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ON THE THERMAL DECOMPOSITION OF $[Ni(H_2O)_6](NO_3)_2$ AND ITS DEUTERATED ANALOGUE

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The methods of TG, DTA and DSC were used to study the thermal decompositions of $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$ in an atmospheric air medium. Intermediates were isolated at 145, 230 and 245°, and were identified by quantitative analysis and IR spectroscopy. The following phase transitions were observed under the conditions of the experiment: melting of the salts, partial dehydration to the tetrahydrate, formation of basic nickel nitrate hydrate stable within a narrow temperature interval, and formation of NiO.

The enthalpies of the phase transitions were calculated from the DSC data.

The DTA and DSC data show that in $[Ni(D_2O)_6](NO_3)_2$ the phase conversions take place at somewhat lower temperatures than those for $[Ni(H_2O)_6](NO_3)_2$.

The experimental decomposition of $[Ni(H_2O)_6](NO_3)_2$ has been studied by a number of authors. Some of the data obtained are contradictory, while others are complementary.

Publications [1-10] deal with thermal decomposition in air. According to these authors, the compound melts in its crystal water and undergoes stepwise dehydration, the intermediate hydrates differing in composition, depending on the heating rate. It is pointed out in [5] that all the phase transitions occur in the solid phase at a low rate of heating of 5-20 deg/min. The pentahydrate was reported in [4]. The tetrahydrate, described in [3, 5, 8], is unstable and is readily converted into the trihydrate [8] or the dihydrate [3, 5]. Some authors [1, 9] report that the hexahydrate is converted into the trihydrate without anu tetrahydrate or dihydrate being observed.

The formation of an intermediate with 1.5 mol H_2O is reported in [4]. In [2], the turn in the TG curve at the thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ is stated to be due to the formation of anhydrous nickel nitrate.

Another group of authors report the formation of basic nickel nitrate. In [5, 6] its composition is given as $Ni(NO_2)_2.2Ni(OH)_2$, while other authors [7] believe it to be $Ni(NO_3)_{1.3}(OH)_{0.67}$. The authors of [8] describe a basic hydrate, $x Ni(NO_3)_2.y Ni(OH)_2.z H_2O$ with $x = 24, y = 1, z = 64\text{-}17$, which is converted into $Ni(NO_3)_2.1.33Ni(OH)_2$. The structural investigations of the hydroxonitrates with the general formula $x Ni(NO_3)_2.y Ni(OH)_2.z H_2O$ are of interest [20]. They are all related to two structural diagrams derived from $Ni(OH)_2$. In [18], the thermal decomposition of $Ni(NO_3)_2$ was studied by using a DSC with a heating rate of 10 deg/min, and the reaction heats for the observed peaks were calculated.

All the above authors reported NiO as the end-product of the thermal decomposition.

The thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ has been studied in different gas media [11, 12], in closed crucibles [10], on various carriers [13] and in vacuum [15, 17, 19]. The data of the TG curves were used to derive a mechanism of the individual stages [13], and their activation energies were calculated as 25, 108 and 99.5 kJ/mol, respectively. The data were obtained via the Avramii-Erofeev kinetic equation. The same parameters are described in [15] from gasometric analysis and TG curve data. The activation energies of thermal decomposition of a number of nitrates are given in [16], the activation energy for $[Ni(H_2O)_6](NO_3)_2$ being 31.6 kJ/mol.

In [19], the intermediates in the thermal decomposition in vacuum were identified by means of IR and Raman spectra up to 600 cm^{-1}.

The objectives of the present study were:

a. To study the non-isothermal decompositions of $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$ in air at two different heating rates and to compare the temperatures of the phase transitions for the two compounds.

b. By means of quantitative analysis and IR spectroscopy (2000-200cm^{-1}), to characterize the starting compounds, the intermediates and the end-products of the thermal decomposition.

c. To calculate the kinetic parameters (E^* and A) separately for the first phase (formation of the hydroxonitrate hydrate) and the second phase (formation of the oxide).

d. By means of DSC to determine the enthalphies of the basic phase transitions for the two compounds.

Experimental

The initial $[Ni(H_2O)_6](NO_3)_2$ was obtained by twofold recrystallization of p.a. grade $[Ni(H_2O)_6](NO_3)_2$, while its deuterated analogue was obtained by severalfold recrystallization from heavy water.

The DTG and TG curves were taken with a MOM apparatus, at two different heating rates (2 and 5 deg/min), in open ceramic crucibles from 20° to 400°. The intermediates were obtained at a heating rate of 2 deg/min to temperatures of 145°, 230° and 245°, respectively. Samples of each were immediately covered with Nujol or with hexachloro-1,3-butadiene and their IR spectra were taken, while other samples were subjected to quantitative analysis. In both intermediates and initial substances, the nickel content was determined complexometrically [20], the content of nitrate groups spectrophotometrically with a Perkin Elmer 323 instrument, and the water by Fisher's method.

The IR spectra were taken with an M-80 spectrophotometer, in a suspension in Nujol, from 2000 to 200 cm^{-1}, and in hexachloro-1,3-butadiene, from 2000 to 1200 cm^{-1}. These conditions were selected with a view to avoiding the overlapping of the absorption bands of the investigated samples with those of Nujol and hexachloro-1,3-butadiene. KBr tablets were not used, as exchange reactions bave been reported to occur between $Ni(NO_3)_2$ and KBr [21].

Determination were also made of the enthalpies of the observed phase transitions, in $[Ni(H_2O)_6](NO_3)_2$ and the deuterated analogue, by means of DSC. These curves were taken with a Mettler-3000 apparatus at a heating rate of 5 deg/min in perforated aluminium capsules.

The kinetic parameters were determined from the TG curve data relating to a heating rate of 5 deg/min.

Experimental results

The DTA and TG curves on the investigated compounds at a heating rate of 2 deg/min are shown in Fig. 1, and those at a heating rate of 5 deg/min in Fig. 2. The temperatures of the phase transitions and the mass losses of the samples from the DTA and TG curves are presented in Table 1, while the chemical compositions of the initial compounds and the intermediates in the thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ are given in Table 2. The DSC

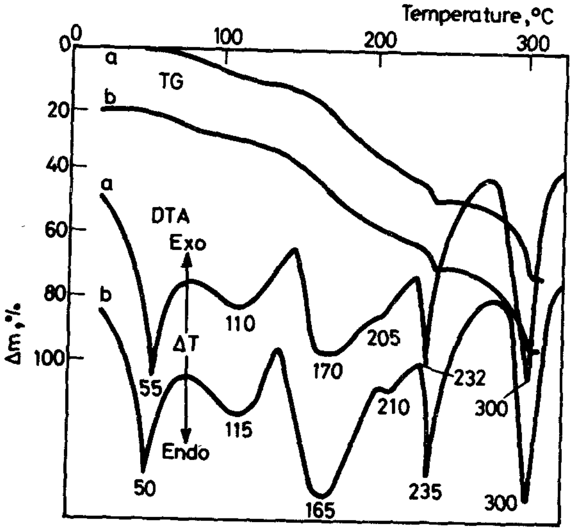

Fig. 1 DTA and TG curves of a – $[Ni(H_2O)_6](NO_3)_2$ b – $[Ni(D_2O)_6](NO_3)_2$ at a heating rate of 2 deg /min ; sample mass 300 mg

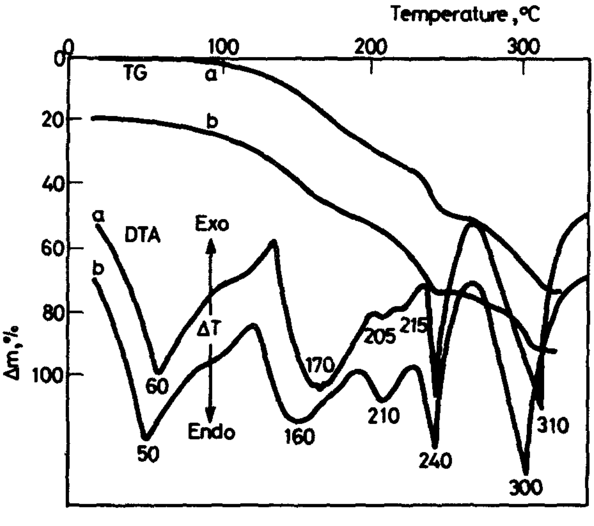

Fig. 2 DTA and TG curves of a – $[Ni(H_2O)_6](NO_3)_2$ b – $[Ni(D_2O)_6](NO_3)_2$ at a heating rate of 5 deg /min ; sample mass 300 mg

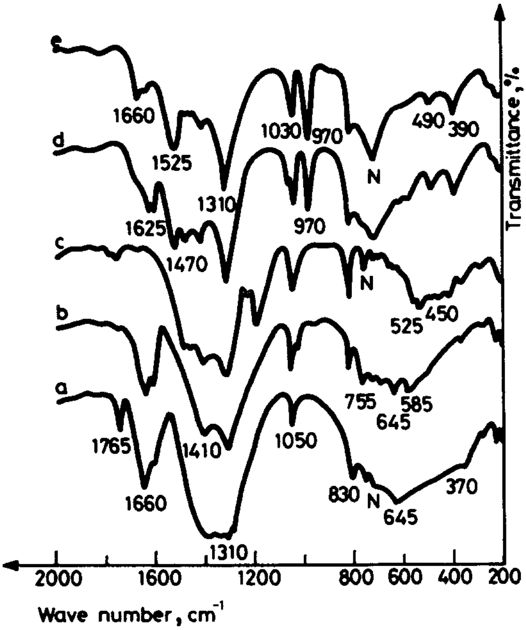

Fig. 3 IR-spectra of $[Ni(H_2O)_6](NO_3)_2$: a – initial product and the intermediate samples; b – at 145°C, d – at 230°C, e – at 245°C; c – of $[Ni(D_2O)_6](NO_3)_2$

data are collected in Table 3. The IR spectra of $[Ni(H_2O)_6](NO_3)_2$ and the intermediates are given in Fig. 3.

The endoeffects observed with maxima in the intermal 50-60° (Figs 1 and 2, Table 1) are due to the melting of the compounds; no change is observed in the respective TG curves. Further the temperatures recorded depend on the heating rate; at both heating rates, the deuterated hydrate has the lower m.p.

The second endoeffect, with $T_{max} = 110°$ (Fig. 1, Table 1), corresponds to a decrease in mass of the sample, $\Delta m_{exp.} = 13.0\%$; accordingly, it may be assumed that it corresponds to the release of two molecules of hydrate water and to the formation of $[Ni(H_2O)_4](NO_3)_2$ (Table 1). This effect is not clearly outlined in the thermal curve taken at 5 deg/min and appears as a shoulder of the first effect. As expected, the courses of the DTA and TG curves of the deuterated analogue were analogous, which was further confirmed by the decrease in mass.

Table 1 Data from DTA and TG curves of $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$ at a heating rate of 2 deg/ min

Phase transition	Form	$\Delta m_{theor.}$ %	$\Delta m_{exp.}$, %	$T_{init.}$ °C	$T_{fin.}$ °C	$T_{max.}$ °C
$[Ni(H_2O)_6](NO_3)_2$ (cr) →	H	-	-	20	70	55
$[Ni(H_2O)_6](NO_3)_2$ (f.)	D	-	-	20	70	50
$[Ni(H_2O)_6](NO_3)_2$ (f.) →	H	12.4	13.0	70	145	110
$[Ni(H_2O)_4](NO_3)_2 + 2H_2O$	D	13.2	14.0	70	135	115
$2[Ni(H_2O)_4](NO_3)_2$ (cr) →	H	34.1	32.6	145	230	170
$Ni_2(OH)_2(NO_3)_2.2H_2O$ + $+ 2HNO_3 + 4H_2O$	D	34.3	33.0	135	230	165
$Ni_2(OH)_2(NO_3)_2.2H_2O$ →	H	3.1	4.0	230	240	232
$Ni_2(OH)_2(NO_3)_2.H_2O + H_2O$	D	3.3	3.8	230	240	235
$Ni_2(OH)_2(NO_3)_2.H_2O$	H and D	-	-	240	260	-
$Ni_2(OH)_2(NO_3)_2.H_2O$ → $2NiO + 2HNO_3 + H_2O$	H and D	24.7	25.0	260	350	300

Since the data in the literature on the stepwise dehydration of the initial compounds are quite different and contradictory, the additional investigations carried out involved the isolation of an intermediate (Table 2, sample 2) which was identified via quantitative analysis and its IR spectrum. The quantitative analysis data fully confirm the picture afforded by stepwise dehydration, according to which $[Ni(H_2O)_4](NO_3)_2$ is obtained as an intermediate. Figure 3 presents a comparison of its spectrum (curve *b*) with that of the initial substance (curve *a*) as regards the symmetry of the NO_3^- group, the presence of the nickel aqua complex, and the vibration oscillations of the coordinated water molecules. For fuller information, curve *c* is given, with the spectrum of the partially deuterated tetrahydrate obtained from solution.

As regards the oscillations of the nitrate group, the spectrum of the tetrahydrate shows its three normal oscillations: the symmetrical valent (ν_1) one 1050 cm^{-1}, the split asymmetric valent ν_3 one with absorption maxima at 1310 cm^{-1} and 1410 cm^{-1}, i.e. $\Delta\nu_3 = 100$ cm^{-1}, and the deformation oscillation at 825 cm^{-1}. The second deformation oscillation is covered by the Nujol absorption. These data indicate violation of the trigonal structure of the NO_3^- group, which is in full accord with the crystalline structure of the tetrahydrate [28].

A comparison of the spectrum of the tetrahydrate isolated during thermal decomposition (Fig. 3, curve *b*) and that of the initial hexahydrate (Fig. 3, curve *a*) in the region of the vibration oscillations of the coordinated water molecules shows a difference only as regards their number. In the two spectra ρ_w is at 755 cm^{-1}, while ρ_v is close to the absorption peak of Nujol, but is also well manifested in the spectrum of the deuterated product at 325 cm^{-1} (isotonic shift $\nu_H / \nu_D = 1.43$; Fig. 3, curve c). Corresponding to the vibration oscillation, ρw in the examined spectrum is at 450 cm^{-1}. These data are in full agreement with those in other publications [22]. The additional weak vibration oscillations observed for the tetrahydrate (Fig. 3, curves *b*, *c*) are to be expected bearing in mind the existence of roentgenostructurally different water molecules in its structure [28], as well as the observed splitting of $\delta H2O$ and δD_2O (Fig. 3, curves *b* and *c*) at 1640-1620 cm^{-1} and, accordingly, at 1220-1180 cm^{-1}. The absorption at 370 cm^{-1}, which for free $[Ni(H_2O)_6]^{2+}$ has been reported at 405 cm^{-1} [22] and at 392 cm^{-1} [24, 25], must be ascribed to the valency oscillation of $Ni\text{-}OH_2$ characterizing the aqua complex as a whole. In the particular case, this oscillation may appear at lower frequencies, since the distance d_{Ni-OH_2} in the hexahydrate is smaller than the corresponding distance in the tetrahydrate [23]: 203 pm and 213 pm, respectively, and this is also in accordance with the structural data on $[Ni(H_2O)_4](NO_3)_2$ [28].

The further courses of the DTA curves (Figs 1 and 2) show the presence of a strong endoeffect with maximum at 165-170° for both $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$. $\Delta m_{exp.} = 32.6\%$ from the TG curve corresponds to this effect (Table 1). With a view to a fuller understanding of the chemistry of the process taking place, an intermediate was isolated and identified at $T = 230°$, i.e. after the completion of the examined endoeffect (Table 2, Fig. 3, curve *d*). Its IR spectrum indicates the presence of NO_3^- groups, and water molecules and OH^- groups. The latter are identified by the appearance of the absorption at 970 cm^{-1}, which is absent in the spectra of the hexa- and tetrahydrates and may be ascribed to the flat deformational oscillation $\delta Ni\text{-}OH$. The contents of nickel, nitrate and hydrate water in the investigated sample were determined by quantitative analysis. However, difficulties were encountered in the quantitative determination of the hydroxy groups, since the customary method [26] proved inapplicable to the system examined. The percentage content of OH^- groups was calculated as the difference between 100 and the total sum of the other components (Table 2).

Table 2 Chemical compositions of initial substances and intermediates in the thermal decomposition of $[Ni(H_2O)_6](NO_3)_2$ at 2 deg/min

No.	T, °C	Δm, %	Chemical composition				Mol ratio			
			Ni	NO_3^-	OH^-	H_2O	Ni	NO_3^-	OH^-	H_2O
1	25	0	20.2	42.6	0	37.1	1.0	2.0	0	6.0
2	145	13.0	23.2	48.7	0	28.1	1.0	2.0	0	4.0
3	230	46.0	37.6	39.9	10.9	11.6	1.0	1.0	1.0	1.0
4	245	49.5	40.1	42.5	11.4	6.1	1.0	1.0	1.0	0.5

On the basis of the data obtained from the quantitative analysis, the TG curve mass changes and the IR spectra, it may be assumed that a binuclear complex $Ni_2(OH)_2(NO_3)_2.2H_2O$ is obtained as a result of the hydrolysis. This assumption is in accord with the published fact, that polynuclear compounds are frequently obtained in the hydrolysis of aqua complexes, and it is also confirmed by the absorption at 1030 cm^{-1} in the spectrum of the compound, which may be ascribed to a bridging OH^- group. From the existing information, it is not possible to give a conclusive reply as to whether the nitrate groups are monodentately or bidentately bonded in the basic salt obtained, for in this case the difference is determined solely by the positions of the split ν_3 oscillations and not their number. The position of the latter suggests bidentate bonding, which accounts for the octahedral coordination of the nickel.

The thermal curves of the investigated compound (Figs 1 and 2) also show a sharp peak with macimum at $T=235°$, which, according to the recorded decrease in mass of the sample, is due to the release of part of the hydrate water content of the basic salt obtained. This process results in a product with composition $Ni_2(OH)_2(NO_3)_2.H_2O$, which is stable in the interval 240-250° (Table 1, Figs 1 and 2). Above this range, decomposition of the basic nickel nitrate begins, leading to nickel oxide, as proved roentgenographically, by quantitative analysis, and via the IR spectrum. The endoeffect at $T_{max}=300\text{-}310°$ corresponds to this process (Figs 1 and 2). The character of this endoeffect is analogous for the two compounds investigated, but the NiO obtained exhibits some difference in particle size [27].

Three endoeffects are to be observed in the DSC curves for $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$, with two maxima in the second endoeffect. The enthalpies of the phase transitions, corresponding to the respective endoeffects, are given in Table 3. The melting enthalphy of $[Ni(H_2O)_6](NO_3)_2$ is higher than that of $[Ni(D_2O)_6](NO_3)_2$, a dependence which correlates with the T_f data on the investigated compounds and indicates a certain destabilization of the crystal lattice of the deuterated analogue. The second endoeffect embraces the processes of stepwise dehydration to $[Ni(H_2O)_6](NO_3)_2$ and hydrolysis of the aqua complex to basic nickel nitrate hydrate, stable in the temperature interval 240-260°. The enthalpy of this transition is considerable: for $[Ni(D_2O)_6](NO_3)_2$ it is 33 kJ/mol higher than that for $[Ni(H_2O)_6](NO_3)_2$. This may be explained by the higher degree of hydrolysis in the deuterated compound, since the overall enthalphy of the process of decomposition from the initial hydrate to the oxide is higher than it would be if it were due to evaporation of the hydrate water alone. Thus, the experimentally determined enthalpy for $[Ni(H_2O)_6](NO_3)_2$ is 499 kJ/mol, whereas that calculated on the basis of the thermodynamic dependences is 482 kJ/mol; for $[Ni(D_2O)_6](NO_3)_2$, the corresponding data are 524 kJ/mol and 489 kJ/mol. The third endoeffect observed in the DSC curve is related only to the transition from the basic salt hydrate to NiO, with an enthalpy of 154 kJ/mol or 157 kJ/mol, respectively. It must be pointed out that in these curves, as in the case of DTA, the maximum of the effect lies at lower temperature for the deuterated compound than that for the ordinary nitrate hydrate.

Table 3 DSC data on $[Ni(H_2O)_6](NO_3)_2$ and $[Ni(D_2O)_6](NO_3)_2$ at 5 deg/min

Phase transition	H form				D form			
	$T_{init.}$ °C	$T_{term.}$ °C	$T_{max.}$ °C	$\Delta H°$, kJ/mol	$T_{init.}$ °C	$T_{term.}$ °C	$T_{max.}$ °C	$\Delta H°$, kJ/mol
$[Ni(H_2O)_6](NO_3)_2$ (cr.) → $[Ni(H_2O)_6](NO_3)_2$ (f.)	25	55	51	43	25	50	46	32
$2[Ni(H_2O)_6](NO_3)_2$ (cr.) → $Ni_2(OH)_2(NO_3)_2.H_2O$	55	260	140 250	302	50	260	100 240	335
$Ni_2(OH)_2(NO_3)_2.H_2O$ → 2NiO	260	350	335	154	260	340	327	157

The data from the TG curve (Fig. 1) were computer-processed on the basis of the general differential method, with determination of the probable mechanisms of thermal decomposition, the activation energies, and the pre-exponential factors separately for the three stages: stage I: from the beginning up to formation of the tetrahydrate; stage II: from the tetrahydrate to basic nickel nitrate hydrate; and stage III: decomposition of basic nickel nitrate hydrate to nickel oxide.

Stage I is best described by the kinetic equation

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

with $E^* = 43$ kJ/mol and $A = 3.7\text{x}10^4$ s^{-1} for H,

and $E^* = 49$ kJ/mol and $A = 5.1\text{x}10^4$ s^{-1} for D.

Stage II is best described by the kinetic equation

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

with $E^* = 78$ kJ/mol and $A = 1.0\text{x}10^6$ s^{-1} for H,

and $E^* = 69$ kJ/mol and $A = 1.8\text{x}10^6$ s^{-1} for D.

The best equation for stage III is

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

with $E^* = 180$ kJ/mol and $A = 5.7\text{x}10^{14}$ s^{-1} for H,

and $E^* = 160$ kJ/mol and $A = 1.1\text{x}10^{10}$ s^{-1} for D.

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Zusammenfassung — Mittels TG, DTA und DSC wurde die thermische Zersetzung von $[Ni(H_2O)_6](NO_3)_2$ und $[Ni(D_2O)_6](NO_3)_2$ in Luft untersucht. Bei Temperaturen von T=145°C, 230°C un 245°C konnten Intermediäre festgestellt werden, welche mittels quantitativer Analyse und IR-Spektroskopie identifiziert wurden. Unter den gegebenen experimentellen Bedingungen wurden folgende Phasenumwandlungen beobachtet: Schmelzen der Salze, partielle Dehydratation zu Tetrahydrat, Bildung von basishem Nickelnitrat-hydrat (stabil innerhalb eines schmalen Temperaturintervalles), schließliche Bildung von NiO.

Aus den DSC-Daten wurden die Enthalpien der Phasenumwaldungen berechnet. DTA- und DSC-Daten zeigen, daß die Phasenunwandlungen bei $[Ni(H_2O)_6](NO_3)_2$ bei etwas niedrigeren Temperaturen liegen als bei $[Ni(D_2O)_6](NO_3)_2$.