Journal of Thermal Analysis, Vol. 18 (1980) 77—85

THERMAL DECOMPOSITION OF COPPER(II)PHTHALATE MONOHYDRATE

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(Received January 23, 1979)

The thermal dehydration and decomposition of copper(II) phthalate monohydrate was studied by isothermal and non-isothermal methods. The decomposition process consisted of three steps: two steps of dehydration and the third of decomposition. The kinetics of isothermal dehydration reactions follow (i) a unimolecular law up to the formation of copper(II) phthalate hemihydrate, and (ii) a phase boundary model giving anhydrous copper(II) phthalate, while the kinetics of isothermal decomposition reaction comply with the Erofeev—Avrami equation, $[-\ln(1-\alpha)]^{1/n} = Kt + C$. The energies of activation for the formation of the decomposition products were calculated. The decomposition products were characterized by elemental analysis, photomicrographic observations, infrared and reflectance spectra and X-ray powder diffraction data.

Currently much work is being done on the thermal decompositions of transition metal carboxylates [1, 2] to understand the mechanisms of decomposition and the nature of the decomposition products. A search of the available literature showed that the thermal decomposition of copper(II) phthalate monohydrate has not been studied so far. In a continuation of our work on the thermal decomposition of copper(II) carboxylates [3—5], we now report the thermal decomposition of $Cu(II)C_6H_4(COO)_2 \cdot H_2O$.

Experimental

Crystals of copper(II) phthalate monohydrate were prepared [6] by the addition of basic copper carbonate (BDH) to an aqueous solution of phthalic acid (Merck) to give a saturated solution. The excess of solid carbonate was removed by filtration, leaving a filtrate of pH ~ 5. The solution was left to evaporate slowly until blue, air-stable crystals appeared. The crystals were separated, washed several times with distilled water and air-dried. Chemical analysis of the compound gave Cu = 25.4 (gravimetric determination by precipitating Cu as CuSCN [7], C = 38.9 and H = 2.5% (microanalysis of carbon and hydrogen). Calculated for $Cu(II)C_6H_4(COO)_2 \cdot H_2O$: Cu = 25.8; C = 39.1 and H = 2.4%.

For the isothermal dehydration and decomposition studies, a known amount of the powdered sample was taken and the reactions were carried out in a manually-operated thermobalance described earlier [8].

Simultaneous TG-DTG-DTA curves were recorded by means of a Paulik–Paulik–Erdey MOM derivatograph (Hungary).

For microscopic studies of the crystals a polarizing microscope was used. The volatile organic decomposition products were collected and analyzed in a separate experiment. The identity of the sublimate product was confirmed from infrared spectra, melting point and other standard organic tests. It was found to be phthalic anhydride.

Infrared spectra were recorded on a Spektromom 2000 MOM Budapest spectrometer, calibrated with polystyrene for the spectral range 4000–650 cm^{-1}, in Nujol mulls. Reflectance spectra of the reactant and intermediates were measured on a VSU-2P spectrophotometer in the range 1000–220 μm, using MgO as the reference.

Powder X-ray diffraction pattern were recorded with an X-ray diffractograph, using nickel-filtered CuKα radiation.

Results and discussion

The isothermal dehydration reaction was studied at 393, 403 and 413 K using a loose powder of parallelopipeds. The reaction product was found by chemical analysis, infrared spectra and from loss in mass to be $Cu(II)C_6H_4(COO)_2 \cdot 0.5\ H_2O$. The dehydration mechanism was supported by microscopic observations. The reaction product after different intervals at 413 K was examined under a polarizing microscope. It was noticed that when the crystal was heated a number of nuclei formed randomly (Plate 1.). These nuclei are compact and crystalline; they grow in all directions, but the growth rate is not uniform (Plate 2.). Ultimately, the whole

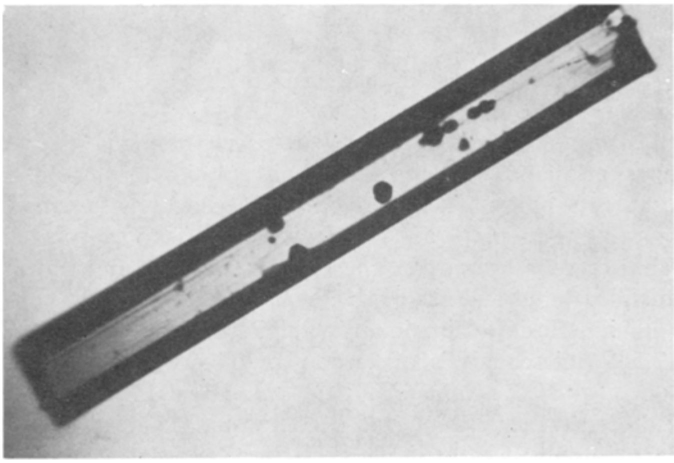

Plate 1. Formation of product nuclei after two minutes 63×

of the reactant is converted to a light-green product. The shape or habit of the product crystal remains unchanged upon reaction completion (Plate 3.).

The kinetics of the reaction follow a unimolecular law

$$-\log(1-\alpha)=Kt \qquad (1)$$

The applicability of Eq. (1) is shown in Fig. 1, where plots of $-\log(1-\alpha)$ *vs.* time t are linear. The energy of activation was found from the Arrhenius plot to be 99 ± 7 kJ/mole. Since the reaction was found to be irreversible, the theoretical order of reaction should also be one [9].

Further isothermal dehydration of copper(II) phthalate hemihydrate was conducted at 443, 458 and 473 K. At 458 K, the reaction product after 53 minutes corresponds to anhydrous copper(II) phthalate. The identity of the product was confirmed on the basis of chemical analysis, infrared and reflectance spectra and X-ray diffraction.

The infrared spectra of the original compound exhibit significant bands, attributed to the vibrational frequency of coordinated water at 810 cm^{-1}, the M–OH bending mode at 900 cm^{-1}, the out-of-plane (O–H) deformation at 970–940 cm^{-1} and the stretching mode of water at 3050–3000 cm^{-1} [10]. The sample heated at 473 K retains all the characteristic infrared features of the original compound except the bands due to water, suggesting thereby that all the water has been removed at this temperature.

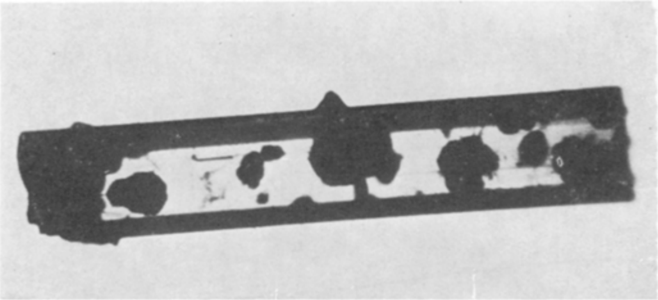

Plate 2. Growth of the nuclei of the product after seven minutes. 63×

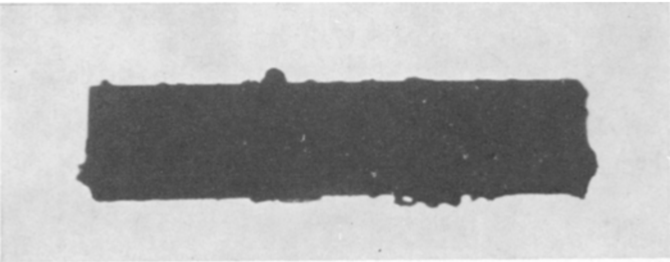

Plate 3. Crystal after reaction completion. 63×

The reflectance spectra of the starting material and the species involved in the dehydration process are shown in Fig. 2. The original band at 525–400 μm (I) gradually shifts to higher frequency, as the dehydration proceeds through the formation of a hemihydrate(II) to the anhydrous product. In the anhydrous carboxylate the band appears at 550–450 μm (III). The visual change in colour during the reaction was from blue to green.

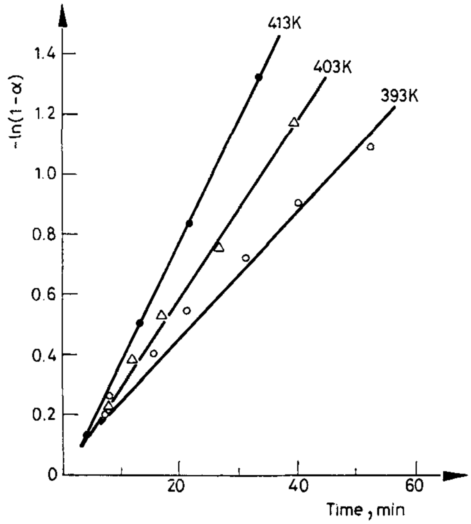

Fig. 1. Plots of $-\log(1-\alpha)^{1/2}$ vs. time for the isothermal dehydration of copper(II) phthalate monohydrate

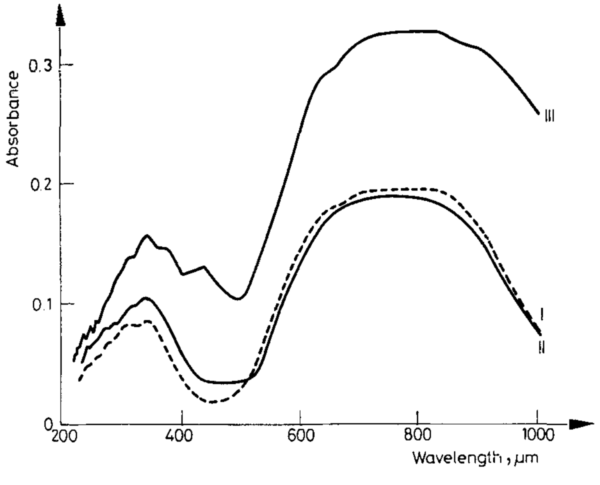

Fig. 2. Reflectance spectra of (I) copper(II) phthalate, (II) reaction product at 413 K (hemihydrate) and (III) anhydrous copper(II) phthalate

The kinetics of the reaction follow the contracting-area Eq. (2) and contracting-volume Eq. (3):

$$1 - (1 - \alpha)^{1/2} = Kt \tag{2}$$

$$1 - (1 - \alpha)^{1/3} = Kt \tag{3}$$

Figure 3 shows the validity of Eq. (2) where the plots of $1 - (1 - \alpha)^{1/2}$ *vs.* time t at various temperatures are straight lines, while the plots of $1 - (1 - \alpha)^{1/3}$ *vs.* time t are shown in Fig. 4, confirming the applicability of Eq. (3). From the

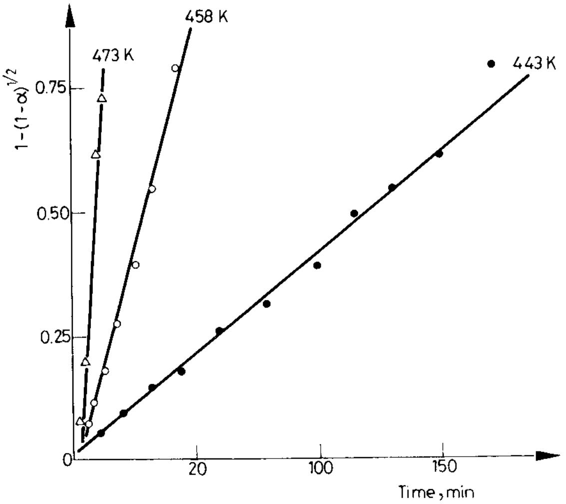

Fig. 3. Plots of $1 - (1 - \alpha)^{1/2}$ *vs.* time for the isothermal dehydration of copper(II) phthalate hemihydrate

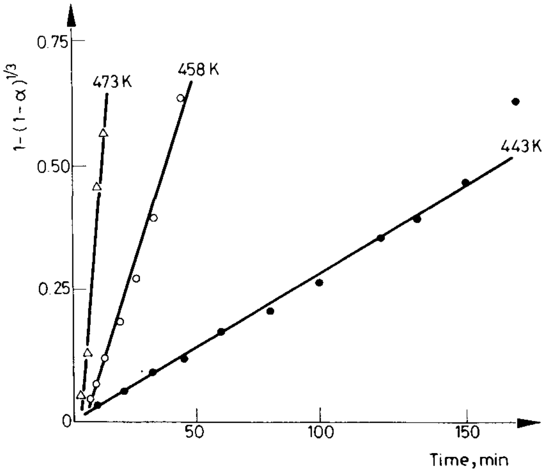

Fig. 4. Plots of $1 - (1 - \alpha)^{1/3}$ *vs.* time for the isothermal dehydration of copper(II) phthalate hemihydrate

Arrhenius plots the activation energies for the stages corresponding to Eqs. (2) and (3) were found to be 171 ± 8 and 178 ± 8 kJ/mole, respectively. The anhydrous salt was found by X-ray analysis to be crystalline, although the sizes of the crystallites were considerably decreased.

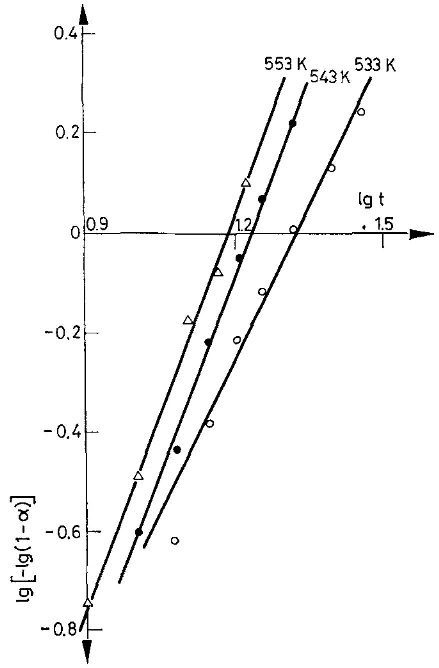

Fig. 5. Plots of ln [−ln (1 − α)] *vs.* ln *t* for the isothermal decomposition of copper(II) phthalate monohydrate

Table 1

X-ray diffraction data of the final decomposition product of copper(II) phthalate monohydrate

Experimental		ASTM data file (refs. [13] and [14])		Product assignment
d, Å	Intensities	*d*, Å	Intensities	
3.021	16	3.020	9	Cu_2O
2.524	50	2.523	100	CuO
2.466	100	2.465	100	Cu_2O
2.325	55	2.323	96	CuO
2.136	55	2.135	37	Cu_2O
1.865	20	1.866	25	CuO
1.583	10	1.581	14	CuO
1.512	60	1.510	27	Cu_2O

The isothermal decomposition of copper(II) phthalate monohydrate was carried out at 533, 543 and 553 K. The final loss in weight corresponded to the formation of cupric oxide. The crystals were examined under a polarizing microscope upon complete decomposition, when black crystals of CuO, diminished in size, were observed.

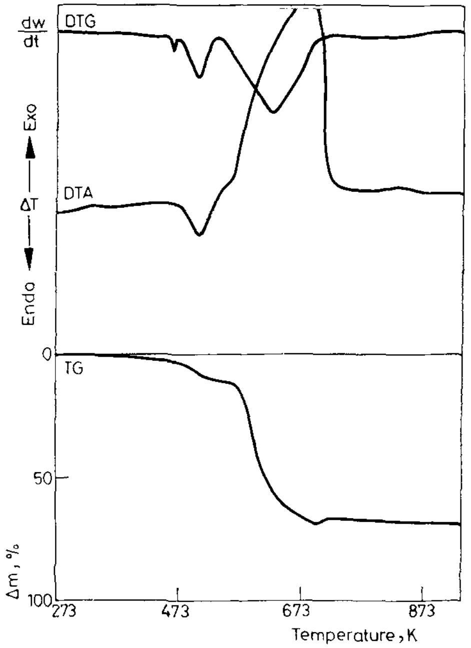

Fig. 6. Simultaneous TG-DTG-DTA curves of copper(II) phthalate monohydrate at a heating rate of 10°/minute

The kinetic data on the final product formation were best fitted by the Erofeev – Avrami equation [11, 12]

$$[-\ln(1-\alpha)]^{1/n} = Kt + C \tag{4}$$

Plots of $\ln[-\ln(1-\alpha)]$ against $\ln t$ (Fig. 5) are linear for α ranging from 0.34 to 0.98. The first part of the reaction ($0 < \alpha < 0.34$) accounts for the dehydration of the hydrated salt. An Arrhenius plot for Eq. (4) gave an energy of activation of 38.8 ± 4.2 kJ/mole. The nature of the final decomposition product of copper(II) phthalate monohydrate was studied with the help of an X-ray diffractogram using nickel-filtered CuK_α radiation. The crystal phase composition of the decomposition product at 823 K indicated that it consists of a mixture of CuO and Cu_2O. The *d* values along with the relative intensities calculated from the diffractogram and the corresponding *d* values and intensities for CuO [13] and Cu_2O [14] reported in literature are given in Table 1 and are comparable.

Dynamic thermal studies: Simultaneous TG-DTG-DTA curves were recorded with 100 mg of sample at heating rates of 5°/minute and 10°/minute with 100 mg sensitivity in static air atmosphere. Figure 6 shows the thermal curves at 10°/minute.

The DTG curve of the sample exhibits one sharp peak and two broad peaks, at 458, 493 and 633 K, respectively. The corresponding DTA indicates one shallow endothermic region and one endothermic peak, both due to dehydration, and one broad exotherm due to decomposition. In the TG curve there is one slackening and two arrests. The loss in weight calculated for the slackening and the first steps of the DTA and DTG corresponds to the formation of $Cu(II)C_6H_4(COO)_2$ $0.5\,H_2O$. The loss in weight calculated for the first arrest is in good agreement for anhydrous copper(II) phthalate as the product. The loss at this stage is slightly more than the expected loss, indicating that decomposition also starts simultaneously.Traces of phthalic anhydride, evolved as a volatile product near the end of the dehydration process, were probably a result of partial decomposition of anhydrous copper(II) phthalate, hence accounting for a slightly enhanced loss near dehydration, whereas the second arrest indicated a continuous weight loss right up to the formation of CuO. Rapid heating increased the proportion of lower-valent copper, as is evident from Fig. 6. The TG curve shows a slight gain in weight, further supported by a small endotherm in the DTA at 823 K. These indications are believed to be due to the reduction process by the evolved gases. Finally, the conversion of the crystal phase composition of the residual products to stable CuO on heating at higher temperatures is clear from the nature of the DTA curve.

The nature of the curves did not change when the heating rate was maintained at 5°/minute.

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One of the authors (C. M. K.) is grateful to the University of Jammu, Jammu, for the award of a Fellowship.

References

1. M. J. McGinn, B. R. Wheeler and A. K. Galwey, Trans. Faraday Soc., 67 (1971) 1.
2. H. Yokobayashi, K. Nagase and K. Muraishi, Bull. Chem. Soc., Japan, 48 (1975) 2789.
3. P. S. Bassi and P. C. Kalsi, Ind. J. Chem., Ser. A, 14 (1976) 967.
4. P. S. Bassi and P. C. Kalsi, J. Thermal Anal., 10 (1976) 375.
5. P. S. Bassi and P. C. Kalsi, J. Thermal Anal., 13 (1978) 363.
6. C. K. Prout, J. R. Carruthers and F. J. C. Rossotti, J. Chem. Soc., Ser. A, (1971) 3350.
7. A. I. Vogel, Quantitative Inorganic Analysis, Longmans, Green and Co., London, p. 497 1962.
8. P. S. Bassi, P. C. Kalsi and C. M. Khajuria, Ind. J. Chem., Ser. A, 15 (1977) 399.
9. D. M. Speros and H. R. Werner, Analytical Calorimetry, (ed. R. R. Porter J. F. Johnson), Plenum Press, New York, Vol. 3 p. 511 1974.

10. K. NAKAMOTO, Infrared Spectra of Inorganic and Co-ordinated compounds (John Wiley and Sons, Inc. London), p. 155 1962.
11. M. AVRAMI, J. Chem. Phys., 9 (1941) 177.
12. B. V. EROFEEV, Compt. Rend. Acad. Sci. (U.R.S.S.), 52 (1946) 54.
13. H. E. SWANSON and E. TATGE, NBS Circular 539 Vol. I (1953) 49.
14. H. E. SWANSON and R. K. FUYAT, NBS Circular 539 vol. II (1953) 23.

RÉSUMÉ — On a étudié, par des méthodes isothermes et non-isothermes, la déshydratation et la décomposition thermique du phtalate de cuivre(II) monohydraté. Le procèssus de décomposition consiste en trois étapes: deux étapes de déshydratation et la troisième de décomposition. La cinétique des réactions de déshydratation isotherme suit (i) une loi unimoléculaire jusqu'à la formation de phtalate de cuivre(II) hémihydraté, et (ii) un modèle de surfaces limites qui donne du phtalate de cuivre(II) anhydre, tandis que la cinétique de la réaction de décomposition isotherme satisfait l'équation d'Eroféev-Avrami: $[-\ln(1-\alpha)]^{1/n} = Kt + C$. On a calculé les énergies d'activation de la formation des produits de décomposition. On a caractérisé les produits de décomposition par analyse élementaire, par des observations micrographiques, des spectres infrarouges et d'émission ainsi que par des données de diffraction sur poudre des rayons X.

ZUSAMMENFASSUNG — Die thermische Dehydratisierung und Zersetzung von Kupfer(II)Phthalat Monohydrat wurde durch isotherme und nichtisotherme Methoden untersucht. Der Zersetzungsvorgang bestand aus drei Stufen: zwei Stufen der Dehydratisierung und die dritte der Zersetzung. Die Kinetik der isothermen Dehydratisierungsreaktionen folgt (i) einem unimolekularen Gesetz bis zur Bildung von Kupfer(II)Phthalat Hemihydrat und (ii) einem Grenzflächen modell, das wasserfreies Kupfer(II)Phthalat ergibt, während die Kinetik der isothermen Zersetzungsreaktion der Erofeev-Avrami Gleichung, $[-\ln(1-\alpha)]^{1/n} = Kt + C$ genügt. Die Aktivierungsenergien für die Bildung der Zersetzungsprodukte wurden berechnet. Die Zersetzungsprodukte wurden durch Elementaranalyse, mikrophotographische Beobachtungen, Infrarot- und Remissionsspektra sowie Röntgen-Pulverdiffraktionsdaten charakterisiert.

Резюме — С помощью изотермического и неизотермического методов анализа были изучены термическая дегидратация и разложение моногидрата фталата меди(II). Процесс разложения протекает в три стадии: две стадии дегидратации и третьей стадии разложения. Кинетика реакций изотермической дегидратации подчиняется мономолекулярному закону до образования полугидрата фталата меди(II) и модели фазовой границы, давая безводный фталат меди(II). Кинетика реакции изотермического разложения подчиняется уравнению Ерофеева-Аврами: $[-\ln(1-\alpha)]^{1/n} = Kt + C$. Вычислены энергии активации образования продуктов разложения. Продукты разложения были охарактеризованы элементарным анализом, фотомикрографией, ИК спектрами и спектрами отражения, а также порошковой рентгенографией.