Journal of Thermal Analysis, Vol. 20 (1981) 459–462

STUDIES ON THE THERMAL DECOMPOSITION OF $Cu(NO_3)_2 \cdot 3\,H_2O$

J. GHOSE and A. KANUNGO*

*Department of Chemistry, I. I. T., Kharagpur, India — *Department of Chemistry, SUNY at Stony Brook, N. Y. 11794, U. S. A.*

(Received July 18, 1980)

The thermal decomposition of $Cu(NO_3)_2 \cdot 3\,H_2O$ was studied using DTA, DTG, TG and X-ray techniques. The three endothermic changes were analyzed and the intermediate compound formed was confirmed as monoclinic basic copper nitrate, $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. With a hot-plate microscope the melting point of $Cu(NO_3)_2 \cdot 2\,H_2O$ was determined as 391 K.

The most common method for the preparation of pure CuO is by the thermal decomposition of crystalline copper nitrate, $Cu(NO_3)_2 \cdot 3\,H_2O$. Although some work has recently been done on the thermal decomposition of basis copper nitrate [1, 2], no qualitative data are available in the literature on the thermal behaviour of crystalline copper nitrate. Some early work has shown that, on heating, this compound melts at 387 K, and in the course of decomposition to cupric oxide, an intermediate basic nitrate is formed [3]. Later, Gordon *et al.* [4] reported three endothermic peaks in the DTA curve of this compound, without discussing their origin. Thermogravimetric studies on this compound have been reported separately by Palei *et al.* [5] and Keeley *et al.* [6]. While Palei *et al.* reported the formation of an intermediate basic nitrate, $Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$, Keeley *et al.* completely ruled out the formation of an intermediate compound and suggested that $Cu(NO_3)_2 \cdot 3\,H_2O$ decomposes directly into CuO in a single step.

Thus, the data in the literature are rather contradictory and hence the present work was taken up to establish quantitatively the course of the thermal decomposition of crystalline copper nitrate using DTA, TG, DTG and X-ray techniques.

Experimental

DTA, TG and DTG of the dried and finely powdered $Cu(NO_3)_2 \cdot 3\,H_2O$ were carried out with a MOM derivatograph in air. 181.5 mg of the sample was weighed in a Pt crucible. The rate of heating was 10 or 15°/min over the temperature range 303 K to 1273 K, with the DTA and DTG sensitivities at 1/10. The X-ray diffraction patterns were obtained with a Dron-I, X-ray diffractograph. CuKs radiation (λ = 1.542 Å) was used.

Results and discussion

The thermoanalytical curves of $Cu(NO_3)_2 \cdot 3\,H_2O$ (10°/min) are shown in Fig. 1. The DTA curve has three endothermic peaks and the DTG curve indicates that only the second and third endothermic peaks are accompanied by weight loss. Thus, the first endothermic peak, at 409 K, is probably due to a physical change, such as melting of the crystals. The reported melting point of crystalline $Cu(NO_3)_2 \cdot 3\,H_2O$ is 387 K [3], which is lower than the peak temperature. However, on determination of the m.p. of the crystals with a hot-plate microscope it was found

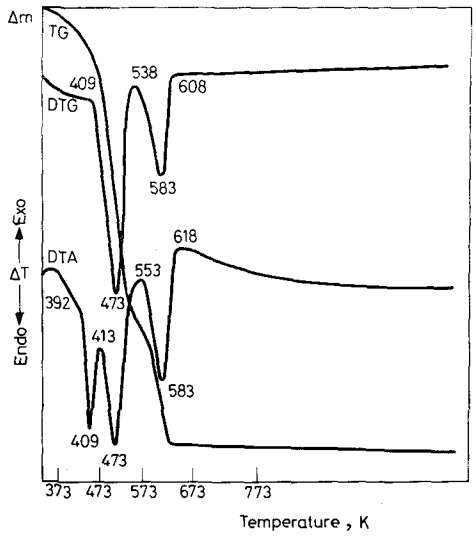


Fig. 1. Thermal curves of $Cu(NO_3)_2 \cdot 3\,H_2O$

to be 391 K and not 387 K. This is also the temperature where the change begins, as shown in the DTA curve. Hence, the first endothermic peak is due to melting of the crystals, but as DTA is a dynamic process the temperature of the melting process is recorded at a higher value, i.e. 409 K.

The second endothermic peak, at 476 K, is probably due to the formation of an intermediate compound. In the literature, there has been some controversy regarding the formation of an intermediate, but both the DTA and DTG curves in Fig. 1 show that an intermediate is formed. This is in contradiction with the reports of Keeley *et al.*, but their reports were based only on thermogravimetric studies, which, unless carried out at a very slow rate, are unable to show the break between the second and third endothermic processes. This has also been observed in the present work; the TG curve at 15°/min shows the total weight loss in a single step, at 10°/min there is a very small step between the second and third DTA peaks, and at 5°/min this step is quite prominent. Nevertheless, in all the runs,

the DTG always showed the weight loss to occur in two steps. The intermediate compound is probably a basic nitrate of copper. Palei *et al.* have reported this compound to be $Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$, whereas Sneed *et al.* have described it as $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. The TG curve shows that the weight loss during the formation of this compound is 51.2%. Now, the calculated weight loss during the conversions

(i) $Cu(NO_3)_2 \cdot 3\,H_2O \rightarrow Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$ and

(ii) $Cu(NO_3)_2 \cdot 3\,H_2O \rightarrow Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$ are 47.35% and 50.51%,

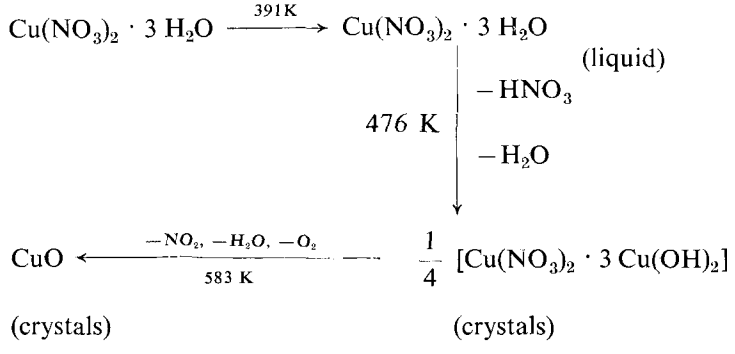
respectively. The experimental weight loss corresponds to conversion (ii), and hence it seems that the intermediate compound is $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. Chemical analysis also confirmed this formula. Finally, the powdered X-ray pattern showed it to be monoclinic copper nitrate hydroxide, $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. The X-ray pattern of the basic nitrate did not have any lines of orthorhombic gerhardtite. This is to be expected, as the orthorhombic form changes to the monoclinic one above 413 K [7], and the basic nitrate was obtained at 476 K. Hence, TG, chemical analysis and X-ray analysis all conclusively show that the intermediate compound formed at 476 K is $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$, and not $Cu(NO_3)_2 \cdot 2\,Cu(OH)_2$ as reported by Palei *et al.*

The third peak, at 583 K, is due to the decomposition of the basic nitrate to cupric oxide, which begins at 553 K. This is similar to the reports of Ilcheva et al. The formation of cupric oxide was also indicated by the 17.63% weight loss in TG as compared to the calculated 16.05% weight loss for the conversion

$$Cu(NO_3)_2 \cdot 3\,Cu(OH)_2 \rightarrow CuO\,.$$

Finally, X-ray analysis of the final product conclusively shows it to be CuO.

Thus, from these results it may be concluded that the thermal decomposition of copper nitrate crystals to cupric oxide occurs in three steps, which can be represented schematically as follows.



References

1. L. ILCHEVA, M. MANEVA and P. BOZADZIEV, J. Thermal Anal., 16 (1979) 205.
2. J. P. AUFFREDIE, D. LOUER and M. LOUER, J. Thermal Anal., 16 (1979) 329.
3. M. C. SNEED, J. L. MAYNARD and R. C. BRASTED, Comprehensive Inorganic Chemistry, Van Nostrand, N. Y. 1954, Vol. 2, p. 87.
4. S. GORDON and C. CAMPBELL, Anal. Chem., 27 (1955) 1102.
5. P. N. PALEI, I. G. SENTYURIN and I. S. SKYARENKO, Zh. Analit. Khim., 12 (1957) 318.
6. W. M. KEELEY and H. W. MAYNOR, J. Chem. Eng. Data, 8 (1963) 297.
7. H. R. OSWALD, Z. Krist., 116 (1961) 210.

RÉSUMÉ — On a étudié par ATD, TGD, TG et rayons X, la décomposition thermique de $Cu(NO_3)_2 \cdot 3\,H_2O$. On a analysé les trois effets endothermiques et confirmé que le composé intermédiaire formé est le nitrate basique de cuivre, $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. Avec un microscope à platine chauffante on a déterminé le point de fusion de $Cu(NO_3)_2 \cdot 2\,H_2O$ égal à 391 K.

ZUSAMMENFASSUNG — Die thermische Zersetzung von $Cu(NO_3)_2 \cdot 3\,H_2O$ wurde durch DTA, DTG, TG und Röntgentechniken verfolgt. Die drei endothermen Änderungen wurden analysiert und die gebildete Zwischenstufe als monoklines basisches Kupfernitrat, $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$ bestätigt. Mit einem Heizplattenmikroskop wurde der Schmelzpunkt von $Cu(NO_3)_2 \cdot 2\,H_2O$ bei 391 K bestimmt.

Резюме — С помощью ДТА, ДТГ, ТГ и рентгенографического анализа изучено термическое разложение $Cu(NO_3)_2 \cdot 3H_2O$. Установлены три эндотермические изменения и структура промежуточного продукта, который представлял собой основной нитрат меди моноклинной структуры $Cu(NO_3)_2 \cdot 3\,Cu(OH)_2$. С помощью микроскопа с нагревом была определена температура плавления $Cu(NO_3)_2 \cdot 2H_2O$ равная 391 К.