

## Thermal Analysis of Copper Salicylate Tetrahydrate

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Kinetics of isothermal dehydration and decomposition of  $\text{Cu}(\text{C}_6\text{H}_4\text{OH.COO})_2 \cdot 4\text{H}_2\text{O}$  have been studied at 70-90° and 220-240° respectively using material in the form of powder and pellet. Chemical analysis and X-ray diffraction technique have been used to identify the decomposition products. Kinetics of isothermal dehydration follow a contracting cube expression and the corresponding energy of activation has been found to be 24.28 kJ/mole. The isothermal decomposition curves have been best fitted by an Erofeev-Avrami equation. The energy of activation for the isothermal decomposition comes out to be 38.09 kJ/mole. The combined DTG, DTA and TGA curves of the sample have also been recorded at heating rates of 5°/min and 10°/min.

MUCH work is being done on the thermal decomposition of metal carboxylates in order to understand the mechanism of decomposition and the nature of the decomposition products. Recently, the thermal decomposition of carboxylates<sup>1-3</sup> have been studied by differential thermal analysis and a classification of these compounds have been done. The isothermal and differential thermal decomposition of  $\text{Cu}(\text{II})(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$  have also been reported<sup>4</sup> recently and it has been shown to occur in three stages. No systematic work is reported on the thermal decomposition of salicylates which are very important biologically. A detailed study of thermal behaviour of  $\text{Cu}(\text{C}_6\text{H}_4\text{OH.COO})_2 \cdot 4\text{H}_2\text{O}$  including kinetics of isothermal dehydration, decomposition and derivatographic studies was therefore undertaken and the results are reported in this paper. For the isothermal decomposition step, the course of the reaction was followed by the loss in weight method. The identity of the product was determined by chemical analysis and X-ray diffraction studies.

### Materials and Methods

$\text{Cu}(\text{C}_6\text{H}_4\text{OH.COO})_2 \cdot 4\text{H}_2\text{O}$  with normal magnetic moment of 1.92 BM corresponding to the spin only value of Cu(II), was prepared by the method given elsewhere<sup>5</sup>. Solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (AR, 1 mole) in water (1 litre) was mixed with an equimolar solution of sodium salicylate (AR) in water (750 ml). When the mixed solution was left to stand, pale blue needle shaped crystals separated. It was recrystallized from water and the composition of the compound established by microanalysis for carbon and hydrogen and by precipitating Cu as  $\text{CuSCN}_6$  (Found: C, 40.5; H, 4.6. Req'd: C, 41.0; H, 4.4%). The identity of the compound was also confirmed from X-ray diffraction of the powder sample.

For the isothermal dehydration and decomposition, same amount of the sample was taken each time in a silica crucible, which was placed on the pan of

a balance in a thermostat set at a constant temperature within  $\pm 0.2^\circ$ . The loss in weight at each temperature was recorded after different time intervals till no further loss in weight was observed. The dehydration was studied at 70°, 80° and 90° while the decomposition was studied at 220°, 230° and 240°.

The decomposition was also studied by removing the crucible from the thermostat after different intervals of time and noting the loss in weight at each temperature till no further loss in weight. The nature of the plots of loss in weight versus time  $t$  was the same in both the cases. The final loss in weight was also the same in both the cases. The decomposition was also studied using the material in the form of pellets and fixing the particle size. It was seen that compacting and particle size have no effect on the nature of the kinetic curves. The decomposition products have been identified using X-ray diffraction technique.

Derivatographic study was carried out using a Paulik-Paulik-Erdey MOM derivatograph (Hungary). The apparatus makes it possible to obtain four thermal curves simultaneously: T (temperature), DTA, DTG and TGA. Thermograms were obtained at heating rates of 5°/min and 10°/min in a circular platinum crucible in static air. The weight of the sample in each case was 200 mg and was loosely kept in the crucible.

### Results and Discussion

**Isothermal dehydration of  $\text{Cu}(\text{C}_6\text{H}_4\text{OH.COO})_2 \cdot 4\text{H}_2\text{O}$**   
— For the dehydration, plots of loss in weight versus time  $t$  at 70°, 80° and 90° are given in Fig. 1. At 90°, the loss in weight after 40 min corresponded to the formation of anhydrous copper salicylate. The identity of the product was confirmed by chemical analysis.

Kinetics of dehydration reaction follow a contracting cube expression of the type:

$$1 - (1 - \alpha)^{1/3} = Kt + C \quad \dots(1)$$

where  $\alpha$  is the fraction decomposed at time  $t$ ;  $K$

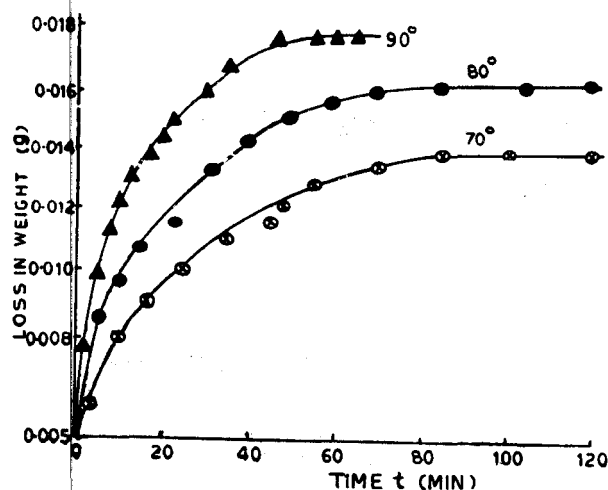


Fig. 1—Plots of loss in weight versus time ( $t$ ) at different temperatures for the isothermal dehydration of copper salicylate tetrahydrate

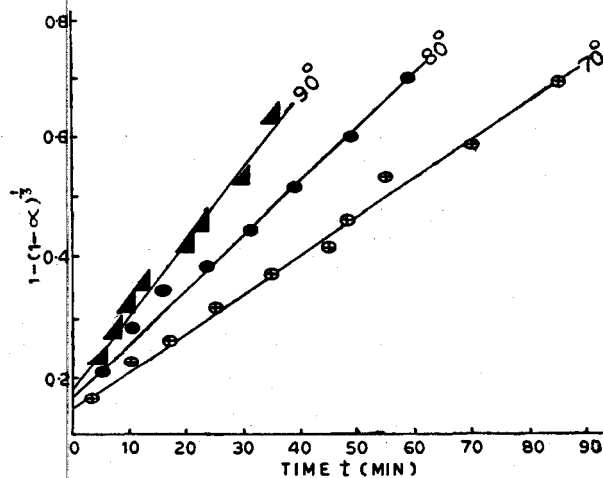


Fig. 2—Plots of  $1 - (1 - \alpha)^{1/3}$  versus time ( $t$ ) at different temperatures for the isothermal dehydration of copper salicylate tetrahydrate

and  $C$  are constants. The applicability of Eq.(1) has been tested by plotting  $1 - (1 - \alpha)^{1/3}$  versus time,  $t$  at various temperatures; such plots are linear (Fig. 2).

The overall activation energy for the dehydration has been found out to be 24.28 kJ/mole from the Arrhenius plot. The contracting cube equation has been deduced on the basis of a reaction interface contracting inwards from the surface of a particle. It was observed under a polarizing microscope that the pale blue crystals of  $\text{Cu}(\text{C}_6\text{H}_4\text{OH}(\text{COO})_2)_2 \cdot 4\text{H}_2\text{O}$  when kept on a slide and placed in a thermostat at  $90^\circ$ , the colour changed from pale blue to yellowish brown after 2 min and finally to green after 40 min. It has also been observed that the change in colour occurs firstly at the surface and then inwards. The volume of the crystal was found to decrease as dehydration proceeded.

**Isothermal decomposition of  $\text{Cu}(\text{C}_6\text{H}_4\text{OH}(\text{COO})_2)_2 \cdot 4\text{H}_2\text{O}$** —Isothermal decomposition of the hydrated salt in the powder (<60 mesh) as well as pellet form was studied at  $220^\circ$ . Dehydration occurs

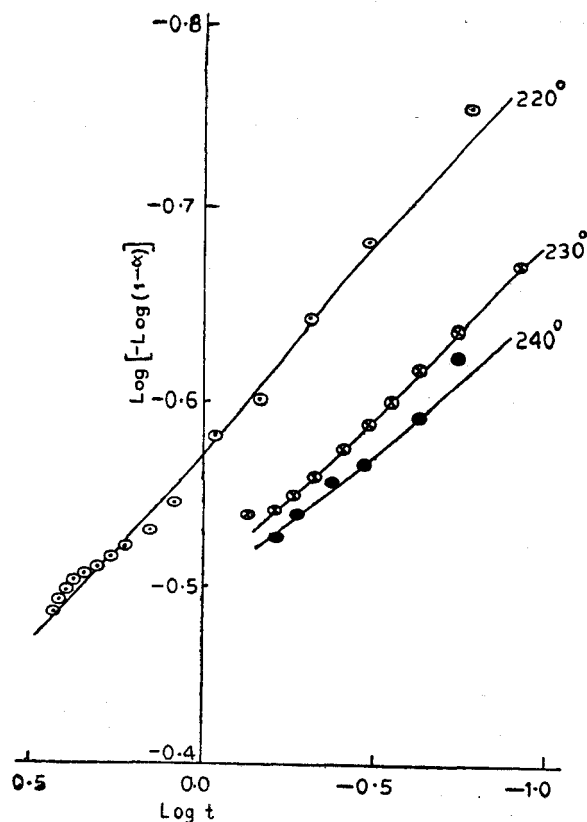


Fig. 3—Plots of  $\ln [-\ln (1 - \alpha)]$  versus  $\log t$  at different temperatures for the isothermal decomposition of copper salicylate tetrahydrate

very rapidly as seen from the steep rise in the plots of loss in weight versus time  $t$ . This is followed by a large slackening in the decomposition. An intermediate stage of the decomposition process is believed to be the cause of this slow process. X-ray powder diffraction of this intermediate showed it to be poorly crystalline. After this stage, the reaction rate increases rapidly and gives the decay curve. The isothermal decomposition of powder  $\text{Cu}(\text{C}_6\text{H}_4\text{OH}(\text{COO})_2)_2 \cdot 4\text{H}_2\text{O}$  at  $220^\circ$ ,  $230^\circ$  and  $240^\circ$  was also investigated. At  $220^\circ$ , the reaction was complete after 190 min and the loss in weight corresponded to the formation of  $\text{CuO}$ . In view of the poor crystalline nature of the intermediate products; isolated by removing the sample after different time intervals, these could not be subjected to X-ray diffraction study.

Final product was identified to be  $\text{CuO}$  by the X-ray diffraction using  $\text{CuK}\alpha$  radiation. The  $d$ -values with the corresponding relative intensities were calculated from the X-ray diffraction study of the end product and compared with the values reported<sup>7</sup> for  $\text{CuO}$ . For each diffraction line from the powdered material, its interplanar spacing ( $d$ ) has been calculated from the Bragg's relation and the relative intensity of each line has been measured by visual comparison of the intensity of the line with the standard scale.

The experimental  $d$ -values\* and the corresponding intensities of the final product were found to be in

\* $d$ -values with corresponding intensities can be had from the authors on request.

good agreement with the  $d$ -values and the intensities reported for CuO in literature<sup>7</sup>.

The isothermal decomposition curves of  $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot 4\text{H}_2\text{O}$  are best fitted by an Erofeev-Avrami equation<sup>8,9</sup>.

$$[-\ln(1-\alpha)]^{1/n} = K't \quad \dots(2)$$

The applicability of the Eq. (2) has been shown in Fig. 3 where the plots of  $\ln[-\ln(1-\alpha)]$  versus  $\ln t$  are linear.

The isothermal decomposition of  $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot 4\text{H}_2\text{O}$  first gives a dark green product. The black product has been found to be CuO by the X-ray diffraction technique using  $\text{CuK}\alpha$  radiation. This equation is applicable up to the formation of this green product. The energy of activation has been found to be 38.09 kJ/mole from the Arrhenius plot.

*Derivatographic study of  $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot 4\text{H}_2\text{O}$*   
 — The combined DTG, TGA and DTA curves of a sample of 200 mg of  $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot 4\text{H}_2\text{O}$  heated at a rate of 5°/min in a circular platinum crucible are given in Fig. 4.

The dehydration occurs in two stages as indicated by two endotherms. In the first step, the dehydration of Cu salicylate tetrahydrate begins at 50° and ends at 125°, as shown by a peak in the DTG. The loss in weight in the range 50-125° calculated from TG curve is 29 mg indicating that the product formed has a composition  $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot \text{H}_2\text{O}$  (reqd = 27 mg). In the DTA curve, the formation of Cu salicylate  $\cdot \text{H}_2\text{O}$  is shown by an endotherm in the range 50-140°. An inflexion point at 90° was also recorded in the DTA curve. The inflexion point did not correspond to any stable portion in the TGA curve, but it corresponded to a loss of 18 mg indicating that two water molecules lost were of different type than the other two. The monohydrate formed is stable up to 150° as shown by the DTG and DTA curves. Then dehydration of the monohydrate starts at 150°. Before the complete dehydration, decomposition also starts as shown by a pseudopause in the TGA curve in the range 160-200°. This step is endothermic in DTA in the range 150-200°. This pseudopause is more

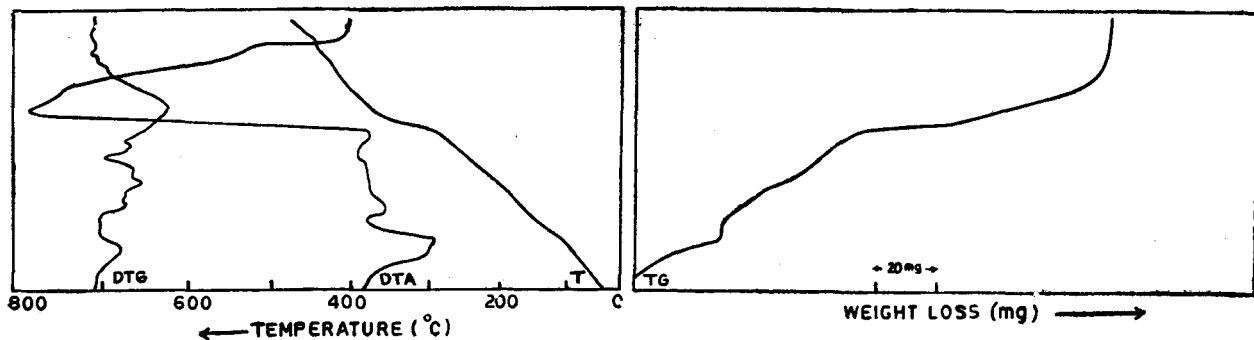


Fig. 4 — Derivatogram of copper salicylate tetrahydrate at a heating rate of 5°/min

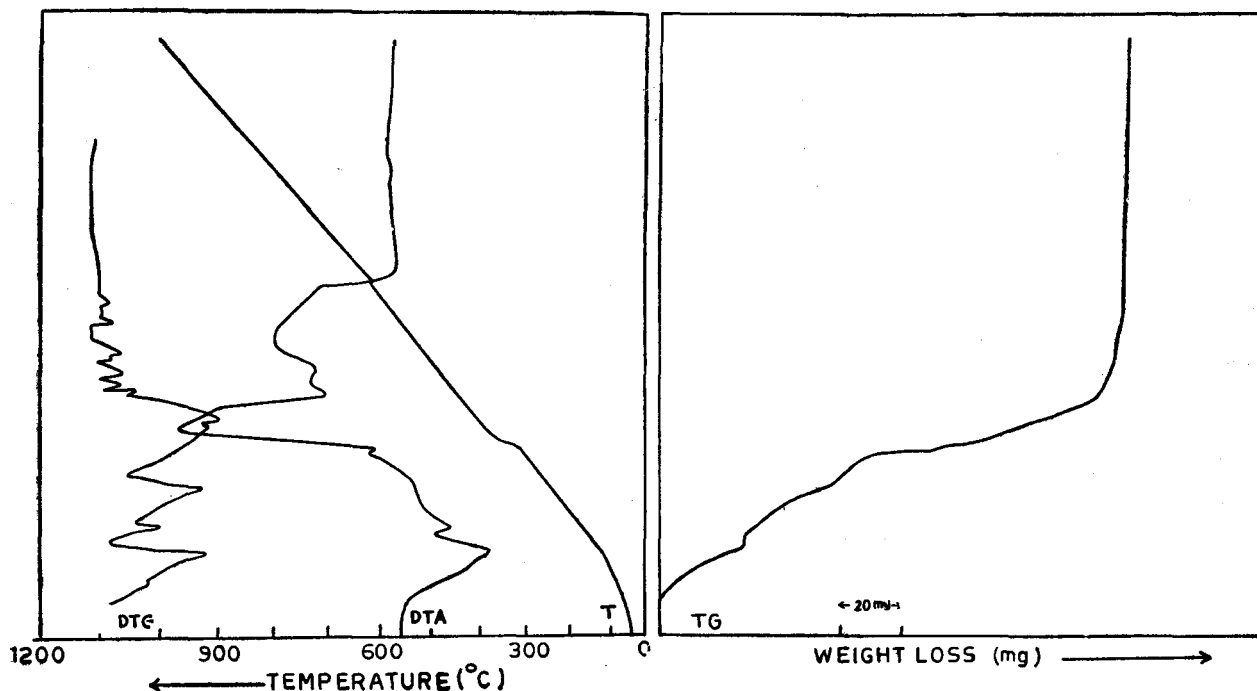


Fig. 5 — Derivatogram of copper salicylate tetrahydrate at a heating rate of 10°/min.

evident when the heating rate was maintained at  $10^\circ/\text{min}$  (Fig. 5). These results indicate that two water molecules are coordinated to the central metal atom and the other two molecules of water are structurally held. Another pseudo-pause was obtained in the temperature range of  $250-300^\circ$  corresponding to loss of weight of 60 mg as indicated in the TGA curve. This weight corresponds to the formation of  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . The formation of this intermediate is shown by a small exotherm in the range  $235-270^\circ$  in the DTA curve. Fourth stage of decomposition as indicated by TGA curve corresponds to the formation of cupric oxide. This stage is indicated by an exotherm in the range  $300-460^\circ$  in the DTA curve and a peak in the range  $250-480^\circ$  in DTG curve.

The four steps of thermal decomposition (two for dehydration, two for decomposition) were also indicated in the DTG and DTA fairly and clearly when the heating rate was maintained at  $10^\circ/\text{min}$  up to  $1000^\circ$  (Fig. 5). A broad exothermic peak in the DTA was observed at  $500-620^\circ$  corresponding to a very little loss in weight indicating recrystallization of the product.

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