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THERMAL STUDY OF $NiC_2O_4 \cdot 2H_2O$ OBTAINED BY A SOLID STATE REACTION AT ROOM TEMPERATURE AND NORMAL PRESSURE

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ABSTRACT

The reaction of mixtures of oxalic acid and different compounds of nickel (chloride, hydroxide carbonate, nitrate and oxide) at room temperature and normal pressure were studied. In all these mixtures the same phenomenon is observed: they become humid very rapidly, indicating the beginning of the reaction. In addition, in the mixtures of the chloride or nitrate, an immediate release of hydrochloric or nitric acid is observed. Depending on the nickel salt employed, the reaction is finished in 48 h ($NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and NiO) or 7 days ($NiCl_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$). In all cases the reaction product is $NiC_2O_4 \cdot 2H_2O$. We evaluated the activation energy and pre-exponential factor for the dehydration step $NiC_2O_4 \cdot 2H_2O \rightarrow NiC_2O_4 + 2H_2O$.

INTRODUCTION

Years ago we began studies on reactions without references in the literature; these were reactions between solid compounds which take place at room temperature and normal pressure [1–5].

This paper presents the reactions carried out between oxalic acid and the chloride, hydroxide carbonate, nitrate and oxide of nickel. The reaction product is $NiC_2O_4 \cdot 2H_2O$ in all cases.

Afterwards, we studied the thermal decomposition of the oxalates obtained in an air stream and a nitrogen stream. We also carried out a kinetic study of the dehydration step of the oxalates. The kinetic parameters computed correspond to the transformation

dihydrated oxalate → anhydrous oxalate

obtained in an air stream at three different temperatures. These temperatures were chosen between 200 and 250 °C, corresponding to the dehydration zone of the TG curves.

The thermal decomposition of the dihydrated nickel oxalate has been studied by various authors, but there is no agreement of results. For Duval

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[6] the decomposition of oxalate leads to nickel oxide. The nickel oxide is not obtained at once but via a basic carbonate which is stable over a range of about 100 °C and conforms very closely to the compound $NiCO_3 \cdot 2NiO$. The pure nickel oxide is not obtained below a temperature of 633 °C. Dollimore et al. [7] reported that when the decomposition is carried out in air the end product is NiO, and in nitrogen the end product is metallic nickel. Finally, Alloun and Nair [8] also studied the decomposition in nitrogen, they did not find metallic nickel but nickel oxide as the end product.

We found the same residue for all of the mixtures prepared: nickel oxide in air and a mixture of nickel oxide and metallic nickel in nitrogen.

EXPERIMENTAL

Products

The following compounds supplied by Merck, r.a. were used: $H_2C_2O_4 \cdot 2H_2O$; NiO; $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$; $Ni(NO_3)_2 \cdot 6H_2O$; $NiCl_2 \cdot 6H_2O$.

The NiO is poorly crystallized with 12.8% of carbonate and water impurities. The nature of the impurities allows us to suppose that this nickel oxide will behave, from the point of view of the reaction studied by us, as the hydroxide carbonate behaves.

In fact, the CO_2 and water in the hydroxide carbonate represent 29.6% of its molecular weight so the NiO supplied by Merck employed in the mixture will be transformed in part into the hydroxide carbonate. The well-crystallized NiO without impurities does not react with oxalic acid [5].

Preparation of the samples

The following mechanical mixtures were prepared:

$H_2C_2O_4 \cdot 2H_2O$ plus NiO (molar ratio, 1 : 1);
$H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3 : 1);
$H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1);
$H_2C_2O_4 \cdot 2H_2O$ plus $NiCl_2 \cdot 6H_2O$ (molar ratio, 1 : 1).

$NiC_2O_4 \cdot 2H_2O$ was obtained in the laboratory by the precipitation of a nickel nitrate solution with an oxalic acid solution. It was used to compare its thermal behaviour with the thermal behaviour of the different nickel oxalates obtained in the studied reactions.

Apparatus

TG

A Chevenard thermobalance (model 93) from Adamel was used with photographic recording. The heating rate was 300 °C h^{-1}. A Mettler TA3000 system was used with a heating rate of 300 °C h^{-1}.

DTA

This apparatus was constructed in the laboratory using a vertical furnace and a temperature regulation system, both from Adamel. A differential chromel–alumel thermocouple was used. The heating rate was 300 °C h^{-1}.

DSC

A Mettler TA3000 system was used. The heating rate was 300 °C h^{-1}.

X-ray powder diffraction

A Siemens D-500 diffractometer was used with a graphite monochromator, K 805 generator and Cu $K\alpha_1$ radiation.

IR spectroscopy

A Perkin–Elmer 599B instrument was used with KBr pellets.

RESULTS

All the mixtures become humid very rapidly. The humidity is accompanied by the release of the corresponding carbonic, nitric and hydrochloric acids. The study by X-ray powder diffraction indicated that in the mixture of oxalic acid and nickel oxide and the mixture of oxalic acid and nickel hydroxide carbonate, the reaction is finished in 48 h, while in the mixture of oxalic acid and nickel nitrate and the mixture of oxalic acid and nickel chloride, the reaction is slower and is not finished before 7 days. In all cases the reaction product is $NiC_2O_4 \cdot 2H_2O$.

Mixtures

The following mixtures were studied: $H_2C_2O_4 \cdot 2H_2O$ plus NiO (molar ratio, 1 : 1) and $H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3 : 1).

Thermal study

The reacted mixtures show similar thermal behaviour in the air stream and in the nitrogen stream. For this reason, we only present here the thermal curves of one mixture.

In an air stream

Figure 1 shows the TG and DTA curves of the reacted mixture, curves (a) and (b) respectively. In the same figure we also show the TG and DTA curves of the nickel oxalate obtained by precipitation from solutions of nickel, curves (c) and (d) respectively. We can see that the curves of the

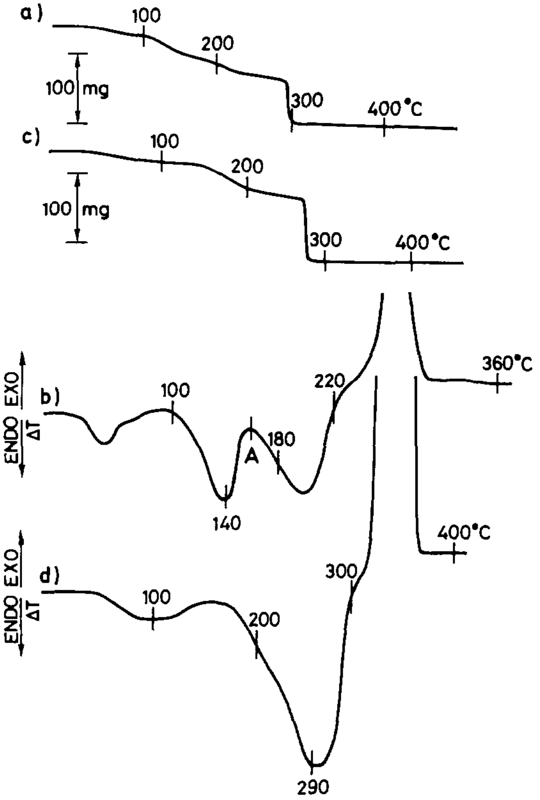

Fig. 1. TG and DTA curves: curve (a) TG and curve (b) DTA, for $H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3:1); curve (c) TG and curve (d) DTA, for $NiC_2O_4 \cdot 2H_2O$ obtained by precipitation.

mixture are similar to the curves of the precipitated oxalate but they are not identical. The intervals of temperature in which the transformations take place do not coincide; the loss of humidity in the mixture occurs at a lower temperature than in the precipitated oxalate.

However, in the TG and DTA curves of the mixture we observed a loss before the loss of the two moles of water of crystallization (endothermic peak at 200 ° C in curve (b)) which does not appear in the curves of the precipitated oxalate.

The X-ray diffraction taken of a sample at point A of curve (b) corresponds to $NiC_2O_4 \cdot 2H_2O$. This means that the endothermic peak at 140 ° C corresponds to the loss of part of the CO_2 released in the formation reaction of the $NiC_2O_4 \cdot 2H_2O$ that has remained retained for the hydrated oxalate.

The X-ray diagram of the sample taken at 220 ° C, which according to the TG curve corresponds to anhydrous nickel oxalate, shows a poorly crystallized compound.

Finally, the X-ray diagram of the sample taken at 350 °C corresponds to NiO.

In a nitrogen stream

Figure 2 gives the TG, DTG and DSC curves of both nickel oxalates: the reacted mixture and the oxalate obtained by precipitation. These curves were obtained in the Mettler TA3000 system. The TG curves (curves (a) and (c)) show the same steps as the curves obtained in air, but they are different owing to an increase in weight that takes place, in both samples, immediately after the decomposition of the anhydrous oxalate has finished.

The X-ray diffraction of samples taken at 400 °C shows mixtures of metallic nickel and nickel oxide.

However, the X-ray diagrams of samples taken at 950 °C correspond to nickel oxide. Therefore, the increase in weight corresponds to the oxidation of metallic nickel; the oxidizer is the oxygen from the equilibrium

$$2CO + O_2 \rightleftarrows 2CO_2$$

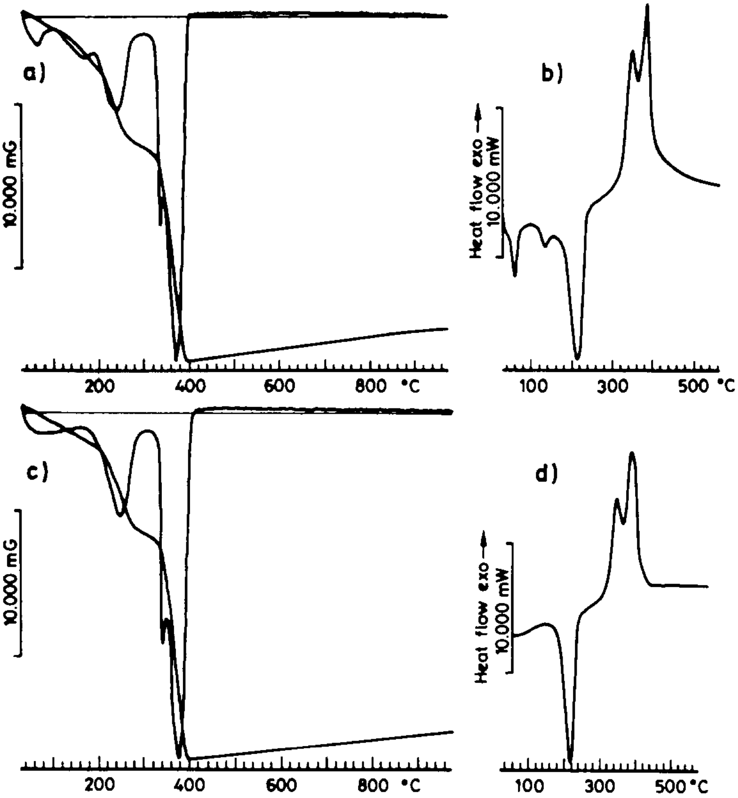

Fig. 2. TG, DTG and DSC curves: curves (a) TG and DTG, and curve (b) DSC for $H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3:1); curves (c) TG and DTG, and curve (d) DSC, for $NiC_2O_4 \cdot 2H_2O$ obtained by precipitation.

The DTG curves allow us to distinguish two peaks of decomposition which indicate that the decomposition of the anhydrous oxalate may be described by the equations

$$NiC_2O_4 \rightarrow NiO + CO + CO_2 \quad \text{(I)}$$

and

$$NiC_2O_4 \rightarrow Ni + 2CO_2 \quad \text{(II)}$$

A thermodynamic treatment of the decomposition of oxalates of divalent metal ions was given in 1963 by Dollimore et al. [7].

The DSC curves (curves (b) and (d)) only differ from the corresponding DTA curves in air of Fig. 1 in the exothermic peak, which appears here as two different oxidation peaks.

Mixtures

The following mixtures were studied: $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1) and $H_2C_2O_4 \cdot 2H_2O$ plus $NiCl_2 \cdot 6H_2O$ (molar ratio, 1 : 1).

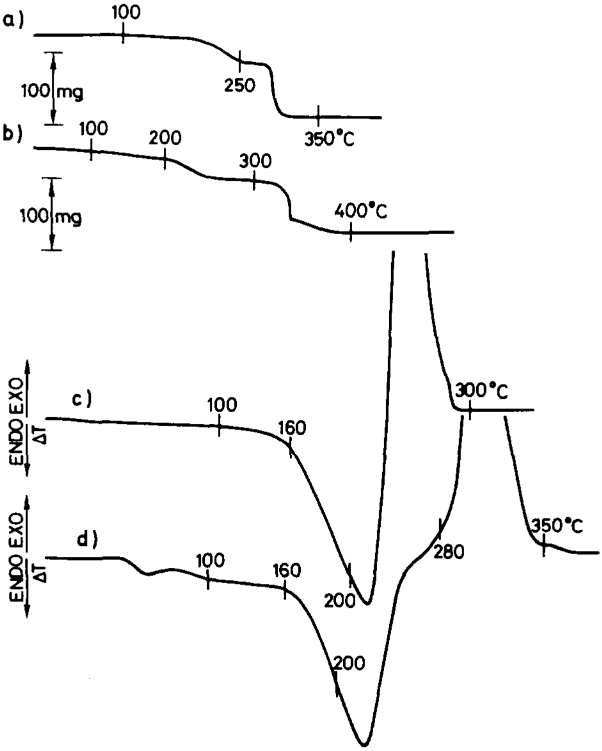

Fig. 3. TG and DTA curves: curve (a) TG and curve (c) DTA, for $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1); curve (b) TG and curve (d) DTA, for $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(Cl)_2 \cdot 6H_2O$ (molar ratio, 1 : 1).

Thermal study

In an air stream

The TG and DTA curves of both samples are reproduced in Fig. 3. The TG curve (curve (a)) of the mixture of oxalic acid and nickel nitrate shows only two losses, the first one between 100 and 250 ° C corresponding to the loss of the hydration water, and the second one corresponding to the release of CO and CO_2 from the decomposition of the anhydrous oxalate. The nickel oxalate originating from the nitrate does not retain any adsorbed volatile components in any estimable measure, unlike the case of the mixture of oxalic acid and nickel hydroxide carbonate.

The DTA curve (curve (c)) with only two peaks confirms the thermogravimetric results; the first, endothermic peak corresponds to a dehydration, and the second, exothermic peak corresponds to a decomposition, coinciding with the curves obtained in air for the two preceding mixtures.

The X-ray powder diffractograms indicate that the sample at 275 ° C is a poorly crystallized anhydrous oxalate of nickel and the sample at 350 ° C is well crystallized nickel oxide.

The thermal behaviour of the dihydrated oxalate obtained from the mixture of oxalic acid and nickel chloride shown in the TG curve (b) and the DTA curve (d) is very similar to the behaviour of the mixture of oxalic acid and nickel nitrate discussed above.

In a nitrogen stream

Figure 4 displays the TG, DTG and DSC curves of both mixtures. Curves (a) and (c) correspond to the mixture of oxalic acid and nickel nitrate and curves (b) and (d) correspond to the mixture of oxalic acid and nickel chloride.

The TG curves (curves (a) and (b)) are identical with the curves of the oxalates in a nitrogen stream mentioned above. We only observe one difference in the DTG curves of the mixture of oxalic acid and nickel chloride; only a single peak appears for the decomposition of the anhydrous oxalate shown by curve (b).

The X-ray diffraction of samples taken at 400 ° C shows mixtures of metallic nickel and nickel oxide. However, in the mixture of oxalic acid and nickel chloride, the amount of metallic nickel is small; this is confirmed by the single decomposition peak of the DTG curve.

In the DSC curves (curves (c) and (d)), the decomposition of both oxalates gives a single exothermic peak.

IR spectroscopy

As far as we know, precedents of the spectrum of dihydrated oxalate of nickel do not exist.

In Fig. 5 we give the IR spectra of the four samples studied, all of them are practically identical.

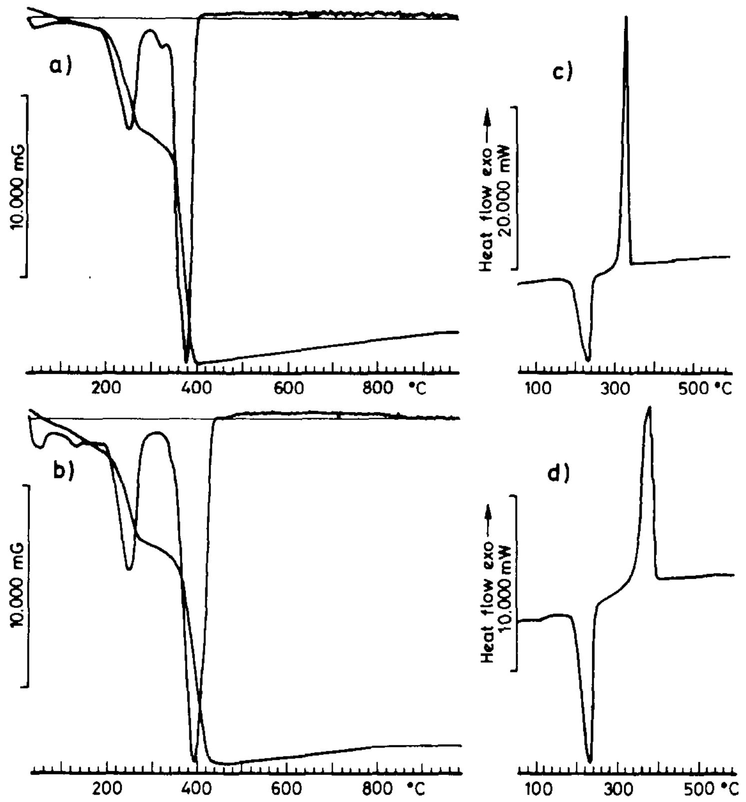

Fig. 4. TG, DTG and DSC curves: curves (a) TG and DTG, and curve (c) DSC, for $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1); curves (b) TG and DTG, and curve (d) DSC, for $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(Cl)_2 \cdot 6H_2O$ (molar ratio 1 : 1).

The spectrum of the nickel oxalate obtained by precipitation, spectrum (b), presents the following bands: a strong band at 3370 cm^{-1} associated with stretching vibrations of crystallization water; a strong band at 1620 cm^{-1} due to H–O–H bending motion and to C=O stretching vibrations; a sharp doublet at 1320 and 1350 cm^{-1} associated with C–O stretching vibrations (this band, without practical significance in the carboxylic acids, has a normal interval between 1440 and 1210 cm^{-1}); a medium band at 815 cm^{-1} due to C–C stretching vibrations; two bands at 475 and 325 cm^{-1} due to Ni–O linkage.

The spectrum of the mixture of oxalic acid and nickel nitrate, spectrum (c), is slightly different; it presents a displacement of the band at 1620 cm^{-1} to 1600 cm^{-1} and a new very weak band at 1380 cm^{-1}. This slight modification could indicate the presence of small amounts of NO_3^- ions adsorbed by the sample. These small amounts are not detected by TG.

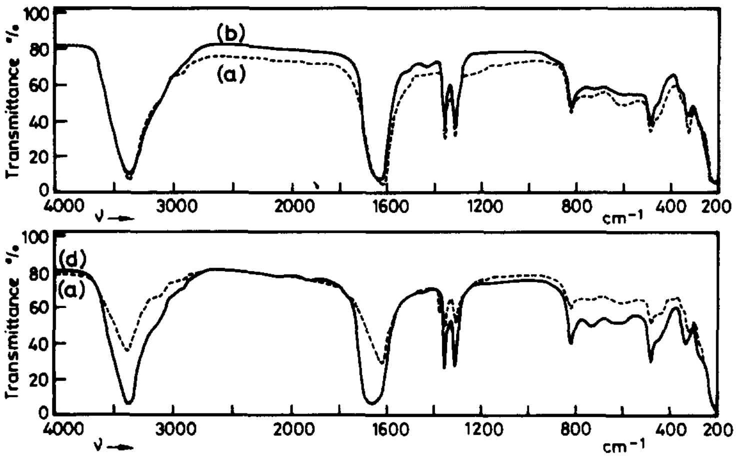

Fig. 5. IR spectra: curve (a) $H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3 : 1); curve (b) $NiC_2O_4 \cdot 2H_2O$ obtained by precipitation; curve (c) $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1); curve (d) $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(Cl)_2 \cdot 6H_2O$ (molar ratio, 1 : 1).

Kinetic study

Using isothermal TG experiments we have studied the mechanism of the thermal dehydration of nickel oxalates mentioned above and have obtained the reaction

$$NiC_2O_4 \cdot 2H_2O(s) \rightarrow NiC_2O_4(s) + 2H_2O(g)$$

The dehydration takes place between 100 and 280 °C when the heating rate is 10 °C min^{-1}. Three isotherms at 210 °C, 220 °C and 230 °C were employed. The TG experiments were carried out in an air stream with a flow of 150 ml min^{-1}.

TABLE 1

Kinetic parameters for the dehydration of $NiC_2O_4 \cdot 2H_2O$ to NiC_2O_4

$NiC_2O_4 \cdot 2H_2O$	E_A (kcal mol^{-1})	K_0 (s^{-1})
obtained by precipitation	14.62	1.7×10^5
from a mechanical mixture of $H_2C_2O_4 \cdot 2H_2O$ plus $Ni(NO_3)_2 \cdot 6H_2O$ (molar ratio, 1 : 1)	24.79	3.3×10^9
from a mechanical mixture of $H_2C_2O_4 \cdot 2H_2O$ plus $NiCl_2 \cdot 6H_2O$ (molar ratio, 1 : 1)	23.29	8.2×10^8
from a mechanical mixture of $H_2C_2O_4 \cdot 2H_2O$ plus $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ (molar ratio, 3 : 1)	30.50	2.3×10^{12}

In all cases the dehydration follows first-order kinetics

$F(\alpha) = \ln(1 - \alpha) = -kt$

The kinetic parameters for the four samples of nickel oxalates studied are given in Table 1.

In Table 1 we can see that the lowest activation energy corresponds to the oxalate obtained by precipitation. Two almost equal activation energies follow, corresponding to oxalates obtained from mechanical mixtures of oxalic acid with the chloride and nitrate salts of nickel, both well crystallized. Finally, we have an activation energy almost double the first activation energy, corresponding to the oxalate obtained from the mixture of oxalic acid and nickel hydroxide carbonate, with the nickel salt poorly crystallized.

DISCUSSION

In our opinion, the formation of the dihydrated oxalate of nickel from the reaction between oxalic acid and different salts of nickel could be explained by looking at the structures of both reactants.

It can be deduced from the crystallographic data [9–12] that oxalic acid has a chain structure of $C_2O_4^{2-}$ groups and molecules of water joined by hydrogen bonds.

The nickel nitrate has its six molecules of water linked to the nickel ion by bonds coordinate with the oxygen, forming a hexaaquonickel complex, $[Ni(H_2O)_6]^{2+}$, with a regular octahedral structure; the Ni–O bond length is 2.03 Å.

The crystal structure of $NiCl_2 \cdot 6H_2O$ contains *trans*-$NiCl_2(H_2O)_4$ units, the Ni–Cl and Ni–O bond lengths being 2.38 Å and 2.10 Å respectively.

Thus, being a hexacoordinated octahedral complex, it is difficult for the reaction to take place according to an associative mechanism because the six ligands around the central atom, Ni(II), do not allow enough space for a new group to enter in the transition period.

Therefore, the main stage in the reaction velocity is the dissociation of the bond between Ni(II) and the leaving groups, accompanied by the demolition of the octahedron.

The mixtures humidify very quickly, which confirms the initial release of coordinate water and demolition of the complex Ni(II) structure, giving an Ni(II) chloride or nitrate saturated solution.

However, the insoluble nickel oxalate is formed by a simple process of precipitation whereas the case of the mixture of the hydroxide carbonate and oxalic acid is different.

The nickel hydroxide carbonate is an insoluble and amorphous salt coming from carbonic acid, whose dissociation constants ($K_1 = 4.6 \times 10^{-7}$ and $K_2 = 4.4 \times 10^{-11}$) are considerably smaller than those of oxalic acid

($K_1 = 6.2 \times 10^{-2}$ and $K_2 = 6.1 \times 10^{-5}$). The formation of the nickel oxalate may be considered as a displacement reaction of a weak acid by a stronger one.

Finally, comparing the times necessary to complete the reaction of the mixtures of nickel salts and oxalic acid allows us to establish that the displacement reaction is much quicker (48 h) than the demolition reaction of the structure of the nickel complexes (7 days).

From all the points mentioned above and from the observed release of hydrochloric and nitric acids, we deduce that the structure of the oxalic acid remains in the nickel oxalate. The ion Ni(II) substitutes the protons of two adjacent acid molecules. The crystalline structure of the dihydrated nickel oxalate given by Deyrieux et al. [13], with chains of metal–oxalate–metal, confirms this scheme.

In relation to the thermal behaviour of the different hydrated nickel oxalates studied, one can observe differences which are related to their formation mechanisms.

In Table 1 we can see that the values of activation energy are practically identical for the mixture of oxalic acid and nickel nitrate and the mixture of oxalic acid and nickel chloride, the nature of the nitrate or chloride anion does not affect the process. However, the activation energy is different for the hydrated nickel oxalate originating from the mixture of oxalic acid and nickel hydroxide carbonate. This confirms the two formation mechanisms of the hydrated nickel oxalate mentioned above.

In relation to the dissociation of the anhydrous oxalate a single dissociation mechanism takes place in the air stream (see eqn. (I)).

As soon as the CO from the decomposition of the oxalate is formed it reacts with oxygen from the air, producing CO_2. This oxidation reaction is extremely exothermic and it occurs simultaneously with the decomposition of the oxalate (endothermic reaction). Therefore, in the DTA curves, both phenomena are shown by only one exothermic peak which appears immediately after the endothermic peak corresponding to the dehydration. Nevertheless, in the nitrogen stream the dissociation is produced by mechanisms (I) and (II) mentioned above. Mechanism (II) is confirmed by X-ray diffraction. The X-ray diagrams of samples taken at 400 °C correspond to mixtures of metallic nickel and nickel oxide, the proportion of both depends on the origin of the oxalate.

At 950 °C all the residues are exclusively nickel oxide. In the TG and DTG curves between 400 and 950 °C an increase in weight is observed, due to the reaction

$$Ni + \tfrac{1}{2}O_2 \rightarrow NiO$$

The nickel takes the necessary oxygen from the equilibrium $2CO + O_2 \rightleftarrows 2CO_2$, which is established between the CO and CO_2 formed in mechanism (I).

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