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DEGRADATION STUDIES ON NICKEL NITRATE HEXAHYDRATE. PART 2. EVOLVED GAS ANALYSIS

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ABSTRACT

The work from Part 1 of this study has been extended by the use of evolved gas analysis. Deaquation and denitration processes have thus been examined in detail and possible mechanisms postulated.

Three factors are involved, namely, the coordination chemistry of nickel, the rate of removal of water from the sample, and the ability of water vapour to hydrolyse the intermediate nickel nitrate dihydrate.

INTRODUCTION

Previous studies of nickel nitrate hexahydrate have shown [1] that on heating, a number of stoichiometric hydrates are formed as intermediates. Not all studies reported the formation of an anhydrous nitrate and many found forms of basic nickel nitrates. In Part 1 [1] we showed that the sometimes conflicting reports can be explained in terms of experimental conditions. The deaquation process was found to be dominated by three factors: the coordination chemistry of nickel and ligand availability, the ease of liberated water removal from the sample, and the reactivity of water vapour.

The aim of this study is to supplement our previously published data [1] on nickel nitrate hexahydrate with results from evolved gas analysis (EGA). Also reported are studies under identical conditions of nickel nitrate hexammine and a nickel nitrate methyl cyanide complex. Together, these enable mechanistic pathways to be determined.

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Limited thermal analysis studies have been made of the ion hydrated forms of nickel nitrate. Wendlandt and Smith [2] noted that the hexammine salt began to lose mass at about 353 K when heated at 5 K min^{-1}. A thermogravimetric analysis (TG) inflection point was observed at 423 K, when the composition approximated $[Ni(NH_3)_4](NO_3)_2$. Further heating resulted in rapid formation of NiO. Rapid dissociation of the nitrate complex was thought to be due to a reaction of nitrate ions with coordinated ammonia groups. Differential thermal analysis (DTA) of the complex showed two endothermic peaks at 423 and 458 K followed by an exothermic peak at 533 K. The former peaks were thought to be caused by evolution of from two to three moles of ammonia while the exotherm by an oxidation–reduction reaction.

Addison et al. [3–5] prepared $Ni(NO_3)_2 \cdot 3MeCN$ which lost one MeCN molecule in vacuum [5]. The product decomposed under vacuum at 443 K leaving anhydrous nickel nitrate as a pure, lime-green powder. The latter gave a large DTA peak at 533 K with a shoulder at 503 K. The shoulder was attributed to the formation of nickel nitrite which then decomposed, giving the main peak.

EXPERIMENTAL

Instrumentation

TG was achieved using a vacuum microbalance system described previously [1,6]. DTA studies utilised a commercial unit which was operated under vacuum [1,6].

For the EGA study [6] an AEI MS10 mass spectrometer was used. This was connected via slow-leak sinters, through an expansion bulb (~ 21), to a previously evacuated sample tube. The latter was heated by a furnace controlled by a Stanton-Redcroft linear temperature programmer (Mk. 3).

Two modes of operation were used for the EGA study. For the measurement of water or ammonia evolution, the sample system was continually evacuated and the gas sampled through the sinters. Thus, the output for a particular mass gave an indication of the rate of evolution of the gas in question. For the study of the denitration process, the system was evacuated prior to heating but then sealed. A final pressure of 10^{-2} Torr was reached and gas loss into the spectrometer was found to be negligible over a 10-h period. Taking into consideration all the possible gases evolved and their equilibrium reactions, then the denitration process can be followed by measuring the m/e 30 (NO) peak height. In addition, to detect the possible formation of a nitrite intermediate, m/e 32 (O_2) was measured.

All experiments used a sample mass of ~ 10 mg, where possible consisting of a single crystal, a heating rate of ~ 1 K min^{-1}, and in vacuum, unless otherwise stated.

Reagents

The hydrated salt was AnalaR grade (BDH) nickel nitrate hexahydrate. This was also used to prepare the hexammine, formed by precipitation using ammonia. The hexammine consisted of small violet crystals and was stored in a desiccator.

The nickel nitrate methyl cyanide complex was prepared using a method described by Addison and Logan [5]. Nickel chloride hexahydrate was kept at 623 K until it had reached the yellow anhydrous form (~ 12 h). Approximately 10 g of the latter was added to 100 cm^3 dinitrogen tetroxide together with a small quantity of methyl cyanide, the mixture being kept at 273 K for 48 h. Finally, the liquid was evaporated off using a rough vacuum. The solid present underwent the colour changes expected [5], going from green through turquoise to a deep green. Care was taken thoughout to exclude moisture and the product stored under vacuum. Infrared analysis showed the salt to contain significant quantities of methyl cyanide and the TG data indicate that the material is $Ni(NO_3)_2 x MeCN$ where $x = 0.732$.

RESULTS

TG data are presented in the form of the fraction decomposed, α, with temperature, T, as are the EGA data for the denitration processes.

Nickel nitrate hexahydrate

Figure 1 shows the EGA results for the rising temperature evolution of water, nitrogen oxides and oxygen from the hexahydrate. The nitrogen oxides trace differs from that obtained previously [7] and this is thought to be due to difficulties in preventing hydrolysis of the nitrate in early experiments.

As discussed earlier, the EGA trace for water (m/e 18) only gives a qualitative indication of the extent of water evolution. A series of peaks are present but although some, notably that at 337 K, reach their maximum almost instantaneously they all show similar decay characteristics. Thus, although water evolution is shown to occur up until 464 K some of that after the last maximum at 445 K may be due to low water throughput.

The oxygen trace is a close parallel of that obtained for the evolution of nitrogen oxides. It thus appears that the products of heating nickel nitrate hexahydrate in vacuum are water only up to a temperature of ~ 460 K and nitrogen oxides/oxygen from 460 K up to 605 K. This suggests that the main nitrate decomposition occurs as either a single step

$$Ni(NO_3)_2 \rightarrow NiO + N_2O_5$$

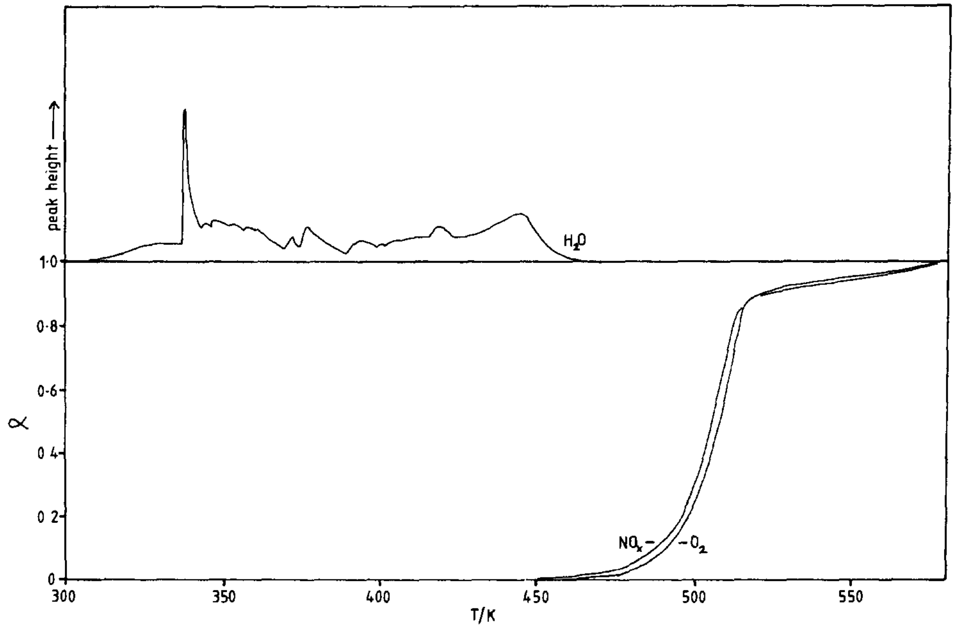

Fig. 1. The EGA traces for the evolution of water, nitrogen oxides and oxygen for the vacuum decomposition of nickel nitrate hexahydrate at 1 K min^{-1}.

or as two steps

$Ni(NO_3)_2 \rightarrow Ni(NO_2)_2 + O_2$

$Ni(NO_2)_2 \rightarrow NiO + N_2O_3$

Nickel nitrate hexammine

The α–T trace for the vacuum TG decomposition of the hexammine is shown in Fig. 2. The final mass loss was 74.8%, this being reached at 610 K. The initial mass loss was significantly slower than that observed [1] for the hexahydrate, probably because of the higher electron-donor properties of ammonia.

A small plateau at $\alpha = 0.24$ corresponds well with the formation of the triammine (theoretical $\alpha = 0.243$). After this point the mass loss is relatively uniform up to 475 K where the sample corresponded to $Ni(NO_3)_2$. At 475 K there is a sharp increase in the decomposition rate followed by a short plateau at 481 K, $\alpha = 0.525$, which does not correspond to any stoichiometric products such as $Ni(NO_2)_2NH_3$ or $Ni(NO_3)(NO_2)$.

Melting was not observed and so the DTA peaks (Fig. 2) for the vacuum decomposition of the hexammine correspond to either chemical processes and/or crystalline changes. All peaks are endothermic except for that at 502.5 K which is exothermic.

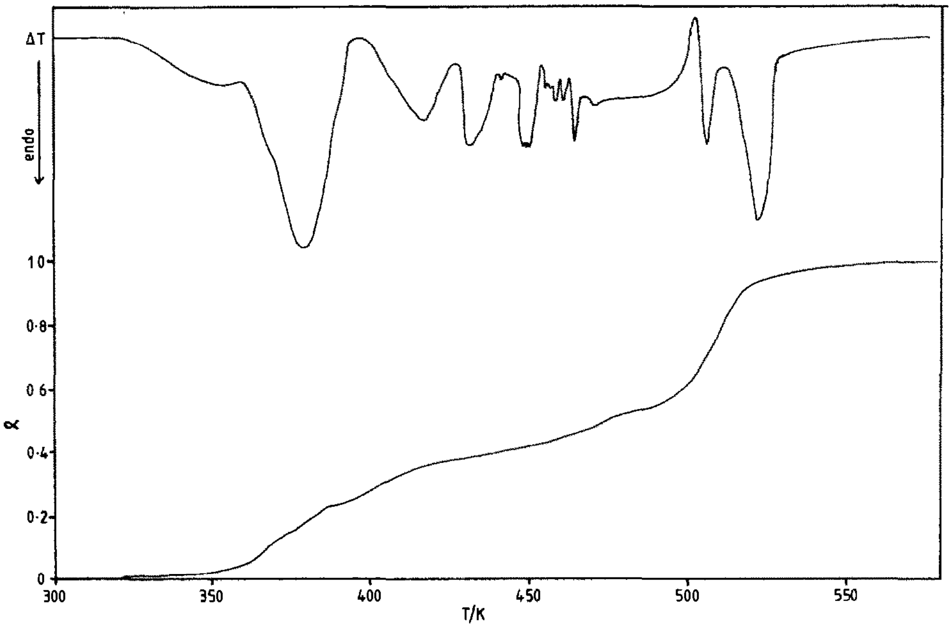

Fig. 2. Plot of α versus T for the vacuum decomposition of nickel nitrate hexammine at 1 K min^{-1} by TG together with the DTA trace for the same process.

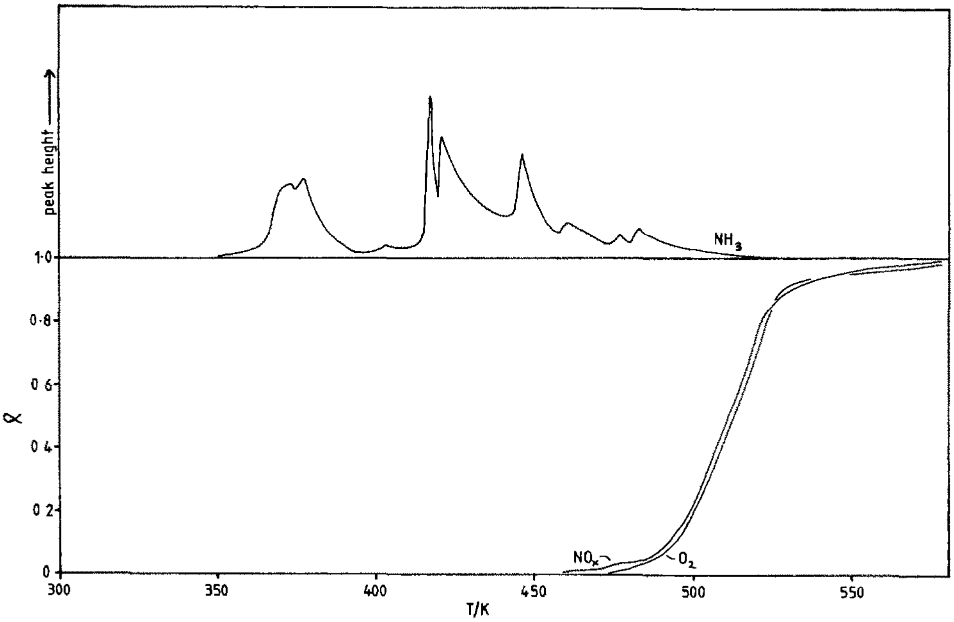

Fig. 3. The EGA traces for the evolution of ammonia, nitrogen oxides and oxygen for the vacuum decomposition of nickel nitrate hexammine at 1 K min^{-1}.

The evolution of nitrogen oxides from the hexammine (Fig. 3) begins at ~ 458 K, the rate rising slowly until a plateau at $\alpha = 0.035$, $T = 478$ K is reached. After this the trace has a sigmoidal shape ending with the formation of NiO at 610 K. The α–T trace for the evolution of oxygen was obtained by pumping on the system until 480 K when virtually all ammonia had been removed (Fig. 3). The trace is similar to that for the nitrogen oxides except for the beginning. The reasons for the early plateau on the nitrogen oxides' trace are unclear.

The evolution of ammonia occurs in a number of stages, each giving rise to a peak (Fig 3). The final two coincide with the initial evolution of nitrogen oxides.

Nickel nitrate methyl cyanide

Figure 4 shows the α–T trace for the vacuum decomposition of the methyl cyanide complex. The mass loss begins at ~ 325 K with the decomposition rate slowly increasing until 391 K, $\alpha = 0.20$. After this point the decomposition is relatively uniform, the rate rising slowly until 501 K, followed by a long decay period, ending with NiO at ~ 610 K.

A series of attempts were made to drive off the methyl cyanide from the nitrate. Addison and Logan [5] reported that $Ni(NO_3)_2 \cdot 2MeCN$ could be

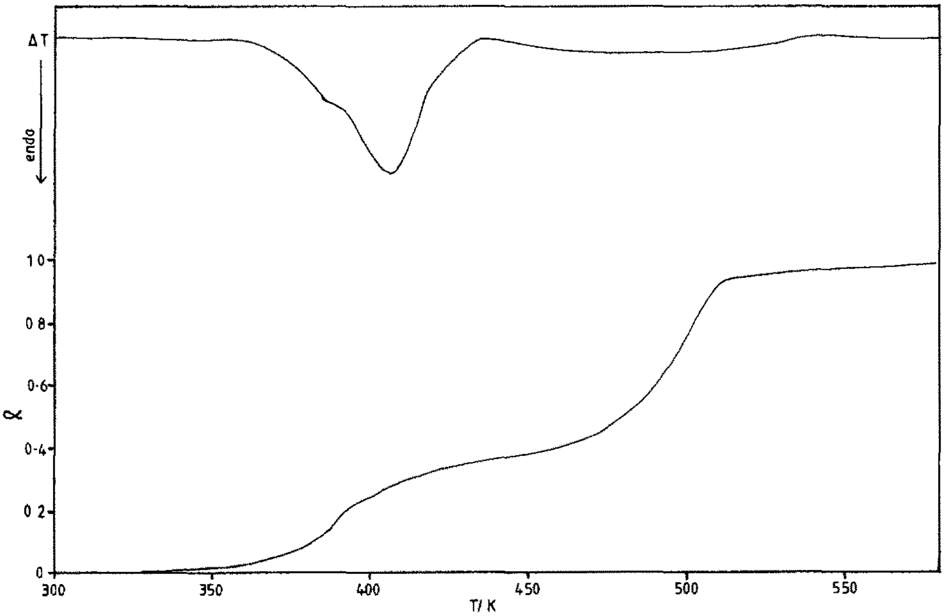

Fig. 4. Plot of α versus T for the vacuum decomposition of nickel nitrate methyl cyanide at 1 K min^{-1} by TG together with the DTA trace for the same process.

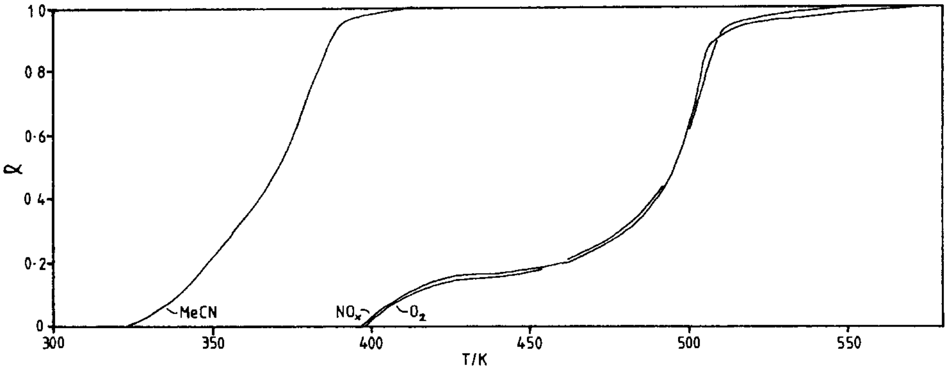

Fig. 5. The EGA traces for the evolution of methyl cyanide, nitrogen oxides and oxygen for the vacuum decomposition of nickel nitrate methyl cyanide at 1 K min^{-1}.

converted to $Ni(NO_3)_2$ by heating under vacuum at 443 K. This could not be reproduced here using a variety of temperatures. Below 353 K the rate of decomposition was insignificant; above this temperature the samples slowly decomposed in a linear fashion to NiO. At no stage was $Ni(NO_3)_2$ formed as a recognisable intermediate.

The DTA for the vacuum decomposition of the methyl cyanide complex using a heating rate of 1 K min $^{-1}$ is shown in Fig. 4. At no point was sample melting observed. The first peak, from ~ 360 K to ~ 437 K has its maximum at 408 K and a shoulder at 386 K. The second is broad and shallow and is between ~ 437 K and ~ 533 K with a maximum at 484 K.

The α–T trace for nitrogen oxides' evolution from the methyl cyanide complex is shown in Fig. 5. The trace begins at 397 K and, after a short induction period, follows a deceleratory mechanism until approximately 430 K. After this point the trace has a sigmoidal appearance, ending at ~ 610 K. The α–T trace for the evolution of oxygen is very similar to that for the nitrogen oxides (Fig. 5).

The α–T trace for the evolution of methyl cyanide from the sample (m/e 41) shows degradation to begin at ~ 324 K. The trace is largely acceleratory, reaching the point $\alpha = 0.95$, $T = 390$ K rapidly. After this there is a short decay period ending at 418 K.

DISCUSSION

Comparison of the TG and DTA results for the vacuum decomposition of nickel nitrate hexahydrate showed that there were many more DTA peaks than there were intermediate hydrates indicated on the TG traces [1]. This suggests that throughout the loss of water there are physical and/or structural changes taking place. These are better shown by comparing the DTA

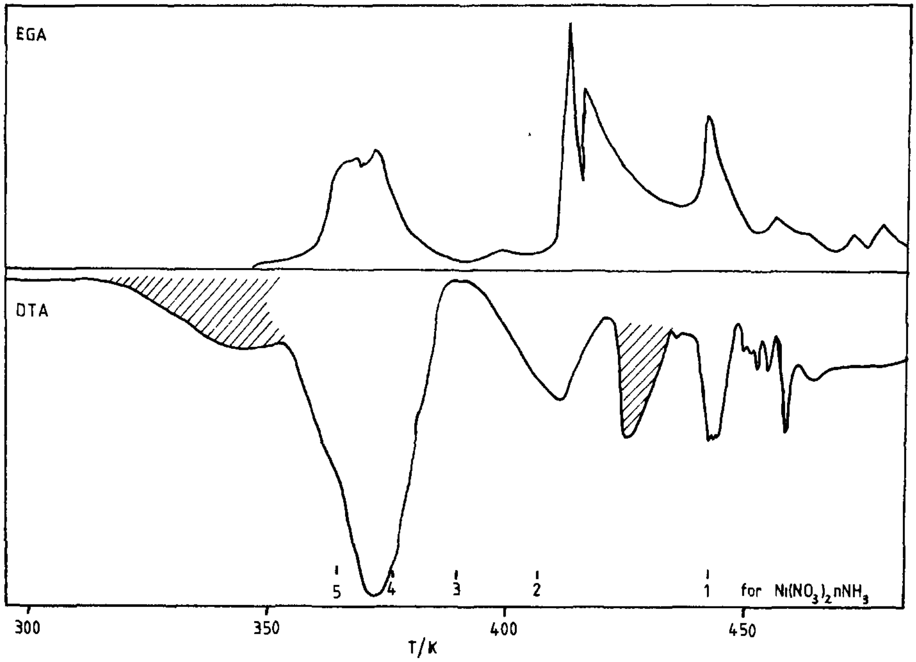

Fig. 6. Comparison of the EGA trace for the evolution of water with the DTA trace for the vacuum decomposition of nickel nitrate hexahydrate.

trace [1] with the EGA trace for the evolution of water (Fig. 6). Non-corresponding peaks on the two traces have been shaded and are discussed below.

The first non-corresponding peak is at 327.5 K on the DTA trace, close to the temperature at which the $5\frac{1}{2}$ hydrate is completely formed. For the compound to lose exactly half a water molecule it is postulated that the water loss and a structural rearrangement, allowing water to act as a bridging ligand, must occur simultaneously

$$[\mathrm{Ni(H_2O)_6}](\mathrm{NO_3})_2 \xrightarrow{-\frac{1}{2}\mathrm{H_2O}} \tfrac{1}{2}[\mathrm{Ni_2(H_2O)_{11}}](\mathrm{NO_3})_4$$

Thus, the peak at 327.5 K must correspond to a further rearrangement. This may involve the formation of "free" water within the lattice which is then rapidly released on liquefaction. Thus, the $4\frac{1}{2}$ hydrate would be formed by two steps.

$$\tfrac{1}{2}[\mathrm{Ni_2(H_2O)_{11}}](\mathrm{NO_3})_4 \rightarrow \tfrac{1}{2}[\mathrm{Ni_2(H_2O)_9(NO_3)_2}](\mathrm{NO_3})_2\mathrm{2H_2O}$$

and

$$\tfrac{1}{2}[\mathrm{Ni_2(H_2O)_9(NO_3)_2}](\mathrm{NO_3})_2\mathrm{2H_2O} \xrightarrow[\text{liquefaction}]{-\mathrm{H_2O}} \tfrac{1}{2}[\mathrm{Ni_2(H_2O)_9(NO_3)_2}](\mathrm{NO_3})_2$$

The next non-corresponding peak is also on the DTA trace, at 316 K, immediately prior to the point at which the 3 hydrate is formed. Water evolution between the $4\frac{1}{2}$ and 3 hydrates is relatively uniform as shown by the EGA trace. The 3 hydrate is unusual since, to retain an octahedral structure, either both unidentate and bidentate nitrate species must be present. There are few examples of such compounds and so the peak at 361 K may signal a change from the previous octahedral structure to a penta-coordinated structure, this involving unidentate nitrate ligands only.

The DTA doublet peak at ~ 377 K has no corresponding EGA peak and coincides with solidification. This occurs after the maximum rate of water evolution in the transition from the 3 to the $2\frac{1}{2}$ hydrate. The formation of a half integral hydrate must encourage solidification since it necessarily involves bridging water ligands with attendant dimerisation of $Ni(H_2O)_n$ units. The structure may be similar to that of the 3 hydrate or have changed during solidification. In any event, further deaquation to the 2 hydrate gives rise to a further non-corresponding DTA peak at 396 K.

The 396 K peak may be associated with a structural change in the sample near the beginning of the transition between the $2\frac{1}{2}$ and the 2 hydrates. Hathaway et al. [8] found that the dihydrate contains nickel in an octahedral field of oxygen atoms. This could occur if the compound contained bidentate or bridging nitrate species. Alternatively, both water molecules could act as bridging ligands. Either structure must be different from that for the $2\frac{1}{2}$ hydrate and the DTA peak at 396 K may be evidence that the $2\frac{1}{2}$ hydrate contains a penta-coordinate nickel species. After the 2 hydrate, the two traces are fairly similar.

Study of the results for the decomposition of the hexammine shows that the processes cannot be so clearly delineated as with the hydrate. However, ammonia cannot act as a bridging ligand, this explaining the absence of half integral ammine intermediates.

Comparing the DTA and EGA traces for the evolution of ammonia (Fig. 7) it can be seen that the first DTA peak does not correspond to a peak on the EGA trace. However, the rate of this transition is very slow and so the fast pumping speed of the EGA system may have prevented its detection. As discussed previously [1], there is no theoretical justification for the existence of a particularly stable coordination number other than the maximum 6. The presence of the 3 ammine as a relatively stable intermediate suggests otherwise. The trihydrate intermediate was the longest lived during the decomposition of the hexahydrate, lasting over a temperature increase of 8 K. In both cases it is the first point at which both nitrate species have become ligands, thus neutralising the central cation's charge.

The transitions after the triammine intermediate are not as straightforward as the transitions before, with respect to the DTA and EGA traces. Not only are they more complex but most of the peaks do not match. However, the TG result does not show the presence of a further ammine intermediate and so no conclusions can be drawn as to possible mechanisms.

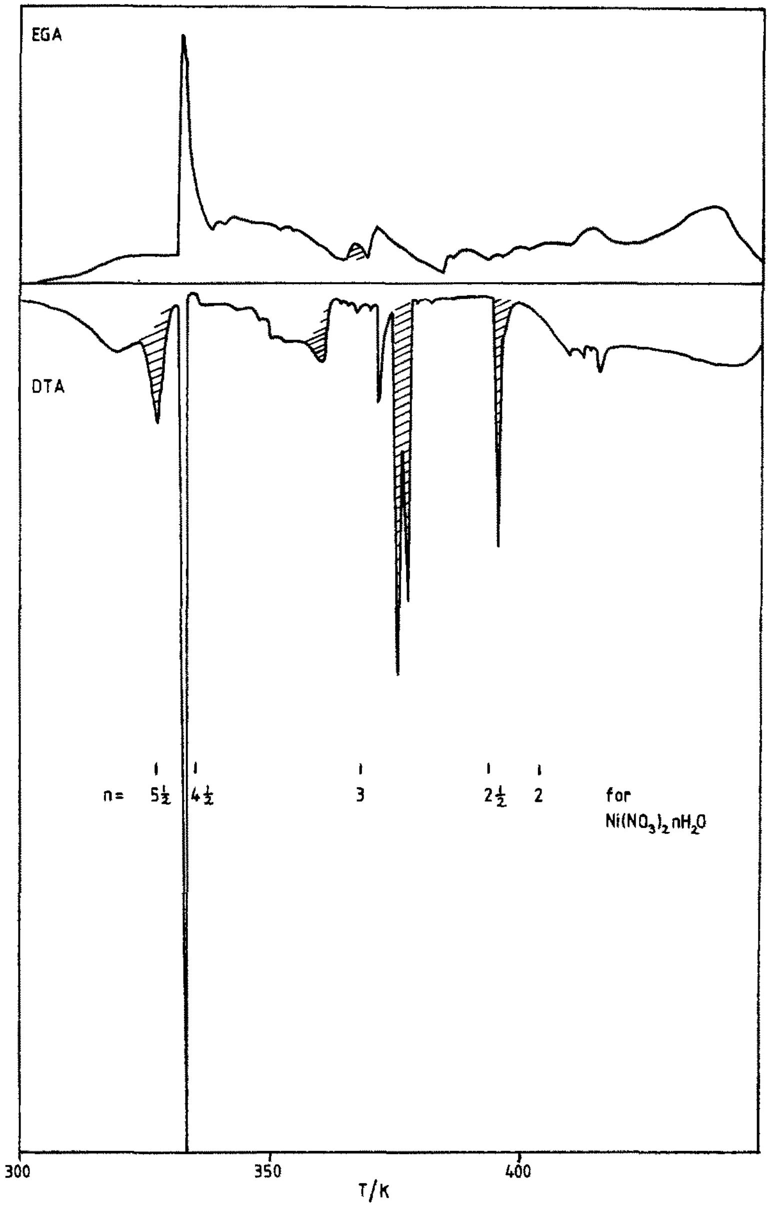

Fig. 7. Comparison of the EGA trace for the evolution of ammonia with the DTA trace for the vacuum decomposition of nickel nitrate hexammine.

The results for the nickel nitrate methyl cyanide complex are more straightforward than was the case for the aquo and ammine compounds. Comparison of the DTA, TG and EGA data (Figs. 4 and 5) indicates that denitration occurs in two stages. The first is very endothermic and leads to the peak at 408 K overlapping that due to the loss of methyl cyanide at 386

K. A second process has given rise to the second, shallow endotherm. The reasons for this are unclear but it may point to the existence of differing forms of anhydrous nickel nitrate.

SUMMARY

Previous work [1] showed that the degradation of nickel nitrate hexahydrate is dominated by three factors: the coordination chemistry of nickel, the rate of removal of water from the sample, and the ability of water vapour to hydrolyse the intermediate nickel nitrate dihydrate. This study has concentrated on the mechanisms in operation when the rate of water removal from the system is very high, i.e., with a low heating rate and in vacuum. Using EGA evidence, mechanisms for the formation of various integral and half integral hydrates have been discussed.

REFERENCES

1 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 86 (1985) 119.
2 W.W. Wendlandt and J.P. Smith, The Thermal Properties of Transition Metal Ammine Complexes, Elsevier, New York, 1967.
3 C.C. Addison and D. Sutton, J. Chem. Soc., (1964) 5553.
4 C.C. Addison and B.J. Hathaway, J. Chem. Soc., (1958) 3099.
5 C.C Addison and N. Logan, in W.L. Jolly (Ed.), Preparative Inorganic Reactions, Vol. 1, Wiley-Interscience, London, 1971, p. 141.
6 T.J. Taylor, Ph.D. Thesis, Salford, 1982.
7 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 51 (1981) 269.
8 B.J. Hathaway, D.G. Holah and M. Hundson, J. Chem. Soc., (1963) 4586.