SYNTHESIS AND PROPERTIES
OF BERYLLIUM IODATES IV

Thermal and calorimetric investigations of $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$

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The thermal decomposition of $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$ was studied by means of DTA and DSC methods. The enthalpies of the more important phase transitions were determined. $Be(IO_3)_2 \cdot I_2O_5$ was isolated and identified as an intermediate.

Acidic salts of iodic acid of the type $M(IO_3)_n \cdot xHIO_3 \cdot yH_2O$, where $n = 1, 2, 3$, are known and their thermal behaviour has been studied to a certain extent.

The valuable physical properties of those compounds or some of their intermediates obtained during thermal decomposition have attracted interest [1]. The synthesis and identification of the acidic beryllium iodate $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$ were described first in [2]. Other data on this compound cannot be found in the literature. Accordingly, in the present work we have studied its thermal and calorimetric behaviour and identified some of its intermediates.

Experimental

The initial acidic beryllium iodate was described first in [2]. It was identified via quantitative analysis, IR spectra and X-ray phase analysis.

The thermal behaviour was investigated with a Paulik–Paulik–Erdey MOM derivatograph at heating rates of 5 and 10 deg/min and a fixed sensitivity of 200 mg up to 1000°. For determination of the enthalpies of the most important phase transitions in the thermal decomposition of $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$, the DSC curve was recorded with a DSC–II Perkin–Elmer apparatus, using a sample of 10 mg in the temperature region from 20 up to 230°. Some of the intermediates were identified by means of quantitative analysis, IR spectra and X-ray phase analysis.

Results and discussion

DTA and TG curves obtained at a heating rate of 5 deg/min are given in Fig. 1. The DSC data are presented in Fig. 2. The most probable scheme for the thermal decomposition, with the corresponding temperatures and the enthalpies of the phase transitions of $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$, is given in Table 1.

The endoeffect with $T_{max} = 80°$ (353 K) in the DTA curve (Fig. 1), which corresponds to an endoeffect at $T = 65°$ (338 K), in the DSC curve, takes place without a weight loss. This phase transition has an enthalpy of 75 kJ/mol and corresponds to melting of the compound analyzed.

The DTA curve next shows a large endoeffect with $T_{max} = 130^b$ (403 K), which corresponds to the process of dehydration:

$$Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O = Be(IO_3)_2 \cdot I_2O_5 + 7H_2O \qquad (1)$$
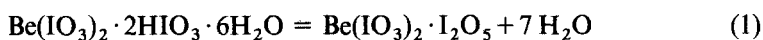
The decrease in weight of the sample according to the TG curve is $\Delta m = 15.7\%$, while the loss calculated via Eq. (1) is $\Delta m = 15.4\%$. This confirms the proposed scheme of dehydration.

In order to identify the intermediate, it was isolated and analyzed by means of quantitative analysis and IR spectroscopy. Its spectrum exhibits the characteristic absorption bands of I_2O_5 as well as those of $Be(IO_3)_2$. The presence of the I–O–I group in the structure of I_2O_5 is proved by the absorption bands observed at
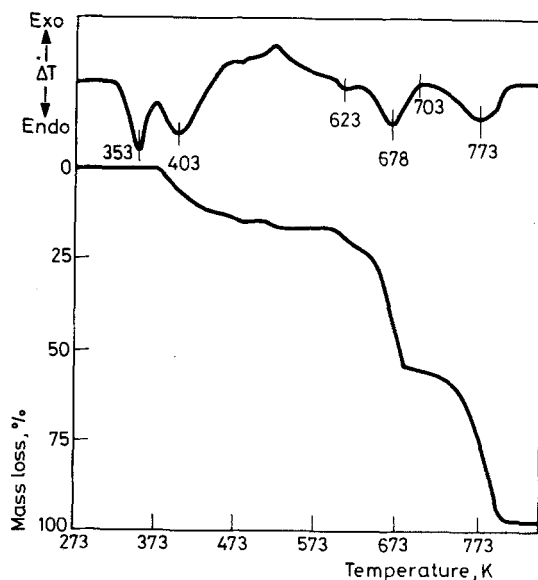

Fig. 1

Fig. 2

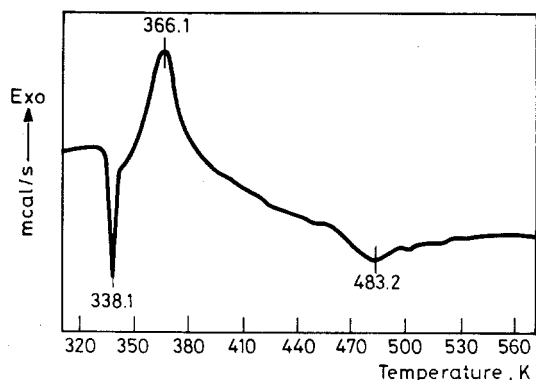Table 1 DTA, TG and DSC data on $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$

Scheme of thermal decomposition	DTA and TG data					DSC data		
	T_{max}, °C	T_{max}, K	Δm theor.	Δm exp.	effect	T_{max}, °C	T_{max}, K	$\Delta H°$ kJ/mol
$Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O_{(s)} \rightarrow$ $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O_{(l)}$	80	353	—	—	(+)	65	338.1	75.0
$Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O_{(l)} \rightarrow$ $Be(IO_3)_2 \cdot I_2O_{5(s)} + 7 H_2O_{(g)}$	130	403	15.4	15.7	(+)	93 210	366.1 483.2	−243 250
$Be(IO_3)_2 \cdot I_2O_5$—stable	260– 310	533– 583	—	—	(−)			
$Be(IO_3)_2 \cdot I_2O_5 \rightarrow Be(IO_3)_2 +$ $+ I_2O_5 \begin{smallmatrix} \nearrow I_2 \\ \searrow 2.5 O_2 \end{smallmatrix}$	350, 405	623, 678	56.2	56.2	(+)			
$Be(IO_3)_2 \rightarrow BeO + I_2 + 2.5 O_2$	430 500	703 773	96.9	96.7	(−) (+)			
BeO residue	over 500	over 773	—	—				

430 cm^{-1} and 620 cm^{-1}, due to the symmetrical and asymmetrical stretching vibration of the I–O bonds (Fig. 3) [3]. The intense absorption bands in the regions 720–840 cm^{-1} and 860–900 cm^{-1} are due to the iodate groups of anhydrous beryllium iodate.

The composition of the intermediate obtained, $Be(IO_3)_2 \cdot I_2O_5$, is confirmed by the thermal curves presented in Fig. 4.
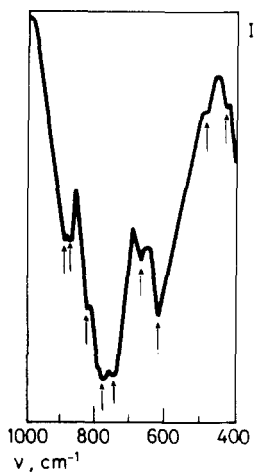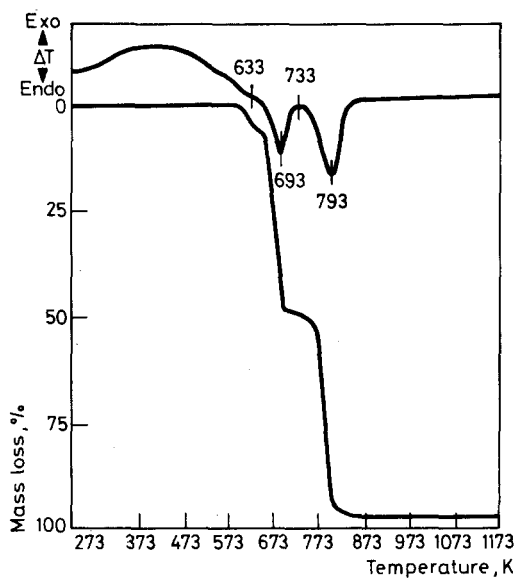
Fig. 3

Fig. 4

A horizontal part is observed in the temperature region 260–310° (535–583 K) in the TG curve, and no effects are seen in the DTA curve. In this region the isolated intermediate is stable.

The endoeffects at 350° (623 K) and 405° (678 K) (Fig. 1) are due to the decomposition of $Be(IO_3)_2 \cdot I_2O_5$ to $Be(IO_3)_2$ and I_2O_5 and to the decomposition

of the latter, respectively. The loss in the TG curve is $\Delta m = 56.2\%$, which coincides with that calculated for the proposed scheme: $\Delta m = 56.2\%$.

The further runs of the DTA and TG curves correspond to the data on the thermal decomposition of $Be(IO_3)_2 \cdot 4H_2O$ [4], i.e. decomposition of the anhydrous product to BeO and the liberation of iodine and oxygen according to the scheme (Table 1).

The data from the DSC curve in the region of the dehydration processes are quite interesting, and yield more complete information on these processes. Whereas the DTA curve gives one endoeffect, at $T_{max} = 130°$ (403 K), the DSC curve (Fig. 2) first exhibits an exoeffect at $T_{max} = 93.1°$ (366 K), with an endoeffect at $T = 210°$ (483 K). A similar picture is observed during analogous investigations of other beryllium iodates we have synthesized, and can be explained in terms of the complex multistep mechanism characteristic of the dehydration process [4]. It is accompanied by simultaneous exo- and endoprocesses, but, whereas DTA registers their total effect at $T_{max} = 130°$ (403 K), the DSC method allows identification of some of the effects of the particular step of the process. It is clear that the dehydration of $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$ in the melt is accompanied by structural exothermal transformations, taking place both before and in parallel with the stage of separation of the differently attached water. Simultaneously, processes of crystallization and recrystallization of the intermediate obtained and evaporation of the evolved water take place. The endoeffect at $T = 210°$ (483 K) corresponds to the evaporation, as the recorded enthalpy of $\Delta H^0_{483} = 250$ kJ/mol coincides very well with the calculated one: $\Delta H^0_{298} = 264$ kJ/mol. The registered exoeffect at $T_{max} = 93.1°$ (366 K) is therefore total, including the effect of the dehydration stage as well as all accompanying exoeffects which have higher values than the first one.

References

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Zusammenfassung — Mittels DTA und DSC Verfahren wurde die thermische Zersetzung von $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$ untersucht. $Be(IO_3)_2 \cdot I_2O_5$ konnte als Zwischenprodukt isoliert und identifiziert werden. Weiterhin wurde die Enthalpien der wichtigeren Phasenübergänge ermittelt.

Резюме — Методом ДТА и ДСК изучено термическое разложение $Be(IO_3)_2 \cdot 2HIO_3 \cdot 6H_2O$. Определены энтальпии некоторых важных фазовых переходов. Выделен и идентифицирован промежуточный продукт разложения состава $Be(IO_3)_2 \cdot I_2O_5$.