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Thermal behavior of alkaline earth metal malonate hydrates and their anhydrides

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Abstract

The thermal dehydration and decomposition of alkaline earth metal malonate hydrates and their anhydrides have been studied using TG-DTA, IR spectroscopy, X-ray diffractometry and evolved gas analysis in atmospheres of N_2, CO_2, O_2 and air. The initial temperatures of the dehydration t_i and decomposition T_i which can measure the relative stabilities of the hydrated and anhydrous malonates are given in various atmospheres. The t_i values on the TG curves were shown to be a measure of the relative strengths of the M^{2+}–OH_2 bond. The plot of the T_i values against Kahwa's parameter for alkaline earth metal malonate anhydrides, except Be, yielded a straight line. Analysis of the first dehydration and decomposition steps indicated that the R2 and A3 mechanisms for the dehydration and decomposition processes give the best fit of the results, respectively.

Keywords: Alkaline earth metal malonates; Malonate hydrate; TG–DTA; Thermal decomposition; Thermal dehydration; Various atmospheres

1. Introduction

The thermal decomposition of alkali and alkaline earth metal dicarboxylates in which both hydrogen and carbon are active, has been investigated by several workers [1], but the reactions are not well established in terms of either the decomposition product or the mechanism.

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The thermal decomposition of alkali and alkaline earth metal dicarboxylates containing cations of s-block elements can be carried out without a subsequent reaction or oxidation step of the central metal ion by the CO and/or CO_2 evolved or the metal or metal oxide produced on heating in the usual experimental conditions.

Recently, several reports were presented on the thermal behavior of alkaline earth metal dicarboxylate hydrates. Kalenikov et al. [2] have shown that the initial dehydration temperatures of alkaline earth metal oxalates, $MC_2O_4 \cdot 2H_2O$ (M is Ca, Sr, Ba) in air are correlated with the polarizing effect of M^{2+}, and the stability of the H_2O of crystallization bond depends on the heat of formation of M^{2+}. Bassi and coworkers [3] have suggested the participation of the liquid phase during the dehydration of Mg malonate trihydrate, while further decomposition is a solid state process and the final decomposition product at 400°C is crystalline MgO. The kinetic and microscopic studies of the thermal decomposition reaction of Ca malonate dihydrate were undertaken by Galwey and Mohamed [4]. The reaction initially proceeded at constant rate.

House and Eveland [5] have shown that the isothermal dehydration of $CaC_2O_4 \cdot H_2O$ followed an R1 rate law, and analysis of the data from nonisothermal experiments gave approximately equal results for the R2 and R3 rate laws. According to Cheng et al. [6], the thermal dehydration of $CaC_2O_4 \cdot H_2O$ is regulated by an A3 mechanism, i.e. random nucleation followed by subsequent growth, and the compensation equation is $\log A = 0.1119\, E - 0.7832$. Li et al. [7] have stated that the process of thermal decomposition of $BaC_2O_4 \cdot 0.5\, H_2O$ is dominated by an A3 mechanism.

This work is a continuation and extension of a previously reported study on the thermal behavior of alkali metal malonate hydrates in various atmospheres [8a, 8b]. The present investigation is concerned with the salts formed by Be(II), Mg(II), Ca(II), Sr(II) and Ba(II) with malonic acid. Although Be^{2+} has a unique covalent character [9] compared with other alkaline earth metal compounds, Be belongs to the same Group IIA elements of s-block configuration. Therefore, this report includes the Be malonate.

2. Experimental

The preparation and elemental analysis of the metal malonate hydrates and the procedures of TG–DTA, evolved gas analysis, infrared measurements, X-ray diffraction analysis [10] and kinetic analysis [11] were described in earlier papers. The C, H and alkaline earth metal contents in the samples are given in Table 1.

3. Results and discussion

The TG–DTA curves of the alkaline earth metal malonate hydrates of Be–Ba obtained at a heating rate of 5°C min^{-1} in the temperature range of RT to 1000°C in atmospheres of N_2 flowing at 60 ml min^{-1} are shown in Fig. 1. The solid lines denote TG curves and the broken lines DTA curves. The TG and DTA data for the thermal

Table 1
Analytical data for alkaline earth metal malonate hydrates

Malonate	C(%)		H(%)		M(%)	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
$BeC_3H_2O_4 \cdot H_2O$	27.95	27.92	3.10	3.12	6.91	6.98
$MgC_3H_2O_4 \cdot 2H_2O$	22.23	22.19	3.75	3.72	14.95	14.97
$CaC_3H_2O_4 \cdot 2H_2O$	20.16	20.23	3.42	3.39	22.43	22.50
$SrC_3H_2O_4 \cdot 2H_2O$	15.94	15.98	2.61	2.68	38.76	38.82
$BaC_3H_2O_4 \cdot 3.5H_2O$	11.88	11.91	2.80	2.83	45.37	45.41

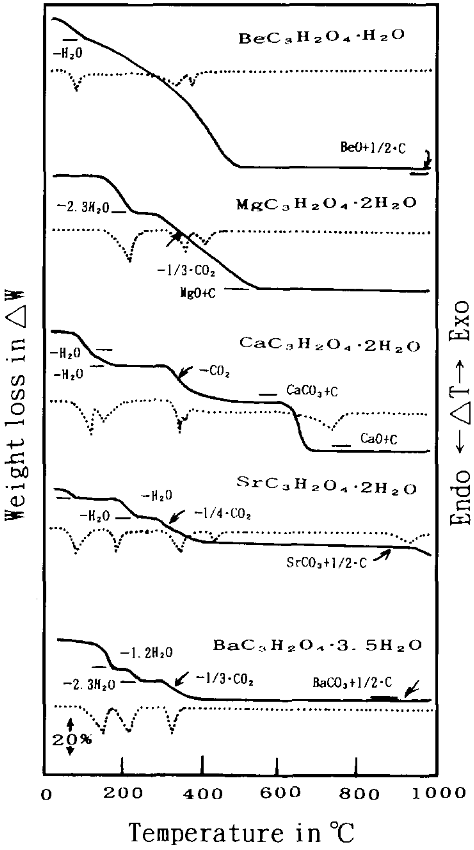


Fig. 1. TG–DTA curves of alkaline earth metal malonate hydrates in a flowing nitrogen atmosphere: —, TG;··· DTA.

dehydration and decomposition of alkaline earth metal malonate hydrates and their anhydrides in various atmospheres are summarized in Tables 2 and 3.

3.1. Dehydration process

The TG–DTA curves of alkaline earth malonate hydrates in a flowing atmosphere of N_2 are given in Fig. 1. On the TG curves, the number of molecules of water of crystallization lost at each point is indicated. The dehydration behaviors in N_2 of Be and Mg malonate hydrates are different from those of Ca, Sr and Ba malonate hydrates. Both the TG and DTA curves for Be and Mg hydrates show a one-step dehydration.

Table 2

Thermal dehydration data of alkaline metal malonate hydrates in various atmospheres: n, number of dehydration stages; t_i, initial dehydration temperatures; t_m, DTA peak temperatures; ΔW, weight loss at each dehydration step; N, moles of dehydrated water

Malonate	Dehydration						
	Atmosphere	Stage n	t_i/°C	t_m/°C	ΔW obsv./%	ΔW calcd./%	N
$BeC_3H_2O_4 \cdot H_2O$	N_2	1	55	80	12.2	14.0	$-H_2O$
	Air	1	52	78	13.5	14.0	$-H_2O$
$MgC_3H_2O_4 \cdot 2H_2O$	N_2	1	132	212	21.5	22.2	$-2H_2O$
	CO_2	1	141	195	21.3		
	O_2	1	113	183	21.2		
	Air	1	143	197	21.2		
$CaC_3H_2O_4 \cdot 2H_2O$	N_2	2	70	110	8.9	10.1 (in first stage): 10.1 (in second stage).	$-H_2O$ $-H_2O$
			110	135	10.1		
	CO_2	2	79	118	9.6		
			121	149	9.9		
	O_2	2	67	112	9.9		
			117	140	9.1		
	Air	2	68	113	9.7		
			118	144	9.1		
$SrC_3H_2O_4 \cdot 2H_2O$	N_2	2	48	87	5.8	5.6	$-0.7H_2O$
			176	192	11.8	10.4	$-1.3H_2O$
	CO_2	2	58	89	5.7	6.0	$-0.75H_2O$
			175	216	11.7	10.0	$-1.25H_2O$
	O_2	2	47	86	6.3	6.4	$-0.8H_2O$
			90	100	12.1	9.6	$-1.25H_2O$
	Air	2	55	87	6.6	6.4	$-0.8H_2O$
			177	191	12.3	10.0	$-1.25H_2O$
$BaC_3H_2O_4 \cdot 3.5H_2O$	N_2	2	85	149	13.9	13.7	$-2.3H_2O$
			175	217	7.3	7.2	$-1.2H_2O$
	CO_2	2	84	151	12.9	12.5	$-2.1H_2O$
			182	218	7.7	7.7	$-1.3H_2O$
	O_2	2	77	152	16.6	17.9	$-3.0H_2O$
			183	220	2.4	3.0	$-0.5H_2O$
	Air	2	81	181	14.3	14.3	$-2.4H_2O$
			181	227	7.1	7.2	$-1.2H_2O$

Table 3

Thermal decomposition data of alkaline earth metal malonate anhydrides in various atmospheres: T_i, initial decomposition temperatures; T_m, DTA peak temperatures; ΔW, weight loss values at each decomposition step

Malonate	Decomposition						
	Atmosphere	Stage n	T_i/°C	T_m/°C	ΔW obsv./%	ΔW calcd./%	Product
				324			
$BeC_3H_2O_4$	N_2	1	211	365	62.0	63.0	BeO + 1/2C
				293			
	Air	1	193	352	66.5	66.6	BeO
			311	362	11.3	9.0	$-1/3CO_2$
$MgC_3H_2O_4$	N_2	2	371	407	43.3	45.6	MgO + C
			299	347	8.9	9.0	$-1/3CO_2$
	CO_2	2	400	–	28.9	25.9	$MgCO_3$
			321	341	8.8	9.0	$-1/3CO_2$
	O_2	2	347	384	50.5	53.0	MgO
			300	343	8.5	9.0	$-1/3CO_2$
	Air	2	358	395	50.0	53.0	MgO
			327	342	7.7	6.7	$-CO_2$
$CaC_3H_2O_4$	N_2	3	–	350	18.4	16.9	$CaCO_3 + C$
			628	736	25.3	24.7	CaO + C
			327	337	8.1	6.7	$-CO_2$
	CO_2	3	–	350	18.4	16.9	$CaCO_3 + C$
			939	957	11.0	–	–
			329	349	20.8	20.2	$CaCO_3 + 1/3C$
	O_2	2	619	750	22.9	24.7	CaO + 1/2C
			325	341	21.5	20.2	$CaCO_3 + 1/2C$
	Air	2	622	733	24.8	24.7	CaO + 1/2C
			318	331	4.6	4.8	$-1/4CO_2$
$SrC_3H_2O_4$	N_2	3	–	423	13.6	12.4	$1/3SrC_3H_2O_4 + 2/3SrCO_3$
			852	931	–	–	→SrO
			318	341	5.6	6.5	$-1/3CO_2$
	CO_2	2	–	388	13.3	15.9	$SrCO_3 + 1/2C$
	O_2	1	291	328	16.8	15.9	$SrCO_3 + 1/2C$
			298	341	15.8	15.9	$SrCO_3 + 1/2C$
	Air	2	930	932	–	–	→SrO
			307	326	5.3	4.8	$-1/3CO_2$
$BaC_3H_2O_4$	N_2	2	337	–	10.3	11.9	$BaCO_3 + 1/2C$
			305	338	5.3	4.8	$-1/3CO_2$
	CO_2	2	339	–	10.3	11.9	$BaCO_3 + 1/2C$
			183	–	8.9	7.5	$-1/2CO_2$
	O_2	2	297	317	12.0	11.9	$BaCO_3 + 1/2C$
			187	333	7.1	7.5	$-1/2CO_2$
	Air	2	299	–	11.6	11.9	$BaCO_3 + 1/2C$

However, the dehydration stages in the TG and DTA curves for Ca, Sr and Ba malonate hydrates are in two stages.

The initial first-stage dehydration temperatures (t_i) of alkaline earth malonate hydrates, except Mg, in various atmospheres are in the range of 48–85°C (Table 2). The TG t_i values are shown as a measure of the relative strengths of the M^{2+}–OH_2 (M is alkaline earth metal) bond [8a, 8b, 12].

The dehydration products, as shown by X-ray diffractometry (XRD) in Fig. 2b, were amorphous, similar to the anhydrides of simple inorganic and organic hydrates, which generally exhibit amorphous X-ray patterns [13]. It is thought that the transition into anhydrous crystalline products after completion of dehydration of the metal malonate hydrates requires a large activation energy. Other hydrated salts were also found to be amorphous to X-rays following the dehydration, supporting former reports on iron [14] and cobalt [15] salts.

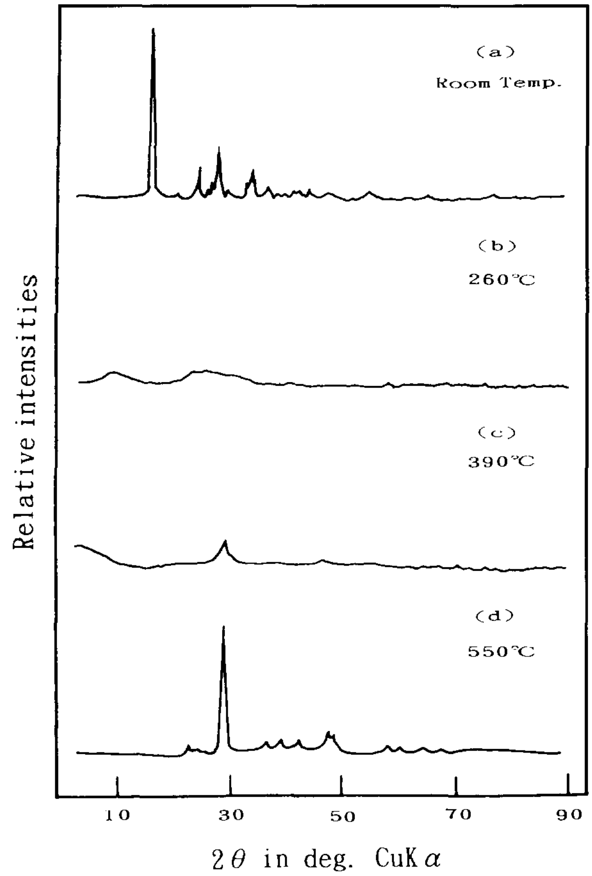


Fig. 2. XRD patterns of (a) $CaC_3H_2O_4 \cdot 2H_2O$ and its products at (b) 260°C, (c) 390°C and (d) 550°C in a flowing nitrogen atmosphere.

3.2. Decomposition process

The TG–DTA curves of alkaline earth malonate anhydrides in a flowing atmosphere of N_2 are given in Fig. 1. The relation between the initial decomposition temperatures (T_i) of the alkaline earth metal malonate anhydrides and their atomic number first rises through a maximum value (327°C for Ca), and then drops with increasing atomic number (Table 3). The decrease of the T_i values for the higher atomic numbers, Sr and Ba, may be because the M^{2+}-malonate bond is weakened due to the bulky molecules of the anhydrides.

To show the effects of various atmospheres (N_2, CO_2 and air), the curves of $SrC_3H_2O_4 \cdot 2H_2O$ are given in Fig. 3. It is indicated that the thermal decomposition pathways on the TG curves of alkaline earth metal malonate anhydrides in N_2 and CO_2 proceed via 3 stages: (i) evolution of CO_2 (Step I); (ii) subsequent formation of carbonate MCO_3 from the anhydrous salt (Step II); and (iii) formation of oxides MO from carbonates at higher temperatures without any detectable intermediate product (Step III).

However, the decomposition in O_2 showed no Step I and indicated a sharp exothermic peak on the DTA curve in Step II due to oxidation of the organic portion.

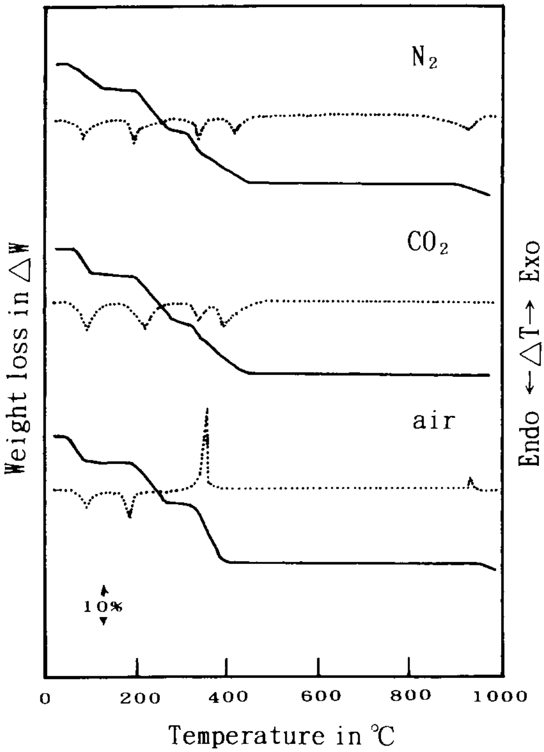


Fig. 3. TG–DTA curves of $SrC_3H_2O_4 \cdot 2H_2O$ in various atmospheres.

The products after Step I of each salt in N_2 and CO_2 were black in color, suggesting the presence of elementary carbon; lower in air and O_2 than in N_2 and CO_2. The products in Step II showed the IR absorption of CO_3^{2-} at 850 cm^{-1} and agreed with the data for alkaline earth carbonates in the JCPDS cards ($MgCO_3$, JCPDS Card, 8-478; $CaCO_3$, 5-453; $SrCO_3$, 5-418; $BaCO_3$, 5-378).

On the basis of the generalized consideration that the highest thermal decomposition temperatures for many compounds will be observed for the largest cations of the smallest charge, Kahwa and Mulokozi [16] have demonstrated a linear relationship of negative slope between the initial decomposition temperature T_i for a number of metal oxalates and the interaction energies, evaluated by

$$T_i = 516 - 1.4006(r_c/r_i)\sqrt{\sum I_i} \tag{1}$$

where r_c, r_i and $\sum I_i$ are the Pauling covalent radius of the metal, its ionic radius in hexacoordination [17] and the sum of the ionization potentials in kcal mol^{-1} [18], respectively. Eq. (1) shows that the T_i value depends on r and I.

Nakamura [19] has proposed the estimation of the decomposition temperature T_d of alkaline earth metal carbonates from the lattice energy U_M calculated using the sum $r_c + r_a$ (r_c and r_a are the radius of the cation and anion, respectively) and the enthalpy change ΔH_M

$$\begin{aligned}\Delta H_M &= 195 - \frac{2320}{r_{M^+} r_{O^{2-}}}\left(1 - \frac{0.345}{r_{M^+} r_{O^2}}\right) + \frac{2320}{r_{M^+} r_{CO_3^{2-}}}\left(\frac{1 - 0.348}{r_{M^+} r_{CO_3^{2\cdot}}}\right) \\ &= 195 - \frac{1392 r_M{}^2 + 3773 r_M + 5531}{(r_M + 1.40)^2 (r_M + 2.00)^2}\end{aligned} \tag{2}$$

where $r_M = r_{c \cdot M^{2+}}$, entropy change $\Delta S_M = 167.4$ kJ mol^{-1} K^{-1}, $r_{a \cdot CO_3^{2-}} = 2.00$ Å. The values of T_d, consequently, are given by the following equation and are shown in Table 4

$$T_d = \Delta H_M / \Delta S_M \tag{3}$$

As Fig. 1 and Table 4 show, the T_d values are comparable, with the tendency that the T_i values for alkaline earth metal carbonates increase with increase in atomic weight.

It is expected that the T_i values for Ca, Sr and Ba malonates in an N_2 atmosphere (327, 318 and 307°C) decrease with increase in the order of increasing atomic number. The thermal stability of Ca, Sr and Ba malonates is the inverse of the order of the thermal stability of their carbonates (Table 4).

Table 4
Thermal decomposition temperatures T_d estimated from the lattice energy U_M of NaCl-type crystals and the entropy change ΔH_M

Carbonate	Mg	Ca	Sr	Ba
T_d/°C	327	1002	1377	1677

The plot of T_i against Kahwa's parameter for alkaline earth metal malonates is shown in comparison with those of alkali [8b] and lanthanide [12] malonates in Fig. 4. Straight lines were obtained. Although the plot for alkali metal malonates is negative, those of alkaline earth metal and lanthanide malonates are positive. The positive slope is in conflict with the mechanism in which the carboxylate decomposition is initiated by C—O bond breaking, suggesting that another characteristic mechanism of the malonate is occurring. A hydrogen atom in the methylene group between two electron-attracting carboxyl groups is known to be highly activated and acts like proton. The mechanism suggested by Shishido and Ogasawara [20] for alkali metal malonates, in which the decomposition of malonate is initiated by the deprotonation of the methylene group, seems likely for the alkaline earth metal elements.

The deviation of Be^{2+} in the plot appears to reflect the abnormal properties of Be^{2+}, i.e. the considerable covalent character expected from high electronegativity, the high charge-to-radius ratio (z/r) of 6.5, the high ionization potentials and high standard electrode potential E°, which indicate the difference between the properties of Be^{2+} and

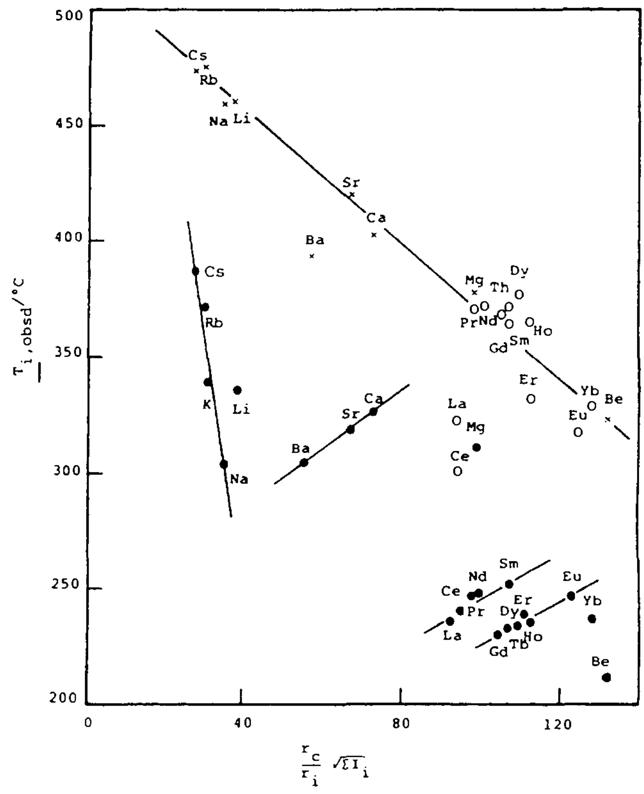


Fig. 4. Initial decomposition temperatures (T_i, obsv.) of metal oxalates (○) and malonates (●) vs. the ratio $r_c/r_i\sqrt{\sum I_i}$; (×) indicates T_i of metal oxalates, observed by Kahwa and Mulokozi.

those of the other alkaline earth metal ions. The plot of Mg^{2+} shows an intermediate nature between that of Be^{2+} and the heavier element ions.

3.3. *Kinetic treatment*

Kinetic analysis of the TG data for alkaline earth metal malonate hydrates and their anhydrides was carried out using a microcomputer to find the kinetic model which gives the best description of the dehydration and decomposition in N_2, CO_2 and air atmospheres [11]. Analysis of the first step of the dehydration of $MC_3H_2O_4 \cdot xH_2O$ indicated that an R2 mechanism, i.e. a two-dimensional phase boundary reaction, gives the best fit of the results for all the atmospheres. The kinetic parameters in the first dehydration, the activation energy E_a and frequency factor A, are given in Table 5. The values of the kinetic parameters for the dehydration are little affected by the ambient atmospheres. The values of E_a thus obtained are approximately consistent with those hitherto reported for the dehydration of many hydrated compounds.

Analysis of the main decomposition process indicates that the random nucleation and growth of nuclei mechanism (A3 model) gives the best fit of the results. The kinetic parameters in the first decomposition are given in Table 6. The activation energy values of the malonate anhydrides in CO_2 show somewhat higher values than in N_2 and air.

From the appearance in the IR spectra of the $C\underset{\cdots}{-}C$ bond at around 1200 cm^{-1} and acetate ion at 1050–1030 cm^{-1} [12, 21], and the CO_2 found in the evolved gas analysis method together with the residual carbon in the decomposition products, it is assumed

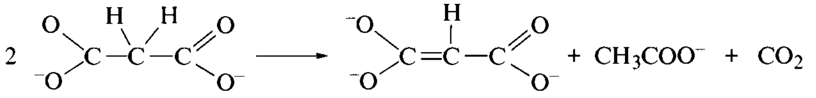
Table 5
Kinetic parameters for the first thermal dehydration of alkaline earth metal malonate hydrates in various atmospheres

Malonate	Atmosphere	E_a/(kJ mol^{-1})	A/(s^{-1})
$BeC_3H_2O_4 \cdot H_2O$	N_2	77.4	3.7×10^{11}
	Air	74.9	8.3×10^{11}
$MgC_3H_2O_4 \cdot 2H_2O$	N_2	92.5	2.8×10^{13}
	CO_2	95.4	4.6×10^{13}
	O_2	81.6	7.1×10^{12}
	Air	85.4	3.7×10^{13}
$CaC_3H_2O_4 \cdot 2H_2O$	N_2	83.3	8.5×10^{12}
	CO_2	84.5	9.0×10^{12}
	O_2	86.2	3.4×10^{13}
	Air	85.4	2.8×10^{13}
$SrC_3H_2O_4 \cdot 2H_2O$	N_2	97.5	5.1×10^{14}
	CO_2	96.2	3.9×10^{14}
	O_2	93.7	9.2×10^{13}
	Air	97.1	2.8×10^{14}
$BaC_3H_2O_4 \cdot 3.5H_2O$	N_2	113.4	7.1×10^{15}
	CO_2	115.5	7.6×10^{15}
	O_2	112.6	6.8×10^{15}
	Air	114.2	3.8×10^{15}

Table 6
Kinetic parameters for the first thermal decomposition of alkaline earth metal malonate anhydrides in various atmospheres

Malonate	Atmosphere	E_a/(kJ mol^{-1})	A/(s^{-1})
$BeC_3H_2O_4$	N_2	127.6	3.7×10^{14}
	Air	120.1	7.8×10^{13}
$MgC_3H_2O_4$	N_2	154.4	2.8×10^{15}
	CO_2	156.9	7.4×10^{15}
	O_2	146.9	3.6×10^{15}
	Air	152.7	5.1×10^{15}
$CaC_3H_2O_4$	N_2	218.8	6.5×10^{17}
	CO_2	230.5	7.3×10^{18}
	O_2	212.1	4.0×10^{16}
	Air	216.7	3.8×10^{16}
$SrC_3H_2O_4$	N_2	189.1	3.8×10^{16}
	CO_2	198.7	7.1×10^{16}
	O_2	177.0	8.5×10^{15}
	Air	188.6	6.2×10^{16}
$BaC_3H_2O_4$	N_2	166.1	7.2×10^{15}
	CO_2	177.0	1.3×10^{16}
	O_2	168.2	5.4×10^{15}
	Air	173.6	5.0×10^{15}

that a hydrogen transfer reaction takes place according to the following mechanism as proposed by Shishido and Ogasawara [21] and Muraishi et al. [12]



(4)

4. Conclusions

The alkaline earth malonate hydrates have been prepared. It is evident that the initial temperatures of dehydration and decomposition of the hydrated and anhydrous malonates in various atmospheres can be shown to be a measure of the thermal stabilities of these malonates.

The first dehydration and decomposition steps of the hydrated and anhydrous malonates follow the R2 and A3 mechanisms, respectively.

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