

DEHYDRATION OF CRYSTALLINE $K_2CO_3 \cdot 1.5 H_2O$

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ABSTRACT

Sesquihydrated potassium carbonate crystals were grown by slow evaporation of its aqueous solution maintained at $40 \pm 1^\circ C$. The thermal dehydration of this crystal was studied by dynamic and isothermal TG measurements. It was observed from dynamic TG that the $K_2CO_3 \cdot 1.5 H_2O$ crystal dehydrates in steps of 0.5 mole and 1 mole at temperatures of 235 ± 4 and $273 \pm 10^\circ C$, respectively. Isothermal TG measurements have been carried out from 190 to $260^\circ C$ at intervals of $10^\circ C$. From isothermal and dynamic TG measurements, kinetic parameters E and Z are calculated using different known forms of the function $F(\alpha)$. It is observed that consistency of E and Z values in isothermal and dynamic TG measurements for the two dehydration steps gives the correct function $F(\alpha)$ as $[-\ln(1 - \alpha)]^{0.5}$. The activation energies for the function $F(\alpha)$ for the two dehydration steps are $\sim 22 \text{ kcal mole}^{-1}$ and $\sim 10 \text{ kcal mole}^{-1}$, respectively.

INTRODUCTION

Sesquihydrated potassium carbonate is formed at temperatures exceeding $38^\circ C$ [1]. Pohl [2] reported that $K_2CO_3 \cdot 1.5 H_2O$ loses 5.59% of water at $100^\circ C$ and forms monohydrated potassium carbonate $K_2CO_3 \cdot H_2O$, which loses all its water in the range 130 – $135^\circ C$.

Our interest in studying the thermal analysis of $K_2CO_3 \cdot 1.5 H_2O$ arises from the fact that it is isostructural with $Na_2CO_3 \cdot H_2O$. We have carried out a thermal analysis of $Na_2CO_3 \cdot H_2O$ and found that it dehydrates in two steps, one of 0.3 mole and the other of 0.7 mole (3). From isothermal and dynamic TG analysis it was shown that the dehydration mechanism is given by the function $F(\alpha) = [-\ln(1 - \alpha)]^{0.5}$. A literature survey shows that very little work has been carried out on the dehydration of K_2CO_3 in general and the mechanism of dehydration in particular.

The present paper reports the kinetics of thermal dehydration of a $K_2CO_3 \cdot 1.5 H_2O$ crystal by means of TG at a constant heating rate and from isothermal data. It is observed from dynamic TG that $K_2CO_3 \cdot 1.5 H_2O$

dehydrates in two steps, one of 0.5 mole and the other of 1 mole at mean temperatures of 235 ± 4 and $273 \pm 10^\circ\text{C}$, respectively. Comparison of the activation energy and frequency factor from dynamic and isothermal measurements shows that the dehydration mechanism in a $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystal is given by the function $F(\alpha) = [-\ln(1 - \alpha)]^{0.5}$.

EXPERIMENTAL

Potassium carbonate of purity 99.5% was obtained from Sarabhai Chemicals. $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystals were grown by slow evaporation of its aqueous solution. The temperature of the solution was maintained at $40 \pm 1^\circ\text{C}$. It was observed that crystalline $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ is less hygroscopic than the powder form.

The thermogravimetry study was carried out using the TG assembly fabricated in this laboratory, details of which are given elsewhere [4]. The measurement of mass loss was carried out in the temperature range $30\text{--}300^\circ\text{C}$. The crystals were heated at a rate of 5°C min^{-1} . The value of $\Delta m/\Delta t$, i.e. the rate of change of mass (mg min^{-1}) was calculated at different temperatures. Change in mass vs. temperature (TG) and rate of change of mass vs. temperature (DTG) curves were plotted.

Isothermal TG measurements were carried out by maintaining the temperature constant within $\pm 1^\circ\text{C}$. Measurements were made in the temperature range $190\text{--}260^\circ\text{C}$ at intervals of 10°C . Kinetic parameters were calculated using different methods.

RESULTS AND DISCUSSION

Figure 1 gives the representative set for the sequence of dehydration steps for a $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystal grown at 40°C . The figure shows that dehydration starts from 160°C . The crystal shows two DTG maxima at 235 and 270°C . The TG measurement also shows changes of slope near these temperatures. It is observed that for a crystal of mass 485 mg, the observed loss in mass corresponded to the liberation of 1.5 water molecules; 0.5 mole is lost at 235°C and the remaining 1 mole is lost at 270°C . Comparison of the area under the two DTG peaks also confirms this observation.

Figure 2 shows the result of isothermal TG measurements. Here α , the fraction dehydrated at time t , is plotted against time. It is seen from the figure that the lower the isothermal temperature the higher is the time required for complete dehydration. It is observed that the crystal dehydrates completely at 140°C when maintained at this temperature for about 20 h. But when the crystal was maintained at 120°C only 0.5 mole of water came out of the crystal in nearly 15 h. It is observed that if sufficient time is

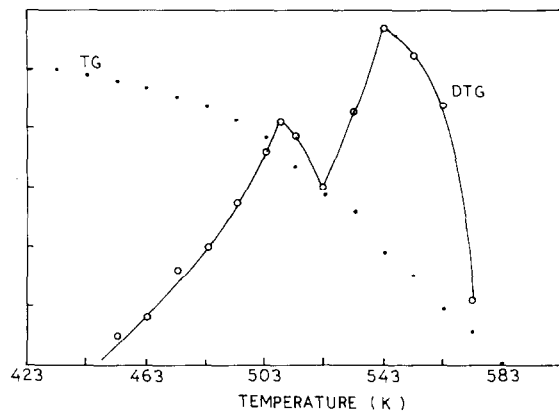


Fig. 1. Plot of TG and DTG curve for the thermal dehydration of $K_2CO_3 \cdot 1.5 H_2O$.

allowed, complete dehydration takes place at $140^\circ C$, a temperature much lower than the final mean dehydration temperature $273^\circ C$ given by dynamic TG.

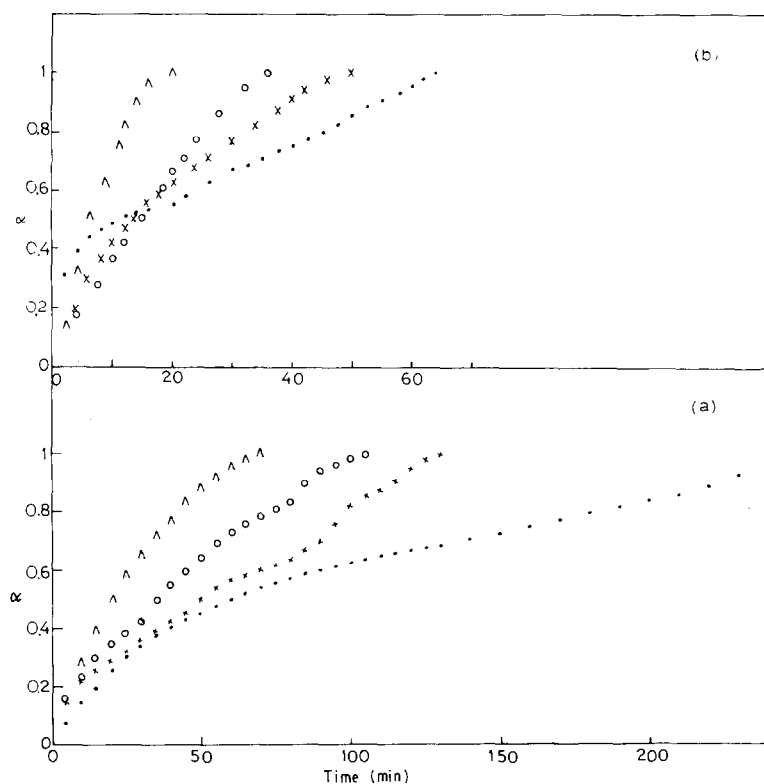


Fig. 2. Plots of fraction reacted vs. time. (a) ●, $190^\circ C$; ×, $200^\circ C$; ○, $210^\circ C$; △, $220^\circ C$. (b) ●, $230^\circ C$; ×, $240^\circ C$; ○, $250^\circ C$; △, $260^\circ C$.

For calculation of kinetic parameters from isothermal measurements we assume that the equation

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

holds good for the thermal dehydration of $K_2CO_3 \cdot 1.5 H_2O$. Here α is the fraction of reactant dehydrated at time t and k is the rate constant. Integration of eqn. (1) gives

$$F(\alpha) = \int \frac{d\alpha}{f(\alpha)} = kt = tZe^{-E/RT} \quad (2)$$

The function $F(\alpha)$ which describes the mechanism for the isothermal dehydration can be determined by plotting various theoretical functions against t ; the correct function should give a straight line with slope k [5]. The functions used in the present study are $-\ln(1-\alpha)$, $[-\ln(1-\alpha)]^{0.66}$, $[-\ln(1-\alpha)]^{0.5}$, $[-\ln(1-\alpha)]^{0.4}$, $[-\ln(1-\alpha)]^{0.33}$ and $[-\ln(1-\alpha)]^{0.25}$. Typical plots of the function $[-\ln(1-\alpha)]^{0.5}$ vs. time at temperatures in the range 190–260°C at intervals of 10°C are shown in Figs. 3 (a) and (b). Figure 3 (a) gives variations of $[-\ln(1-\alpha)]^{0.5}$ vs. time from 190 to 220°C and Fig. 3 (b) gives variations of the same function with time from 230 to 260°C. It is observed that all the functions except $-\ln(1-\alpha)$ give good straight lines. They also show bilinear variation with a change of slope. A change of slope indicates the presence of two distinct dehydration steps. Though $F(\alpha)$ vs. time plots show bilinear variation for all the temperatures from 190 to 260°C and for all the functions mentioned, it was observed that at higher temperatures a part of the water molecules corresponding to the second step (1 mole) is lost with the water molecules for the first step (0.5 mole). The lower the isothermal temperature the lower is the fraction of water molecules corresponding to second step that goes along with the first step.

A typical plot of $-\log k$ vs. $1/T$ for temperatures 190 to 260°C is shown in Fig. 4 for the function $[-\log(1-\alpha)]^{0.5}$. It is seen from the figure that there is a discontinuity in the curve near 230°C. The two parts of the curve for the first dehydration step have the same slopes but the curve for the second step has different slopes. Table 1 gives the kinetic parameters obtained in terms of the Arrhenius equation for different $F(\alpha)$. It is seen from the table that the activation energy values for the two dehydration steps calculated from the $-\log k$ vs. $1/T$ curve for a set of temperatures from 190 to 220°C are nearly the same, whereas for a set of temperatures from 230 to 260°C quite different values are shown for the two dehydration steps. It is observed in the case of the $K_2CO_3 \cdot 1.5 H_2O$ crystal that if the isothermal dehydration temperature is lower than the first dehydration temperature given by dynamic TG, then the set of isothermal temperatures give the correct activation energy value only for the first step even though water molecules corresponding to the second dehydration step are lost at

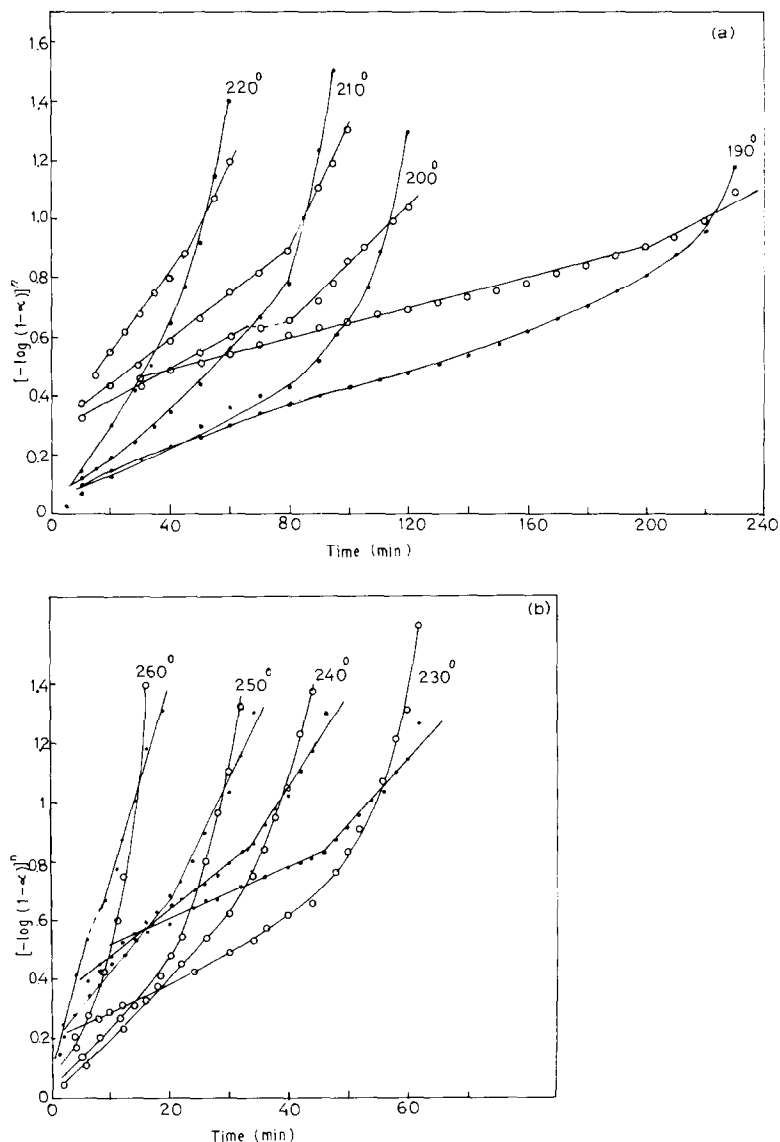


Fig. 3 (a) Plots of $[-\log(1-\alpha)]^n$ (isothermal) vs. time at 190–220°C. ●, $n=1$; ○, $n=0.5$. (b) Plots of $[-\log(1-\alpha)]^n$ (isothermal) vs. time at 230–260°C. ○, $n=1$; ●, $n=0.5$.

these temperatures. If the isothermal dehydration temperatures are higher than the dehydration temperature for the first step as given by dynamic TG, then the set of isothermal temperatures give quite different values for the two dehydration steps. As will be seen later, the correct value of the activation energy can be known only when these values from isothermal and dynamic measurements are compared.

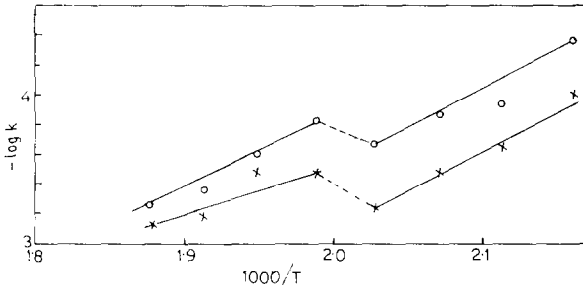


Fig. 4. Arrhenius plots for the isothermal dehydration of $K_2CO_3 \cdot 1.5 H_2O$. \circ step 1; \times , step 2.

The kinetic parameters may also be obtained from analysis of the dynamic TG curve by using the Coats–Redfern equation [6]

$$\ln \frac{F(\alpha)}{T^2} = \ln \frac{ZR}{\phi E} \left(1 - \frac{2RT}{E} \right) - \frac{E}{RT} \quad (3)$$

where T is the absolute temperature, Z is the frequency factor, R is the gas constant, ϕ is the linear heating rate, and E is the activation energy. typical plots of $-\log\{[-\log(1-\alpha)]^{0.5}/T^2\}$ vs. $1/T$ are shown in Fig. 5. It is observed that all the functions including $-\log(1-\alpha)$ give straight line plots. Each functional plot is bilinear, indicating that there are two distinct dehydration steps. Kinetic parameters obtained for the dehydration of the

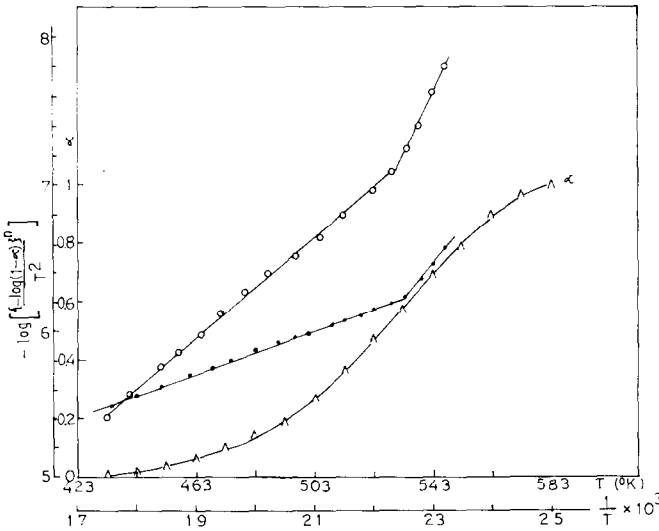


Fig. 5. Plots of α and $-\log\{[-\log(1-\alpha)]^n/T^2\}$ vs. $1/T$ for the thermal dehydration of $K_2CO_3 \cdot 1.5 H_2O$ (dynamic). \circ , $n = 1$; \bullet , $n = 0.5$.

TABLE I (continued)

F(α)	Step	Temperature range 230–260°C		Temperature range 190–220°C	
		E (kcal mole ⁻¹)	Z (s ⁻¹)	E (kcal mole ⁻¹)	Z (s ⁻¹)
F(α) ^{0.66}	1	22.75	(4.30 ± 0.99) 10 ⁶	27.30	(1.40 ± 0.11) 10 ⁹
	2	12.74	(2.47 ± 0.47) 10 ²	21.23	(4.33 ± 0.93) 10 ⁶
F(α) ^{0.5}	1	22.02	(1.93 ± 0.46) 10 ⁶	24.65	(8.15 ± 3.67) 10 ⁷
	2	10.01	(15.37 ± 4.15)	22.75	(1.99 ± 0.20) 10 ⁷
F(α) ^{0.4}	1	29.40	(2.79 ± 0.52) 10 ⁹	25.78	(1.17 ± 0.160) 10 ⁸
	2	21.36	(1.84 ± 0.20) 10 ⁶	22.75	(1.49 ± 0.12) 10 ⁷
F(α) ^{0.33}	1	30.34	(7.28 ± 1.79) 10 ⁹	22.75	(6.05 ± 0.76) 10 ⁶
	2	10.32	11.62 ± 1.82	18.20	(9.46 ± 0.23) 10 ⁴
F(α) ^{0.25}	1	23.90	(9.64 ± 3.84) 10 ⁴	22.75	(5.25 ± 0.67) 10 ⁶
	2	6.82	0.24 ± 0.05	18.20	(6.80 ± 0.68) 10 ⁴

TABLE 2
 Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of the $K_2CO_3 \cdot 1.5 H_2O$ crystals from dynamic TG

$F(\alpha)$	E (kcal mole ⁻¹)	Z (s ⁻¹)		Dehydration temp. (°C)	
		Step 1	Step 2	Step 1	Step 2
$-\log(1-\alpha)$	39.14 ± 0.19	19.24 ± 0.69	$(6.29 \pm 1.11) \times 10^7$	$235 \pm 4^\circ C$	$273 \pm 10^\circ C$
$[-\log(1-\alpha)]^{0.66}$	30.05 ± 0.62	11.80 ± 0.94	$(1.53 \pm 0.40) \times 10^6$	$(7.61 \pm 2.33) \times 10^3$	
$[-\log(1-\alpha)]^{0.5}$	21.18 ± 0.47	9.55 ± 0.30	$(2.94 \pm 0.39) \times 10^4$	$(2.71 \pm 1.01) \times 10^2$	
$[-\log(1-\alpha)]^{0.4}$	18.70 ± 0.34	5.09 ± 0.20	$(10.03 \pm 1.49) \times 10^3$	100.46 ± 9.32	
$[-\log(1-\alpha)]^{0.33}$	14.80 ± 0.77	3.99 ± 0.07	$(16.52 \pm 4.93) \times 10^2$	11.03 ± 1.03	
$[-\log(1-\alpha)]^{0.25}$	9.43 ± 0.33	2.95 ± 0.04	$(1.14 \pm 0.32) \times 10^2$	7.05 ± 0.45	
				5.85 ± 0.23	

$\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystal for the two steps, using different forms of the function $F(\alpha)$ are tabulated in Table 2.

It has been pointed out by Criado and Morales [7] from their theoretical analysis, that the linearity of the $F(\alpha)$ vs. $1/T$ plot obtained from dynamic TG study is a necessary but not sufficient criterion. They reiterated the necessity of recording at least one isothermal measurement of the same reaction in the temperature interval of TG measurement in order to assign the proper form of $F(\alpha)$. This is in agreement with the views of Dharwadkar et al. [8] and Tang and Choudhari [9]. The dehydration study of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ also shows that, to determine the proper form of $F(\alpha)$, consistency in the values of E and Z obtained from isothermal and dynamic TG should be considered. Thus, on comparing the E and Z values for different forms of $F(\alpha)$ in Tables 1 and 2, it is seen that for $F(\alpha) = [-\ln(1 - \alpha)]^{0.5}$, the E and Z values are comparable. For other functions a large variation in E and Z values are observed in the isothermal and dynamic study. Thus the possible mechanism for the dehydration of the $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystal is one of random nucleation and subsequent growth. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals also showed this mechanism of dehydration [3].

CONCLUSIONS

It is concluded that: (i) the $\text{K}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}$ crystal dehydrates in two distinct steps of 0.5 mole and 1 mole at temperatures of 235 ± 4 and $273 \pm 10^\circ\text{C}$, respectively; (ii) to determine the proper form of the function for the dehydration, consistency in the values of E and Z obtained from isothermal and dynamic experiments should be considered; (iii) for calculation of kinetic parameters isothermal TG should be carried out near the second dehydration step temperature; and (iv) the value of E very much depends upon the form of the function $F(\alpha)$.

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