Short Communication

THERMAL DECOMPOSITION OF Cu(II) ADIPATE

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The kinetics of isothermal decomposition of $Cu(CH_2CH_2COO)_2$ were studied at 483—503 K. The end-product was identified as CuO by X-ray diffraction and chemical analysis. The kinetics follow the Prout—Tompkins equation with an activation energy of 191 ± 10 kJ/mole. The activation energies and the order of reaction were also evaluated from analysis of the DTG, DTA and TG curves of the sample.

Much work is currently being done on the isothermal decomposition reactions of transition metal carboxylates [1]. Recently, the thermal decomposition of copper carboxylates [2, 3] have been studied by differential thermal techniques. The thermal decompositions of Cu(II) benzoate, Cu(II) salicylate and Cu(II) malonate have recently been reported by Bassi and Kalsi [4, 6]. The present work deals with the kinetics of isothermal decomposition of Cu(II) adipate. For the isothermal decomposition, the rate of the reaction was followed by the thermal method, while the decomposition products were analyzed by chemical analysis and X-ray diffraction.

Material and methods

Cu(II) adipate was prepared as reported earlier [7]. The composition of the anhydrous sample was determined by analyzing the sample gravimetrically by precipitating copper as cuprous thiocyanate [8] and by microanalysis of carbon and hydrogen. The carbon and hydrogen were found to be 34.3 and 3.7% (calculated: C = 34.6 and H = 3.8%), respectively. The sample taken for the isothermal decomposition studies was homogenized by sieving below 100 mesh. A known weight of the sample was taken in a silica crucible and placed in a thermostat set at a constant temperature within ± 0.2°. The change in weight was noted after different intervals of time till no further loss in weight. The final decomposition product was found crystalline under a polarizing microscope and by X-ray diffraction.

Thermal analysis were carried out by means of a Paulik – Paulik – Erdey MOM derivatograph (Hungary). The weight of the sample was 250 mg. The curves were recorded at a heating rate of 10°/minute.

Results and discussion

Isothermal decomposition

Plots of loss in weight versus time t at various temperatures for Cu(II) adipate are given in Fig. 1. The decomposition was studied at 483, 493 and 503 K. At 483 K, the reaction was complete after 14 hours and the weight loss corresponded to the formation of cupric oxide. The decomposition product was further identified (to be CuO) by chemical analysis, by precipitating Cu as CuSCN [8], and

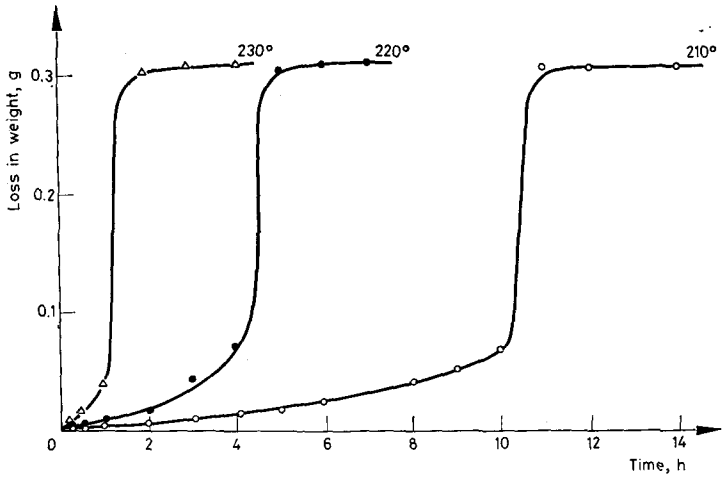

Fig. 1. Plots of loss in weight versus time at various temperature for the isothermal decomposition of Cu(II)-adipate

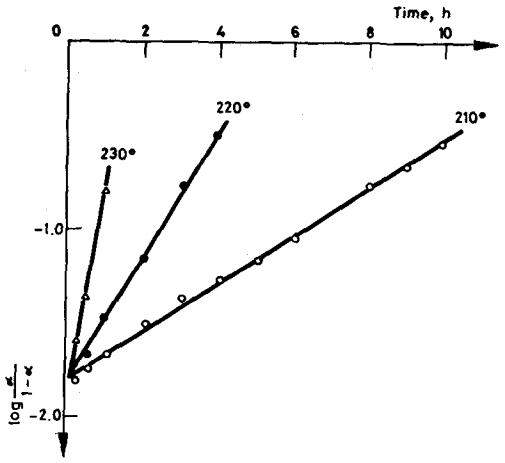

Fig. 2. Test of Prout—Tompkins equation for the thermal decomposition of copper adipate

by X-ray diffraction using CuK_α radiation. The d values and the corresponding relative intensities, calculated from the X-ray diffraction study of the final product, are presented in Table 1, along with the values reported for CuO [9]. The relative intensity of each line was measured by visual comparison of the intensity of the line with the standard scale. The experimental d values were found to be in good agreement with the d values reported for CuO [9].

Table 1

d-values and the intensities of the final decomposition product of Cu(II) adipate calculated from the X-ray diffraction pattern alongwith the values reported for CuO in literature[9]

Final product		CuO	
d, Å	Intensity	d, Å	Intensity
2.70	4	2.75	12
2.49	100	2.52	100
2.40	80	2.31	30
2.29	100	2.32	96
2.10	17	1.96	3
1.85	40	1.86	25
1.69	15	1.71	8
1.57	16	1.58	14
1.49	55	1.50	20
1.40	15	1.41	15
1.36	15	1.37	19
1.28	10	1.30	7
1.25	12	1.26	7
1.22	3	1.19	2
1.15	6B	1.15	4
1.08	5	1.09	6
0.97	12	0.98	4
0.95	6	0.95	3
0.93	5	0.94	4
0.92	3	0.93	4
0.88	9	0.92	2
0.87	5B	0.91	2
0.85	6B	0.90	1
0.83	4	—	—

B=Broad

The rate of the reaction obeys the Prout–Tompkins equation [10]:

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

where k and C are constants. The applicability of Eq. (1) is shown in Fig. 2, where $\log \frac{\alpha}{1-\alpha}$ is plotted *vs.* time t. This equation assumes that the rate of

reaction is proportional to the number of nuclei present, and the rate of nucleation is given by linear branching of nuclei and termination of branching chains. The activation energy for the overall reaction was computed from the Arrhenius plot and the value was found to be 191 ± 10 kJ/mole.

Thermal study of Cu(II) *adipate*

The combined DTG, DTA and TG curves of a sample of 250 mg heated at the rate of 10°/min with 200 mg sensitivity in a platinum crucible in static air are given in Fig. 3.

The decomposition of Cu(II) adipate begins at about 553 K and is completed at 708 K, as shown by a peak in the DTG curve. The loss in weight calculated from the TG curve is 61.6%. This corresponds to the formation of CuO (calculated loss = 61.7%). Thus, DTG and TG curves show that only one decomposition reaction accompanied by loss in weight takes place, and no stable inter-

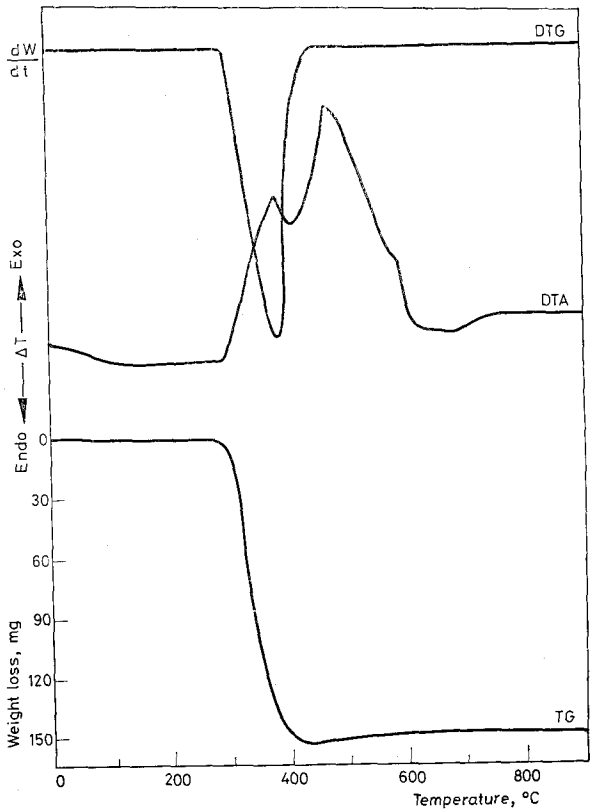

Fig. 3. TG, DTG, DTA curves of Cu(II)-adipate at a heating rate of 10°/min

mediate are formed. The corresponding DTA curve indicates a large exothermic region (550 – 883 K) with peaks at 653 and 733 K. Isothermal heating of a sample of Cu(II) adipate for 2 hr at 840 K also gave CuO as the final product.

The order of reaction, n, was determined by applying the Horowitz – Metzger equation [11], $C_s = (n)^{\frac{1}{1-n}}$, where C_s is the weight fraction of the substance present at the peak temperature T_s (the DTG peak temperature). The order of decomposition was calculated to be one. The order of reaction (n) and activation energy (E) were also determined graphically using the Freeman – Carroll method [12] and were found to be one and 183 ± 10 kJ/mole, respectively. The Coats – Redfern relation [13] was also employed in the following form (suitable when $n = 1$, as in the present case):

$$\log \frac{\log C^{-1}}{T^2} = \log \frac{ZR}{\Phi E} - \frac{E}{2.303\, RT} \qquad (2)$$

Here $C = \frac{W_{oc} - W}{W_{oc}}$; W_{oc} = total mass loss for the particular stage; W = mass loss at temperature T (K); Z = pre-exponential factor; R = gas constant; and Φ = heating rate in degrees sec^{-1}. Plotting $\log \frac{\log C^{-1}}{T^2}$ against T^{-1}, a linear plot was obtained. The activation energy was found to be 186 ± ± 10 kJ/mole from the linear plot. It may be noted that activation energies obtained from isothermal and non-isothermal studies are close to each other.

It is interesting to compare the activation energy for Cu(II) adipate with the activation energies for similar decompositions [14 – 16] for which a decomposition scheme to account for the activation energy values has been proposed by Galwey. This scheme may be applied to the decomposition of Cu(II) adipate also. Accordingly, it is proposed that decomposition is controlled by nucleation and the activation involves two –COOCu groups at a single cation. The energy required for activation of one such group is 111 kJ/mole [14]. In Cu(II) adipate, there being two carboxyl groups, the activation energy should be twice (i.e. 111 × 2 = = 222 kJ/mole) the energy for one group. However, the experimental (isothermal) value of the energy is 191 ± 10 kJ/mole. This can be explained if the structure of Cu(II) adipate is kept in mind. The steric considerations preclude the approach of two carboxyl groups of an adipate radical to a single Cu atom. It is concluded, therefore, that the activated complex for decomposition involves a bond between one carboxyl group and the nucleus surface, and the second carboxyl group remains within the undecomposed reactant matrix. The activation energy predicted [14] for this model is 205 kJ/mole, in agreement with the value of 191 ± ± 10 kJ/mole measured for Cu(II) adipate.

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