THERMAL BEHAVIOUR OF SOME DERIVATIVES OF MALIC ACID WITH CALCIUM AND STRONTIUM

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Abstract

Results are presented on the thermal behaviour of two derivatives of malic acid. The decomposition intermediates obtained at about 400°C were identified as derivatives of malonic acid. For some individual thermal decomposition steps, the values of the non-isothermal kinetic parameters were determined.

Introduction

Following research into thermal behaviour and non-isothermal decomposition kinetics in solid-gas systems [1], we now present results relating to the thermal stabilities of $CaMa \cdot 2H_2O$ and $SrMa \cdot 1.5H_2O$, where Ma is the dianion of malic acid: $HOOC-CH_2-CHOH-COOH$.

Experimental

Powders of the above-mentioned compounds were synthesized and characterized by means of elemental chemical analyses (for Ca, Sr, C, H) and IR spectra obtained in the range $400-4000 \ cm^{-1}$.

The thermal curves were recorded with MOM Budapest Q-1500 D, Paulik-Paulik-Erdey type derivatograph in static air atmosphere, with $\alpha\text{-}Al_2O_3$ as inert reference compound, at various heating rates in the range $1.5-10 \ K \ min^{-1}$, in the temperature range $20-1000°C$.

A Philips PW 1140 X-ray diffractometer was used for an initial characterization of the crystalline states of the studied compounds. The powder diffractograms were recorded by using CuK_α radiation. The crystallite mean size, l, was calculated for the most intense diffraction line by using Scherrer's formula [2].

The IR spectra were obtained in the range $400-4000 \ cm^{-1}$ with an IR Specord M-80 spectrophotometer.

The derivatographic data were used to evaluate the decomposition non-isothermal kinetic parameters by three integral methods: those of Coats-Redfern [3], Flynn-Wall (for a constant heating rate) [4] and Urbanovici-Segal [5], who modified the Coats-Redfern method.

For automatic processing of the data, a program written in BASIC language by Dragoe and Segal [6] was used. Besides the optimal values of the non-isothermal kinetic parameters, this program utilizes the values obtained by means of the Coats-Redfern method to regenerate the TG curve in coordinates (α, $T\,^\circ$C) and the experimental points are then recorded in the same coordinates. If these points lie on the regenerated curve, this confirms the accuracy of the measurements and verifies the correctness of the approximations on which the applied integral methods are based.

Results and discussion

The molecular formulae of the investigated malates were established by corroboration of the results of the elemental chemical analyses with the IR spectra obtained in the range 400–4000 cm^{-1}. IR spectral data on malic acid and the investigated compounds are listed in Table 1.

Inspection of this Table shows that the IR spectra of the two studied malates are similar. The broad band occurring in the range 3000–3600 cm^{-1} (with a peak at 3400 cm^{-1}) in both IR spectra can be assigned to the formation of hydrogen-bonds in water or/and alcohol. The band confirms the presence of the water molecules in the investigated compounds.
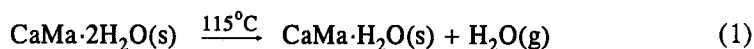
The formation of the malates can be diagnosed by the presence of two strong bands at ca. 1600 cm^{-1} ($\nu_{OCO\,asym.}$) and ca. 1420 cm^{-1} ($\nu_{OCO\,sym.}$), which can be assigned to the ionized carboxylate group, as malic acid exhibits a band at 1730 cm^{-1} due to the free carboxyl group.
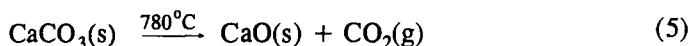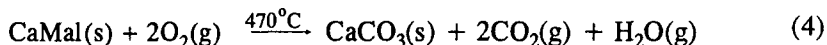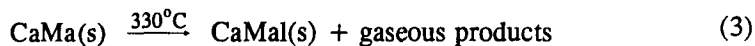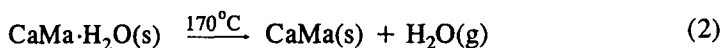
A sharp and strong band was evidenced at 1090 cm^{-1} both in the malic acid spectrum and in the spectra of the investigated compounds, and it was assigned to ν_{C-OH}. The IR spectra of these compounds do not reveal no shift of this band, which allows the conclusion that the interactions between the metal ions and the alcoholic group of the malic dianion are minimal.

As shown by the X-ray diffractograms, CaMa·2H$_2$O exhibits a crystalline state, while SrMa·1.5H$_2$O is an amorphous material. The interplanar distance d, relative intensities I/I_0 and crystallite mean size l for the most intense diffraction lines given by CaMa·2H$_2$O are listed in Table 2.

Thermal decomposition of CaMa·2H$_2$O

The derivatographic data obtained at $\beta = 8.5$ K min^{-1} suggest that the thermal decomposition occurs through the reactions described by the equations

$$\text{CaMa·2H}_2\text{O(s)} \xrightarrow{\;115^\circ\text{C}\;} \text{CaMa·H}_2\text{O(s)} + \text{H}_2\text{O(g)} \tag{1}$$

$$CaMa \cdot H_2O(s) \xrightarrow{170^\circ C} CaMa(s) + H_2O(g) \tag{2}$$

$$CaMa(s) \xrightarrow{330^\circ C} CaMal(s) + \text{gaseous products} \tag{3}$$

$$CaMal(s) + 2O_2(g) \xrightarrow{470^\circ C} CaCO_3(s) + 2CO_2(g) + H_2O(g) \tag{4}$$

$$CaCO_3(s) \xrightarrow{780^\circ C} CaO(s) + CO_2(g) \tag{5}$$

The temperatures written above the arrows correspond to the maximum decomposition rate, as shown by the DTG curve. In the above equations, Mal means the dianion of malonic acid (HOOC–CH$_2$–COOH).

Table 1 IR spectral data of malic acid, CaMa$\cdot$2H$_2$O and SrMa$\cdot$1.5H$_2$O in the wave numbers range 400–4000 cm^{-1}

Malic acid	CaMa$\cdot$2H$_2$O	SrMa$\cdot$1.5H$_2$O	Assignment
~3400 vs	~3400 vs	~3400 vs	$\nu_{OH \text{ alcohol, water}}$
1730 vs	–	–	ν_{CO}
1650 m	1600 vs	1580 vs	$\nu_{OCO\text{asym.}}$
1438 m	–	–	$\nu_{CO} + \delta_{OH}$
1420 m	–	–	$\delta_{CH_2 \text{bond.}}$
–	1420 vs	1415 vs	$\nu_{OCO\text{sym.}}$
–	1310 m	1320 m	$\delta_{OH} + \nu_{CO}$
1295 m	–	–	
1268 w	–	–	
1230 w	–	–	
1195 m	1200 m	1200 m	$\nu_{(CC)\text{sym.}}$
1120 s	1090 s	1090 s	ν_{C-OH}
1100	–	–	
–	1030 m	1035 m	
960 m	–	–	$\nu_{(CC)\text{sym.}}$
935 m	950 w	950 w	
910 w	–	–	$\pi_{(OH)}$
–	860 m	870 m	$\nu_{H_2O\text{rock.}}$
762 w	–	–	$\delta_{(COOH)}$
668 m	680 m	680 m	$\delta_{CH \text{ of } CH_2}$
642 m	–	–	
–	560 m	550 m	
542 w	–	–	

vs – very strong; s – strong; m – medium; w – weak

Table 2 X-ray powder diffraction data for CaMa·2H$_2$O

The line number	d/Å	I/I$_o$	l/Å
1.	4.08	44	
2.	3.90	100	130
3.	3.82	56	
4.	3.45	12	
5.	3.33	56	
6.	3.12	25	
7.	2.94	25	
8.	2.81	25	
9.	2.74	100	125
10.	2.65	23	
11.	2.53	15	
12.	2.47	18	
13.	2.41	18	
14.	2.27	39	
15.	2.18	30	
16.	2.14	43	
17.	2.05	25	
18.	2.02	39	
19.	2.00	39	
20.	1.89	21	
21.	1.83	13	
22.	1.76	26	
23.	1.70	16	
24.	1.64	17	
25.	1.50	10	

The product of the reaction (3), CaMal, was isolated at about 410°C and characterized by means of elemental chemical analysis and the IR spectrum in the range 400–4000 cm^{-1}.

The IR spectrum of CaMal was compared with that of malonic acid in the range 400–4000 cm^{-1}, and the results are shown in Table 3.

The IR spectrum of CaMal exhibits two very strong bands, assigned to the carboxylate group at about 1400 cm^{-1} ($v_{OCOsym.}$) and 1580 cm^{-1} ($v_{OCOasym.}$). The band at 1090 cm^{-1} assigned to the frequency v_{C-OH} has disappeared, which supports our assumption.

The IR spectrum of the reaction intermediate isolated at about 420°C exhibits some bands assigned to the carbonate group: a very strong band at 1430 cm^{-1}

Table 3 IR spectral data of malonic acid, CaMal and SrMal in the wave numbers range 400–4000 cm^{-1}

Malonic acid	CaMal	SrMal	Assignment
~3400 vs	~3400 vs	~3400 vs	ν_{OH}
1700 vs	–	–	ν_{CO}
–	1580 vs	1560 vs	$\nu_{OCOasym.}$
1410 s	1400 s	1400 s	$\nu_{OCOsym.}$
1300 s	1300 m	1300 w	
1200 s	1200 w	–	
1150 s	–	–	
900 vs	–	–	
850 w	870 w	850 w	$\nu_{H_2O\ rock.}$
650 s	650 w	650 w	
580 m	550 w	–	

vs – very strong; s – strong; m – medium; w – weak

($\nu_{CO_3asym.}$), which replaces the bands assigned to the carboxylate group, a strong and narrow band at 880 cm^{-1} ($\delta_{CO_3out-of-plane}$) and a medium band at 700 cm^{-1} ($\delta_{CO_3in-plane}$).

The values of the non-isothermal kinetic parameters, reaction order n, pre-exponential factor A and activation energy E for reactions (1) and (2) are listed in Tables 4 and 5, respectively.

Inspection of these results demonstrates a quite satisfactory agreement among the non-isothermal kinetic parameter values obtained by means of the three applied methods.

The reaction order $n=0.7$ for reaction (1), obtained by the three integral methods, is quite close to the value corresponding to a contracting sphere model [7].

The regenerated TG curves for reactions (1) and (2) in the coordinates (α, T °C) are given in Figs 1 and 2.

The experimental points may be seen to lie practically on the calculated curve, thereby illustrating the reliability of the method applied to evaluate the non-isothermal kinetic parameters and their determined values.

Table 4 Values of non-isothermal kinetic parameters for reaction (1) at β=2.29 K min^{-1}

Method	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	0.7	0.7	0.7
E/kJ mol^{-1}	48.6	51.5	49.8
A/s^{-1}	1.47·10^4	6.87·10^4	2.41·10^4
r^*	–0.9997	–0.9997	–0.9996

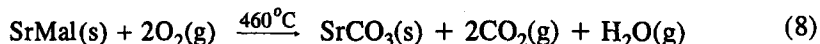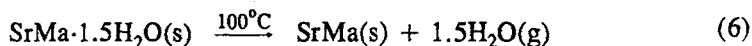*r is the correlation coefficient of the corresponding linear regression

Table 5 Values of non-isothermal kinetic parameters for reaction (2) at $\beta = 1.95$ K min^{-1}

Method	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.6	1.6	1.5
$E/\text{kJ mol}^{-1}$	124.7	125.1	124.8
A/s^{-1}	$2.28 \cdot 10^{13}$	$2.53 \cdot 10^{13}$	$2.44 \cdot 10^{13}$
r	-0.9944	-0.9950	-0.9927
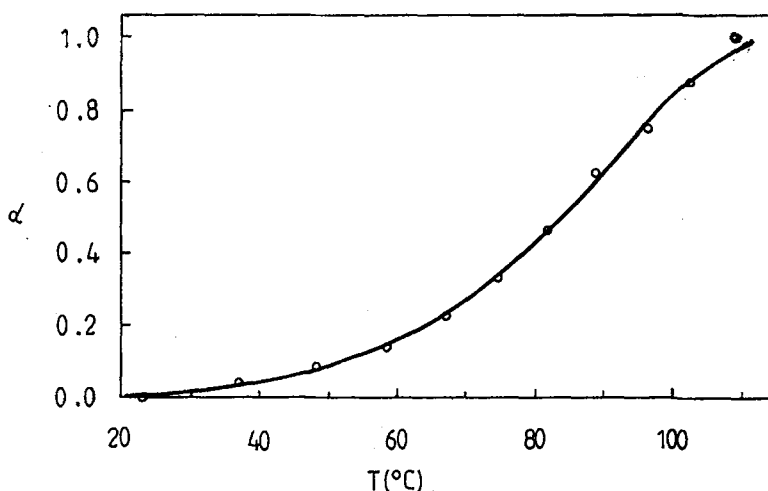
Fig. 1 Regenerated (α, T °C) curve for reaction (1) at $\beta = 2.29$ K min^{-1}: (—) calculated curve; (o) experimental points

Thermal decomposition of SrMa·1.5H$_2$O

The curves recorded at a programmed heating rate of $\beta = 8.4$ K min^{-1} reflect the following decomposition steps:

$$SrMa \cdot 1.5H_2O(s) \xrightarrow{100°C} SrMa(s) + 1.5H_2O(g) \qquad (6)$$

$$SrMa(s) \xrightarrow{320°C} SrMal(s) + \text{gaseous products} \qquad (7)$$

$$SrMal(s) + 2O_2(g) \xrightarrow{460°C} SrCO_3(s) + 2CO_2(g) + H_2O(g) \qquad (8)$$

The existence of SrMal as a product of reaction (7) at about 380°C was confirmed by the IR spectrum, which was similar to that of CaMal (Table 3). Noteworthy points are the absence of the band at 1090 cm^{-1}, and the presence of the bands assigned to the ionized carboxylate group at 1400 cm^{-1} ($\nu_{OCOsym.}$) and 1560 cm^{-1} ($\nu_{OCOasym.}$).

Table 6 Values of non-isothermal kinetic parameters for reaction (6) at $\beta = 2.03$ K min^{-1}

Method	Coats-Redfern	Flynn-Wall	Modified Coats-Redfern
n	1.3	1.3	1.2
$E/kJ\ mol^{-1}$	47.3	50.6	46.5
A/s^{-1}	$7.35 \cdot 10^3$	$4.02 \cdot 10^4$	$6.27 \cdot 10^3$
r	–0.9968	–0.9975	–0.9961
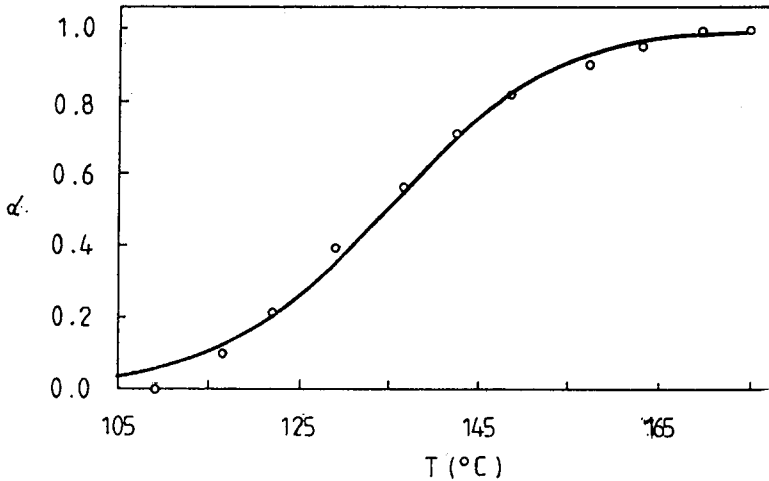
Fig. 2 Regenerated (α, T °C) curve for reaction (2) at $\beta = 1.95$ K min^{-1}: (—) calculated curve; (o) experimental points
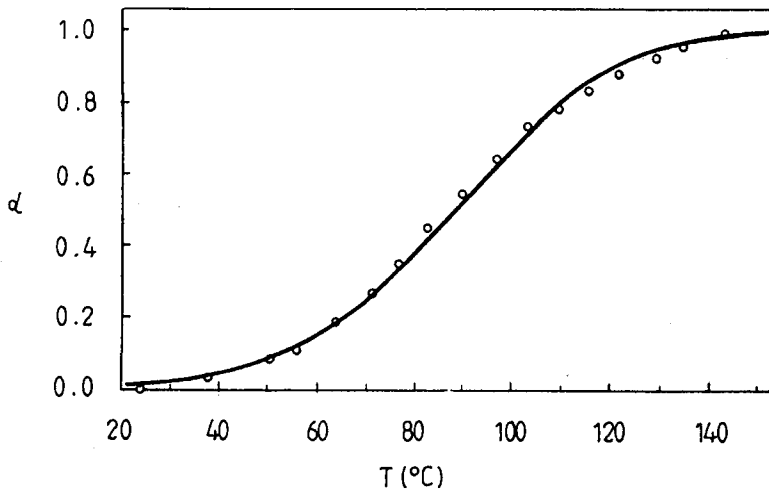
Fig. 3 Regenerated (α, T °C) curve for reaction (6) at $\beta = 2.03$ K min^{-1}: (—) calculated curve; (o) experimental points

Only reaction (6) proved to be kinetically processable. The values of the non-isothermal kinetic parameters for this reaction are listed in Table 6. Satisfactory agreement among the values of the non-isothermal kinetic parameters can be observed for this case too.

The fractional and higher than unity values of the reaction order for reaction (6) and reaction (2) can be ascribed to the decomposition of structural units consisting of more than one molecule, coexisting in variable ratios in the investigated system.

The TG curve regenerated in the coordinates (α, T °C) is given in Fig. 3. The experimental points lie on the curve, thereby indicating the validity of the applied method and the accuracy of the results.

Conclusions

1. The thermal behaviour of two derivatives of malic acid was investigated.

2. The decomposition processes of these compounds led to malonic acid compounds in an intermediate stage.

3. The values of the non-isothermal kinetic parameters for certain individual decomposition steps were determined by using three integral methods.

4. The determined values exhibit satisfactory agreement.

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