

NON-EQUIVALENT WATER MOLECULES IN $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ AND IN $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$ IN THE THERMOGRAVIMETRIC INVESTIGATIONS

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The thermal decomposition of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$ were studied by thermogravimetric analysis (TG) and simultaneous differential thermal analysis (SDTA) at a constant heating rate. The gaseous products of the decomposition were on-line identified by a quadrupole mass spectrometer (QMS). In both cases the process of decomposition starts at ca. 410 K and is connected with removal of water molecules in a stepwise way; at the beginning the first water molecule is lost, then the second and at higher temperature the third one. The rest of the water molecules are lost in the temperature region of ClO_4^- decomposition.

The energy of activation of the process was calculated in both cases.

Keywords: DTA, hexaaquanickel(II) perchlorates, QMS, TG, thermal decomposition

Introduction

$[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ (hereafter abbreviated to NiHP) has three solid phases in the temperature range 77–320 K: a low-temperature phase (Phase III), an intermediate-temperature phase (Phase II) and a high-temperature phase (Phase I). Evidence for the existence of these phases was obtained through specific heat measurements carried out using adiabatic calorimetry [1] and differential scanning calorimetry (DSC) methods for NiHP and $[\text{Ni}(\text{D}_2\text{O})_6](\text{ClO}_4)_2$ (NiDP) [2]. The calorimetric experiments showed that Phase III–Phase II phase transition appears in NiDP at a temperature higher by about 3 K than in NiHP, namely at 314.6 K (NiDP) vs. 311.3 K (NiHP). Phase II–Phase I transition appears at approximately the same temperature, i.e., 362.4 K (NiDP) and 362.8 K (NiHP), in the DSC method [2]. Both Phase III–Phase II and the Phase II–Phase I phase transitions have a dynamical [3–5] and structural character [6, 7]. A small change of structure is exhibited at the III–II phase transition [7], i.e., a symmetry reducing the deformation of the water-ligand octahedron [6], and a greater structural change is exhibited at the II–I phase transition [7]. Low-frequency vibrations and molecular motions of H_2O molecules in NiHP and of D_2O in NiDP were investigated by IINS method [8] and by FTIR one [9]. Evidence of 3 types of water molecules was presented using those methods [8, 9] in Phase III showing three groups of frequencies of molecular motions for water molecules in

both compounds. The effect of non equivalence of water molecules in octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{D}_2\text{O})_6]^{2+}$ is probably connected with hydrogen bonds' net existing in the sample till the temperature of the phase transition III–II [9] (ca. 312 K). Some articles [10, 11] show that such nonequivalent water molecules can exist in other perchlorate hexahydrates, e.g., in CoHP or in MnHP. It seems to us that one can easily confirm the existence of water molecules bounded on different way in NiHP and NiDP when investigating the process of dehydration in those substances by the thermogravimetric method. Dehydration takes place in the temperature region above 365 K, i.e. above the phase transition II–I. Therefore, such a measurement has been undertaken. It was the main aim of the work. We wanted also to show that the phase transitions: III–II, II–I are reversible (using DSC method and comparing directly the results for those two compounds on one picture) and to analyze the process of decomposition using TG and QMS method on the possible way. Using TG method we wanted to estimate energy of activation for dehydration. It was also an aim of the work.

Experimental

Thermogravimetric measurements were carried out on a derivatograph, type TGA/SDTA 851^e (Mettler Toledo), in an argon atmosphere (flow rate: $80 \text{ cm}^3 \text{ min}^{-1}$) at a heating rate $\beta=10 \text{ K min}^{-1}$, starting

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Table 1 Parameters of NiHP – thermal analysis; sample mass=40.3 mg

Stage	Temperature range/K	Mass loss/%	Mass after decomposition		Products of the decomposition
I	300–440	4.9	38.3 mg	95.1%	$[\text{Ni}(\text{H}_2\text{O})_5](\text{ClO}_4)_2$
II	440–490	4.9	36.3 mg	90.2%	$[\text{Ni}(\text{H}_2\text{O})_4](\text{ClO}_4)_2$
III	490–520	4.9	34.4 mg	85.3%	$[\text{Ni}(\text{H}_2\text{O})_3](\text{ClO}_4)_2$
IV	520–700	64.3	8.5 mg	21.0%	NiO

Table 2 Parameters of NiDP – thermal analysis; sample mass=33.5 mg

Stage	Temperature range/K	Mass loss/%	Mass after decomposition		Products of the decomposition
I	300–440	5.3	31.7 mg	94.7%	$[\text{Ni}(\text{D}_2\text{O})_5](\text{ClO}_4)_2$
II	440–490	5.3	20.0 mg	89.4%	$[\text{Ni}(\text{D}_2\text{O})_4](\text{ClO}_4)_2$
III	490–520	5.3	28.2 mg	84.1%	$[\text{Ni}(\text{D}_2\text{O})_3](\text{ClO}_4)_2$
IV	520–700	63	7.1 mg	21.1%	NiO

from room temperature up to 700 K. NiHP and NiDP were prepared on the way described carefully in [2]. The number of hydrogen atoms (resulting mainly from using 94% D_2O) in the obtained compound was estimated by NMR method to be not greater than 6%. Samples of masses given in Tables 1 and 2 were placed in 150 μL platinum crucibles.

A simultaneous differential thermal analysis curve (SDTA) and a DSC curve were also recorded to confirm evidence of the above mentioned phase transitions and also to follow the process of decomposition. Additionally, on-line quadrupole mass spectrometry (QMS), via a Balzer GSD 300T apparatus, was used to allow easier interpretation of all results. Temperature was measured by a Pt–Pt/Rh thermocouple with an accuracy of ± 0.5 K.

Results and discussion

Thermal methods

Figure 1 presents TG, DTG, SDTA and QMS curves for NiHP, and Fig. 2 presents the same results for NiDP. At the very beginning of both experimental runs (for NiHP and NiDP) we can see the mass increasing, distinctly shown on DTG curves (Figs 3 and 4). We should state that the effect could be treated as an artifact. Probably it is connected with the influence of a magnetic field, emanating from an active heating system surrounding the sample, on the sample's paramagnetic ions. Our results distinguish 4 stages of decomposition in NiHP as well as in NiDP. The results are presented in Tables 1 and 2, and graphically displayed in Figs 1 and 2. The results are shown more distinctly, as they pertain to the first stage of dehydration, on Figs 3 and 4. In the first stage the first water molecule is lost, in the second stage the second water molecule is lost and in the third stage, again, another water mole-

cule is lost. It can be seen from the QMS results (Figs 1 and 2) that subsequent water molecules are lost in a stepwise process which is now associated with the release of oxygen and Cl_2 . This stage starts at ca. 550 K and ends at ca. 700 K. The SDTA curve shows us also the thermal effects connected with heating of our samples in investigated temperature region. We do not want to analyze the curve from room temperature till ca. 400 K because we have got more detailed DSC results in the temperature region. On DSC curve (Fig. 5)

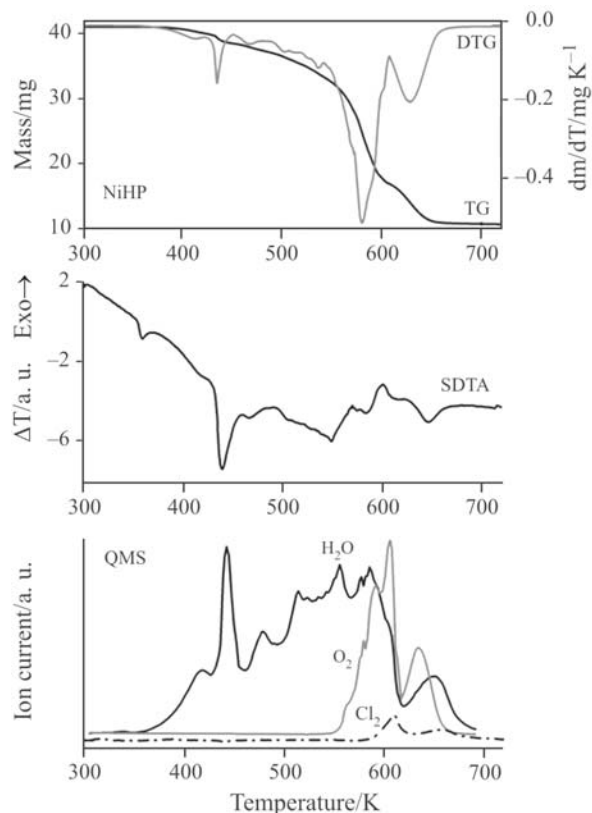


Fig. 1 TG, DTG, SDTA and QMS curves for NiHP in the range of 330–700 K, heated at a constant heating rate of 10 K min^{-1}

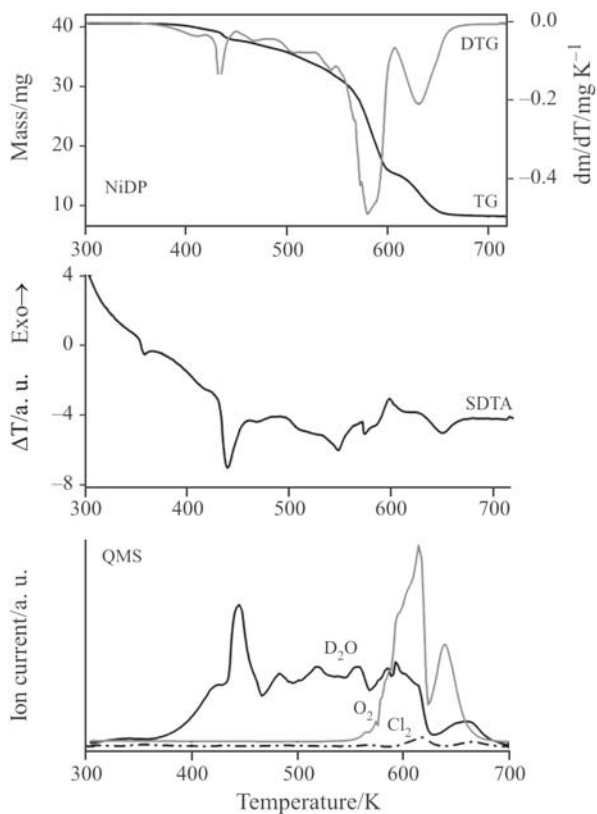


Fig. 2 TG, DTG, SDTA and QMS curves for NiDP in the range of 330–700 K, heated at a constant heating rate of 10 K min^{-1}

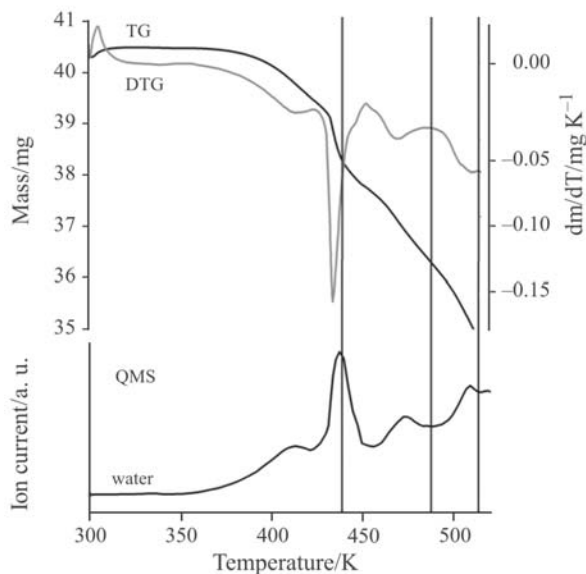


Fig. 3 TG and DTG curves for NiHP in the temperature region where the first, the second and the third water molecule is removed

we can see a large endothermic split peak, (about 470 K) which is in correspondence with a distinctly shown peak on the SDTA curve at the temperature. The effect is connected with losing of two water molecules (as we can see from Tables 1 or 2). No smooth

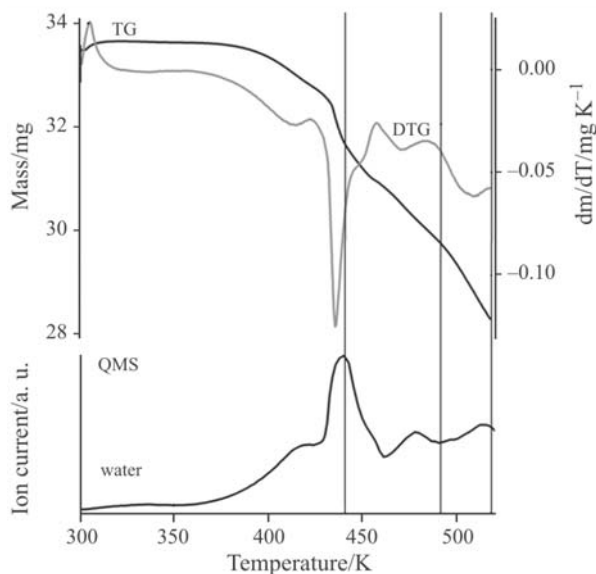


Fig. 4 TG and DTG curves for NiDP in the temperature region where the first, the second and the third water molecule is removed

DSC curve above ca. 520 K is the sign that our crucible is not tight. Therefore, we had to stop our DSC experimental run at ca. 550 K. Figure 5 shows that the process of heating of our samples is connected only with endo-thermic effects till 520 K. The first two peaks are connected with phase transitions in the solid-state at ca. 313 and 363 K. They confirm well our previous DSC results [2]. A comparison of DSC results for NiHP and NiDP samples is shown in Fig. 6. These results correspond well to our previous results [2]. They show distinctly that phase transitions in the solid modification at ca. 313 and 363 K are reversible, which was not so carefully investigated in [2]. One can easily see a shift of phase transition temperatures connected with deuteration.

A comparison of the process of dehydration for NiHP and NiDP is of interest. From Fig. 7 it can be seen that the process by which the first water molecule

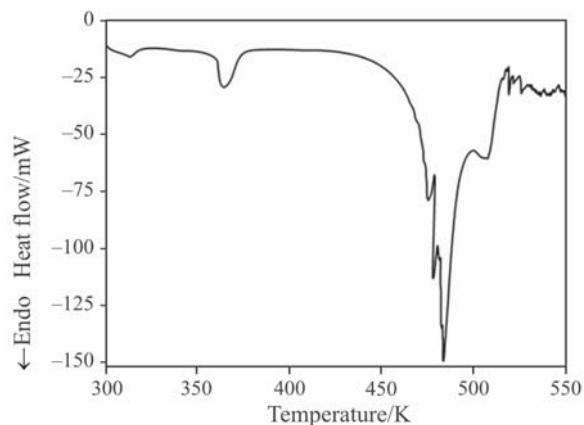


Fig. 5 DSC curve for NiHP. At ca. 450 K one can see that the process of NiHP decomposition starts

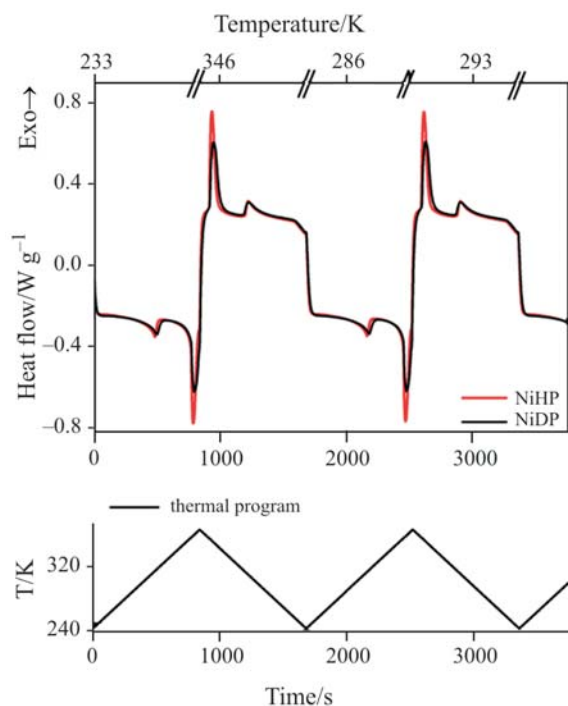


Fig. 6 DSC curves for NiHP and NiDP when heating, cooling and again heating and cooling these samples. In the lowest part of the figure the thermal program is shown

is lost starts at a temperature for NiDP comparable to that for NiHP. This further suggests that the activation energy of the process of dehydration for NiDP is close to that for NiHP. However, it should be noted that a main extreme on the DTG curve (Fig. 7), corresponding to release of the first water molecule, appears at a distinctly lower temperature for NiHP than for NiDP. Total decomposition of those samples seems to go on the following way: the product of three first steps of dehydration transforms in the following way: $[\text{Ni}(\text{H}_2\text{O})_3](\text{ClO}_4)_2 \rightarrow \text{NiO} + \text{Cl}_2 + 4\text{O}_2 + 3\text{H}_2\text{O}$. On the QMS curve (Figs 1 and 2) we can see signs of oxygen and water even at the highest temperature of the measurements i.e. at ca. 650 K. More detailed interpreta-

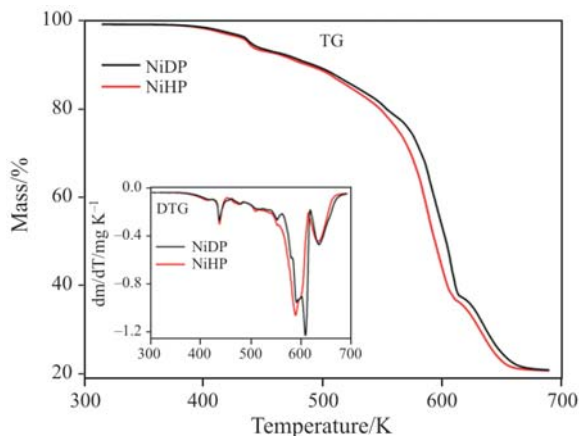


Fig. 7 Comparison of TG and DTG curves for NiHP and NiDP

tion of the total decomposition of our samples is difficult because of its decomposition with explosion well seen as an exothermic effect at ca. 600 K (SDTA) and on QMS curve as great oxygen peaks. In connection with the effect of explosion an estimation of intermediate decomposition's products is difficult. The curve signed by Cl_2 on QMS results does not show without a doubt that chlorine is one of decompositions' products. Chlorine can appear as a product of decomposition of ClO_2 in our samples or as a result of ionization of ClO_2 and of ionization of some another compounds composed of oxygen and chlorine in QMS spectrometer. Speaking about NiO we should sign rather the chemical formula as NiO_x . The value of x calculated from TG results is equal to 1.14 for NiHP and 1.31 for NiDP. Because x is not exactly equal to 1 we can state that obtained NiO compound is not stoichiometric one.

Calculation method

Based on the results from TG, the integral method of Coats and Redfern [12] was used to study the kinetics of dehydration of NiHP and NiDP. The kinetic parameters can be derived using a modified Coats–Redfern equation [15]:

$$\ln \left[\frac{g(\alpha)}{T^2} \right] = \ln \frac{AR}{qE} - \frac{E}{RT}$$

where α is the degree of transformation defined as

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty}$$

where W is the mass of the solid and the subscripts 0 and ∞ refer to the initial and residual amounts, respectively, q refers to the heating rate, and $g(\alpha)$ is a function, the expression of which depends on the kinetic model of the specific reaction. If a correct $g(\alpha)$ is used, a plot of $\ln[g(\alpha)/T^2]$ vs. $1/T$ should give a straight line, from which some values of the activation energy E and the pre-exponential factor A in the Arrhenius equation can be calculated. The formal expressions of the functions $g(\alpha)$ depend on the conversion mechanism and its mathematical model [13]. The latter usually represents the limiting stage of the reaction – the chemical reactions; random nucleation and nuclei growth; phase boundary reaction or diffusion. If the correct $g(\alpha)$ is used, the corresponding linear dependence should give the highest correlation coefficient from the linear regression analysis. The most common kinetic models and their algebraic expressions one can find in [13]. Figure 8 presents Coats and Redfern plots of dehydration of NiHP and Fig. 9 presents the dehydration of NiDP. The energy of activation value obtained for dehydration (the first step of the process) of NiHP is equal to $77.74 \pm 0.24 \text{ kJ mol}^{-1}$ and for NiDP is equal to

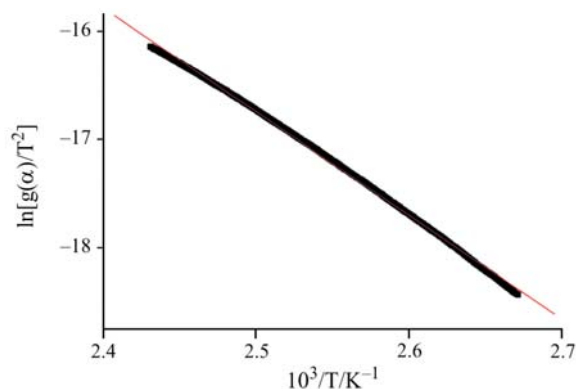


Fig. 8 Coats and Redfern plot of NiHP dehydration (the first water molecule is removed)

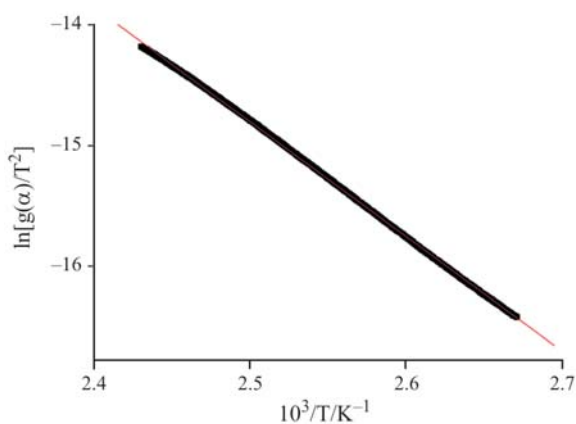


Fig. 9 Coats and Redfern plots of NiDP dehydration (the first water molecule is removed)

$76.26 \pm 0.13 \text{ kJ mol}^{-1}$. Thus the energy of activation for NiDP is comparable to that for NiHP. The best model used for experimental values of α was $F_{3/2}$ i.e. reaction model: three-halves order kinetics

$$f(\alpha) = (1 - \alpha)^{3/2}$$

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt = 2[(1 - \alpha)^{-1/2} - 1]$$

An important conclusion from those measurements is that there are at least 3 kinds of water molecules in NiHP and NiDP. This result agrees with our previous results [8, 9]. We can admit that the problem discussed in the article from the main point of view is comparable with similar problems considered in another publications for example [14, 15].

Conclusions

- The two-phase transitions in solid NiHP (311.3, 362.8 K) and NiDP (314.6, 362.4 K) are reversible.
- When heating those two samples lose water molecules and then they decompose. Losing of 3 first molecules is realized in three separate steps. The rest

water molecules are lost in the time of perchlorate ions' decomposition (clearly seen on QMS results). These results are compatible with those obtained in [8, 9] showing three groups of frequencies for water molecules in each of both compounds. The effect of non equivalence of water molecules in octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{D}_2\text{O})_6]^{2+}$ is probably connected with hydrogen bonds' net existing in the sample till the temperature of the phase transition III–II [9].

- Total decomposition of both samples is connected with losing of 3 and then losing of rest of water molecules and also with decomposition of perchlorate anion to O_2 , Cl_2 . NiO is the solid remainder of the process.
- The value of energy of activation obtained for dehydration (the first step of the process) of NiDP is comparable to that for NiHP and is equal ca. 77 kJ mol^{-1} .

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