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THERMAL AND CALORIMETRICAL INVESTIGATIONS OF ORDINARY AND DEUTERATED HYDRATES OF BARIUM ACETATE

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The percentage of thermal dehydration and decomposition of ordinary and deuterated hydrates of barium acetate (tri- and monohydrates) were studied with a derivatograph and by DSC method. The observed phase transitions were identified and their corresponding enthalpy changes determined. The latter were compared with those estimated on thermodynamic data. The conclusions made on the dehydration process in correlation with IR spectra were used as information about the structure of the dehydrated water in the compounds investigated. The end product was also identified as barium carbonate.

It is reported [1] that at 423 K dehydration of $Ba(Ac)_2 3H_2O$ into $Ba(Ac)_2$ occurs. There are not other data on the dehydration of ordinary and deuterated hydrates of $Ba(Ac)_2 nH_2O$ $n = 1,3$ while the thermal decomposition of $Ba(Ac)_2$ is studied by several authors. On basis of thermodynamic data it has been determined [2] that $Ba(Ac)_2$ decomposes into barium carbonate and acetone and the reaction is of topochemical type occurring in the kinetic range. The mechanism of this process is discussed also in [3] and the products are identified by IR spectroscopy. The intermediates obtained have not been determined.

The object of this investigation is to study the process of thermal dehydration and the decomposition of ordinary and deuterated hydrates of barium acetate by DTA and DSC methods.

Experimental

The primary compounds necessary for the experiment were obtained as follows. $Ba(Ac)_2 \cdot 3H_2O$: by double recrystallization of $Ba(Ac)_2$ from solution at a temperature 278–288 K; $Ba(Ac)_2 \cdot 3D_2O$: under the same conditions but from heavy water; $Ba(Ac)_2H_2O$ and $Ba(Ac)_2D_2O$: at vacuum evaporation of the corresponding solutions at 298–303 K.

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The hydrates obtained were identified by the determination of barium and water contents gravimetrically. The TG and DTA curves were recorded with a sensitivity of 200 mg and rate of 5 deg/min up to a temperature 900 K. A derivatograph type MOM system was used. DSC curves proved to be in the temperature range 273–500 K at a rate of 5 deg/min if recorded with Perkin–Elmer apparatus. IR spectra are at a range of 3600–400 cm^{-1} in KBr pellets and in 3600–1800 cm^{-1} in Hostaflon suspension.

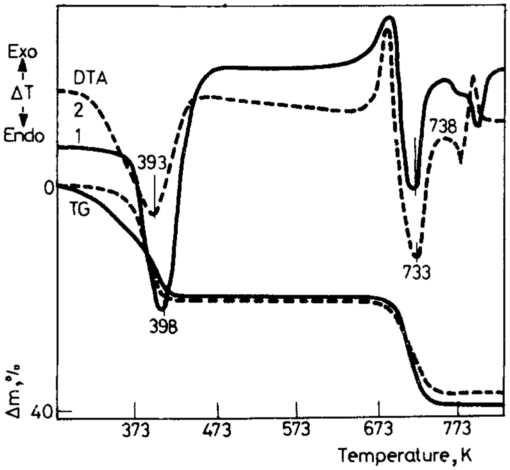

Fig. 1 DTA and TG curves of $Ba(OOCCH_3)_2 \cdot 3H_2O$ (1) and $Ba(OOCCH_3)_2 \cdot 3D_2O$ (2)

Results and discussions

Thermal data for $Ba(Ac)_2 \cdot 3H_2O$ and $Ba(Ac)_2 \cdot 3D_2O$ are shown in Fig. 1, and DSC data of the same compounds in Fig. 2. Figures 3 and 4 represent analogous curves for $Ba(Ac)_2 \cdot H_2O$ and $Ba(Ac)_2 \cdot D_2O$, respectively and parts of their IR spectra in Fig. 5.

Thermal data as well as the estimated phase transitions are summarised in Table 1. The determination of ΔH° ph.tr. (estimated) is done as described in Ref. [4].

It is seen from DTA and TG curves for $Ba(OOCCH_3)_2 \cdot 3H_2O$ as well as for $Ba(OOCCH_3)_2 \cdot 3D_2O$ (Fig. 1) that under these experimental conditions no stepwise dehydration of the compounds investigated is recorded. The dehydration process of $Ba(Ac)_2 \cdot 3H_2O$ is observed in the temperature range 323–418 K (temperatures recorded on TG curves) and the maximum of the corresponding endoeffect is at 398 K, while for $Ba(Ac)_3 \cdot 3D_2O$ that range is 313–418 K with maximum at 393 K. These data show that dehydration of the deuterated analog starts at lower temperature than that for $Ba(Ac)_2 \cdot 3H_2O$ and the difference is also observed on the curves obtained by a derivatograph at different heating rates.

The information about the dehydration is further extended by the data of the DSC curves for the trihydrate (Fig. 2).

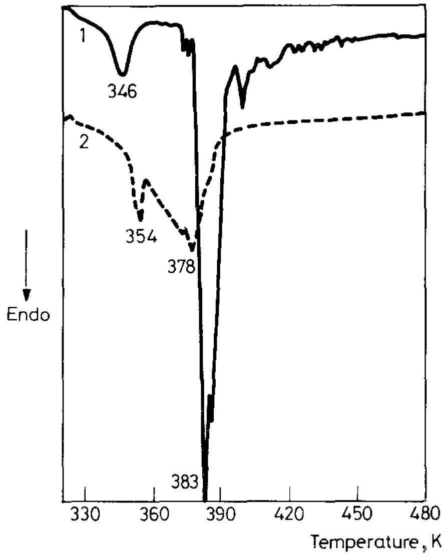

Fig. 2 DSC curves of $Ba(OOCCH_3)_2 \cdot 3H_2O$ (1) and $Ba(OOCCH_3)_2 \cdot 3D_2O$ (2)

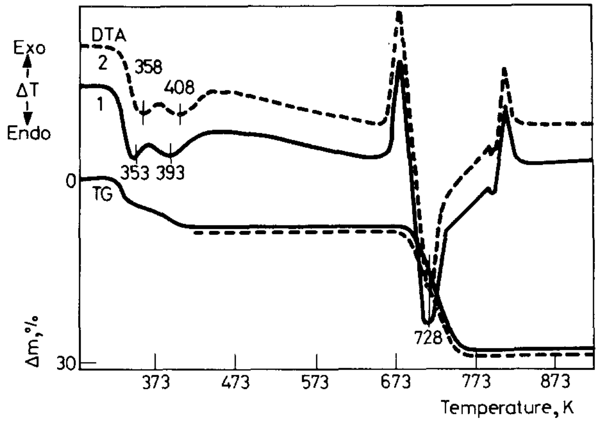

Fig. 3 DTA and TG curves of $Ba(OOCCH_3)_2 \cdot H_2O$ (1) and $Ba(OOCCH_3)_2 \cdot D_2O$ (2)

The different experimental conditions of the calorimetrical investigations make it possible to record stepwise dehydration of the trihydrate. The temperatures of the dehydration process are a little lower than those, recorded by DTA and the difference between ordinary and deuterated trihydrates remain the same.

The information about the character of the investigated phase transitions is fulfilled by data from the recorded enthalpies of dehydration of $Ba(Ac)_2 \cdot 3H_2O$ and of $Ba(Ac)_2 \cdot 3D_2O$, compared with theoretically estimated ones for the case of dehydration water in gas phase or in liquid state. Those data compared in Table 1

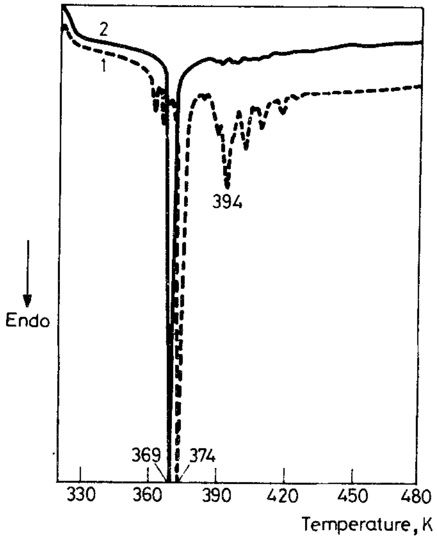

Fig. 4 DSC curves of $Ba(OOCCH_3)_2 \cdot H_2O$ (1) and $Ba(OOCCH_3)_2 \cdot D_2O$ (2)

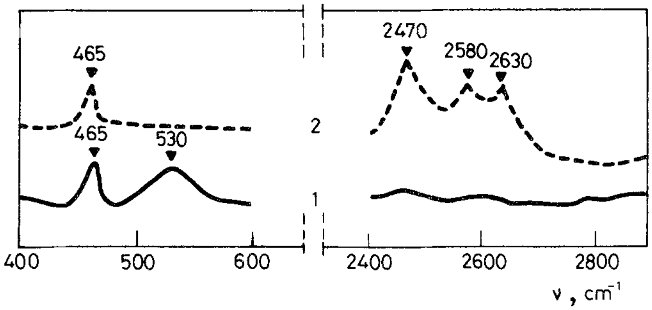

Fig. 5 Parts of IR spectrum of $Ba(OOCCH_3)_2 \cdot H_2O$ (1) and $Ba(OOCCH_3)_2 \cdot D_2O$ (2)

Table 1 DTA, TG and DSC data for $Ba(OOCCH_3)_2 \cdot nH_2O$ and $Ba(OOCCH_3)_2 \cdot nD_2O$ ($n = 1, 3$)

	DSC data				DTA, TG data		
Transformation	T, K	$\Delta H^{\circ}_{exp.}$, kJ/mol	$\Delta H^{\circ}_{theor.}$, kJ/mol		T, K	$\Delta m_{exp.}$, %	$\Delta m_{theor.}$ %
			$\Delta H^{\circ}_{f H_2O_{(L)}}$	$\Delta H^{\circ}_{f H_2O_{(g)}}$			
$Ba(OAc)_2 \cdot 3H_2O \rightarrow Ba(OAc)_2 + 3H_2O_{(1+g)}$	383	79.60	43.8	156.91	398	16.36	17.47
$Ba(OAc)_2 \rightarrow BaCO_3 + CH_3COCH_3$					738	22.10	22.70
$Ba(OAc)_2 \cdot 3D_2O \rightarrow Ba(OAc)_2 + 3D_2O_{(L)(l)}$	378	49.39	47.70	186.60	393	18.43	19.04
$Ba(OAc)_2 \rightarrow BaCO_3 + CH_3COCH_3$					733	18.76	22.70
$Ba(OAc)_2 \cdot H_2O \rightarrow Ba(OAc)_2 \cdot 0.5H_2O + 0.5H_2O_{(1+g)}$	374	33.68	21.36	65.33	353	3.25	3.29
$Ba(OAc)_2 \cdot 0.5H_2O \rightarrow Ba(OAc)_2 + 0.5H_2O$					393	3.30	3.29
$Ba(OAc)_2 \rightarrow BaCO_3 + CH_3COCH_3$					728	21.14	22.70
$Ba(OAc)_2 \cdot D_2O \rightarrow Ba(OAc)_2 \cdot 0.5D_2O + 0.5D_2O_{(L)(l)}$	369	18.14	14.54	59.94	358	3.65	3.63
$Ba(OAc)_2 \cdot 0.5D_2O \rightarrow Ba(OAc)_2 + 0.5D_2O$					408	2.84	3.63
$Ba(OAc)_2 \rightarrow BaCO_3 + CH_3COCH_3$					728	22.10	22.70

enable us to draw the conclusion that, under the conditions of the calorimetrical investigations, the evaporation of the total quantity of water becomes difficult and there are solid, liquid, and gaseous phases in the system at the same time. But while for $Ba(OOCCH_3)_2 \cdot 3H_2O$ the dehydrated water evaporates to a greater extent, for the deuterated analog it is entirely in liquid state. An evidence for that is the recorded $\Delta H^\circ_{\text{deh.}}$, which is near to the estimated one for the case when $\Delta H^\circ_{f_{(l)}}$ stands for water. The difference of the behaviour of the two hydrates can be explained by the different values of $\Delta H^\circ_{\text{evap.}}$ for ordinary and deuterated water.

DTA and TG data for $Ba(Ac)_2 \cdot H_2O$ and for $Ba(Ac)_2 \cdot D_2O$ (Fig. 3) are analogous and are characterized with two endoeffects: two steps which can be explained as follows:

$$Ba(OOCCH_3)_2 \cdot H_2O \rightarrow Ba(OOCCH_3)_2 \cdot 1/2H_2O \rightarrow Ba(OOCCH_3)_2$$

and analogously for $Ba(OOCCH_3)_2 \cdot D_2O$. This type of dehydration is confirmed also by the decrease of the weight, which corresponds to two steps on TG. For the deuterated hydrate, this decrease is lower by 0.8% for the second step than the theoretical one which is due to the presence of traces of DOH because of isotope interchange during the experiment.

The first step of dehydration for ordinary monohydrate occurs in the temperature range 343–363 K (recorded by TG) and with maximum in the DTA curve at 353 K, while the second—in the temperature range 363–423 K with maximum 393 K. The effects for the deuterated hydrate are analogous, but start at higher temperature—by 5° for the first step and by 15° for the second step, i.e. the relationship is reversed to that observed for the trihydrate. This fact can be considered as a proof for the fact that hydrate water in the crystal structure of the monohydrate is bound to the anion by hydrogen bonds. The information about the character of these bonds is supported by the facts observed on the stepwise dehydration of $Ba(OOCCH_3)_2 \cdot H_2O$ and $Ba(OOCCH_3)_2 \cdot D_2O$ during which $Ba(OOCCH_3)_2 \cdot 1/2H_2O$ is obtained. The recording of this intermediate hydrate can be explained by the presence of different kinds of hydrogen bonds, namely: $CH_3COO—H_2O$ and $H_2O—H_2O$. The conclusions made on the basis of the thermal investigations correlate quite well with IR spectra (Fig. 5). The split observed in the stretching vibrations (DO) of the deuterated hydrate at 2470, 2580, 2630 cm^{-1} is a characteristic spectroscopical criterion for the participation of water molecules in two kinds of hydrogen bonds, i.e. for the asymmetry of the water molecule [5]. The observed librational frequency $\nu_{\text{lib}} = 530\ cm^{-1}$ for $Ba(Ac)_2 \cdot H_2O$ indicates the lattice nature of the hydrate water [6]. The analogous vibration for $Ba(Ac)_2 \cdot D_2O$ is not observed because it is out of the observable region.

The information about the dehydration process of the monohydrate is supported with DSC data and the recorded enthalpies and phase transitions are compared with the estimated ones (Table 1). The data show that the quantity of released water in the dehydration of $Ba(Ac)_2 \cdot D_2O$ is almost entirely in liquid state in analogy with the trihydrate.

The data in Figs 1 and 3 show that the resultant dehydrated salt is stable up to 683 K. After that the TG curves show a sudden decrease of weight by 22.1% up to 798 K. That corresponds to the following thermal decomposition:

$$Ba(OOCCH_3)_2 \rightarrow BaCO_3 + CH_3COCH_3$$

That scheme is confirmed by the defractogramm of the solid product obtained—barium carbonate (calcite modification)—and corresponds to the one reported in Ref. [2] where it has been prooved that this process is thermodynamically preferable in comparison to others.

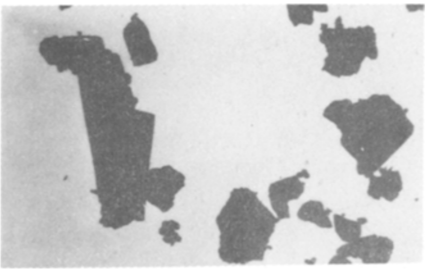

Fig. 6 Electron microscopic picture of $BaCO_3$ prepared by thermal decomposition of $Ba(OOCCH_3)_2 \cdot 3H_2O$ (×3400)

The endoeffect of the decomposition of $Ba(Ac)_2$ shows a maximum at 728 K. It is of interest, however, to point out the little observable effect at 798 K, which is not connected with any change of weight. Its corresponding temperature is very low and one cannot expect that polymorphic conversion of barium carbonate occurs. Electron microscopy is applied for analysing the latter and the average size of the particles of the barium carbonate are 3–5 μm (Fig. 6). These data are of interest because they show an opportunity for preparation of $BaCO_3$ through thermal decomposition of barium acetate.

Zusammenfassung — Mittels DTA- und DSC-Methoden wurde das Verhältnis von Dehydrierung und Zersetzung normaler und deuterierter Hydrate von Bariumazetat (Tri- und Monohydrate) untersucht. Die beobachten Phasenübergänge wurden identifiziert und die dazugehörigen Enthalpieveränderungen bestimmt. Letztere wurden mit den auf der Grundlage thermodynamischer

Daten gewonnenen Schätzwerten verglichen. Die aus den Dehydrierungsprozessen und den IR-Spektren gezogenen Schlußfolgerungen dienen zur Erkenntnisgewinnung über die Struktur des dehydrierten Wassers in den untersuchten Verbindungen. Das Endprodukt der Zersetzung ist Bariumcarbonat.

Резюме — Методом ДТА и ДСК был изучен процесс термической дегидратации и разложения моно- и тригидрата ацетата бария и его дейтеропроизводных. Идентифицированы наблюдаемые фазовые переходы и определены для них изменения энтальпии. Последние были сопоставлены с таковыми, найденными на основе термодинамических данных. Сделаны заключения о процессе дегидратации, которые коррелировались с ИК-спектроскопическими данными о структуре гидратной воды. Конечным продуктом термического разложения являлся карбонат бария.