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THERMAL DECOMPOSITION OF Cu(II) MALONATE

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The isothermal decomposition of anhydrous Cu(II) malonate of uniform particle size has been studied at 170, 180 and 190°. Decomposition to cupric oxide takes place via the intermediate formation of $2CuCO_3.Cu(OH)_2$. X-ray diffraction has been employed to identify the decomposition products. The experimental kinetic data for Cu(II) malonate decomposition are best fitted by two stages: (i) a linear process and (ii) a first-order expression. The activation energies for the two kinetic stages have been found to be 45.7 and 57.2 kcal/mole, respectively. A DTA study of Cu(II) malonate decomposition has also been made. Activation energies have been determined via analysis of the DTA curve using the Borchardt and Piloyan equations.

The isothermal decompositions of Cu(II) benzoate and Cu(II) acetate were recently studied, and the results were very interesting as both the intermediates and the final products were crystalline [1, 2].

The ionization, magnetic susceptibility, magnetic properties and structure of Cu(II) malonate have also been reported recently [3, 4]. In the present paper we describe the results of an investigation of the isothermal decomposition of Cu(II) malonate. The rate of the reaction was followed gravimetrically, while the decomposition products were analyzed by X-ray diffraction. The DTA curve was also recorded.

Experimental

Cu(II) malonate was prepared as reported earlier [5]. The composition of the anhydrous sample was established by analyzing the sample gravimetrically by precipitating copper as cuprous thiocyanate [6], and by microanalysis of carbon and hydrogen. The carbon and hydrogen contents were found to be 21.2% and 1.8% (calculated: C = 21.5% and H = 1.2%).

The sample taken for the isothermal decomposition studies was sieved through a 140 mesh to give uniform particle size. A known weight of the sample (0.2187 g) was taken in a silica crucible, which was placed in a thermostat set at a constant temperature within $\pm 0.2°$ variation. The silica crucible was removed from the thermostat after known intervals of time and the loss in weight at each temperature was noted till weight constancy. The products after different time intervals

were examined under a polarizing microscope and in each case were found to be crystalline. The differential thermal analysis curve was recorded up to 300° using a DTA apparatus, with alumina as reference material. The nature of the curve obtained was independent of the mass of sample used. The heating rate was maintained at 7.5 °/min.

Results and discussion

DTA study of Cu(II) malonate: Two endothermic peaks (Fig. 1.) werf observed at 100–190° and 210–240° in the DTA study of Cu(II) malonate oe uniform particle size at a heating rate of 7.5 °/min. This indicates that two reactions are involved in the decomposition of Cu(II) malonate.

The activation energies of the two decomposition reactions were determined by analysis of the DTA curve using the Borchardt [7] equation (1) for a first-order reaction:

$$k = \frac{Cp\,\frac{d\Delta T}{dt} + K\Delta T}{K(A - a) - Cp(\Delta T)} \qquad (1)$$

Table 1

d-Values and the intensities of the intermediate product of Cu(II) malonate calculated from the X-ray diffraction study along with the values reported for $2CuCO_3.Cu(OH)_2$

Intermediate		$2CuCO_3 \cdot Cu(OH)_2$	
d, Å	Intensities	*d*, Å	Intensities
6.18	25B	—	—
5.13	20	5.15	55
4.48	30B	—	—
3.95	3B	3.86	3
3.63, 3.26 } 3.44	20B, 20B } 20B	3.51	100
3.14	25	3.10	11
2.92	4B	2.92	9
2.77	5B	2.81	7
2.62	10	2.59	11
2.53	15	2.52	20
2.46	10	2.50	30
2.34	7	2.33	17
2.23	7	2.29	13
1.95	4	1.90	7
1.85	5	1.85	3

B = Broad

Table 2

d-Values and the intensities of the final product of Cu(II) malonate calculated from the X-ray diffraction study along with the values reported for CuO

Final product		CuO	
d, Å	Intensities	*d*, Å	Intensities
2.96	4	—	—
2.70	4	2.75	12
2.47	100	2.52	100
2.39	90	2.32	96
2.27	60	2.31	30
2.08	65	—	—
1.77	20	1.86	25
1.70	4	1.71	8
1.56	5	1.58	14
1.49	80	1.50	20
1.40	15	1.41	15
1.35	12	1.37	19
1.27	40	1.30	7
1.25	7	1.26	7
1.22	8	1.26	6
1.15	5B	1.15	4
0.97	25	0.98	4
0.95	12	0.95	3
0.93	3	0.93	2
0.88	9B	0.91	2
0.87	9B	0.90	1
0.82	10B	—	—

where k = rate constant for the reaction; A = total DTA area; Cp = total heat capacity; K = cell constant; a = area at time t; $\frac{d\Delta T}{dt}$ = slope of the curve at time t; and ΔT = height at time t. As the quantities $Cp \frac{d\Delta T}{dt}$ and $Cp\,\Delta T$ are negligible, the equation reduces to

$$k = \frac{\Delta T}{A - a} \tag{2}$$

From plots of $\log k$ *vs.* T^{-1}, activation energies of 43.5 and 52.3 kcal/mole, respectively were found for the two decomposition reactions involved in the DTA study of Cu(II) malonate of uniform particle size.

The activation energies were also determined via analysis of the DTA curve using the equation of Piloyan et al. [8] for solids:

$$\ln \Delta t = C' - E/RT \tag{3}$$

where Δt is the deviation of the DTA curve from the baseline, which can be obtained in units of length (cm), and C' is a constant. By plotting log Δt against T^{-1}, the activation energies for the two stages were found to be 48.0 and 52.0 kcal/mole, respectively.

Plots of the loss in weight *vs.* time t, at various temperatures and for Cu(II) malonate with the same particle size are given in Fig. 2. The decomposition was studied at 170, 180 and 190°. At 170°, the reaction was complete after 47 hours and the loss in weight corresponded to the formation of cupric oxide. To identify

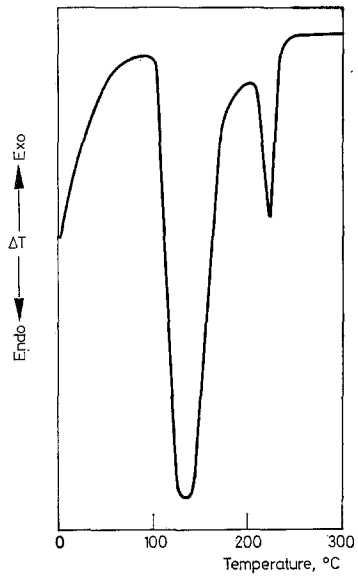

Fig. 1. DTA curve of Cu(II) ($C_3H_2O_4$)

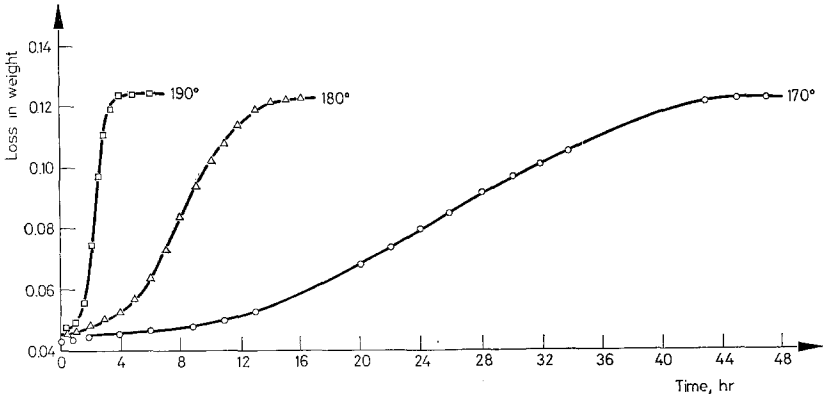

Fig. 2. Plots of loss in weight *vs.* time for the isothermal decomposition of Cu(II) ($C_3H_2O_4$)

the intermediate products, these were isolated by removing the samples from the thermostat after different time intervals. The only intermediate found in the isothermal decomposition by X-ray diffraction using CuK_α radiation was $2CuCO_3.Cu(OH)_2$.

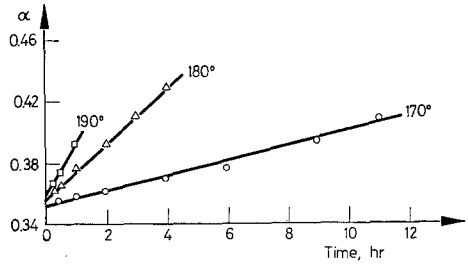

Fig. 3. Linear plots for the isothermal decomposition of Cu(II) ($C_3H_2O_4$)

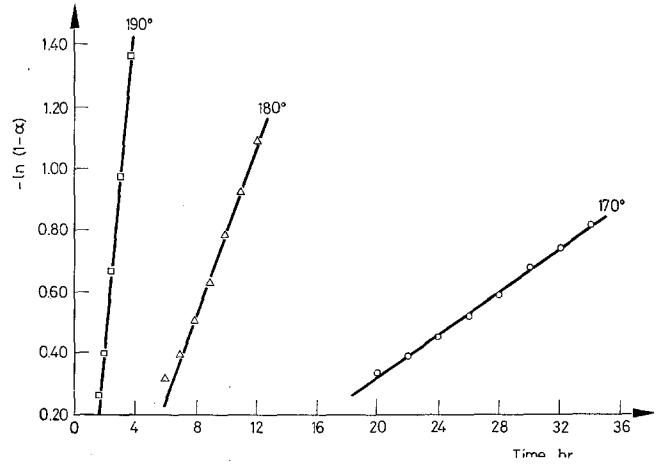

Fig. 4. Plots of $-\ln(1-\alpha)$ *vs.* time for the isothermal decomposition of Cu(II) ($C_3H_2O_4$)

The *d* values and the corresponding relative intensities calculated from the X-ray diffraction patterns of the intermediate and the final product of Cu(II) malonate are given in Tables 1 and 2, along with the values reported for $2CuCO_3.Cu(OH)_2$ and CuO in the literature [9, 10]. For each diffraction line from the powdered material, its interplanar spacings (*d*) were calculated using the Bragg equation, $2d \sin \Theta = n\lambda$. The relative intensity of each line was measured by visual comparison of the intensity of the line with a standard scale.

The experimental *d* values and intensities for the intermediate and the final product were found to be in good agreement with the corresponding literature values for $2CuCO_3.Cu(OH)_2$ and CuO [9, 10]. $2CuCO_3.Cu(OH)_2$ undergoes decomposition to cupric oxide.

It can be seen from Fig. 2 that the plots for the isothermal decomposition are linear in the initial stages. The kinetics of the reaction were found to obey (i) a linear process and (ii) a first-order expression of the type

$$-\ln(1-\alpha) = K't \tag{4}$$

where α, the fractional decomposition, is defined as the ratio of the loss in weight at any time to the final loss in weight. The linear plots for isothermal decomposition of Cu(II) malonate are shown in Fig. 3, and the applicability of Eq. (4) in Fig. 4, where the plots of $-\ln(1-\alpha)$ *vs.* time t are linear. The energies of activation for the first and second stages were found from the Arrhenius plots to be 45.7 and 57.2 kcal/mole, respectively.

The activation energies can be compared with those determined for the two steps from the DTA curve. In view of the inherent uncertainty in the DTA study, the agreement is very good.

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RÉSUMÉ — On a étudié la décomposition thermique du malonate de cuivre(II) anhydre à 170, 180 et 190°. La décomposition du malonate en CuO se produit avec formation intermédiaire de $2CuCO_3.Cu(OH)_2$. Les produits de décomposition ont été identifiés par diffraction des rayons X. Les données expérimentales correspondent à deux étapes de cinétique différente: (i) un processus linéaire et (ii) une expression du premier ordre. Les énergies d'activation respectives des deux étapes cinétiques s'élèvent à 45.7 et 57.2 kcal.mol^{-1}. Le malonate de cuivre(II) a aussi été étudié par ATD. Les énergies d'activation ont été déterminées à partir de la courbe ATD en appliquant les équations de Borchardt et de Piloyan.

ZUSAMMENFASSUNG — Die isotherme Zersetzung von wasserfreiem Cu(II)-malonat einheitlicher Partikelgröße wurde bei Temperaturen von 170°, 180° und 190° untersucht. Die Zersetzung von Cu(II)-malonat zu Kupfer(II)-oxid erfolgt über die intermediäre Bildung von $2CuCO_3.Cu(OH)_2$. Die Röntgendiffraktionstechnik wurde zur Identifizierung der Zersetzungsprodukte eingesetzt. Die Versuchsergebnisse von Cu(II)-malonat können am besten zwei kinetischen Zuständen angepaßt werden: (1) einem linearen Prozeß und (2) einem Ausdruck erster Ordnung. Die entsprechenden Aktivierungsenergien für die zwei kinetischen Zustände waren 45.7 Kcal/Mol bzw. 57.2 Kcal/Mol. Eine DTA-Untersuchung von Cu(II)-malonat wurde ebenfalls durchgeführt. Die Aktivierungsenergien wurden aus der Analyse der DTA-Kurve mittels der Gleichungen von Borchardt und Piloyan bestimmt.

Резюме — Было изучено изотермическое разложение частиц одного и того же размера малоната меди (II) при температурах 170°, 180° и 190°. Разложение малоната меди (II) до окиси меди протекает через стадию образования $2CuCO_3 . Cu(OH)_2$. Для идентификации продуктов разложения была использована техника диффракции рентгеновых лучей. Экспериментальные результаты по малонату меди (II) наилучше соответствуют двум кинетическим стадиям: (1) линейному процессу и (2) уравнению первого порядка. Было найдено, что соответствующие энергии активации этих двух кинетических стадий, соответственно, равны 45,7 ккал/моль 57,2 ккал/моль. Изучено также ДТА малоната меди (II). Из кривых ДТА, используя уравнения Борхардта и Пилояна, определены энергии активации.