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The thermal and calorimetric studies of $Ni(H_4IO_6)_2{\cdot}4H_2O$

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Abstract

A new nickel orthoperiodate hydrate has been synthesized, whose composition is $Ni(H_4IO_6)_2{\cdot}4H_2O$. It has been identified by quantitative analysis, DTA, TG and DSC. Based on data from the DTA and DSC curves, a thermal decomposition scheme has been proposed. The formal kinetic parameters have been determined. © 1997 Elsevier Science B.V.

Keywords: Nickel orthoperiodate hydrate; $Ni(H_4IO_6)_2{\cdot}4H_2O$; Thermal decomposition

1. Introduction

Nickel orthoperiodates is presented in the literature either as $Ni_2HIO_6{\cdot}3H_2O$ [1] or $NiH_3IO_6{\cdot}6H_2O$ [2]. In Ref. [1] the authors determined the thermodynamic parameters of the compound from the temperature dependence of its solubility at different temperatures. In Ref. [2] the synthesis $NiH_3IO_6{\cdot}6H_2O$ is described and its thermal properties are measured. The crystal structure of $NiH_3IO_6{\cdot}6H_2O$ has been determined in Ref. [3] and vibration spectra characterized. It is of interest to synthesize the acidic orthoperiodates with a view to determine changes in their properties with structure.

The purpose of this study was to synthesize the primary orthoperiodate of nickel and study its thermal characteristics.

2. Experimental

$Ni(H_4IO_6)_2{\cdot}4H_2O$ was obtained by adding $x Ni(OH)_2{\cdot}y NiCO_3{\cdot}z H_2O$ to a solution of H_5IO_6 in the molar ratio 1 : 2. The suspension was stirred for 2 h at room temperature. After that it was filtered and then left to crystallize. The compound was identified as a nickel salt by determining it complexometrically [4], as containing iodine iodometrically [5], and water using Fisher's method.

The IR spectrum was measured in the region 4000–200 cm^{-1} using CsI plates and Philips spectrophotometer, model PU 9700. DTA curves were measured by a Paulik–Paulik–Erdey derivatograph MOM OD-102 with a simple mass of 137 to 200 mg at a heating rate of 10 and 5 K min^{-1}, respectively, at 600°C. DSC traces were measured by a Perkin–Elmer calorimeter, model DSC-4 in the temperature region 20–420°C with a sample mass of 2 mg and at a heating rate of 5 K min^{-1}. The thermal and calorimetric parameters were measured with the help of samples of different

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synthesis. They have shown identity, as the difference of the temperatures during transition in DTA was 1–2°C and in DSC - 0.1°C.

3. Results and discussion

Quantitative analysis data of the newly synthesized compound coincided with that calculated for $Ni(H_4IO_6)_2{\cdot}4H_2O$:

	Ni/%	I/%	H_2O/%
Computed	10.03	43.44	12.3
Experimental	10.14	43.68	12.3

but this composition also corresponded with the methaperiodate – $Ni(IO_4)_2{\cdot}8H_2O$. To resolve them it was necessary, with the help of IR spectroscopy, to determine the structural groups present at 745 cm^{-1}(m), 760 cm^{-1}(sh) and 640 cm^{-1}(m). Absorption bonds showed the presence of H_4IO_6-groups. Spectroscopic assignment of this group is an unsymmetrical stretching vibration (v_3) of I–O and I=O bonds giving absorption bands at 745 cm^{-1}(m), 760 cm^{-1}(sh) and 640 cm^{-1}(m) [6–8], respectively.

Also, the presence of H_4IO_6-ion revealed the availability of the additional stretching vibration δ_{I-OH} at 1020 cm^{-1}(w) at lower frequencies as compared with that of $NiH_3IO_6{\cdot}6H_2O$ [7,8]. In the spectrum, the other absorption bands can also be observed. The band at 435 cm^{-1}, according to Ref. [9], is due to the Ni–O band, and the absorption bands at 340 and 300 cm^{-1} – to the unsymmetrical deformation vibration v_4 of the periodate group.

The presence of the water of crystallization is proven by wide absorption band at 3400 cm^{-1}, due to the stretching vibration of OH-group, and by an absorption band at 1630 cm^{-1} due to a deformation vibration of water (δ_{H_2O}). This data proved that the salt was primarily the orthoperiodate hydrate, i.e., $Ni(H_4IO_6)_2{\cdot}4H_2O$.

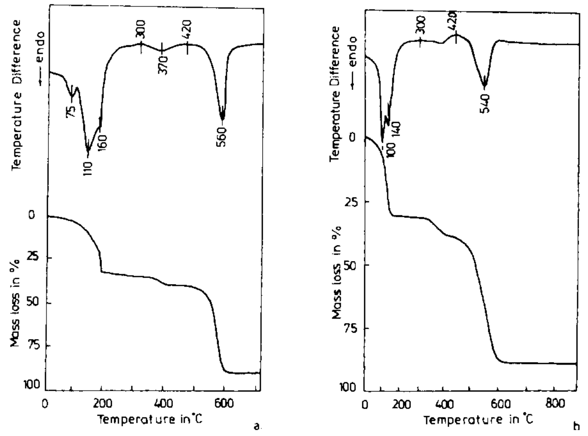

Fig. 1. DTA and TG curves of $Ni(H_4IO_6)_2{\cdot}4H_2O$ at heating rates (a) of 10 K min^{-1} and (b) 5 K min^{-1}.

The thermal and calorimetric parameters of the newly synthesized compound was measured by DTA (see Fig. 1(a)) at a heating rate of 10 K min^{-1}. A large endothermic process was observed at 110°C with a distinct shoulder at 160°C. At the temperature of this shoulder the TG curve showed that the sample mass had decreased by 30.7% that corresponded to loss of H_2O (calculated 30.1%). An inflection occurred at 160°C. Both TG and DSC early SCS showed that the dehydration process, in this region, occurred in two steps. From the measured mass change observed in the initial compound, the processes which occur up to 200°C are:

$$Ni(H_4IO_6)_2 \cdot 4H_2O \rightarrow Ni(IO_4)_2 + 8H_2O$$

$$Ni(IO_4)_2 \rightarrow \alpha\text{-}Ni(IO_3)_2 + O_2$$

The shoulder in the DTA curve at 110°C, as well as the inflexion point in the TG curve at 160°C, corresponds with the second reaction, i.e., the decomposition of methaperiodate to the form of nickel iodate α-$Ni(IO_3)_2$. Corroboration of this, came from production of $Ni(IO_4)_2$, in the derivatogram obtained from $Ni(H_4IO_6)_2{\cdot}4H_2O$ at a heating rate of 5 K min^{-1} in that a split peak with T_{max} at 100 and 140°C (Fig. 1(b)) was observed. The presence of the low exothermic process with $T_{max} = 300°C$ is due to the crystallization of the primary amorphous $Ni(IO_3)_2$ to α-$Ni(IO_3)_2$. The latter was identified by analyzing the sample taken from the derivatogram at 350°C. Chemical analysis, X-Ray analysis, IR spectrum and green colour showed that the intermediate product was α-$Ni(IO_3)_2$, according to Refs. [10,11]. A broad exothermic process with $T_{max} = 420°C$ is due to the decomposition of α-$Ni(IO_3)_2$ to β-$Ni(IO_3)_2$ [10,11]. The small decrease in the sample mass during this transition shows that the polymorphic transformation has been accompanied with little decomposition of $Ni(IO_3)_2$.

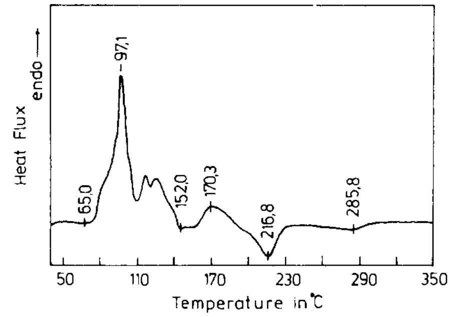

Fig. 2. DSC curves of $Ni(H_4IO_6)_2{\cdot}4H_2O$.

Two small exothermic processes were also clearly shown in the derivatogram of $Ni(H_4IO_6)_2{\cdot}4H_2O$ measured at a heating rate of 5 K min^{-1} (Fig. 1(b)). Immediately after the polymorphic transition of α-$Ni(IO_3)_2$ to β-$Ni(IO_3)_2$, an endothermic transition was observed at $T_{max} = 540°C$ which corresponds to decomposition of $Ni(IO_3)_2$ into NiO,I_2 and O_2. The data in the derivatogram is in agreement with those obtained from the thermal decomposition of $Ni(IO_3)_2{\cdot}2H_2O$ [11]. The decrease in sample mass during the whole process of thermal dehydration and decomposition was 87.6% which was then compared with that calculated 87.3%.

The thermal properties of $Ni(H_4IO_6)_2{\cdot}4H_2O$, was also measured by DSC at a heating rate of 5 K min^{-1} (Fig. 2). An endothermic process of complex character was observed in the range 65–192°C, corresponding to the dehydration process. This picture is more complicated than that observed in the DTA curve because of the greater resolving ability of the scanning calorimetry, and lower sample mass was required to resolve the processes clearly. Initially, it separated the water of crystallization and then the constitutional water. The latter dehydration process ended with the production of $Ni(IO_4)_2$, produced a peak with T_{max} at 170.3°C. Then it was further proven that the dehydration occurred through $Ni(IO_4)_2$. The total dehydration enthalpy was $\Delta H_{ph.tr.} = 441.30$ kJ mol^{-1}. The basic part of this value is due to ΔH_{vap} of water of crystallization and loss of constitutional water, namely: $38.63 \times 8 = 309.04$ kJ mol^{-1} ($\Delta H^0_{vap} = 38.63$ kJ mol^{-1} at $T_{max} = 130°C$) [12]. The difference between them is 441.30 kJ mol^{-1} which is due to the energy connected with phase transition of the final compound to $Ni(IO_4)_2$. The next exothermic process with $T_{min} = 216.8°C$ is due to the decomposition of $Ni(IO_4)_2$, and it leads to obtain more stable thermodynamic $Ni(IO_3)_2$. It corresponded to a $\Delta H_{ph.tr.} = -44.00$ kJ mol^{-1}. The second small exothermic effect with $T_{max} = 285.85°C$ corresponds to the polymorphic transformation of α-$Ni(IO_3)_2$ to β-$Ni(IO_3)_2$ with $\Delta H_{ph.tr.} = -14.28$ kJ mol^{-1}. This value has not been measured before permitting the phase transformation of $Ni(IO_3)_2$ to be characterized thermodynamically, which information was needed to study its electrical properties.

From the kinetic analysis of DSC, the parameters of the thermal decomposition of $Ni(H_4IO_6)_2{\cdot}4H_2O$ were calculated using the DSC-4 Standard Program Manual (Perkin–Elmer Pat. No.: 0993-9864). The program data are findings of two calorimetric studies at a heating rate of 5 K min^{-1} and sample mass 2 mg. The particle sizes of the different samples were the same and corresponded to the intermediate fraction of the mesh analysis.

Accordingly, following data were obtained:

Temperature range/°C	E^*/kJ mol^{-1}	lnA/s^{-1}	Corr. coeff. R
80–140	150.53 ± 3.25	45.54 ± 0.98	0.87 ± 0.10
113–139	109.68 ± 2.37	28.89 ± 0.62	0.97 ± 0.02
160–183	183.14 ± 3.95	45.82 ± 0.99	1.09 ± 0.02
198–225	254.67 ± 5.50	59.46 ± 1.28	0.95 ± 0.02
255–302	167.92 ± 3.62	31.84 ± 0.68	0.99 ± 0.02

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