curves and weightloss calculated from TGA curve (percentage and molar ratio) of dried and non-dried $MgBr_2$ recorded at differen heating rates, under nitrogen and in static air.

Peak	Peak temp. (°C)	Temperature range (°C)	Weight loss (%)	Weight loss Cumulative (%)	Molar ratio $HOH/MgBr_2$	Molar ratio $HBr/MgBr_2$
I. Dried $MgBr_2.6HOH$ in flowing nitrogen						
Heating rate: 10°C min^{-1}						
A	125	70-130	5.0	5.0	0.81	-
B	145	130-150	5.0	10.0	0.81	-
C	160w	150-165	5.5	15.5	0.89	-
D	170	165-180	10.5	26.0	1.70	-
E	195	180-210	10.5	36.5	0.79	0.21
F	225	210-240	11.5	48.0	-	0.42
		240-360	3.0	51.0	-	0.11
G	400	360-410	10.0	61.0	-	0.36
		410-680	25.0	86.0	-	0.90
Heating rate: 25°C min^{-1}						
A	130sh	70-135	2.0	2.0	0.32	-
B	155	135-160	5.5	7.5	0.89	-
D	170	160-185	5.5	13.0	0.89	-
C	200w,230w	185-235	12.0	25.0	1.95	
E	245	235-250	13.0	38.0	0.95	0.25
F	260	250-270	11.5	49.5	-	0.41
		270-375	1.0	50.5	-	0.03
G	410	375-435	4.5	55.0	-	0.16
	455	435-480	6.0	61.0	-	0.21
H	715	480-855	26.5	87.5	-	0.94
II. Non-dried $MgBr_2.6HOH$ in flowing nitrogen.						
Heating rate: 10°C min^{-1}						
A	110	40-120	6.0	6.0	0.97	-
B	145	120-150	9.5	15.5	1.54	-
C	160	150-165	5.0	20.5	0.81	-
D	170	165-180	5.0	25.5	0.81	-
E	190	180-210	10.5	36.0	0.87	0.19
F	230	210-255	14.0	50.0	-	0.51
		255-360	2.0	52.0	-	0.07

TABLE 1 (Cont.)

Peak	Peak temp. (°C)	Temperature range (°C)	Weight loss			
			(%)	Cumulative (%)	Molar ratio	
					HOH/$MgBr_2$	HBr/$MgBr_2$
G	400	360-410	10.0	62.0	-	0.36
		410-660	24.0	86.0	-	0.87
Heating rate: 25°C min^{-1}						
A	130	40-135	3.5	3.5	0.57	-
B	155	135-160	6.0	9.5	0.97	-
D	170	160-185	6.5	16.0	1.05	-
C	200w,215w	185-225	11.0	27.0	1.79	-
E	230	225-240	13.0	40.0	0.92	0.30
F	245	240-255	10.5	50.5	-	0.37
		255-375	1.0	51.0	-	0.04
G	415	375-435	7.0	58.0	-	0.25
	445	435-470	6.5	64.5	-	0.24
		470-725	22.0	86.5	-	0.80
III. Non-dried $MgBr_2.6HOH$ in static air.						
Heating rate: 10°C min^{-1}						
A	125	40-130	4.0	4.0	0.65	-
B	145	130-160	7.0	11.0	1.14	-
D	170	160-185	9.0	20.0	1.46	-
C	200w	185-220	8.0	28.0	1.30	-
E	225w,230	220-235	4.5	32.5	0.45	0.06
F	240	235-245	10.0	42.5	-	0.36
	260	245-265	9.5	52.0	-	0.35
		265-390	6.0	58.0	-	0.21
G	435,445sh					
	475w	390-485	28.0	86.0	-	1.02
Heating rate: 25°C min^{-1}						
A		40-130	3.0	3.0	0.49	-
B	145,160w	130-165	6.0	9.0	0.97	-
D	185	165-195	10.0	19.0	1.62	-
C	210w	195-230	8.0	27.0	1.30	-
E	240	230-255	13.5	40.5	0.92	0.32
F	265	255-280	10.5	51.0	-	0.38
		288-400	3.0	54.0	-	0.10
G	440,465m					
	525w	400-540	33.0	87.0	-	1.20

The last stages of weightloss were recorded at 485 and 540°C with heating rates of 10 and 25°C min^{-1}, respectively. Under nitrogen, weightloss continued till 660 and 725°C, respectively.

The sample was studied by a Fisher-Johns melting point apparatus. The evolved gases were examined by litmus paper. Evolution of an acid (HBr) started with peak E at 180°C, but was very weak. It became very intense during peak F at about 220°C. Table 1 shows weightloss expressed as mole HOH or HBr per mole Mg. For these calculations we assumed that water is lost in stages to form a mono-hydrate and that the dehydration is followed by thermal hydrolysis of the mono-hydrate which leads to the formation of Mg(OH)Br. We also assumed that the magnesium hydroxy bromide loses HBr at higher temperatures and is transformed to MgO. These assumptions were based on the stepwise isothermal TGA, IR and X-ray spectroscopy and on the chemical analysis of $MgBr_2.6HOH$ which had been heated at various temperatures.

Stepwise Isothermal TGA

This TGA curve shows four stages of thermal weightloss up to 300°C, which may be related to our different DTA peaks (Table 2).

TABLE 2

Thermal weightloss (weight percent and molar ratio) obtained by stepwise isothermal TGA of dried $MgBr_2$

Peak	Furnace temp. (°C)	Weightloss			
		(%)	Cumulative (%)	Molar ratio	
				$HOH/MgBr_2$	$HBr/MgBr_2$
A,B,C	140	15.5	15.5	2.50	-
D	160	14.5	30.0	2.35	-
E	180	6.6	36.6	0.15	0.21
	200	0.4	37.0	-	0.01
F	220	2.8	39.8	-	0.10
	240	8.2	48.0	-	0.30
	260	0.2	48.2	-	
	280	0.8	49.0	-	0.03
	300	0.0	49.0	-	-

Infrared spectra

The decomposition products of $MgBr_2$ isolated at various stages of the thermal analysis, were investigated by infrared spectroscopy. No hydroxyl groups were detected in the spectra of samples which were heated up to 200°C, showing that no significant hydrolysis took place below this temperature. Weak OH bands were detected in the spectra of samples heated above 200°C. The intensity of the OH bands increased when the samples were heated to higher temperatures. The most intense OH bands were observed in the temperature range between peaks F and G. At temperatures higher than that of peak G the OH bands became weak. These bands disappeared at 800°C. In this temperature range absorption bands which are characteristic for MgO were detected.

X-ray diffraction data

Diffractograms of samples which were heated to temperatures below 250°C showed only minor changes from that of the untreated $MgBr_2.6H_2O$. Characteristic peaks of $MgBr_2.6H_2O$ persisted above 250°C but most peaks became very weak and broad, relative to the 20.98 and 32.90 2θ peaks, indicating a low degree of crystallinity. However, small characteristic peaks of $MgBr_2.6H_2O$ were detected even at 700°C. We assume that initially, when the sample came out of the furnace, it contained anhydrous $MgBr_2$ which was rehydrated during the period between the thermal treatment and the X-ray diffraction measurements. No $MgBr_2$ was detected after heating the sample to 800°C.

Small characteristic peaks of MgO were detected in the diffractogram recorded after heating the sample to 520°C. The peaks intensified with the temperature. The diffractogram of the sample heated to 800°C showed that this sample was composed of crystalline MgO. No other compounds were identified in this diffractogram.

Chemical analysis

The Mg and Br contents were determined in the non-dried sample which had been heated to various temperatures (Table 3). The table shows that the molar ratio Mg:Br increases with the heating temperature and that MgO is the end product of the thermal analysis.

TABLE 3

Determination of molar ratio Mg:Br and Mg:O in MgBr.6HOH samples heated to various temperatures

Temperature	Molar	ratio
(°C)	Mg:Br	Mg:O
180	0.551	-
400	0.960	-
520	1.174	-
650	4.179	-
800	-	0.972

DISCUSSION

The following reactions may occur during the course of the thermal analysis:

(1) Drying of the solid salt (dehydration)
$MgBr_2$.xHOH(s) -> $MgBr_2$.(x-y)HOH(s) + yHOH(g) and
$MgBr_2$.zHOH(s) -> $MgBr_2$(s) + zHOH(g)
(2) Melting of hydrate (accompanied by partial dehydration)
$MgBr_2$.xHOH(s) -> $MgBr_2$.(x-y)HOH(l) + yHOH(g)
(3) Boiling of the melt
$MgBr_2$.xHOH(l) -> $MgBr_2$.(x-y)HOH(s) + yHOH(g)
(4) Thermal hydrolysis
$MgBr_2$.HOH(s) -> Mg(OH)Br(s) + HBr(g) or
2$MgBr_2$.3HOH(s) -> $Mg_2(OH)_3Br$(s) + 3HBr(g), etc.
(5) Dehydroxylation by dehydrobromidization
Mg(OH)Br(s) -> MgO(s) + HBr(g)
$Mg(OH)_2$(s) + $MgBr_2$(s) -> 2MgO(s) + 2HBr(g)
2Mg(OH)Br(s) -> MgO.$MgBr_2$(s) + HOH(g), etc.
(6) Melting of $MgBr_2$
$MgBr_2$(s) -> $MgBr_2$(l)

Reactions 1-5 are associated with weightloss. Most peaks in the DTG curves do not return to the base-line before the start of the next peak. This is an indication that the various reactions overlap. Furthermore, the differences observed between curves recorded under a flow of nitrogen or in static atmosphere, at different heating rates or in the isothermic technique demonstrate that the extent of each of the reactions depends on the experimental conditions.

Although several reactions may occur simultaneously, from TG, X-ray , infrared and chemical analysis, together with previous findings, it is possible to attribute certain peaks to certain reactions. Peak A is very weak. It corresponds mainly to the drying of the salt (reaction 1). Table 1 shows that the amount of water which is lost during the appearance of peak A depends on the rate of heating. From these results and from the results which are given in Table 2, it is obvious that the dehydration of the salt which is associated with peaks B and C, starts at the same time as peak A.

The melting of $MgBr_2.6HOH$ is incongruent. The melting point which is reported in the literature ranges between 153 and 172°C [12]. Peak B in the DTA curve is more intense than peak C whereas in the DTG curve the intensity of peak C is always equal or higher than that of peak B. The location of peak B changes very little with the experimental conditions whereas that of peak C shifts to higher temperatures with increasing heating rates or when recorded in static atmosphere. These are indications that peak B is predominantly due to the melting of $MgBr_2.6HOH$ [1] whereas peak C is due to the boiling of the melt (reactions 2 and 3, respectively). From the stepwise isothermal TGA it is obvious that mainly $MgBr_2.4HOH$ and to some extent also $MgBr_2.2HOH$ are obtained at this stage. It should be mentioned here that TGA of magnesium chloride showed previously that $MgCl_2.2HOH$ was the principal dehydration product of the hexahydrate, being formed during the appearance of peak C.

Peak D does not change with the heating rate. This is characteristic for a peak which is associated with melting, probably of $MgBr_2.4HOH$. From the TGA (Table 1) it is obvious that this melting leads to dehydration and the formation of $MgBr_2.2HOH$. In the stepwise isothermal TGA (Table 2) most of the salt is converted to the monohydrate. In our previous DTA study of $MgCl_2.6HOH$ an equivalent peak D was used for the identification of the tetrahydrate. This DTA peak was detected in the dried salt but not in the non-dried salt. From these observations it was concluded that the dried magnesium chloride contained some $MgCl_2.4HOH$ in addition to $MgCl_2.6HOH$ crystals, whereas the non-dried salt contained $MgCl_2.6HOH$ plus humidity. In the present study peak D appears in the DTA curves of both samples, the dried and the non-dried. However, from the present results it is obvious that $MgBr_2.4HOH$ is obtained from dried or non-dried $MgBr_2.6HOH$ by reaction 3.

According to Table 1, peak E represents dehydration of the dihydrate and formation of the monohydrate (reaction 1). Table 2 shows that this reaction started before the start of peak E. Table 1 shows that during the conventional thermal analysis the accumulated weightloss at this stage was much higher than that responsible for the evolution of five water molecules. This is due to the fact that the dehydration was accompanied by a small amount of hydrolysis (reaction 4). The appearance of small OH bands in the IR spectra of samples taken from the DTA furnace after the completion of this peak confirms that thermal hydrolysis starts, but contributes only little to the weightloss at this stage. This was proven by heating the salt in a "Melting point apparatus" and examining the evolved gases with litmus paper. This is in agreement with the HBr evolution curve obtained by Naumann, Emons and Pohl [8]. According to these authors the basic magnesium hydroxide bromide $MgBr_{1.42}(OH)_{0.58}(HOH)_{0.27}$ is obtained at this stage. On the other hand, according to our X-ray study, most magnesium bromide consists as non-hydrolyzed $MgBr_2$.

The IR spectra of samples heated to 270 or 400°C exhibited very intense OH bands. This is an indication that thermal hydrolysis (Reaction 4) is the principal reaction which is associated with peak F. This peak splits to several peaks when the reaction is carried out in static atmosphere and a heating rate of 10°C, indicating that the reaction associated with this peak is complicated. At the end of peak F and before the start of peak G the total weightloss depends on whether the thermal treatment was carried out under a flow of nitrogen or in static air. Under a flow of nitrogen the weightloss at this stage is 51%, indicating that only part of the monohydrate was hydrolyzed. A complete hydrolysis deserves a weightloss of 58.5%. In static air weightloss is equal to 58% indicating that the thermal hydrolysis is accomplished. In static air water vapour which is obtained remains in the heating cell to react with the magnesium salt at the temperature of peak F. Consequently, the thermal hydrolysis reaction terminates before the start of peak G. According to Naumann, Emons and Pohl [8] $Mg(OH)_{0.81}Br_{1.19}$ is formed. According to our X-ray study $MgBr_2$ persisted at this stage.

Peak G splits into several peaks when the thermal analysis is performed in a static atmosphere or at high heating rates. It should be noted that when the thermal analysis is carried out under a flow of nitrogen, weightloss (and hydrolysis) continues after the completion of peak G. Under a flow of nitrogen all the evolved water molecules have escaped from the heating cell before the system reaches the temperature of peak G.

At the end of the thermal analysis the total weightloss is equal to 86%. This is the expected weightloss for the transformation of $MgBr_2.6HOH$ into MgO. The last process should be the dehydroxylation by dehydrobromidization of the magnesium hydroxy bromide. This assumption is supported by chemical analysis (decreasing percentage of Br), IR spectra (disappearance of OH bands and appearance of MgO bands) and X-ray data (the crystallization of MgO). It is obvious that in static air peak G represents dehydrobromidization of the system and the formation of MgO (reaction 5). It should be noted that under the flow of nitrogen this reaction occurs at temperatures above that of peak G. It shpuld also be noted that in static air the dehydrobromidization occurs at lower temperatures and is accomplished together with peak G.

Peak H at 715°C in the DTA curve does not have a parallel DTG peak. It may represent the melting of anhydrous $MgBr_2$, (reaction 6). In the present study this peak was recorded only in one case, in the DTA curve of dried salt recorded under a flow of nitrogen, at a heating rate of 25°C min^{-1}. According to Table 1 this run differs from all other runs by loosing weight up to 800°C. This means that, at the melting point of $MgBr_2$, the sample still contained magnesium salt which did not hydrolyze. This is in agreement with the X-ray study.

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