

THERMAL AND CALORIMETRIC INVESTIGATIONS OF $\text{Mg}(\text{IO}_3)_2 \cdot n\text{H}_2\text{O}$ ($n = 10, 4$) AND THEIR DEUTERATED ANALOGUES

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Abstract

A DTA and DSC study was made of the thermal dehydration and decomposition of $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$. The data obtained show that the dehydration takes place in one stage. The $\Delta H_{\text{deh}}^\circ$ obtained were used to calculate ΔH_f° , and comparisons were made with the literature data. It was confirmed that the thermal decomposition passes through an intermediate $\text{Mg}_5(\text{IO}_6)_2$, which is unstable and immediately decomposes to MgO . An isotope effect is observed in both DTA and DSC curves. Thermogravimetric data on $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ are also presented.

Keywords: TG, DTA, DSC, dehydration, iodate hydrates of Mg, isotope effect

Introduction

This study forms part of a series of investigations on the thermal and calorimetric properties of compounds of the type $\text{M}(\text{IO}_3)_2 \cdot n\text{D}_2\text{O}$ and their deuterates.

Thermogravimetric data on $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ are presented in [1, 2], while differential thermal analysis was carried out in [3] at a low heating rate of $100 \text{ deg}\cdot\text{h}^{-1}$. However, there appears to be a certain lack of correspondence in the data on the thermal decomposition of anhydrous magnesium iodate. According to [1, 4] it has a one-stage course until MgO is obtained, while according to [3] an intermediate orthoperiodate $\text{Mg}_5(\text{IO}_6)_2$ is obtained in this process, analogously as in the thermal decomposition of the alkaline earth iodates. However, unlike $\text{M}_5(\text{IO}_6)_2$ ($M^{2+} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$), immediately after it is obtained $\text{Mg}_5(\text{IO}_6)_2$ begins to decompose to MgO . The kinetics of the process of thermal decomposition is investigated in [5, 6], with determinations being made both of

the changes in enthalpy of decomposition in the two stages and of their activation energies.

There are no data on the thermal properties of $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ and the deuterated derivatives $\text{Mg}(\text{IO}_3)_2 \cdot n\text{D}_2\text{O}$ ($n = 10, 4$).

The aim of the present study was to specify and supplement the available information on the thermal and calorimetric behaviour of $\text{Mg}(\text{IO}_3)_2 \cdot n\text{H}_2\text{O}$:

a. From the TG and DTA data, to establish which of the two schemes of thermal decomposition of $\text{Mg}(\text{IO}_3)_2$ is more authentic, and whether there is any difference in the behaviour of $\text{Mg}(\text{IO}_3)_2$ samples obtained from $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$.

b. To obtain data on the thermal dehydration of $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$.

c. To record the DSC curves in the region of the thermal dehydration of $\text{Mg}(\text{IO}_3)_2 \cdot n\text{H}_2\text{O}$ and the deuterates, in order to determine the changes in enthalpy of the phase transitions observed and, if possible, to calculate ΔH_f° for the deuterates.

d. To survey the direction and size of the isotope effect.

Experimental

The investigated tetrahydrates (ordinary and deuterated) were synthesized as described in [7]. The decahydrates were obtained by slow crystallization at $2-3^\circ\text{C}$ from saturated solutions of anhydrous magnesium iodate, which were prepared in ordinary and heavy water, respectively. In the preparation of the deuterate, the crystallization was carried out in a desiccator in an inert medium. The crystals of $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ are unstable in air and quickly lose some of their hydrate water. They are most efficiently kept in the mother liquor at $2-3^\circ\text{C}$. The samples were filtered off and dried in a flow of inert gas immediately before the analysis. The hydrates obtained were identified by quantitative analysis, while the tetrahydrates were identified roentgenographically as well. Attempts were made to record the diffractograms of $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{D}_2\text{O}$ (there are no such data in the literature). It was established that, even when the initial sample was prepared in collodion dissolved in amyl acetate, it underwent dehydration.

The thermal and calorimetric investigations ($V = 5 \text{ deg}\cdot\text{min}^{-1}$) were performed under the same conditions and with the same apparatus as in [8]. DSC curves were taken additionally in standard pans. The thermogravimetric data on $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ were obtained on a Thermowaage 'Linseis' instrument at heating rates of 5 and $2 \text{ deg}\cdot\text{min}^{-1}$.

Discussion

TG and DTA curves for $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$ are depicted in Fig. 1, which also shows the thermogravimetric curve of $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ (curve c). Figure 2 presents DSC curves for $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$ in volatile sample pans (2a) and in standard pans (2b). Table 1 outlines the most probable course of thermal dehydration and decomposition of the tetrahydrates on the basis of the DTA and DSC data.

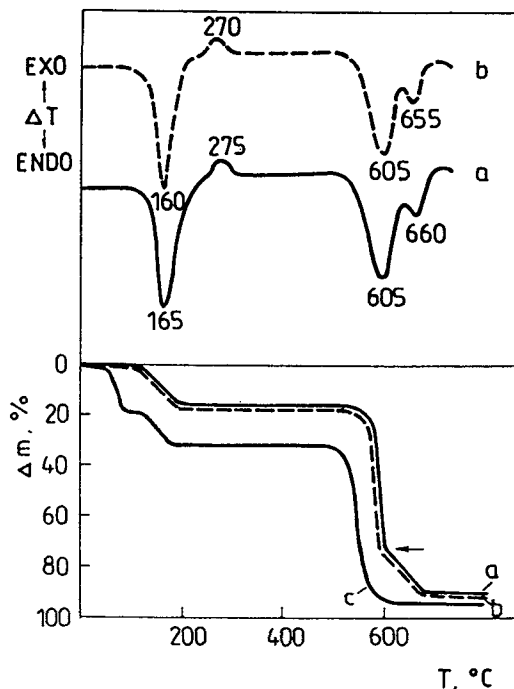


Fig. 1 TG and DTA curves for $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ (a) and $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$ (b); TG curve for $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ (c)

The presented data (Fig. 1 and Table 1) indicate one-stage dehydration of the tetrahydrates (ordinary and deuterated) to anhydrous magnesium iodate, and are analogous to those on $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ in [3]. The recorded exoeffect at 270°C for the ordinary hydrate and at 275°C for the deuterated one is due to crystallization of the amorphous magnesium iodate obtained. Crystalline $\text{Mg}(\text{IO}_3)_2$ is stable up to 520°C, followed by a process of decomposition. The course of the TG curve and the effects in the DTA curve registered in the interval 520–680°C show that the process of $\text{Mg}(\text{IO}_3)_2$ decomposition is a two-stage one, the bend in the TG curve corresponding to the formation of an intermediate. The established decrease in mass of the sample, in conjunction with the results obtained

from the quantitative and X-ray phase analyses of a sample isolated in the temperature region 600–620°C, reveal that this intermediate is $\text{Mg}_5(\text{IO}_6)_2$. Immediately after its formation, this product decomposes to MgO , with the release of iodine and oxygen. Our results confirm the findings in [3].

The thermogravimetric data ($V = 5 \text{ deg}\cdot\text{min}^{-1}$) indicate that $\text{Mg}(\text{IO}_3)_2\cdot 10\text{H}_2\text{O}$ undergoes dehydration in two stages: $10 \rightarrow 4 \rightarrow 0$. At a lower heating rate, $V = 2 \text{ deg}\cdot\text{min}^{-1}$, three stages are recorded in the TG curve: $10 \rightarrow 9 \rightarrow 4 \rightarrow 0$. However, it proved impossible to isolate and confirm the intermediate $\text{Mg}(\text{IO}_3)_2\cdot 9\text{H}_2\text{O}$.

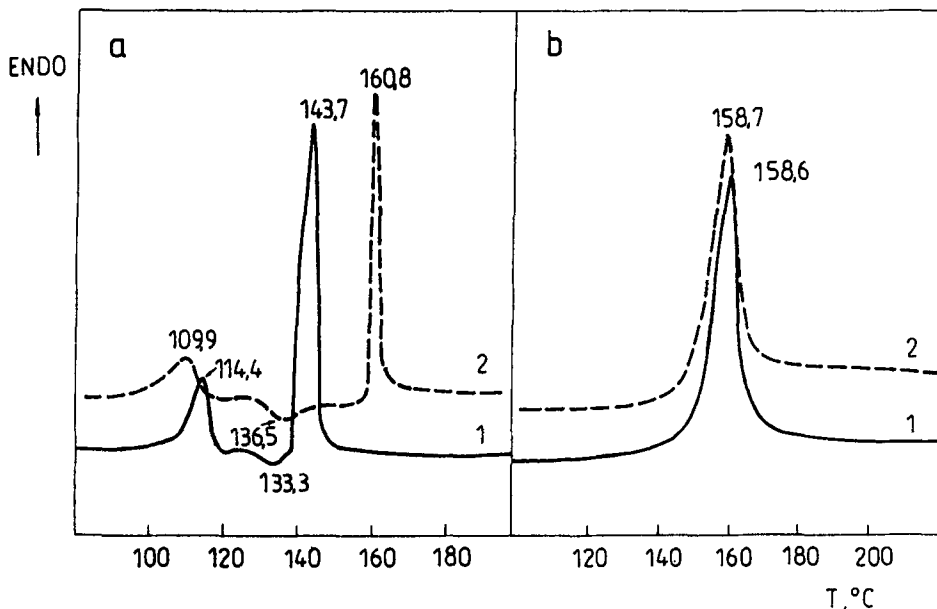


Fig. 2 DSC curve of $\text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$ (curve 1) and $\text{Mg}(\text{IO}_3)_2\cdot 4\text{D}_2\text{O}$ (curve 2) obtained in: a. volatile sample pans; b. standard pans

The DSC curves of $\text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}(\text{D}_2\text{O})$ in Fig. 2 show that their courses differ essentially, depending on the conditions under which they were obtained. For instance, the DSC curve from a standard pan (Fig. 2b) exhibits only one endoeffect, at $T_{\text{onset}} = 153.4^\circ\text{C}$ ($T_{\text{max}} = 158.6^\circ\text{C}$), which corresponds to the dehydration process (the first stage in Table 1), and $\Delta H_{\text{deh}}^\circ = 198.1 \text{ kJ}\cdot\text{mol}^{-1}$. A comparison of this value with that calculated theoretically according to Hess's Law (Table 1, calculated from data for ΔH_f° in [9]) shows that the experimentally determined $\Delta H_{\text{deh}}^\circ$ is about 10% lower. This may be due to the extremely vigorous course of the dehydration process leading to heat losses. Different values for $\Delta H_{\text{deh}}^\circ$ were obtained upon repetition of the measurements, and in many

Table 1 DTA and DSC data for Mg(IO₃)₂·4H₂O and its deuterated analogue

Phase transition	Form	DTA data		DSC data (volatile sample pan)			$\Delta H_{\text{det}}^{\circ}$ -calc. / kJ·mol ⁻¹				
		Δm / %		$T_{\text{ph.t.}}/^{\circ}\text{C}$	T_{onset}	T_{max}		$\Delta H_{\text{ph.t.}}^{\circ}$ / kJ·mol ⁻¹			
		exp.	theor.						$^{\circ}\text{C}$	H ₂ O _(g)	H ₂ O _(l)
Mg(IO ₃) ₂ ·4H ₂ O → Mg(IO ₃) ₂ + 4 H ₂ O	H	16.0	16.2	165	>0	108.4	114.4	53.8	219.1	43.0	
	D	17.3	17.6	160	>0	101.3	109.9	39.9	138.6	143.7	162.0
Mg(IO ₃) ₂ (em) → Mg(IO ₃) ₂ (e)	H	-	-	275	<0	130.6	136.5	-14.6	159.6	160.8	85.6
	D	-	-	270	<0						
Mg(IO ₃) ₂ (e) → 1/5 Mg ₅ (IO ₆) ₂ + 4/5 I ₂ + 9/5 O ₂	H	75.0	74.6	605	>0						
	D	76.0	75.1	605	>0						
Mg ₅ (IO ₆) ₂ → 5MgO + I ₂ + 7/2 O ₂	H	90.0	91.0	660	>0						
	D	92.0	91.2	655	>0						

cases the experiments themselves proved impossible. The DSC curve taken in a volatile sample pan (Fig. 2a) shows a more complicated course. Two endoeffects appear, the second (larger) one being preceded by a small exoeffect. We have observed the same pattern in investigations of the tetrahydrates of cobalt and nickel (in press). The first recorded endoeffect (Fig. 2, Table 1) corresponds to incongruent melting of the hydrate. Evidence of this is the relatively high temperature ($T_{\max} = 114.4^{\circ}\text{C}$) for ordinary melting, as well as the recorded $\Delta H_{\text{ph.t.}}^{\circ}$, which is higher than the calculated $\Delta H_{\text{deh}}^{\circ}$ for liquid water. Consequently, three phases are present in the system at that moment: solid, liquid and gaseous. The appearance of an exoeffect immediately before the complete dehydration and evaporation of the water is further evidence for its taking place in the melt. The overall change in enthalpy (obtained as a sum of the three $\Delta H_{\text{ph.t.}}^{\circ}$), corresponding to $\Delta H_{\text{deh}}^{\circ}$, is $211.9 \text{ kJ}\cdot\text{mol}^{-1}$ which is in good agreement with the theoretically calculated value for water in a gaseous state (Table 1). The error here is $\approx 3\%$.

The course of the DSC curves for $\text{Mg}(\text{IO}_3)_2\cdot 4\text{D}_2\text{O}$ (Fig. 2, Table 1) is analogous to that for the ordinary hydrate, the recorded temperatures being about 5–7 deg lower. A similar dependence is to be observed in the DTA curve. The recording of this temperature difference by both methods confirms the correctness of the results and the direction of the isotope effect. Such an effect has been observed for other iodate hydrates (in the press), though it is higher in value. The established overall change in enthalpy for $\text{Mg}(\text{IO}_3)_2\cdot 4\text{D}_2\text{O}$ is $110.3 \text{ kJ}\cdot\text{mol}^{-1}$ and, when compared with that calculated from data for ΔH_f° [7] (Table 1), shows that a small part of the hydrate water released is evaporated. ΔH_f° for $\text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{IO}_3)_2\cdot 4\text{D}_2\text{O}$ were calculated on the basis of the DSC data for $\Delta H_{\text{deh}}^{\circ}$.

The values obtained are:

	$\Delta H_f^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$ (acc. to DSC)	$\Delta H_f^{\circ} / \text{kJ}\cdot\text{mol}^{-1}$ (lit. data)	Error/ %
$\text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$	2083.2	2092.8 [9]	0.45
$\text{Mg}(\text{IO}_3)_2\cdot 4\text{D}_2\text{O}$	2192.8	2133.6 [7]	2.70

A comparison of the DTA data for $\text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$ with those for the isostructural $\text{Co}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$ and $\beta\text{-Ni}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$ [8] shows that the thermal stability increases in the following sequence: $\text{Co}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O} < \beta\text{-Ni}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O} < \text{Mg}(\text{IO}_3)_2\cdot 4\text{H}_2\text{O}$. This fact is fully reasonable if the stable electronic configuration of Mg^{2+} ($2s^2p^6$) is compared with that of the *d*-elements Co^{2+} ($3s^2p^6d^7$) and

$\text{Ni}^{2+}(3s^2p^6d^8)$. The thermal stability of the anhydrous salts varies in the same sequence.

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Zusammenfassung — Mittels DTA und DSC wurde die thermische Dehydratation und Zersetzung von $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{H}_2\text{O}$ und $\text{Mg}(\text{IO}_3)_2 \cdot 4\text{D}_2\text{O}$ untersucht. Die Resultate ergeben eine Dehydratation in einem Schritt. Anhand der erhaltenen ΔH_{deh} wurden ΔH_f Werte berechnet und mit den entsprechenden Literaturangaben verglichen. Man stellte fest, daß die thermische Zersetzung über das instabile und sich gleich in MgO zersetzende Zwischenprodukt $\text{Mg}_5(\text{IO}_6)_2$ erfolgt. Sowohl bei DTA- als auch bei DSC-Kurven konnte ein Isotopeneffekt beobachtet werden. Auch TG-Daten von $\text{Mg}(\text{IO}_3)_2 \cdot 10\text{H}_2\text{O}$ werden vorgelegt.