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

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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, $Cu(NO_3)_2 \cdot$ $\cdot\,3\,Cu(OH)_2$. 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 ($\lambda = 1.542$ 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
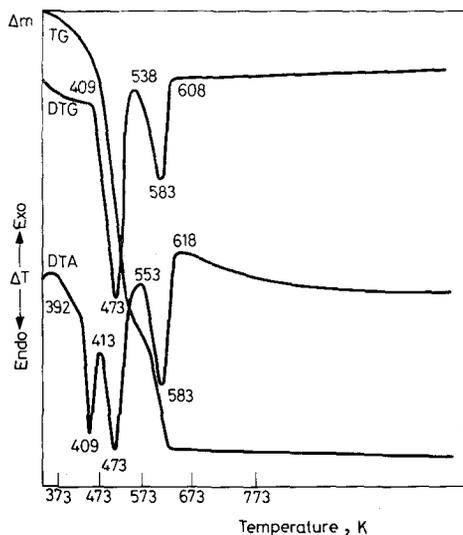

Fig. 1. Thermal curves of $Cu(NO_3)_2 \cdot 3 H_2O$

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,