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THERMAL AND CALORIMETRIC INVESTIGATIONS OF $M(IO_3)_2 \cdot 2H_2O$ FOR $M^{2+} = Ni^{2+}$ AND Zn^{2+} AND THEIR DEUTERATED ANALOGUES

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Abstract

The thermal dehydration and decomposition of $M(IO_3)_2 \cdot 2H_2O$ ($M^{2+} = Ni^{2+}$ and Zn^{2+}) and their deuterates were investigated by DTA and DSC methods. The data obtained confirm their one-stage dehydration and their decomposition to the respective oxides. $Ni(IO_3)_2 \cdot 2H_2O$ and $Ni(IO_3)_2 \cdot 2D_2O$, were more stable than $Zn(IO_3)_2 \cdot 2H_2O$ and $Zn(IO_3)_2 \cdot 2D_2O$. A considerable isotope effect was observed in relation to T_{deh} for $Ni(IO_3)_2 \cdot 2H_2O$ and $Ni(IO_3)_2 \cdot 2D_2O$, which was explained by the presence of structural changes well differentiated from the dehydration process for the deuterate. The data obtained for both pairs of dihydrates were used to determine ΔH_f^0 for $Ni(IO_3)_2 \cdot 2H_2O$ and $Ni(IO_3)_2 \cdot 2D_2O$.

Keywords: TG, DTA, DSC; dehydration; iodate dihydrates of Ni^{2+} and Zn^{2+}; isotope effect

Introduction

The thermal behaviour of $Ni(IO_3)_2 \cdot 2H_2O$ has previously been investigated in an argon medium at a heating rate of $V = 10$ deg·min^{-1} [1], and in an air medium at $V = 5$ deg·min^{-1} [2]. The derivatograms reveal no essential differences as concerns release of the hydrate water, but the reported temperatures are higher in [1]. Furthermore, the DTA curve in [1] does not reveal the polymorhous transformation of α- to β-$Ni(IO_3)_2$ (observed as an exoeffect in [2]), and it has not been established which of the two polymorphous modifications of the anhydrous salt is that obtained on thermal dehydration.

The reported data on the thermal dehydration and decomposition of $Zn(IO_3)_2 \cdot 2H_2O$ and $Zn(IO_3)_2 \cdot 2D_2O$ involve only the recording of T_{max} of the two phase transitions [3], while in [4, 5] the examination covers only the process of thermal decomposition of $Zn(IO_3)_2$ up to the formation of ZnO.

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No data have been published on DSC studies of the calorimetric behaviour of the ordinary and deuterated hydrates.

The aims of the present study were to compare the data of DTA and DSC investigations of $Ni(IO_3)_2 \cdot 2H_2O(D_2O)$ and $Zn(IO_3)_2 \cdot 2H_2O(D_2O)$ and to determine the changes observed in the enthalpies of the phase transitions.

Experimental

The ordinary and deuterated dihydrates investigated were synthesized by crystallization from solutions of the anhydrous iodates in ordinary water or in heavy water. The necessary anhydrous iodates were obtained by heating the respective hydrates to constant weight at 300°C. (The latter were obtained upon precipitation of 30% solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with iodic acid.) When D_2O was used, the procedures of dissolution and filtration were carried out in special vessels under argon. The solutions obtained were left to crystallize over $CaCl_2$ in a desiccator filled with argon and place in a box for about 2 weaks. The crystals thus obtained were ground in an agate mortar, and the fraction with particle size below 0.063 mm (230 mesh) was selected.

The investigated hydrates and the intermediates (the anhydrous saats) were identified by quantitative and X-ray analyses. The diffractograms of the pairs of ordinary – deuterated hydrates show that they are crystallographically identical.

The thermal investigations were carried out on a Paulik-Paulik-Erdey MOM OD-102 derivatograph at $V = 5$ deg·min^{-1}, with 100 mg of samples. The DSC curves were taken on a DSC-4 Perkin Elmer instrument in the temperature interval 50–300°C, at the same heating rate and $m = 5$ mg (standard crucible).

Experimental and discussion

The TG and DTA curves for $Ni(IO_3)_2 \cdot 2H_2O(D_2O)$ in Fig. 1 and for $Zn(IO_3)_2 \cdot 2H_2O(D_2O)$ in Fig. 2, while the DSC curves are presented in Fig. 3. Table 1 outlines the thermal behaviour of the investigated compounds with the respective temperatures and changes in enthalpies of the phase transitions observed.

The DTA data, in combination with the quantitative and X-ray phase analyses, reveal that for both compounds dehydration takes place in one stage. The anhydrous salt obtained is stable within in temperature interval, after which it undergoes decomposition to the respective oxide, iodine and oxygen, analogously as in [1, 2, 4].

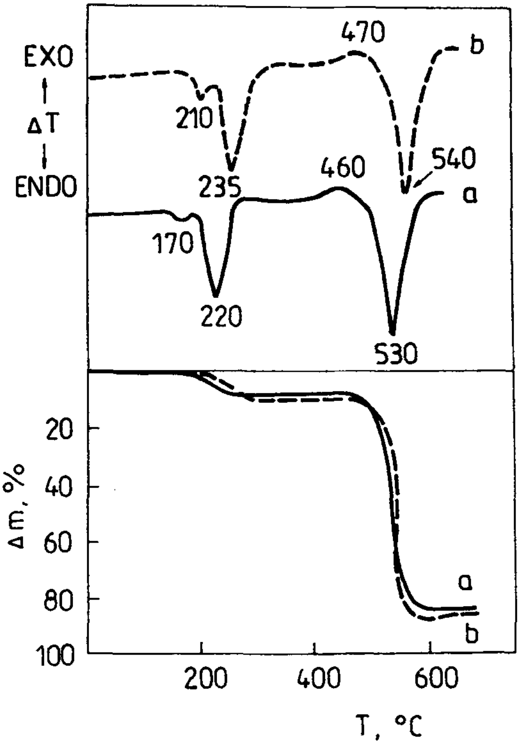

Fig. 1 TG and DTA curves of $Ni(IO_3)_2{\cdot}2H_2O$ (a) and $Ni(IO_3)_2{\cdot}2D_2O$ (b)

Immediately before the dehydration effect, the DTA curves of both $Ni(IO_3)_2{\cdot}2H_2O$ and $Ni(IO_3)_2{\cdot}2D_2O$ show a small endoeffect (which is more marked and stronger for the deuterate) with T_{max} = 170 and 210°C, respectively, with no corresponding change in the mass of the sample in the TG curve. It could be due either to melting or to a polymorphous transformation so far unregistered in the literature. In favour of the latter assumption are the high value of the recorded temperature and the small value measured in the DSC curve: $\Delta H^{o}_{ph.t.} = 6.4$ kJ·mol^{-1} (Table 1). However, the immediate proximity of this effect to the dehydration effect makes it impossible to isolate and analyze a suitable sample.

The first compound obtained in the dehydation of $Ni(IO_3)_2{\cdot}2H_2O(D_2O)$ is the less stable α-$Ni(IO_3)_2$ which, at a temperature close to that of decomposition of the salt, is transformed into β-$Ni(IO_3)_2$. This transition is registered with an exoeffect at T_{max} = 460 and 470°C, respectively for the ordinary and deuterated hydrates. The data we have obtained are in accordance with those in [2], though the temperatures now recorded for the polymorphous transformation and de-

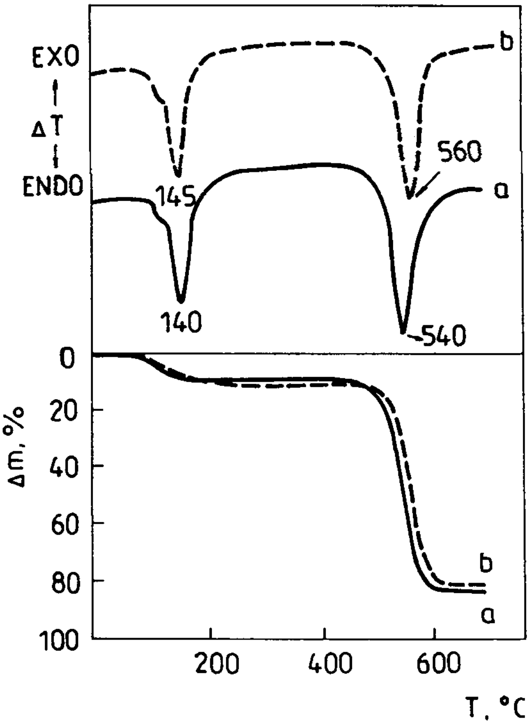

Fig. 2 TG and DTA curves of $Zn(IO_3)_2 \cdot 2H_2O$ (a) and $Zn(IO_3)_2 \cdot 2D_2O$ (b)

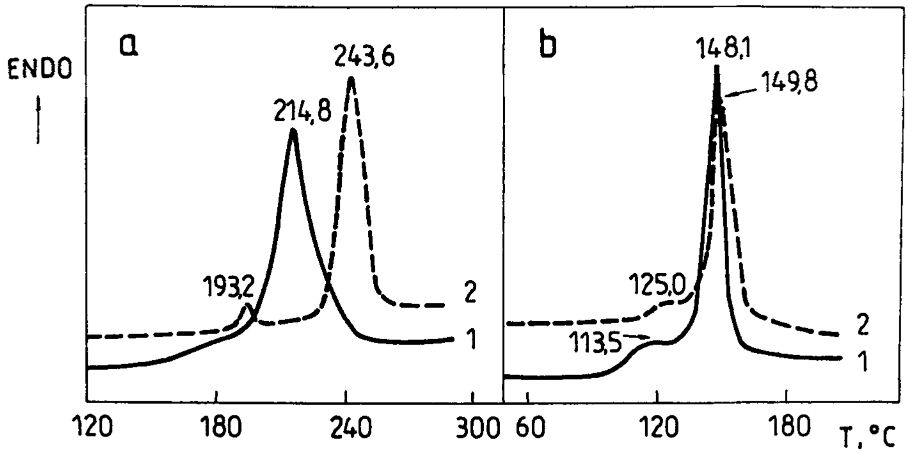

Fig. 3 DSC curves of: (a) $Ni(IO_3)_2 \cdot 2H_2O$ (curve 1) and $Ni(IO_3)_2 \cdot 2D_2O$ (curve 2); (b) $Zn(IO_3)_2 \cdot 2H_2O$ (curve 1) and $Zn(IO_3)_2 \cdot 2D_2O$ (curve 2)

Table 1 DTA and DSC data for $M(IO_3)_2{\cdot}2H_2O$ and $M(IO_3)_2{\cdot}2D_2O$ ($M^{2+} = Ni^{2+}, Zn^{2+}$)

Compound	Phase transition	Form	DTA data				DSC data		
			Δm / %		T_{max}/ °C	$\Delta H^o_{ph.t}$ / kJ·mol^{-1}	$T_{ph.t}$ / °C		$\Delta H^o_{ph.t}$ / kJ·mol^{-1}
			exp.	theor.			T_{onset}	T_{max}	
$Ni(IO_3)_2{\cdot}2H_2O$	$Ni(IO_3)_2{\cdot}2H_2O_{(c)} \rightarrow Ni(IO_3)_2{\cdot}2\,H_2O_{(polymf.?)}$	H	–	–	170	>0	–	–	–
		D	–	–	210	>0	188.3	193.0	6.4
	$Ni(IO_3)_2{\cdot}2H_2O \rightarrow \alpha\text{-}Ni(IO_3)_2 + 2\,H_2O$	H	8.5	8.1	220	>0	199.3	214.8	156.9
		D	9.0	8.9	235	>0	232.8	243.6	153.6
	$\alpha\text{-}Ni(IO_3)_2 \rightarrow \beta\text{-}Ni(IO_3)_2$	H	–	–	460	<0			
		D	–	–	470	<0			
	$\beta\text{-}Ni(IO_3)_2 \rightarrow NiO + I_2 + \frac{5}{2}O_2$	H	82.5	83.2	530	>0			
		D	83.0	83.4	540	>0			
$Zn(IO_3)_2{\cdot}2H_2O$	$Zn(IO_3)_2{\cdot}2H_2O \rightarrow Zn(IO_3)_2 + 2\,H_2O$	H	8.0	8.0	140	>0	–	113.5	
							140.3	148.1	131.9
		D	9.0	8.9	145	>0	–	125.0	
							142.0	149.8	115.1
	$Zn(IO_3)_2 \rightarrow ZnO + I_2 + \frac{5}{2}O_2$	H	81.5	82.1	540	>0			
		D	81.5	82.2	560	>0			

composition are lower than those indicated there. The two polymorphous modifications, α- and β-$Ni(IO_3)_2$, were characterized on the basis of their X-ray powder patterns which coincide with those published in the literature [6].

Comparison of the DTA data for the ordinary deuterated nickel iodate dihydrates reveals a difference in the temperatures of the phase transitions in favour of the deuterate. The difference is larger for the dehydration temperatures (ΔT_{max} = 15 deg), while for the remaining phase transitions it is ΔT_{max} = 10 deg.

The derivatogram of $Zn(IO_3)_2{\cdot}2H_2O$ (Fig. 2) shows some analogy with that of $Ni(IO_3)_2{\cdot}2H_2O$. An area of stability of $Zn(IO_3)_2$ is established in the temperature interval 200 to 450°C. These are also the conditions for obtaining the anhydrous product. The isotope effect for the pair $Zn(IO_3)_2{\cdot}2H_2O(D_2O)$ in relation to T_{deh} is 5 deg in favour of the deuterate. In this case there is again a difference in the decomposition temperatures of the anhydrous salts obtained from the ordinary and deuterated hydrates. Such an effect has been observed in an earlier study [3].

As regards thermal stability, the presented derivatograms show that $Ni(IO_3)_2{\cdot}2H_2O$ is more stable than $Zn(IO_3)_2{\cdot}2H_2O$, while for the anhydrous salts the difference is inessential. The different thermal stabilities of the examined iodate hydrates could be explained by the difference in their structures, but such a comparison is impossible because of the absence of such data for $Zn(IO_3)_2{\cdot}2H_2O$.

The DSC curves (Fig. 3) taken in the region of thermal dehydration for both pairs of hydrates show full analogy with the DTA curves, i.e. there is a strong endoeffect corresponding to the single-stage dehydration of the initial compound. However, in the cases of $Zn(IO_3)_2{\cdot}2H_2O$ and $Zn(IO_3)_2{\cdot}2D_2O$ (Fig. 3), immediately before it there is a not very distinct endoeffect, corresponding to which the DTA curve exhibits a slight expansion at the beginning of the dehydration effect.

The DSC curve of $Ni(IO_3)_2{\cdot}2D_2O$ (Fig. 3a, curve 2) also displays a small endoeffect prior to that of dehydration, but it is a distinct one. In this case it corresponds to the analogous peak, already observed by us in the derivatogram of the compound (Fig. 1), which corresponds to the polymorphous transformation.

The large difference, observed by means of DTA, in the T_{deh} for $Ni(IO_3)_2{\cdot}2H_2O(D_2O)$ is confirmed by the DSC data (ΔT_{max} = 28.8 deg), which shows that this is not a case of experimental error. It is rather possible that this difference is due to structural transformations, which are particularly marked in the deuterate and connected just with the observed effect (Fig. 1 and Fig. 3a) prior to the dehydration. These assumptions could be confirmed or rejected after high-temperature X-ray or Raman investigations have been carried out.

In the $Zn(IO_3)_2\cdot 2H_2O$–$Zn(IO_3)_2\cdot 2D_2O$ pair, the DSC isotope effect observed is 1.8 deg again in favour of the deuterate.

Calculations of ΔH_f^0 for $Ni(IO_3)_2\cdot 2H_2O$ and $Ni(IO_3)_2\cdot 2D_2O$ were made on the basis of the data obtained for ΔH_{deh}^0 (Table 1). There are no thermodynamic data for the latter. The following values were obtained:

$$\Delta H_f^0 = 1128.9\ \mathrm{kJ\cdot mol^{-1}}\ \text{for}\ Ni(IO_3)_2\cdot 2H_2O\ \text{and}$$

$$\Delta H_f^0 = 1140.6\ \mathrm{kJ\cdot mol^{-1}}\ \text{for}\ Ni(IO_3)_2\cdot 2D_2O.$$

The determined value of ΔH_f^0 for $Ni(IO_3)_2\cdot 2H_2O$ show a fairly good coincidence (error 1.7%) with the literature value of 1109.4 $\mathrm{kJ\cdot mol^{-1}}$. Such calculations cannot be made for the pair $Zn(IO_3)_2\cdot 2H_2O$ – $Zn(IO_3)_2\cdot 2D_2O$ because of the non-availability of the necessary value of ΔH_f^0 for $Zn(IO_3)_2$.

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Zusammenfassung — Mittels DTA- und DSC-Methoden wurde die thermische Dehydratation und Zersetzung von $M(IO_3)_2\cdot 2H_2O$ ($M^{2+} = Ni^{2+}$ und Zn^{2+}) und deren Deuteraten untersucht. Die erhaltenen Ergebnisse bestätigen die einstufige Dehydratation und die Zersetzung in die entsprechenden Oxide. $Ni(IO_3)_2\cdot 2H_2O$ und $Ni(IO_3)_2\cdot 2D_2O$ waren stabiler als $Zn(IO_3)_2\cdot 2H_2O$ und $Zn(IO_3)_2\cdot 2D_2O$. Für T_{deh} wurde ein beträchtlicher Isotopeneffekt für $Ni(IO_3)_2\cdot 2H_2O$ und $Ni(IO_3)_2\cdot 2D_2O$ beobachtet, der mit der Gegenwart von Strukturabweichungen erklärt wird, die sehr gut vom Dehydratationsprozeß des Deuterates unterschieden werden können. Die für beide Paare der Dihydrate erhaltenen Angaben wurden zur Bestimmung von ΔH_f^0 von $Ni(IO_3)_2\cdot 2H_2O$ und $Ni(IO_3)_2\cdot 2D_2O$ verwendet.