Infrared spectra and thermal decompositions of metal acetates and dicarboxylates[1]

K. C. Patil, G. V. Chandrashekhar, M. V. George, and C. N. R. Rao[2]
Department of Chemistry, Indian Institute of Technology, Kanpur, India

Received June 1, 1967

The infrared spectra of rare earth acetates have been studied to examine the metal-acetate bonding. The thermal decomposition of rare earth acetates as well as lead and copper acetates have been investigated in detail by employing thermogravimetric analysis and differential thermal analysis. Thermal decomposition of calcium dicarboxylates (malonate to sebacate) have been studied employing t.g.a. and d.t.a. Infrared spectra of the dicarboxylates have also been studied. Preliminary results on the products of decomposition of dicarboxylates have been reported.

Canadian Journal of Chemistry, 46, 257 (1968)

Introduction

The thermal decomposition of calcium acetate to acetone and calcium carbonate is a well-known reaction. There is, however, little or no information on the thermal decomposition of other metal acetates in the literature. In the present study, the thermal decompositions of copper acetate, lead di- and tetra-acetates, as well as of a few rare earth acetates, have been investigated employing differential thermal analysis (d.t.a.), thermogravimetric analysis (t.g.a.), and infrared spectroscopy. In addition, the infrared spectra of rare earth acetates have been examined in order to study the nature of the metal-acetate bonding in the rare earth series.

The thermal decompositions of several metal oxalates, particularly those of rare earths, have been studied exhaustively in the past few years (1, 2 and references cited therein, 3, 4). Preparation of ketones by the decarboxylation of the metal salts of long chain dicarboxylic acids has long been known to organic chemists. While this method was found to be somewhat useful for the preparation of some ketones, the pyrolysis of many of the salts are found to give rise to a variety of products, many of which have not been identified. It was therefore considered interesting to examine the thermal decomposition of the calcium salts of a few dicarboxylic acids (malonic to sebacic) employing t.g.a. and d.t.a. Such a study would throw light on the mode of decomposition and indicate, at least, the main inorganic residue left over after the removal of the organic part. Results of a preliminary study of the decomposition products have also been presented.

Experimental

All the rare earth acetates were prepared by dissolving the oxides in boiling 50% acetic acid and evaporating the solutions to dryness, as reported by Witt and Onstott (5). The resulting compounds were recrystallized from water and heated to ~ 220 °C in vacuum to obtain anhydrous acetates (5). Both lead and copper acetates were available commercially.

All the dicarboxylic acids used were commercial samples. The calcium salts were prepared by the reaction of calcium carbonate with the acid solutions in water. Calcium malonate and succinate were obtained as insoluble salts, whereas calcium glutarate, adipate, and pimelate were obtained by the evaporation of the resulting solutions, after completely neutralizing the acids. Dysprosium sebacate was prepared by the interaction of the sodium salt of the acid with the chloride solution.

The t.g.a. curves were recorded with an Aminco thermobalance. The heating rate employed was 10 °C/min and the ambient pressure was $\sim 3 \times 10^{-2}$ mm Hg. The d.t.a. curves were obtained by employing an Aminco thermoanalyzer with a temperature-programmed furnace (fitted with a voltage stabilizer), differential amplifier, and an *X–Y* recorder. Alumina was used as the reference. The heating rate employed was 16 °C/min. The enthalpy changes, ΔH, for the different reactions were obtained by measurement of peak areas with respect to a standard transformation. Dehydration of $CuSO_4.5H_2O$ and decomposition of $CaCO_3$ were employed as standards. Uncertainties in the ΔH values were of the order of ±15%.

The infrared spectra of all the acetates and the dicarboxylates were recorded on a Perkin–Elmer model-521 double-grating spectrometer. Samples were prepared as KBr pellets or mulls in Nujol. The vapor phase spectra were taken using 10 cm gas cells (NaCl).

Vapor phase chromatographic (v.p.c.) analysis was done using F and M 700 (thermal conductivity detector) chromatograph fitted with 12 ft. × 1/8 in. stainless steel column packed with fire brick powder. The temperature

---

[1] Forms part of the Ph.D. Thesis of K. C. P.
[2] To whom all correspondence should be addressed.

TABLE I

Infrared frequencies of metal acetates (cm^{-1})*

Acetates	$\nu_{asym}(COO^-)$	$\nu_{sym}(COO^-)$	$\delta_{asym}(CH_3)$	$\delta_{sym}(CH_3)$	$\rho(CH_3)$	ν(C—C)	δ(OCO)	$\pi(COO^-)$ or π(CH)
Na	1575	1422 (153)	1438	1341	1046, 1014	923	650	620
La	1545	1440 (105)	1460	1335	1050, 1030, 1015	965, 952, 940	674, 660, 640	610, 604
Pr	1550	1440 (110)	1455	1345, 1315	1052, 1024	955, 948	675	610
Nd	1569	1439 (130)	1464	1341	1048, 1016	940	675	610
Sm	1550	1420 (130)	1458	1342	1050, 1018, 1008	960, 945	660, 645	608
Gd	1546	1420 (126)	1465	1341	1050, 1017	952, 943	675	608
Dy	1545	1418 (127)	1460	1341	1047, 1017	963, 941	675	606
Lu	1551	1412 (139)	1462	1348	1049, 1022	954	684	606

*Nomenclature of the bands is similar to that of Nakamoto (9). Values in parenthesis in the ν_{sym} column are the $\Delta\nu(\nu_{asym}(COO^-) - \nu_{sym}(COO^-))$ values.

of the column was maintained at 58 or 98 °C. Hydrogen was used as the carrier gas (at 35 cc/min).

Results and Discussion

Infrared Spectra of Rare Earth Acetates

The free acetate ion has 15 infrared active fundamentals of which the asymmetric and symmetric stretching modes of the CO_2^- group have been employed for structural studies. The various characteristic frequencies of the acetate ion in a number of metal acetates have been reported in the literature (6–8). Since the symmetry of the free ion is C_{2v}, no major differences in the spectra are expected for the different coordinated structures of the acetate ion (9). Nakamoto and co-workers (10) have shown that the separation $\Delta\nu$ between the asymmetric and the symmetric frequencies of the CO_2^- group is an indication of the nature of the coordination in a related group of acetates. The major frequencies of rare earth acetates characteristic of the acetate ion are shown in Table I along with the data on sodium acetate. It can be seen that the separation ($\Delta\nu$) in the rare earth acetates varies between 105 and 140 cm^{-1}, the largest separation being in the case of lutetium acetate. These separations are smaller than the $\Delta\nu$ in sodium acetate. Further, ν_{asym} and ν_{sym} are both lower than in sodium acetate, just as in the case of nickel acetate (9). It is possible that the acetate ion in rare earth acetates is present as a unidentate ligand, as in the case of nickel acetate, rather than as the symmetrical bridged structure (11). The bidentate structure proposed by Nakamoto (9) cannot also be ruled out, since all the rare earth acetates were anhydrous. Since $\Delta\nu$ in rare earth acetates does not vary much with the rare earth ion, it appears likely that the metal–oxygen bonds in all these cases are nearly of the same strength. The relatively high $\Delta\nu$ in lutetium acetate could be taken as indicative of the slightly stronger metal–oxygen bonding in the heavier rare earth acetates.

TABLE II

Thermogravimetric analysis data on the thermal decomposition of rare earth acetates, $Ln(CH_3CO_2)_3$

Ln	Oxycarbonate formation temperature $Ln_2O_3.CO_2$ (°C)	Minimum oxide formation temperature Ln_2O_3 (°C)
La	450	910
Pr	450	720 (Pr_6O_{11})
Nd	420	820
Sm	460	750
Gd	450	740
Dy	450	650
Lu	430	600

Thermal Decomposition of Rare Earth Acetates

All the rare earth acetates prepared were hydrates and the number of water molecules varied from 1 to 4. The water molecules were lost on heating the hydrates to 200–220 °C in all cases. For the tetrahydrates of gadolonium, dysprosium, and lutetium acetates, the d.t.a. curves showed that dehydration took place in two stages at ~ 120 °C and ~ 220 °C, indicating two types of water molecules bound differently.

The anhydrous acetates prepared from the decomposition of the hydrated rare earth acetates were stable and decomposed only above 400 °C.

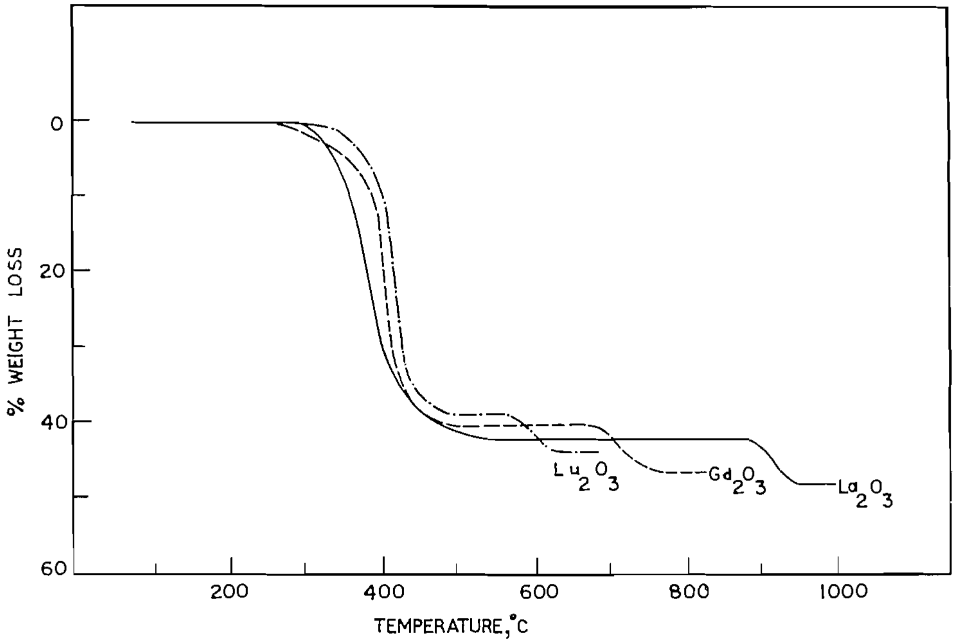


FIG. 1. The t.g.a. curves of anhydrous rare earth acetates (heating rate 10 °C/min).

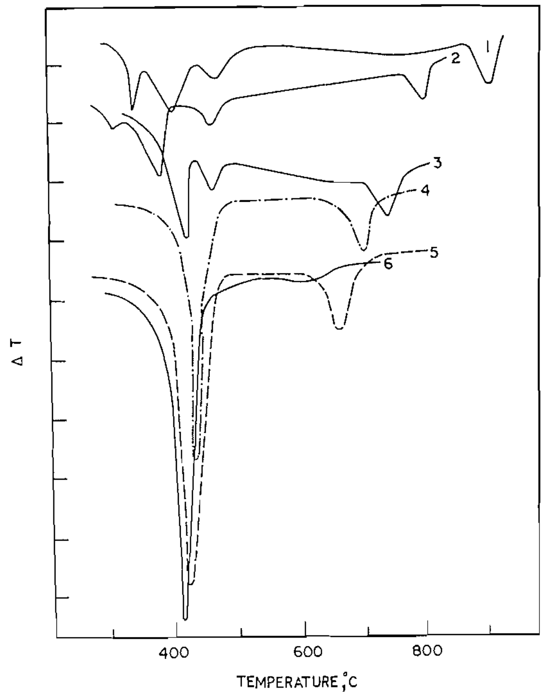


FIG. 2. The d.t.a. curves (in air) of anhydrous rare earth acetates $Ln(CH_3CO_2)_3$. Curve 1, La; 2, Nd; 3, Sm; 4, Gd; 5, Dy; and 6, Lu.

The results from the t.g.a. and d.t.a. of the anhydrous rare earth acetates are shown in Tables II and III. Typical t.g.a. and d.t.a. curves are shown in Figs. 1 and 2 respectively. The t.g.a. curves of all the rare earth acetates showed evidence for only two stages of decomposition: the first stage between 420–460 °C corresponding to the decomposition of the anhydrous acetate, $Ln(CH_3CO_2)_3$, to the oxycarbonate, $Ln_2O_3.CO_2$ and the second stage corresponding to the formation of the sesquioxide, Ln_2O_3 (with the exception of praseodymium acetate where the end product is the nonstoichiometric Pr_6O_{11})[3].

[1] $2Ln(CH_3CO_2)_3 \rightarrow Ln_2O_3.CO_2 + 2CO_2 + 3CH_3COCH_3$

[2] $Ln_2O_3.CO_2 \rightarrow Ln_2O_3 + CO_2$

There is no evidence for the formation of the normal carbonate, $Ln_2(CO_3)_3$, in the t.g.a. curves. The formation of the oxycarbonate, $Ln_2O_3.CO_2$, has been found to be the first stage

---

[3] Pr_6O_{11} is found to be the final product of decomposition of praseodymium salts. Oxidation of Pr^{3+} accompanies the last stage of decomposition.

TABLE III

Differential thermal analysis data on the thermal decompositions of rare earth acetates, $Ln(CH_3CO_2)_3$

Ln	Anhyd. acetate to carbonate T (°C)	ΔH (kcal mole^{-1})	Carbonate to oxycarbonate T (°C)	ΔH (kcal mole^{-1})	Oxycarbonate to oxide T (°C)	ΔH (kcal mole^{-1})
La	335, 405	70	465	40	900	77
Nd	300, 370	17	450	12	790	12
Sm	435	16	475	8	750	25
			Anhyd. acetate to oxycarbonate T (°C)	ΔH (kcal mole^{-1})	Oxycarbonate to oxide T (°C)	ΔH (kcal mole^{-1})
Gd			435	38	700	20
Dy			425	54	660	15
Lu			420	80	590	11

in the decomposition of normal rare earth carbonates (12, 13). The decomposition temperatures of rare earth carbonates are summarized in Table IV for purposes of comparison.

TABLE IV

Decomposition temperatures of rare earth carbonates from d.t.a. data

Ln	Decomposition of $Ln_2(CO_3)_3$ to $Ln_2O_3.CO_2$ (peak temperature (°C))	Decomposition of $Ln_2O_3.CO_2$ to Ln_2O_3 (peak temperature (°C))
La	530	900
Pr	485	615 (Pr_6O_{11})
Nd	510	730
Sm	450	700
Gd	420	600

The d.t.a. curves of lanthanum, neodymium, and samarium acetates showed evidence for the initial formation of the normal carbonate, $Ln_2(CO_3)_3$, prior to its decomposition to $Ln_2O_3.CO_2$.

$$[3] \quad 2Ln(CH_3CO_2)_3 \rightarrow Ln_2(CO_3)_3 + 3CH_3COCH_3,$$

where Ln = La, Nd, or Sm. Further, formation of the normal carbonate in the case of lanthanum and neodymium was found to take place in two stages, as can be seen from the d.t.a. curves (Fig. 2). The first of these two stages is unlikely to arise from the formation of oxyacetates, since oxyacetates cannot yield normal carbonates as the decomposition products. It should be noted that the decomposition temperatures of lanthanum, neodymium, and samarium carbonates are appreciably higher than the temperatures for these two stages (Table IV). The reactions for the two stages[4] of formation of the normal carbonates may be written as

$$[4] \quad Ln(CH_3CO_2)_3 \rightarrow LnCO_3(CH_3CO_2) + CH_3COCH_3$$

$$[5] \quad LnCO_3(CH_3CO_2) \rightarrow \tfrac{1}{2}Ln_2(CO_3)_3 + \tfrac{1}{2}CH_3COCH_3,$$

where Ln = La, Nd, or Sm. The lanthanum, neodymium, and samarium carbonates then decompose to the $Ln_2O_3.CO_2$, finally yielding Ln_2O_3 (Tables III and IV).

The d.t.a. curves of all the other rare earth acetates showed only two peaks corresponding to the decomposition of the acetate directly to the oxycarbonate and the subsequent decomposition of the basic salt to the oxide.[5] The decomposition temperatures of the carbonates agree well with those reported in the literature (12, 13). The formation of the oxycarbonate was also confirmed by infrared spectroscopy (Table V). The infrared data show that the carbonate ion is strongly coordinated to the metal ion, possibly as a unidentate ligand (9). The temperature of formation of the basic carbonate does not vary much with the rare earth ion. Apparently, the coordination between with acetate and the metal ion does not vary appreciably in the rare earth series (as already inferred from infrared spectra). The minimum oxide formation temperature (from the basic carbonate), however,

---

[4] These stages could not be seen in the t.g.a. curves. The differences in the t.g.a. and the d.t.a. results are not due to the different rates of heating employed.

[5] These results are in conformity with the known data on the stabilities of rare earth carbonates (12). The normal carbonates are found to be stable only in the case of the more basic (lighter) rare earths, while the heavier rare earths generally form the oxycarbonates.

TABLE V

Infrared frequencies of oxycarbonates (cm^{-1}), $Ln_2O_3.CO_2$

Ln	ν_{CO}			*	δ_{CO_3}	
La	1506	1442	1355	1048	870	845
Pr	1526	1462	1355	1050	870	841
Nd	1534	1460	1352	1053	873	840
Sm	1524	1459	1370	1055	873	844
Dy	1512	1449	1394	1055	870	844
Gd	1504	1440	1389, 1333	1053	860	844

*Assignment not clear.

decreases markedly as one goes down the rare earth series, possibly indicating that the coordination of carbonate ion to the metal ion becomes stronger as one goes to heavier rare earths. The variation in the enthalpies of the various reactions (Table III) are, however, difficult to interpret.

Thermal Decomposition of Lead and Copper Acetates

The t.g.a. curve of lead tetraacetate (Fig. 3) shows three distinct stages corresponding to the formation of the diacetate, carbonate, and oxide (PbO), the last two stages being confirmed by an independent t.g.a. curve of lead diacetate. The formation of lead diacetate from the tetraacetate will involve reactions of the acetoxy radical. The d.t.a. curve (Fig. 3) shows two exothermic peaks[6] at ~ 150 °C and 190 °C, probably corresponding to the formation of diacetate as well as the products from the acetoxy radical. However, the d.t.a. results are difficult to understand. The products from the acetoxy radical were found to be mainly CO_2 and methyl acetate by vapor phase infrared spectroscopy. Ethane, if formed, must be present in small proportions. Thus, the different reactions in the decomposition of $Pb(CH_3CO_2)_4$ are:

[6] $Pb(CH_3CO_2)_4 \rightarrow Pb(CH_3CO_2)_2 + 2CH_3CO_2\cdot$

[7] $2CH_3CO_2\cdot \rightarrow CH_3CO_2CH_3 + CO_2$

[8] $Pb(CH_3CO_2)_2 \rightarrow PbCO_3 + CH_3COCH_3$

[9] $PbCO_3 \rightarrow PbO + CO_2$.

The t.g.a. curve of copper acetate, $Cu_2(CH_3CO_2)_4.2H_2O$, showed the first stage due to the dehydration at ~ 180 °C. After the dehydration, there was only one rapid stage of decomposition. The decomposition was complete by ~ 310 °C, but the t.g.a. curve showed a slight mass increase up to 550 °C. The mass increase indicated that some oxidation of Cu or Cu_2O formed in the decomposition may be taking place above ~ 350 °C. The composition of the final product at 550 °C is CuO. The t.g.a. results from the present study agree with the d.t.a. studies of Hill and co-workers (14), who have also reported the product analysis by mass

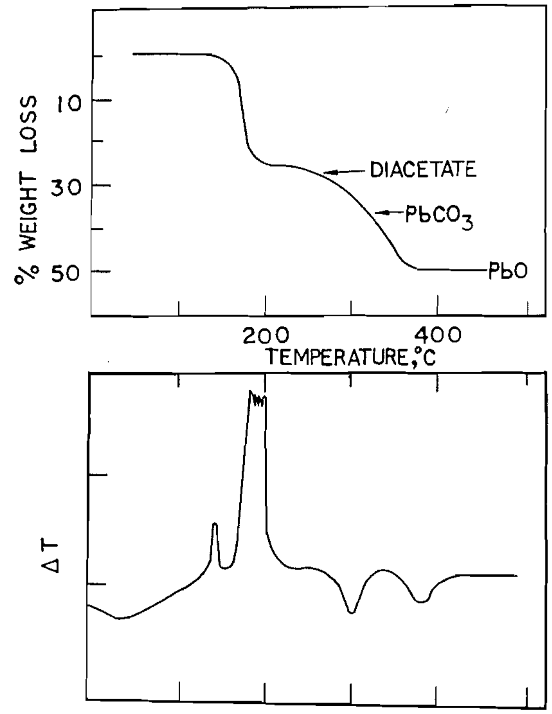


FIG. 3. The t.g.a. (3 × 10^{-2} mm Hg) and d.t.a. (in air) curves of lead tetraacetate. The heating rate was 10 °C/min in the t.g.a. and 16 °C/min in the d.t.a.

---

[6] The t.g.a. and d.t.a. curves may not be exactly comparable, particularly with respect to the reaction temperatures, since the heating rates are not identical. Further, the t.g.a. was in vacuum (3 × 10^{-2} mm Hg) while d.t.a. was in air.

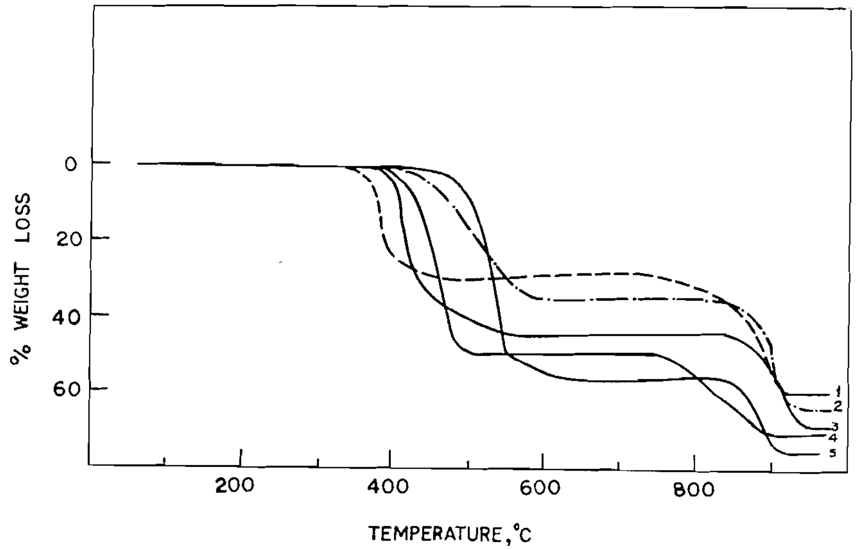


FIG. 4. The t.g.a. curves of anhydrous calcium dicarboxylates: (1) malonate, (2) succinate, (3) adipate, (4) pimelate, and (5) sebacate (heating rate 10 °C/min).

spectrometry. Considering water, acetone, and CO_2 to be the main products, the following reactions can be written for the decomposition of $Cu_2(CH_3CO_2)_4.2H_2O$.

[10] $Cu_2(CH_3CO_2)_4.2H_2O \rightarrow Cu_2(CH_3CO_2)_4 + 2H_2O$

[11] $Cu_2(CH_3CO_2)_4 \rightarrow 2CuO + 2CH_3COCH_3 + 2CO_2$

Methane and acetic acid, which have been found as (minor) products (14), are possibly formed from ketene (produced by the pyrolysis of acetone).

Infrared Spectra of Dicarboxylates

Infrared spectra of calcium dicarboxylates were studied with a view to examining the metal-carboxylate bonding. It has been shown that the magnitude of covalency of the metal–oxygen bonding in metal dicarboxylates can be inferred from the separation between the symmetric and asymmetric stretching frequencies of carboxylate ion (9). The separation between the symmetric and asymmetric stretching frequencies of the carboxylate ion in the various calcium dicarboxylates (malonate to sebacate) was nearly the same ($\sim$ 140 cm^{-1}), indicating that the metal–oxygen bonding is about the same in all these calcium salts.

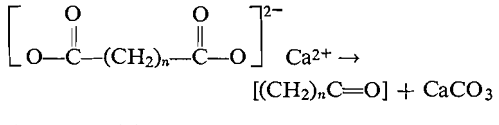
Results from T.G.A. and D.T.A. of Dicarboxylates

The t.g.a. data of a number of calcium dicarboxylates are summarized in Table VI and typical t.g.a. curves are shown in Fig. 4. It can be seen that all the dicarboxylates (from malonate to sebacate) give $CaCO_3$ as the residue[7] by losing elements of the ketone in one step.

TABLE VI

Thermogravimetric analysis data on the thermal decomposition of calcium salts of dicarboxylic acids

	Formation of anhyd. salt (°C)	Formation of $CaCO_3$ (°C)	Formation of CaO (°C)
Oxalate.H_2O	250	530	910
Malonate.$2H_2O$	250	400	910
Succinate.$2H_2O$	200	580	920
Glutarate.$4H_2O$	290	550	940
Adipate.H_2O	200	550	950
Pimelate.H_2O	220	490	870
Sebacate.$3H_2O$	200	550	900

[12] 

$$\left[O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_n-\overset{\overset{\displaystyle O}{\|}}{C}-O \right]^{2-} Ca^{2+} \rightarrow [(CH_2)_nC{=}O] + CaCO_3$$

The decomposition temperatures of the various calcium dicarboxylates do not seem to vary widely, confirming that the metal–oxygen bonding in these carboxylates does not vary with the

---

[7] The $CaCO_3$ formed decomposes to CaO at $\sim$ 900 °C (see Table VI and Fig. 4).

anion. Further, the formation of $CaCO_3$ as the solid residue precludes the formation of anhydrides as the initial products of decomposition.[8]

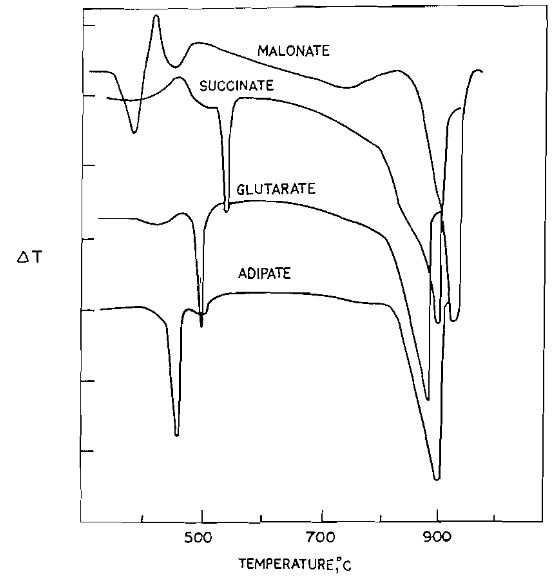


FIG. 5. The d.t.a. curves in air of anhydrous calcium dicarboxylates (heating rate 10 °C/min).

TABLE VII

Differential thermal analysis data on the thermal decomposition of calcium dicarboxylates (peak temperatures in °C)

	Dehydration	Decomposition to $CaCO_3$*	Decomposition to CaO
Malonate.$2H_2O$	190, 240	385	930
Succinate.$2H_2O$	185	540	910
Glutarate.$4H_2O$	190, 300	500	880
Adipate.H_2O	190	460	900
Pimelate.H_2O	100, 160, 320	410	840
Sebacate.$3H_2O$	190	340	840

*Better agreement with t.g.a. data is found if the temperatures (at the base line) after the peaks are considered.

The d.t.a. curves (Fig. 5) of calcium dicarboxylates showed several endothermic peaks (below 320 °C) due to dehydration. After the dehydration, the major peak in the curves corresponds to the endothermic decomposition of the dicarboxylate to $CaCO_3$ and there is fair agreement between the results from d.t.a. (Table VII) and t.g.a. (Table VI). In the case of calcium malonate, there seems to be some evidence for an exothermic reaction after the decomposition. All the d.t.a. curves show the decomposition of $CaCO_3$ to CaO in the 840–910 °C range, again showing that $CaCO_3$ is the only residue left after the decomposition of calcium dicarboxylates. The decomposition temperature of $CaCO_3$ varies slightly from one carboxylate to another.

The t.g.a. curve of dysprosium sebacate showed that the decomposition proceeded through the formation of the oxycarbonate. There was, however, clear evidence for the loss of the elements of nonanone in the first stage of decomposition.

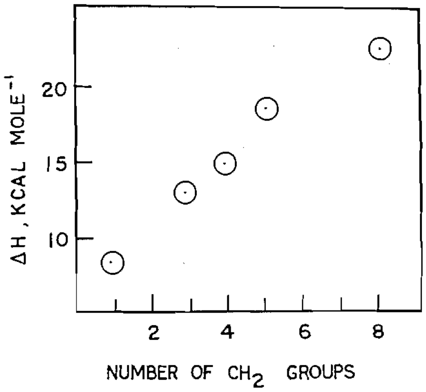


FIG. 6. Variation of ΔH of the decomposition of dicarboxylates with the number of CH_2 groups in the dicarboxylate.

By employing the endothermic decomposition peak of $CaCO_3$ as the internal standard ($\Delta H \sim 40$ kcal $mole^{-1}$), the enthalpies for the decomposition of calcium dicarboxylates to $CaCO_3$ were estimated by measuring the areas of the endothermic peaks. The ΔH values thus obtained show an interesting trend in the series of metal dicarboxylates (Fig. 6). The ΔH for the decomposition of dicarboxylates varies linearly with the number of methylene groups, showing an increment of $\sim$ 2 kcal per methylene group. Apparently, the enthalpy of decomposition of dicarboxylates is a thermomolecular property. This finding indicates that the organic products obtained in the decompositions of dicarboxylates are produced by the vapor phase decompositions of the elements of the ketones.

---

[8] Anhydrides have been found to be initially formed in the thermal decompositions of dicarboxylic acids (15).

TABLE VIII

Characterization of the products obtained by the thermal decomposition of calcium dicarboxylates

		Positions of important infrared bands, particularly in the $\nu_{C=O}$ region* (cm^{-1})			No. of peaks in v.p.c.	Some of the likely products	References†
Malonate[a]	(V)	2310 (w) 2115 (w)	1720 (m)	1640 (s)	—	Ketene[b]	
	(L)	2105 (w)	1695 (s)	1640 (s)	—	Acetic acid[b]	
Succinate[a,c]	(M)	3270 (m)	1700 (s)	1600 (s)	2[d]	1,4-Cyclohexane dione[b]	(21)
Glutarate[a]	(L)		1780 (m)	1720 (m) 1709 (s)	6–7[c]	Cyclohexanone cyclobutanone[b] acetone	(19)
Adipate	(L)		1750 (m)	1710 (s) 1646 (m)	6[f]	Cyclopentanone	(16, 20)
Pimelate[a]	(L)		1709 (s)		7[g]	Cyclohexanone	(16)
Sebacate[a]	(L)		1702 (s)		3[e,h]	[i]	

*V = vapor; L = pure liquid; M = mull in Nujol.

†Reference to the earlier literature on the thermal decomposition of calcium dicarboxylates.

[a] Also broad absorption in the OH region (~ 3200–3400 cm^{-1}). [b] Likely to be one of the products, but not very certain. [c] Semi-solid. [d] V.p.c. in diethyl ether solution. [e] V.p.c. in diethyl ether solution, some high boiling liquid insoluble in ether was left over. [f] Major fraction was cyclopentanone. [g] Major fraction was cyclohexanone. [h] More components likely to be present in the high boiling fraction. [i] Present studies cannot establish the identity of any of the compounds.

Preliminary Studies on the Characterization of the Decomposition Products

Results of a preliminary examination of the decomposition products of a few metal dicarboxylates by employing infrared spectroscopy and vapor phase chromatography are presented below.

Sufficient quantities of the products obtained by the distillation of the calcium dicarboxylates were collected and their infrared spectra were recorded; in the case of calcium malonate the spectrum of the vapors was recorded. The products were also passed through a firebrick column in a gas chromatograph. The findings from the infrared and vapor phase chromatographic experiments are summarized in Table VIII.

From the data in Table VIII it can be seen that thermal decompositions of calcium dicarboxylates give a number of products. The major components have been identified in the decomposition of some of the dicarboxylates: acetic acid from malonate, cyclopentanone from adipate, and cyclohexanone from pimelate.The formation of these products is in conformity with the early literature (16–21) on the subject and lends support to the observation that the elements of ketones are removed in the decarboxylation reaction. The variety of products formed in the decomposition, however, results from the fragmentation and subsequent reactions of the elements of ketone, many of which are likely to involve free radical mechanisms. It appears that a thorough study of the decomposition products will yield interesting results.

1. C. Duval. Inorganic thermogravimetric analysis. 2nd ed. Elsevier, Amsterdam. 1963.
2. A. Glasner and M. Steinberg. J. Inorg. Nucl. Chem. **22**, 39 (1961).
3. A. Glasner, E. Levy, and M. Steinberg. J. Inorg. Nucl. Chem. **25**, 1415 (1963).
4. W. W. Wendlandt. Thermal methods of analysis. Interscience Publishers, John Wiley and Sons, New York. 1964.
5. J. R. Witt and E. I. Onstott. J. Inorg. Nucl. Chem. **24**, 637 (1962).
6. (*a*) K. Ito and H. J. Bernstein. Can. J. Chem. **34**, 170 (1956). (*b*) F. Vratny, C. N. R. Rao, and M. Dilling. Anal. Chem. **33**, 1455 (1961).
7. C. N. R. Rao. Chemical applications of infrared spectroscopy. Academic Press, New York. 1963.
8. K. Nakamura. J. Chem. Soc. Japan, **79**, 1411, 1420 (1958).
9. K. Nakamoto. Infrared spectra of inorganic and coordination compounds. John Wiley and Sons, New York. 1963.
10. K. Nakamoto, F. Fujita, S. Tanaka, and M. Kobayashi. J. Am. Chem. Soc. **79**, 4904 (1957).
11. K. Nakamoto, Y. Morimoto, and A. E. Martell. J. Am. Chem. Soc. **83**, 4528 (1961).
12. (*a*) R. L. N. Sastry, S. R. Yoganarasimhan, P. N. Mehrotra, and C. N. R. Rao. J. Inorg. Nucl. Chem. **28**, 1165 (1966). (*b*) P. N. Mehrotra. Ph.D. Thesis, Indian Institute of Technology, Kanpur, India. 1967.
13. W. W. Wendlandt and T. D. George. Texas J. Sci. **13**, 316 (1961).
14. J. A. Hill, C. B. Murphy, and G. P. Schacher. Anal. Chim. Acta, **24**, 496 (1961).

15. W. W. WENDLANDT and J. A. HOIBERG. Anal. Chim. Acta, **28**, 506 (1963); **29**, 539 (1963).
16. L. RUZICKA, W. BRUGGER, M. PFEIFFER, H. SCHINZ, and M. STOLL. Helv. Chim. Acta, **9**, 499 (1926).
17. L. RUZICKA, W. BRUGGER, C. F. SLIDEL, and H. SCHINZ. Helv. Chim. Acta, **11**, 496 (1928).
18. L. RUZICKA, M. STOLL, and H. SCHINZ. Helv. Chim. Acta, **11**, 670 (1928).
19. G. A. ROBERTSON. J. Chem. Soc. **119**, 810 (1921).
20. J. F. THORPE and G. A. R. KON. Organic synthesis. Coll. Vol. I. 2nd ed. 1941. p. 192.
21. F. FEIST. Ber. **28**, 739 (1898).