

THERMAL ANALYSIS OF $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ CRYSTALS

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ABSTRACT

Monohydrated sodium carbonate crystals have been grown by slow evaporation of its aqueous solution maintained at $40 \pm 1^\circ\text{C}$. The thermal dehydration of this crystal has been studied by dynamic and isothermal TG measurements. It is observed from dynamic TG that the single molecule of water of crystallization is lost in two steps of 0.3 mole and 0.7 mole at temperatures 426 ± 5 and 454 ± 5 K, respectively. From isothermal and dynamic TG measurements, the 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 $F(\alpha) = -[\log(1 - \alpha)]^{0.5}$. The activation energies for this function for the two dehydration steps are ≈ 6 and ≈ 9 kcal mole $^{-1}$, respectively.

INTRODUCTION

Monohydrated sodium carbonate is a stable solid phase in the presence of aqueous solution at temperatures exceeding 32.5°C , which is the transition point for the transformation of decahydrated sodium carbonate to heptahydrated carbonate [1]. According to Haidinger [2], the monohydrated salt is formed when the decahydrated salt is melted in its own water of crystallization. Schindler [3] found that when a higher hydrate is kept at a temperature between 32.5 and 37.5°C , monohydrated carbonate is formed. Haidinger pointed out that the monohydrate does not melt when heated but loses its combined water between 87 and 100°C . We have studied dehydration steps in $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals and found that the single water molecule comes out of the crystal in two steps, one of 0.3 mole and the other 0.7 mole at mean temperatures 426 ± 5 and 454 ± 5 K, respectively [4].

The present paper deals with the kinetics of thermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystals by means of TG at a constant heating rate and from isothermal data.

EXPERIMENTAL

Analar grade sodium carbonate was obtained from Sarabhai Chemicals. Sodium carbonate monohydrate crystals were grown by slow evaporation of its aqueous solution. The temperature of solution was maintained at $40 \pm 1^\circ\text{C}$.

The thermogravimetric study was carried out using the TG assembly fabricated in the laboratory, details of which are given elsewhere [5]. The measurement of mass loss was carried out in the temperature range 30 to 225°C . The crystals were heated at a rate of 5°C min^{-1} . The value of $\Delta m/\Delta t$, i.e. 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 at 90, 100, 110, 120, and 130°C . Kinetic parameters were calculated using different methods.

RESULTS AND DISCUSSION

Figure 1 represents the sequence of dehydration steps for a $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystal grown at $40 \pm 1^\circ\text{C}$. The crystal shows two DTG maxima at 153 and 185°C . The TG measurement also shows a change of slope near these temperatures. For a crystal of mass 423 mg, the observed loss in mass corresponds to the liberation of one water molecule. Out of this one water molecule, 30% is lost at 153°C and the remaining 70% is lost at 185°C . This suggests that the single water molecule is not removed from the crystal in one step but is lost in two fractions. Comparison of the area under the two DTG peaks confirms this fact.

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 Fig. 2 that the time required for the loss of one water molecule at 90°C is 320 min, at 100°C , 180 min, at 110°C , 120 min, at 120°C , 90 min and at 130°C , 80 min. Complete dehydration takes place at 90°C , a temperature which is much lower than the actual dehydration temperature (185°C) given by the dynamic TG.

For the 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 $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Here, α is the fraction of reactant dehydrated at time t and k is the rate constant. Integration of eqn. (1) gives

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

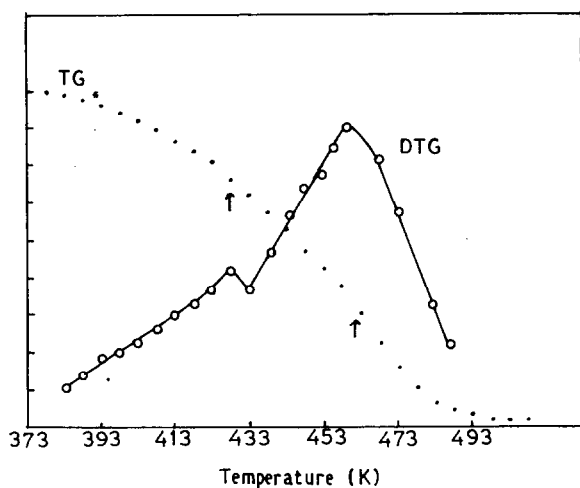


Fig. 1. Plots of TG, DTG curves for the thermal dehydration of the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystal.

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 [6]. The functions used in the present study are $-\ln(1 - \alpha)$, $\{-\ln(1 - \alpha)\}^{1/2}$ and $\{-\ln(1 - \alpha)\}^{2/5}$. Typical plots of these functions vs. time at temperatures 100, 110 and 120°C are shown in Fig. 3. It is seen from Fig. 3 that the functions $\{-\ln(1 - \alpha)\}^{2/5}$ and $\{-\ln(1 - \alpha)\}^{1/2}$ give good straight lines. Both the functions show bilinear variations with a change of slope. The change of slope indicates the

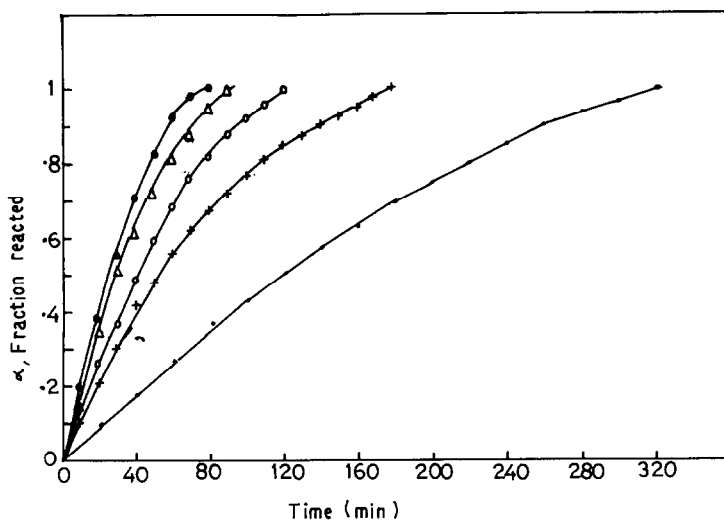


Fig. 2. Plots of fraction reacted vs. time. ·, 90°C; ×, 100°C; ○, 110°C; △, 120°C; ●, 130°C.

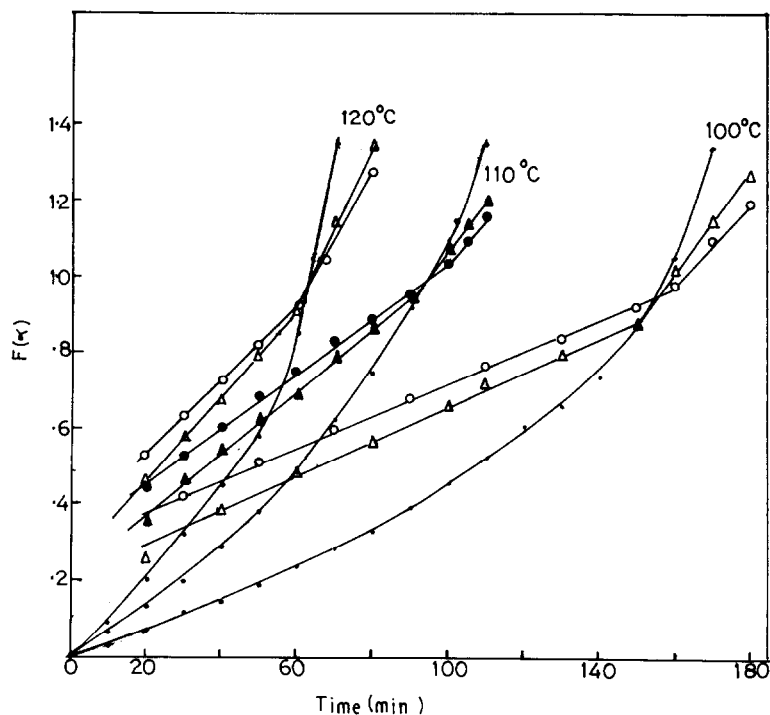


Fig. 3. Plots of $F(\alpha)$ (isothermal) vs. time at 100, 110 and 120°C. ·, $-\log(1-\alpha)$; ○, 0 ; Δ , $\{-\log(1-\alpha)\}^{0.5}$.

presence of two distinct dehydration steps. A typical plot of $-\log k$ vs. $1/T$ is shown in Fig. 4. Table 1 gives the kinetic parameters obtained in terms of the Arrhenius equation for different $F(\alpha)$. It is seen from Table 1 that the

TABLE 1

Kinetic parameters for the thermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ from isothermal TG

Temp. (K)	$k(\text{s}^{-1})$ for $F(\alpha)^{0.4}$		$k(\text{s}^{-1})$ for $F(\alpha)^{0.5}$	
	Step I $\times 10^{-5}$	Step II $\times 10^{-5}$	Step I $\times 10^{-5}$	Step II $\times 10^{-5}$
403	16.22	33.33	18.84	39.54
393	15.83	30.30	17.28	35.71
383	12.20	22.25	13.64	22.22
373	7.58	14.29	8.33	15.15
363	4.29	5.95	4.76	8.33

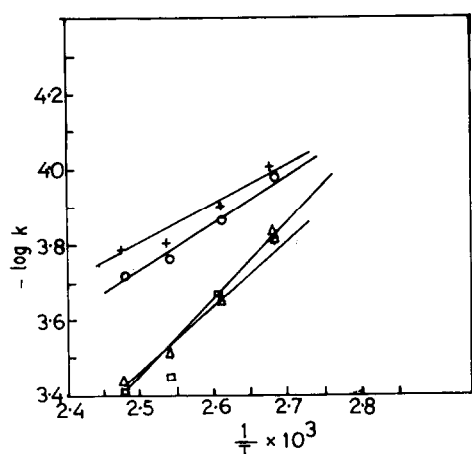


Fig. 4. The Arrhenius plots for the isothermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$. Step I: +, 0.4; O, 0.05, Step II: Δ , 0.4; $\square$, 0.5.

activation energies for the first dehydration step for $F(\alpha) = \{-\log(1 - \alpha)\}^{0.4}$ and $F(\alpha) = \{-\log(1 - \alpha)\}^{0.5}$ are 4.73 and 6.13 kcal mole $^{-1}$, respectively. The activation energies for the second dehydration step in the above functions are 6.91 and 9.01 kcal mole $^{-1}$, respectively.

One can also obtain kinetic parameters from the analysis of dynamic TG curves by using the Coats and Redfern [7] equation

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

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

E (kcal mole $^{-1}$)				Z (s $^{-1}$)			
Step I		Step II		Step I		Step II	
$F(\alpha)^{0.4}$	$F(\alpha)^{0.5}$	$F(\alpha)^{0.4}$	$F(\alpha)^{0.5}$	$F(\alpha)^{0.4}$	$F(\alpha)^{0.5}$	$F(\alpha)^{0.4}$	$F(\alpha)^{0.5}$
4.73	6.13	6.91	9.01	0.07	0.56	2.7	50.0
				± 0.01	± 0.08	± 0.3	± 4.9

plots of $-\ln[F(\alpha)/T^2]$ vs. $1/T$ are shown in Fig. 5. It is seen from the figure that all the functions used in the isothermal study give straight line plots. Each functional plot is bilinear indicating that there are two distinct steps of dehydration. Kinetic parameters, obtained for the dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ for the two steps using different forms of function $F(\alpha)$, are tabulated in Table 2.

It is seen from Table 2 that for function $F(\alpha) = -\log(1 - \alpha)$ the activation energy for the two steps is 15.15 and 21.58 kcal mole⁻¹. This value is much higher than the value calculated from isothermal study. Activation energy values corresponding to functions $F(\alpha) = \{-\log(1 - \alpha)\}^{0.4}$ and $F(\alpha) = \{-\log(1 - \alpha)\}^{0.5}$ for the two steps are 4.66 and 6.89 and 5.96 and 8.97 kcal mole⁻¹, respectively. If these values are compared with those obtained from isothermal study, it is seen that there is a good agreement between them.

It has been pointed out by Criado and Morales [8] from their theoretical analysis, that the linearity of $-\log[F(\alpha)/T^2]$ vs. $1/T$ 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 forms of function α . The same point of view has also been expressed by Dharwadkar et al. [9] and Tang et al. [10]. The close agreement of the E values for the functions $F(\alpha) = \{-\log(1 - \alpha)\}^{0.4}$ and $F(\alpha) = \{-\log(1 - \alpha)\}^{0.5}$ in the iso-

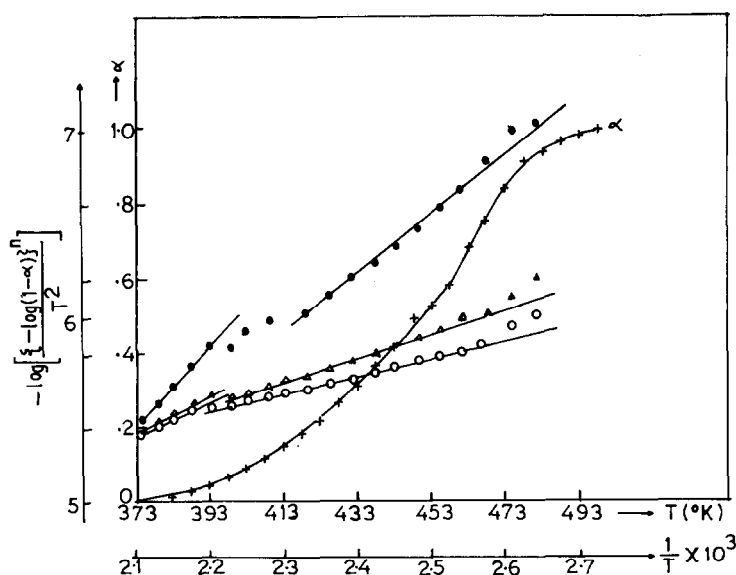


Fig. 5. Plots of α and $-\ln[F(\alpha)/T^2]$ vs. $1/T$ for the thermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ (dynamic). $\times$, α ; $\bullet$, $(-\log\{-\log(1 - \alpha)\})/T^2$; $\circ$, $(-\log\{-\log(1 - \alpha)\}^{0.4})/T^2$; $\triangle$, $(-\log\{-\log(1 - \alpha)\}^{0.5})/T^2$.

TABLE 2
Functions $F(\alpha)$ and kinetic parameters for the thermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ from dynamic TG^a

$F(\alpha)$	E (kcal mole ⁻¹)	Z (s ⁻¹)		Dehydration temp. (K)	
		Step I	Step II	Step I	Step II
$\{-\log(1-\alpha)\}$	15.15 ± 0.01	21.58 ± 1.7	$(3.8 \pm 0.68) \times 10^3$	$(3.03 \pm 1.5) \times 10^5$	
$\{-\log(1-\alpha)\}^{0.4}$	4.66 ± 0.17	6.89 ± 0.33	11.43 ± 1.06	49.7 ± 1.9	454 ± 5
$\{-\log(1-\alpha)\}^{0.5}$	5.96 ± 0.10	8.97 ± 0.16	25.4 ± 1.8	153.8 ± 3.9	

^a Mean of five observed values and its mean deviation.

thermal and dynamic TG study shows that these may be proper forms of function $F(\alpha)$.

Tables 1 and 2 also give Z values obtained from the isothermal and dynamic TG study. It is seen from the Tables that only for $F(\alpha) = \{-\log(1 - \alpha)\}^{0.5}$ the Z values are comparable. For other functions a very large difference in Z values in the isothermal and dynamic study is observed. The comparison of E values and Z values together from isothermal and dynamic TG studies shows that the proper form of $F(\alpha)$ is $F(\alpha) = \{-\log(1 - \alpha)\}^{0.5}$. Thus the possible mechanism for the dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ is random nucleation and subsequent growth.

CONCLUSIONS

It is concluded from the study that (i) the $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ crystal dehydrates in two distinct steps at temperatures 426 ± 5 and $454 \pm 5^\circ\text{K}$; (ii) to determine the proper form of $F(\alpha)$ for the thermal dehydration of $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, consistency in the value of E and Z from isothermal as well as dynamic experiments should be considered; and (iii) the value of E very much depends on the form of the function $F(\alpha)$.

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