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THERMAL AND CALORIMETRIC STUDIES OF $M(IO_3)_2{\cdot}6H_2O$ AND $M(IO_3)_2{\cdot}6D_2O$ FOR $M^{2+}=Ca^{2+}$ AND Sr^{2+}

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Thermal and calorimetric studies were carried out on $M(IO_3)_2{\cdot}6H_2O$ and $M(IO_3)_2{\cdot}6D_2O$ for $M^{2+}=Ca^{2+}$ and Sr^{2+}, using DTA and DSC methods. The thermal behaviour of the ordinary and deuterated hydrates is outlined and the differences observed between them are discussed. The enthalpies of the phase transitions were determined. The ΔH_f° for $Ca(IO_3)_2{\cdot}6H_2O$, $Ca(IO_3)_2{\cdot}6H_2O(D_2O)$ and $Sr(IO_3)_2{\cdot}6H_2O(D_2O)$ were calculated from the ΔH_{deh} data and comments are made on the isotope effect observed.

Keywords: DSC, DTA, $M(IO_3)_2{\cdot}6H_2O$, $M(IO_3)_2{\cdot}6D_2O$

Introduction

The thermal dehydration of $M(IO_3)_2{\cdot}6H_2O$ ($M^{2+}=Ca^{2+}$ and Sr^{2+}) was investigated by means of DTA in [1]. The two-stage course of the dehydration process was established: first until the corresponding monohydrates, and then until the anhydrous salts were obtained. There are analogous data for $Ca(IO_3)_2{\cdot}6H_2O$ in [2]. Similar DTA and DSC studies of the thermal behaviour of $Ca(IO_3)_2{\cdot}6H_2O$ were presented in [3]. There are no data on the thermal and calorimetric behaviour of the corresponding deuterates.

The aim of the present study was to record the DTA and DSC curves of $M(IO_3)_2{\cdot}6H_2O$ ($M^{2+}=Ca^{2+}$ and Sr^{2+}) and the corresponding deuterates and thereby to examine the dehydration processes. An attempt was made to determine ΔH_f° for the ordinary and deuterated hydrates from ΔH_{deh}.

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Experimental

The hexahydrates investigated were synthesized by treating 30% solutions of the corresponding nitrates with iodic acid at ≈25°C for $Ca(IO_3)_2 \cdot 6H_2O$ and≈ 5°–6°C for $Sr(IO_3)_2 \cdot 6H_2O$. The deuterates were synthesized by using 30% solutions of the anhydrous nitrates and iodic acid in heavy water. The crystalline phases obtained were filtered off, then dried in a flow of argon, and were kept cold in special boxes in an inert medium. All reagents used were of p.a. grade, while the heavy water was 99.75% (p.a. Merck). The hexahydrates obtained were subjected to quantitative analyses: Ca^{2+} and Sr^{2+} complexometrically [4], iodine iodometrically [5], and water was identified by Fisher's method [6] and determined thermogravimetrically. The thermal investigations were carried out on a Paulik-Paulik-Erdey MOM OD-102 derivatograph. The DTA and TG curves were taken up to 500°C at a heating rate of 5 deg·min^{-1} with a sample weight of 200 mg. In order to determine the enthalpies of the phase transitions observed during the thermal dehydration of $M(IO_3)_2 \cdot 6H_2O(D_2O)$ ($M^{2+}=Ca^{2+}$ and Sr^{2+}), the corresponding DSC curves were also recorded on a Perkin-Elmer DSC-4 apparatus in the range 50°–250°C with a sample weight of 1 mg in volatile sample pans. The enthalpies of the phase transitions were determined with an accuracy of ±0.5%. The X-ray powder diffraction patterns of the investigated compounds were recorded on a TUR-M-62 instrument with CuK_α irradiation, and were also used to determine the particle size.

Results and discussion

The DTA and TG curves of $Ca(IO_3)_2 \cdot 6H_2O(D_2O)$ are shown in Fig. 1 and the DSC curves in Fig. 2. For $Sr(IO_3)_2 \cdot 6H_2O(D_2O)$, the corresponding DTA and TG curves can be seen in Fig. 3 and the DSC curves in Fig. 4. Table 1 presents diagrams of the thermal dehydration of the investigated compounds from the DTA data, and Table 2 those from the DSC data.

It follows from the data presented in Fig. 1 and Table 1 that the thermal dehydrations of $Ca(IO_3)_2 \cdot 6H_2O$ and $Ca(IO_3)_2 \cdot 6D_2O$ take place in two stages, the corresponding monohydrates being obtained in the first stage. It is noteworthy, however, that the endoeffect corresponding to the first dehydration stage for the deuterate has a lower T_{max} (by about 20 deg) than that of the ordinary hydrate, and appears split, with T_{max}=75° and 90°C. This split may be due either to a two-stage separation of the first five molecules of water or to a consecutive course of dehydration and evaporation of the liquid water released. It is not possible to determine which of the two possibilities is involved, since the TG curves do not provide additional information.

Table 1 DTA and TG data for $M(IO_3)_2 \cdot 6H_2O$ resp. $M(IO_3)_2 \cdot 6D_2O$ ($M^{2+} = Ca^{2+}, Sr^{2+}$)

Substance	Phase transition	Mass loss / %		T_{max} /	$\Delta H^{o}_{p.t.}$ /
		exp.	theor.	°C	kJ·mol^{-1}
	$Ca(IO_3)_2 \cdot 6H_2O \rightarrow Ca(IO_3)_2 \cdot H_2O + 5H_2O$	18.3	18.1	110	>0
$Ca(IO_3)_2 \cdot 6H_2O$	$Ca(IO_3)_2 \cdot H_2O \rightarrow \beta\text{–}Ca(IO_3)_2 + H_2O$	4.3	4.4	160	>0
	$\beta\text{–}Ca(IO_3)_2 \rightarrow \frac{1}{5}Ca_5(IO_6)_2 + \frac{4}{5}I_2 + \frac{9}{5}O_2$	–	–	T_{init} 450	>0
	$Ca(IO_3)_2 \cdot 6D_2O \rightarrow Ca(IO_3)_2 \cdot D_2O + 5D_2O$	19.4	19.6	75.9	>0
$Ca(IO_3)_2 \cdot 6D_2O$	$Ca(IO_3)_2 \cdot D_2O \rightarrow \alpha\text{–}Ca(IO_3)_2 + D_2O$	4.6	4.9	160	>0
	$\alpha\text{–}Ca(IO_3)_2 \rightarrow \beta\text{–}Ca(IO_3)_2$	–	–	275	>0
	$\beta\text{–}Ca(IO_3)_2 \rightarrow \frac{1}{5}Ca_5(IO_6)_2 + \frac{4}{5}I_2 + \frac{9}{5}O_2$	–	–	T_{init} 450	>0
	$Sr(IO_3)_2 \cdot 6H_2O \rightarrow Sr(IO_3)_2 \cdot H_2O + 5H_2O$	16.1	16.5	95	>0
$Sr(IO_3)_2 \cdot 6H_2O$	$Sr(IO_3)_2 \cdot H_2O \rightarrow \alpha\text{–}Sr(IO_3)_2 + H_2O$	4.3	4.3	175	>0
	$\alpha\text{–}Sr(IO_3)_2 \rightarrow \gamma\text{–}Sr(IO_3)_2$	–	–	280	>0
	$\gamma\text{–}Sr(IO_3)_2 \rightarrow \frac{1}{5}Sr_5(IO_6)_2 + \frac{4}{5}I_2 + \frac{9}{5}O_2$	–	–	T_{init} 470	>0
	$Sr(IO_3)_2 \cdot 6D_2O \rightarrow Sr(IO_3)_2 \cdot D_2O + 5D_2O$	17.6	17.9	75	>0
$Sr(IO_3)_2 \cdot 6D_2O$	$Sr(IO_3)_2 \cdot D_2O \rightarrow \alpha\text{–}Sr(IO_3)_2 + D_2O$	2.3	2.2	165	>0
	$\alpha\text{–}Sr(IO_3)_2 \rightarrow \gamma\text{–}Sr(IO_3)_2$	2.2	2.1	280	>0

Table 2 DSC data for $M(IO_3)_2 \cdot 6H_2O$ resp. $M(IO_3)_2 \cdot 6D_2O$ ($M^{2+} = Ca^{2+}, Sr^{2+}$)

Substance	Phase transition	$T_{p.t.}$ / °C T_{onset}	 T_{max}	$\Delta H_{p.t.}$ exp. / kJ·mol^{-1}	ΔH_{deh} calc. / kJ·mol^{-1} $\Delta H^0_{f,H_2O(g)}$	 $\Delta H^0_{f,H_2O(l)}$
$Ca(IO_3)_2 \cdot 6H_2O$	$Ca(IO_3)_2 \cdot 6H_2O(s) \rightarrow Ca(IO_3)_2 \cdot 6H_2O(l)$	80.3	82.6	74.7	–	–
	$Ca(IO_3)_2 \cdot 6H_2O(l) \rightarrow Ca(IO_3)_2 \cdot H_2O + 5H_2O(g)$	115.9 154.8 160.9	119.6 156.1 162.6	–42.4 24.9 215.6	276.0	56.9
	$Ca(IO_3)_2 \cdot H_2O(s) \rightarrow Ca(IO_3)_2(s) + H_2O(g+l)$	206.3	215.2	41.8	49.5	2.2
$Ca(IO_3)_2 \cdot 6D_2O$	$Ca(IO_3)_2 \cdot 6D_2O(s) \rightarrow Ca(IO_3)_2 \cdot 6D_2O(l)$	68.6	72.2	42.1	–	–
	$Ca(IO_3)_2 \cdot 6D_2O(l) \rightarrow Ca(IO_3)_2 \cdot D_2O(s) + 5D_2O(g+l)$	114.9 141.2	119.5 143.1	–62.5 150.8	306.0	79.0
	$Ca(IO_3)_2 \cdot D_2O(s) \rightarrow Ca(IO_3)_2(s) + D_2O(g+l)$	198.8	205.8	64.31	59.9	14.5
$Sr(IO_3)_2 \cdot 6H_2O$	nonidentified phase transition	117.2	120.2	–57.9	–	–
	$Sr(IO_3)_2 \cdot 6H_2O(s) \rightarrow Sr(IO_3)_2 \cdot H_2O(s) + 5H_2O(g+l)$	156.3	156.9	212.4	269.0	48.8
	$Sr(IO_3)_2 \cdot H_2O(s) \rightarrow Sr(IO_3)_2(s) + H_2O(g+l)$	168.8	173.5	29.8	49.3	5.2
$Sr(IO_3)_2 \cdot 6D_2O$	nonidentified phase transition	76.7	89.1	–18.6	–	–
	nonidentified phase transition	126.3	130.3	–47.08	–	–
	$Sr(IO_3)_2 \cdot 6D_2O(s) \rightarrow Sr(IO_3)_2 \cdot D_2O(s) + 5D_2O(g+l)$	151.8	152.6	104.4	306.0	78.7
	$Sr(IO_3)_2 \cdot D_2O(s) \quad Sr(IO_3)_2(s) + D_2O(g)$	174.7	186.6	22.25	56.9	11.5

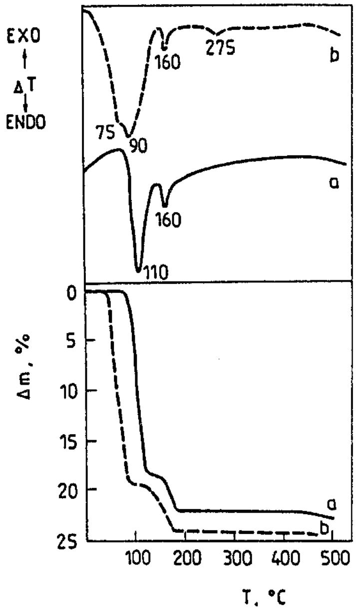

Fig. 1 DTA and TG curves of $Ca(IO_3)_2 \cdot 6H_2O$ (a) and $Ca(IO_3)_2 \cdot 6D_2O$ (b)

The second stage of the thermal dehydration is also interesting: $Ca(IO_3)_2 \cdot 6H_2O$ yields β–$Ca(IO_3)_2$, while $Ca(IO_3)_2 \cdot 6D_2O$ yields α–$Ca(IO_3)_2$. The IR spectrum of the latter differs from that of β–$Ca(IO_3)_2$ [3]. The formation of α–$Ca(IO_3)_2$ was corroborated by the small endoeffect with T_{max}=275°C in the derivatogram of the deuterate, due to the polymorphous transformation of the α–form into the β–form. The fact that the latter was obtained is proved by the fact that the IR spectrum of a sample isolated at 300°C is identical with that obtained following the dehydration of $Ca(IO_3)_2 \cdot H_2O$ and coincides with published data on this polymorphous form [3].

Decomposition of β–$Ca(IO_3)_2$ begins at temperatures over 460°C and calcium orthoperiodate, iodine and oxygen are obtained in accordance with [7].

The data from the DSC curves for $Ca(IO_3)_2 \cdot 6H_2O(D_2O)$ (Fig. 2 and Table 2), compared with those from the DTA curves (Fig. 1 and Table 1), show differences in the phase transitions taking place. First of all the initial hydrate melts (first endoeffect not observed in the DTA curve). Next immediately before the large endoeffect of the dehydration, there is a clearly expressed exoeffect, which shows that the dehydration process takes place in the melt. An analogous pattern has been observed for other hydrates [8, 9].

The DTA and TG curves for $Sr(IO_3)_2 \cdot 6H_2O$ and $Sr(IO_3)_2 \cdot 6D_2O$ (Fig. 3 and Table 1) show analogous phase transitions. The dehydration process is a two-stage one, as in the case of $Ca(IO_3)_2 \cdot 6H_2O(D_2O)$, and the small endoeffect with T_{max}=280°C is related to the polymorphous transformation of the α-form into the γ-form. Since there are no roentgenographic data on the latter in the literature, identification was made via the IR spectra (Fig. 5) of samples isolated according to the DTA curve before and after 280°C. The IR spectra obtained coincide with

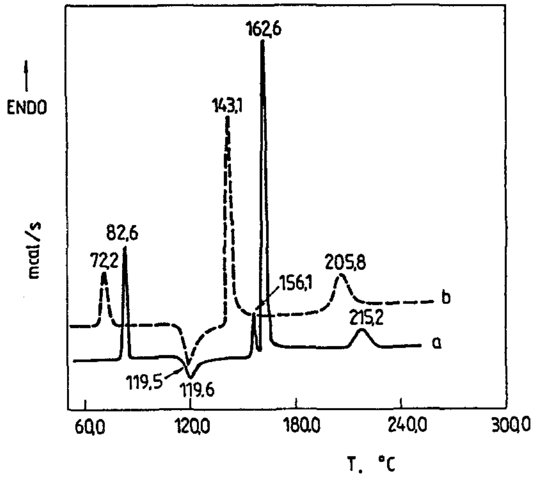

Fig. 2 DSC curves of $Ca(IO_3)_2 \cdot 6H_2O$ (a) and $Ca(IO_3)_2 \cdot 6D_2O$ (b)

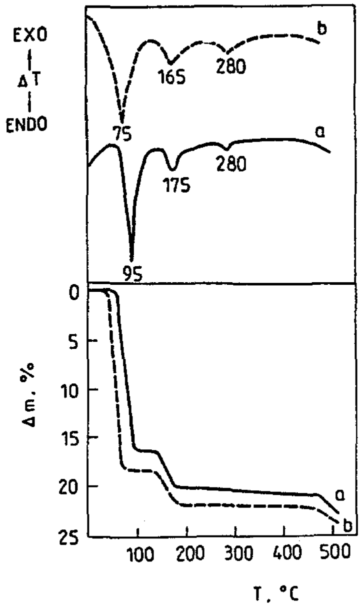

Fig. 3 DTA and TG curves of $Sr(IO_3)_2 \cdot 6H_2O$ (a) and $Sr(IO_3)_2 \cdot 6D_2O$ (b)

those given for these polymorphous forms in [3]. It must be pointed out that this transition is not registered when the DTA curve is obtained at a higher heating rate (8 or 10 deg·min^{-1}). The γ-$Sr(IO_3)_2$ obtained begins to decompose at a temperature of over 470°C, analogously to β-$Ca(IO_3)_2$ [7, 10].

The DTA data indicate that $Sr(IO_3)_2 \cdot 6H_2O$ has a lower thermal stability than that of $Ca(IO_3)_2 \cdot 6H_2O$. A general explanation of this fact may be the weaker polarizing action of Sr^{2+} (due to its larger radius) on the surrounding structural groups.

The DSC curves of $Sr(IO_3)_2 \cdot 6H_2O(D_2O)$ (Fig. 4 and Table 2) differ from the corresponding DTA curves in the existence of an exoeffect (one for the ordinary and two for the deuterated hydrate) before the dehydration endoeffects. In this particular case these effects can be explained only by processes of polymorphous transformation or recrystallization. Roentgenographic or Raman studies at different temperatures could provide a clear-cut answer to this question.

The last recorded endoeffects in the DSC curves of $M(IO_3)_2 \cdot 6H_2O(D_2O)$ ($M^{2+}=Ca^{2+}$ and Sr^{2+}) correspond to the second stage of dehydration of the corresponding monohydrates to the anhydrous salts. However, it is not possible to say which of the existing polymorphous forms is the one obtained under the conditions of the experiment.

Data on the enthalpies of the recorded phase transitions were also obtained from the DSC curves (Table 2). As regards the dehydration process, the values for $\Delta H_{\rm deh}$ were compared with those calculated according to the Hess law in order to obtain information about the state of aggregation of the hydrate water released. For the deuterates, because of the absence of data in the literature, the necessary ΔH_f^0 were calculated from an equation in [11, 12], due use being made of increments from [14]. The comparison showed that in $Ca(IO_3)_2 \cdot 6H_2O$, $Ca(IO_3)_2 \cdot H_2O$ and $Ca(IO_3)_2 \cdot D_2O$ the water released is completely evaporated. In $Sr(IO_3)_2 \cdot 6D_2O$ most of it is in a liquid state, while in the remaining cases there is a mixture of liquid and vapour. For $Ca(IO_3)_2 \cdot 6H_2O$ the value obtained for $\Delta H_{\rm deh}$ (calculated as the sum of the effects of melting and dehydration) is 272.8 kJ·mol^{-1}. However, there is a noteworthy difference in $T_{\rm max}$ i.e. the isotope effect is greater than that observed for other hydrates [13, 14]. Hence, the question arises as to the cause of this effect. In this respect, it was first checked whether the initial pairs of hydrates (ordinary and deuterated) have the same structure or are different polymorphous modifications of a given hydrate, with different hydration temperatures. Their X-ray powder diffraction patterns were taken to examine this, and were found to be roentgenographically identical for each pair of ordinary and deuterated hydrates. Consequently, the difference in $T_{\rm max}$ for the ordinary and deuterated hydrates is not related to a difference in polymorphous modification. However, a slight unidirectional shift of the diffraction reflexes appears, which may be taken as evidence of the expansion of the crystal lattice of the deuterate. The latter undoubtedly influences the thermal stability, i.e. it determines the isotope effect to some degree.

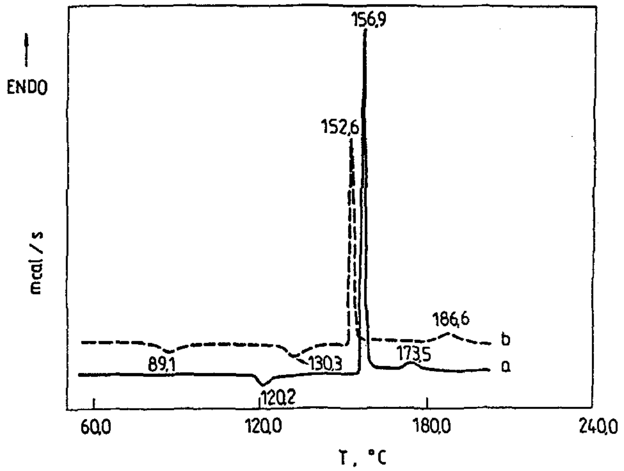

Fig. 4 DSC curves of $Sr(IO_3)_2{\cdot}6H_2O$ (a) and $Sr(IO_3)_2{\cdot}6D_2O$ (b)

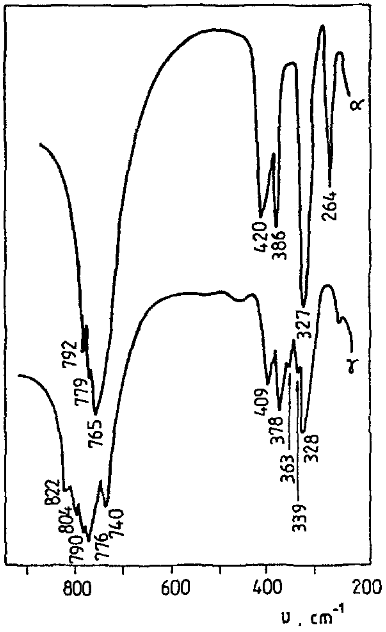

Fig. 5 IR spectra of α- and γ-$Sr(IO_3)_2$

As regards ΔH_{deh} the appreciable isotope effect is explained primarily by the difference in the amount of hydrate water evolved in the dehydration process. Together with the kinetic factors, its value is also determinant for T_{max}.

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Zusammenfassung — Mittels DTA- und DSC-Methoden wurden $Me(IO_3)_2 \cdot 6H_2O$ und $Me(IO_3)_2 \cdot 6D_2O$ (mit $Me^{2+}=Ca^{2+}$ und Sr^{2+}) thermisch und kalorimetrisch untersucht. Es wird ein Überblick über das thermische Verhalten ordentlicher und deuterierter Hydrate gegeben, in dem auch die Unterschiede zwischen beiden diskutiert werden. Die Enthalpien der untersuchten Phasenumwandlungen wurden bestimmt. Aus den Daten für H_{deh} wurde H_f von $Ca(IO_3)_2 \cdot 6H_2O$, $Ca(IO_3)_2H_2O(D_2O)$ und $Sr(IO_3)_2 \cdot 6H_2O(D_2O)$ berechnet und Bemerkungen zum beobachteten Isotopeneffektes gemacht.