

THERMAL DECOMPOSITION OF MAGNESIUM MALONATE TRIHYDRATE

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The decomposition of magnesium malonate trihydrate has been studied isothermally and non-isothermally using TG, DSC, scanning electron microscope etc. The activation energy and frequency factor for isothermal dehydration are $100 \pm 5 \text{ kJ mol}^{-1}$ and 10^{10} s^{-1} respectively and the corresponding values for decomposition from DSC are $332.9 \pm 113 \text{ kJ mol}$ and 10^{17} s^{-1} respectively. The participation of liquid phase during dehydration is suggested while further decomposition is a solid state process. Final decomposition product at 673 K is crystalline magnesium oxide.

In studies dealing with the thermal dehydration reactions of certain metal malonates it has been reported that dehydration is a solid state process at the phase boundary [1]. From decomposition studies of anhydrous malonates [2–4] it has been further demonstrated that these processes are individual ones and that similar compounds decompose differently. For example crysolysis of silver malonate is a solid state process while participation of a liquid in the decomposition of copper malonate has been observed. Out of the various alkaline earth metal malonates, only barium salt [5] has been decomposed with an activation energy of $481 \pm 125 \text{ kJ mol}^{-1}$ and apparently did not melt. Similar studies on magnesium malonate have not been made although few reports on other magnesium carboxylates are known [6, 7]. Many applications of magnesium carbonate and magnesium oxide depend upon the state and nature of subdivisions of its powder, which also depend upon the precursor from which it is obtained by decomposition. Magnesium malonate was therefore selected for thermal decomposition studies. In such studies mere obedience to a solid state kinetic model is not sufficient to conclude that a reaction takes place in the solid state. Reactions which appear to occur in the solid state may have local melting at the reactant product interface or a liquid or even a vapour phase may participate [8]. A solid state kinetic model may be applied only if the liquid phase does not participate. Decomposition of hydrated magnesium malonate was undertaken to explore the above stated characteristics.

Experimental

Magnesium malonate trihydrate was prepared by adding small amounts of magnesium carbonate to aqueous solution of malonic acid in small amounts with constant stirring until effervescence ceased. The excess magnesium carbonate was filtered off. The solution was then concentrated on water bath and precipitates formed were filtered and washed with methanol and finally dried in air. The compound was characterized by chemical analysis and infrared spectrum. The percentage of magnesium was determined titrimetrically. Estimated percentages of elements are Mg = 13.10, C = 21.60, H = 3.75 (Calc. Mg = 13.30, C = 20.00, H = 4.40). Derivatograph was recorded on a Standon Red-Croft Model (STA-780) at a heating rate of $10^{\circ} \text{ min}^{-1}$. Differential scanning calorimetry was taken on Mettler TA 3000 system. The X-ray powder diffraction pattern of the end product was recorded using nickel-filtered CuK_{α} radiation.

Results and discussion

Infrared spectrum of magnesium malonate trihydrate resemble with the spectra of Mn and Fe malonates which belong to orthorhombic crystal system¹ and shows a band near 3450 cm^{-1} due to $\nu_{(\text{OH})}$ of lattice water, a small but distinct band at 2930 cm^{-1} due to $\nu_{(\text{C}-\text{H})}$ of the carboxylate group and a broad band in the range $1560\text{--}1610 \text{ cm}^{-1}$ due to $\nu_{\text{asym}}(\text{C}=\text{O})$ of the carboxylate and bending mode of H_2O group. The band at 1380 cm^{-1} is due to $\nu_{\text{sym}}(\text{C}=\text{O})$ of the Co-ordinated carboxylate group [9]. A sharp and distinct band at 340 cm^{-1} indicates the presence of (Mg—O) bonding.

Non-isothermal decomposition analysis of magnesium malonate (Fig. 1) shows two stages of decomposition, first due to dehydration (30% loss) and the second due to decomposition. DTG however, shows that decomposition occurs in many steps. DTA shows two endothermic steps with peak temperatures 506 K and 660 K respectively. An exothermic peak starts immediately after the second endotherm which implies that the two correspond to a single step process which started as endothermic but becomes exothermic subsequently. This endotherm (648 K) attributed to the decomposition of the compound at a higher temperature (the temperature is being continuously raised) is converted into an exothermic peak due to the oxidation of organic moiety in air. The salt was heated (525–700 K) isothermally for different time intervals (5 min to 2 hr) but no stable intermediate could be separated and therefore the steps in DTG are probably due to the changing mode of decomposition of the volatile organic moiety only. The X-ray diffraction pattern of the decomposition product obtained at various temperatures showed it

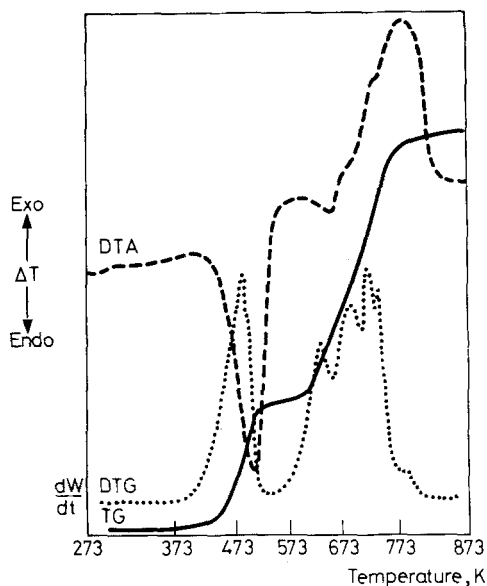


Fig. 1 Simultaneous DTG-DTA-TG curves of magnesium malonate trihydrate

to be crystalline magnesium oxide only. The experimental d -values and intensities for the products are found to be in good agreement with the corresponding literature values for MgO (Table 1). Elemental analysis of the solid product showed it to contain traces (0.83%) of elemental carbon. Evolved gases were analysed for ketene, acetic acid, acetic anhydride using NMR. No gas other than carbon dioxide could be detected. Efforts to obtain MgCO_3 as an intermediate failed and in this respect decomposition of magnesium malonate is similar to that of magnesium oxalate, since both directly give MgO although the carbonate is an intermediate in the decomposition of other alkaline earth metal carboxylates [10] at about 873 K.

Table 1 X-ray diffraction data for thermolysis product of magnesium malonate trihydrate

Experimental data for MgO		ASTM data for MgO		
d lines	intensity	d lines	intensity	hkl
2.390	10	2.431	10	111
2.160	100	2.106	100	200
1.456	52	1.489	52	220
1.257	4	1.270	4	311
1.193	12	1.216	12	222
1.029	5	1.053	5	400
0.9309	17	0.9419	17	420
0.8704	15	0.8600	15	422

Figure 2 shows DSC of magnesium malonate trihydrate recorded from 313 K to 873 K and it shows a fairly symmetrical endotherm for dehydration and an unsymmetrical exothermic peak for decomposition. The peak temperatures for dehydration and decomposition are 511 K and 676 K respectively. For the enthalpy of dehydration i.e. ΔH is $166.3 \text{ kJ mol}^{-1}$ with a reaction order of 0.54 and

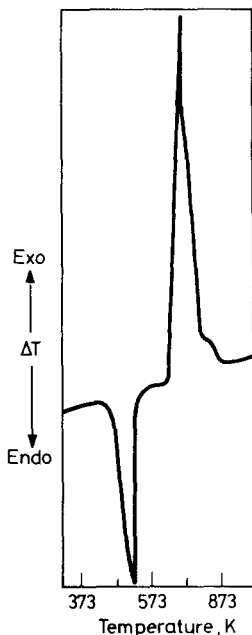


Fig. 2 DSC curve of magnesium malonate trihydrate

an activation energy (E_a) of $118.75 \text{ kJ mol}^{-1}$ with a frequency factor $A = 10^{10} \text{ s}^{-1}$. The enthalpy change per molecule of H_2O is 55.4 kJ mol^{-1} , is a value close to the value of heat of sublimation of ice (52 kJ mol^{-1}). For the decomposition of anhydrous salt not very accurate values for activation energy, enthalpy of reaction etc. were obtained from DSC. The enthalpy of decomposition (ΔH) is 185 kJ mol^{-1} , reaction order being 2.17 while the energy of activation is $332.9 \pm 113 \text{ kJ mol}^{-1}$ with a value of $A = 10^{17} \text{ s}^{-1}$. The α -t plots as obtained from DSC were deceleratory for dehydration as well as for decomposition. Since no endotherm, other than due to dehydration, characteristic of melting was observed in either DTA or DSC, the participation of liquid phase in dehydration as seen in SEM is transient.

The mode of decomposition of this salt was further studied using scanning electron microscope. SEM patterns of the original magnesium malonate trihydrate

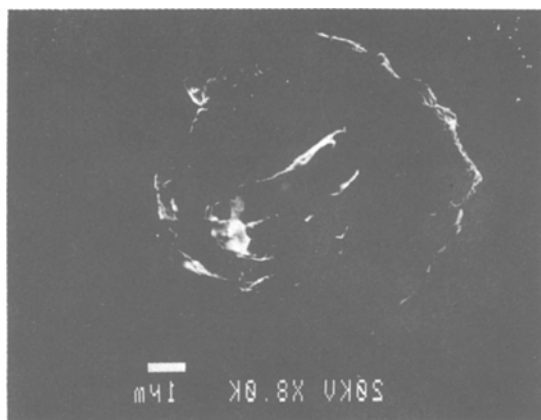


Plate 1 SEM of magnesium malonate trihydrate

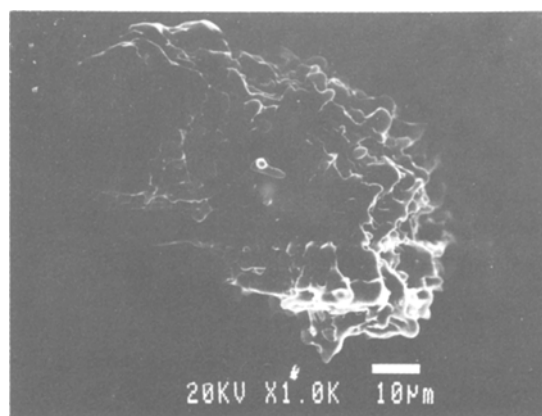


Plate 2 SEM of anhydrous sample obtained after dehydrating magnesium malonate trihydrate at 493 K

is shown in (Plate 1). In the SEM taken after dehydrating a large reactant crystal, one sees capillaries and round corners as if created by bubbling and are characteristic of froath formation (Plate 2), and thus gives evidence for the participation of liquid phase in dehydration. The scanning electron micrographs of the magnesium malonate recorded after decomposition at higher temperature show definite geometrical shapes characteristic of solids. Thus on heating at 673 K for one hour (Plate 3) shows that the material is in the form of crystalline needles. The SEM taken after heating at 873 K for different times only showed microcrystalline powders. The photographs indicate that in dehydration there is participation of

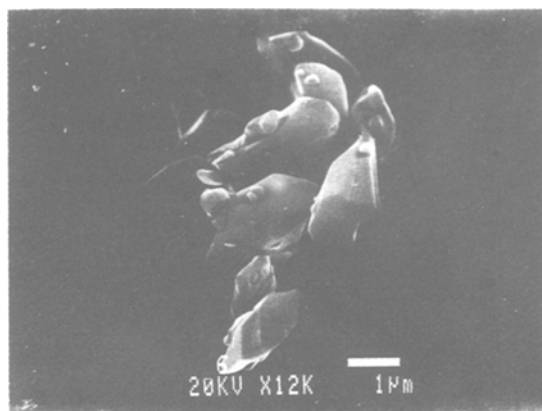


Plate 3 SEM of magnesium oxide, the decomposition product of magnesium malonate trihydrate at 673 K

liquid phase although melting of the solid as a whole was not observed in either DTA or DSC. It can be concluded from these studies that the quantity of liquid is very small and that dehydration is facilitated in the liquid phase, since the stabilizing forces of crystal structure are released and steric constants are diminished. Since the bulk solid does not melt, a localized and transient melt formation on the interface is anticipated as described for the decomposition of Cu(II) malonate and ammonium dichromate [11]. However further decomposition of the anhydrous salt does not involve any liquid intermediate.

Kinetics for dehydration were also studied isothermally at 463 K, 473 K, 483 K and 493 K. In a plot between α vs. t (Fig. 3) the intercepts on y -axis indicate that a large number of product nuclei are already present and that a major part of the reaction is deceleratory. Better correlation coefficients i.e. more than 0.99 was obtained only in those cases where the deceleratory mechanism applies. In all these cases as shown in Table 2, the value of activation energy is around 100 kJ mol^{-1} .

The first four mechanisms are based on diffusion models in the solid state and will involve very high activation energy and low frequency factor. Thus the activation energy and frequency factor obtained in the present investigation are appropriate only for interface reactions to which Polyani–Wigner equation applied. Therefore the most suitable mechanism is the contracting disc mechanism for dehydration where $1 - (1 - \alpha)^2 = kt$. The deceleratory process is due to decreasing size of particles. Dehydration thus occurs in two stages.

1. Local melting of the crystal and the deceleratory process is due to the decreasing size of the disc particles.

2. Dehydration from the melt and is of constant rate.

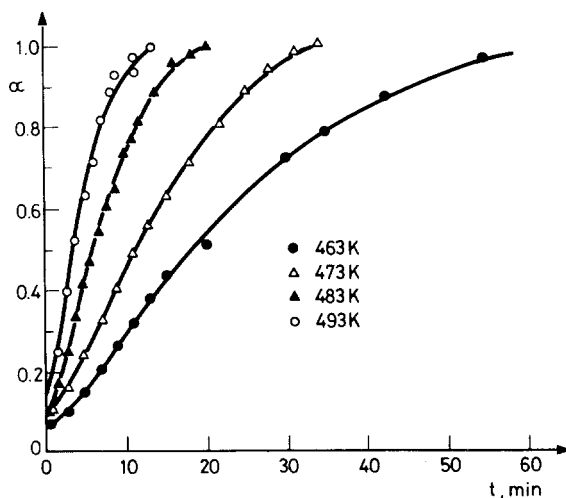


Fig. 3 α vs. t plots for isothermal dehydration of magnesium malonate trihydrate

Table 2 Energy of activation in the dehydration of magnesium malonate trihydrate with different kinetic models

Mechanism	Correlation coefficient	Energy of activation kJ mol^{-1}
$\alpha^2 = kt$.9949	104.17
$(1 - \alpha) \ln(1 - \alpha) + \alpha = kt$.9956	106.38
$(1 - (1 - \alpha)^{2/3}) = kt$.9942	99.15
$1 - 2/3\alpha - (1 - \alpha)^{2/3} = kt$.9950	104.05
$1 - (1 - \alpha)^{1/2} = kt$.9952	102.20

This model is complementary to SEM studies also. The activation energy is characteristic of break of $\text{M}-\text{O}-\text{(H}_2\text{O)}$ bond and subsequent decomposition giving magnesium oxide occurs at moderate temperature of 673 K, when the oxide is crystalline and which becomes amorphous at higher decomposition temperature.

References

- 1 K. Nagase, K. Murishi, K. Sonf and N. Tanaka, *Bull. Chem. Soc. Jpn* 48(11) (1975) 3184.
- 2 A. K. Galwey, A. Mohamed and J. Mohamed, *J. Chem. Soc. Faraday Trans. 1*, 81 (1985) 2503.
- 3 N. J. Carr and A. K. Galwey, "Materials Science Monographs" 28B on "reactivity of solids" (Ed. by Pierre Barret and Louis-Claude Dufour) Elsevier, New York 28 (1985) 697.
- 4 A. K. Galwey and M. A. Mohamed, "Materials Science Monographs" 28B on "reactiv-

- ity of solids" (Ed. by Pierre Barret and Louis-Claude Dufour), Elsevier, New York, 28 (1985) 699.
- 5 S. Shishido and K. Ogaswara, *Sci. Rep. Nigata Univ., Ser C*, 3 (1971) 23.
 - 6 K. Isa and M. Nagava, *Thermochim. Acta*, 75 (1984) 197.
 - 7 W. E. Mourad and S. Nasued, *Thermochim. Acta*, 41 (1980) 117.
 - 8 A. K. Galwey, "Thermal Analysis" (Ed. by Bernard Miller), John Wiley and Sons, New York, 1, 1982, p. 38.
 - 9 K. Nakamoto, "Infrared and Raman spectra of inorganic and co-ordination compounds", John Wiley and Sons, New York 1978.
 - 10 D. Dollimore and D. L. Griffiths, *J. Thermal Anal.*, 2 (1970) 229.
 - 11 N. J. Carr, A. K. Galwey and N. J. Swindell, *Proc. 7th Int. Conf. "Thermal Analysis"*, Heyden, Philadelphia 1982.

Zusammenfassung — Mittels TG, DSC, Scanningelektronenmikroskop usw. wurde die Zersetzung des Trihydrates von Magnesiummalonat isotherm und nicht isotherm untersucht. Die Aktivierungsenergie und der Frequenzfaktor für die isotherme Dehydratation betragen $100 \pm 5 \text{ kJ} \cdot \text{mol}^{-1}$ bzw. 10^{10} s^{-1} . Die entsprechenden DSC Werte für die Zersetzung betragen $332.9 \pm 113 \text{ kJ} \cdot \text{mol}^{-1}$ bzw. 10^{17} s^{-1} . Während der Dehydratation scheint auch eine flüssige Phase aufzutreten, die weitere Zersetzung ist jedoch eine Feststoffreaktion. Das Endprodukt der Zersetzung bei 673 K ist kristallines Magnesiumoxid.

Резюме — Используя методы ТГ, ДСК и сканирующую электронную микроскопию, изучено изотермическое и неизотермическое разложение тригидрата малоната магния. Значения энергии активации и частотного множителя для реакции изотермической дегидратации составляли, соответственно, $100 \pm 5 \text{ кдж} \cdot \text{моль}^{-1}$ и 10^{10} сек^{-1} , тогда как данные, полученные методом ДСК, равнялись, соответственно $332 \pm 113 \text{ кдж} \cdot \text{моль}^{-1}$ и 10^{17} сек^{-1} . Установлено участие жидкой фазы в процессе дегидратации, тогда как дальнейшее разложение является твердотельным процессом. Конечным продуктом разложения при 673 К является кристаллический оксид магния.