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# THERMAL DEHYDRATION REACTIONS OF $Na^I$, $K^I$, $Rb^I$ AND $Cs^I$ MALONATE HYDRATES IN THE SOLID STATE

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## ABSTRACT

The thermal dehydration of alkali metal malonate hydrates was studied by means of thermogravimetry, differential thermogravimetry, differential thermal analysis and X-ray diffraction analysis, mainly in a nitrogen atmosphere. The reaction order of dehydration obtained by the TG method is found to be 2/3 for all the salts examined; the values of activation energy $E_a$ and frequency factor $A$ for all the salts examined in the first step were 68–96 kJ $mol^{-1}$ and $10^{10}$–$10^{13}$ $s^{-1}$, and these values for rubidium and caesium salts in the second step were 185–194 kJ $mol^{-1}$ and $10^{20}$–$10^{22}$ $s^{-1}$, respectively.

The dehydration temperature reflecting the strength of the metal–$OH_2$ bond is lower in sodium and potassium malonate hydrates than in rubidium and caesium malonate hydrates.

## INTRODUCTION

The chemical importance of carboxylic acids can be readily understood, because their nomenclature is widely used as a basis for that of other organic compounds. Furthermore, they can be used as the starting materials in the preparation of many organic compounds [1]. The constituents of metal carboxylates comprise carboxylate groups, metal ions and water molecules. The structures of metal carboxylates have been determined mainly by X-ray diffraction and infrared spectral studies [2]. The crystal structures of the malonates $Li_2C_3H_2O_4$ [3a], $Na_2C_3H_2O_4 \cdot H_2O$ [3b], $CaC_3H_2O_4 \cdot 2H_2O$ [3c], $SrC_3H_2O_4$ [3c], $CdC_3H_2O_4 \cdot H_2O$ [3d], $MnC_3H_2O_4 \cdot 2H_2O$ [3e], $Fe(C_3H_2O_4)_2 \cdot 2H_2O$ [3f], $Nd_2(C_3H_2O_4)_3 \cdot 8H_2O$ [3g] and $Eu_2(C_3H_2O_4)_3 \cdot 8H_2O$ [3h] are known. Metal malonates have therefore been selected as fundamental substances in order to explain the physical and chemical properties in the solid state compared with those of other metal salts. However, there are difficulties in determination of the mechanism of thermal decomposition of

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metal malonates, as the solid products result not only from the particular metal ions but also by condensation, rearrangement or autocatalysis of the initial products of decomposition.

Although the thermal decomposition of metal carboxylates has been studied by a number of investigators [4], these studies have been focused chiefly on metal formates and oxalates. Work on the thermal decomposition of higher metal dicarboxylates is complex, and has been started only recently. The thermal decomposition of metal malonates containing cations of s-block elements can be carried out without a subsequent reduction or oxidation step of the central metal ion by the CO or $CO_2$ evolved or the metal produced on heating; this behaviour is, in general, different from that of the complexes of 3d transition metals and leads to products having a well defined composition. For this reason, the malonates of the s-block elements seem suitable materials for the first part of a series of studies. Metal malonates possess some organic character, but at the same time their nucleation and growth processes on thermal decomposition are similar to the behavior of various inorganic substances. Because the thermal decomposition of malonates indicates their dual character, it is also interesting to investigate and compare the mechanisms during thermal decomposition for a series of malonates possessing different anionic or cationic environments. Little attention has been paid to malonates, and there have been only a few investigations of these compounds. Of the investigations up to now on the thermal decomposition reactions of malonates, the only reports in the literature are on $Na_2C_3H_2O_4 \cdot H_2O$ [5a], $K_2C_3H_2O_4 \cdot 2H_2O$ [5a], $BaC_3H_2O_4 \cdot 0.8H_2O$ [5a], $CoC_3H_2O_4 \cdot 2H_2O$ [5b], $NiC_3H_2O_4 \cdot 2H_2O$ [5c], $CuC_3H_2O_4$ [5d], $CuC_3H_2O_4 \cdot 4H_2O$ [5e], $Ag_2C_3H_2O_4$ [5f], $Tl_2C_3H_2O_4$ [5g] and lanthanon malonate hydrates [5h], and most reports are on individual compounds.

In this paper, the influence of the alkali metal ions on the thermal behavior of malonates was systematically studied by thermal analysis as part of a general program on the study of the thermal properties of metal carboxylates. The thermal dehydration reactions of alkali metal malonate hydrates in flowing nitrogen and static air atmospheres have been studied by TG, DTG and DTA.

## EXPERIMENTAL

### *Preparation of alkali metal malonates*

The alkali metal malonates were prepared by reaction of the corresponding metal carbonates in an aqueous solution of malonic acid (10% excess) at 70 ° C. Precipitation occurred immediately, but the solutions were allowed to stand overnight. The white crystalline precipitates were filtered off, washed

TABLE 1

Thermal dehydration data of alkali metal malonate hydrates in flowing nitrogen and static air atmospheres. $N'$, water molecules lost by dehydration

| Malonate | Atmosphere | Dehydration | | | | | |
|---|---|---|---|---|---|---|---|
| | | TG temp. range (°C) | DTA peak temp. (°C) | DTG peak temp. (°C) | Weight loss (%) | | $N'$ |
| | | | | | Obs. | Calc. | |
| $Na_2C_3H_2O_4 \cdot H_2O$ | $N_2$ | – | 77 | 72 | – | – | – |
| | | 67– 88 | 85 | 85 | 10.2 | 10.8 | $-H_2O$ |
| | Air | – | 78 | 77 | – | – | – |
| | | 65– 95 | 85 | 82 | 10.3 | 10.8 | $-H_2O$ |
| $K_2C_3H_2O_4 \cdot H_2O$ | $N_2$ | – | 76 | 74 | – | – | – |
| | | 53–145 | 84 | 83 | 10.7 | 9.1 | $-H_2O$ |
| | Air | 55–151 | 75 | 72 | 10.0 | 9.1 | $-H_2O$ |
| $Rb_2C_3H_2O_4 \cdot 5H_2O$ | $N_2$ | 153–168 | 170 | 159 | 4.6 | 4.9 | $-H_2O$ |
| | | 168–185 | 175 | 175 | 21.7 | 19.9 | $-4H_2O$ |
| | Air | 138–154 | – | – | 4.7 | 4.9 | $-H_2O$ |
| | | 154–201 | 200 | 197 | 17.4 | 19.9 | $-4H_2O$ |
| $Cs_2C_3H_2O_4 \cdot 6H_2O$ | $N_2$ | 118–153 | 138 | 139 | 4.6 | 5.7 | $-1.5H_2O$ |
| | | 153–173 | 160 | 161 | 17.5 | 17.0 | $-4.5H_2O$ |
| | Air | 120–172 | 118 | 116 | 5.7 | 5.7 | $-1.5H_2O$ |
| | | 172–180 | 175 | 176 | 17.6 | 17.0 | $-4.5H_2O$ |

with water and a 2 : 1 mixture of ethanol and ether, and dried over $P_2O_5$ and then $SiO_2$ in a desiccator for several days. The water of crystallization was determined by isothermal dehydration at a suitable temperature. The results of elemental analyses for C, H and metals agreed with calculated values within $\pm 0.3\%$. From the results of the elemental analyses and dehydration curves, reasonable empirical formulae were found to be those shown in Table 1.

## *Apparatus*

The TG–DTG–DTA curves were simultaneously recorded on a Shinku Riko TGD-3000RH apparatus at a heating rate of 5 °C min$^{-1}$ in atmospheres of nitrogen, flowing at 60 ml min$^{-1}$, and static air. About 10 mg of powdered sample in a platinum crucible (3 mm diam.) was used in each measurement. The X-ray diffractograms were obtained with a Rigaku Denki DS diffractometer, using Cu *Kα* radiation. The infrared absorption spectra in the region 4000–650 cm$^{-1}$ were obtained by the KBr disk method with a Hitachi 215 spectrophotometer.

### Kinetic treatment

The kinetic parameters, namely reaction order $n$, activation energy $E_a$, and frequency factor $A$ for the dehydration stages were calculated from TG curves using the Coats–Redfern equation, which is a typical integral method [6]. The equation was initially derived for an $f(\alpha)$ function of the type $f(\alpha) = (1 - \alpha)^n$. The general form of the equation used is

$$\ln\left[g(\alpha)/T^2\right] = \ln\left(AR/\phi E_a\right) - \left(E_a/RT\right) \tag{1}$$

where

$$g(\alpha) = -\ln(1 - \alpha) \qquad \text{when } n = 1 \tag{2}$$

and

$$g(\alpha) = \left[1 - (1 - \alpha)^{1-n}\right]/(1 - n) \qquad \text{when } n \neq 1 \tag{3}$$

where $\alpha$ is the degree of reaction, $\phi$ is the heating rate $(\mathrm{d}T/\mathrm{d}t)$, $T$ is the temperature at time $t$, and $R$ is the gas constant. Plotting the left-hand side of eqns. (2) and (3) against $1/T$ gave linear graphs with slopes of $E_a/2.303R$ for the correct value of $n$. The activation energy and the frequency factor were thus calculated from the slope and the intercept of the Coats–Redfern plot.

## RESULTS AND DISCUSSION

### Dehydration process

Simultaneous TG–DTG–DTA data for the thermal dehydration of alkali metal malonate hydrates at a heating rate of 5 °C $\mathrm{min}^{-1}$ in various atmospheres are summarized in Table 1. Typical TG–DTG–DTA curves for $Na_2C_3H_2O_4 \cdot H_2O$ and $Cs_2C_3H_2O_4 \cdot 6H_2O$ in a flowing nitrogen atmosphere are shown in Fig. 1. The lines on the TG curves signify the numbers of molecules of water of crystallization lost at those points. The dehydration behavior of sodium and potassium malonate hydrates is different from those of rubidium and caesium malonate hydrates. Although the dehydration stages in the TG curves of the monohydrates of sodium and potassium salts appear to be single steps, the corresponding stages in their DTG and DTA curves comprise two steps. Slight variations in thermal behavior are more readily detected in the DTG curves [7]. The DTG peaks of dehydration of sodium and potassium malonate hydrates are not symmetrical, and the corresponding DTA peak is broad, which indicates more than one step of dehydration. The TG and DTA curves for $Rb_2C_3H_2O_4 \cdot 5H_2O$ and $Cs_2C_3H_2O_4 \cdot 6H_2O$ show two dehydration steps. The initial dehydration temperatures $T_i$ of sodium and potassium salts in nitrogen are relatively low,

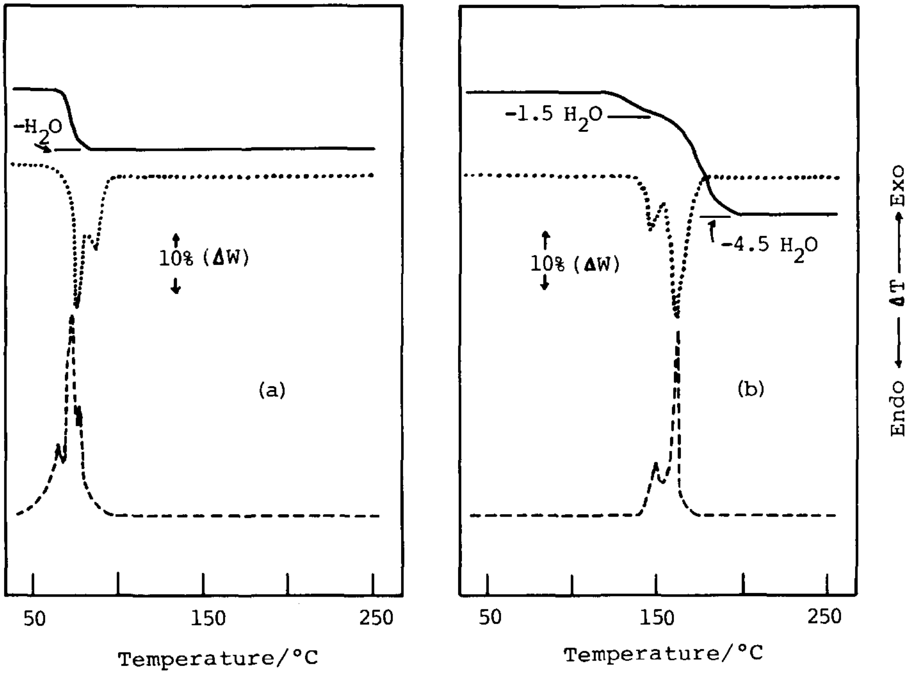

Fig. 1. TG–DTG–DTA curves for the thermal dehydration of (a) $Na_2C_3H_2O_4 \cdot H_2O$ and (b) $Cs_2C_3H_2O_4 \cdot 6H_2O$ in a flowing nitrogen atmosphere: ———, TG; — — —, DTG; ······, DTA. Positions corresponding to the calculated weight loss are indicated by short horizontal lines.

below 80 °C, whereas those of the rubidium and caesium salts are higher, at 153 and 118 °C. The dehydration temperature gives information about the dissociation energy of the metal-coordinated water bonding [8]. If the strength of the $M-OH_2$ bond was assumed to depend on the electrostatic force between the metallic ion and the lone pair of electrons in the water molecules, the $Na-OH_2$ and $K-OH_2$ bonds would be presumed to be stronger than the $Rb-OH_2$ and $Cs-OH_2$ bonds. However, the data from TG–DTA indicate the reverse. These findings may be attributed to weakening of the $M-OH_2$ linkage. Thus, as the oxygen atoms in carboxylates have greater polarity than the oxygen atoms of water molecules, a decrease in the ionic radius of the $M^+$ ion results in strengthening of the M–O bond in the carboxylates.

Alkali metal malonate hydrates show pronounced crystallinity at the beginning of the dehydration process. Significant structural changes, however, occur during their dehydration. The products from the Na, K, Rb, and Cs salts just after dehydration, as shown by X-ray diffractometry, were amorphous, similarly to the anhydrides of simple inorganic and organic hydrated compounds, which generally exhibit amorphous X-ray patterns [9]. It is thought that the transition into anhydrous crystalline products after

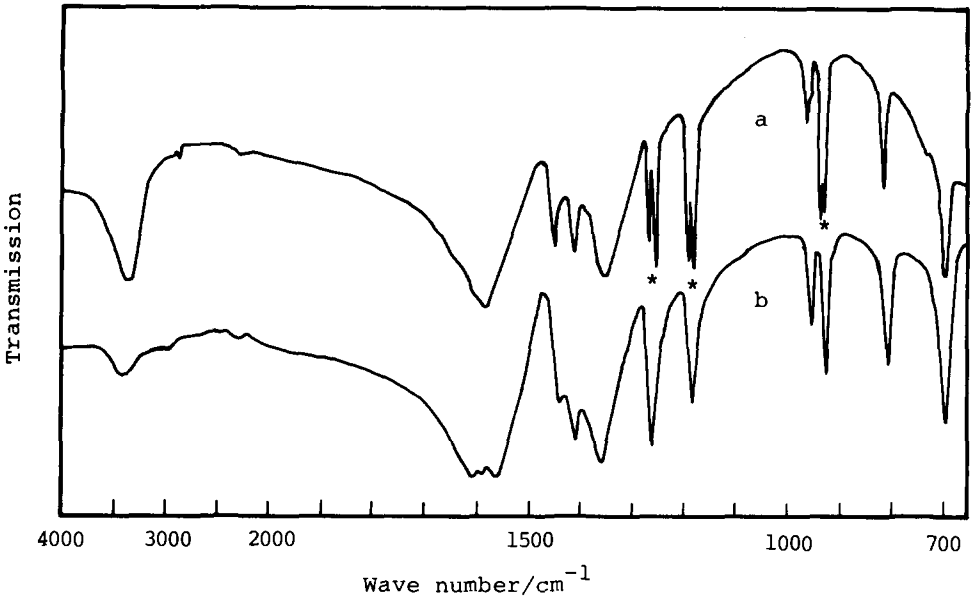

Fig. 2. IR absorption spectra of (a) sodium malonate monohydrate and (b) sodium malonate after dehydration.

completion of dehydration of the metal malonate hydrates requires a large activation energy.

Since the sets of frequencies in the IR absorption spectra of all the alkali metal malonates are broadly similar, the malonates could be regarded as being isomorphous. Typical IR spectra for sodium malonate monohydrate $Na_2C_3H_2O_4 \cdot H_2O$, the starting material, and dehydrated sodium malonate,

TABLE 2

Assignments of spectra of sodium malonate monohydrate and of sodium malonate after dehydration at 110 °C

| $Na_2C_3H_2O_4 \cdot H_2O$ (cm$^{-1}$) | $Na_2C_3H_2O_4$ (cm$^{-1}$) | Assignment |
|---|---|---|
| 3420 s, br; 3350 s, br | 3500 m, br; 3300 m, br | $\nu_{as}$, $\nu_s$ OH |
| 1589 s, br | 1568 s, br | $\nu_{as}$ OCO |
| 1450 m, sp | 1440 w | sci $CH_2$ |
| 1416 m; 1360 s, br | 1410 m; 1360 s, br | $\nu_s$ OCO |
| 1273 s, sp; 1259 s, sp | 1261 s | wag $CH_2$ |
| 1198 s, sp; 1185 s, sp | 1183 s | $\nu_{as}$ CC |
| 980 m, sp; 968 w, sh | 955 s | $\nu_s$ CC |
| 941 s, sp; 934 s, sp | 928 s | rock $CH_2$ |
| 822 s, sp; 701 s, br | 808 s; 694 s | wag OCO |

Key: s, strong; m, medium; w, weak; br, broad; sp, sharp; sh, shoulder; sci, scissoring; rock, rocking; wag, wagging.

$Na_2C_3H_2O_4$, are presented in Fig. 2. The assignments of the major IR frequencies of the compounds are given in Table 2. The spectra have been assigned on the basis of existing data in the literature [10]. The IR spectrum (Fig. 2b) of $Na_2C_3H_2O_4$ dehydrated at 110 °C shows slight differences from that of $Na_2C_3H_2O_4 \cdot H_2O$ (Fig. 2a). It is noteworthy that the splitting of the absorption bands of $Na_2C_3H_2O_4 \cdot H_2O$ at the following wavenumbers (marked by asterisks in the figure)—(i) 1273 and 1259 $cm^{-1}$, resulting from $CH_2$ wagging, (ii) 1198 and 1185 $cm^{-1}$, indicative of $\nu_{as}CC$; and (iii) 941 and 934 $cm^{-1}$, due to $CH_2$ rocking, disappear after the dehydration step, indicating the appearance of a new spectrum.

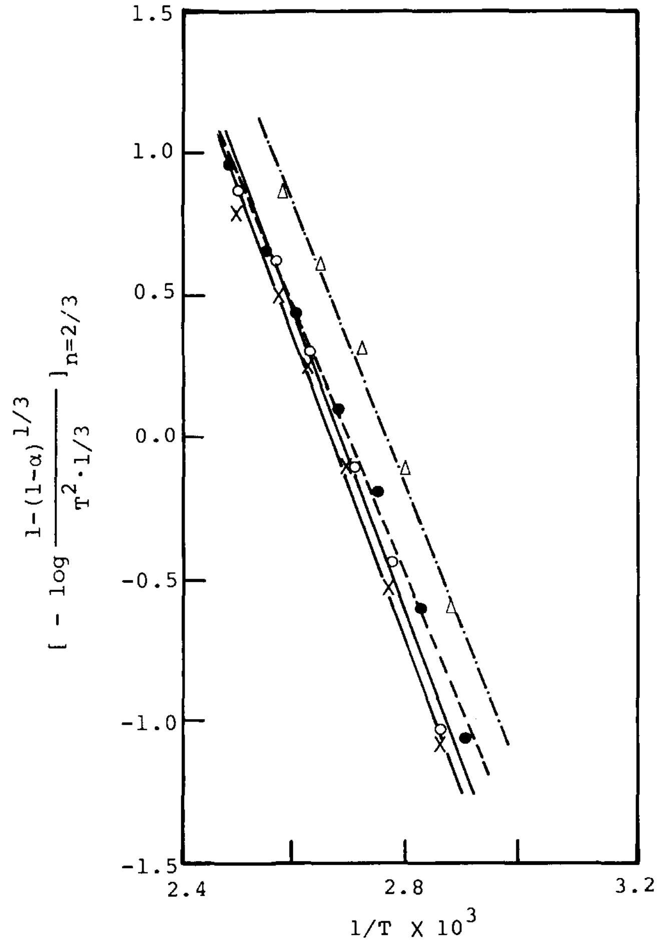

Fig. 3. Plots using the Coats–Redfern method for the reaction $Na_2C_3H_2O_4 \cdot H_2O(s) \rightarrow Na_2C_3H_2O_4(s) + H_2O(g)$ in various atmospheres. ○———○, $N_2$; ×———×, $CO_2$; △–·–·–△, Air; ●------●, $O_2$.

TABLE 3

Kinetic parameters for thermal dehydration of alkali metal malonate hydrates. *N*, Step of dehydration stage

| Malonate | Atmosphere | *N* | $E_a$ (kJ mol$^{-1}$) | *A* (s$^{-1}$) |
|---|---|---|---|---|
| $Na_2C_3H_2O_4 \cdot H_2O$ | $N_2$ | I | 92.5 | $2.0 \times 10^{13}$ |
| | $CO_2$ | I | 95.8 | $4.4 \times 10^{13}$ |
| | Air | I | 84.5 | $3.4 \times 10^{12}$ |
| | $O_2$ | I | 81.6 | $6.8 \times 10^{11}$ |
| $K_2C_3H_2O_4 \cdot H_2O$ | $N_2$ | I | 67.8 | $6.1 \times 10^{10}$ |
| $Rb_2C_3H_2O_4 \cdot 5H_2O$ | $N_2$ | I | 96.2 | $9.3 \times 10^{11}$ |
| | | II | 193.7 | $2.8 \times 10^{22}$ |
| $Cs_2C_3H_2O_4 \cdot 6H_2O$ | $N_2$ | I | 72.0 | $8.6 \times 10^{10}$ |
| | | II | 184.9 | $6.4 \times 10^{20}$ |

## *Kinetics*

The activation energy and the frequency factor for the first dehydration step of the alkali metal malonate hydrates were calculated from TG data. When the reaction order was assumed to be $\frac{2}{3}$ the plot gave a straight line (Fig. 3), indicating that the dehydration begins on the surface of the crystals and then proceeds uniformly to their centers. The kinetic parameters for the dehydration calculated by the Coats–Redfern method are given in Table 3. The values of activation energy so obtained are approximately consistent with those hitherto reported for the dehydration of many hydrated compounds. The activation energies of dehydration of sodium malonate monohydrate in oxidizing atmospheres are slightly lower than those in inert atmospheres. It is also evident that the values for the activation energy and frequency factor in the second step of dehydration of rubidium and caesium malonate hydrates are much larger than those in the first step.

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