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# THERMAL INVESTIGATIONS OF THE CALCIUM SALTS OF MONOCARBOXYLIC ALIPHATIC FATTY ACIDS

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Calcium salts of acetic and mono, di and trichloroacetic acids were investigated with respect to their dehydration and decarboxylation, using a derivatograph. A phase transition was noticed only in the case of calcium acetate. Effects of crucible and diluent on the thermal behaviour of the above salts were also studied. The decomposition products were investigated qualitatively, and from these gaseous products and also from the residue after pyrolysis the probable mechanisms of decompositions have been suggested. Activation energies for the decarboxylation processes were evaluated from the TG curves.

Thermal decompositions of the metal salts of monocarboxylic acids have been carried out by several workers [1–11]. Most of the studies were confined to the pyrolysis of the salts. Synthesis of symmetrical aliphatic ketones from the pyrolysis of metal salts of simple aliphatic acids is well known. However, it appears from the pyrolysis that various compounds, simple or complex, are generated along with the ketones. In our earlier work [12] on the decomposition of calcium propionate monohydrate we observed decarboxylation to take place in multiple steps when a ceramic crucible was used. In view of the possibility of synthesizing simple ketones, the present paper reports the pyrolysis of calcium acetate by derivatograph with variation of the crucible and with or without diluent. Attempts have also been made with calcium propionate to see whether this pyrolysis is dependent on the nature of the crucible used with or without diluent. This paper also reports whether the decarboxylation phenomena of the calcium salts of mono, di and trichloroacetic acids take place like those of simple acid salts *via* the formation of metal carbonate and ketone besides other possible products. Thermal stabilities, temperature ranges of decomposition and activation energies are also reported. The probable mechanisms of decarboxylation have been derived from chemical analysis of the gaseous products and the residue after pyrolysis in the cases of the chloroacetates.

## Experimental

Salts were prepared adopting standard procedures. Purities of the samples were confirmed by elemental analysis. A Paulik - Paulik - Erdey type MOM derivatograph was used for simultaneous thermogravimetry, derivative thermogravimetry and differential thermal analysis in dynamic air. The particle size of the sample and alumina preheated to 1400° used as diluent was within 150 - 200 mesh. Ceramic and platinum crucibles were used, and the heating rate was maintained at 2.5° $\text{min}^{-1}$. The diluent used was four times the weight of the sample.

The derivatograph we employed has no device for gas detection. As a result we pyrolyzed the salts separately in a quartz boat in dynamic air and detected the gaseous products by chemical tests [13].

## Results

Thermal curves of calcium acetate monohydrate in a ceramic crucible with and without diluent are shown in Fig. 1, and those in a platinum crucible in Fig. 2.

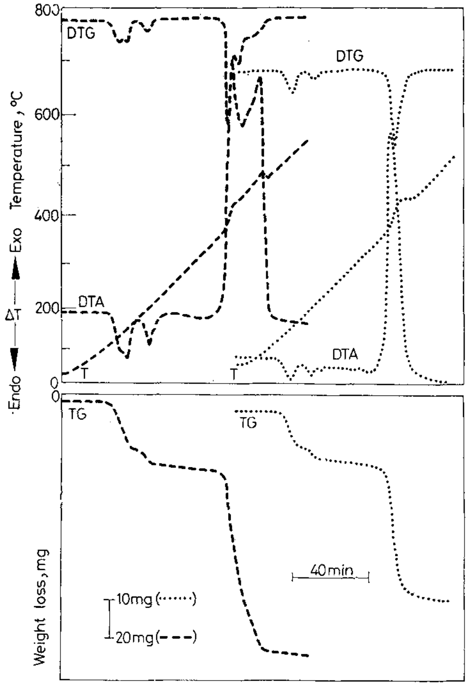

Fig. 1. Thermal curves for $Ca(CH_3COO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 300 | Ceramic | Nil |
| . . . . | 115 | Ceramic | Alumina |

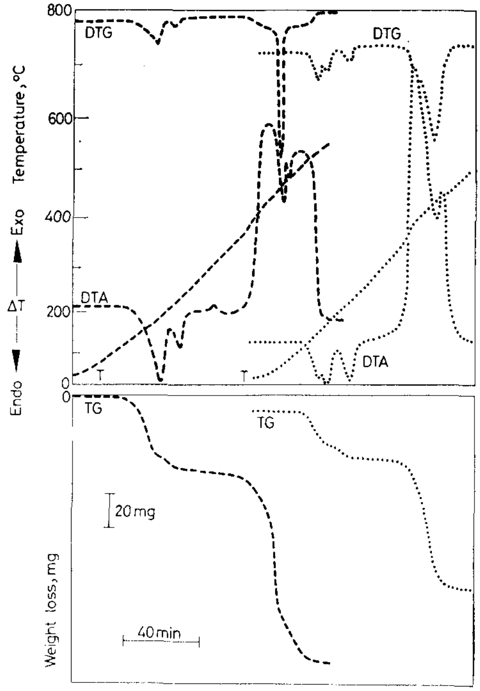

Fig. 2. Thermal curves for $Ca(CH_3COO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 324 | Platinum | Nil |
|  | 220 | Platinum | Alumina |

Calcium acetate monohydrate becomes anhydrous upon heating in a ceramic crucible, first passing through an unstable hemihydrate and then a stable $(CH_3COO)_2Ca.O.25\ H_2O$, as observed from its TG curve. The DTG curve shows two overlapping peaks for the formation of the two intermediate hydrates, and a peak for the dehydration of $(CH_3COO)_2Ca.O.25\ H_2O$ to anhydrous salt, but the corresponding DTA curve shows a shoulder followed by a peak for the above two intermediate hydrates, and a peak followed by a shoulder for the dehydration of $(CH_3COO)_2Ca.O.25\ H_2O$. If diluent is used in a ceramic crucible, the existence of the hemihydrate is not observed in the thermal curves, and the dehydration $(CH_3COO)_2Ca.O.25\ H_2O$ takes place in a single step as observed from the TG and DTG curves, but its DTA curve shows two overlapping peaks. On the other hand, upon heating in a platinum crucible, the monohydrate becomes anhydrous *via* unstable $(CH_3COO)_2Ca.O.25\ H_2O$. The corresponding DTA and DTG curves show two overlapping peaks, whereas on heating in a platinum crucible with alumina, the monohydrate becomes anhydrous by first passing through an unstable hemihydrate and then $Ca(CH_3COO)_2.O.25\ H_2O$. The anhydrous salt undergoes a phase transition. It appears from the DTA curve that the phase transition is prominent in a platinum crucible without diluent. The decomposition of the anhydrous salt takes place in a single step when the pyrolysis is carried out in a ceramic crucible with diluent. Upon heating of the salt in a platinum crucible with alumina, the TG curve shows single-step decarboxylation, but its DTA and DTG curves show the decarboxylation to take place in more than one step. In contrast, in a platinum or ceramic crucible without diluent, the TG curve of the salt shows decarboxylation to take place in more than one step.

Thermal curves of calcium propionate monohydrate in a ceramic crucible with alumina and in a platinum crucible without alumina are shown in Fig. 3. Single-step dehydration and phase transition before decarboxylation are observed in both cases. As observed from the TG curve the process of decarboxylation occurs in a single step, but in a ceramic crucible with alumina the DTA curve shows two peaks, whereas in a platinum crucible without alumina the DTA curve shows a number of peaks. In the case of a ceramic crucible with alumina, the DTG curve shows a peak followed by a hump, whereas in a platinum crucible first a hump is observed, followed by a peak. Thermal curves of calcium propionate monohydrate in a platinum crucible with or without alumina are similar.

Thermal curves of calcium monochloroacetate monohydrate in a platinum crucible with diluent are shown in Fig. 3. Dehydration occurs in a single step. After dehydration, the rate of weight loss is very small up to 225° and then increases rapidly. The decomposition takes place in multiple overlapping steps. The corresponding DTA curve shows two endothermic peaks for the decomposition process where the rate of weight loss is very small, and an endotherm followed by two exotherms for the latter part of the decomposition. The residue after pyrolysis contains calcium oxide, calcium chloride and traces of carbon, while the gaseous products are CO, $COCl_2$, $ClCH_2COOH$ and $CH_3COOH$. The pattern of dehydration and decarboxylation of the salt and the products after pyrolysis remain the same even if a ceramic crucible is used with diluent. Attempts to carry out the pyrolysis in crucibles without diluent failed due to the tendency of the salt to undergo overswelling.

Thermal curves of calcium dichloroacetate monohydrate in a ceramic crucible with or without diluent are shown in Fig. 4, and those in a platinum crucible in Fig. 5. Thermal curves for calcium dichloroacetate monohydrate using a ceramic crucible with or without diluent show the dehydration to take place in a single step. If the dehydration is performed in a platinum crucible with diluent, a single step is observed in the TG curve, whereas its DTA and DTG curves show two overlapping peaks. On the other hand, on pyrolysis in a platinum crucible without diluent, the TG curve shows single-step dehydration. However, its DTA curve shows three overlapping peaks, while the DTG curve is broad. The anhydrous salt undergoes decomposition first to calcium chloride, calcium oxide and traces of carbon, and then to calcium chloride and calcium oxide on further heating. When a ceramic crucible is used without alumina, the TG and DTG curves show the decomposition to take place in a single step, but its DTA curve shows an endotherm followed by an exotherm. If diluent is used the patterns of the TG

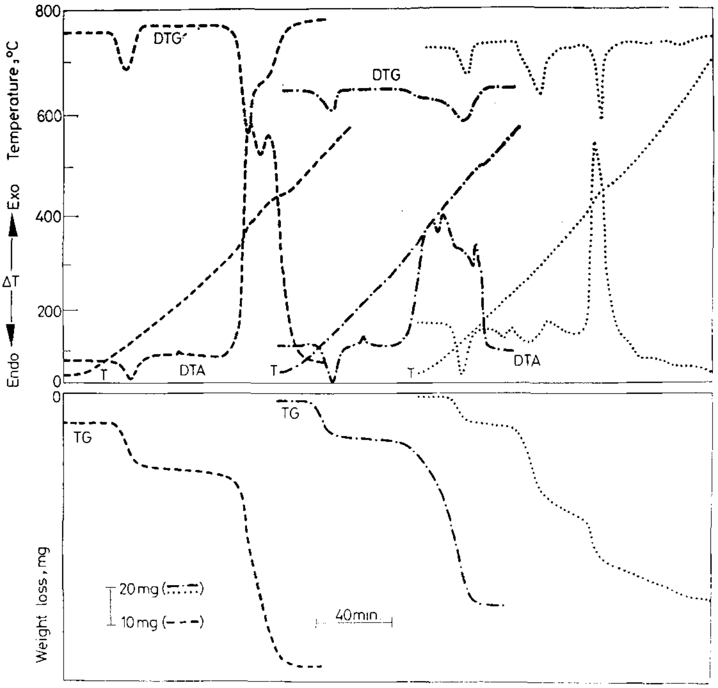

Fig. 3. Thermal curves for $Ca(C_2H_5COO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 125 | Ceramic | Alumina |
| — · — | 200 | Platinum | Nil |

Thermal curves for $Ca(CH_2ClCOO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| . . . . | 150 | Platinum | Alumina |

and DTG curves remain unaltered, whereas its DTA shows an exotherm just after dehydration and an endotherm for decomposition. With a platinum crucible and diluent, the decomposition takes place in a single step as observed from its TG and DTG curves, but its DTA curve shows an exotherm followed by an endotherm for the decomposition. With a platinum crucible without diluent, single-step decomposition is observed from its TG and DTG curves, but its DTA curve shows two endothermic peaks followed by several exothermic peaks. The product after decarboxylation on further heating does not contain any carbon particles. For this process of carbon elimination one sharp exotherm is noticed in the DTA curve. The gaseous products CO, $COCl_2$ and $Cl_2CHCOOH$ are detected during pyrolysis.

Thermal curves of calcium trichloroacetate trihydrate in a ceramic crucible with or without diluent are shown in Fig. 6 and those in a platinum crucible in Fig. 7.

Upon heating in a ceramic crucible, calcium trichloroacetate trihydrate becomes anhydrous in a single step. The dehydration pattern appears to be the same when alumina is used in a ceramic crucible, whereas dehydration in a platinum crucible with alumina takes place in two steps, passing through the monohydrate. On the other hand, the existence of an intermediate hydrate is indicated from the DTA and DTG curves when dehydration is carried out in a platinum crucible without alumina, though its TG curve shows single-step dehydration. The anhydrous salt decomposes to calcium chloride. The TG and DTG curves show decomposition to take place in more than one overlapping step when a ceramic crucible is used. The corresponding DTA curve shows an endotherm followed by two exothermic peaks. In a ceramic crucible with diluent, the decomposition is also found to take place in overlapping multiple steps as observed from its TG and DTG curves and also from two endothermic peaks followed by an exothermic peak in the DTA curve. On the other hand, when the decarboxylation is carried out in a platinum crucible with alumina, one endothermic peak followed by an exothermic peak is

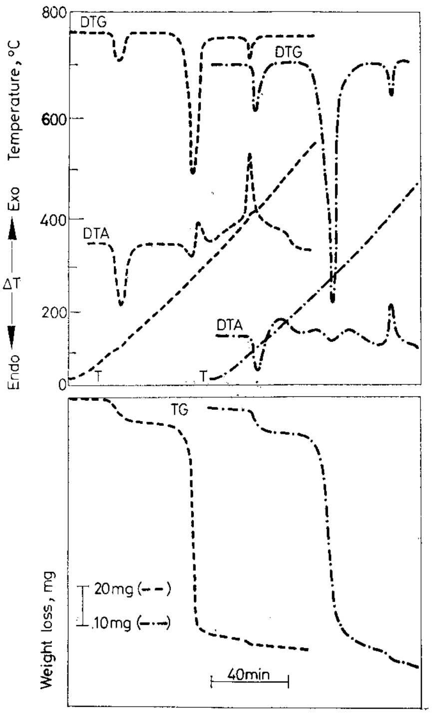

Fig. 4. Thermal curves for $Ca(CHCl_2COO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 200 | Ceramic | Nil |
| — · — | 100 | Ceramic | Alumina |

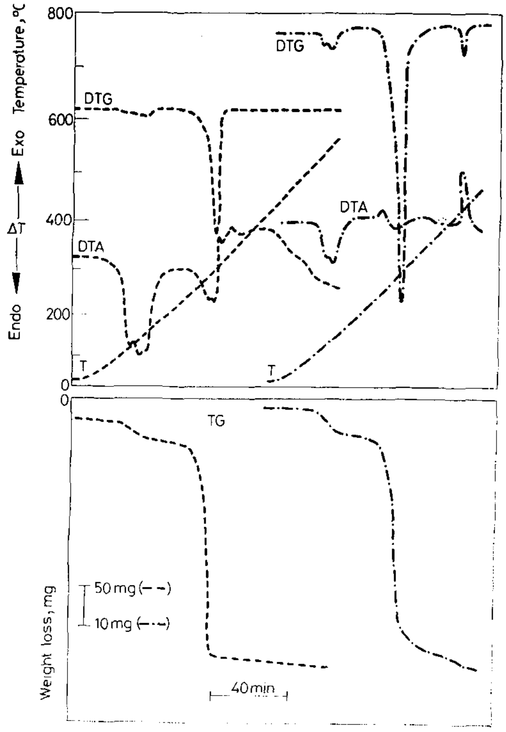

Fig. 5. Thermal curves for $Ca(CHCl_2COO)_2.H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 500 | Platinum | Nil |
| — · — | 200 | Platinum | Alumina |

observed as soon as the dehydration ceases. Decomposition in a platinum crucible without alumina is found to take place in multiple overlapping steps. The gaseous products HCl, CO, $COCl_2$, $CCl_3COCl$ and $Cl_3CCOOH$ are detected during pyrolysis.

Temperature ranges and DTG peak temperatures for the dehydration and decarboxylation processes are given in Table 1. Activation energies for the decomposition processes are evaluated from analysis of the TG curves using Freeman and Carroll's equation [14] and the values are tabulated in Table 1.

## Discussion

We find a difference in the pattern of dehydration of calcium acetate monohydrate from that we reported for calcium propionate monohydrate, where the dehydration takes place in a single step when a ceramic crucible is used. The pattern

Table 1

Thermal parameters of decomposition of calcium salts of monocarboxylic aliphatic fatty acids

| | Decomposition reactions | Crucible | Diluent | Temp. ranges, °C | DTG peak temperature, °C | Activation energy for decarboxylation, kcal mol$^{-1}$ TG |
|---|---|---|---|---|---|---|
| I | a) $Ca(CH_3COO)_2.H_2O \rightarrow Ca(CH_3COO)_2.0.5H_2O$ | Ceramic | Nil | 105–140 | 138 | |
| | b) $Ca(CH_3COO)_2.0.5H_2O \rightarrow Ca(CH_3COO)_2.0.25H_2O$ | | | 140–160 | 150 | |
| | c) $Ca(CH_3COO)_2.0.25H_2O \rightarrow Ca(CH_3COO)_2$ | | | 180–210 | 200 | |
| | d) $Ca(CH_3COO)_2 \rightarrow CaCO_3$ | | | 359–480 | 400, 435 | * |
| II | a) $Ca(CH_3COO)_2.H_2O \rightarrow Ca(CH_3COO)_2.0.25H_2O$ | Ceramic | Alumina | 134–190 | 160 | |
| | b) $Ca(CH_3COO)_2.0.25H_2O \rightarrow Ca(CH_3COO)_2$ | | | 190–220 | 210 | |
| | c) $Ca(CH_3COO)_2 \rightarrow CaCO_3$ | | | 360–448 | 420 | 52.5 |
| III | a) $Ca(CH_3COO)_2.H_2O \rightarrow Ca(CH_3COO)_2.0.25H_2O$ | Platinum | Nil | 118–172 | 160 | |
| | b) $Ca(CH_3COO)_2.0.25H_2O \rightarrow Ca(CH_3COO)_2$ | | | 172–210 | 210 | |
| | c) $Ca(CH_3COO)_2 \rightarrow CaCO_3$ | | | 320–518 | 445 | * |
| IV | a) $Ca(CH_3COO)_2.H_2O \rightarrow Ca(CH_3COO)_2.0.5H_2O$ | Platinum | Alumina | 120–148 | 142 | |
| | b) $Ca(CH_3COO)_2.0.5H_2O \rightarrow Ca(CH_3COO)_2.0.25H_2O$ | | | 148–167 | 165 | |
| | c) $Ca(CH_3COO)_2.0.25H_2O \rightarrow Ca(CH_3COO)_2$ | | | 167–217 | 213 | |
| | d) $Ca(CH_3COO)_2 \rightarrow CaCO_3$ | | | 325–500 | 420 | 33.9 |
| V | a) $Ca(C_2H_5COO)_2.H_2O \rightarrow Ca(C_2H_5COO)_2$ | Ceramic | Alumina | 88–158 | 110 | |
| | b) $Ca(C_2H_5COO)_2 \rightarrow CaCO_3$ | | | 282–490 | 375 | 28.4 |
| VI | a) $Ca(C_2H_5COO)_2.H_2O \rightarrow Ca(C_2H_5COO)_2$ | Platinum | Nil | 100–144 | 130 | |
| | b) $Ca(C_2H_5COO)_2 \rightarrow CaCO_3$ | | | 270–502 | 462 | 23.0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| VII | a) $Ca(ClCH_2COO)_2.H_2O \rightarrow Ca(ClCH_2COO)_2$<br>b) $Ca(ClCH_2COO)_2 \rightarrow CaCl_2 + CaO + C$ | Platinum | Alumina | 98–135<br>170–670 | 120<br>282, 431 | * |
| VIII | a) $Ca(Cl_2CHCOO)_2.H_2O \rightarrow Ca(Cl_2CHCOO)_2$<br>b) $Ca(Cl_2CHCOO)_2 \rightarrow CaCl_2 + CaO + C$ | Ceramic | Nil | 100–130<br>213–512 | 112<br>400 | 42.5 |
| IX | a) $Ca(Cl_2CHCOO)_2.H_2O \rightarrow Ca(Cl_2CHCOO)_2$<br>b) $Ca(Cl_2CHCOO)_2 \rightarrow CaCl_2 + CaO + C$ | Ceramic | Alumina | 100–150<br>212–479 | 110<br>280, 410 | 46.0 |
| X | a) $Ca(Cl_2CHCOO)_2.H_2O \rightarrow Ca(Cl_2CHCOO)_2$<br>b) $Ca(Cl_2CHCOO)_2 \rightarrow CaCl_2 + CaO + C$ | Platinum | Nil | 100–160<br>210–570 | <br>300 | 37.7 |
| XI | a) $Ca(Cl_2CHCOO)_2.H_2O \rightarrow Ca(Cl_2CHCOO)_2$<br>b) $Ca(Cl_2CHCOO)_2 \rightarrow CaCl_2 + CaO + C$ | Platinum | Alumina | 100–170<br>209–462 | 117, 131<br>280, 420 | 34.5 |
| XII | a) $Ca(Cl_3CCOO)_2.3H_2O \rightarrow Ca(Cl_3CCOO)_2$<br>b) $Ca(Cl_3CCOO)_2 \rightarrow CaCl_2$ | Ceramic | Nil | 60–143<br>179–248 | 110<br>225, 247 | * |
| XIII | a) $Ca(Cl_3CCOO)_2.3H_2O \rightarrow Ca(Cl_3CCOO)_2$<br>b) $Ca(Cl_3CCOO)_2 \rightarrow CaCl_2$ | Ceramic | Alumina | 88–110<br>132–255 | 105<br>150, 165,<br>200, 225 | * |
| XIV | a) $Ca(Cl_3CCOO)_2.3H_2O \rightarrow Ca(Cl_2CCOO)_2$<br>b) $Ca(Cl_3CCOO)_2 \rightarrow CaCl_2$ | Platinum | Nil | 75–154<br>174–242 | 124, 135<br>228, 240 | * |
| XV | a) $Ca(Cl_3CCOO)_2.3H_2O \rightarrow Ca(Cl_3CCOO)_2.H_2O$<br>b) $Ca(Cl_3CCOO)_2.H_2O \rightarrow Ca(Cl_3CCOO)_2$<br>c) $Ca(Cl_3CCOO)_2 \rightarrow CaCl_2$ | Platinum | Alumina | 90–150<br>150–208<br>208–310 | 140<br>170<br>230 | 40.6 |

* Evaluation of activation energy is not possible due to poor resolution of the curve.

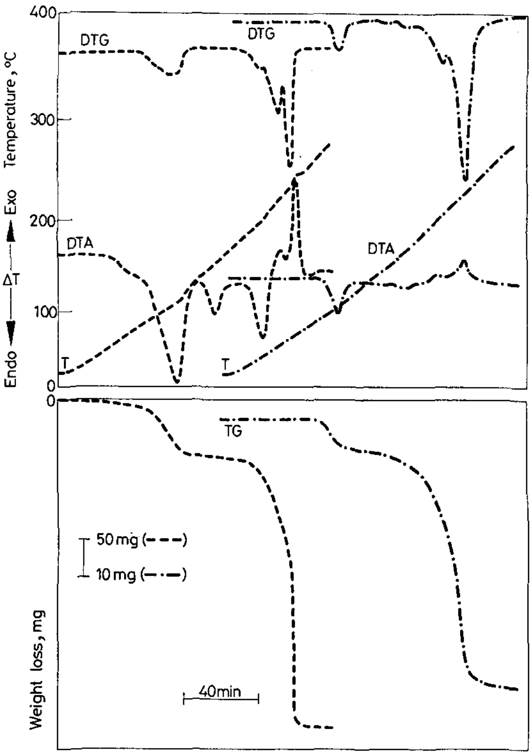

Fig. 6. Thermal curves for $Ca(Cl_3COO)_2 \cdot 3H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 600 | Ceramic | Nil |
| — · — | 100 | Ceramic | Alumina |

of dehydration of calcium propionate monohydrate remains unaltered when a ceramic or platinum crucible is used with or without diluent. A similar phenomenon is also noticed in the case of calcium monochloroacetate monohydrate. On the other hand, the mode of dehydration of both dichloro and trichloroacetates is affected by a change in the crucible. With respect to the pattern of dehydration, a diluent effect is not observed for either of the salt hydrates when a ceramic crucible is used. However, this effect is noticed with a platinum crucible. In the case of calcium acetate monohydrate, the pattern of dehydration changes with variation of the crucible with or without diluent. We reported the phase transition of anhydrous calcium propionate. A similar transition is observed in the case of anhydrous calcium acetate. However, the DTA peak area for this transition is very small, even when maximum DTA sensitivity is employed. Judd et al. [5] carried out the thermal decomposition of calcium acetate. They did not report such a transition of the anhydrous salt as observed by us. The phase transition of anhydrous calcium acetate is reversible, as that for calcium propionate [12].

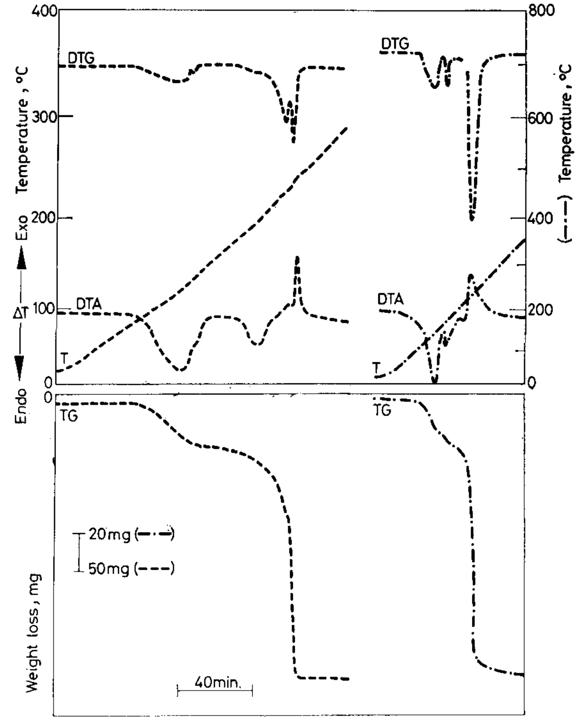

Fig. 7. Thermal curves for $Ca(Cl_3COO)_2.3\ H_2O$

| Notation | Wt. taken in mg | Crucible | Diluent |
|---|---|---|---|
| — — — | 500 | Platinum | Nil |
| — · — | 200 | Platinum | $Al_2O_3$ |

We reported the decarboxylation of calcium propionate in a ceramic crucible, where it takes place in multiple steps, and suggested the free radical mechanism of Hites [15]. It is observed that the nature of the DTA curve for decarboxylation remains the same when diluent is used in a ceramic crucible (Fig. 3). This is also observed in a platinum crucible with or without diluent (Fig. 3). However, it is noticed that on exchange of the ceramic crucible for platinum, the number of DTA peaks increases, indicating that the decarboxylation takes place in a more complex fashion (Fig. 3). Such an observation is not prominent in the decarboxylation of other salts. We could not restrict the formation of possible products other than the symmetrical diethyl ketone. However, in the case of calcium acetate we get acetone alone only when the decarboxylation is carried out in a ceramic crucible with alumina. Here, we think that alumina is acting as a catalyst in a ceramic crucible, which restricts the formation of other possible intermediate products as in the mechanism proposed by Hites [12, 15].

The expected decomposition of calcium monochloroacetate is *via* the ketone as for simple acid salts, but in practice we could not detect symmetrical haloketones from the gaseous products during pyrolysis. We obtained CaO, $CaCl_2$ and traces of carbon, but Malihovoski et al. [10] reported the presence of calcium chloride and calcium carbonate in the residue after pyrolysis of calcium monochloroacetate, and also reported the existence of HCl, PhOH, CO, $CO_2$, MeCl, $C_2H_4$ and $HOCH_2COOH$ in the gaseous products. The mechanism cited by them is through the formation of metal oxide and acid anhydride. However, this mechanism cannot predict the formation of calcium chloride reported by them. Hence, the possible mechanisms of decomposition may be as follows:

(I) $Ca(CH_2ClCOO)_2 \rightarrow CaCl_2 + CH_3COOH + 2\,CO$
(II) $Ca(CH_2ClCOO)_2 \rightarrow CaO + (CH_2ClCO)_2O$
$(ClCH_2CO)_2O \xrightarrow{H_2O} ClCH_2COOH$
$(ClCH_2CO)_2O \rightarrow COCl_2 + CH_3COOH + C$

If the decomposition occurs through the proposed pathway I, the formation of calcium oxide, carbon, phosgene and monochloroacetic acid cannot be justified. We think that the decomposition follows both pathways simultaneously, though we could not confirm the liberation of the anhydride.

We propose the following mechanisms for the decomposition of calcium dichloroacetate:

(I) $Ca(Cl_2CHCOO)_2 \rightarrow CaCl_2 + Cl_2CHCOOH + 2\,CO$
(II) $Ca(Cl_2CHCOO)_2 \rightarrow CaO + (Cl_2CHCOO)_2O$
$(Cl_2CHCOO)_2O \rightarrow Cl_2CHCOOH + COCl_2 + C$

Here also, as the product after pyrolysis contains mostly $CaCl_2$, it is suggested that the decomposition is favoured by pathway I while the presence of $COCl_2$, $Cl_2CHCOOH$ and carbon supports the fact that the decomposition takes place by pathway II, although the formation of the anhydride could not be confirmed.

In the case of the trichloroacetate, we obtained only $CaCl_2$ in the residue after pyrolysis, just like Malihovoski et al. [10], with the gaseous products $Cl_3COCl$, CO and $COCl_2$. Malihovoski et al. reported the formation of $(Cl_3CCOO)_2O$ and traces of hexachloroethane in addition to the products detected by us. On repeated analysis we could not detect the anhydride. We think that the decomposition occurs through the following mechanisms, where formation of $CaCl_2$, $Cl_3CCOOH$, $Cl_3CCOCl$, $COCl_2$, HCl, CO and $C_2Cl_6$ are justified, though we have failed to detect the presence of hexachloroethane:

$Ca(Cl_3CCOO)_2 \rightarrow CaCl_2 + Cl_3CCOCl + CO + CO_2$
$Cl_3CCOCl \rightarrow Cl_3C^{\cdot} + COCl^{\cdot}$
$2\,Cl_3C^{\cdot} \rightarrow C_2Cl_6$
$2\,COCl^{\cdot} \rightarrow COCl_2 + CO$
$Cl_3CCOCl + H_2O \rightarrow HCl + Cl_3CCOOH$

In the work of Judd et al. [11] the thermal decomposition of copper salts of chloroacetic acids carried out in an inert atmosphere. They reported a mechanism of decomposition of copper dichloroacetate similar to pathway (I) reported by us, with the simultaneous reduction of $CuCl_2$ to CuCl and $Cl_2$, but expressed their inability to confirm the presence of $Cl_2$ or $COCl_2$ which could have been formed by the reaction of $Cl_2$ and CO. In the case of copper trichloroacetate, the mechanism suggested by them is almost the same as ours, but here too the possibility of formation of $COCl_2$ is not reported by them. In our case there is no possibility of generation of $Cl_2$ from $CaCl_2$; naturally the mechanisms of formation of phosgene suggested by us in the cases of the calcium salts of mono, di and trichloroacetic acids are justified.

It appears from the Table that the value of the activation energy does not differ much with the change of the crucible in the decarboxylation process, except in the case of calcium acetate.

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Résumé — La déhydratation et la décarboxylation des sels de calcium des acides acétique, mono, di et trichloroacétique ont été étudiées à l'aide d'un Derivatograph. Seul l'acétate de calcium présente une transition de phase. Les effets respectifs du creuset et du diluant sur le comportement thermique de ces sels ont également été suivis. Les produits de décomposition ont été analysés qualitativement. D'après la nature des gaz émis et celle des résidus de pyrolyse, un mécanisme est proposé pour ces décompositions. Les énergies d'activation des réactions de décarboxylation sont calculées à partir des courbes TG.

ZUSAMMENFASSUNG — Die Calciumsalze von Essigsäure sowie von Mono-, Di- und Trichloressigsäure wurden mittels eines Derivatographen hinsichtlich ihrer Dehydratisierung und Decarboxylierung untersucht. Ein Phasenübergang wurde nur im Falle des Calciumacetats beobachtet. Der Effekt des Tiegels und des Verdünners auf das thermische Verhalten obiger Salze wurde ebenfalls untersucht. Die Zersetzungsprodukte wurden qualitativ geprüft und aus diesen gasförmigen Produkten sowie aus ihren Pyrolyseresten wurde ein wahrscheinlicher Zersetzungsmechanismus vorgeschlagen. Die Aktivierungsenergien der Decarboxylierungsvorgänge wurden aus den TG-Kurven ermittelt.

Резюме — С помощью дериватографа исследованы кальциевые соли уксусной кислоты, моно-, ди- и трихлоруксусных кислот относительно их дегидратации и декарбоксилирования. Фазовые переходы отмечены только в случае ацетата кальция. Также изучено влияние тигля и разбавителя на термическое поведение названных выше солей. Продукты разложения исследованы количественно и исходя из газообразных продуктов и остатка после пиролиза, предложены возможные механизмы их разложения. Исходя из ТГ кривых оценены энергии активации процессов декарбоксилирования.