Thermochimica Acta, 103 (1986) 333–340
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DEAQUATION AND DENITRATION STUDIES ON COPPER NITRATE TRIHYDRATE

T.J. TAYLOR * D. DOLLIMORE ** and G.A. GAMLEN

Department of Chemistry and Applied Chemistry, University of Salford, Salford, M5 4WT (Gt. Britain)

(Received 17 December 1985)

ABSTRACT

Previous studies on the thermal degradation of copper nitrate trihydrate have been reviewed. These indicate that the conditions used strongly influence the processes involved. The degradation has been studied here using slow heating rates and in vacuum, so reducing these effects. Possible mechanisms using these conditions have been discussed, using data for the degradation of the ammine complex to supplement the study.

INTRODUCTION

The thermochemistry of inorganic nitrates has been a little studied field. Transition metal nitrates are sometimes used as precursors in the production of metal oxide supported catalysts although little appears to be known about the processes occurring when the oxysalts are converted thermally to the oxides. Most oxysalts are, in fact, hydrated and so do not decompose in simple stages. Previous studies, as described here, often have not examined these stages in detail.

Mellor [1] noted that anhydrous copper nitrate was reported to begin to decompose at 428–433 K. The trihydrate was said to melt at 387.49 K, freeze at 368.56 K and boil at 443 K with the evolution of nitric acid and the formation of a basic salt; indeed the formation of a basic salt has been noted at 338 K. The hexahydrate was stated to melt at 331 K although the salt has been observed to decompose to the trihydrate and water 299.4 K and to form the trihydrate in air.

Gordon and Campbell [2] conducted DTA studies on a wide range of nitrates and perchlorates. They found that copper nitrate trihydrate gave a

---

* Present address: Corporate Technology, Allied-Signal Inc., P.O. Box 1021R, Morristown, NJ 07960, U.S.A.

** Present address: Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606, U.S.A.

0040-6031/86/$03.50 © 1986 Elsevier Science Publishers B.V.

large endotherm from 377 to 719 K with minor peaks at 425.49 and 583 K.

Wendlandt [3] in a study of a series of nitrates found that copper nitrate trihydrate began to lose water at 343 K. After a region of rapid mass loss a break in the curve was observed at 438 K. The composition at this point corresponded approximately to an oxynitrate ($Cu_2O(NO_3)_2$). This basic nitrate had been previously reported by Pettier and Duval [4]. They found that copper nitrate hexahydrate evolved water and nitrogen oxides above 331 K but, in the region of 421 to 473 K a green, basic nitrate of composition $Cu(NO_3)_2 2Cu(OH)_2$ was detected. This compound decomposed between 473 and 880 K, the residue consisting of CuO.

Keely and Maynor [5] found that the decomposition to cupric oxide was complete at 623 K although with a much lower heating rate it was observed to finish at 483 K. They found no evidence for the formation of the oxynitrate as had been reported by Sneed et al. [6] and Wendlandt [3]. The decomposition of the trihydrate in air has also been briefly investigated by Pierron et al. [7] when considering the preparation of copper oxide on an alumina support. Using differential thermal analysis (DTA) they assumed that an alumina impregnated with $Cu(NO_3)_2 3H_2O$ and dried for 20 h at 393 K resulted in supported $Cu(NO_3)_2$. This decomposed endothermically to CuO between 473 and 573 K, the maximum rate being near 533 K.

Also, Addison and Hathaway [8] as part of a study of anhydrous metal nitrates, found that the copper nitrate sublimed slowly at 373 K and rapidly at 473 K.

The aim of this work was to characterize the degradation processes occurring on heating copper nitrate trihydrate in vacuum. This has been supplemented by work on the ammine complex also.

EXPERIMENTAL

Thermogravimetry was achieved using a vacuum microbalance system previously described [9]. DTA utilized a Stanton Redcroft 671 unit operated under vacuum. Evolved gas analysis (EGA) was performed using a mass spectrometer (MS) based system described elsewhere [10]. This could be operated in one of two modes but both involved a vacuum environment around the sample. The first was essentially a leak into the MS with a vacuum bypass to carry away most of the gaseous products. The second was a rising pressure method in which the system was sealed after an initial vacuum of 10^{-6} Torr was reached. Thereafter the sample environment was continuously monitored via a slow leak sinter such that negligible gas loss was achieved. Pressure rise was to approximately 10^{-2} Torr. All experiments used a sample mass of ~ 10 mg, where possible consisting of a single crystal, and a heating rate of 1 K min^{-1}.

The hydrated salt was "Analar" grade copper nitrate trihydrate. This was also used to prepare the ammine complex; precipitated as deep blue crystals by passing ammonia through an ammoniacal solution of the trihydrate.

RESULTS

The TG data is presented here in the form of the fraction decomposed, α, versus temperature, T.

Two α–T traces were derived from the TG system for the vacuum decomposition of copper nitrate trihydrate (Fig. 1). These were based on the actual total mass loss of 73.19% and the theoretical mass loss of 67.08% (assuming an end product of CuO), respectively. The difference is probably due to sublimation of anhydrous copper nitrate [8]. Evidence of this was found at the end of the experiment when a surface layer of copper oxide was observed on the hangdown tube outside the hot zone. The α–T trace based on the theoretical mass loss is useful for determining the composition of intermediates formed during the decomposition and it is this trace which will be used to describe the steps occurring.

The initial mass loss, beginning at 314 K, is deceleratory ending at $\alpha = 0.05$, $T = 330$ K with the formation of an intermediate corresponding to $Cu(NO_3)_2 \cdot 2\ 1/2\ H_2O$ (theoretical $\alpha = 0.055$). Further, rapid, mass loss begins at 338 K and ends after an uneven trace at $\alpha = 0.43$, $T = 380$ K with an inflection. The mass loss at this point corresponds to an intermediate $3Cu(NO_3)_2Cu(OH)_2$ (theoretical $\alpha = 0.433$). Further loss takes place at a reduced rate and in an uneven fashion until approximately 455 K. After this point a long decay period takes place, ending with the formation of CuO at 585 K. It is not possible to say at which point sublimation began although

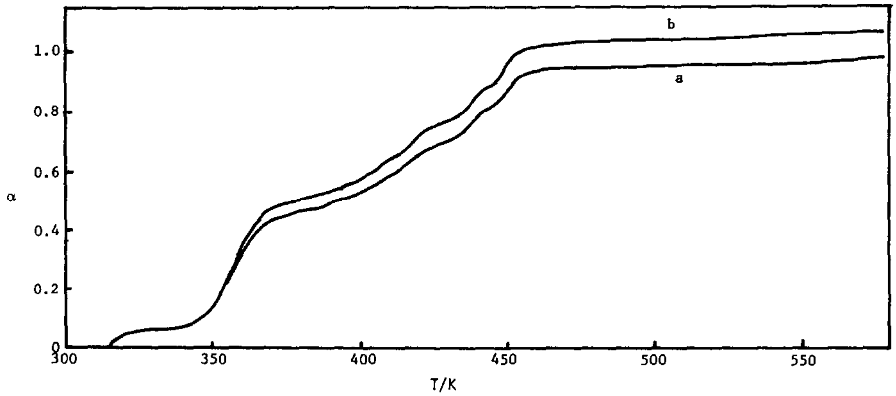

Fig. 1. Plots of α versus T for the vacuum decomposition of copper nitrate trihydrate; based on (a) the actual and (b) the theoretical mass losses.

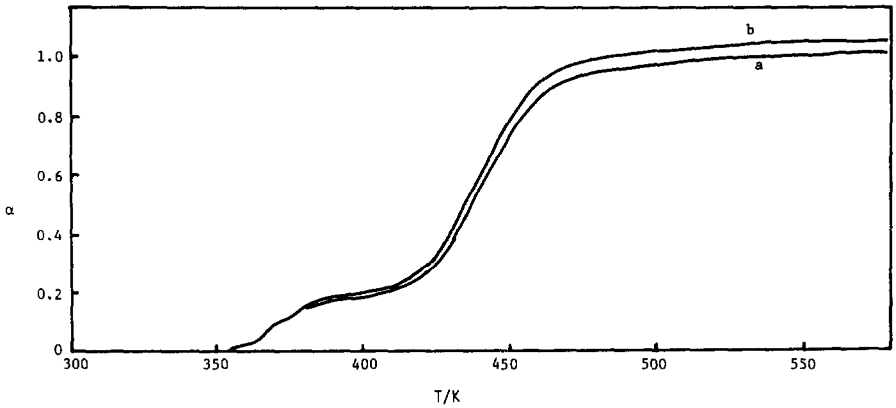

Fig. 2. Plots of α versus T for the vacuum decomposition of copper nitrate tetrammine; based on (a) the actual and (b) the theoretical mass losses.

from the matching of the inflection to a stoichiometric compound it is thought to be at 370 K.

Again, two α–T traces, both shown in Fig. 2, were derived from the TG system for the vacuum decomposition of copper nitrate tetrammine. These were based on the actual total mass loss of 72.45% and the theoretical mass loss of 68.88%, respectively, the difference again probably due to the sublimation of anhydrous copper nitrate. The α–T trace based on the theoretical mass loss is used to describe the decomposition.

The initial mass loss, beginning at 352 K is acceleratory ending in an inflection at 370 K. The mass at this point corresponds with an intermediate of formula $Cu(NO_3)_2 3NH_3$. Further mass loss is deceleratory ending at 395 K with the formation of $Cu(NO_3)_2 2NH_3$. After this point the α–T trace is sigmoidal in shape with a long decay period starting at 480 K and ending at 605 K with the formation of CuO.

The DTA trace for the decomposition of the trihydrate is shown in Fig. 3. As can be seen, the trace consists of two main peaks, at 357 and 458 K, both with shoulders, and three minor peaks, at 325, 395 and 434 K. The tetrammine trace is shown in Fig. 4 and, indicates that, there are "minor" peaks, at 404 and 495 K and two main peaks, the first being at 378 K and the second having maxima at 458, 467, and 475 K.

Figure 5 shows the α–T trace derived from an EGA study of the vacuum decomposition of copper nitrate trihydrate at 1 K min^{-1}; this refers to the total evolution of all nitrogen oxides. As can be seen, the evolution begins at approximately 341 K, the trace being approximately linear until 368 K after which it assumes a sigmoidal shape until 430 K where a second sigmoidal period begins. The latter ends at 460 K, after which there is a long decay period ending at $\alpha = 1.0$, $T = 585$ K.

The EGA trace for water evolution is also shown in Fig. 5. The trace has three main features; two small peaks of similar proportions with maxima at

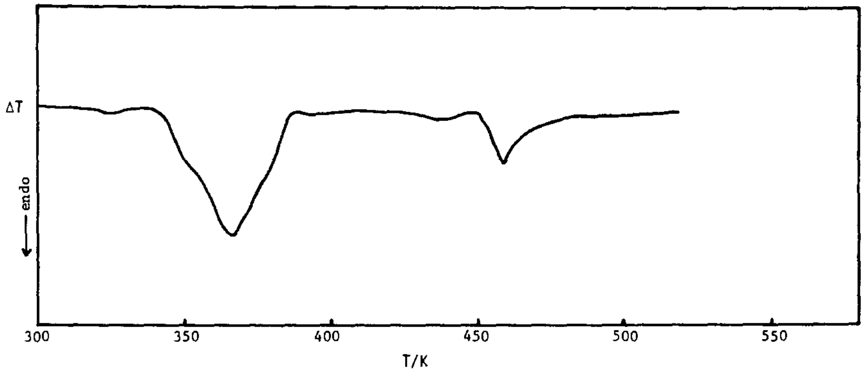

Fig. 3. The DTA trace for the vacuum decomposition of copper nitrate trihydrate.

325 and 456 K, and a larger peak consisting of a number of smaller overlapping peaks. The latter are indicated by the presence of a number of shoulders. Thus the overall maximum is at 370 K with shoulders at 364, 377, 386 and 408 K.

Comparison of the H_2O and NO_x traces shows that the evolution of these products overlaps considerably. Therefore, it was not possible to study the main decomposition process after pumping off the evolved water. The *m/e* 32 peak, due to oxygen was monitored during decomposition but this remained constant at the background level. This suggests that the following equilibrium was in operation:

$$H_2O + 2NO_2 + \frac{1}{2}O_2 \rightleftharpoons 2HNO_3$$

the RHS being favoured.

Figure 6 shows the EGA traces for the decomposition of the copper nitrate tetrammine; the α–T trace refers to the evolution of NO_x. As can be seen, the trace begins at 395 K and rises with an increasing rate, to $\alpha = 0.30$,

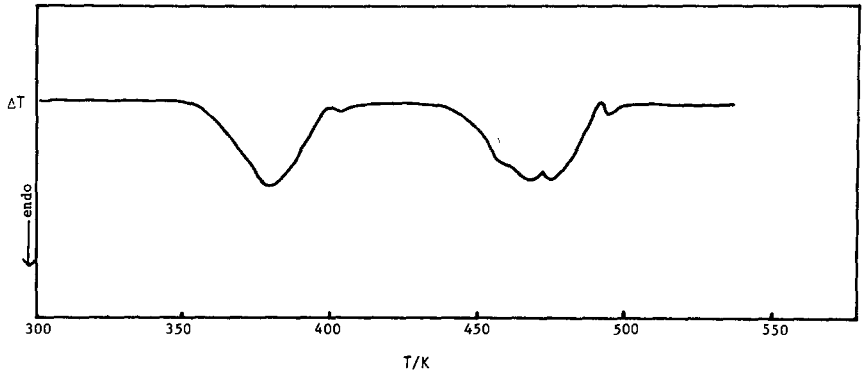

Fig. 4. The DTA trace for the vacuum decomposition of copper nitrate tetrammine.

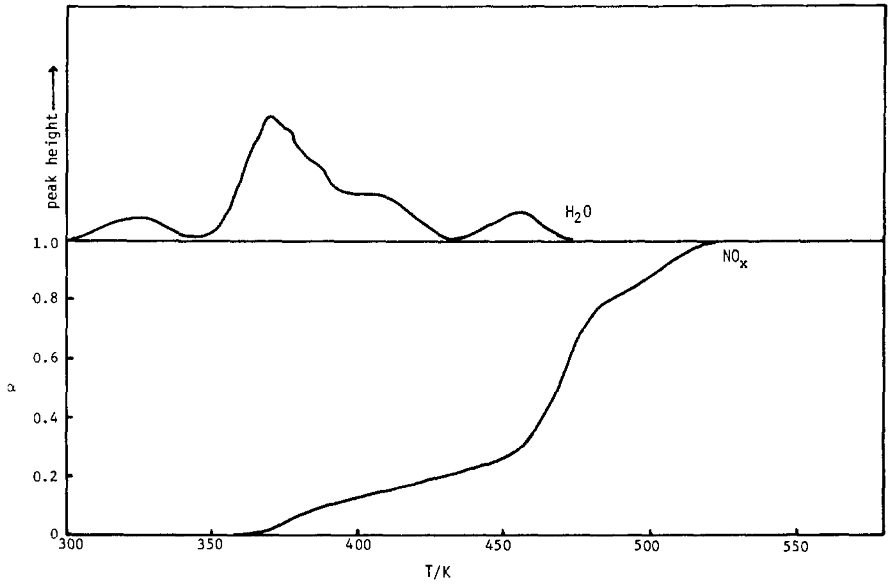

Fig. 5. The normalized EGA trace for the evolution of water and NO_x for the vacuum decomposition of copper nitrate trihydrate.

$T = 435$ K. After this point, the trace is approximately linear until $\alpha = 0.87$, $T = 475$ K after which the trace is deceleratory ending at 610 K.

The second trace in Fig. 6 shows the evolution of ammonia from the

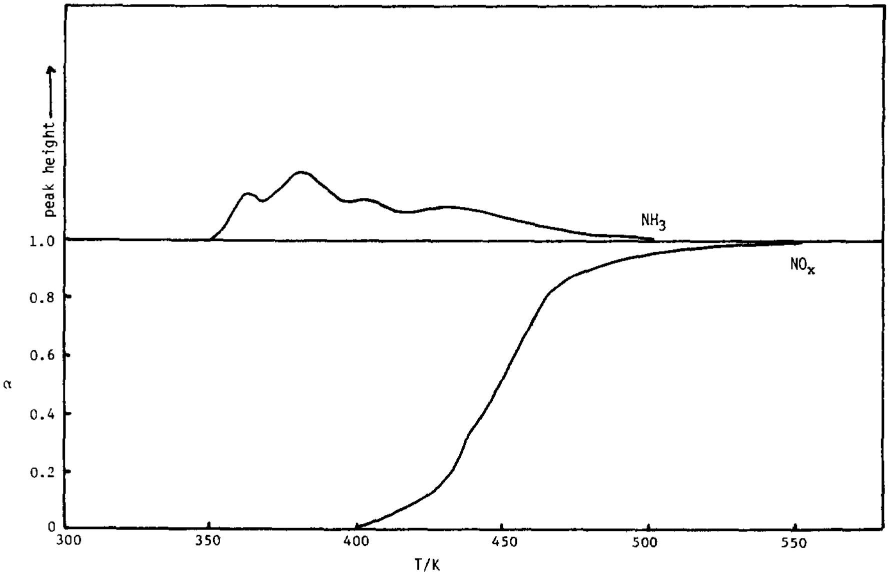

Fig. 6. The normalized EGA trace for the evolution of ammonia and NO_x for the vacuum decomposition of copper nitrate tetrammine.

sample. The evolution begins at 350 K rising to a peak at 363 K. This overlaps with a second larger peak, the latter having a maximum at 379 K. After this there are two, broad overlapping peaks with maxima at approximately 402 and 437 K.

It proved impossible to follow the evolution of oxygen from this compound. The traces were variable and very dependent on sample mass. It was thought that this was due to complex equilibria processes involving the nitrogen oxides, oxygen and ammonia.

DISCUSSION

The thermal analysis studies of copper nitrate trihydrate indicate the existence of a number of separate processes. As with nickel [11], these may be concerned with the coordination properties of divalent copper.

The typical coordination number of divalent copper is four and the arrangement of these four ligands is square planar. However, other potential ligands may be weakly associated above and below the complex, so forming a distorted octahedral. In addition, copper forms a number of polynuclear complexes, often consisting of chains of copper and ligand species. Thus the trihydrate is capable of forming a dimeric type of structure of formula $[Cu_2(H_2O)_6]^{2+}$ with two of the water molecules acting as bridging ligands. The initial loss of half a water molecule points to an extension of the structure to form a trimeric type of structure.

Subsequent decomposition of the compound ended with the formation of the basic nitrate $3Cu(NO_3)_2 \cdot Cu(OH)_2$. This must have involved a reaction between the water present in the compound and the copper nitrate since the decompositions were performed in vacuum. It should be noted that the TG trace did not show the formation of any intermediates between the 5/2 hydrate and the basic nitrate. Also, the EGA traces (Fig. 5) show that water loss and the evolution of nitrogen oxides occurred simultaneously during this transition. The temperature of formation of the basic nitrate was 367 K and the EGA results show that $\alpha = 0.22$ for NO_x evolution at this point. Given the differences between the equipment this is reasonably close to the theoretical value of $\alpha = 0.25$. The difference may have been caused by the subsequent sublimation of copper nitrate, this leading to a mass loss observable using TG but not necessarily EGA as discussed below.

After the formation of the basic copper nitrate there are large differences in the shapes of the TG and EGA traces. The studies on anhydrous copper nitrate described by Addison and Logan [12] indicate that the gaseous compound does not decompose below 499 K but at this temperature decomposition occurs suddenly and completely. Thus, in the experiments performed here, it would appear that copper nitrate may sublime, causing mass loss, and condense on a cooler part of the equipment with no attendant NO_x evolution over most of the temperature range studies.

The EGA trace for the evolution of water (Fig. 5) indicates that the hydroxide species are present in the sample during sublimation and that therefore copper nitrate is possibly subliming from the basic copper nitrate compound. Alternatively, copper nitrate molecules may be able to leave the sections of the lattice disrupted by evolving water molecules.

Unlike water, ammonia cannot act as a bridging ligand, this explaining the absence of any half integral ammine intermediates. The starting compound is a square planar complex with the four ammonia molecules acting as ligands [13]. In order to retain this type of structure then the first stable intermediate, the 2 ammine, must have two unidentate nitrate species as ligands. Further deammination would have to involve the nitrate species as unidentate ligands to further retain the structure but this does not seem to have occurred. After the 2 ammine intermediate the TG trace (Fig. 2) shows the compound breaking down to CuO in a single step. The EGA traces (Fig. 6) show that the ammonia evolution is more rapid at the beginning of the final stage of the decomposition.

The DTA trace (Fig. 4) for the final stage of the decomposition indicates that there is more than one process occurring but the reasons for this are unclear.

Wallwork et al. [14] found that anhydrous copper nitrate consists of infinite chains of copper atoms bridged by unidentate nitrate groups. This compound is clearly not very stable and has not been observed in these studies. In addition, none of the work described earlier has reported the formation of solid anhydrous copper nitrate during the decomposition of a copper nitrate compound.

REFERENCES

1 J.W. Mellor, Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 3, Longmans, London, 1923, p. 280.
2 S. Gordon and C. Campbell, Anal. Chem., 27 (1955) 1102.
3 W. Wendlandt, Texas J. Sci., 10 (1958) 392.
4 S. Peltier and C. Duval, Compt. Rend., 226 (1948) 1727.
5 W.M. Keely and H.W. Maynor, J. Chem. Eng. Data, 8 (1963) 297.
6 M.C. Sneed, J.L. Maynard and R.C. Brasted, Comprehensive Inorganic Chemistry, Vol. 2, Van Nostrand, New York, 1954, p. 87.
7 E.D. Pierron, J.A. Rashkin and J.F. Roth, J. Catal., 9 (1967) 38.
8 C.C. Addison and B.J. Hathaway, J. Chem. Soc., (1958) 3099.
9 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 86 (1985) 119.
10 D. Dollimore, G.A. Gamlen and T.J. Taylor, Thermochim. Acta, 91 (1985) 287.
11 T.J. Taylor, D. Dollimore, G.A. Gamlen, A.J. Barnes and M.A. Stuckey, Thermochim. Acta, in press.
12 C.C. Addison and N. Logan, Adv. Inorg. Radiochem., 6 (1963) 71.
13 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd edn., Interscience, New York, 1972, p. 528.
14 S.C. Wallwork, Proc. Chem. Soc., London, (1952) 311; B. Duffin and S.C. Wallwork, Acta Crystallogr. Sect. A, 33 (1963) 16.