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Synthesis, thermal and calorimetric studies of $NiH_3IO_6 \cdot 6H_2O$

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Abstract

A new nickel orthoperiodate hydrate has been synthesized, whose composition is $NiH_3IO_6 \cdot 6H_2O$. It has been identified by quantitative analysis, DTA, TG, DSC and by IR spectroscopy. Based upon data from the DTA and DSC curves a thermal decomposition scheme has been proposed. The formal kinetic parameters have been determined.

Keywords: DSC; DTA; Kinetic properties; Nickel orthoperiodate hydrate; Solubility measurements; Thermodynamic properties

1. Introduction

Interest in the study of orthoperiodates has been prompted by the valuable properties they possess: electrical and corrosion inhibition properties, and practical analysis, etc. [1]. The only nickel orthoperiodate known in the literature is $Ni_2HIO_6 \cdot 3H_2O$ [2]. The authors have prepared $NiH_3IO_6 \cdot 6H_2O$ and determined its thermodynamic parameters by solubility measurements at different temperatures.

2. Experimental

Nickel orthoperiodate hexahydrate ($NiH_3IO_6 \cdot 6H_2O$) was first obtained by adding 2.6 g $NiCO_3$ stepwise to a solution containing 4.9 g H_5IO_6 in 100 cm^3 of water. The suspension was stirred for 2 h at room temperature. Green, well shaped crystals

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separated from the filtrate after 48 h. The compound was identified by quantitative analysis: Ni^{2+} complexometrically [3], iodine iodometrically [4]. The IR spectra were taken in the region 4000–2500 cm^{-1} in hexachloro-1,3-butadiene suspension, in the region 1400–200 cm^{-1} in Nujol suspension, and in the region 1000–200 cm^{-1} in KBr tablets on a PU 9700 Philips apparatus. The DTA curves were measured on a MOM OD-102 Paulik-Paulik-Erdey derivatograph with a sample mass of 100 mg and at a heating rate of 10° min^{-1} to 600°C. The DSC curves were obtained using a DSC-4 Perkin-Elmer apparatus in the temperature region 20–420°C, with a sample mass of 2 mg and at a heating rate of 10° min^{-1}. The X-ray powder diffraction patterns were taken on a TUR-M-62 apparatus with FeKα radiation.

3. Results and discussion

Quantitative analysis of the newly synthesized compound coincided most satisfactorily with that calculated for $NiH_3IO_6 \cdot 6H_2O$:

	Ni/%	I/%	H_2O/%
Computed	14.95	32.32	52.73
Experimental	14.66	31.99	53.35

The compound was also identified by means of its IR spectrum (Fig. 1(right)). The characteristic absorption bands–deformation vibration of the I-OH group at 1100 and 1190 cm^{-1}–can be observed in these IR spectra, as proof of the acidic character of the compound (Fig. 1(right)). The presence of $H_3IO_6^{2-}$ can be proven by the observed absorption bands at 620 and 760 cm^{-1}, due to stretching vibrations of I-O, whereas the same absorption band of IO_4^- lies at higher frequencies. The presence of two types of water within the structure of the compound–constitutional and crystallization water–is most satisfactorily exhibited in the stretch vibration region of water molecules at 3400, 3320, 3100, 3000 cm^{-1} (Fig. 1 (left)). Observed in the spectrum is also absorption at 540 cm^{-1}, which according to [1] is due to deformation vibration of O-I-O.

The phase transitions observed in the DTA curves gave some information on the chemical nature of the thermal decomposition, as outlined in Table 1.

Table 1
DTA, TG and DSC data for $NiH_3IO_6 \cdot 6H_2O$

Phase transition	DTA, TG			DSC	
	T/°C	Δm_{theor}/%	Δm_{exp}/%	T/°C	$\Delta H_{ph.tr}$/kJ mol^{-1}
$2NiH_3IO_6 \cdot 6H_2O \rightarrow$ $Ni(IO_3)_2 \cdot 2H_2O + 13H_2O + NiO + O_2$	25–300	33.9	34.4	83.1	388.9
$Ni(IO_3)_2 \cdot 2H_2O_{(am)} \rightarrow$ β-$Ni(IO_3)_{2(c)} + 2H_2O$	300–480	11.2	10.0	317	−4.2
β-$Ni(IO_3)_{2(c)} \rightarrow NiO + I_2 + 2.5O_2$	480–560	83.2	82.5	–	–

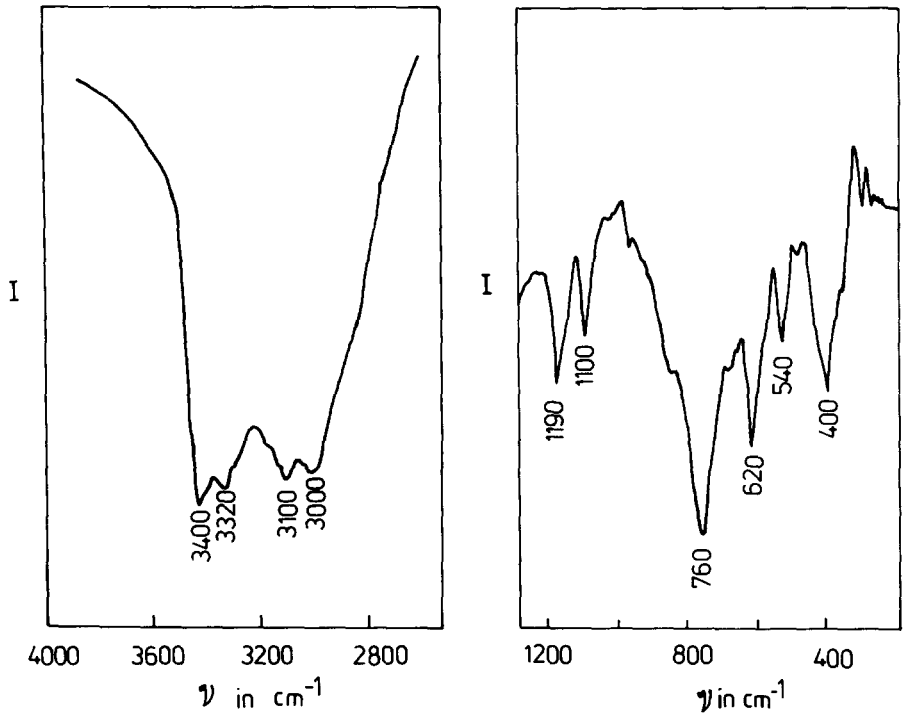

Fig. 1. IR spectra of $NiH_3IO_6 \cdot 6H_2O$ (right) in suspension from Nujol in the region 1400–200 cm^{-1} and (left) in suspension of hexachloro-1,3-butadiene in the region 4000–250 cm^{-1}.

It is of interest to see if it is possible to isolate intermediate periodates with the correct composition. However this was not possible, since it was not registered in the TG curve as a region of constant weight (Fig. 2). Thus the first phase of the dehydration process corresponds to the endothermic peak with $T_{max} = 100°C$ observed within the DTA curve, and was related to a gradual emission of water of crystallization until $Ni(IO_3)_2 \cdot 2H_2O$ was obtained and to a partial periodate decomposition to NiO. Distinction between the two processes by DTA is impossible because they combine into a common endothermal peak. The dehydration and decomposition scheme corresponds to the observed variation of sample mass, 34.4%, which coincides most satisfactorily with the calculated 33.9%. Despite the greater resolution of the DSC method, the curve does not separate dehydration and decomposition (Fig. 3). $\Delta H_{ph.tr.}$ of the total is 388.9 kJ mol^{-1}, due to the considerable energy changes accompanying the processes. The isolated intermediate phase at $T_{max} = 180°C$ is green and amorphous, by X-ray diffraction, which is to be expected since similar cases are reported in the literature [5]. The data from the IR spectra of this intermediate phase (Fig. 4a) show absorption bands at 800 and 757 cm^{-1}, which according to [6] prove that $Ni(IO_3)_2 \cdot 2H_2O$ has been obtained and those at 560, 460, 430 cm^{-1}, which belong to NiO [7]. Of interest is the fact that the intermediate phase shows a pronounced crystallinity at 400°C (Fig. 5) and is yellow. The read interplanar distances coincide

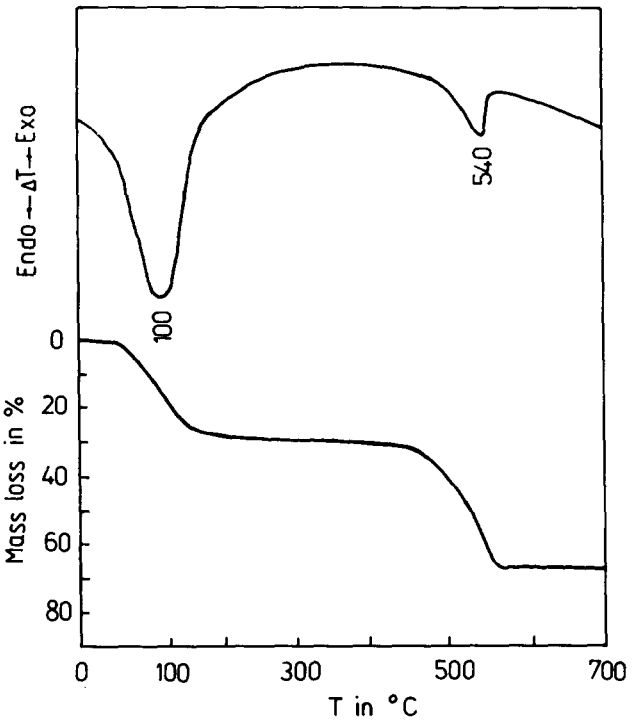

Fig. 2. DTA and TG curves of $NiH_3IO_6 \cdot 6H_2O$.

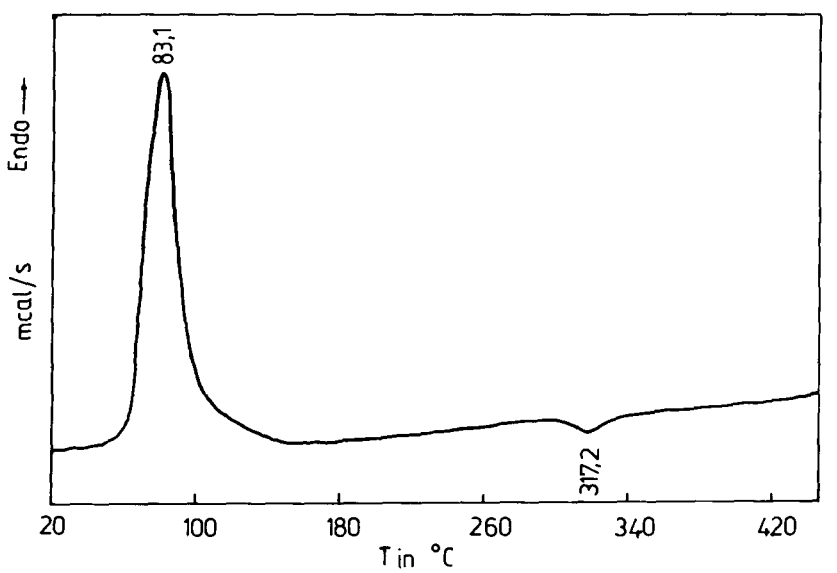

Fig. 3. DSC curves of $NiH_3IO_6 \cdot 6H_2O$.

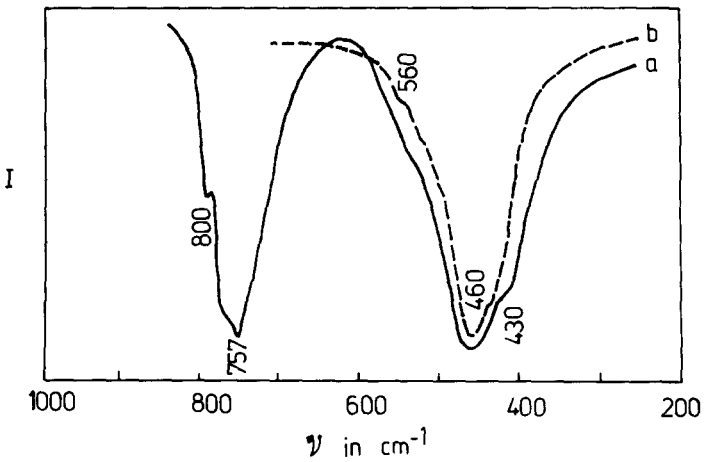

Fig. 4. IR spectra of sample isolated at 180°C (a) and 580°C (b) in KBr tablets, in the region 1000–200 cm^{-1}.

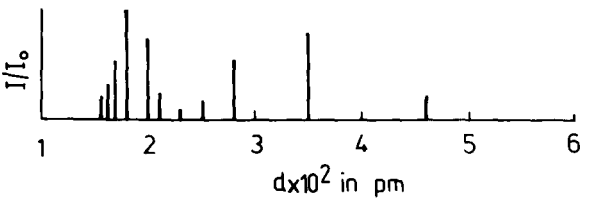

Fig. 5. Interplanar distance of sample isolated at 400°C.

most satisfactorily with the data in the literature for β-$Ni(IO_3)_2$ [8]. Such process of crystallization and obtaining of stable β-$Ni(IO_3)_2$ can be observed in the DSC curve as well, where the exothermic peak with $\Delta H_{ph.tr.} = -4.2\,kJ\,mol^{-1}$ is relatively low. The endothermic peak with $T_{max} = 540°C$, observed within the DTA curve, corresponds to decomposition of β-$Ni(IO_3)_2$ to NiO, I_2 and O_2. The change in the sample mass during such transition completely corresponds to the theoretical calculations. The final product is NiO, proven by the IR spectra (Fig. 4b).

The formal kinetic parameters of the two principal phase transitions were determined with a view to obtain information on the kinetics of thermal dehydration and decomposition, using a program [9, 10].

For first phase transition (60–140°C):
$NiH_3IO_6 \cdot 6H_2O \rightarrow Ni(IO_3)_2 \cdot 2H_2O$
$E^* = 112\,kJ\,mol^{-1}$, correlation coefficient 0.9976 and rate equation $F = (1 - \alpha)$.

For second phase transition (500–560°C):
$Ni(IO_3)_2 \cdot 2H_2O \rightarrow NiO$
$E^* = 333\,kJ\,mol^{-1}$, correlation coefficient 0.9958 and rate equation $F = \alpha(1 - \alpha)$.

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