

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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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 $\text{Ni}(\text{mal}), 2.5\text{H}_2\text{O} > \text{Co}(\text{mal}), 2\text{H}_2\text{O} > \text{Mn}(\text{mal}), 2\text{H}_2\text{O} > \text{Zn}(\text{mal}), 2\text{H}_2\text{O} > \text{Ca}(\text{mal}), 2\text{H}_2\text{O} > \text{Cu}(\text{mal}), 2\text{H}_2\text{O}$. But in the decarboxylation process the trend observed is $\text{Ca}(\text{mal}) > \text{Ni}(\text{mal}) > \text{Co}(\text{mal}) > \text{Mn}(\text{mal}) > \text{Zn}(\text{mal}) > \text{Cu}(\text{mal})$. 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 subsequent crystallisation. The other compounds of malonic acid (those of Co^{2+} , Ni^{2+} and Cu^{2+}) were prepared in a similar manner. The compounds of malonic acid with Mn^{2+} and Zn^{2+} were prepared by reacting the respective metal carbonates with malonic acid in hot aqueous solution keeping malonic 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_2 .

Simultaneous DTA, TG and DTG determination of the salts were carried out by the procedure described elsewhere¹. 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^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) 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 $\nu_{\text{O-H}}$ band in the $3600\text{-}3400\text{ cm}^{-1}$ 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	C	H
$\text{Ca}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	22.38 (22.50)	20.18 (20.21)	3.32 (3.37)
$\text{Mn}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	28.35 (28.47)	18.61 (18.65)	3.05 (3.11)
$\text{Co}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	29.86 (29.92)	18.25 (18.28)	2.98 (3.05)
$\text{Zn}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	32.04 (32.14)	17.68 (17.70)	2.91 (2.95)
$\text{Cu}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$	31.50 (31.53)	17.82 (17.86)	2.93 (2.98)
$\text{Ni}(\text{C}_2\text{H}_3\text{O}_4)_2 \cdot 2.5\text{H}_2\text{O}$	28.49 (28.54)	17.47 (17.50)	3.37 (3.40)

Results and Discussion

On gradual heating from room temperature the hydrated salts were completely dehydrated within the temperature range $112\text{-}298^\circ$. 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

Sl. no.	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	E _a † kcal mol ⁻¹	ΔH kcal mol ⁻¹	Order of reaction
1.	Ca(mal).2H ₂ O → Ca(mal).H ₂ O + H ₂ O	118	169	178	10.32 (10.11)	30.28	5.45	1
	Ca(mal).H ₂ O → Ca(mal) + H ₂ O	178	201	236	11.19 (11.25)	39.97	6.68	1
2.	Mn(mal).2H ₂ O → Mn(mal) + 2H ₂ O	150	212	250	18.47 (18.66)	34.48	35.41	1
3.	Co(mal).2H ₂ O → Co(mal) + 2H ₂ O	160	220	250	18.26 (18.28)	37.78	27.1	1
4.	Ni(mal).2.5H ₂ O → Ni(mal) + 2.5H ₂ O	219	271	298	22.08 (21.87)	53.21	31.01	1
5.	Cu(mal).2H ₂ O → Cu(mal).H ₂ O + H ₂ O	112	122	137	8.88 (8.93)	59.41	8.66	1
	Cu(mal).H ₂ O → Cu(mal) + H ₂ O	137	158	188	10.16 (9.80)		10.07	1
6.	Zn(mal).2H ₂ O → Zn(mal) + 2H ₂ O	138	161	200	17.60 (17.70)	55.30	19.82	1

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 methods³ and the activation energies for each dehydration process were computed from an analysis of the corresponding TG curves using the method of Horowitz and Metzger⁶. The $\ln \ln (w_0 - w_f^i)/(w - w_f^i)$ vs θ 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^{3,4} 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

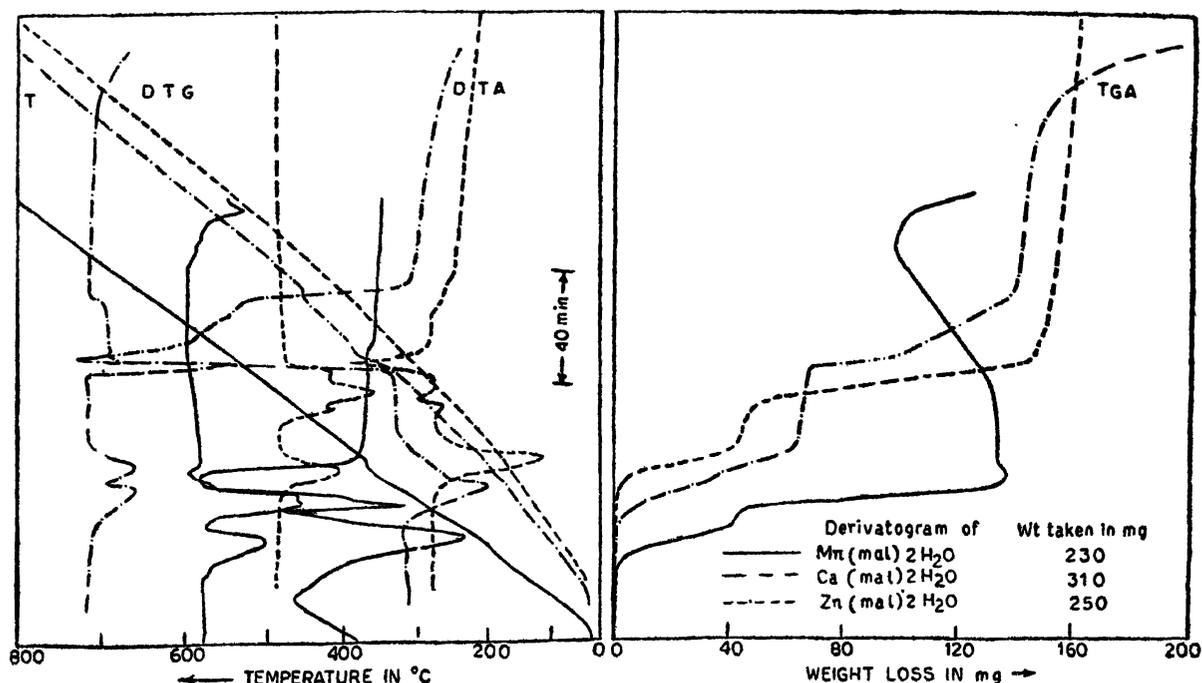


Fig. 1

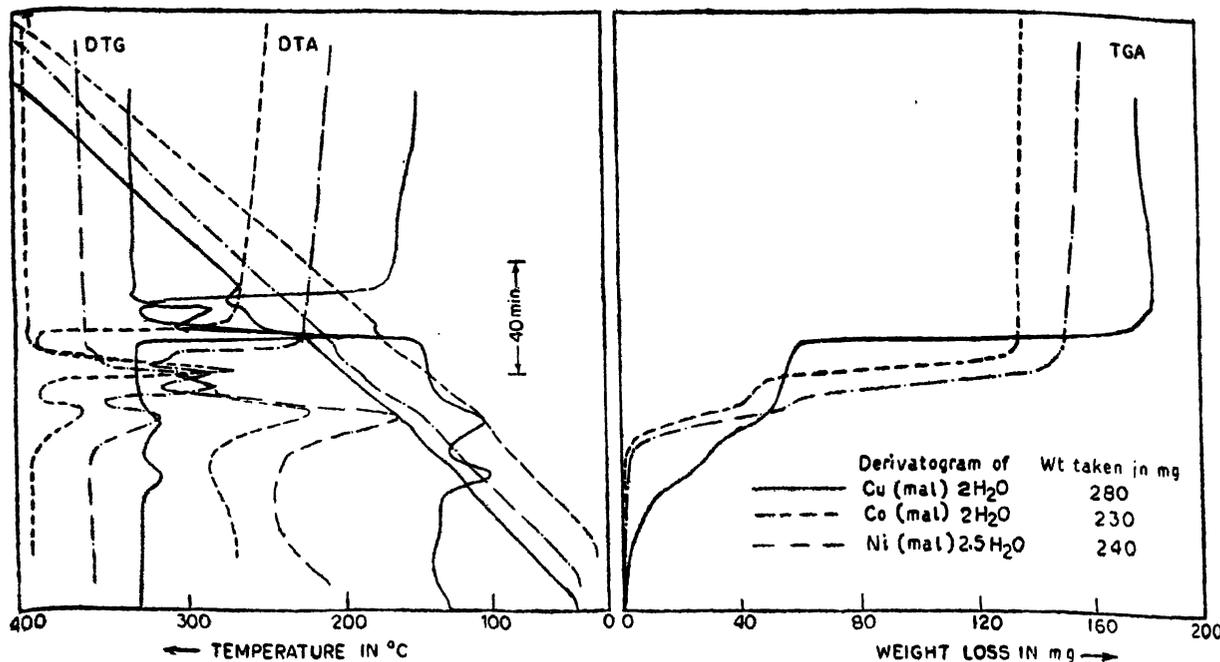


Fig. 2

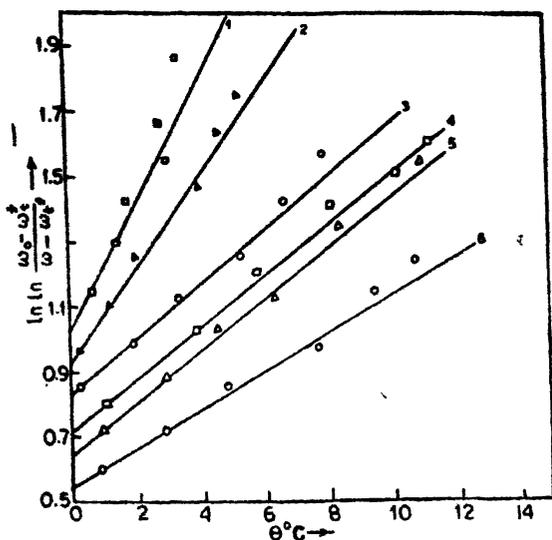


Fig. 3. Plot of $\ln \ln (w_0 - w_f^i) / (w - w_f^i)$ vs θ for dehydration of metal malonates: (1) $\text{Cu(mal)} \cdot 2\text{H}_2\text{O}$, (2) $\text{Zn(mal)} \cdot 2\text{H}_2\text{O}$, (3) $\text{Ni(mal)} \cdot 2.5\text{H}_2\text{O}$, (4) $\text{Co(mal)} \cdot 2\text{H}_2\text{O}$, (5) $\text{Ca(mal)} \cdot 2\text{H}_2\text{O}$ (first stage), and (6) $\text{Mn(mal)} \cdot 2\text{H}_2\text{O}$.

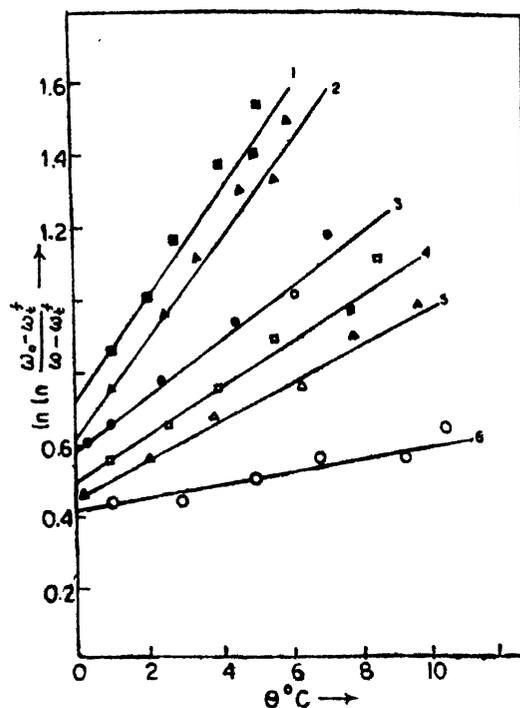


Fig. 4. Plot of $\ln \ln (w_0 - w_f^i) / (w - w_f^i)$ vs θ for decarboxylation of metal malonates: (1) Cu(mal) , (2) Co(mal) , (3) Zn(mal) , (4) Ni(mal) , (5) Mn(mal) , and (6) Ca(mal) .

temperatures for the decarboxylation processes of the anhydrous compounds along with the corresponding 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 calcium carbonate.

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

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

TABLE 3—DECARBOXYLATION STAGE

Sl. No	Reaction	Initiation temp. °C	Peak temp. °C	Completion temp. °C	Weight loss % Found/(Calcd.)	E _{act} kcal mol ⁻¹	ΔH kcal mol ⁻¹	Order of reaction
1.	Ca(mal) → CaCO ₃ + products	331	358	452	29.75 (29.57)	15.75	106.29	1
2.	Mn(mal) → Mn ₂ O ₃ + products	250	293	370	50.53 (50.35)	34.67	63.43	1
3.	Co(mal) → Co ₃ O ₄ + products	258	294	360	47.25 (47.04)	86.34	75.28	1
4.	Ni(mal) → NiO + products	298	338	390	54.59 (53.51)	49.28	71.89	1
5.	Cu(mal) → CuO + products	212	226	273	53.18 (51.96)	69.44	82.57	1
6.	Zn(mal) → 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 formation⁵ of the respective metal oxides (Fig. 5) exhibit interesting trends along with the rise of the values of $-\Delta H_f^\circ$. 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.

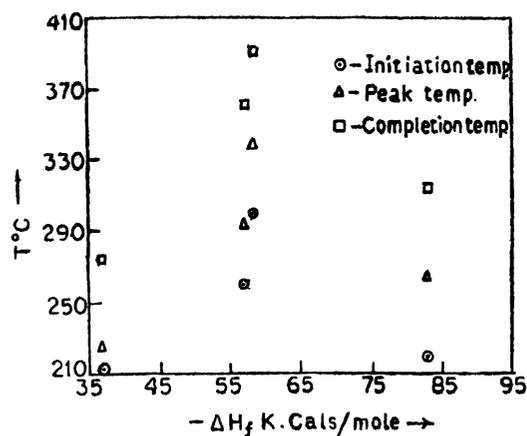


Fig. 5

Compounds	Initiation temp. °C	Peak temp. °C	Completion temp. °C	ΔH _f ^o of oxides* kcal mol ⁻¹
Mn(mal)	250	293	370	-92.00
Co(mal)	258	294	360	-57.20
Ni(mal)	298	338	390	-58.40
Cu(mal)	212	226	273	-37.10
Zn(mal)	220	265	314	-83.17

* Ref. 13.

The plots of initiation temperature of thermal decarboxylation of the metal malonates against the corresponding reciprocal ionic radii⁶ (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

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

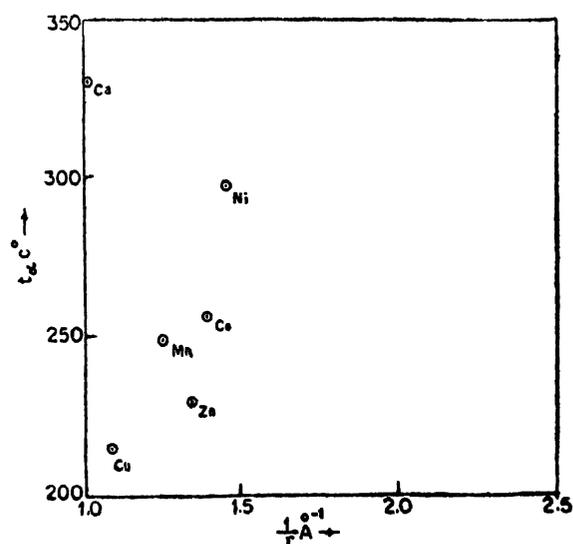


Fig. 6

TABLE 5

Compound	Initial weight loss temp. °C	1/r* Å ⁻¹
Ca(mal)	331	1.000
Mn(mal)	250	1.219
Co(mal)	258	1.351
Ni(mal)	298	1.428
Cu(mal)	212	1.369
Zn(mal)	220	1.333

*Ref. 14.

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 >

the presence of the $-\text{COO}^-$ band was established by ir spectrum.

Route-II: The decomposition products were passed into a ice-cooled trap containing Br_2 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_2Br . CH_2Br under similar condition. The presence of $\text{CH}_2=\text{CH}_2$ was confirmed. Carbon monoxide was detected by the I_2O_5 -method and cyclopropane characterised by ir and nmr spectra.

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