Kinetics of Isothermal Decomposition of Copper Benzoate [Cu(C₆H₅COO)₂]

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Differential thermal analysis and kinetics of isothermal decomposition at 220°, 230° and 240° of anhydrous [Cu(II)(C₆H₅COO)₂] of uniform size have been reported. Isothermal decomposition of [Cu(II)(C₆H₅COO)₂] to CuO takes place via the intermediate formation of $CuCO_3.Cu(OH)_2$. Chemical analysis, X-ray diffraction and IR spectral studies have been used to identify the intermediate and the final products. The reaction kinetics up to the formation of $CuCO_3.Cu(OH)_2$ follow Prout-Tompkins equation with 249 kJ/mole as the energy of activation.

COPPER benzoate [Cu(II)(C₆H₅COO)₂] is a very important compound capable of giving large number of useful adducts[1,2]. The structure[3], magnetic properties[1], the mass spectra[4] and diffuse-reflectance spectra[2] of [Cu(II)(C₆H₅COO)₂] have been determined. It is reported to exist as a dimer, giving Cu-Cu bridging and each Cu atom is linked to four oxygen atoms of different benzoate groups. No attempt has been made to study the differential thermal analysis and isothermal decomposition of [Cu(II)(C₆H₅COO)₂]. Previous reports[3] about oxidative decarboxylation under different conditions in aqueous and non-aqueous systems have been reported to give different types of products.

In the present investigation, the decomposition of anhydrous [Cu(II)(C₆H₅COO)₂] has been studied by differential thermal analysis and the rate of the reaction was followed gravimetrically. Chemical analysis, X-ray diffraction and IR spectral studies were employed to identify the intermediate products formed during the decomposition. Final product was identified by chemical analysis and X-ray diffraction study. The kinetics of the reaction have also been studied at different temperatures.

Materials and Methods

[Cu(II)(C₆H₅COO)₂.3H₂O] was prepared by the method given elsewhere[1]. Benzoic acid, sodium hydroxide and cupric sulphate used for the preparation were of Analar grade. Drying of [Cu(II)(C₆H₅COO)₂.3H₂O] crystals in air, then over CaCl₂ in vacuo and finally over P₂O₅ at 110-20° in vacuo for 30 hr, yielded the anhydrous compound. The composition of the anhydrous sample was established by analysing the sample gravimetrically by precipitating copper as cuprous thiocyanate[5] (Found: C, 55·4; H, 3·5. Reqd: C, 55·0; H, 3·3%).

For the isothermal decomposition studies, the sample was powdered and the particle size taken was 75 microns. The sample (1 g) was taken in a silica crucible and kept in a thermostat (accuracy ±0·2°). It did not decompose up to 200° and therefore the kinetics of isothermal decomposition of copper benzoate was studied in the temperature range 220-240°. The loss in weight at each temperature was noted after different time intervals till no further loss in weight. The differential thermal analysis curves were recorded using a DTA apparatus (GDR, Berlin) up to 300° using alumina as the reference material. The nature of the curve was independent of the mass of the sample used. The heating rate was maintained at 5°/min.

Chemical analysis and microscopic studies — A known weight of the intermediate product (dark green) was analysed for Cu by precipitating Cu as CuSCN[5]. The results suggested the formula of the compound to be $CuCO_3.Cu(OH)_2$. Similarly, final product (black) was found to be CuO. It was observed under a polarizing microscope that these two products were crystalline in nature.

Results and Discussion

Thermogravimetric analysis of anhydrous copper benzoate did not show any appreciable loss in weight up to 220°. The reaction became appreciable at 200° and was complete after 16 hr. Beyond 16 hr, no further loss in weight was noticed and the weight loss corresponded to the formation of CuO. To identify the intermediate compounds, these were isolated by removing the samples from the thermostat after different time intervals. The only definite intermediate compound (dark green) formed was identified as $CuCO_3.Cu(OH)_2$ by chemical analysis, X-ray diffraction studies using Cu-Kα radiation and IR spectrum. The d-values with the corresponding relative intensities calculated from the X-ray diffraction patterns of the intermediate product and the product at the end of the reaction are given in Tables 1 and 2 respectively alongwith the values reported[6,7] for $CuCO_3.Cu(OH)_2$ and CuO. Interplanar spacings have been calculated from Bragg's relation, $2d \sin \theta = \lambda n$ and the relative intensity of each line has been measured by visual comparison of the intensity of the line with the standard scale.

The close agreement between some d-values and the intensities of the intermediate compound and

TABLE 1 — d-VALUES WITH CORRESPONDING INTENSITIES CALCULATED FROM THE X-RAY DIFFRACTION STUDY OF THE INTERMEDIATE PRODUCT ALONG WITH THE VALUES REPORTED FOR $CuCO_3.Cu(OH)_2$

Intermediate compound		$CuCO_3.Cu(OH)_2$ (ref. 6)	
d (Å)	Intensities	d (Å)	Intensities
7·47	40	7·41	11
5·46	20	5·99	55
4·83	80	5·05	75
4·69	60	4·69	13
4·30	15	—	—
3·85	10	—	—
3·42	70	3·69	85
3·23	5	—	—
3·02	13	3·02	17
2·88	40	2·86	100
2·75	19	2·77	45
2·47	25	2·47	30
2·41	20	2·42	20
2·16	7	2·16	7
2·07	7	2·05	9
2·02	5	2·02	5
1·90	3	1·90	13

TABLE 2 — d-VALUES WITH THE CORRESPONDING INTENSITIES CALCULATED FROM THE X-RAY DIFFRACTION STUDY OF THE FINAL DECOMPOSITION PRODUCT ALONG WITH THE VALUES REPORTED FOR CuO

Final product		CuO (ref. 7)	
d (Å)	Intensities	d (Å)	Intensities
2·72	12	2·75	12
2·51	55	2·53	49
2·45	80	2·52	100
2·31	90	2·32	96
2·12	20	—	—
1·86	25	1·86	25
1·71	4	1·71	8
1·69	3	—	—
1·57	8	1·58	14
1·50	40	1·50	20
1·41	9	1·41	12
1·30	8	1·30	7
1·28	9	1·26	7

$CuCO_3.Cu(OH)_2$ gave support to the conclusion that the intermediate is $CuCO_3.Cu(OH)_2$. Some d-values and the intensities of the intermediate compound do not match with the d-values and the intensities of $CuCO_3.Cu(OH)_2$. The identity of intermediate compound was further confirmed by recording its IR spectrum in nujol. The infra red group frequencies for CO_3^{2-} in the intermediate are observed at 720 (s), 870 (s), 1090-1130 (s) and 1390 cm^{-1} (s) corresponding to the infrared group frequencies at 650-750, 800-900 cm^{-1}, 1050-1100 and 1400-1450 cm^{-1} given in literature[7,8]. The $\overline{OH}$ infrared frequencies appeared at 3410-3450 (m, b) and 3600-3650 cm^{-1} corresponding to the infrared group frequency at 3600-3200 cm^{-1} given in literature[9]. The IR spectrum of $CuCO_3.Cu(OH)_2$ (Analar grade) was also taken. The IR spectra of the intermediate compound and of the Analar sample were superimposable. The intermediate, $CuCO_3.Cu(OH)_2$, further decomposed to give the final product, cupric oxide.

The kinetic data were analysed with the help of two kinetic equation on different models, viz. (i) Avrami equation[10] and (ii) Prout-Tompkins equation[11]. No single equation is applicable for the entire decomposition. However, the kinetic data comply fairly well with Prout-Tompkins equation

$$\ln \frac{\alpha}{1-\alpha} = kt+C \qquad \ldots(1)$$

where

$$\alpha = \frac{\text{Loss in weight/g at any time}}{\text{Final loss in weight/g}}$$

and k is specific rate constant and C is a constant. This equation is applicable only up to the formation of intermediate, $CuCO_3.Cu(OH)_2$. The applicability of this equation, in the decomposition at different temperatures and for the same size of particles, has been shown in Fig. 1 where the plots of ln $(\alpha/1-\alpha)$ versus time t are linear. The energy of activation has been found out to be 249 KJ/mole from the Arrhenius plot.

Eq. (1) describes the kinetics of a reaction progressing via linear branching chains which can be terminated on reaching any part of the product phase. Eq. (1) has been applied to the decomposition kinetics of solids[12]. This equation has been derived under the assumption that the rate of reaction is proportional to the number of nuclei (N) present, i.e.

$$\frac{d\alpha}{dt} = K'N \qquad \ldots(2)$$

and the rate of nucleation is given by
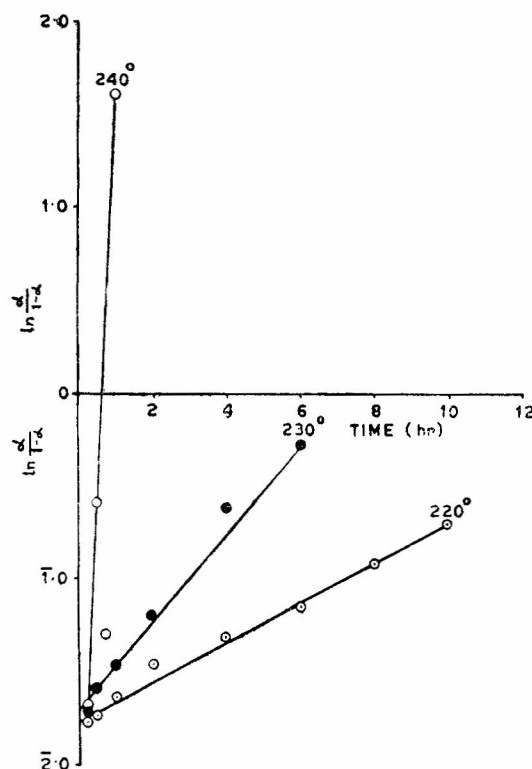
$$\frac{dN}{dt} = K_1N_0+(K_2-K_3)N \qquad \ldots(3)$$

Fig. 1 — Plots of ln $(\alpha/1-\alpha)$ versus time (t)

where K_1, K_2 and K_3 are the probabilities of nucleation, linear branching of nulcei and termination of branching chains respectively.

Differential thermal analysis — Three endothermic peaks at 235°, 255° and 265° have been recorded in DTA of $Cu(II)(C_6H_5COO)_2$ of uniform size at a heating rate of 5°/min. The first endothermic peak at 235° is due to the decomposition of $Cu(II)(C_6H_5COO)_2$ to $CuCO_3.Cu(OH)_2$ as the intermediate product. The second endothermic peak at 255° is due to loss of some water molecules from the basic carbonate while the third endothermic peak at 265° is due to the further decomposition of the intermediate to cupric oxide. Repeated thermal analysis indicates three endotherms showing that three decomposition reactions are invloved; although this is not indicated in the isothermal decomposition. The isothermal decomposition is found to proceed with one definite intermediate, which could be separated, during kinetic study. However, both DTA and kinetics studies do indicate the presence of $CuCO_3.Cu(OH)_2$ as the intermediate. It appears that near the completion of decomposition, two to three reactions occur simultaneously and give the other products as obtained in the DTA. Kinetics fail to give these products. Due to coexisting of different phases and the competing reactions, the kinetics become an overall one during the final stages of decomposition.

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