

THERMAL DECOMPOSITIONS OF FORMATES. PART VI. THERMAL DEHYDRATION REACTION OF COPPER(II) FORMATE DIHYDRATE

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ABSTRACT

The thermal dehydration reactions of two kinds of copper(II) formate dihydrate, which differ in origin and preparation history, have been investigated by means of TG, DTA and DSC. The kinetics of isothermal dehydration were studied by weight loss, and the difference in kinetic behavior between these two samples was related to the difference in origin and preparation history. On the whole, the dehydration mechanisms of these two samples were found to be phase boundary controlled contracting interface reactions.

INTRODUCTION

It is well known that a chemical reaction in the solid state is influenced by the history of the preparation of the solid. In this paper, the thermal dehydration reactions of two kinds of $\text{Cu}(\text{HCO}_2)_2 \cdot 2 \text{H}_2\text{O}$, which differ in origin and preparation history, were investigated by means of TG, DTA and DSC in order to elucidate the influence of the preparation methods. Isothermal kinetic experiments, X-ray and IR analyses and scanning electron microscopic (SEM) observations were also carried out to give some indication of the dehydration processes.

Basic kinetic constants, such as the order of reaction, enthalpy change and activation energy, were determined in order to compare the dehydration reactions of these samples. The differences in these reaction parameters were related to the chemical and physical properties of the two samples.

EXPERIMENTAL

Materials

Two kinds of $\text{Cu}(\text{HCO}_2)_2 \cdot 2 \text{H}_2\text{O}$ were prepared as follows. The first sample (A) was obtained by very slow evaporation at 328 K, from aqueous solution containing free formic acid [1,2]. The second sample (B) was obtained by heating $\text{Cu}(\text{HCO}_2)_2 \cdot 4 \text{H}_2\text{O}$ for 1 h at 320 K in air. These samples were ground in a pestle and mortar and sieved to a narrow fraction of 270–325 mesh size in order to carry out the dehydration processes under the same conditions.

Measurements

TG and DTA curves were simultaneously recorded on a Rigaku Thermoflex TG-DTA M 8075 at a heating rate of 5 K min⁻¹ in air. About 10 mg of specimen were weighed into an aluminium crucible, and measured using α -alumina as reference material.

The enthalpy change for the dehydration was determined from the DSC curve recorded on a Rigaku Thermoflex DSC 8055, at a heating rate of 5 K min⁻¹. The instrument was calibrated by measuring the heat of transition of KNO₃ ($\Delta H = 5.414$ kJ mole⁻¹ at 401 K).

IR absorption spectra were measured from 250 to 4000 cm⁻¹ in KBr disks with a Hitachi 295 spectrophotometer. X-Ray diffraction patterns were recorded on a Rigaku Geigerflex diffractometer. CuK α radiation and a nickel filter were used in all measurements. A Shimadzu EMXSM type SEM apparatus was used.

RESULTS AND DISCUSSION

The thermal dehydration reaction of sample A was studied by the static and dynamic methods described previously [1], and basic kinetic constants, such as the order of reaction, activation energy, enthalpy change of dehydration and frequency factor, were determined (Table 1). The dehydration reaction appeared to proceed in two steps, which obeyed a phase boundary controlled and a unimolecular decay expression. However, it actually took

TABLE 1

Experimental rate constants and Arrhenius parameters for the thermal dehydration of sample A

T (K)	Stage 1 *		Stage 2 **
	logk ₁	α_0 ***	logk ₂
350	-0.671	0.96	-0.159
353	-0.541	0.98	0.012
355	-0.453	0.97	0.142
358	-0.325	0.97	0.284
360	-0.242	0.96	0.395
	A (sec ⁻¹)		E (kJ mole ⁻¹)
Stage 1	1.6 × 10 ¹³		104.3
Stage 2	2.2 × 10 ¹⁷		129.2

Enthalpy change for dehydration $\Delta H = 127.9$ kJ mole⁻¹

* Phase boundary controlled contracting interface reaction.

** First-order reaction.

*** α_0 is the fraction at which the transition from stage 1 to stage 2 occurred.

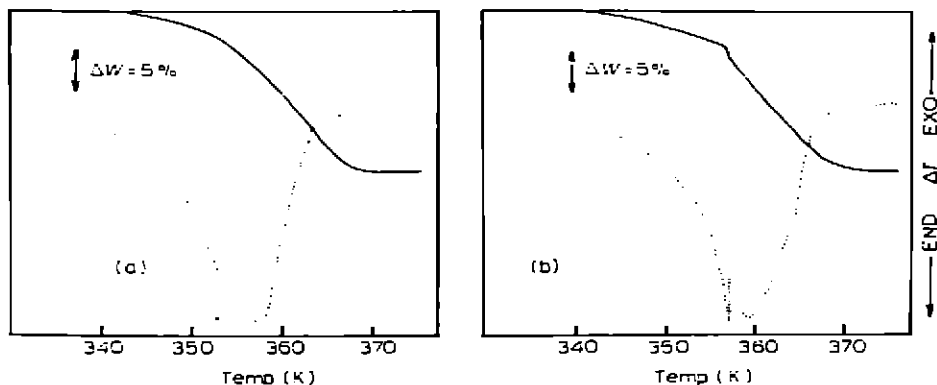


Fig. 1. TG (solid line) and DTA (broken line) for the dehydration of $\text{Cu}(\text{HCO}_2)_2 \cdot 2 \text{H}_2\text{O}$. (a) Sample A; (b) sample B.

place as a one-step reaction and the rate was controlled by a chemical process at a phase boundary.

Although the X-ray diffraction pattern and IR spectra of sample B were similar to those of A, the thermal behavior was different. In particular the DTA curve of sample B showed two endothermic peaks and, corresponding to these peaks, the TG curve was divided into two regions, i.e. the dehydration started at 333 K and the weight fell slowly to 4.2% at 357 K; above this temperature the dehydration proceeded rapidly and a constant level was reached from 373 K (19% weight loss), corresponding to $\text{Cu}(\text{HCO}_2)_2$ (Fig. 1). These thermal analysis results suggested that the dehydration reaction of sample B proceeded in two steps.

The dehydration of sample B was studied in more detail by the static method under isothermal conditions. The relation between the fraction of dehydration, α , and time of reaction, t , for the isothermal dehydration are shown in Fig. 2. $\alpha(t)$ curves obtained at lower temperature (348 and 351 K)

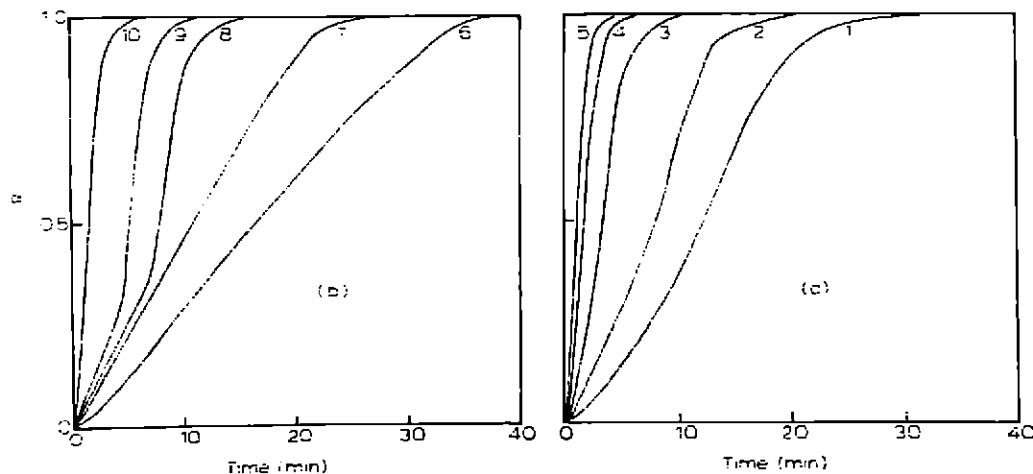


Fig. 2. $\alpha-t$ curves for $\text{Cu}(\text{HCO}_2)_2 \cdot 2 \text{H}_2\text{O}$. (a) Sample A; (b) sample B. 1, 350 K; 2, 353 K; 3, 355 K; 4, 358 K; 5, 360 K; 6, 348 K; 7, 351 K; 8, 352.5 K; 9, 354 K; 10, 357 K.

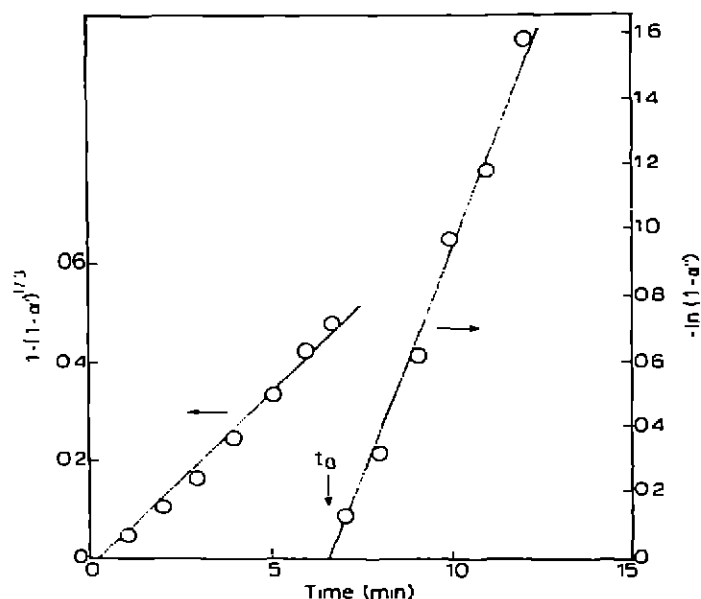


Fig. 3. Plots of $1 - (1 - \alpha')^{1/3}$ vs. time and $-\ln(1 - \alpha'')$ vs. time for sample B at 352.5 K.

were similar to those of other formate dihydrates [1]. However, in the curve obtained at 352.5 K a flexion was observed when α reached about 0.35, and for $\alpha > 0.35$ the reaction was greatly accelerated. The $\alpha(t)$ curve obtained at 354 K was similar to that obtained at 352.5 K and a flexion was also observed when α reached 0.29. The form of these curves suggested that the dehydration mechanism changed at these flexion points.

TABLE 2

Experimental rate constants and Arrhenius parameters for the thermal dehydration of sample B

T (K)	Stage 1 *		Stage 2 **
	$\log k_1$	α_0 ***	$\log k_2$
348	-0.721	0.78	-0.804
351	-0.621	0.59	-0.714
352.5	-0.601	0.34	-0.535
354	-0.451	0.29	-0.508
357		0	-0.290
	A (sec^{-1})		E (kJ mole^{-1})
Stage 1	7.1×10^{11}		93.8
Stage 2	1.1×10^{18}		135.7

Enthalpy change for dehydration $\Delta H = 119.5 \text{ kJ mole}^{-1}$

* Phase boundary controlled contracting interface reaction.

** First-order reaction.

*** α_0 is the fraction at which the transition from stage 1 to stage 2 occurred.

Analyzing the curve obtained at 352.5 K, the reaction conformed with a phase boundary controlled expression [3] up to the flexion point

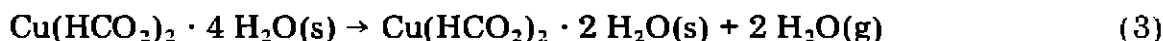
$$1 - (1 - \alpha')^{1/3} = k_1 t \quad (1)$$

where k_1 is a rate constant, α' is α/α_0 and α_0 is the fraction at which a flexion occurred. The remainder of the reaction fitted a first-order reaction [3]

$$-\ln(1 - \alpha'') = k_2(t - t_0) \quad (2)$$

where α'' is $(\alpha - \alpha_0)/(1 - \alpha_0)$, k_2 is a rate constant for a first-order reaction and t_0 is the time at which α becomes α_0 (Fig. 3). Experimental rate constants and Arrhenius parameters for the thermal dehydration of sample B are given in Table 2.

It is noteworthy that the activation energy for the phase boundary controlled process of sample B was somewhat lower than that of A, and the induction period of the former was shorter than that of the latter. In addition to the above results, the value of α_0 decreased with increasing reaction temperature and it seemed to converge to zero at the highest temperature examined (357 K). Since the dehydration starts at the corners and edges of the particles which are nucleated within an induction period, a shorter induction period and a lower activation energy for sample B must be related to its structure and preparation history. If the nuclei were formed during the preparation process



the thermal behavior mentioned above is reasonable.

The activation energy and frequency factor for the first-order reaction of sample B were comparable to those of A. It appears that the transition from the phase boundary controlled process to the first-order reaction must be virtually the same as that for sample A, i.e. the dehydration reaction seems to obey essentially the phase boundary controlled expression.

From the SEM observations (Fig. 4), sample B has a porous solid structure formed by evolution of the water vapor in reaction (3). Therefore, the fact that the α_0 value was found to be smaller than that of sample A ($\alpha_0 \sim 0.96$) is ascribable to the porous structure of sample B. It is reasonable that the dehydration which begins on the porous surface of the crystal and propagates to its center shows an appearance of a quasi first-order reaction more rapidly than one which begins on an even surface. At higher temperatures it appears as though the reaction occurring throughout the bulk of the solid exhibits a kinetic behavior which is characteristic of a homogeneous first-order reaction, for the dehydration proceeds too rapidly from the porous surface to the inside of the powder specimen. Consequently, it may be concluded that the kinetic behavior of sample B is almost the same as that of A.

The enthalpy change for the dehydration gives the difference in potential energy between the hydrated and anhydrous copper(II) formate. Therefore, sample A is more stable than B by about 8 kJ mole⁻¹, which is not contradictory to the fact that sample B is more activated than A by about 10 kJ mole⁻¹.

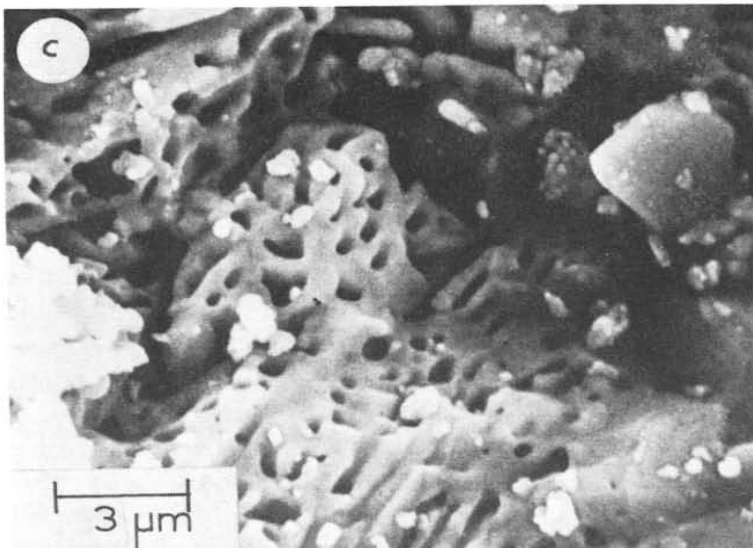
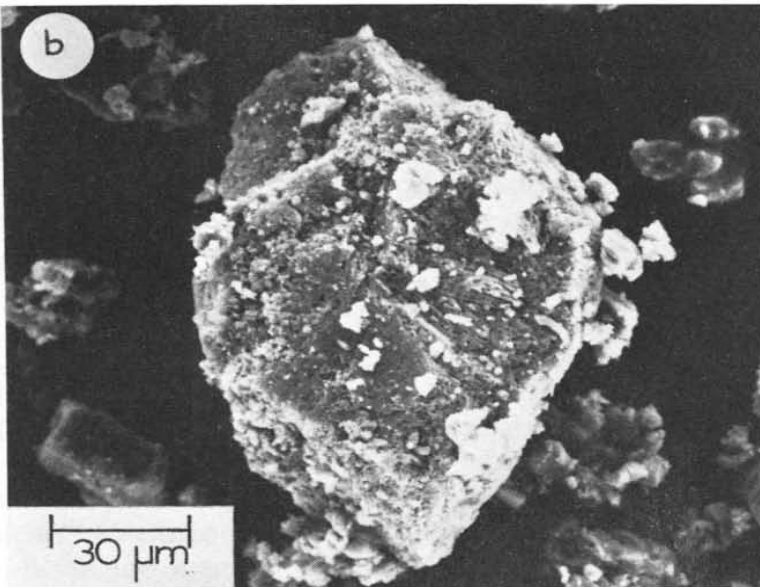
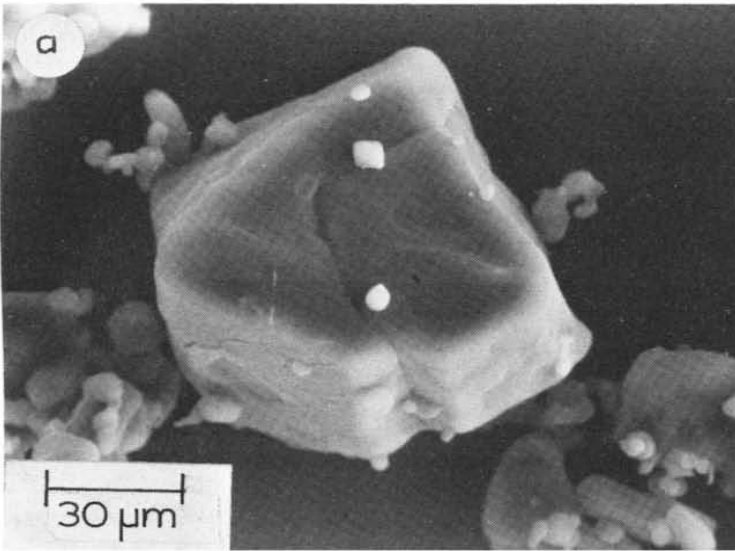


Fig. 4. SEM photographs of samples A and B. (a) Sample A; (b), (c), sample B.

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