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THERMAL DECOMPOSITION OF STRONTIUM AND BARIUM MALONATES

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Abstract

The thermal decomposition of strontium and barium malonates has been studied isothermally and non-isothermally employing simultaneous TG–DTG–DTA, DSC, XRD and IR spectroscopic techniques. DSC of these malonates has been recorded both in oxygen and nitrogen atmospheres. The decomposition is a single step process and the end product formed is carbonate. The energy of activation and frequency factor values for the decomposition of strontium malonate are 547 kJ mol^{-1} and 10^{41} s^{-1} respectively. The activation energy and frequency factor values for isothermal dehydration of barium malonate sester-hydrate are 57–111 kJ mol^{-1} and 10^{7}–10^{12} s^{-1} respectively and the corresponding values for decomposition from DSC are 499.5 kJ mol^{-1} and 10^{44} s^{-1} respectively. The higher thermal stability of strontium malonate as compared to that of barium salt is ascribed to its being anhydrous so that decomposition proceeds without restructuring. Their thermal stabilities have also been compared with that of respective oxalate salts.

Keywords: alkaline earth malonates, DSC, DTA, kinetic parameters, TG, thermal decomposition

Introduction

Since alkaline earth metal carboxylates and their decomposition products are extensively used in industry as pharmaceuticals, catalysts, ceramics, glasses etc., so their decomposition has become a fascinating subject of interest [1]. Also the interest in the decomposition of this series is two-fold viz. i) comparison with respective oxalates [2] and ii) comparison of the decomposition pattern of the anhydrous malonates with hydrated ones, the former decompose in crystallites as prepared rather than after recrystallization and restructuring processes which are inevitable when dehydration precedes the anion breakdown reaction. The present work is a systematic extension of the decomposition studies earlier reported by us on magnesium and calcium malonates [3, 4].

Experimental

Strontium and barium malonates were prepared by a method similar to that reported for magnesium malonate trihydrate [3]. The identities of the com-

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pounds were established by chemical analysis. The percentage of strontium and barium were determined titrimetrically [5]. Estimated percentages of the elements are:

			%C	%H	%Sr/Ba	
i)	$SrCH_2C_2O_4$	obsd.	19.01	1.14	46.14	(Sr)
		calc.	18.95	1.05	46.32	
ii)	$BaCH_2C_2O_4 \cdot 2.5H_2O$	obsd.	12.87	2.25	49.08	(Ba)
		calc.	12.68	2.46	48.24	

The experimental details of STA (TG–DTG–DTA), DSC, IR and XRD are reported elsewhere [3].

Results and discussion

Infrared spectrum of strontium malonate shows a small but distinct band at 2940 cm^{-1} due to $\nu_{(C-H)}$ of the malonate group and a broad band in the range 1565–1620 cm^{-1} due to $\nu_{asym(C=O)}$ of the carboxylate. A band centred at 1390 cm^{-1} is due to $\nu_{sym(C=O)}$ of the coordinated malonate group. A sharp band at 390 cm^{-1} is assigned to the presence of (Sr–O) bonding [6]. The IR spectrum of the barium salt resembles to that of strontium, except an additional broad band centred at about 3430 cm^{-1} due to $\nu_{(OH)}$ of lattice water. A band indicating (Ba–O) bonding lies at 418 cm^{-1}.

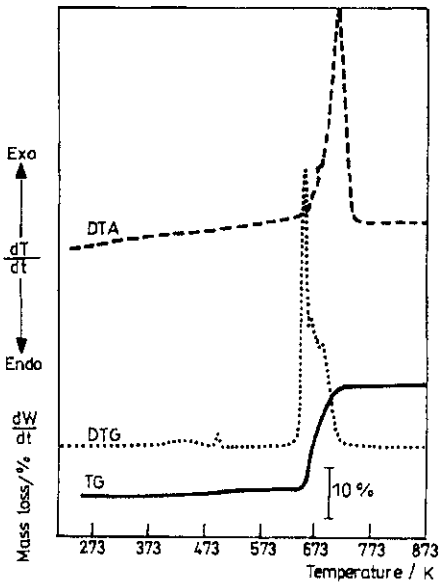

Fig. 1 Simultaneous TG–DTG–DTA curves of strontium malonate

Figure 1 shows the simultaneous TG, DTG and DTA curves for strontium malonate at a heating rate of 10°C min^{-1}. There is only one stage of decomposition as the compound is anhydrous and crystalline. DTA shows one endotherm corresponding to a DTG peak at 657 K but two shoulders are also present in DTA and DTG. Since any intermediate formed could not be detected, so these shoulders are not attributed to any stable intermediate species but to a change in the pyrolysis of gaseous decomposition products only or to a phase transformation involving no melting. TG curve shows a change in slope at a mass loss of 15.0%. It may be due to the removal of one CO molecule. The end product formed is strontium carbonate at a mass loss of 22.15% (calc. loss=22.11%). Strontium carbonate as the ultimate product has been confirmed by IR, estimation of strontium titrimetrically and XRD powder pattern of the final thermolysis residue [7]. IR spectrum exhibits a strong band due to ν_1 (1070 cm^{-1}), characteristic of strontium carbonate with aragonite structure [8] in which strontium ion has nine nearest oxygen atoms. There was no elemental carbon in the residue, elemental analysis showed 8.1% carbon due to strontium carbonate only.

Figure 2 displays the DSC curves for strontium malonate both in oxygen and nitrogen atmospheres at a heating rate of 10°C min^{-1}. An exotherm lies at 627 K in oxygen and an endotherm exists at 663 K in nitrogen atmosphere. The shape of α–t plots in nitrogen atmosphere is deceleratory without any induction period (Fig. 3) thus indicating that product particles are formed rapidly. The most appropriate mechanism for isothermal decomposition was $(1-\alpha)^{-1}=kt$. Kinetic parameters for the endotherm at 663 K in nitrogen atmosphere are E_a=547 kJ mol^{-1}, ΔH=29.54 kJ mol^{-1}, n=1.54 and $A=10^{41}$ s^{-1}. A large difference in the values of E_a and ΔH may be explained by possible contribution of nuclea-

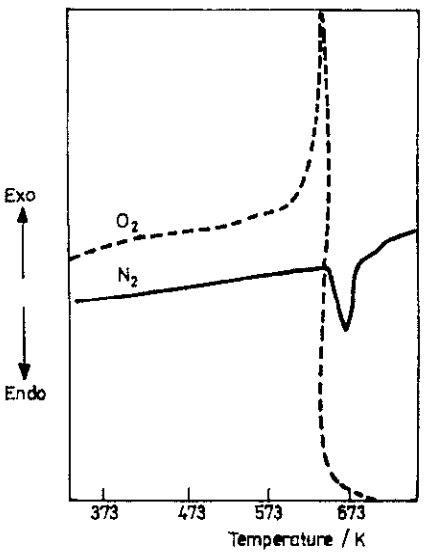

Fig. 2 DSC curves of strontium malonate in nitrogen and oxygen

tion of solid product to energy of activation. Since E_a (547 kJ mol^{-1}) is much higher than the C–C bond energy (347 kJ mol^{-1}) or C–O bond energy (359 kJ mol^{-1}), it means the activation process involves the breaking of C–C or C–O bonds. The unusually high value of frequency factor, A (10^{41} s^{-1}) signifies

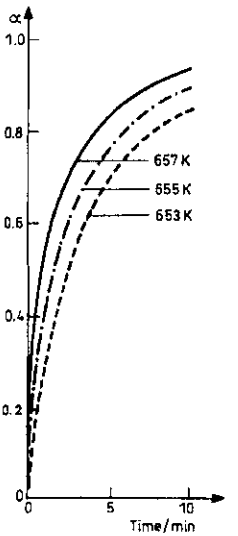

Fig. 3 α–t plots for decomposition of strontium malonate in nitrogen atmosphere

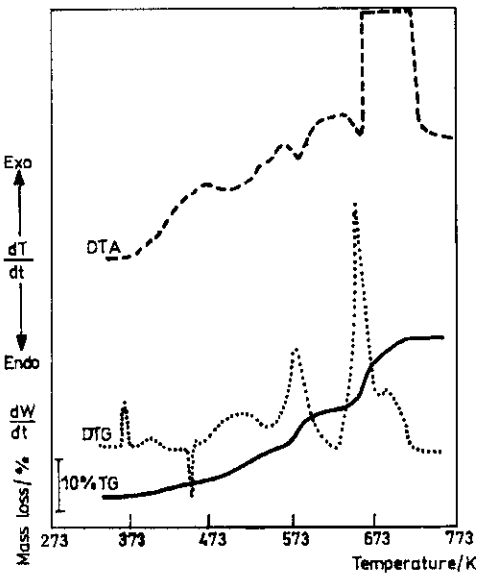

Fig. 4 Simultaneous TG–DTG–DTA curves of barium malonate sester-hydrate

more than one process occurring simultaneously which accelerate the rate of decomposition.

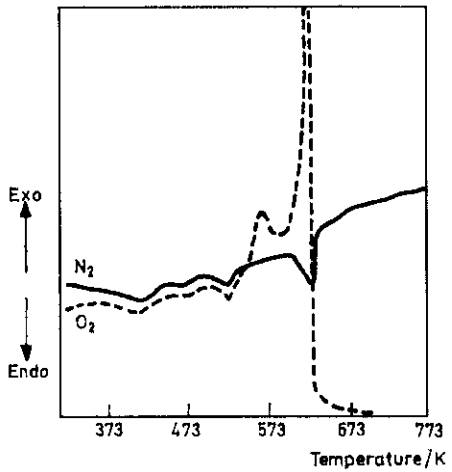

Fig. 5 DSC curves of barium malonate sester-hydrate in nitrogen and oxygen

Figure 4 shows the simultaneous TG, DTG and DTA curves of barium malonate sester-hydrate, $BaCH_2C_2O_4 \cdot 2.5H_2O$, at a heating rate of 10°C min^{-1}. There are three steps in TG apart from a small (~1%) mass loss due to desorption of adsorbed gases. The first two steps are due to dehydration and the third one is due to decomposition. The removal of 1.5 water molecules at a mass loss of 8.0% occurs with a DTG peak at 517 K whereas the complete dehydration is at a mass loss of 16% (calc. loss=15.85%) with the DTG peak at 577 K, both peaks being endo in DTA. After dehydration, a change in slope in TG at a mass loss of 28% is attributed to the removal of one CO molecule. There is complete correspondence between DTA (668 K, endo) and DTG (663 K) peaks suggesting that there is no phase change or melting in the system. Final product is barium carbonate as shown by a mass loss of 30% (calc. loss-30.63%) in TG at 715 K. It was charac-

Table 1 Kinetic parameters of dehydration and decomposition from DSC of barium malonate sester-hydrate

T_{peak}	Atmosphere	E_a/kJ mol^{-1}	A/s^{-1}
415	oxygen	112.65	10^{12}
417	nitrogen	110.00	10^{12}
526	oxygen	772.36	10^{75}
525	nitrogen	361.06	10^{34}
628	oxygen	499.49	10^{44}
631	nitrogen	1000.00	10^{123}

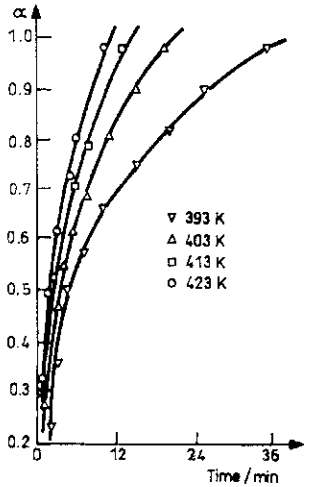

Fig. 6 α–t plots for isothermal dehydration of barium malonate sester-hydrate (393–423 K)

terized by IR and estimation of barium titrimetrically from the final thermolysis residue.

Figure 5 exhibits DSC curves of barium malonate sester-hydrate both in oxygen and inert atmospheres at a heating rate of 10°C min^{-1}. The peak temperatures in nitrogen atmosphere lie at 417 (endo), 525 (endo) and 631 K (endo) while the corresponding peaks in oxygen atmosphere exist at 415 (endo), 526 (endo) and 628 (exo). Kinetic parameters for different peak temperatures in oxygen and ni-

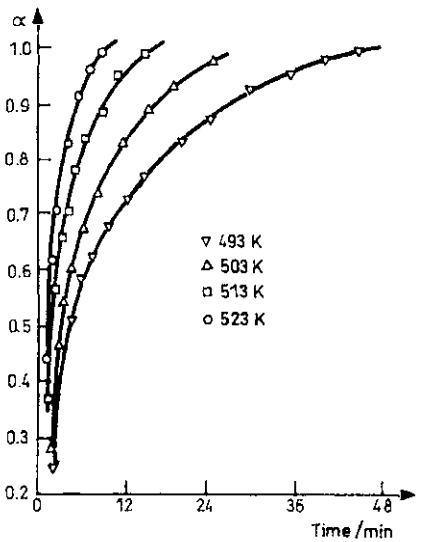

Fig. 7 α–t plots for isothermal dehydration of barium malonate sester-hydrate (493–523 K)

trogen atmospheres are listed in Table 1. Although the parameters corresponding to the first endotherm (~415 K) are of the same magnitude in both atmospheres, the values for the second endotherm (~526 K) are much higher as compared to those in nitrogen atmosphere. It may be due to the restructuring of products or adsorbed water vapours from air which causes Smith-Topley effect. Kinetic parameters for the peak around 631 K (endo in nitrogen and exo in oxygen) are very high in nitrogen atmosphere. This is because of the very high energy needed to fragment the organic moiety which would otherwise require a low energy of activation in oxygen as oxidation of organic species is more favourable than its fragmentation.

Table 2 Kinetic parameters for isothermal dehydration of barium malonate sester-hydrate

Mechanism	Symbol	Rate controlling step	T_{range}/K	E_a/kJ mol^{-1}	A/s^{-1}
$\alpha^2=kt$	D_1	one dimensional	393–423	57.0	10^8
		diffusion	493–523	105.0	10^{11}
$(1-\alpha)\ln(1-\alpha)+\alpha=kt$	D_2	two dimensional	393–423	58.5	10^8
		diffusion	493–523	110.7	10^{12}
$1-2/3\alpha-(1-\alpha)^{2/3}=kt$	D_4	three dimensional	393–423	57.0	10^7
		diffusion	493–523	101.2	10^{10}
$1-(1-\alpha)^{1/2}=kt$	R_2	contracting	393–423	58.0	10^8
		area	493–523	110.8	10^{11}

Kinetics for dihydration of barium malonate sester-hydrate have also been studied isothermally at 393, 403, 413 and 423 K for the elimination of one water molecule while at 493, 503, 513 and 523 K for the removal of remaining water. The α–t plots are deceleratory (Figs 6 and 7) and show no induction period indicating that product nuclei are formed very rapidly. A correlation coefficient greater than 0.99 has been obtained only for deceleratory models where the kinetic parameters do not differ much (Table 2). For the low temperature dehydration stage (393–423 K), although the value of frequency factor is low yet the magnitude of activation energy is the one expected from dehydration occurring at the product-reactant interface. In case of high temperature dehydration stage (493–523 K) the frequency factor is of right magnitude obtained using Polyani-Wigner equation. The high value of activation energy is probably due to cooperative surface phenomenon [9].

An important feature of these studies is the obtention of unusually high values for frequency factor and activation energy in dehydration and subsequent decomposition giving the intermediate end products. Due to difference in structure and molar volume of reactant and products, the reactant-product interface remains strained and hence develops cracks, pores, etc. and enhance its reactivity, thereby increasing the magnitude of kinetic parameters.

Strontium malonate decomposes at a higher temperature (643 K) than that of barium malonate sester-hydrate (604 K). A tentative reason for higher thermal stability is that the former is an anhydrous salt while the latter is hydrated. The dehydration prior to decomposition produces a loose and labile malonate which then decomposes easily.

Alkaline earth metal malonates decompose at lower temperatures (Mg=583, Ca=610, Sr=643, Ba=604 K) as compared to the respective oxalates [2] (Mg=728, Ca=667, Sr=680, Ba=663 K). This is due to the difference in the size of their chelate rings as the metal-ligand bond strength in the five-membered ring (oxalate) is expected to be more as compared to the six-membered one (malonate) [10]. The higher thermal stability of oxalates can also be explained on the basis of high temperature acid-base theory according to which the weaker the anion-base the higher the decomposition temperature [11] and the oxalate ion is a weaker anion-base than a malonate ion. The anhydrous malonates are reported to be composed of a network of more loosely linked polymers with higher potential energy than the anhydrous oxalates [12].

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