THERMAL AND CALORIMETRIC INVESTIGATIONS ON BERYLLIUM PERIODATE HYDRATES

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The thermal decompositions of two beryllium periodate hydrates, $Be(IO_4)_2 \cdot 8H_2O$ and $Be(H_4IO_6)_2 \cdot 2H_2O$, were studied by DTA and TG in the temperature range from 298 to 1073 K, and by DSC from 298 to 723 K. The intermediates of the thermal decompositions were identified via quantitative analysis, IR spectroscopy and the TG curves. The data obtained were utilized to suggest a scheme for the thermal decompositions of the two periodates. Both compounds decompose via an anhydrous beryllium iodate, and the final residue is beryllium oxide.

The enthalpies of the phase transitions were determined from the DSC curves.

There are only a few literature data on the syntheses and properties of beryllium periodates. The synthesis of $Be_2(IO_5)_2 \cdot 12H_2O$ [1] was confirmed by Dratovsky and Prejkova [2]. The same authors investigated the $Be_3(IO_5)_2$–H_3IO_6–H_2O system, and isolated and identified another compound, $BeI_2O_8 \cdot 13H_2O$. The thermal behaviour of $Be_3(IO_5)_2 \cdot 12H_2O$ has been studied [3, 4]. According to [3], this thermal decomposition leads to an intermadiate $Be_2I_2O_9 \cdot 3.9H_2O$, but it was not decided whether this is a compound of I(VI) or a mixture of two products. According to [4], $Be_3(IO_5)_2 \cdot 12H_2O$ decomposes to $Be(IO_3)_2$. There are data about the preparation of $Be(IO_4)_2 \cdot 8H_2O$ [5], but its thermal behaviour has not been studied. A method for the preparation of a new beryllium periodate, $Be(H_4IO_6)_2 \cdot 2H_2O$, was investigated in [6]. The product was analyzed and identified by means of quantitative analysis, IR spectroscopy and X-ray diffraction. The present paper reports a detailed study of the thermal and calorimetric behaviour of two beryllium periodate hydrates: $Be(IO_4)_2 \cdot 8H_2O$ and $Be(H_4IO_6)_2 \cdot 2H_2O$.

Experimental

$Be(IO_4)_2 \cdot 8H_2O$ and $Be(H_4IO_6)_2 \cdot 2H_2O$ were prepared as described previously [6]. They were identified by means of quantitative analysis, IR spectroscopy and X-ray diffraction, as were some of the decomposition intermediates.

The DTA and TG curves of those compounds were recorded with a MOM derivatograph at a heating rate of 10 deg min^{-1} up to 1173 K.

The DSC curves were recorded with a Mettler TA 3000 apparatus at a heating rate of 10 deg min^{-1} up to 723 K. The enthalpies recorded for the phase transitions were recalculated into kJ/mol.

Results and discussion

The DTA and TG curves of $Be(IO_4)_2 \cdot 8H_2O$ are presented in Fig. 1, and those of $Be(H_4IO_6)_2 \cdot 2H_2O$ in Fig. 3. The DSC curves are given in Figs 2 and 4, respectively. The most probable scheme of thermal decomposition and the respective temperatures and enthalpies of the phase transition for $Be(IO_4)_2 \cdot 8H_2O$ are listed

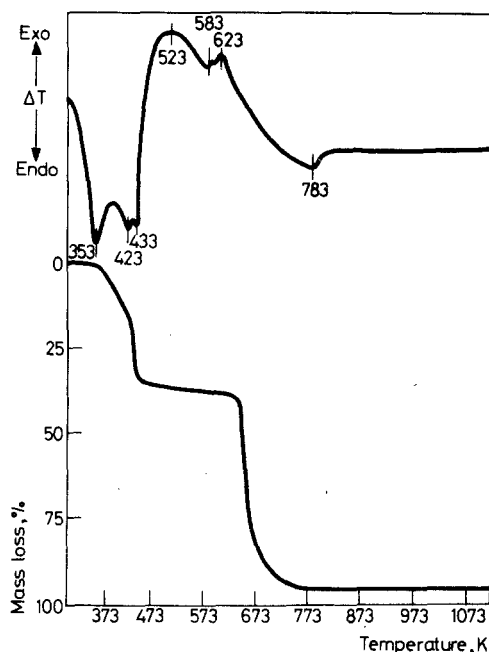Fig. 1 DTA and TG curves of $Be(IO_4)_2 \cdot 8H_2O$
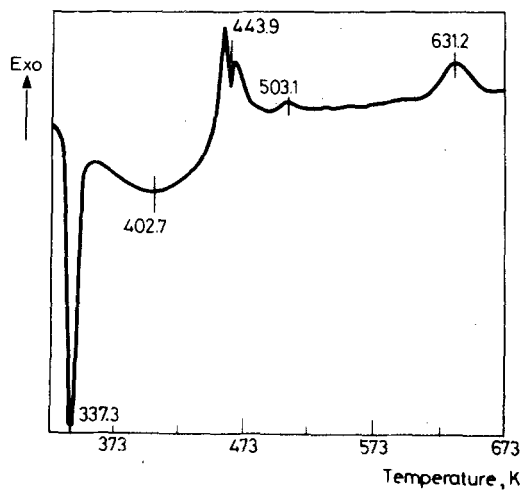
Fig. 2 DSC curve of $Be(IO_4)_2 \cdot 8H_2O$
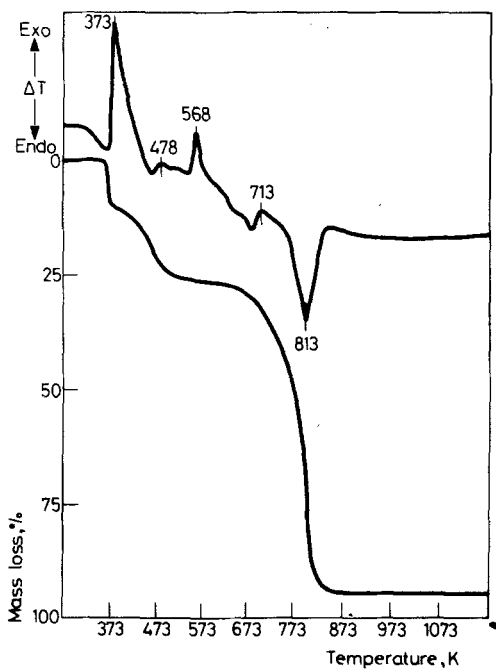
Fig. 3 DTA and TG curves of $Be(H_4IO_6) \cdot 2H_2O$

Table 1 DTA, TG and DSC data on $Be(IO_4)_2 \cdot 8H_2O$

Scheme of thermal decomposition	Data from DTA and TG				Data from DSC		
	T_{max}, K	Δm, % (TG)		Effect exo (−) endo (+)	T_{max}, K	$\Delta H°$, J/g	$\Delta H°$, kJ/mol
		found	calcd.				
1	2	3	4	5	6	7	8
$Be(IO_4)_2 \cdot 8H_2O_{(s)} \rightarrow$ $\rightarrow Be(IO_4)_2 \cdot 8H_2O_{(l)}$	353			+	337.3	181.44	97.07
$Be(IO_4)_2 \cdot 8H_2O_{(l)} \rightarrow$ $\rightarrow Be(IO_4)_2 + 8 H_2O$	423 433	26.5	26.91	+	402.7	122.68	65.63
$Be(IO_4)_2 = Be(IO_3)_2 +$ $+ O_2$	523	8.4	8.18	−	443.9	− 19.31	− 7.55
$Be(IO_3)_2 \rightarrow Be(IO_3)_2$ (amor.) (cryst.)	583			−	503.2	− 7.93	− 2.84
1	2	3	4	5	6	7	8
$Be(IO_3)_2 = BeO +$ $+ I_2O_{5(s)}$	623	93.3	93.04	−	631.4	− 63.41	−22.76
$I_2O_5 = I_2 + 2.5 O_2$	783			+			
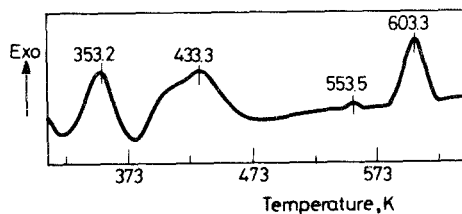
Fig. 4 DSC curve of $Be(H_4IO_6) \cdot 2H_2O$

in Table 1, and those for $Be(H_4IO_6)_2 \cdot 2H_2O$ in Table 2. IR spectra of the initial compounds and some intermediates are shown in Fig. 5.

The observed exo and endo effects in the DTA and DSC curves (Figs 1 and 3) are analogous, but the temperatures corresponding to their maxima are different in most cases. This is to be expected in view of the different experimental conditions.

The observed endo effect with maximum at 353 K is due to melting of the compound investigated, which is seen from the character of the TG curve as well as from visual observations. The second endo effect is split, with maxima at 423 and 433 K, and the change in the direction of the TG and 423 K corresponds to this. This result can be explained by the step of dehydration to an intermediate

$Be(IO_4)_2 \cdot 3H_2O$. The latter is very probable, because it corresponds to a weight change $\Delta m = 16.5\%$ compared with the calculated value of $\Delta m = 16.8\%$.

It is seen that the observed exo effect with maximum at 523 K (on DTA), corresponding to the conversion $Be(IO_4)_2 \rightarrow Be(IO_3)_2 + O_2$, is round, while on DSC it is split. This shows that the conversion occurs by a mechanism which is more complex than that of the above scheme, and the end-product is $Be(IO_3)_2$. The latter is identified through quantitative analysis and the IR spectra (Fig. 5). The $Be(IO_3)_2$ obtained is stable in the temperature range from 573 to 623 K, in which range there is a phase transition from an amorphous state into a crystalline one. The corresponding exo effect has its maximum at 583 K.

This behaviour was also observed in other investigations on beryllium periodates [7]. The exo effect with maximum at 623 K (in the DTA and DSC curves) corresponds to the decomposition of $Be(IO_3)_2$ to BeO and I_2O_5. The presence of the latter is recorded in the IR spectra of the product isolated at that temperature. Its decomposition to oxygen and iodine corresponds to the endo effect at 783 K.

In the DTA curves of $Be(H_4IO_6)_2 \cdot 2H_2O$ (Fig. 3), four exo effects are observed with maxima at 373, 478, 568 and 713 K. They also appear in the DSC curves (Fig. 4), but the characters of the first two differ in the two curves. On DTA, the first peak is significantly bigger in area and the second one is small, whereas in the DSC curve they are approximately equal. These peaks (DTA and DSC) are probably a result of
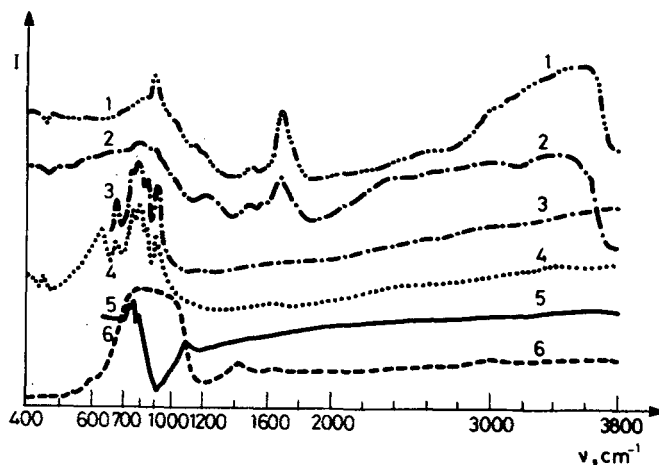

Fig. 5 IR spectra of the initial compounds and of some intermediate products:
1 – of $Be(IO_4)_2 \cdot 8H_2O$,
2 – of $Be(H_4IO_6) \cdot 2H_2O$,
3 – of an intermediate product at 600 K (from 1),
4 – of an intermediate product at 600 K (from 2),
5 – of I_2O_5,
6 – of BeO

Table 2 DTA, TG and DSC data on $Be(H_4IO_6)_2 \cdot 2H_2O$

Scheme of thermal decomposition	Data from DTA and TG				Data from DSC		
	T_{max}, K	Δm, % (TG)		Effect exo (−) endo (+)	T_{max}, K	$\Delta H°$, J/g	$\Delta H°$, kJ/mol
		found	calcd.				
$Be(H_4IO_6)_2 \cdot 2H_2O \rightarrow$ $\rightarrow Be(H_2IO_5)_2 \cdot H_2O +$ $+ 3 H_2O$	373		10.82	−	353	− 84.12	− 41.97
$Be(H_2IO_5)_2 \cdot H_2O \rightarrow$ $\rightarrow Be(IO_3)_2 + 3 H_2O +$ $+ O_2$	513	18.98	19.32	−	433	− 145.5	− 64.75
$Be(IO_3)_2 \rightarrow Be(IO_3)_2$ (amor.) (cryst.)	513–573			−	553	− 8.53	− 3.05
$Be(IO_3)_2$ stable	573–643						
$Be(IO_3)_2 = BeO +$ $+ I_2O_5$	713	93.5	93.04	−	603	− 63.41 ,	− 22.76
$I_2O_5 = I_2 + 2.5 O_2$	813						

overlapping endo and exo processes, the latter being stronger. The total weight decrease $\Delta m = 27.5\%$ corresponds to that calculated for conversion into $Be(IO_3)_2$ (28.05%). The TG curve is rather steep up to $\Delta m = 9.45\%$, after which the weight changes more gradually up to $\Delta m = 27.5\%$. The effects show that the thermal dehydration and decomposition pass through intermediate steps. The TG curve suggests that the intermediate is acid beryllium mesoperiodate (Table 2). Its isolation is impossible, however, because of the continuation of the process to $Be(IO_3)_2$. In the temperature region investigated (298 to 573 K), other phase transitions are not excluded, but they are difficult to identify. The formation of $Be(IO_3)_2$ during the thermal decomposition can be confirmed by its IR spectrum (Fig. 5) in the region of its thermal stability. The latter is very distinct in the TG curve (573–643 K) and accords with other investigations on this compound [7].

The remaining parts of the DTA and TG curves are analogous to those for $Be(IO_4)_2 \cdot 8H_2O$. The exo effect with maximum at 713 K is due to the decomposition of $Be(IO_3)_2$, and the endo effect at 813 K to the decomposition of I_2O_5. The recorded Δm corresponds to the complete removal of iodine and oxygen.

The enthalphies of the phase transitions (listed in Table 2) were determined from the DSC data.

References

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Zusammenfassung — Die thermische Zersetzung der Berylliumperiodat-hydrate $Be(IO_4)_2 \cdot 8H_2O$ und $Be(H_4IO_6) \cdot 2H_2O$ wurde im Temperaturbereich 298—1073 K durch TG—DTA und von 298—723 K mittels DSC untersucht. Zwischenprodukte der thermischen Zersetzung wurden durch quantitative Analyse, IR-Spektroskopie und TG-Kurven identifiziert. Im Ergebnis wird ein Schema für die thermische Zersetzung der beiden Periodat-Hydrate vorgeschlagen. Beide Verbindungen zersetzen sich über wasserfreies Berylliumiodat $Be(IO_3)_2$ als Zwischenprodukt, das feste Endprodukt ist BeO. Die Umwandlungsenthalpien werden aus den DSC-Kurven abgeschätzt.

Резюме — Термическое разложение двух гидратов перйодата бериллия — $Be(IO_4)_2 \cdot 8H_2O$ и $Be(H_4IO_6) \cdot 2H_2O$ — было изучено методами ДТА и ТГ в температурном интервале 298—1073 К и методом ДСК в области температур 298—723 К. Промежуточные продукты термического разложения были идентифицированы количественным анализом, ИК спектроскопией и кривыми ТГ. На основе полученных данных предложена схема термического разложения двух перйодатов. Оба соединения первоначально разлагаются до безводного продукта с последующим образованием оксида бериллия в качестве конечного продукта разложения. На основе кривых ДСК определены энтальпии фазовых переходов.