

KINETICS OF ISOTHERMAL DECOMPOSITION OF CU(II) SUCCINATE

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The isothermal decomposition of $\text{Cu}(\text{CH}_2\text{COO})_2$ has been studied at 473–523 K using material in the form of powder and pellets. The isothermal decomposition of Cu(II) succinate to cupric oxide takes place *via* the intermediate formation of $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The X-ray diffraction technique has been employed to identify the decomposition products. The decomposition curves are best fitted by two kinetic stages: (i) a linear law, and (ii) a unimolecular law. The activation energies for the two stages are 153 ± 10 kJ/mole, and 115 ± 8 kJ/mole, respectively. It has been observed that pelleting has no effect on the kinetics. DTG, DTA and TG curves of the sample have also been recorded. The order of reaction has been calculated from these curves.

The thermal decomposition of metal carboxylates has initiated great interest during recent years. Thermal decompositions of metal formates and oxalates have been widely investigated [1, 2]. However, the work on the thermal decomposition of higher metal dicarboxylates is quite complex and has been started only recently [3]. The work on the thermal decomposition of succinates is very limited [3]. Recently, the isothermal decompositions of Cu(II) adipate and Cu(II) malonate have been reported [4a, b]. Cu(II) succinate differs [5] from Cu(II) malonate structurally as well as in having higher proportions of carbon and hydrogen. Therefore, the isothermal and non-isothermal decompositions of Cu(II) succinate are described in this paper.

Materials and methods

Cu(II) succinate was prepared by the method of Burkin [6]. The composition of the sample was established by analysing the sample gravimetrically by precipitating copper as cuprous thiocyanate [7] (Cu: found = 35.6%, calcd. = 35.4%) and by the elemental analysis of carbon and hydrogen. The carbon and hydrogen were found to be 27.2% and 2.4%, respectively (reqd. C = 26.7% and H = 2.2%). The sample taken for the isothermal decomposition studies was sieved below 80

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mesh. Equal weights (0.2 g) of the powder and of pellets made by compression in a stainless steel press were taken, and the decomposition was studied by the method reported earlier [8]. The decomposition was studied at 473, 503, 513 and 523 K. At 473 K, the rate of the reaction was very slow, only 3% of the material being decomposed after 15 hours of heating. Pelleting has no effect on the nature of the kinetics of the reaction, but the reaction became fast. The products after different time intervals were examined under a polarizing microscope and in each case were found to be crystalline. The simultaneous DTG, DTA and TG curves of the sample heated at 5°/minute in a static air atmosphere were recorded using a Paulik–Paulik–Erdey MOM (Budapest) derivatograph.

Results and discussion

For Cu(II) succinate at 503 K, the reaction was complete after 20 hours, and the loss in weight corresponded to the formation of cupric oxide. Samples were withdrawn at different degrees of decomposition for identification of any intermediate. The only intermediate compound found in the isothermal decomposition of Cu(II) succinate after 13 hr of reaction at 503 K was $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$. This was identified by X-ray diffraction using CuK_α radiation.

The experimental d values and the corresponding relative intensities, calculated from the X-ray diffraction patterns of the intermediate product and the final product of Cu(II) succinate decomposition are given in Tables 1 and 2, along with

Table 1

d -values and the intensities of the intermediate decomposition product of Cu(II) succinate calculated from the X-ray diffraction pattern along with the values reported for $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$

Intermediate product		$2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$	
$d, \text{Å}^\circ$	Intensity	$d, \text{Å}^\circ$	Intensity
5.13	30	5.15	55
4.15	25	—	—
3.80	30	3.67	50
3.50	35	3.51	100
2.96	20	2.92	9
2.44	60	2.50	30
2.25	50	2.22	70
2.16	10	2.16	15
2.12	5	2.10	7
1.82	7	1.83	7
1.56	3	1.56	5
1.48	10	1.59	15
1.39	10	—	—
1.35	7	—	—
1.24	4	—	—

Table 2

d -values and the intensities of the final decomposition product of Cu(II) succinate calculated from the X-ray diffraction pattern alongwith the values reported for CuO

Final product		CuO	
$d, \text{Å}^\circ$	Intensity	$d, \text{Å}^\circ$	Intensity
2.48	80	2.51	100
2.41	50	2.53	49
2.31	70	2.32	96
2.09	12	1.96	3
1.84	20	1.86	25
1.70	5	1.71	8
1.76	12	1.58	14
1.49	30	1.50	20
1.40	15	1.41	12
1.36	13	1.37	19
1.28	7	1.30	7
1.26	5	1.26	6
1.09	7	1.09	6
0.88	6	0.90	1

the known X-ray diffraction data [9, 10] for $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$ and CuO. The experimental and known d values and their intensities for $2 \text{CuCO}_3 \cdot \text{Cu(OH)}_2$ and CuO are found to be in good agreement.

The kinetics of the reaction were found to obey (i) a linear relationship between α , the fractional decomposition, and time t , and (ii) a unimolecular law

$$-\log(1 - \alpha) = Kt. \quad (1)$$

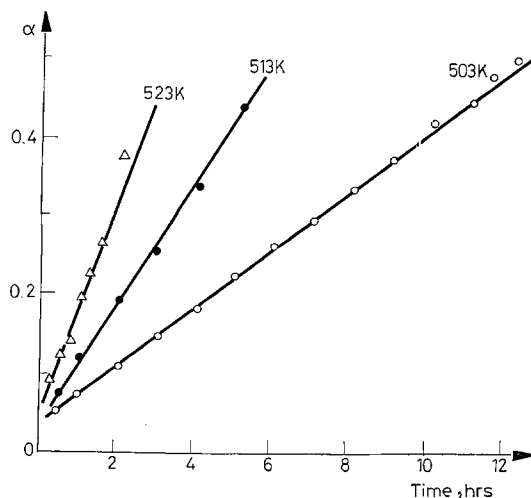


Fig. 1. Plots of α vs time for the decomposition of copper succinate

The linear plots are shown in Fig. 1, and the applicability of Eq. (1) is illustrated in Fig. 2, where the plots of $-\log(1 - \alpha)$ vs. t are straight lines. The energy of activation from the linear plots was found to be 153 ± 10 kJ/mole. This behaviour cannot be ascribed to induction, and the indications are that the reaction centers [11, 12] are already present in larger quantities. The fast linear reaction at 523 K, and the absence of a sigmoid curve initially, can be regarded as evidence in favour of the presence of reaction centers. This general linear kinetic expression was also deduced by Erofeev [13] as follows:

$$\alpha = 1 - e^{(-\int_0^t p dt)} \quad (2)$$

when

$$\frac{d\alpha}{dt} = p \cdot e^{(-\int_0^t p dt)} = p(1 - \alpha) \quad (3)$$

where p represents the probability that an individual molecule will react in the interval $t, t + dt$. Applying this to certain isothermal decomposition reactions, Erofeev found that

$$\alpha = 1 - e^{-kt^n} \quad (4)$$

where n is an integer. The linear law follows from the Erofeev equation with $n = 1$, when

$$\alpha = 1 - e^{-kt} = \sum_{n'=1}^{n'=\alpha} \frac{(-kt)^{n'}}{n'!} \quad (5)$$

For small values of t , this becomes $\alpha = \text{constant} \cdot t$. The energy of activation for Eq. (2) turns out from the Arrhenius plot to be 115 ± 8 kJ/mole. The isothermal decomposition of Cu(II) succinate has also been studied using the material in the form of pellets. Pelleting has no effect on the nature of the kinetics of the reaction but the reaction became fast.

Study of Cu(II) succinate with a derivatograph

The thermal curves (Fig. 3) were recorded with 90 mg of sample heated at $5^\circ/\text{minute}$ with 100 mg sensitivity. In the DTA curve, the decomposition of Cu(II) succinate is shown by an exothermic peak at 498–683 K. The loss in weight recorded by the TG curve in this range corresponds to the formation of CuO. Similarly, the corresponding DTG curve shows one peak at 498–658 K. Two more, small endothermic peaks at 373 K and 463 K, corresponding to 0.5 and 1 mg loss in weight, respectively were recorded in the DTA curve. These peaks are due to the release of moisture taken up by the sample at room temperature.

The order of reaction, n , was obtained using the following equation suggested by Horowitz and Metzger [14]

$$C_s = n^{1/1-n} \quad (6)$$

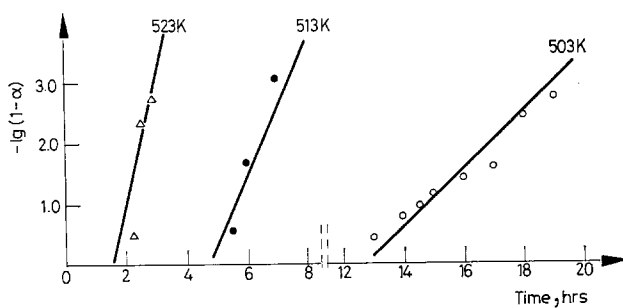


Fig. 2. Plots of $-\log(1-\alpha)$ vs time for the decomposition of copper succinate

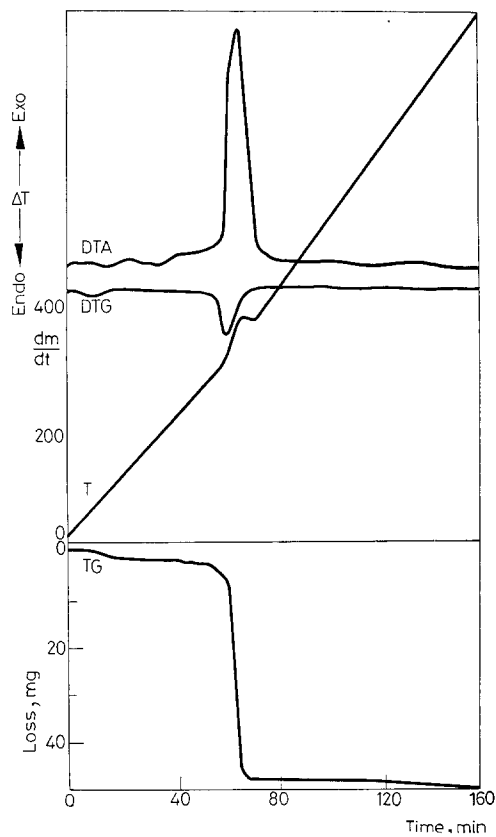


Fig. 3. TG, DTG and DTA curves of Cu(II) succinate sample. Weight: 90 mg. Heating rate: $5^{\circ}/\text{min}$

where C_s is the weight fraction of the substance present at the DTG peak temperature, $T_s \cdot C_s$ is given by

$$C_s = \frac{W - W_t^f}{W_0 - W_t^f} \quad (7)$$

where W = weight at the temperature T_s , W_t^f = final weight and W_0 = initial weight of the substance. The order of decomposition of Cu(II) succinate is obtained by comparing the C_s value yielded by the above method with the values given in the Horowitz and Metzger [14] table. The order is calculated to be one.

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