# A Study on Solid State Thermal Decomposition Characteristics of Some Metallo-Organic Compounds. Part-II. Thermal Dehydration and Decomposition Characteristics of Some Hydrated Metal Malonates

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Manuscript received 2 June 1982, revised 4 April 1984, accepted 20 September 1984

Solid state dehydration of the hydrated, Ca, Mn, Co, Ni, Cu and Zn salts of malonic acid and subsequent decarboxylation of the anhydrous salts have been studied by simultaneous DTA, TG and DTG techniques. The thermal stability order of the hydrates has been found to be Ni(mal),  $2.5H_3O > Co(mal).2H_3O > Mn(mal).2H_3O > Zn(mal).2H_3O > Ca(mal).2H_3O > Ca(mal).2H_3O > Ca(mal).2H_3O > Cu(mal).2H_3O > Mn(mal) > Zn(mal) > Cu(mal) > Ni(mal) > Co(mal) > Mn(mal) > Zn(mal) > Cu(mal). Thermal parameters like activation energy, enthalpy change and order of reaction for each process have been computed by standard methods.$ 

# Experimental

MALONIC acid used was of L.R. grade and the acid was recrystallised several times from water. The calcium salt was prepared by reacting slight excess of G.R., E. Merck calcium carbonate with the acid in hot aqueous solution, filtration and subscquent crystallisation. The other compounds of malonic acid (those of Co<sup>II</sup>, Ni<sup>II</sup> and Cu<sup>II</sup>) were prepared in a similar manner. The compounds of malonic acid with Mn<sup>II</sup> and Zn<sup>II</sup> were prepared by reacting the respective metal carbonates with malonic acid in hot aqueous solution keeping malonio acid in slight excess whereby metal malonates were precipitated. These were filtered, washed with cold water, recrystallised from hot water and finally dried over fused CaCl<sub>2</sub>.

Simultaneous DTA, TG and DTG determination of the salts were carried out by the procedure described elsewhere<sup>1</sup>. TG curves were utilised for calculating the activation energies of the processes involved, whereas, DTA curves were used to evaluate the enthalpy change accompanying the reactions. The initiation, peak and completion temperatures for the dehydration and the decarboxylation processes were noted from the corresponding DTG curves. The hydrated calcium and other metal salts (those of  $Mn^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$ ,  $Cu^{II}$  and  $Zn^{II}$ ) as well as their dehydrated varieties were characterised by recording their ir spectra (nujol) on a Beckman IR. 20A spectrophotometer by the presence and absence of the  $v_{O-H}$  band in the 3600-3400 cm<sup>-1</sup> region. All the hydrated and the anhydrous compounds were analysed for their metal contents.

For calcium compounds, the calcium content was determined by titration with a standard EDTA solution and for the determination of other metals (Mn, Co, Ni, Cu and Zn), standard methods were used. Carbon and hydrogen were determined by microanalytical techniques. The analytical results are given in Table 1.

TABLE 1—ANALYTICAL DATA OF THE COMPOUNDS							
Compound	Analysis % : Found/(Calcd.)						
	M	С	Н				
$C_4(C_8H_9O_4).2H_8O$	22.38	20.18	3.32				
Mn(C,H,O,) 2H,O	28.35	18.61	3.05				
Co(C,H,O,).2H,O	(28.47) 29.86	(18.65) 18.25	(3.11) 2.98				
Zn(C,H,O,) 2H,O	(29,92) 32,04	(18.28) 17.68	(3.05) 2 91				
Cu(C, H, O,).2H, O	(32.14) 31.50	(17.70) 17.82	(2.95) 2.93				
Ni(C <sub>3</sub> H <sub>3</sub> O <sub>4</sub> ).2.5H <sub>3</sub> O	(31.53) 28.49 (28.54)	(17.86) 17.47 (17,50)	(2.98) 3.37 (3.40)				

### **Results and Discussion**

On gradual heating from room temperature the hydrated salts were completely dehydrated within the temperature range 112-298°. From the TG, DTG and DTA traces of the dehydration stage it was found that all the metal malonates lost their respective water molecules in a single step excepting those of calcium and copper salts which lost their water molecules in two steps. All these dehydration reactions are presented in Table 2.

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	TABLE 2—DEHYDRATION STAGE								
SI. po	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	Eact kcal mol <sup>-1</sup>	∆H kcal mol <sup>-1</sup>	Order of reaction	
1.	$Ca(mal).2H_sO \rightarrow Ca(mal).H_sO + H_sO$	118	169	178	10.32	30,28	5.45	1	
	$Ca(mal).H_{s}O \rightarrow Ca(mal)+H_{s}O$	178	201	236	11.19	39.97	e <b>6.68</b>	1	
2.	$Mn(mal).2H_{g}O \rightarrow Mn(mal)+2H_{g}O$	150	21 <b>2</b>	250	(11.25) 18.47 (18.66)	34.48	35.41	1	
3.	$Co(mal).2H_sO \rightarrow Co(mal) + 2H_sO$	160	220	250	18.26	37.78	27.1	1	
4.	$Ni(mal).2.5H_{s}O \rightarrow Ni(mal) + 2.5H_{s}O$	219	271	298	(18.28) 22.08 (21.87)	53 <b>.21</b>	31.01	1	
5.	$Cu(mal).2H_{2}O \rightarrow Cu(mal).H_{2}O + H_{2}O$	112	1 <b>22</b>	137	8.88	59.41	8.66	1	
	$Cu(mal).H_sO \rightarrow Cu(mal)+H_sO$	137	158	188	(8.93) 10.16 (9.80)		10.07	1	
6.	$Zn(mal).2H_9O \rightarrow Zn(mal)+2H_9O$	138	161	200	17.60 (17.70)	55.30	19.82	1	

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Initiation, peak and completion temperatures of the dehydration processes, as obtained from the relevant DTG curves, along with the corresponding weight loss are given in Table 2. Enthalpy changes accompanying each dehydration process were determined by standard methods<sup>2</sup> and the activation energies for each dehydration process were computed from an analysis of the corresponding TG curves using the method of Horowitz and Metzger<sup>2</sup>. The lnln  $(w_0 - w_1^2)/(w - w_1^2)$  vs  $\theta$ plots for the dehydration processes are presented in Fig. 3, while the corresponding plot for decarboxylation reactions are presented in Fig. 4. The orders of both dehydration and decarboxylation reactions were determined by standard methods<sup>3,4</sup> and were found to be unity in all the cases. The results obtained are presented in Table 2 (dehydration) and Table 3 (decarboxylation) and the corresponding curves in Figs. 1 and 2 (dehydration), and Fig. 3. (decarboxylation). Ir spectra of the hydrated and anhydrous varieties were recorded and compared to ascertain the completion of the dehydration process.

Decarboxylation process: All the anhydrous salts exhibit considerable thermal stability and undergo decarboxylation within the temperature range 212°-452°. Initiation, peak and completion





Fig. 4. Plot of lnln  $(w_0 - w_1^d)/(w - w_1^d) vs \theta$  for decarboxylation of metal malonates : (1) Cu(mal), (2) Co(ma)l, (3) Zn(mal), (4) Ni(mal), (5) Mn(mal), and (6) Ca(mal).

metal oxides (which varies in the order: MnO>ZnO>NiO>CoO>CuO) may be related to the strength of the M-O bond in the different metal malonates. Hence, the plots of the initiation, peak

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calcium carbonate.

the anhydrous compounds along with the corres-

ponding weight losses are given in Table 3. The final product left in the crucible was found to be the metallic oxide in all the cases, excepting for calcium malonate where the final product left was

The metal oxides being the stable end-products in all the cases, the negative heat of formation of the

	TABLE 3—DECARBOXYLATION STAGE								
SI. No	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	Eact kcal mol <sup>-1</sup>	∆H kcal mol <sup>-1</sup>	Order of reaction	
1.	$Ca(mal) \rightarrow CaCO_s + products$	331	358	452	29.75	1 <b>5.75</b>	106 <b>.2</b> 9	1	
2.	$Mn(mal) \rightarrow Mn_sO_s + products$	250	293	370	(29.57) 50.53	34 <b>.67</b>	<b>63.4</b> 3	1	
3.	$Co(mal) \rightarrow Co_9O_8 + products$	258	294	360	47.25	86.34	75.28	1	
4.	Ni(mal) -> NiO + products	298	338	3 <b>9</b> 0	54 <b>.5</b> 9	49.28	71.89	1	
5.	$Cu(mal) \rightarrow CuO + products$	212	226	273	(53.51) 53.18	<b>69.4</b> 4	82.57	1	
6.	$Zn(mal) \rightarrow ZnO + products$	220	265	314	50.48 (51.38)	43.68	17.40	1	

and completion temperatures of thermal decarboxylation of anhydrous metal malonates against the negative heat of formation<sup>5</sup> of the respective metal oxides (Fig. 5) exhibit interesting trends along with the rise of the values of  $-\Delta H_{2}^{o}$ . Such variation as reflected in Fig. 5 is close to the behaviour expected from the thermal stability order observed in this study. Only manganese and zinc malonates exhibit departures from this general trend.



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ionic radii, cobalt and nickel malonates exhibiting departure from this general trend.



INDLE T				temp.				
Compounds Mn(mal) Co(mal) Ni(mal) Cu(mal) Zn(mal)	Initiation temp. °C 250 258 298 212 220 Ref. 13	Peak temp. °C 293 294 338 226 265	Completio temp. °C 370 360 390 273 314	<sup>n</sup> △H <sup>0</sup> <sub>f</sub> of oxides <sup>*</sup> kcal mol <sup>-1</sup> - 92.00 - 57.20 - 58.40 - 37.10 - 83.17	Ca(mal) Mn(mal) Co(mal) Ni(mal) Cu(mal) Zn(mal) *Ref. 14.	C 331 250 258 298 212 220	A 1.000 1.219 1.351 1.428 1.369 1.333	
								_

The plots of initiation temperature of thermal decarboxylation of the metal malonates against the corresponding reciprocal ionic radii<sup>6</sup> (Fig. 6) exhibit some definite trends. This behaviour is close to the general behaviour of gradual decrease of the stability of metal salts with the decrease in the In the single-step dehydration as well as in the first-stage of the two-step dehydration processes, represented by the equations in Table 2, the activation energies are in the order, Cu > Zn > Ni > Co > Mn > Ca, while the overall enthalpy changes for dehydration processes are found to follow the order, Mn > Ni > Co > Zn > Cu >

Ca. The thermal stability of the metal malonate hydrates obtained from the DTG initiation and peak temperatures follow the order, Ni > Co > Mn > Ca > Zn > Cu.

In the decarboxylation of the anhydrous metal malonates represented by equations given in Table 3, the activation energies follow the order, Co > Cu > Ni > Zn > Mn > Ca, while the enthalpy changes for the same process are found to follow the order, Ca > Cu > Co > Ni > Mn > Zn. The thermal stability of the anhydrous metal malonates obtained from the DTG initiation and peak temperatures follow the order, Ca > Ni > Ca > Ni > Ca > Ni > Co > Mn > Zn > Cu.

The general series found by Irving and Williams<sup>\*</sup> for the stability of complexes in solution is almost the reverse of the above series for the thermal stability in the solid state. The same sequence, as suggested by us, was reported for the thermal stability of other compounds of the same metal ions by earlier workers<sup>8-12</sup>. This behaviour may be accounted for by assuming that the strength of intermolecular bonds play a significant role in determining the thermal stability of compounds in solid state. represented as



The solid decomposition product was analysed for its copper content and characterised by X-ray powder pattern and was found to be cupric oxide. Carbon dioxide was detected by precipitation as calcium carbonate from a solution of calcium hydroxide while carbon monoxide was detected by reduction of iodine pentoxide into iodine, and ethylene was detected by passing the gaseous decomposition products through bromine water and studying the uv spectra of the dibromoethylene produced.

Probable mechanism: On the basis of the different products detected and characterised, it is suggested that the initial decomposition of copper malonate produced CuO,  $CO_{s}$  and a ketene which is then further decomposed to other products probably through the following Route.



#### ROUTE-I

In an attempt to study the mode of decomposition of the transition metal malonates, to detect and characterise the decomposition products and to suggest a probable mechanism, copper malonate dihydrate was taken as representative example. This was heated under gradually increasing temperature. At the initiation temperature (212°) for the decarboxylation stage it started decomposing. The process continued for a definite temperature range of 212-273° and became complete at 273° which is exactly its completion temperature. The decomposition process leading to the generation of the heterogeneous products obtained thereof may be

#### ROUTE-II

Route-I: (i) The decomposition products were passed into a trap containing carbon tetrachloride cooled in ice whereby the ketene produced immediately dimerised to produce (D) which was detected by recording its ir spectrum which exhibited the strong carbonyl band in the region 1760-1780 cm<sup>-1</sup> corresponding to the  $v_{C=0}$  of the cyclobutane-1,3dione.

(ii) In another experiment the above CCl, solution was shaken with water containing a little NaOH in which the diketone was hydrolysed and formed  $CH_{a}COONa$ . This was evaporated to dryness and

the presence of the  $-COO^-$  band was established by ir spectrum.

Route-II: The decomposition products were passed into a ice-cooled trap containing  $Br_s$  in  $CCl_4$ when its yellow colour discharged completely. The  $CCl_4$  solution in the trap was subjected to vapour phase chromatography and the peaks were noted, and compared with an authentic sample of  $CH_sBr$ .  $CH_sBr$  under similar condition. The presence of  $CH_2=CH_2$  was confirmed. Carbon monoxide was detected by the  $I_2O_8$ -method and cyclopropane characterised by ir and nmr spectra.

# Acknowledgement

The authors are grateful to Dr. N. Ray Chaudhuri and Mr. Sasanka Mukherjee of our department for recording TG, DTA and DTG curves.

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