Journal of Thermal Analysis, Vol. 6 (1974) 555–563

THE THERMAL DECOMPOSITION OF CALCIUM, SODIUM, SILVER AND COPPER(II) ACETATES

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(Received December 22, 1972; in revised form March 2, 1973)

The thermal decomposition of the acetates of calcium, sodium, silver and copper(II) have been investigated using thermogravimetry and differential thermal analysis, together with analysis of the gaseous products formed during the decomposition process. The results indicate that the major organic product formed is either acetone or acetic acid, depending on whether the final solid product is the oxide or the metal

Much work has been published on the thermal decomposition of metal acetates (see for example refs. [1–4]) although interest has mainly been centred on the nature of the solid products formed. The acetates of the Group IIA metals have been extensively studied and it has been shown [5, 6] that decomposition yields the corresponding carbonate, with acetone as the other major product. The decomposition of calcium acetate has, in fact, long been used as a student exercise to demonstrate the formation of acetone. It is generally accepted that breakdown of the acetate group is a complicated process, since the formation of oxides of carbon plus hydrocarbons can lead to many side reactions occurring.

We have studied the decomposition of the acetates of sodium, copper and silver using thermogravimetry (TG) and differential thermal analysis (DTA). The processes have also been investigated using a flow system, which enables decomposition products either to be trapped out or collected in gas bulbs for subsequent identification. To check the results produced by this equipment, the thermal decomposition of calcium acetate has also been studied.

Experimental

The samples of sodium acetate used were Analar grade material, whereas the samples of cupric and calcium acetate were general laboratory reagent grade (not less than 98% and 95% pure, respectively). Silver acetate was prepared by mixing equal volumes of 1 M aqueous solutions of Analar silver nitrate and sodium acetate. The precipitated silver acetate was filtered, washed with distilled water, recrystallized from hot distilled water, and dried at room temperature in a vacuum oven.

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Care was taken to exclude light at all stages of the preparation. Analysis for carbon and hydrogen gave values of 14.2% and 1.78%, respectively, compared with 14.4% and 1.80% expected for silver acetate.

Thermogravimetric studies were carried out using a Stanton Redcroft TG 750 thermobalance. Since small sample weights (<5 mg) were used, it was possible to operate at a high heating rate of 10°/min without any loss in resolution. All experiments were performed with the sample under a flowing stream of nitrogen.

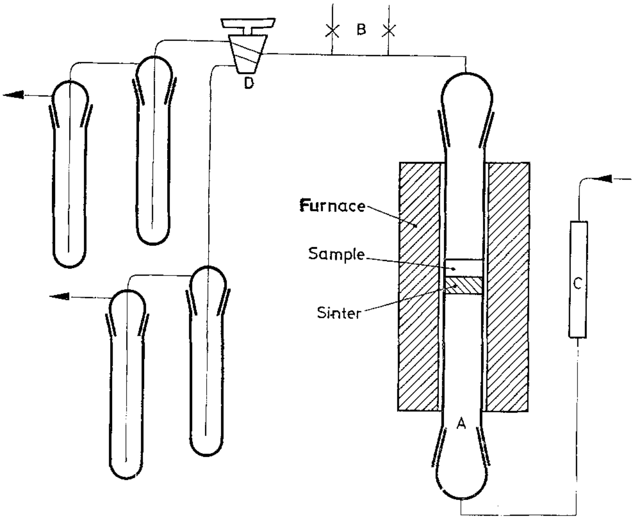

Fig. 1. Schematic diagram of apparatus used for product separation

Differential thermal analysis traces were obtained using a Standata 6–25 differential thermal analyser. Samples (ca. 50 mg) were heated under flowing nitrogen at a nominal heating rate of 10°/min. A twin stem head assembly was employed with the sample and inert reference material (alumina) contained in dimped platinum crucibles (8 × 6.2 mm dia.).

Product analyses were carried out using the flow apparatus shown in Figure 1. A reaction vessel (*A*), consisting of a pyrex tube (3 cm I. D.) with a sinter (porosity 2) situated at its midpoint, was mounted vertically in a furnace and connected via a two way tap (*D*) to a series of traps cooled in liquid air. To the lower end of *A* was connected, via the flow meter *C*, a helium supply. The acetate (5 g) was placed on the sinter and the apparatus swept out with helium for half an hour at a flow rate similar to that used in the decomposition experiments (300 cm^3/min, with a lower rate of 100 cm^3/min for sodium acetate). The furnace temperature was raised at 4.5°/min to a final temperature of ca. 400° and the traps changed at temperatures suggested by the DTA trace for the acetate under study. Gas samples were taken at intervals by attaching evacuated bulbs to the side arms (*B*).

Analyses of the gaseous and liquid samples were performed by gas chromatography and infrared absorption spectroscopy. The apparatus used for gas chromatography was:

1. A model LC2 chromatograph (Phase Separations Ltd.), fitted with a katharometer detector. The column employed was molecular sieve 5A, maintained at 45° with helium at a flow rate of 60 cm^3/min, as the carrier gas.

2. A model F11 chromatograph (Perkin Elmer Ltd.). The column used was Carbowax 1540 at a temperature of 110°. Detection was by flame ionization with nitrogen as the carrier gas at a flow rate of 25 cm^3/min.

Infrared spectra were obtained using a model 457 grating spectrophotometer, manufactured by Perkin Elmer Ltd.

Results and discussion

1. Calcium acetate Ca $(CH_3COO)_2$. (B.D.H. "anhydrous". Laboratory reagent grade).

The decomposition of this material has been studied in detail elsewhere [5]. We therefore used calcium acetate as a standard substance in order to check the results obtained with the flow system.

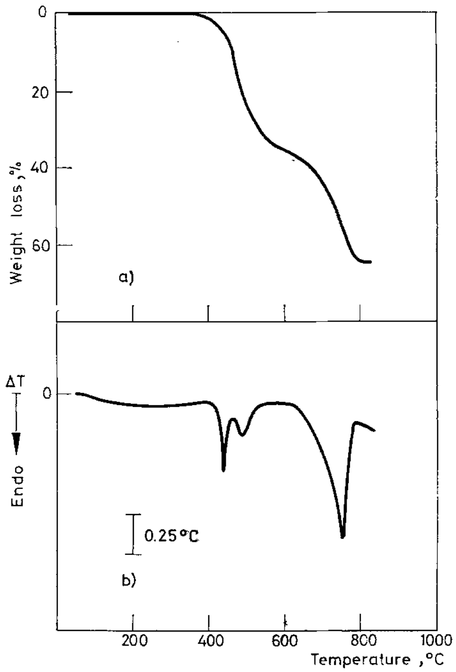

Fig. 2. Thermal decomposition of calcium acetate (a) TG-, (b) DTA curves

In general, the results obtained with this material agree with other published data, in that the decomposition process initially yielded the carbonate plus acetone, followed by formation of the oxide on further heating. However, the first stage decomposition to the carbonate appears on both the TG (Fig. 2a) and DTA (Fig. 2b) traces to be a two stage process. This was somewhat surprising but a closer look at the DTA trace suggested an explanation. The initial endothermic peak is very sharp and resembles that obtained during melting; therefore if the calcium acetate had melted during decomposition, this would be expected to affect the rate of decomposition. To check whether or not melting had occurred, a sample was heated on a hot stage microscope (Leitz 1750) and it was readily apparent that the acetate did in fact melt during decomposition. The endotherm at 440° can therefore confidently be attributed to the melting of calcium acetate. McAdie [7] has shown that strontium acetate melts prior to decomposition at a temperature of 350° and therefore a melting point of 440° is not unreasonable for the calcium salt.

The decomposition of calc ium acetate may therefore be represented as follow

$$Ca(CH_3COO)_2 \xrightarrow[\text{phase}]{\text{via liquid}} CaCO_3 + (CH_3)_2CO\uparrow \rightarrow CaO + CO_2\uparrow$$

2. Sodium acetate $Na(CH_3COO)\ 3H_2O$ (B.D.H. Analar).

This material has been studied by Duval [2] in connection with its use as a standard substance in volumetric analysis. He states that the anhydrous material is stable over the temperature range 170–440°.

DTA (Fig. 3b) shows that loss of the three molecules of water of crystallization is a two stage process with peak temperatures of 70° and 150°. TG (Fig. 3a), however, shows a smooth weight loss up to a value of 40% (theoretical weight loss for the formation of the anhydrous acetate is 39.6%), although there is a marked change in the rate of weight loss at ca. 70°. This change in rate does not occur at a value which corresponds to the loss of an integral number of molecules of water of crystallization and is presumably associated with the boiling of water liberated at an early stage of the process. The TG trace given here was obtained on a finely divided powder (necessary because of the violent nature of the dehydration). When the experiment was repeated using the solid as supplied by the Manufacturer, the dehydration appeared to be a multistage process, although the nature of the trace obtained was very dependent on the sample weight used. Therefore it is not possible to state categorically whether or not the dehydration process occurs via a number of distinct steps.

A horizontal on the TG trace is obtained over the temperature range 160–385°. Above 385° a further weight loss occurs, leading to a final value of 70.5% at 680° (theoretical weight loss for the formation of sodium carbonate is 72.0%). DTA, however, shows that an additional effect occurs before the onset of the second decomposition process; a sharp endotherm, with a peak maximum at

335° is observed. Since this process is not accompanied by any noticeable change is sample weight, it must be associated with a phase transition. Observation of the sample under the hot stage microscope confirmed that this endotherm was due to the melting of the anhydrous acetate. It therefore appears that a more realistic temperature range for the stability of the anhydrous acetate would be 170–300°, rather than Duval's figures of 170–440°.

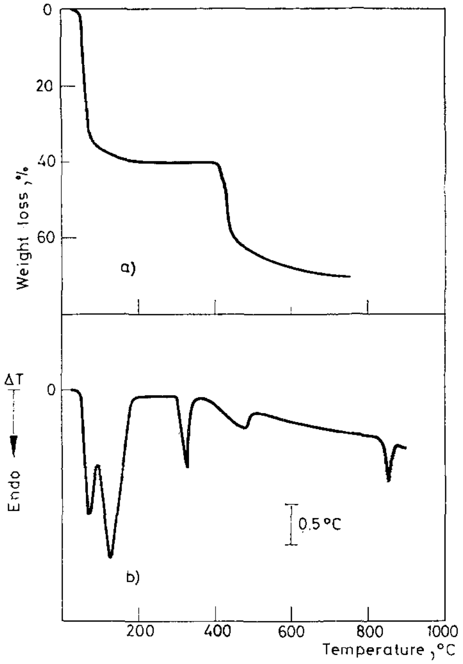

Fig. 3. Thermal decomposition of sodium acetate (a) TG-, (b) DTA curves

The melting of the sodium acetate prior to decomposition caused problems in handling this material in the flow system. However, by using a lower helium flow, it was found possible to keep most of the sample in the furnace hot zone. The major product identified was once again acetone, together with some carbon dioxide.

Further heating led to a DTA endotherm with a peak maximum at 860°; this can be attributed to the melting of the sodium carbonate (lit. value 851°). The decomposition of sodium acetate, in the temperature range of this study, may therefore be represented as follows

$$2Na(CH_3COO)3H_2O \rightarrow 2Na(CH_3COO)_{(s)} \rightarrow 2Na(CH_3COO)_{(l)}$$
$$\rightarrow Na_2CO_3 + (CH_3)_2CO + \text{traces of } CO_2.$$

3. Silver acetate $Ag(CH_3COO)$ (Laboratory preparation)

In both of the previous examples, the final product of decomposition has been the carbonate (or ultimately the oxide on further heat treatment). Silver oxide is known to be unstable above 300° and in fact all silver oxysalts undergo thermal decomposition to yield metallic silver. It was therefore of interest to observe whether this tendency to form the metal rather than the oxide would affect the nature of the gaseous products evolved on decomposition.

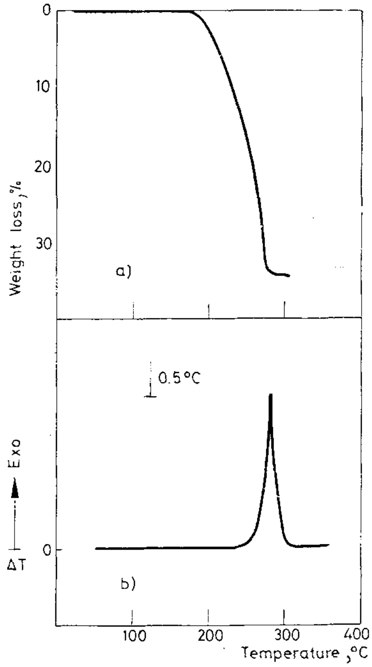

Fig. 4. Thermal decomposition of silver acetate (a) TG-, (b) DTA curves

Both TG (Fig. 4a) and DTA (Fig. 4b) show that decomposition occurs in a single stage. TG indicates the reaction to occur over the temperature range 180–280° with an accompanying weight loss of 34.0% (theoretical to give silver is 35.2%). DTA yields a single sharp exotherm over the temperature range 240–310°. The most interesting result, however, was obtained from the gas analyses. No trace of acetone was detected in the evolved material; instead the major product was acetic acid, together with a small amount of carbon dioxide. It is difficult to understand by what mechanism the acetate groups interact to yield acetic acid as the product, but the process may be represented by the following stoichiometric equation

$$2Ag(CH_3COO) \rightarrow 2Ag + CH_3COOH + CO_2 + H_2 + C.$$

DTA shows clearly that the decomposition is exothermic with a relatively small enthalpy change involved. Calculations using standard free energy and enthalpy change data show that at 25° the values of ΔG and ΔH for the above process are -154.7 kJ mole^{-1} and -50.2 kJ mole^{-1} respectively. Thus the mechanism suggested by the DTA data is thermodynamically feasible. (It was not possible to calculate values of ΔG and ΔH at the reaction temperature, ca. 250°, but it is unlikely that they will differ sufficiently to indicate a different reaction path.)

The other products indicated by this equation are carbon dioxide, carbon and hydrogen. However, it would be expected that many side reactions could occur between these compounds on the surface of the active silver formed, together with breakdown of some of the acetic acid. Only carbon dioxide, plus traces of carbon, were detected by our analytical tests, although the presence of hydrogen cannot be ruled out since our system was insensitive for its detection.

It therefore appears that decomposition of silver acetate proceeds by the stoichiometric equation given above, although it is not clear by what mechanism the reaction occurs.

4. Cupric acetate $Cu_2(CH_3COO)_4 2H_2O$ (B.D.H. laboratory reagent grade)

Cupric acetate (in the hydrated form) exists as a dimeric molecule [8] with the metal atoms surrounded in an approximately square plane by the four oxygens of the bridging acetate groups. Each copper also has a water oxygen bound to it and the copper atoms are sufficiently close to allow orbital overlap, leading the metal–metal interaction. As in the case with the oxysalts of silver, the corresponding cupric salts tend to yield the metal on thermal decomposition in an inert atmosphere.

The results obtained by TG (Fig. 5a) show that the decomposition is essentially two stage although DTA (Fig. 5b) suggests that the process is rather more complicated. The first stage, as shown by TG, occurs over the temperature range 100–180°; the weight loss of 9.3% is a little higher than that expected for the loss of two molecules of water (9.0%). Product analysis at this stage of the reaction indicated that small amounts of acetic acid were produced although this is probably due to the presence of some acetic acid adsorbed on the sample, since the original material smelt strongly of the acid.

The second stage commences at ca. 200° (from TG), proceeds slowly until 290°, when the reaction becomes extremely rapid leading to a final weight loss of 70.0%. This value is much higher than that predicted for formation of metallic copper (59.3%). On removing the furnace it was found that metallic copper was present on the cooler parts of the tube, indicating that part of the sample had volatilized during decomposition. DTA showed a small peak at around 220° followed by a larger endotherm between 250 and 320°. The nature of this peak is typical of the type frequently encountered in the decomposition of oxysalts (e.g. ref. [9]) and results from the combination of an endothermic and an exothermic process.

Much more useful information, however, was obtained using the flow system. On heating above 200° a white solid was seen to volatilize into the cooler parts of the gas line; on further heating this material would revert to the blue colour as product gases passed over it. Some of this material was removed for chemical analysis and it was found to be the corresponding cuprous salt Cu(CH_3COO).

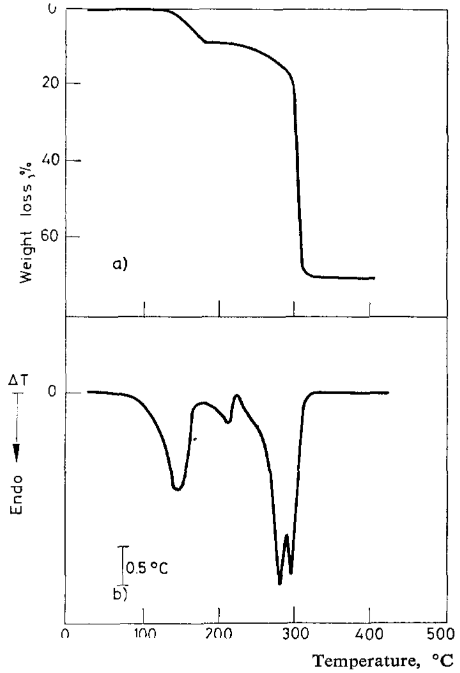

Fig. 5. Thermal decomposition of cupric acetate (a) TG-, (b) DTA curves

(Whether this material is dimeric or not is a matter of conjecture.) Supporting evidence for its being the cuprous salt was provided by the reaction with water, which produced a red precipitate of cuprous oxide. The gaseous products identified during this second stage of the process (from 200° upwards) confirmed that by far the most abundant component was acetic acid.

Since the cuprous salt is formed, it is then reasonable to assume that the decomposition follows a pattern analagous to that already described for silver acetate. Therefore the decomposition of cupric acetate may be described as follows

$$Cu_2(CH_3COO)_4 2H_2O \rightarrow Cu_2(CH_3COO)_4 \rightarrow Cu_2(CH_3COO)_2 + 2CH_3COOH$$

$$\rightarrow 2Cu + CH_3COOH + CO_2 + H_2 + C.$$

Conclusion

The data we have obtained, taken in conjunction with that reported elsewhere, suggests that where the final solid product formed on decomposition of a metal acetate (in an inert atmosphere) is a metal oxide, then the major organic product is acetone. However, when decomposition yields the metal as the solid product, then the major organic material produced is acetic acid.

Evidence is also put forward for suggesting that decomposition of cupric acetate proceeds via the formation of the corresponding cuprous salt, which then decomposes in a manner analogous to that of the silver acetate.

In the case of both the sodium and calcium salts, it is shown that melting occurs either before or during decomposition. Values obtained for the melting points are 335° and 440° respectively.

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Résumé — On a étudié la décomposition thermique des acétates de calcium, sodium, argent et cuivre(II) par thermogravimétrie et analyse thermique différentielle, en effectuant également l'analyse des produits gazeux formés. Les résultats indiquent que le principal produit organique formé est l'acétone ou l'acide acétique, suivant que le produit final solide est l'oxyde ou le métal.

Zusammenfassung — Unter Anwendung der Thermogravimetrie und der Differential-Thermoanalyse, in Verbindung mit der Analyse der während der Zersetzungsvorganges entstehenden gasförmigen Produkte, wurde die thermische Zersetzung der Acetate von Kalcium, Natrium, Silber und Kupfer(II) untersucht. Die Ergebnisse zeigen, daß — in Abhängigkeit davon, ob das feste Endprodukt das Oxid oder das Metall ist, das organische Hauptprodukt entweder Aceton oder Essigsäure ist.

Резюме — Исследовался термораспад ацетатов кальция, натрия, серебра и меди методами термогравиметрии и дифференциального термического анализа, совместно с анализом газообразных продуктов, образующихся при процессах распада. Результаты показали, что основным образующихся органическим продуктом является либо ацетон, либо уксусная кислота, в зависимости от качества конечного твердого продукта, который является окисью или металлом.