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THERMAL AND CALORIMETRIC INVESTIGATIONS ON CRYSTALLINE HYDRATES OF BARIUM HYDROXIDE AND THEIR DEUTERATED ANALOGS

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SUMMARY

By the methods of DSC and DTA, the thermal decompositions of $Ba(OH)_2.8H_2O$, $Ba(OH)_2.8D_2O$, $Ba(OH)_2.H_2O$ and $Ba(OH)_2.D_2O$ had been studied as the phase transitions were identified; the corresponding enthalpy changes have been determined and a comparison between the values determined and those calculated ones on the basis of thermodynamical data, has been carried out. Some decrease in the thermal stability of the deuterated crystal hydrates as compared to that of the normal ones has been proved.

INTRODUCTION

Recently, utilisation of the phase transitions in the crystal hydrates as a way of heat energy storage, has roused in this sort of compounds, a particular interest. Namely, barium hydroxide and its crystal hydrates are of great interest both in this respect as well as Electronics.

By Differential Thermal Analysis (DTA), thermal behaviours of $Ba(OH)_2.8H_2O$ have been studied (1,2,3,4,5), but the data concerning the lower crystal hydrates produced, as well as those concerning the phase transition temperatures, have been found as contradictory. Besides, respective data for the $Ba(OH)_2.D_2O$ deuterated analogs, were missing.

The purpose of the present work is to examine the thermal dissociation of $Ba(OH)_2.8H_2O$, $Ba(OH)_2.H_2O$, $Ba(OH)_2.8D_2O$ and $Ba(OH)_2.D_2O$ by means of two different methods - Differential Thermal Analysis (DTA) and Differential Scanning Calorimetry (DSC)-in order to expand and to enrich the information available, regarding the above mentioned compound thermal behaviours and differences between the normal and the deuterated analogs, as well as to determine the enthalpy changes in the most important phase transitions.

EXPERIMENTAL

The starting materials with which the examinations had been carried out, were with purity 99,5%. Some experiments for producing also $Ba(OH)_2.3H_2O$

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by the methods reported in (6,7,8) had been carried out too, but even at the better storage conditions under nitrogen which had been provided for, the samples always converted in $Ba(OH)_2H_2O$. The TG - and the DTA-curves of the compounds produced, were recorded by means of derivato graph of the MOM type, system Paulik-Paulik-Erday at the following operation regime: range of 200 mg, heating rate of 5^o/min and temperature up to 770K. The DSC-curves were recorded by DSC of the firm Perkin-Elmer at temperature ranging form 273 up to 570K and heating rate of 5^o/min, whereas were determined the enthalpies of the most important phase transitions during dehydration of $Ba(OH)_2.nH_2O$, respectively of $Ba(OH)_2.nD_2O$.

RESULTS AND DISCUSSION

In Table 1 are summarized the read out by the DSC approach enthalpy changes on the most important phase transitions determined at the respective temperatures and the data obtained from the DTA and TG-curves.

The ΔH_f^o values of the normal and the deuterated crystal hydrates which are necessary for the $\Delta H_{ph.tr.}$ calculations, are determined by the equation of Rozenfeld-Karapetianz (9,10), using an initial value of $\Delta H_f^o, Ba(OH)_2 =$ -946,42 kJ/mol.

Teble 1. Data obtained from DTA-and TG-curves

Phase transition		T,K	t,°C	$\Delta H_{ph.tr.}$ kJ/mol		Δm,%	
				read by DSC	calculated	read by TG	calculated
1		2	3	4	5	6	7
$Ba(OH)_2.8H_2O$	$Ba(OH)_2.8H_2O_{(s)} \rightarrow Ba(OH)_2.8H_2O_{(1)}$	349,6	76,6	86,3	94,5	-	-
	$Ba(OH)_2.8H_2O_{(1)} \rightarrow Ba(OH)_2.H_2O_{(s)}$ $+7H_2O_{(g)}$	365- 419	92-146	28,7	331,1	35,9	36,1
	$Ba(OH)_2H_2O_{(s)} \rightarrow Ba(OH)_2H_2O_{(1)}$	481	208	20,4		-	-
	$Ba(OH)_2H_2O_{(1)} \rightarrow Ba(OH)_{2(s)}+H_2O$	503	230	40,1	-	9,1	9,5
	$\alpha\text{-}Ba(OH)_{2(s)} \rightarrow \beta\text{-}Ba(OH)_{2(s)}$	533	260	-	-		
	$Ba(OH)_{2(s)} \rightarrow Ba(OH)_{2(1)}$	669	396	-	14,2		

	1	2	3	4	5	6	7
$Ba(OH)_2.8D_2O$	$Ba(OH)_2.8D_2O_{(s)} \rightarrow Ba(OH)_2.8D_2O_{(l)}$	349	76	84,4			
	$Ba(OH)_2.8D_2O_{(l)} \rightarrow BaOH)_2.D_2O_{(s)}+$ $+7D_2O$	372- 422	99- 149	25,1	277,5	37,12	37,83
	$Ba(OH)_2.D_2O_{(s)} \rightarrow Ba(OH)_2.D_2O_{(l)}$	438	165	15,7	-	-	-
	$Ba(OH)_2.D_2O_{(l)} \rightarrow Ba(OH)_{2(s)}+D_2O$	491	218	49,7	51,8	9,8	10,4
	α-$Ba(OH)_{2(s)} \rightarrow \beta$-$Ba(OH)_{2(s)}$	534,2	261,2	-	-	-	-
	$Ba(OH)_{2(s)} \rightarrow Ba(OH)_{2(l)}$	663	390	-	-	-	-
$Ba(OH)_2.H_2O$	$Ba(OH)_2.H_2O_{(s)} \rightarrow Ba(OH)_{2(s)}+H_2O_{(g)}$	422,2	149,2	63,7	65,6	9,1	9,5
	α-$Ba(OH)_{2(s)} \rightarrow \beta$-$Ba(OH)_{2(s)}$	485,2	212,8	-	-	-	-
$Ba(OH)_2.D_2O$	$Ba(OH)_2.D_2O_{(s)} \rightarrow Ba(OH)_2.D_2O_{(l)}$	356,1	83	5,8	-	-	-
	$Ba(OH)_2.D_2O_{(l)} \rightarrow Ba(OH)_{2(s)}+D_2O_{(l)}$	425,9	152,9	20,08	22,02	-	-
	$D_2O_{(l)} \rightarrow D_2O_{(g)}$	456,7	183,7	46,1	45,4	9,7	10,4
	α-$Ba(OH)_{2(s)} \rightarrow \beta$-$Ba(OH)_{2(s)}$	484,9	211,9	4,2	-	-	-

When studying the thermal behaviours of $Ba(OH)_2.8H_2O$, respectively $Ba(OH)_2.8D_2O$, as the data in Table 1 also illustrate, it can be observed that these compounds indergo analogical phase transitions (described in the Table 1). The fact that the reported in the table temperatures Tm of the crystal hydrates are a little bit higher than those of the deuterated analogs, points to slight destabilization of the $Ba(OH)_2.8D_2O$ crystal structure.

Must be noted the difference observed in the DSC- and DTA-curves of the two compoungs in the temperature range from 365K up to 422K: while on the DTA-curve one only endothermic peak could be seen, on the DSC-curve an exothermic peak appears first, which later moves in a larger endothermic one. The enthalpy changes for the two peaks as well as the addative enthalpy change are also read out. In the DTA the endothermic peak is considered only, as a predominative one for the two compounds. The total ΔHfor the $Ba(OH)_2.8H_2O$ is 28,7 kJ/mol, while that for the $Ba(OH)_2.8D_2O$ is 25,1kJ/mol.

The data indicate the processes as analogical, having close enthalpy changes. Anyway, the enthalpy changes of the $Ba(OH)_2.8D_2O$ are smaller. The complicated picture could be explained by the fact that in the melt are simultaneously taking place processes of structural that in the melt are simultaneously taking place processes of structural transitions, step dehydration, crystallization of the lower crystal hydrates in the crystallization water produced and partial evaporation of the latter. In other words, in the system simultaneously exist the solid, liquid and the gas phases. That fact itself, as well as the exothermic peak observed in the temperature range of question, is the reason for the difference existing between the ΔH values read out on the DSC basis and those thermodynamically calculated for the phase transition: $Ba(OH)_2.8H_2O \rightarrow Ba(OH)_2.H_2O_{(s)}+7H_2O_{(g)}$ and respectively for the deuteriated compound.

Indentification of the remaining phase transitions of $Ba(OH)_2.8H_2O$, respectively $Ba(OH)_2.8D_2O$, described in the Table, is realized by comparison of the DTA- and the DSC-curves on the basis of the data in the literature existing (12,13). In the $Ba(OH)_2.D_2O$ DSC-curve is observed an endothermic peak having maximum at 356,1K and $\Delta H_{pf.tr.}$ =5,8 kJ/mol for which, no weight change by TG-curve is considered. Therefore, the peak under question could not correspond to a polymorphic transition of α-$Ba(OH)_2.D_2O$ in β-$Ba(OH)_2.D_2O$, but could be existing due to the fussing of the latter. Analogical peak for $Ba(OH)_2.H_2O$ on the DSC-curve cannot be precisely read out, since it coincides with the considerably bigger endothermic peak of the phase transition of $Ba(OH)_2.H_2O \rightarrow Ba(OH)_{2(s)}+H_2O_{(g)}$, for which the $\Delta H_{ph.tr.}$ is 63,7 kJ/mol, a value corresponding to the calculated one of $\Delta H_{ph.tr.}$ =65,6 kJ/mol. On the basis of the comparison made between these data, we may assume that the starting monohydrate undergoes a polymorphic transition.

The two endothermic peaks appearing at 425,9K and 456,7K on DSC-curve of $Ba(OH)_2.D_2O$ and to which on the DTA-curve correspond an endothermic peak with a maximum at 418K, are fue to the phase transition of $Ba(OH)_2.D_2O_{(s)} \rightarrow Ba(OH)_{2(s)}+D_2O_{(l)}$ and the evaporation of the crystallization water respectively. This kind of interpretation is in compliance with the ΔH calculated for these processes (Tabl.1) as well as with the alteration of the TG-curve in the temperature range examined.

CONCLUSIONS

On the basis of the examinations reported, the following conclusions could be drawn: the compounds in examination under the conditions of thermal decomposition undergo complex phase transitions, the enthalpies read out by the phase transitions correspond to the thermodynamically calculated ones and point to a reduced thermal stability of the deuteriated crystal hydrates as compared with the normal ones.

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