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

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The thermal decompositions of $Ba(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8D_2O$, $Ba(OH)_2 \cdot H_2O$ and $Ba(OH)_2 \cdot D_2O$ were studied and the phase transitions were identified by DSC and DTA methods. The corresponding enthalpy changes were determined and compared with those calculated from the thermodynamic data. A decrease of the thermal stability was demonstrated for the deuterated crystal hydrates in comparison with the normal ones.

The utilization of phase transitions in crystal hydrates as a kind of heat-energy storage explains the particular recent interest in this type of compounds. Specially, barium hydroxide and its crystal hydrates are of great interest both for the above-mentioned purpose and for electronics applications.

The thermal behaviour of $Ba(OH)_2 \cdot 8H_2O$ has been studied by differential thermal analysis (DTA) [1–5], but the data obtained for the lower crystal hydrates and for the transition temperatures were contradictory. There are no corresponding data on $Ba(OH)_2 \cdot nD_2O$.

The object of the present work was to examine the thermal dissociations of $Ba(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot H_2O$, $Ba(OH)_2 \cdot 8D_2O$ and $Ba(OH)_2 \cdot D_2O$ by two different methods, DTA and differential scanning calorimetry (DSC), in order to enrich the information available on the thermal behaviours of the above compounds and on the differences between normal and deuterated analogues, as well as to determine the enthalpy changes in the most important phase transitions.

Experimental

The initial compounds for the investigations were prepared in the following ways: $Ba(OH)_2 \cdot 8H_2O$—by double recrystallization of $Ba(OH)_2 \cdot 8H_2O$ using CO_2-free water, $Ba(OH)_2 \cdot 8D_2O$—by double recrystallization of initial $Ba(OH)_2 \cdot H_2O$ from heavy water, $Ba(OH)_2 \cdot H_2O$ by the method from [6], and $Ba(OH)_2 \cdot D_2O$ from $Ba(OH)_2 \cdot 8D_2O$ according to the same method. To prevent the absorption of CO_2, the compounds were kept under nitrogen. They were identified by measuring the barium and water contents. Their purity was 99.5%.

Experiments were also carried out to try to obtain $Ba(OH)_2 \cdot 3H_2O$ by the methods described in references [7–9], but even under good storage conditions (under nitrogen), the composition of the samples was $Ba(OH)_2 \cdot H_2O$.

The TG and DTA curves of the compounds obtained were recorded with a Paulik–Paulik–Erdey MOM derivatograph at the following operating parameters: range—200 mg, heating rate 5 deg/min to 770 K.

The DSC curves were recorded with a Perkin–Elmer DSC in the temperature range 273 to 570 K, at a rate of 5 deg/min, and the enthalpies were determined for the most important phase transitions of dehydration of $Ba(OH)_2 \cdot nH_2O$ or $Ba(OH)_2 \cdot nD_2O$.

Results and discussion

The DTA and TG curves are shown in Fig. 1, and the DSC curves of $Ba(OH)_2 \cdot 8H_2O$ in Fig. 2. The curves of the normal and deuterated monohydrates are presented in Figs 3 and 4, respectively.

The enthalpy changes (from DSC data) of the most important phase transitions, which are determined at the respective temperatures, are given in Table 1, together with the DTA and TG data. The ΔH_f° values of the normal and deuterated crystal hydrates, necessary for the $\Delta H_{ph.tr.}$ calculations were determined from the Rozenfeld–Karapetianz equation [10–12], using the initial value of $\Delta H^0_{f\,Ba(OH)_2} = -946.42$ kJ/mol.

The thermal behaviours of $Ba(OH)_2 \cdot 8H_2O$ and $Ba(OH)_2 \cdot 8D_2O$ (see tabulated data) reveal that these compounds undergo analogous phase transitions. The T_m of $Ba(OH)_2 \cdot 8H_2O$ is slightly higher than that of the deuterated analogue, which is accounted for by the weak destabilization of the $Ba(OH)_2 \cdot 8D_2O$ crystal structure.

A noteworthy difference is observed in the DSC and DTA curves of the two compounds in the temperature range from 365 to 422 K; while the DTA curve (Fig.

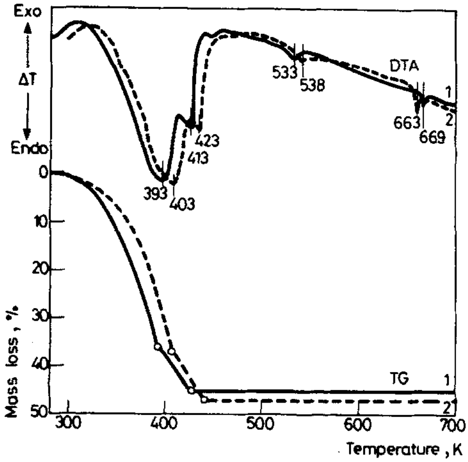

Fig. 1 DTA and TG curves of $Ba(OH)_2 \cdot 8H_2O$ — 1; $Ba(OH)_2 \cdot 8D_2O$ — 2

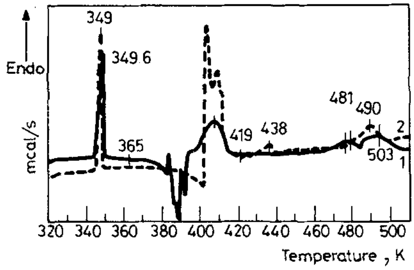

Fig. 2 DSC curves of $Ba(OH)_2 \cdot 8H_2O$ — 1; $Ba(OH)_2 \cdot 8D_2O$ — 2

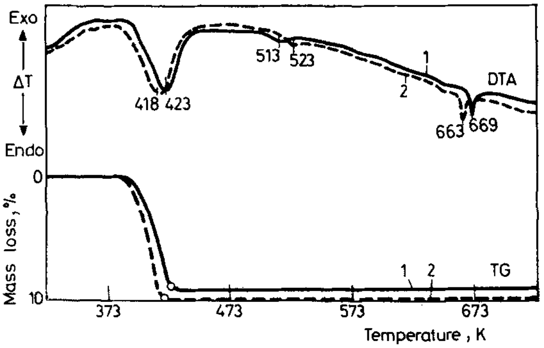

Fig. 3 DTA and TG curves of $Ba(OH)_2 \cdot H_2O$ — 1; $Ba(OH)_2 \cdot D_2O$ — 2

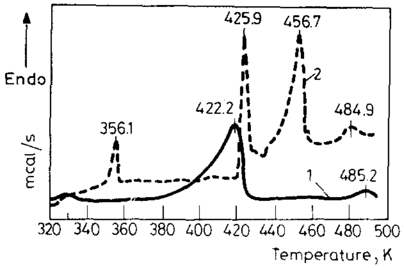

Fig. 4 DSC curves of $Ba(OH)_2 \cdot H_2O$ — 1; $Ba(OH)_2 \cdot D_2O$ — 2

Table 1

	Phase transition	Data from DSC			DTA	Δm, % (TG)	
		peak temp., K	$\Delta H_{ph.tr.}$, kJ/mol		peak temp., K	found	calcd.
			found	calcd.			
$Ba(OH)_2 \cdot 8D_2O_{(l)}$ →	$Ba(OH)_2 \cdot 8H_2O_{(s)} \to Ba(OH)_2 \cdot 8H_2O_{(l)}$	349.6	86.3	94.5	—	—	—
	$Ba(OH)_2 \cdot 8H_2O_{(l)} \to Ba(OH)_2 \cdot H_2O_{(s)} + 7H_2O_{(l+g)}$	365–419	8.7	8.02	393	35.9	36.1
	$Ba(OH)_2 \cdot H_2O_{(s)} \to Ba(OH)_2 \cdot H_2O_{(l)}$	481	20.4	—	—	—	—
	$Ba(OH)_2 \cdot H_2O_{(l)} \to Ba(OH)_{2(s)} + H_2O_{(l)}$	503	40.1	45.2	413	9.1	9.5
	$\alpha\text{-}Ba(OH)_{2(s)} \to \beta\text{-}Ba(OH)_{2(s)}$	—	—	—	533	—	—
	$Ba(OH)_{2(s)} \to Ba(OH)_{2(l)}$	—	—	—	699	—	—
$Ba(OH)_2 \cdot 8D_2O$	$Ba(OH)_2 \cdot 8D_2O_{(s)} \to Ba(OH)_2 \cdot 8D_2O_{(l)}$	349	84.4	—	—	—	—
	$Ba(OH)_2 \cdot D_2O \to Ba(OH)_2 \cdot D_2O_{(s)} + 7D_2O_{(l)}$	372–422	25.1	26.22	403	37.12	37.83
	$Ba(OH)_2 \cdot D_2O_{(s)} \to Ba(OH)_2 \cdot D_2O_{(l)}$	438	15.7	—	—	—	—
	$Ba(OH)_2 \cdot D_2O_{(l)} \to Ba(OH)_{2(s)} + D_2O_{(l+g)}$	491	49.7	44.2	423	9.8	10.4
	$\alpha\text{-}Ba(OH)_{2(s)} \to \beta\text{-}Ba(OH)_{2(s)}$	—	—	—	538	—	—
	$Ba(OH)_{2(s)} \to Ba(OH)_{2(l)}$	—	—	—	663	—	—
	$Ba(OH)_2 \cdot H_2O_{(s)} \to Ba(OH)_{2(s)} + H_2O_{(g)}$	422.2	63.7	65.6	423	9.1	9.5
	$\alpha\text{-}Ba(OH)_{2(s)} \to \beta\text{-}Ba(OH)_{2(s)}$	485.2	—	—	513	—	—
	$Ba(OH)_2 \cdot D_2O_{(s)} \to Ba(OH)_2 \cdot D_2O_{(l)}$	356.1	5.8	—	—	—	—
	$Ba(OH)_2 \cdot D_2O_{(l)} \to Ba(OH)_{2(s)} + D_2O_{(l)}$	425.9	20.08	22.02	—	—	—
	$D_2O_{(l)} \to D_2O_{(g)}$	456.7	46.1	45.4	418	9.7	10.45
	$\alpha\text{-}Ba(OH)_{2(s)} \to \beta\text{-}Ba(OH)_{2(s)}$	484.9	4.2	—	523	—	—

1) exhibits only one endothermic peak, in the DSC curve there appears first an exothermic peak, which is then transformed into a larger endothermic one. The exothermic peak of $Ba(OH)_2 \cdot 8H_2O$ is sharp and split threefold, while that of $Ba(OH)_2 \cdot 8D_2O$ is wider and not so deep (Fig. 2).

The individual enthalpy changes of the two effects were recorded, as well as the additive change for the corresponding phase transition in question. The endoeffect predominated for both compounds; for $Ba(OH)_2 \cdot 8H_2O$ the additive $\Delta H_{ph.tr.} = +28.7$ kJ/mol, and for $Ba(OH)_2 \cdot 8D_2O$ $\Delta H_{ph.tr.} = +25.1$ kJ/mol. The data show that processes for the normal and deuterated hydrates with similar enthalpy changes are analogous. Only the additive endoeffect is observed in the corresponding DTA curves (Fig. 1). The complicated picture of the DSC curves, however, can be explained by the fact that under scanning calorimetry conditions structuring processes, step dehydration, crystallization of lower crystal hydrates and partial evaporation only of separated crystallization water occur simultaneously in the initial melt obtained, i.e. solid, liquid and gas phases coexist in the system. The calculated values for $\Delta H_{ph.tr}$ with $dH^0_{fH_2O}$ (g) = 331.1 kJ/mol and for $\Delta H^0_{fH_2O}$ (l) = 8.02 kJ/mol can be used as substantiation of the above. Comparison of these values with those determined by DSC shows that only small proportion of the crystallization water evaporates. This is to be expected in view of the experimental conditions of this method and the relatively large quantity of separated crystallization water in the transition of the type $Ba(OH)_2 \cdot 8H_2O = Ba(OH)_2 \cdot H_2O + 7\,H_2O$. In dehydration investigations on initial $Ba(OH)_2 \cdot H_2O$ or $Ba(OH)_2 \cdot D_2O$, the picture is simpler, as the smaller quantity of crystallization water evaporates completely. This agrees with the calculations (Table 1).

The other phase transitions of $Ba(OH)_2 \cdot 8H_2O$ and of $Ba(OH)_2 \cdot 8D_2O$ (listed in Table 1) were identified from a comparison of the DTA and DSC data and also reference data [13, 14].

The DTA, TG and DSC data on $Ba(OH)_2 \cdot H_2O$ and $Ba(OH)_2 \cdot D_2O$ show a certain distinction as regards the temperatures at which the respective endothermic peaks are observed. In the DSC curve of $Ba(OH)_2 \cdot D_2O$ (Fig. 4), there is an endothermic peak with maximum at 356.1 K and $\Delta H_{ph.tr.} = 5.82$ kJ/mol for which no weight change is recorded by the TG curve. Therefore, the peak in question could correspond to a polymorphic transition of γ-$Ba(OH)_2 \cdot D_2O$ into β-$Ba(OH)_2 \cdot D_2O$, but it could also be due to the fusion of the latter. As analogous peak in the DSC curve for $Ba(OH)_2 \cdot H_2O$ cannot be precisely detected since it coincides with the considerably larger endothermic peak of the phase transition $Ba(OH)_2 \cdot H_2O_{(s)} \rightarrow Ba(OH)_{2(s)} + H_2O_{(g)}$, for which $\Delta H_{ph.tr.} = 63.7$ kJ/mol, but the calculated $\Delta H^0_{ph.tr.} = 65.6$ kJ/mol.

The two endothermic peaks at 425.9 K and 456.7 K in the DSC curve of $Ba(OH)_2 \cdot D_2O$, with a corresponding endothermic peak with maximum at 418 K in the DTA curve (Figs 3, 4), are due to the phase transition of $Ba(OH)_2 \cdot D_2O_{(s)} \rightarrow Ba(OH)_{2(s)} + D_2O_{(l)}$ and to the evaporation of the crystallization water, respectively. This interpretation is in agreement with the ΔH calculated for these processes (Table 1), as well as with the alteration of the TG curve in the temperature range examined.

Conclusions

The following conclusions could be drawn on the basis of the above investigations: the compounds examined undergo complex phase transitions under the conditions of thermal decomposition; the enthalpies measured for the phase transitions correspond to the thermodynamically calculated ones, which is of help for shedding light on the thermal dissociation mechanisms of the above compounds; a reduced thermal stability is proved for the deuterated crystal hydrates in comparison with the normal ones.

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Zusammenfassung — Die thermische Zersetzung von $Ba(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8D_2O$, $Ba(OH)_2 \cdot H_2O$ und $Ba(OH)_2 \cdot D_2O$ wurde untersucht. Phasenübergänge wurden mittels DSC und DTA ermittelt. Die entsprechenden Enthalpieveränderungen wurden bestimmt und mit den aus thermodynamischen Daten berechneten Werten verglichen. Die deuterierten Kristallhydrate sind thermisch weniger stabil als die leichtes Kristallwasser enthaltenden Verbindungen.

Резюме — Методами ДСК и ДТА изучено термическое разложение и фазовые переходы соединений $Ba(OH)_2 \cdot 8H_2O$, $Ba(OH)_2 \cdot 8D_2O$, $Ba(OH)_2 \cdot H_2O$ и $Ba(OH)_2 \cdot D_2O$. Определены соответствующие энтальпии изменения, которые были сопоставлены с вычисленными на основе термодинамических данных. Показано уменьшение термоустойчивости дейтерированных производных по сравнению с обычными кристаллогидратами.