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# Thermal Analysis of Certain Alkali Metal Malonates

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The thermal analysis of alkali metal malonates (M = Li, Na, K, $NH_4$) has been studied using TG—DTG—DTA, DSC and IR. M—O bond frequency in IR shows increasing trend with increase in electronegativity/polarizing power of the substituent cation. Kinetic parameters for various steps have been reported and high values for activation energy and frequency factor are attributed to the coupling of phase changes and the chemical steps. The stability order of decomposition in nitrogen atmosphere is

$$Li > Na > K > NH_4.$$

## INTRODUCTION

Since alkali metal carboxylates and their decomposition products are extensively used in industry as pharmaceuticals, catalysts, ceramics, glasses etc. so their decomposition is of much interest. Although considerable work on the decomposition of alkali metal oxalates is reported[1-6], similar studies on malonates are rudimentary; yet important studies on decomposition of certain anhydrous malonates have been reported which show that these processes are individual ones even for similar compounds. *e.g.* crystolysis of silver malonate[7] is a solid state process while participation of liquid in the thermal decomposition of copper malonate[8] and magnesium malonate[9] has been observed. The present work is a systematic extension of the decomposition studies reported by us.

A fortunate consequence of the selection of this series was that lithium and ammonium malonates were anhydrous while sodium and potassium malonates were hydrated. The decomposition (crystolysis) in the former thus occurs in crystallites as prepared rather than after recrystallisation and retexturing processes which are inevitable when dehydration precedes the anion breakdown reaction. Also ammonium malonate gives no solid residue while all others give solid residue.

## EXPERIMENTAL

Alkali metal malonates were prepared by mixing equimolar aqueous solutions of respective alkali metal carbonates and malonic acid. The resultant solutions were concentrated on water bath. The precipitates of alkali metal malonates formed by the addition of excess of acetone were dried in air. Composition of alkali metal malonates was established by chemical analysis. The malonate group was estimated by ion exchange method[10]. The percentages of carbon, hydrogen, and malonate groups are given in Table 1. Derivatographs were recorded on a Paulih-Paulik-Erdey MOM derivatograph (Hungary) at a heating rate of 10° $min^{-1}$ in static air atmosphere. Differential scanning calorimetry was taken on Mettler TA 3000 system.

TABLE 1

MICROANALYTICAL DATA FOR ALKALI METAL MALONATES

| Compound | | % C | % H | % Malonate |
|---|---|---|---|---|
| $Li_2CH_2C_2O_4$ | obsd. | 30.77 | 1.75 | 85.40 |
| | calcd. | 31.00 | 1.72 | 87.90 |
| $Na_2CH_2C_2O_4 \cdot H_2O$ | obsd. | 22.25 | 2.00 | 61.74 |
| | calcd. | 21.60 | 2.40 | 61.90 |
| $K_2CH_2C_2O_4 \cdot 3H_2O$ | obsd. | 16.06 | 2.93 | 44.38 |
| | calcd. | 15.38 | 3.41 | 43.58 |
| $(NH_4)_2CH_2C_2O_4$ | obsd. | 26.94 | 6.69 | 72.52 |
| | calcd. | 26.00 | 7.24 | 73.18 |

## RESULTS AND DISCUSSION

The identity of various malonates was confirmed from elemental analysis (Table 1) and infrared spectra of alkali metal malonates which show a band near 3400 $cm^{-1}$ due to $\nu(OH)$ of lattice water for hydrated ones, a small band around 2950 $cm^{-1}$ due to $\nu(C-H)$ of carboxylate group and a broad band in the region 1565–1615 $cm^{-1}$ due to $\nu_{asy}(C=O)$ of carboxylate[11] and bending mode of water group. The band at 1390 $cm^{-1}$ is due to $\nu_{sym}(C=O)$ of the coordinated carboxylate group. In the far IR region (Table 2) the frequency of M—O bonding increases as the electropositive character of metal increases.

TABLE 2

M—O BOND STRETCHING FREQUENCIES IN ALKALI MALONATES

| Compound | M—O bond frequency ($cm^{-1}$) |
|---|---|
| $Li_2CH_2C_2O_4$ | 415 |
| $Na_2CH_2C_2O_4 \cdot H_2O$ | 455 |
| $K_2CH_2C_2O_4 \cdot 3H_2O$ | 480 |

All the compounds were crystalline as many sharp diffraction lines were recorded in room temperature XRD powder pattern.

### Lithium Malonate

The simultaneous TG-DTG-DTA (Fig. 1) of lithium malonate shows a single stage of decomposition to lithium carbonate at a mass loss of

36.5% (calcd. loss = 36.5%). The decomposition temperature interval is 593–673 K which is a considerable lower value than that of oxalate[2] (717–787 K) each taken from DTA. Lithium carbonate as the end product has been confirmed by infrared spectrum and elemental analysis. Elemental analysis of the solid decomposition product showed it to contain 16.09% of elemental carbon and IR spectrum displayed distinct bands at 1430 and 1505 $cm^{-1}$ due to lithium carbonate[12]. DSC recorded from 323 to 773 K in nitrogen atmosphere at a heating rate of 10 K $min^{-1}$ (Fig. 2a) shows an endothermic peak at 650 K. Kinetic parameters of

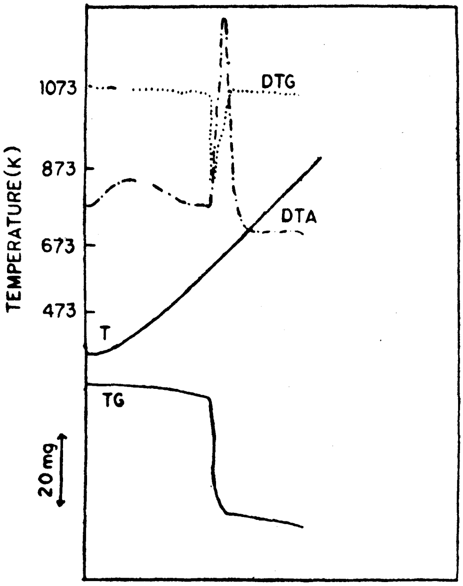


Fig. 1. Simultaneous DTG-DTA-TG curves of lithium malonate.

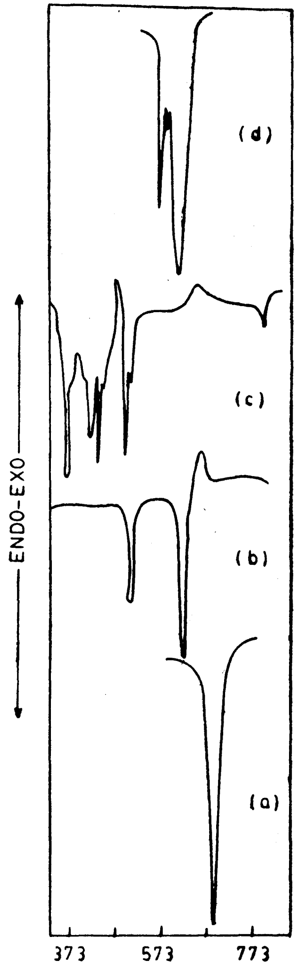


Fig. 2. DSC curves of (a) Lithium malonate, (b) Sodium malonate monohydrate, (c) Potassium malonate trihydrate, (d) Ammonium malonate, in nitrogen atmosphere.

decomposition were calculated from DSC data on the basis of relationship:

$$\frac{d\alpha}{dt} = A \cdot \exp(-E_a/RT)(1-\alpha)^n \tag{1}$$

where $\alpha$ is the fraction of the reaction completed at time t, and $E_a$, n and A are energy of activation, order of reaction and frequency factor respectively. On the basis of the assumption that in DSC, heat of reaction evolved or absorbed at any time t is proportional to the number of moles of reactant consumed, an equation for heat of reaction may be expressed in the form:

$$\frac{1}{H_T} \cdot \frac{dH}{dt} = A \cdot \exp(-E_a/RT)\,(1-\alpha)^n \frac{(H_T - H)^n}{H_T} \tag{2}$$

where $H_T$ = total heat of reaction (J/g) (area under the DSC curve), H = heat of reaction at a given time and temperature (partial area under the curve) and dH/dt = rate of heat flow (J/s) (peak height). Based on this principle the values of n, A, $E_a$ and $H_T$ for the decomposition have been calculated from the programme available in the Tc–10 microprocessor provided with the thermal analysis system. The value of these parameters are $n = 1.87$, $A = 10^{84}\,s^{-1}$, $E_a = 1944\ kJ\ mol^{-1}$ and $H_T = 48\ kJ\ mol^{-1}$ respectively. Very high values for A and $E_a$ show that decomposition is only apparently a single step process and that coupling of chemical reactions with textural change or/and phase change takes place as also seen in the single (unsplit) peak.

## Sodium Malonate Monohydrate

Figure 3 shows the non-isothermal analysis of sodium malonate monohydrate. The TG curve indicates three main stages of decomposition. A plateau in TG with maximum rate peak at 453 K corresponds to the formation of anhydrous salt. Another stable step in TG is the formation of sodium carbonate with a weight loss of 36% (calcd. loss = 36.2%) and this remained stable upto 723 K. DTA exothermic region shows that the decomposition is oxidative. The decomposition temperature of synthetic sodium carbonate is reported to be very high dependent upon the crucible and impurities[13]. However sodium carbonate formed in the present case starts decomposing at a fairly low temperature showing thereby that this compound is only chemically sodium carbonate and not structurally. The high heat produced during the course of its decomposition, the absence of a solvent and the non-equilibrium conditions in a continuously heated system prohibit the formation of a stable structure. Further decomposition of this sodium carbonate leads to the formation of sodium oxide as shown by a mass loss of 64.5%. A complete correspondence between all the steps of DTA and DTG peaks shows that there is no phase change or melting in this system. In the DSC recorded from 323 to 773 K in nitrogen atmosphere (Fig. 2b), the peak temperatures lie at 491 (endo), 596 (endo) and 633 K (exo). The kinetic parameters (*i.e.* $H_T$, $E_a$, n, A) obtained from DSC for the dehydration step are 7.76 kJ mol$^{-1}$, 264.40 mol$^{-1}$, 0.71 and $10^{26}$ s$^{-1}$ respectively. For the decomposition step at 596 K, $H_T$, $E_a$, n and A are 49.36 kJ mol$^{-1}$, 986.63 kJ mol$^{-1}$, 1.65 and $10^{85}$s$^{-1}$. The α-t plots in DSC for dehydration and decomposition in nitrogen are linear.

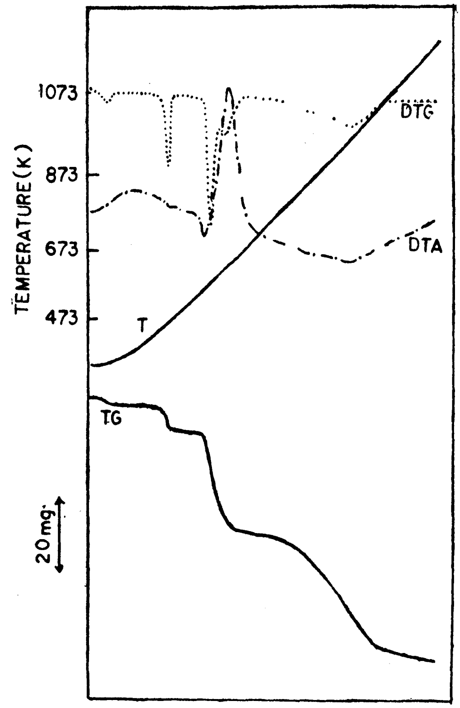
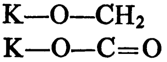


Fig. 3. Simultaneous DTG-DTA-TG curves of sodium malonate.

The high values for kinetic parameters are typical of coupling in these processes. The absence of peaks due to phase change or textural changes only shows that the chemical processes and physical changes occur simultaneously. A large difference in the molar volumes of the product and reactant cause large strain and hence cracks etc. at the product-reactant interface to enhance its reactivity and thus increase the value of A.

**Potassium Malonote Trihydrate**

Since thermal analysis curves for potassium malonate trihydrate are complex, only the main peaks are described. Thermal curve shows that dehydration occurs in three stages with DTG peak temperature at 352, 421 and 447 K implying that all water molecules are not equivalent. Subsequent decomposition is endothermic with a loss of 35% giving a compound of formula  $\begin{matrix}\text{K—O—CH}_2\\ \text{K—O—C=O}\end{matrix}$ whose identity could not be determined. This compound is not stable and decomposes in oxygen exothermally with a peak temperature of 723 K and mass loss of 41.0% to show the formation of potassium carbonate. This however does not possess the stable crystal structure of potassium carbonate and hence starts decomposing at about 853 K endothermally, giving ultimately potassium oxide by IR and chemical analysis. The low temperature decomposition of potassium carbonate is ascribed to its being energy rich because (i) It was formed during an exothermic process, (ii) could not crystallize because of absence of any solvent, (iii) was not kept for long to attain equilibrium structure.

DSC of potassium malonate trihydrate (Fig. 2c) also confirmed the complexity of its decomposition. The peak at 495 K has heat of reaction $= 12$ kJ mol$^{-1}$ with a reaction order of 0.64 and $E_a = 181.51$ kJ mol$^{-1}$ and frequency factor of $10^{21}$s$^{-1}$. The value of $H_T$, n, $E_a$ and A of the stage with a peak temperature 775 K were 8.46 kJ mol$^{-1}$, 0.12, 264 kJ mol$^{-1}$ and $10^{16}$ s$^{-1}$ respectively.

## Ammonium Malonate

TG-DTG-DTA and DSC for ammonium malonate recorded in oxygen and nitrogen atmospheres. After a phase change at 410 K, the decomposition occurs at 448 K. Corresponding peaks have been observed in DSC at 396.5 K and 444 K. This compound leaves no solid residue as all the products were volatile. The evolved gases were confirmed to be $NH_3$, CO and $CO_2$. For a peak in DSC at 396.5 K, the values of $E_a$, A, $H_T$ and n are 252 kJ mol$^{-1}$, $10^{37}$ s$^{-1}$, 4.815 kJ mol$^{-1}$ and 0.32 respectively. The values of these parameters associated with decomposition peak at 444 K are $E_a = 243$ kJ mol$^{-1}$, $A = 10^{30}$ s$^{-1}$, $H_T = 112.84$ kJ mol$^{-1}$ and $n = 1.40$ respectively.

Any generalization about the decomposition behaviour of this malonate series cannot be stated because all the salts are although chemically related but are either anhydrous or have different degrees of hydration and also possess different crystal structures. Ti for dehydration and decomposition are given in Table 3.

One notes that sodium malonate dehydrates at a higher temperature than potassium malonate showing thereby that it is more stable. The stability order for decomposition from Ti as well as from peak temperatures of DSC or even the activation energy in nitrogen atmosphere is

Li > Na > K > $NH_4$. This order is consistent with their electronegativity order and is of course different from the order in oxalates.

Maximum stability of lithium malonate is due to its (i) comparatively high electronegativity and (ii) stable structure—being anhydrous does not have to undergo reorganisation/restructuring after dehydration.

TABLE 3

DECOMPOSITION TEMPERATURE OF ALKALI METAL MALONATES/OXALATES

| Metal | Malonate | | Oxalate |
|---|---|---|---|
| | Dehydration Ti(K) | Decomposition Ti(K) | Decomposition Ti(K) |
| Li | — | 613 | 717* |
| Na | 453 | 573 | 713* |
| K | 383 | 503 | 731* |
| $NH_4$ | — | 393 | 451** |

*Ref. 2, **Ref. 1.

Table 3 shows that alkali metal oxalates are stabler than malonates. This order agrees with the high temperature acid-base theory according to which weaker the anion base the higher the temperature of decomposition[1] and the oxalate ion is a weaker anion base than the malonate ion. A very high value for $E_a$ and A for many of the decomposition steps is attributed to many processes occurring simultaneously.

## REFERENCES

1. L. Erdey, S. Gal and G. Liptay, *Talanta*, **11**, 913 (1964).
2. D. Dollimore and D. L. Griffiths, *J. Therm. Anal.*, **2**, 229 (1970).
3. D. Dollimore and D. Tinsley, *J. Chem. Soc. (A)*, 3043 (1971).
4. A. H. Verdonk, *Therm. Anal.* (Proc. 3rd ICTA, Basel, 1971), **2**, 651 (1972).
5. G. G. T. Guarini, R. Spinicci and D. Donals, *Therm. Anal.* (Proc. 4th ICTA, Heyden, London, 1974), **1**, 185 (1975).
6. J. E. Jr. House, J. Cardat Richard, D. McCormock and E. McCrotly Stephen, *Trans. Ill, State Acad. Sci.*, **71**, 183 (1978).
7. A. K. Galway and M. A. Mohamed, *J. Chem. Soc. Faraday Trans. I*, **81**, 2503 (1985).
8. N. J. Carr, A. K. Galwey and W. J. Swindall, Proc. 10th Int. Conf., "Reactivity of Solids", (Ed.) Pierre-Barret and Louis Claude Dufour), Elsevier, New York, p. 697 (1985).
9. P. S. Bassi, B. S. Randhawa and Sandeep Kaur, *J. Thermal. Anal.* (in press).

10. J. Inczedy, Analytical Applications of Ion Exchange, Pergamon Press, Oxford, p. 81 (1966).

11. K. Nakamoto, Infrared nnd Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York (1978).

12. R. A. Nyquist and R. O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press (1971).

13. W. Wendlandt, Thermal Analysis, 3rd edn., (Ed.) P. J. Elving, J. D. Wine Fordner and I. M. Kollhoff; John Wiley & Sons, New York, 1986.

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