

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Sasol's FT technology has dominated the petrochemical industry locally and to a lesser extent internationally since the 1950's. In the FT process, coal and/or natural gas are converted to an array of hydrocarbon products over cobalt or iron catalysts. In many instances, oxygenated products such as carboxylic acids are also formed.

Various refinery operations downstream of FT synthesis involve hydrotreating. Unsulfided nickel catalysts are the preferred catalysts of choice for hydrotreating operations. However, the presence of organic acids in the FT product stream precludes the use of these catalysts as they result in acid leaching of the nickel catalyst. It is therefore desirable to find catalysts that can decarbonylate the organic acids prior to hydrotreating.

In an initiative undertaken at Sasol, scientists have been engaged in studies to establish the best possible candidates for commercial decarbonylation catalysts. It has been suggested that metal carboxylate interactions could be used to narrow the field in search of commercial decarbonylation catalysts¹. Metals that yield carboxylates that decompose at low temperatures may also be capable of decomposing carboxylic acids at low temperature. Many metal carboxylates have thus been synthesized and their physical properties and thermal decomposition behaviour explored.

More recently it has also become crucial to investigate the physical properties of cobalt carboxylates since such species could potentially form under FT operating conditions where cobalt catalysts are employed. This project describes a study of cobalt carboxylates, ranging from the acetate (C_2) to decanoate (C_{10}). The synthesis, purity of the samples and their thermal decomposition behaviour will be discussed in this chapter.

4.2 Synthesis of Materials

Various synthetic methods were attempted to synthesize the compounds. The fusion method, which involves refluxing an aqueous solution of the metal salt (carbonate, oxide or hydroxide) with a molar equivalent of carboxylic acid², was used extensively in this project.

Although only partially soluble in water, $CoCO_3$ dissolved readily at elevated temperatures. Stoichiometric quantities of each respective acid ($C_2 - C_9$) were added to the $CoCO_3$ solutions. The solutions were then refluxed. The solubility of the acids in water also decreased with increasing chain length, however the higher temperatures and longer reaction times proved to be sufficient for the acids to react with the carbonate, as was evident by the formation of dark purple solids (product).

Products formed were mostly insoluble in water and precipitated out of solution upon cooling. The acetate, propionate and to a lesser extent the butyrate, were soluble in water and the products were isolated by reducing the volume of the solvent until the solution became saturated and the solids began to crystallize out. The solubility of the products in various solvents was tested, revealing that the shorter chain compounds are soluble in polar solvents such as water, ethanol and acetone. Upon shifting to longer chain compounds, solubility in polar solvents is decreased and non-polar solvents such as hexane and petroleum ether are

favoured. The products ranged from ruby red to violet in colour but upon drying, formed amorphous lilac powders.

A variety of solvents were used, including ethanol, water and hexane, in an effort to obtain crystals suitable for X-ray analysis. Slow evaporation under ambient conditions was the preferred method tested. However, other methods such as seeding and evaporation under vacuum were also attempted. Despite numerous attempts to obtain crystals, none suitable for X-ray diffraction could be obtained.

Infrared spectra of these compounds revealed that the synthesis reactions were successful since the two characteristic COO^- absorption bands associated with carboxylates were evident in all cases. Elemental analysis and thermogravimetric analyses provided further evidence that synthesis reactions were successful and that compounds formed were pure. No NMR spectra were recorded due to the paramagnetic nature of cobalt(II).

Some experiments were repeated using CoCl_2 as a source of cobalt(II). Following the same methodology discussed in the previous paragraph, aqueous solutions of CoCl_2 were refluxed with the appropriate molar ratio of carboxylic acid ($\text{C}_2 - \text{C}_8$). Unlike the carbonate, CoCl_2 is highly soluble in water but heating was still required to dissolve the acids which are generally insoluble in water. Acetone was used as a solvent for the longer chain acids.

Products arising from the CoCl_2 syntheses were ruby red in colour but became pink-purple and flaky in nature after drying. These products had limited solubility in most solvents and would not readily dissolve unless heated.

Infrared spectra of the samples revealed very broad, undefined peaks which could not be assigned. On the basis of the poor infrared data it was decided that the CoCl_2 syntheses were unsuccessful and samples were not analyzed any further.

A different approach was used for the decanoate: Stoichiometric amounts of NaOH and decanoic acid were refluxed in hot aqueous solution. A molar equivalent of CoCl_2 was added to this solution after some time and the solution was heated until a purple product precipitated out³. The product was filtered, washed and dried, yielding a violet amorphous powder.

The infrared spectrum of this compound revealed the two characteristic COO^- peaks associated with carboxylates, confirming that this reaction was successful. Additional analyses conducted on this sample provided evidence to support the conclusion that the product formed was pure.

4.3 Characterisation of Materials

4.3.1 Elemental analysis

Elemental analysis data for selected cobalt carboxylates is summarized in Table 4.1. The data reveals fair agreement between the expected C- and H- values and the actual C- and H- values. The larger variance in the %C values could be an indication that some residual CoCO_3 is present in the samples.

Table 4.1 Elemental analysis data for cobalt carboxylates

Compound	% C	% H
Cobalt acetate	Obs. 22.7 Calc. 22.5	Obs. 4.6 Calc. 4.7
Cobalt propionate	Obs. 32.1 Calc. 35.1	Obs. 4.8 Calc. 4.9

Cobalt valerate	Obs. 43.0 Calc. 46.0	Obs. 6.6 Calc. 6.9
Cobalt nonanoate	Obs. 54.6 Calc. 57.9	Obs. 8.7 Calc. 9.2
Cobalt decanoate	Obs. 56.7 Calc. 59.8	Obs. 9.5 Calc. 9.5

4.3.2 Infrared spectroscopy

Infrared spectroscopy is a useful tool for studying the structure of transition metal carboxylates.

As discussed previously, the two carbon-oxygen bonds in the carboxylate group exhibit delocalization. Since the degree of interaction between a cationic centre (metal) and the coordinated carboxylate ligand affects the delocalization and hence the stretching frequencies of the carboxylate ion appreciably, the importance of infrared spectroscopy becomes clearer.

The carbon-oxygen stretching frequencies of the carboxylate ion can to some extent be related to the bonding modes of the carboxylate ligand. Nakamoto and co-workers proposed that the differences between the symmetric and asymmetric stretching frequencies for the COO^- ion could be used to indicate the carboxylate bonding mode⁴.

In this study, infrared spectroscopy was used for three purposes. The first was to confirm that a reaction had taken place in each case. The second was to check if starting materials were removed during purification. Spectra of the prepared samples are compared with those of their precursors (i.e. the pure acids and cobalt carbonate) and used to confirm the purity of each product. Table 4.2 summarizes the characteristic infrared signals for a typical carboxylic acid,

CH₃COOH. Figs. 4.1 - 4.2 show the spectra of CH₃COOH and cobalt carbonate, two of the starting materials.

A third function of infrared spectroscopy in this study was to make inferences about the carboxylate bonding mode in each compound by applying the idea that the difference between the symmetric and asymmetric stretching frequencies for the COO⁻ ion could be used as an indication of the carboxylate bonding mode⁴.

The infrared spectrum of a typical acid, CH₃COOH, is shown in Fig. 4.1 and the various peaks associated with CH₃COOH are summarized in Table 4.2.

Table 4.2 Characteristic infrared signals of CH₃COOH⁴

Frequency (cm ⁻¹)	Assignment
3100 (broad)	O-H stretch
1714	C=O stretch
1405, 1310	O-H bend
1000	C-O stretch

The characteristic C=O stretch of the free carboxylic acids is observed at around 1715 cm⁻¹. C-O and O-H stretches are also observed within their characteristic ranges at 1294 cm⁻¹ and a broad band at 3000 cm⁻¹ respectively.

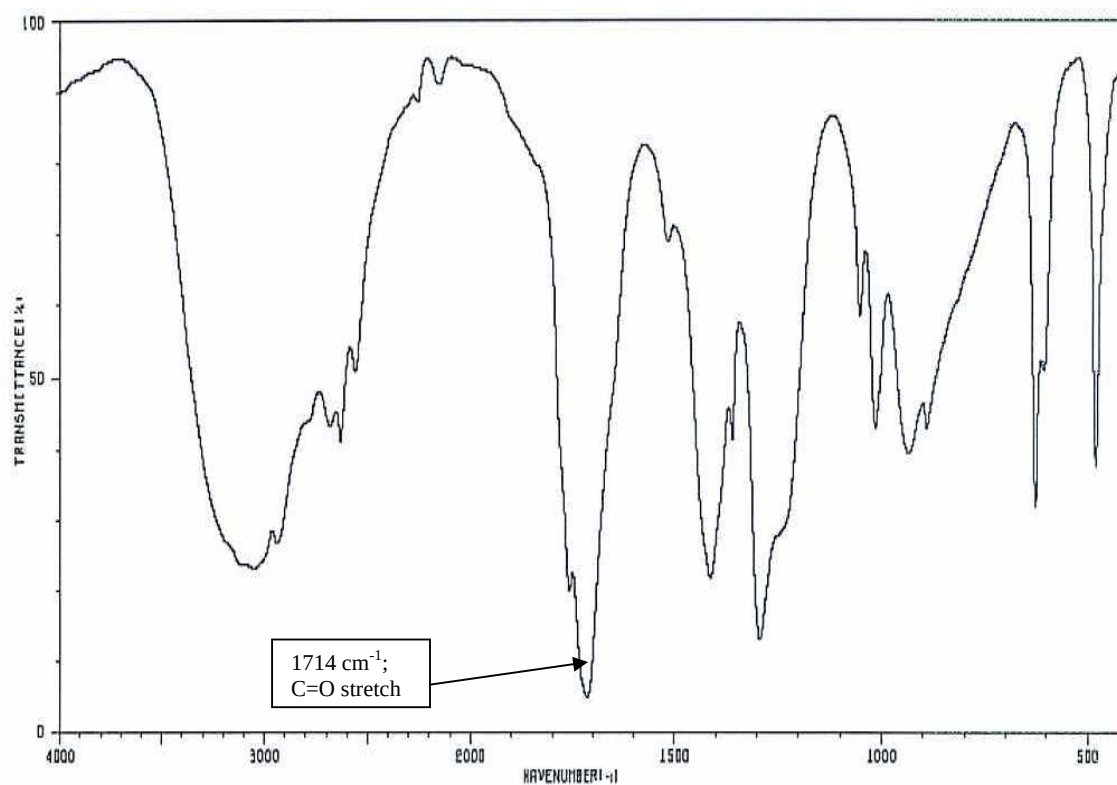


Fig. 4.1 Infrared spectrum of CH₃COOH (liquid film) ⁵

The spectrum for cobalt carbonate is shown in Fig. 4.2 (see p. 59).

A small peak is observed at 3351 cm⁻¹ suggesting that the sample contained some moisture. An intense peak is observed at ~1397 cm⁻¹, which is most likely associated with CO₂. Two small peaks at 2166 cm⁻¹ and 2025 cm⁻¹ were established to be an artifact of the analysis and are not related to the sample. Two smaller peaks are observed at 861 cm⁻¹ and 736 cm⁻¹. These arise due to O-C-O interactions (rocking and bending modes)⁴.

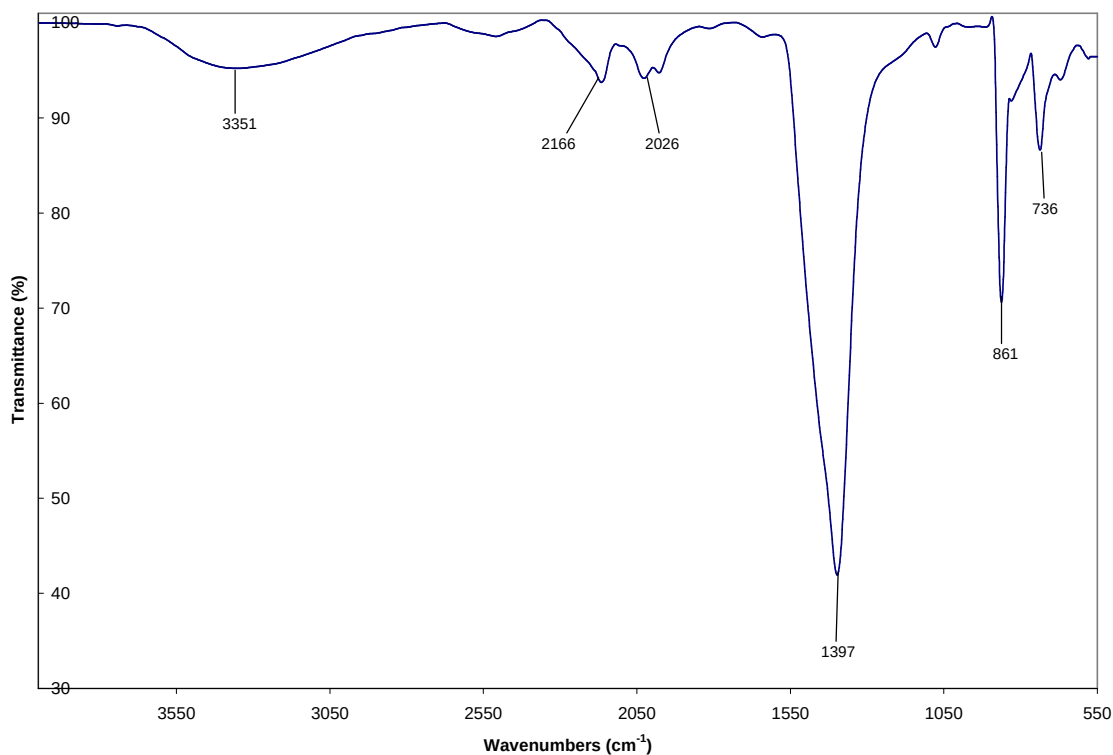


Fig. 4.2 Infrared spectrum of CoCO_3 (KBr)

Initially spectra were recorded in Nujol. However, interpretation of the results is complicated unnecessarily due to interference from the Nujol (C-C and C-H vibrations) and it was thus decided to record all spectra in KBr. Spectra for both sets of products i.e. products obtained from the CoCl_2 syntheses and CoCO_3 syntheses were recorded. Examination of the data revealed that the CoCl_2 syntheses were unsuccessful since the characteristic COO^- peaks associated with carboxylates were not observed. Therefore all further discussions in this chapter are based on the products of the CoCO_3 synthesis reactions*. Assignments of infrared absorptions for the compounds prepared in this project were made using standard infrared absorption tables and charts⁴.

*Additional spectra of the CoCl_2 derived products can be viewed in Appendix A

(a) Cobalt acetate

The spectrum for cobalt acetate is shown in Fig. 4.3.

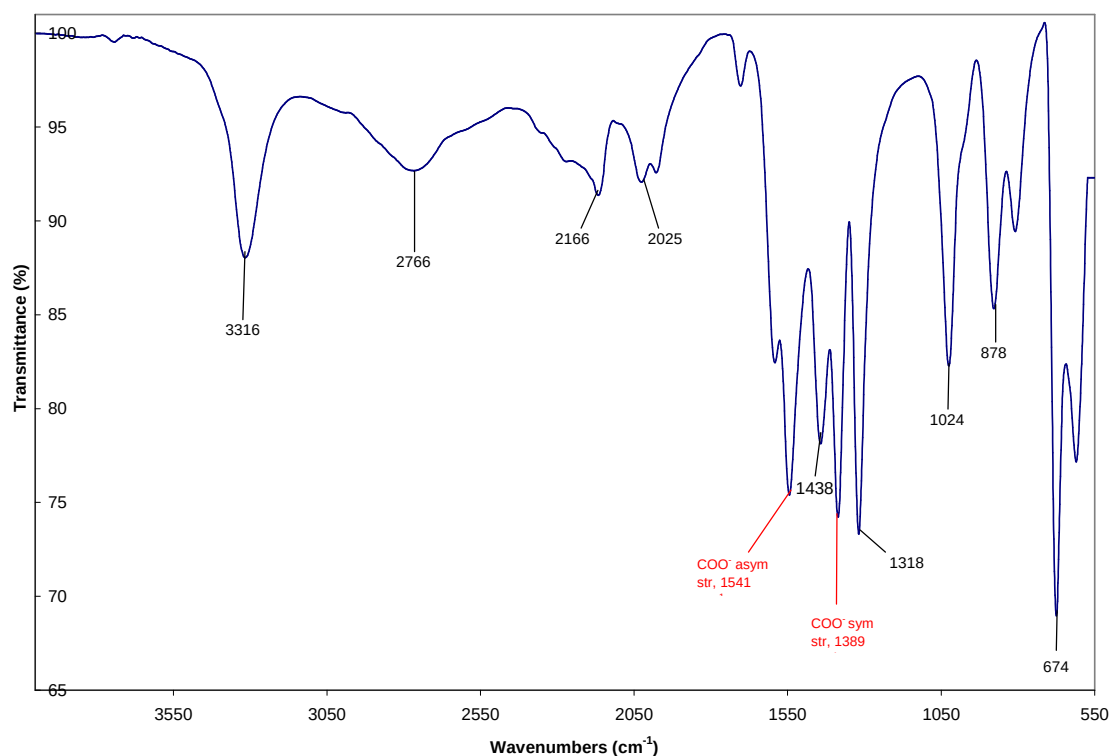


Fig. 4.3 Infrared spectrum of cobalt acetate (KBr)

A prominent -OH peak at 3316 cm^{-1} is observed in Fig. 4.3, suggesting that this compound contains water of crystallization^{4,6}. The peaks typical of aliphatic -CH stretches appear to be hidden under a broad band at 2766 cm^{-1} and could not be assigned definitively. This peak broadening could be as a result of hydrogen bonding between the acetate groups and the crystal water molecules. As discussed previously, the peaks at 2166 cm^{-1} and 2025 cm^{-1} are an artifact of the instrument and are not related to the sample (Refer to p.58). From the spectrum it can be seen that the characteristic C=O peak associated with carboxylic acids ($\sim 1700\text{ cm}^{-1}$) is absent. This serves to confirm that no residual acetic acid is present in the sample and suggests that the sample is pure. Similarly, the very intense peak associated with CoCO_3 at $\sim 1400\text{ cm}^{-1}$ is not observed in the spectrum of cobalt acetate also confirming that no CoCO_3 impurities are present.

The characteristic twin peaks for the symmetric and asymmetric COO^- stretches are observed in the spectrum of cobalt acetate at 1389 cm^{-1} and 1541 cm^{-1} respectively. The presence of a small shoulder peak on the asymmetric COO^- peak suggests that there is a possibility that two different types of carboxylate coordination may occur in this compound⁷. The various peaks observed below 800 cm^{-1} arise from COO^- rocking and bending modes. Unfortunately the Co-O stretches which are typically found below $500\text{ cm}^{-1(4)}$, could not be observed in any of the spectra.

The infrared assignments discussed above are summarized in Table 4.3 below:

Table 4.3 Infrared assignments of cobalt acetate

Band (cm^{-1})	Assignment
3316	-OH stretch
2766 region	Aliphatic -CH stretches
1541	Asymmetric COO^- stretch
1438	Aliphatic -CH bend
1389	Symmetric COO^- stretch
1318	Aliphatic -CH bend
1024	Aliphatic -CH rock
878	C-C stretch
674	COO^- bend

Nickolov & Stoilova reported values of 1394 cm^{-1} and 1559 cm^{-1} for the symmetric and asymmetric COO^- stretches for cobalt acetate respectively⁶. Haywards and Edwards also reported similar results in an independent study, where they found values of 1405 cm^{-1} and 1590 cm^{-1} for the symmetric and asymmetric COO^- peaks respectively⁸.

When the spectrum observed for cobalt acetate (Fig. 4.3) is compared to the spectra obtained by Nickolov and Stoilova in their studies⁶, Fig. 4.4, many similarities become evident between the spectrum for cobalt acetate dihydrate (CADH) and our spectrum. In both of these spectra a very intense -OH peak is observed at $\sim 3400\text{ cm}^{-1}$ as opposed to the much weaker -OH peak observed for cobalt acetate tetrahydrate (CATH). Furthermore the COO^- peaks observed in CADH resemble the COO^- peaks observed in our spectrum more closely in terms of shape and intensity than those of CATH. These similarities would seem to suggest that the product formed in this project is CADH as opposed to CATH. The results of the elemental analyses confirm this idea, as the hydrogen percentage observed (4.6%) corresponds to that expected for a dihydrated product (4.7% vs. 5.7% for a tetrahydrated product).

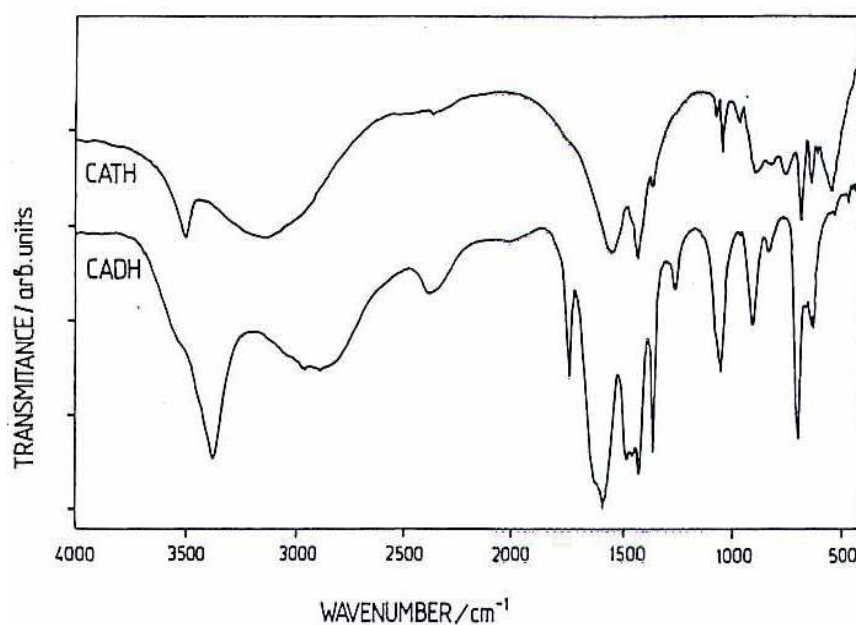


Fig. 4.4 Infrared spectra of CADH and CATH (KBr)⁶

(b) Cobalt propionate

Fig. 4.5 shows the spectrum obtained for cobalt propionate.

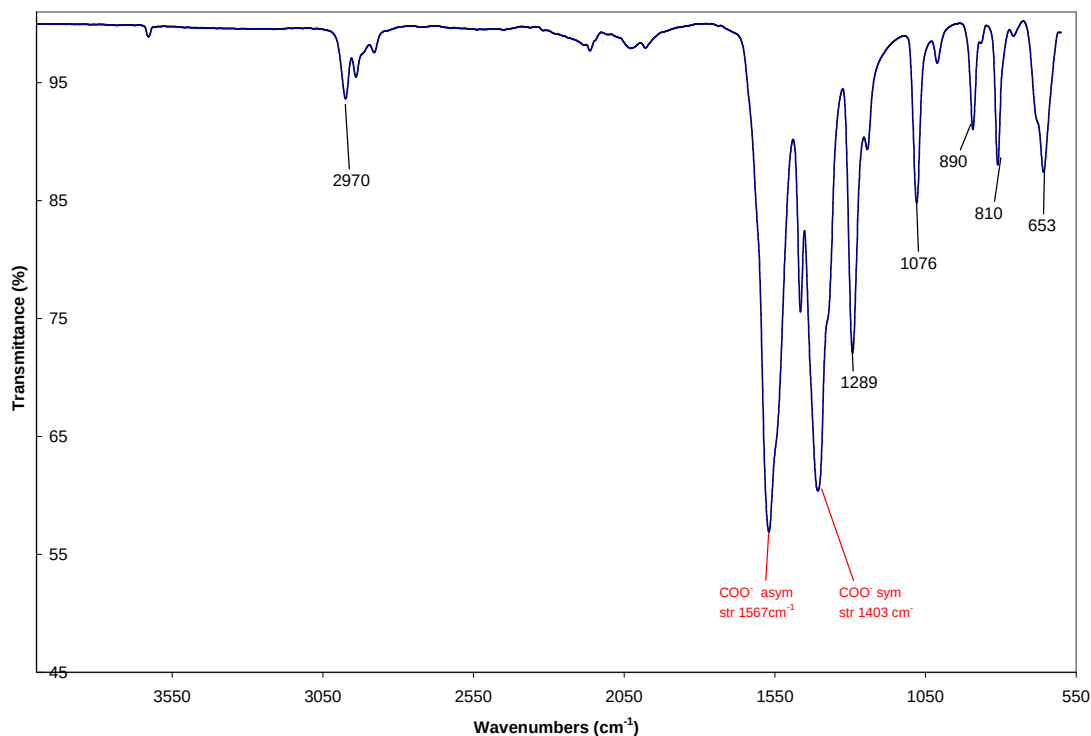


Fig. 4.5 Infrared spectrum of cobalt propionate (KBr)

There is no carbonyl peak evident ($\sim 1700\text{ cm}^{-1}$), suggesting that all propionic acid residues were removed during purification and the characteristic peak associated with CoCO_3 (1397 cm^{-1}) appears to be absent, although a slight shoulder is observed on the symmetric COO^- stretch which may be associated with traces of CoCO_3 . No $-\text{OH}$ peaks are observed in this spectrum which indicates that this sample does not contain water of crystallization. Weak peaks are observed for the aliphatic $-\text{CH}$ stretches in the 2970 cm^{-1} region. The characteristic COO^- stretches are clearly visible at 1567 cm^{-1} for the asymmetric stretch and 1403 cm^{-1} for the symmetric stretch. Typical COO^- interactions (bending and rocking modes) are observed below 890 cm^{-1} . Data are summarized in Table 4.4.

Table 4.4 Infrared assignments of cobalt propionate

Band (cm^{-1})	Assignment
2970 region	Aliphatic -CH stretches
1567	Asymmetric COO^- stretch
1403	Symmetric COO^- stretch
1289	Aliphatic -CH bend
1076	Aliphatic -CH rock
890	C-C stretch
810	COO^- bend
653	COO^- rock

(c) Cobalt butyrate

Fig. 4.6 shows the infrared spectrum of cobalt butyrate. Data are summarized in Table 4.5.

This compound appears to be pure as no C=O peaks are observed and the characteristic peak associated with CoCO_3 at 1397cm^{-1} is not discernable. No -OH peaks are observed indicating that this compound does not contain water of crystallization. As expected, aliphatic -CH stretches are observed at 2959 cm^{-1} . Strong peaks are observed for both the asymmetric and symmetric COO^- stretches at 1560 cm^{-1} and 1401 cm^{-1} respectively. A number of COO^- bending and rocking interactions are observed below 800 cm^{-1} .

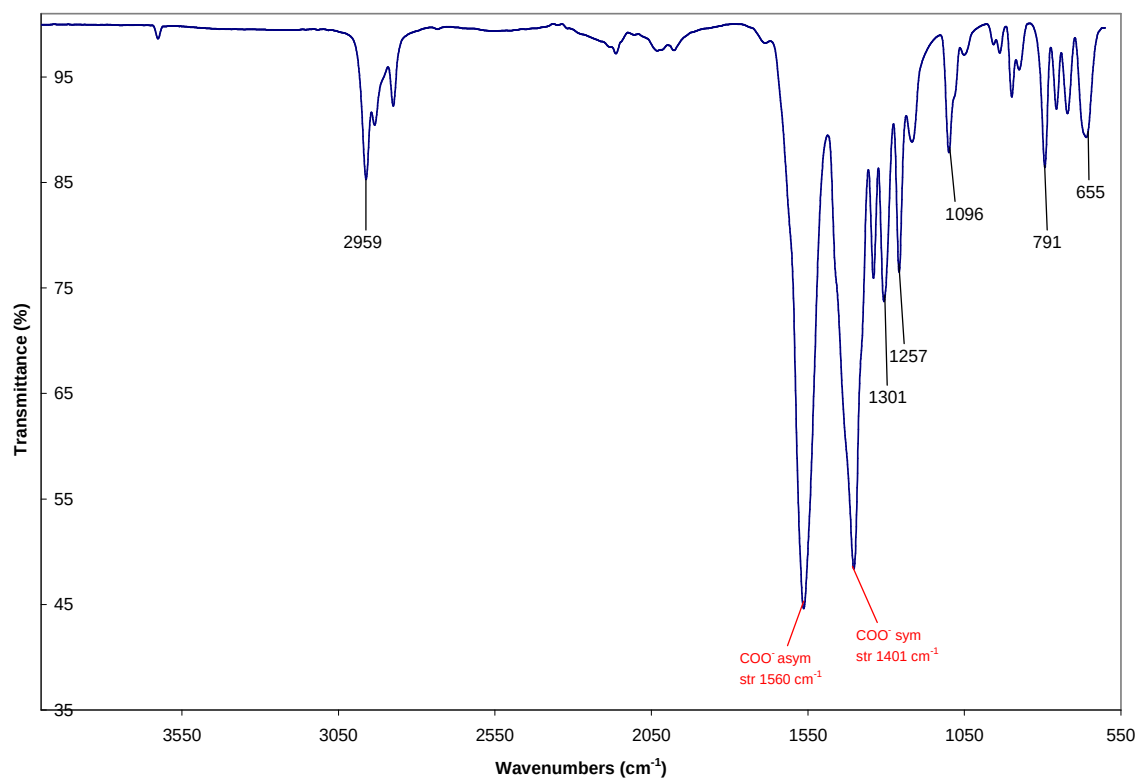


Fig. 4.6 Infrared spectrum of cobalt butyrate (KBr)

Table 4.5 Infrared assignments of cobalt butyrate

Band (cm^{-1})	Assignment
2959 region	Aliphatic -CH stretches
1560	Asymmetric COO^- stretch
1401	Symmetric COO^- stretch
1301	Aliphatic -CH bend
1257	Aliphatic -CH bend
1096	Aliphatic -CH rock
791	COO^- bend
655	COO^- rock

(d) Cobalt valerate

The infrared spectrum of cobalt valerate is shown below in Fig. 4.7 and the data is summarized in Table 4.6.

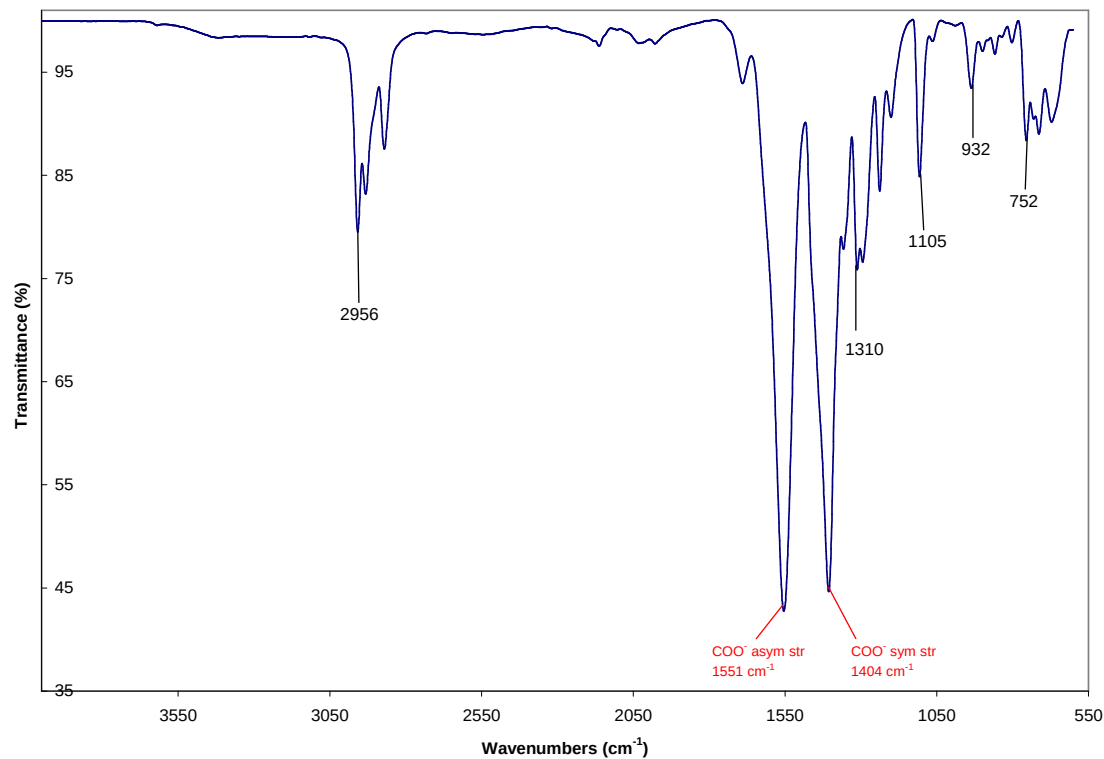


Fig. 4.7 Infrared spectrum of cobalt valerate (KBr)

Table 4.6 Infrared assignments of cobalt valerate

Band (cm ⁻¹)	Assignment
2956 region	Aliphatic -CH stretches
1551	Asymmetric COO ⁻ stretch
1404	Symmetric COO ⁻ stretch
1310	Aliphatic -CH bend
1105	Aliphatic -CH rock
932	C-C stretch
752	COO ⁻ bend

No peaks associated with the starting materials, CoCO_3 and valeric acid, are observed confirming that the material is pure. Aliphatic $-\text{CH}$ stretches are observed at 2956 cm^{-1} . The asymmetric COO^- stretch is evident at 1551 cm^{-1} and the symmetric COO^- stretch is observed at 1404 cm^{-1} . Additional COO^- interactions (rocking and bending) are observed at lower frequencies. No $-\text{OH}$ peaks are observed confirming that this compound contains no crystal water.

(e) Cobalt hexanoate

Fig. 4.8 illustrates the infrared spectrum obtained for cobalt hexanoate.

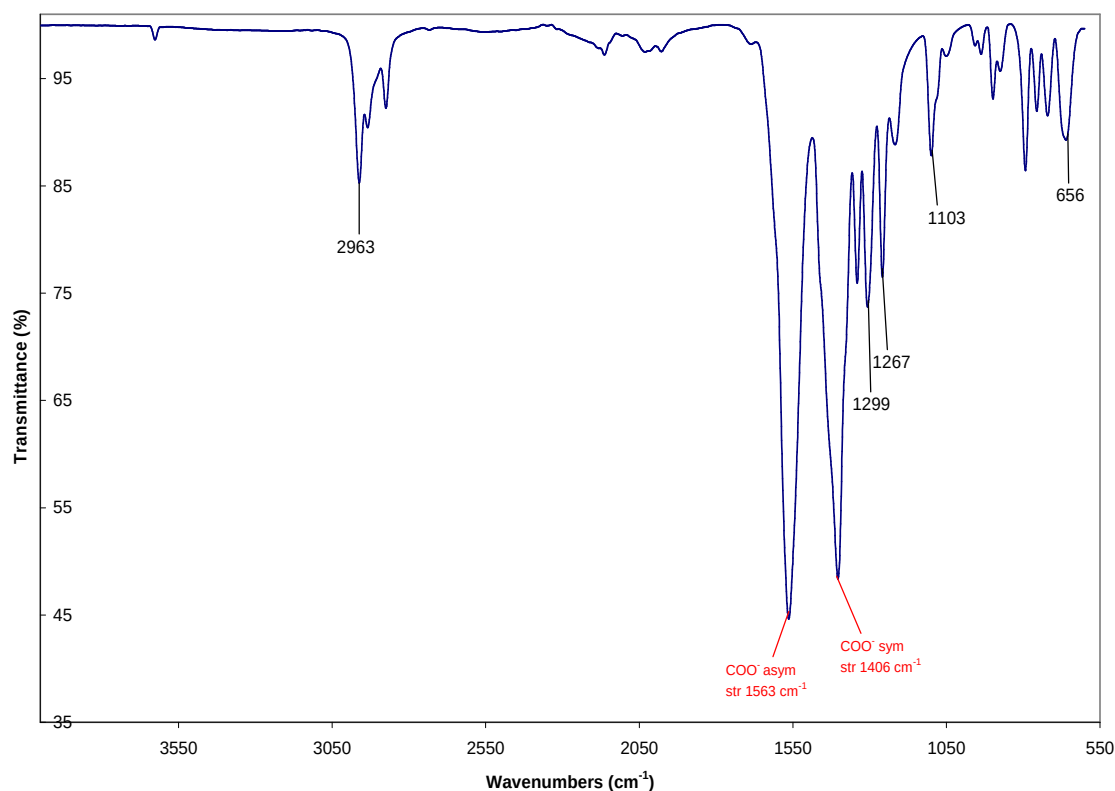


Fig. 4.8 Infrared spectrum of cobalt hexanoate (KBr)

No $-\text{OH}$ stretches are evident in the 3500 cm^{-1} region confirming that this compound contains no water of crystallization. Aliphatic $-\text{CH}$ stretches are observed in the region of $\sim 2960\text{ cm}^{-1}$. Asymmetric and symmetric COO^- stretches are observed at 1563 cm^{-1} and 1406 cm^{-1} respectively. No $\text{C}=\text{O}$ stretches are

observed and the peak associated with CoCO_3 is absent, confirming the purity of this sample. (Refer to Table 4.7 for summary of the data). COO^- bending modes are observed at 656 cm^{-1} .

Table 4.7 Infrared assignments of cobalt hexanoate

Band (cm^{-1})	Assignment
2963	Aliphatic $-\text{CH}$ stretches
1563	Asymmetric COO^- stretch
1406	Symmetric COO^- stretch
1299	Aliphatic $-\text{CH}$ bend
1267	C-O stretch
1103	Aliphatic $-\text{CH}$ rock
656	COO^- bend

(f) Cobalt heptanoate

The infrared spectrum for cobalt heptanoate is shown in Fig. 4.9.

The compound appears to be pure as no peaks associated with the starting materials are observed. No $-\text{OH}$ peaks are present and the sample does not contain water of crystallization. Three peaks are observed for the $-\text{CH}$ stretches in the 2952 cm^{-1} region. The characteristic COO^- peaks are observed at 1548 cm^{-1} and 1402 cm^{-1} for the asymmetric and symmetric stretches respectively.

A summary of the data can be found in Table 4.8.

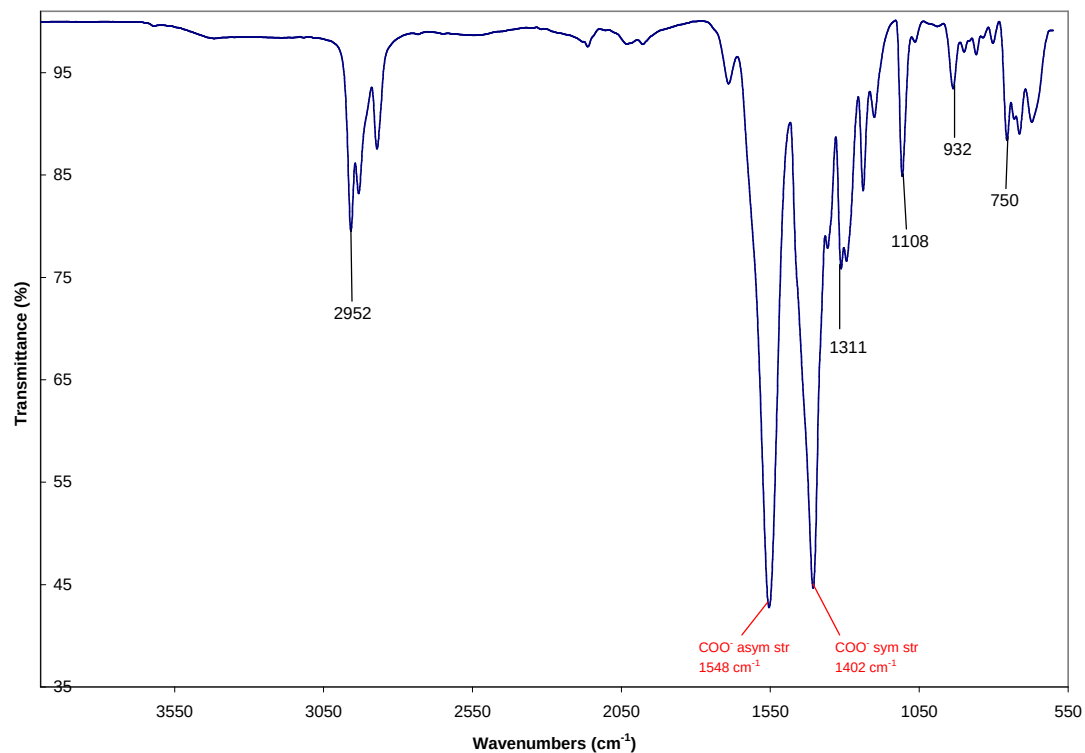


Fig. 4.9 Infrared spectrum of cobalt heptanoate (KBr)

Table 4.8 Infrared assignments of cobalt heptanoate

Band (cm ⁻¹)	Assignment
2952	Aliphatic -CH stretches
1548	Asymmetric COO ⁻ stretch
1402	Symmetric COO ⁻ stretch
1311	Aliphatic -CH bend
1108	C-O stretch
932	C-C stretch
750	COO ⁻ bend

(g) Cobalt octanoate

Shown below in Fig. 4.10 is the spectrum obtained for cobalt octanoate.

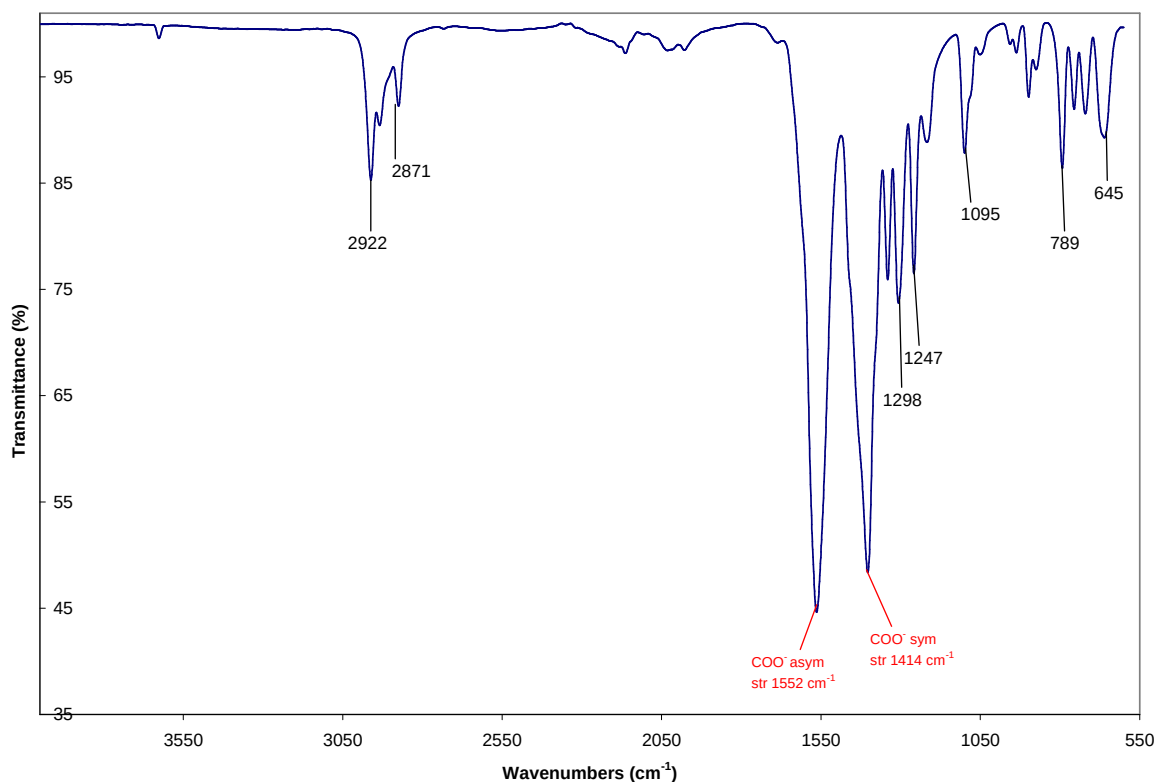


Fig. 4.10 Infrared spectrum of cobalt octanoate (KBr)

No C=O stretches are evident (1700 cm^{-1}) confirming that the sample contains no free acid. Similarly the peak associated with CoCO_3 is not evident indicating that this sample is pure. The compound appears to be anhydrous as no -OH absorptions are observed. Strong aliphatic -CH stretches are observed at $\sim 2922\text{ cm}^{-1}$ and 2871 cm^{-1} . This is not surprising considering the length of the aliphatic carbon chain in this compound. The COO^- peaks are still clearly present at 1552 cm^{-1} and 1414 cm^{-1} . As with the other samples, no peaks were observed below 500 cm^{-1} for the Co-O stretches but COO^- bending and rocking modes are evident below 790 cm^{-1} . Data are summarized in Table 4.9.

Table 4.9 Infrared assignments of cobalt octanoate

Band (cm^{-1})	Assignment
2922, 2871	Aliphatic -CH stretches
1552	Asymmetric COO^- stretch
1414	Symmetric COO^- stretch
1298, 1247	Aliphatic -CH bends
1095	Aliphatic -CH rock
789	COO^- bend
645	COO^- bend

(h) Cobalt nonanoate

The spectrum of cobalt nonanoate is illustrated in Fig. 4.11.

Various peaks are observed in the -OH band suggesting that this compound does contain some water of crystallization. The fact that there are multiple absorptions in this area could suggest that more than one type of water molecule is bound to the carboxylate⁷. Due to the longer aliphatic carbon chain of the carboxylate, prominent -CH stretches are observed at around 2920 cm^{-1} . The asymmetric COO^- peak occurs at 1543 cm^{-1} . The asymmetric stretch is seen at 1406 cm^{-1} . No C=O absorptions or peaks associated with CoCO_3 are observed and the sample appears to be pure. The data is summarized in Table 4.10.

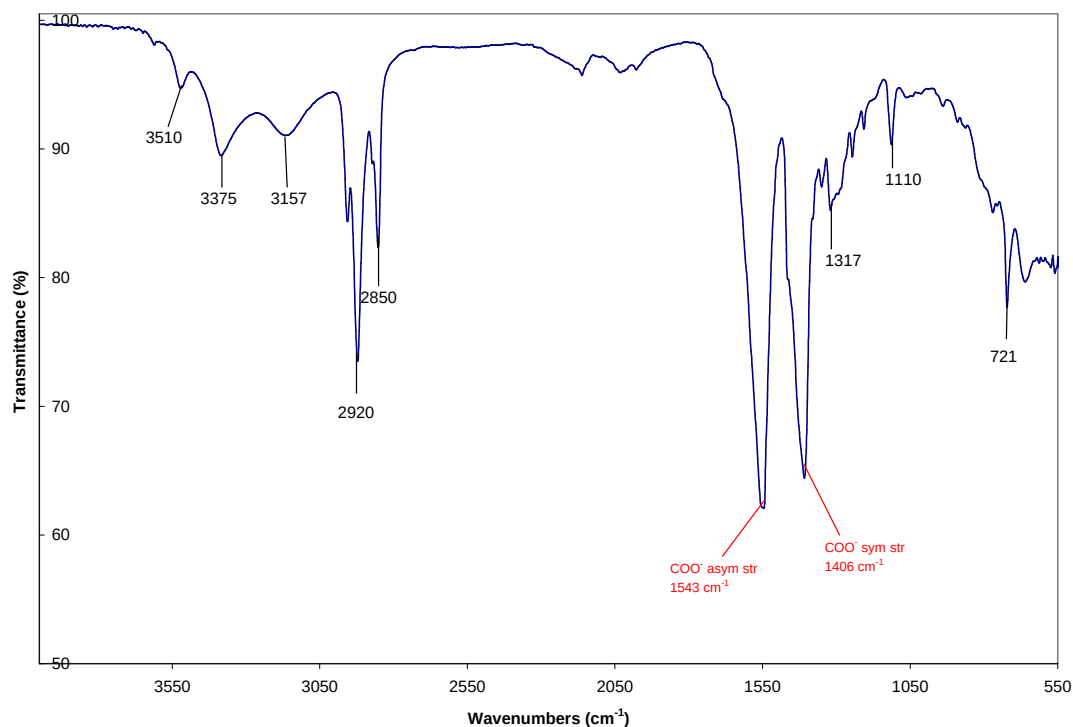


Fig. 4.11 Infrared spectrum of cobalt nonanoate (KBr)

Table 4.10 Infrared assignments of cobalt nonanoate

Band (cm ⁻¹)	Assignment
3510, 3375	-OH stretches
2920, 2850	Aliphatic -CH stretches
1543	Asymmetric COO ⁻ stretch
1406	Symmetric COO ⁻ stretch
1317	Aliphatic -CH bend
1110	Aliphatic -CH rock
721	COO ⁻ bend

(i) Cobalt decanoate

The infrared spectrum of cobalt decanoate is shown in Fig. 4.12.

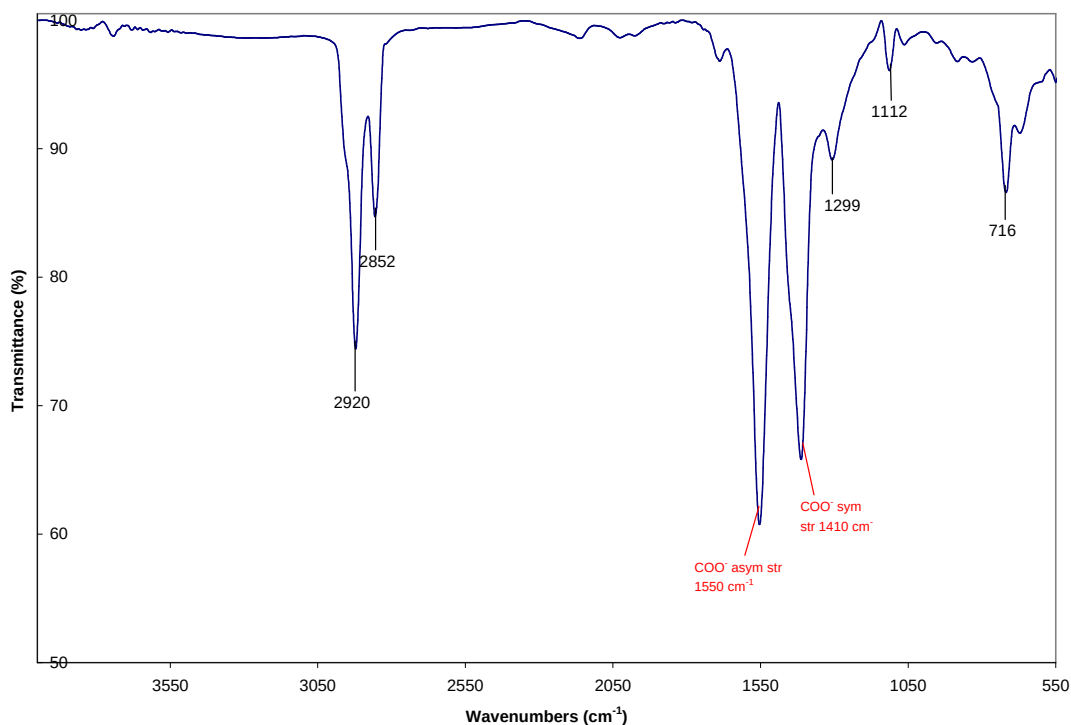


Fig. 4.12 Infrared spectrum of cobalt decanoate (KBr)

Cobalt decanoate does not appear to contain any water of crystallization since no -OH absorptions are observed in the infrared spectrum of this compound. Strong aliphatic -CH stretches are observed at 2920 and 2852 cm⁻¹. These are to be expected due to the long length of the carbon chain in the carboxylate ligand. When compared to the infrared spectrum for pure decanoic acid (Fig. 4.13), it becomes evident that no decanoic acid is present in the sample as none of the characteristic absorptions of decanoic acid are seen in the product spectrum (especially the C=O absorption at 1700 cm⁻¹). Strong asymmetric and symmetric COO⁻ stretches are observed at 1550 cm⁻¹ and 1410 cm⁻¹ respectively. COO⁻ bending modes are observed at 716 cm⁻¹. Table 4.11 summarizes the data.

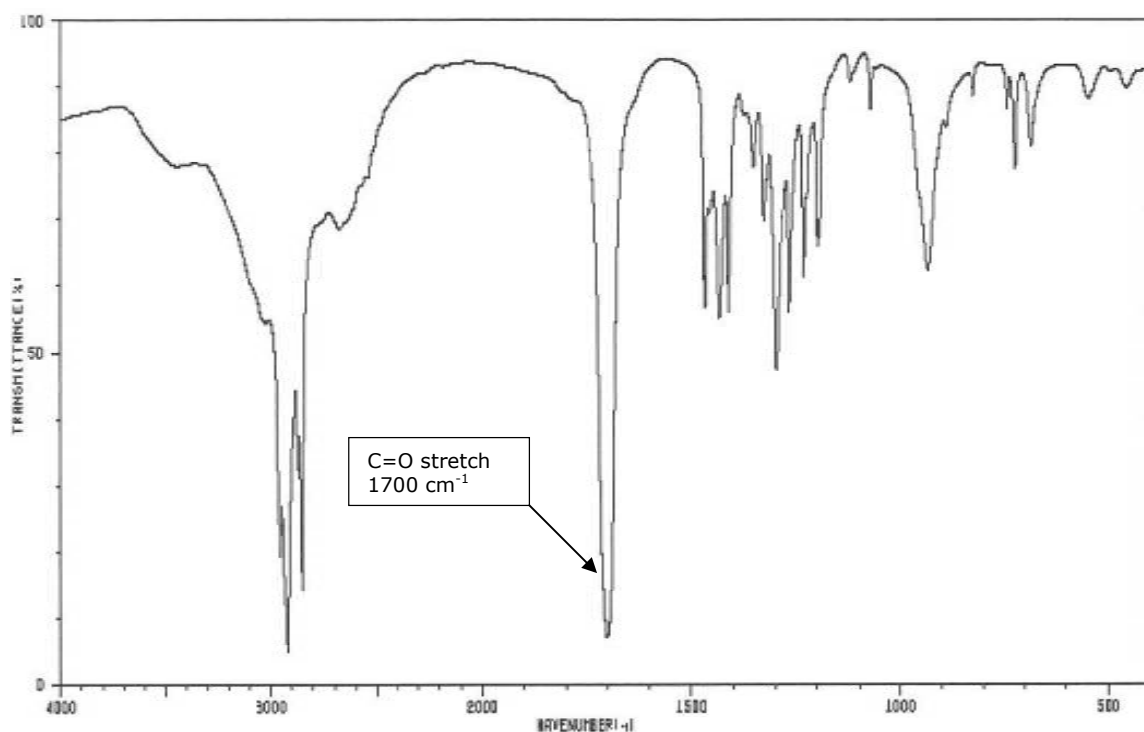


Fig. 4.13 Infrared spectrum of decanoic acid (KBr)⁹

Table 4.11 Infrared assignments of cobalt decanoate

Band (cm ⁻¹)	Assignment
2920, 2852	Aliphatic -CH stretches
1550	Asymmetric COO ⁻ stretch
1410	Symmetric COO ⁻ stretch
1299	Aliphatic -CH bend
1112	Aliphatic -CH rock
716	COO ⁻ bend

An interesting feature observed for the cobalt carboxylates is the breadth of the COO⁻ peaks. When our spectra are compared to spectra of various other carboxylates reported in the literature, the COO⁻ peaks appear broader than observed for many other compounds. This could indicate the formation of

polymeric structures or also possibly that multiple carboxylate bonding modes are found within the same structure⁷.

The separation of the asymmetric and symmetric COO^- stretching frequencies ($\Delta\nu$) was determined for each compound and used to generate information about the possible carboxylate bonding modes in each compound. The proposed structures are based on the findings of a comprehensive study by Stoilova et al⁶ of a range of metal acetates. The authors suggested that a separation of 105 – 140 cm^{-1} could be associated with monodentate bonding, 145 – 185 cm^{-1} could be associated with bidentate chelate bonding and 180 – 190 cm^{-1} could be an indication of bidentate bridging bonding, although values as high as 200 cm^{-1} have been observed. These values were *only proposed for acetates* and it is important to note that in this study we have extended these ideas to the higher carboxylates.

Table 4.12 shows the values of $\Delta\nu$ for the compounds and their proposed structure as per Stoilova's proposals⁶.

Table 4.12 $\Delta\nu$ for cobalt carboxylates

Compound	$\nu_{\text{COO}^- \text{ asym}}$ (cm^{-1})	$\nu_{\text{COO}^- \text{ sym}}$ (cm^{-1})	$\Delta\nu$ (cm^{-1})	Proposed structure
Acetate	1541	1389	152	Chelating
Propionate	1567	1403	164	Chelating
Butyrate	1560	1401	159	Chelating
Valerate	1551	1404	147	Chelating
Hexanoate	1563	1406	157	Chelating
Heptanoate	1548	1402	146	Chelating
Octanoate	1552	1414	138	Monodentate/Chelating

Nonanoate	1543	1406	137	Monodentate/Chelating
Decanoate	1550	1410	140	Monodentate/Chelating

The data suggests that a chelating mode of coordination is favoured by the shorter chain cobalt carboxylates ($C_2 - C_7$). The heavier cobalt carboxylates ($C_8 - C_{10}$) are on the threshold to give monodentate rather than chelating bonding modes. However based on the trend observed for the shorter cobalt carboxylates, it seems more likely that these compounds exhibit chelating coordination. Thus it appears that the general preference amongst the cobalt carboxylates is chelating coordination.

The structure of cobalt acetate has however been confirmed as monodentate¹⁰. This contradiction of our findings proves that Stoilova's ideas should be interpreted with caution when applied to our data. Ideally the proposed structures could be confirmed using single crystal X-ray diffraction. However, no crystals suitable for X-ray diffraction analysis could be obtained during the project (as discussed in section 4.2).

4.3.3 Thermal analysis

The thermal decomposition behaviour of the cobalt carboxylates has been explored using a combination of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectrometry (MS).

TGA evaluates mass changes as a function of temperature and DSC in turn shows changes in heat flow (or energy) as a function of temperature. The combination of these two techniques yields a powerful tool for thermal characterization. TGA can confirm which peaks in the DSC thermograms correspond to decompositions and which are unrelated to decomposition. The additional peaks in the DSC

thermograms could indicate phase changes, which in many cases for the carboxylates, is quite complex due to their phase rich behaviour⁷.

Mass spectrometry coupled to TGA (often abbreviated TG-MS) is a very useful tool to aid in the identification of decomposition products obtained when a compound is heated. Molecular ions and fragments that are evolved upon heating can be identified by their mass to charge ratio, or m/z value. This can help to shed light on the possible mechanisms of decomposition of the compound in question. However, elucidating exact decomposition mechanisms based on this information alone can be quite difficult. This is largely due to two reasons: (1) further degradation of organic molecules occurs in transit from the TG furnace to the mass spectrometer leading to break up of the molecular ions before they can be identified (2) mass fragments arising from the break up of molecular species often share common m/z values and it is impossible to determine how much of a particular fragment arises from which parent molecule without prior separation of the components.

(a) Cobalt acetate

Fig. 4.14 shows the TG and DTG profiles of cobalt acetate (dihydrate).

The TG profile (Fig. 4.14a) of cobalt acetate dihydrate in argon, shows that this compound decomposes via a three step process: In the first step, the acetate begins to lose its water of crystallization at $\sim 101^\circ\text{C}$ to yield an anhydrous intermediate. The second and third mass loss steps of 12.1% and 34% respectively yield a black powdery product. Gravimetric calculations (refer to appendix B for all gravimetric calculations) suggest that this product is CoO , as confirmed by literature^{8,11}.

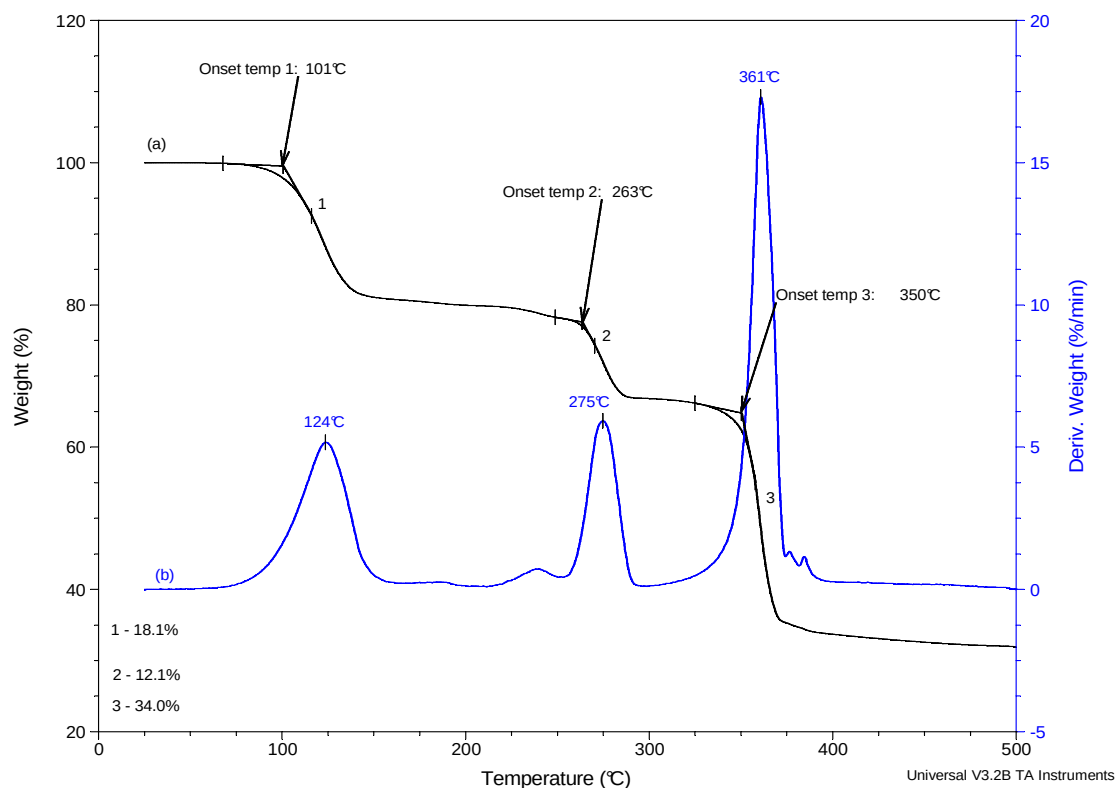


Fig. 4.14 (a) TG and (b) DTG profiles of cobalt acetate dihydrate (argon)

There is literature to suggest that acetic acid and acetic anhydride are evolved during the decomposition process, yielding two intermediate crystalline products $\text{Co}_6\text{O}(\text{CH}_3\text{COO})_{10}$ and $\text{Co}_3\text{O}(\text{CH}_3\text{COO})_4$ which ultimately decompose to CoO ¹². Other workers have suggested that acetaldehyde is liberated, forming a cobalt acetate hydroxide intermediate which then further decomposes to yield CoO and acetic acid as the main volatile product¹¹.

The mass spectrum obtained when cobalt acetate is heated in argon is shown in Fig. 4.15. The mass spectrum shows a plot of the ion current for various mass fragments against relative time in seconds. The mass fragments evaluated were chosen based on the possible decomposition products that may arise when cobalt acetate is heated and are summarized in Table 4.13. This data can be correlated to the temperatures on the TG profile since the number and frequency of cycles

recorded by the mass spectrometer correlates to the heating rate used on the TGA.

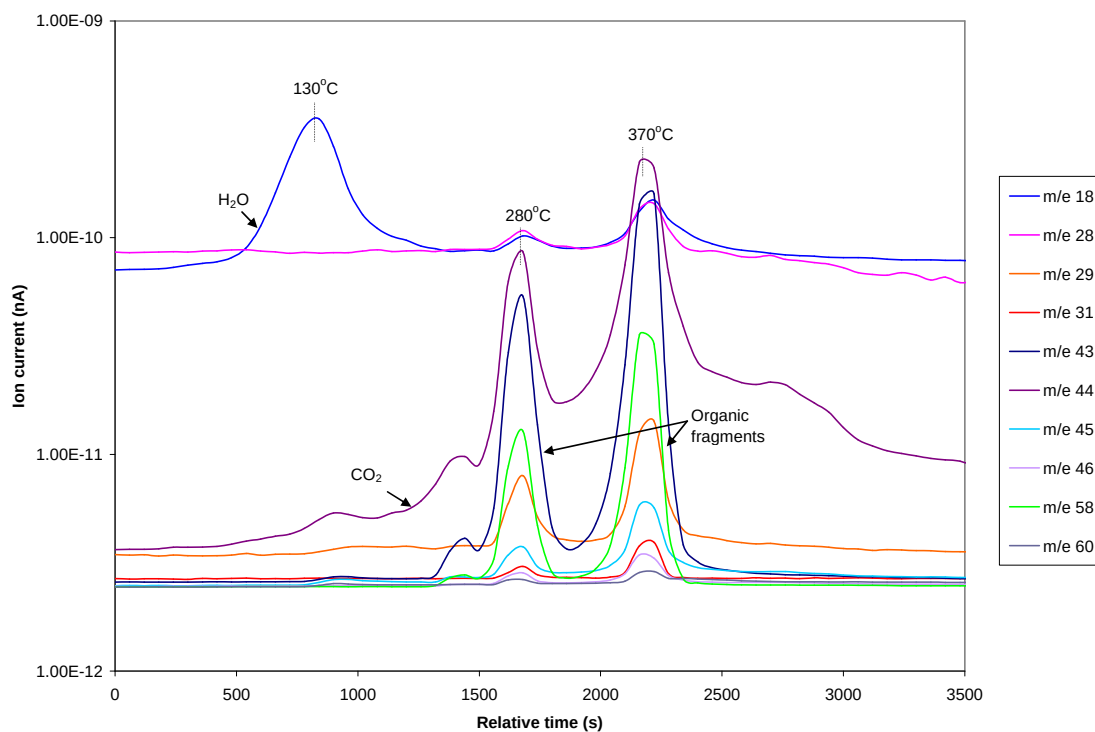


Fig. 4.15 Mass spectrum for cobalt acetate dihydrate heated at 10°C/min (argon)

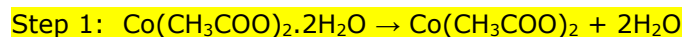
Table 4.13 Mass fragments evaluated for cobalt acetate dihydrate

Mass number (m/z)	Probable parent molecule	Key fragment
18	H ₂ O	H ₂ O ⁺
28	N ₂	N ₂ ⁺
	CO	CO ⁺
	CO ₂	CO ⁺
29	C _x H _y	C ₂ H ₅ ⁺
	C ₂ H ₄ O	CHO ⁺
31	C ₂ H ₅ OH	CH ₂ OH ⁺
43	C ₂ H ₄ O	C ₂ H ₃ O ⁺
	C ₃ H ₆ O	C ₂ H ₃ O ⁺
	CH ₃ COOH	C ₂ H ₃ O ⁺
44	CO ₂	CO ₂ ⁺

	C ₂ H ₄ O	C ₂ H ₄ O ⁺
45	C ₂ H ₅ OH	C ₂ H ₅ O ⁺
46	C ₂ H ₅ OH	C ₂ H ₅ OH ⁺
58	C ₃ H ₆ O	C ₃ H ₆ O ⁺
60	CH ₃ COOH	CH ₃ COOH ⁺

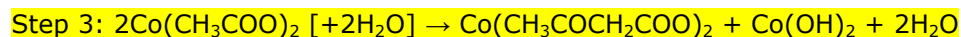
The data observed in the mass spectrum correlates well with the mass losses seen in the TG profile (Fig. 4.14a). The presence of an H₂O peak (m/z 18) at 140°C confirms that the first mass loss step is associated with dehydration. The other fragments observed in the spectrum suggest that the volatile products liberated during the second and third mass loss steps include acetic acid (m/z 43, 45, 60), acetaldehyde (m/z 29, 43, 44), acetone (m/z 43, 58) and possibly traces of ethanol (m/z 31, 45, 46). Although the molecular ion associated with acetic anhydride was not observed, acetic anhydride can not necessarily be excluded as a decomposition product since ions arising from fragmentation of this compound were observed (m/z 43).

Based on the information revealed in the mass spectrum in Fig. 4.15 as well as gravimetric calculations, a plausible decomposition mechanism is discussed step by step^{11,13}:



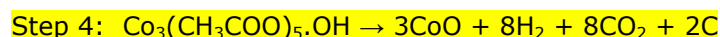
Step 1 is associated with dehydration and yields an anhydrous intermediate. The presence of a water peak (m/z 18) at 140°C in the mass spectrum corroborates this idea.

In steps 2 and 3 the anhydrous intermediate, $\text{Co}(\text{CH}_3\text{COO})_2$, undergoes a set of parallel-consecutive reactions with the water generated in step 1.



Step 2 shows the formation of a cobalt acetate hydroxide intermediate, $\text{Co}_3(\text{CH}_3\text{COO})_5.\text{OH}$, liberating water and acetic acid¹³. Step 3 shows the formation of an acetyl cobalt acetate intermediate, $\text{Co}(\text{CH}_3\text{COCH}_2\text{COO})_2$, liberating water¹¹. There is evidence in the mass spectrum (Fig. 4.15) that supports the idea that both water (m/z 18) and acetic acid (m/z 43, 45, 60) is released in the second decomposition step observed at $\sim 280^\circ\text{C}$.

The intermediate products, cobalt acetate hydroxide and acetyl cobalt acetate, then decompose via another set of parallel-consecutive reactions (steps 4 and 5).



Step 4 shows the decomposition of cobalt acetate hydroxide to CoO , H_2 and CO_2 ¹³. A large CO_2 peak (m/z 44) observed in the mass spectrum, corresponding to the third decomposition step at 370°C , supports this theory. Step 5 shows the parallel decomposition of the acetyl cobalt acetate intermediate to yield CoO , acetaldehyde, water and CO ¹¹. The presence of water (m/z 18), CO (m/z 28) and acetaldehyde (m/z 29, 43) peaks in the mass spectrum for this step observed at 370°C provide evidence in support of this theory.

Endotherms observed in the DSC thermogram of cobalt acetate dihydrate (Fig. 4.16) correspond well to mass losses observed using TG (see Fig. 4.14a). The first endotherm at 128°C is due to the dehydration of the sample. The second and third endotherms correspond to the two decomposition steps observed in the TG. Although it is unclear from the DSC profile where the melting point of cobalt acetate occurs, melting point measurements in the lab revealed that this compound melts at ~ 230°C suggesting that the shoulder to the right of the first endotherm (Indicated as * in Fig. 4.16) could correspond to the melting point of the sample.

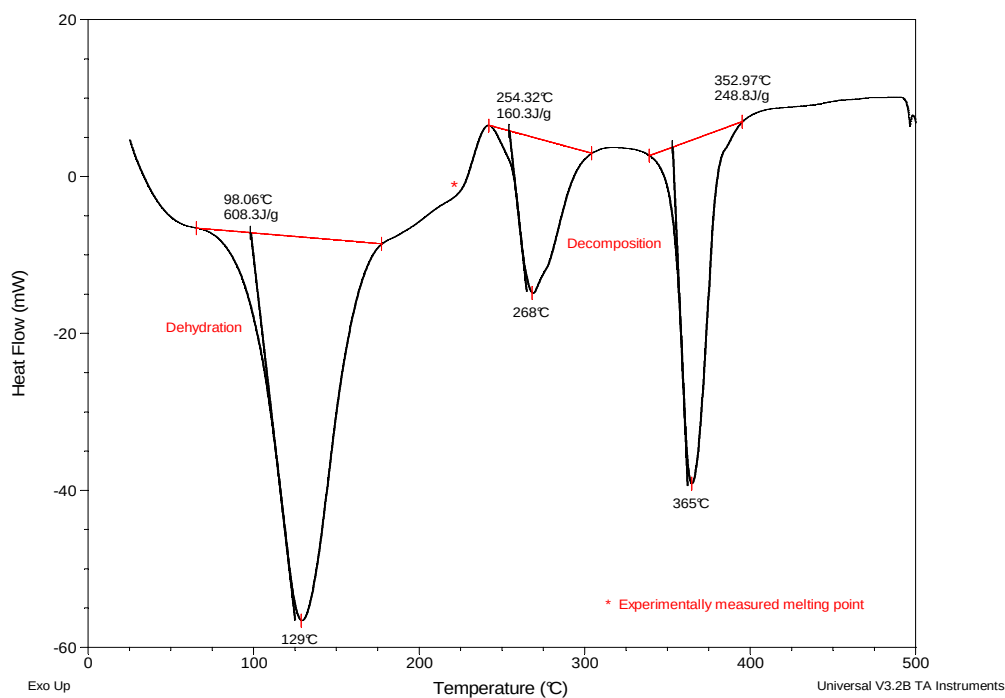


Fig. 4.16 DSC thermogram of cobalt acetate dihydrate (argon)

(b) Cobalt propionate

The TG and DTG profiles for cobalt propionate are shown in Fig. 4.17.

The TG profile for cobalt propionate in argon (Fig. 4.17a) reveals that this compound follows a single step decomposition process. Since this compound is

anhydrous, the mass loss expected for the formation of CoO is 63.4% and that for metallic cobalt 71.2%. Since the observed mass loss of 72.2% correlates closely with the mass loss expected for the formation of metallic cobalt, it appears that metallic cobalt is formed during this reaction.

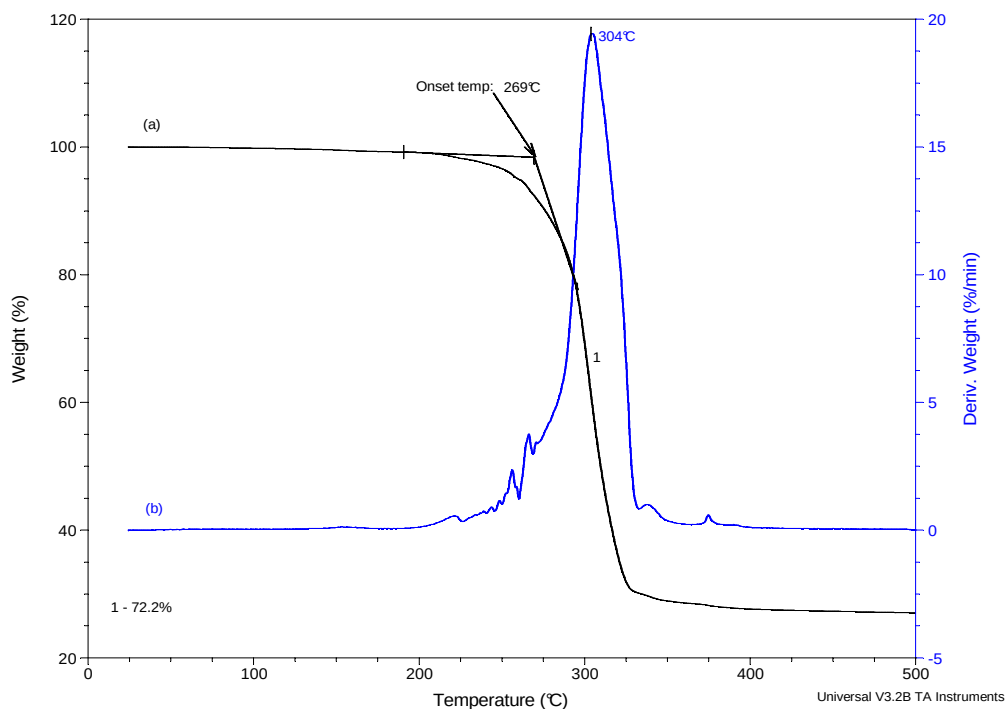


Fig. 4.17 (a) TG and (b) DTG profiles of cobalt propionate (argon)

The formation of metallic cobalt in inert atmosphere is unexpected since, firstly the acetate formed CoO under the same conditions and secondly, there are reports that cobalt propionate yields CoO under inert conditions¹⁴.

Heating in a reducing atmosphere such as hydrogen would yield cobalt metal as a decomposition product, as confirmed in the literature¹¹. One possible explanation is that, assuming the decomposition mechanism of cobalt propionate is similar to that of cobalt acetate (refer to p. 79 – 80), H₂ is generated as a gas product

during the decomposition process in inert conditions and may then facilitate the reduction of CoO to Co as a secondary process¹³.

Since decomposition in air would not generate H₂ as a product, the plausibility of this theory was explored by performing an additional experiment: heating cobalt propionate in air. The TG and DTG profiles are shown in Fig. 4.18.

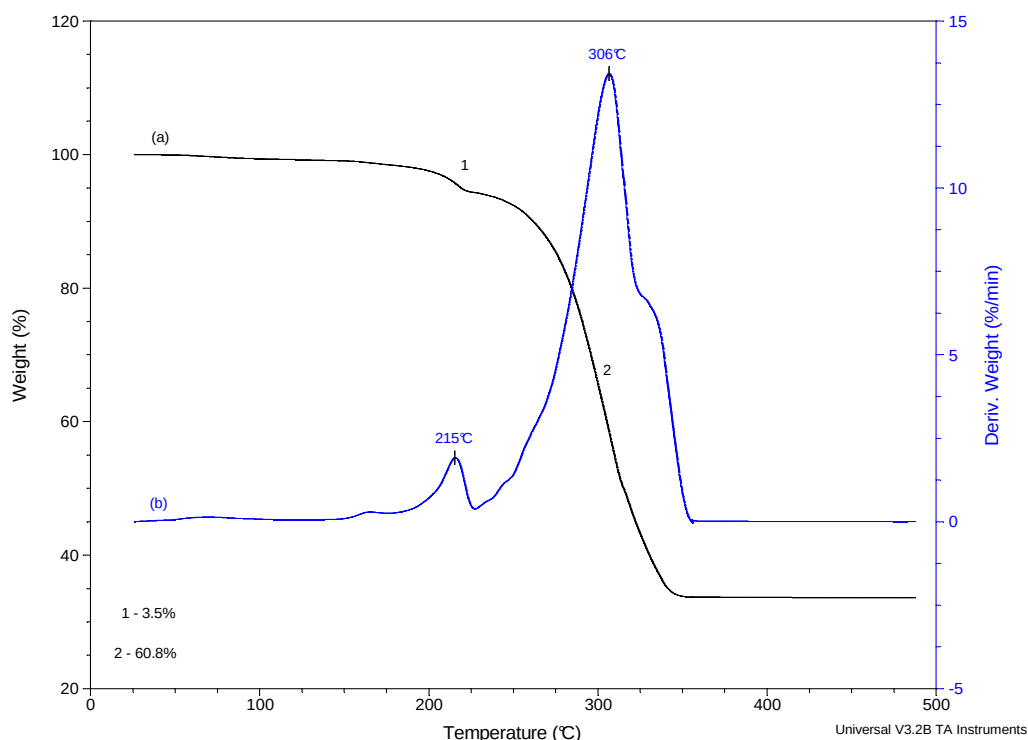


Fig. 4.18 (a) TG and (b) DTG profiles of cobalt propionate (air)

Fig. 4.18 reveals that when heated in air, the total mass loss observed for cobalt propionate is 64.3% which correlates well with the mass loss expected to accompany the formation of CoO (63.4%). The fact that our sample formed cobalt oxide in air supports the idea that metallic cobalt formation under argon may be a secondary process caused by the reduction of CoO by H₂ formed during the decomposition process.

Another possible explanation to account for the formation of metallic cobalt is based on claims that cobalt carboxylate species yield metallic cobalt when heated rapidly in either a limited air supply or under nitrogen¹⁵. To determine whether this idea could account for our findings, additional TG data was obtained using slower heating rates of 2 and 5°C/min (Fig. 4.19a and b). In both instances the final mass loss observed was consistent with the mass loss observed when the sample was originally heated at 10°C/min. This result would seem to suggest that the heating rate does not have a marked effect on the final decomposition product.

Based on the results observed, it would seem that the more plausible explanation to account for the formation of metallic cobalt in cobalt propionate is that CoO is reduced in a secondary process by H₂ formed during decomposition.

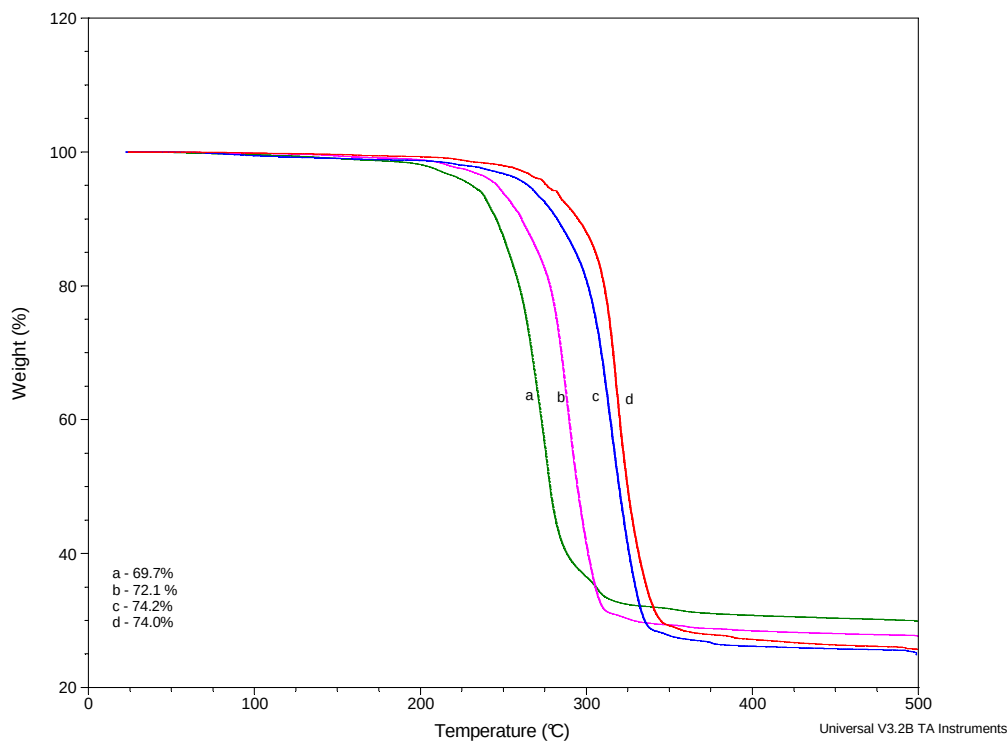


Fig. 4.19 TG profiles of cobalt propionate heated at (a) 2°C/min, (b) 5°C/min, (c) 15°C/min and (d) 20°C/min (argon)

Two additional TG experiments were undertaken using a heating rate of 15 and 20°C/min (See Fig. 4.19c and d). The average mass loss observed for the five experiments was 72.4%. The DTG profiles for each experiment were consistent with the DTG profile observed when cobalt propionate was heated at 10°C/min (Fig. 4.17b) i.e. single peaks and as expected the $T_{\max}$ values are shifted to higher values as the heating rate is increased.

The data from these five thermal experiments was used to estimate the activation energy for the decomposition of cobalt propionate using the Kissinger method¹⁶.

The Kissinger equation:

$$E_a \beta (RT_{\max}^2) = Ae^{-E_a/RT_{\max}} \quad (1)$$

Where: A = Frequency factor

β = Heating rate (K/min)

E_a = Activation energy (J.mol⁻¹)

R = Gas constant (8.315 J.K⁻¹.mol⁻¹)

$T_{\max}$ = Corresponding temperature at DTG peak maxima (See Fig 4.16b)

Can be converted by taking the natural logarithm of equation (1):

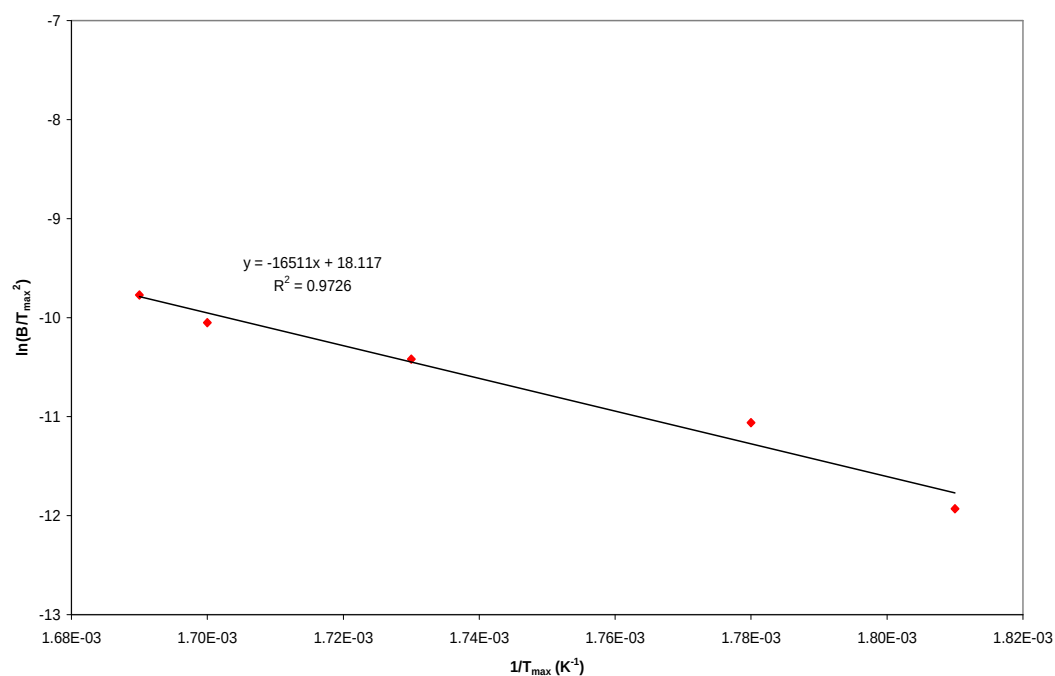
$$\ln (\beta/T_{\max}^2) = -\ln (AR/E_a) + E_a/RT_{\max} \quad (2)$$

Thus the activation energy, E_a , can be obtained by plotting $\ln (\beta/T_{\max}^2)$ against $1/T_{\max}$, where the slope of the straight line is equal to $-E_a/R$.

Data for our thermal experiments are summarized in Table 4.14 and the corresponding kinetic plot is illustrated in Fig. 4.20.

Table 4.14 Data for non-isothermal TG experiments of cobalt propionate

β (K/min)	$T_{\max}$ (K)	$1/T_{\max}$ (K^{-1})	$\ln(\beta/T_{\max}^2)$
2	551	1.81×10^{-3}	- 11.93
5	563	1.78×10^{-3}	- 11.06
10	579	1.73×10^{-3}	- 10.42
15	589	1.70×10^{-3}	- 10.05
20	593	1.69×10^{-3}	- 9.77

**Fig. 4.20** Kinetic plot for the decomposition of cobalt propionate

As stated previously, the slope of the straight line is used to calculate the activation energy, E_a , using the following relationship:

$$\text{Slope} = -E_a/R$$

$$\text{Thus: } E_a = - (\text{Slope} \times R)$$

$$E_a = - (-16\,511\text{ K} \times 8.315\text{ J.K}^{-1}.\text{mol}^{-1})$$

$$E_a = 1.373 \times 10^5\text{ J.mol}^{-1} \equiv 137.3\text{ kJ.mol}^{-1}$$

The activation energy for the decomposition of cobalt propionate is $\sim 137.3\text{ kJ.mol}^{-1}$. This large value suggests that cobalt propionate has a high thermal stability.

The DSC thermogram of cobalt propionate is shown in Fig. 4.21

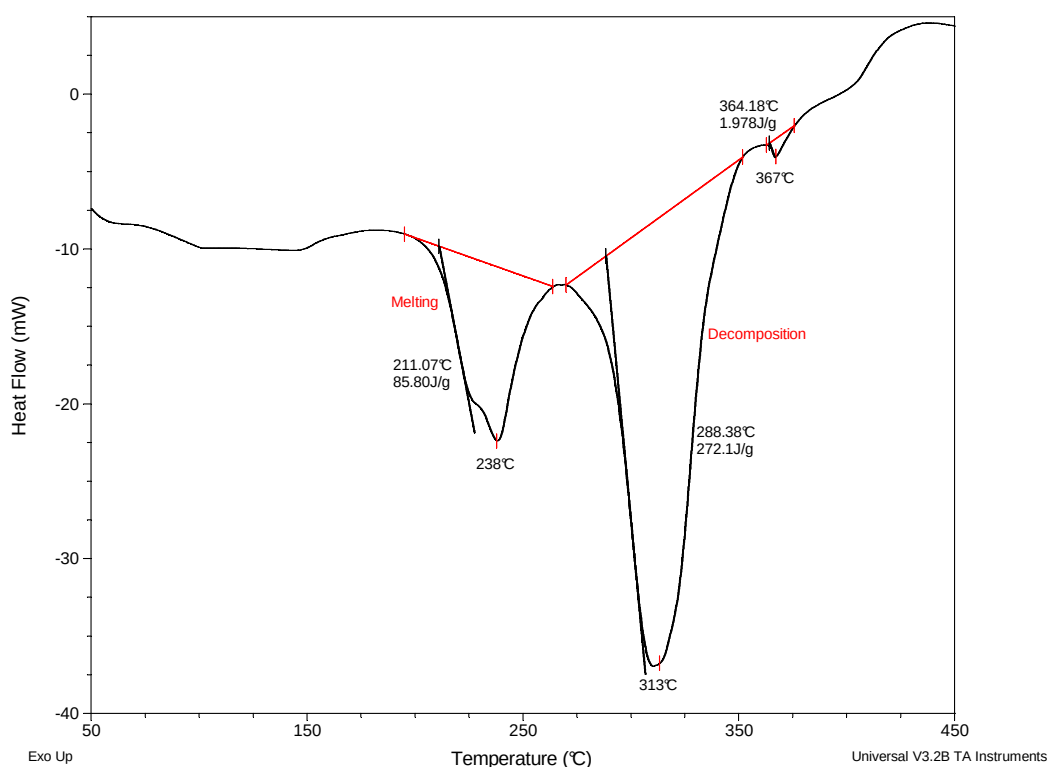


Fig. 4.21 DSC thermogram of cobalt propionate (argon)

Four endotherms are observed in the DSC thermogram of cobalt propionate. The first peaks correspond to the melting point of the compound. Separate determination of the melting point for cobalt propionate using a melting point apparatus, revealed a gradual phase change commencing at $\sim 228^\circ\text{C}$. The second larger endotherm at 313°C corresponds to the mass loss observed in the TG

profile, confirming that this endotherm corresponds to decomposition. A third significantly smaller endotherm at 367°C does not correspond to any measurable mass loss. This could be a phase change of metallic cobalt to a high temperature cubic form as cobalt is known to exhibit complex polytypic behaviour¹⁷.

The mass spectrum obtained when cobalt propionate is heated is shown in Fig. 4.22. The mass fragments evaluated are summarized in table 4.15.

Table 4.15 Mass fragments evaluated by TG-MS

Mass number (m/z)	Probable parent molecule	Key fragment
18	H ₂ O	H ₂ O ⁺
28	N ₂	N ₂ ⁺
	CO	CO ⁺
	CO ₂	CO ⁺
29	C _x H _y	C ₂ H ₅ ⁺
	C ₃ H ₆ O	CHO ⁺
31	C ₃ H ₇ OH	CH ₂ OH ⁺
43	C ₂ H ₄ O	C ₂ H ₃ O ⁺
	C ₃ H ₆ O	C ₂ H ₃ O ⁺
	CH ₃ COOH	C ₂ H ₃ O ⁺
44	CO ₂	CO ₂ ⁺
	C ₂ H ₄ O	C ₂ H ₄ O ⁺
45	C ₂ H ₅ COOH	C ₂ H ₅ O ⁺
57	C ₅ H ₁₀ O	C ₃ H ₅ O ⁺
58	C ₃ H ₆ O	C ₃ H ₆ O ⁺
74	C ₂ H ₅ COOH	C ₂ H ₅ COO ⁺
86	C ₅ H ₁₀ O	C ₅ H ₁₀ O ⁺

The data reveals that the main components evolved during the decomposition of this compound are CO₂ (m/z 44), acetone (m/z 43, 58), propionaldehyde (m/z 29, 58) and 3-pentanone (m/z 57, 86). Our findings concur with the results published by Barnes et al, wherein the authors describe similar results when

using TG-GLC-MS to investigate the decomposition of calcium propionate¹⁸. Barnes and his co-workers proposed that calcium propionate decomposes via calcium carbonate to CaO via a set of radical reactions which generate 3-pentanone as the major gaseous product. Since our TG profile reveals a single step decomposition process, it seems unlikely that the decomposition mechanism of cobalt propionate follows a similar pattern i.e. no carbonate intermediate is formed.

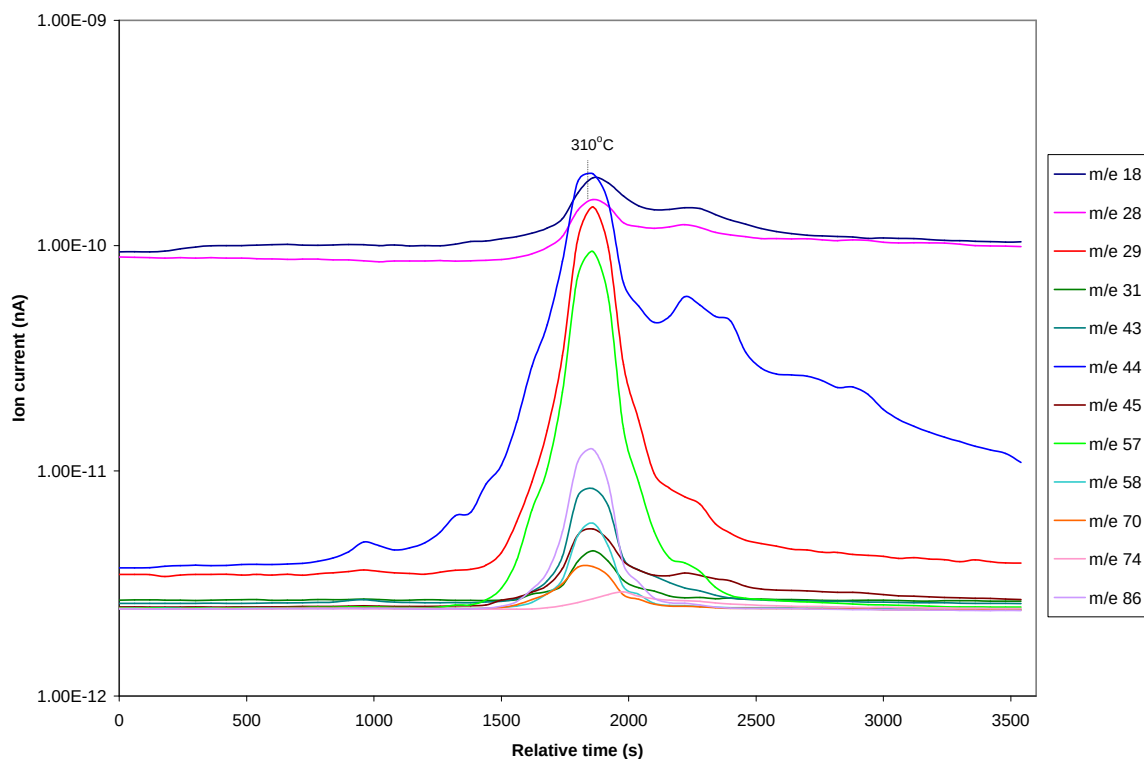


Fig. 4.22 Mass spectrum for cobalt propionate heated at 10°C/min (argon)

(c) Cobalt butyrate

The TG and DTG profiles of cobalt butyrate are shown in Fig. 4.23.

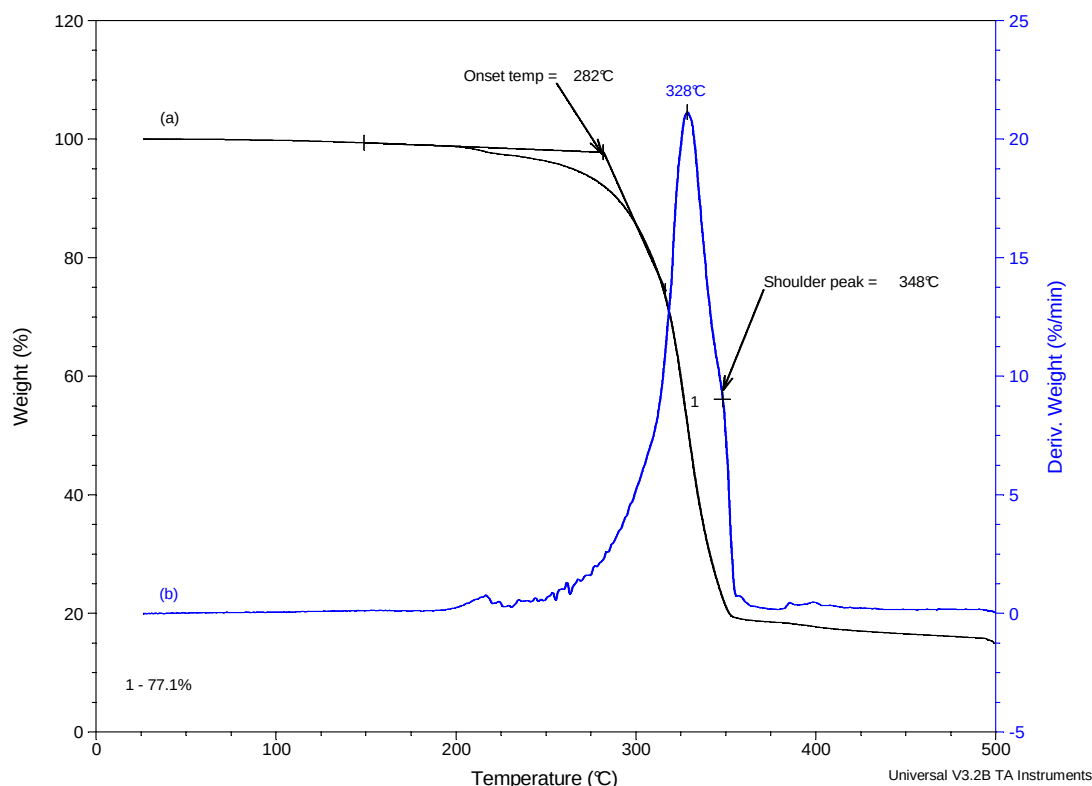


Fig. 4.23 (a) TG and (b) DTG profiles of cobalt butyrate (argon)

The TG profile of cobalt butyrate (Fig. 4.23a) reveals a $\sim 3\%$ mass loss upon heating which is most likely due to the loss of adsorbed moisture on the sample. A total mass loss of 77.1% is observed. For pure anhydrous cobalt butyrate, CoO formation would be accompanied by a 67.8% mass loss. Similarly, 74.1% mass loss is expected when metallic cobalt is formed. Thus the observed mass loss corresponds to the mass loss expected for metallic cobalt formation, bearing in mind that the initial 3% mass loss is not due to the sample decomposition and that the actual mass loss due to decomposition is actually $\sim 74.1\%$.

The DTG profile (Fig. 4.23b) reveals a shoulder peak at 348°C on the main decomposition peak. This shoulder indicates that the decomposition reaction speeds up at this point and could be as a result of the reaction being interrupted by caking (fusion) prior to this point in the process¹⁵.

No mass spectrum was recorded for this compound but in an article published by Leicester and Redman, the authors reported that the condensable products of cobalt butyrate decomposition are mainly butyrone $\text{CO}(\text{C}_3\text{H}_7)_2$ and a little butyric acid¹⁵. They claim that the high yield of ketone results from the breakdown of acid or acid anhydride in the presence of the solid decomposition residue.

Fig. 4.24 shows the DSC thermogram obtained for cobalt butyrate.

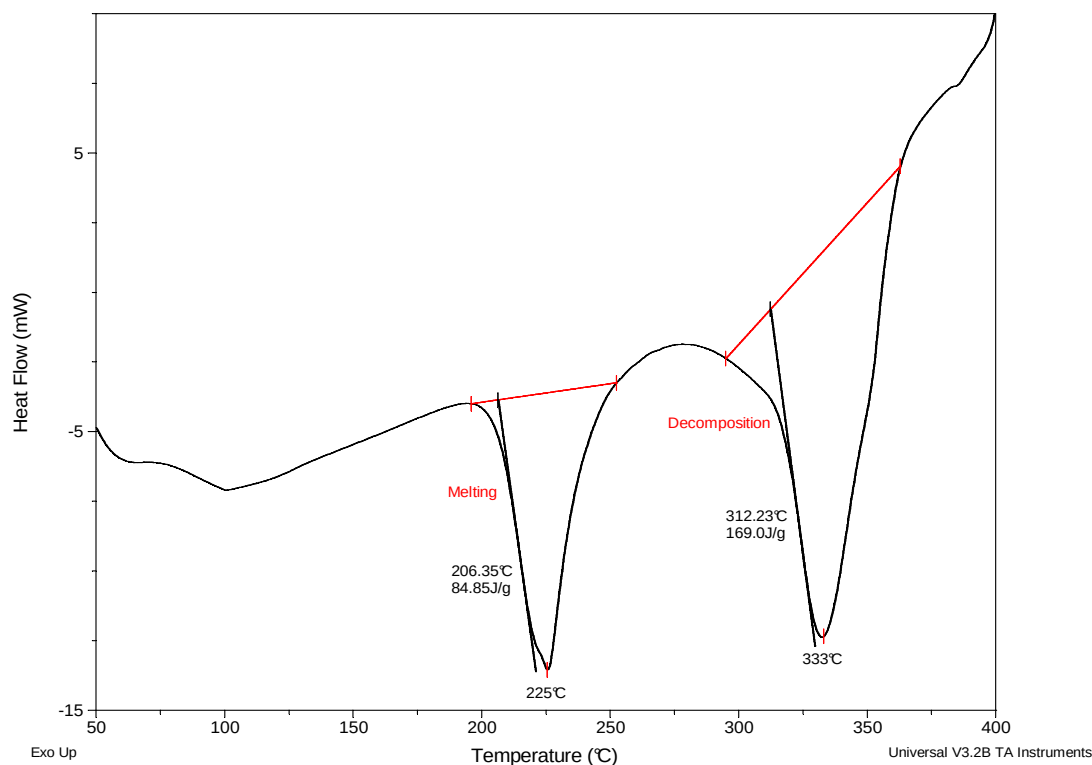


Fig. 4.24 DSC thermogram of cobalt butyrate (argon)

The DSC thermogram shows two endothermic peaks. The first endotherm at 225°C is the confirmed melting point of the compound (measured at ~220°C with a melting point apparatus). At 333°C decomposition takes place as indicated by the second slightly larger endotherm which correlates with the 77% mass loss observed in the TG profile (see Fig. 4.23a).

(d) Cobalt valerate

Fig. 4.25 shows the TG and DTG profiles for cobalt valerate.

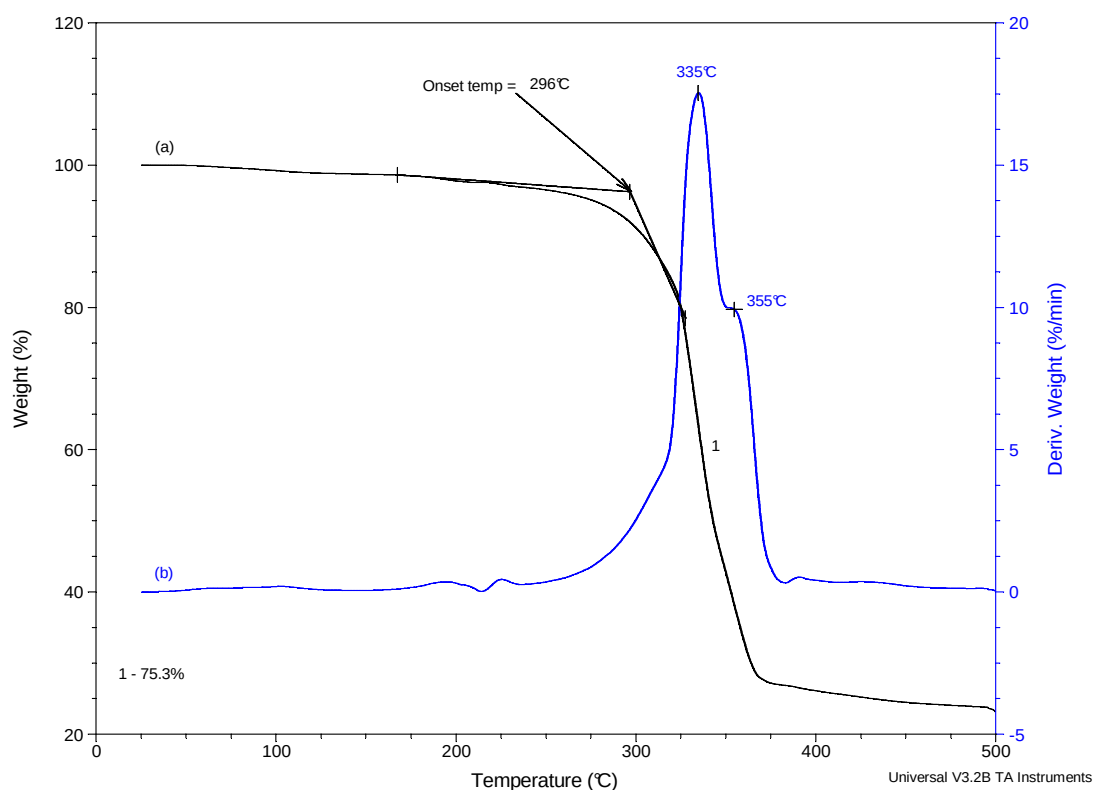


Fig. 4.25 (a) TG and (b) DTG profiles of cobalt valerate (argon)

The TG profile of cobalt valerate (Fig. 4.25a) also reveals a ~3% mass loss upon heating which is most likely due to the loss of adsorbed moisture on the sample. A total mass loss of 75.3% is observed. Calculations show that the expected mass loss for the formation of metallic cobalt is 77.4% for pure anhydrous cobalt valerate. Similarly CoO formation would be accompanied by a 71.3% mass loss. Thus, bearing in mind that the initial 3% mass loss is not due to the sample decomposition and that the actual mass loss due to decomposition is actually 72.3%, the observed mass loss correlates to the expected mass loss for CoO formation.

The DTG profile (Fig. 4.25b) shows a two step decomposition process. Two peaks are observed at 335 and 355°C. The splitting of the DTG peak may be due to the formation of short-lived unstable intermediates which subsequently decompose to CoO. It could also be a result of complex physical behaviour exhibited by the compound as there have been reports in literature indicating that cobalt carboxylates tend to cake badly when heated¹⁵ i.e. fusion occurs forming a crust or diffusional layer that results in interruptions in the decomposition process.

Fig. 4.26 shows the DSC thermogram for cobalt valerate

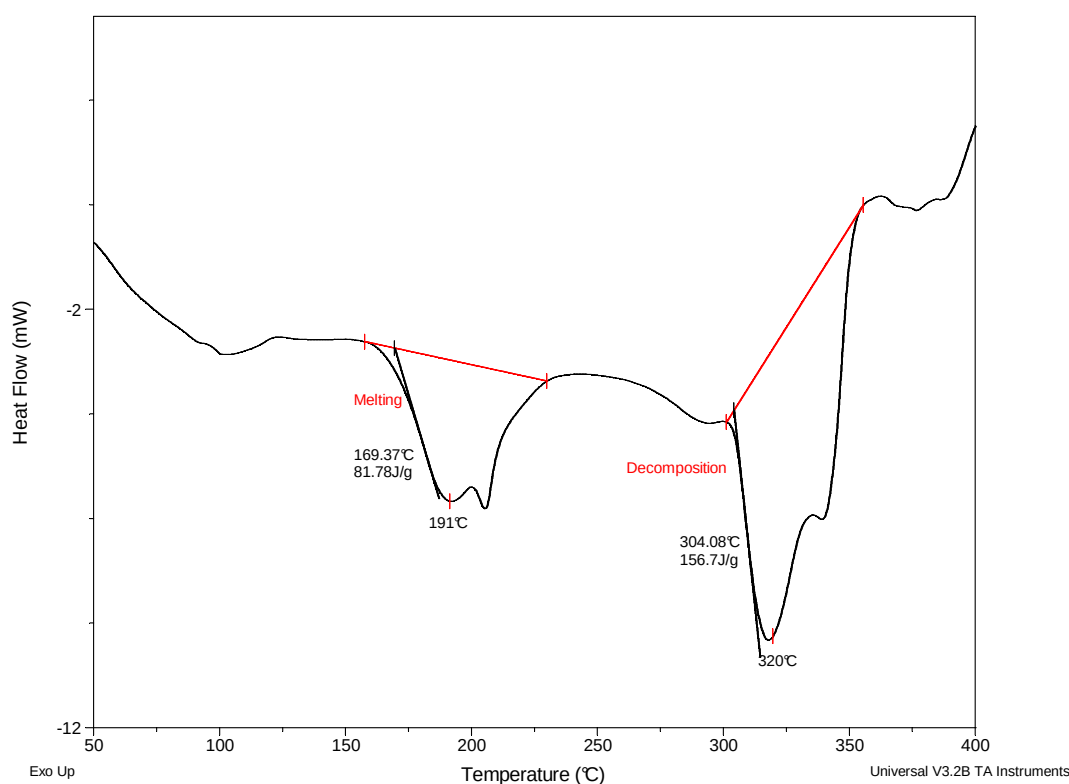


Fig. 4.26 DSC thermogram of cobalt valerate (argon)

Four endotherms are identified in the DSC thermogram of cobalt valerate. Melting point measurements done in the lab showed that this compound melts at ~192°C, confirming that the first peak at 191°C corresponds to melting of the compound. The breadth of this peak as well as the fact that the peak is split suggests that

this compound melts gradually, alluding to the idea that the cobalt carboxylates cake when heated¹⁵. The second endotherm at 320°C corresponds to the 71 % mass loss observed in the TG profile (Fig. 4.25a), confirming that this corresponds to decomposition. A shoulder observed on this peak correlates with the peaks observed in the DTG profile (Fig. 4.25b), confirming that decomposition takes place in two steps.

The mass spectrum obtained when cobalt valerate is heated is shown in Fig. 4.27. From the mass fragments observed in the mass spectrum, it becomes evident that cobalt valerate decomposes to yield primarily valeraldehyde (m/z 27, 29, 58, 57, 55) and some 2-pentanone (m/z 43, 58, 71) and 3-pentanone (m/z 29, 57). Traces of valeric acid also present. A large quantity of CO₂ is liberated. No literature is available on the decomposition of valerates for comparative purposes.

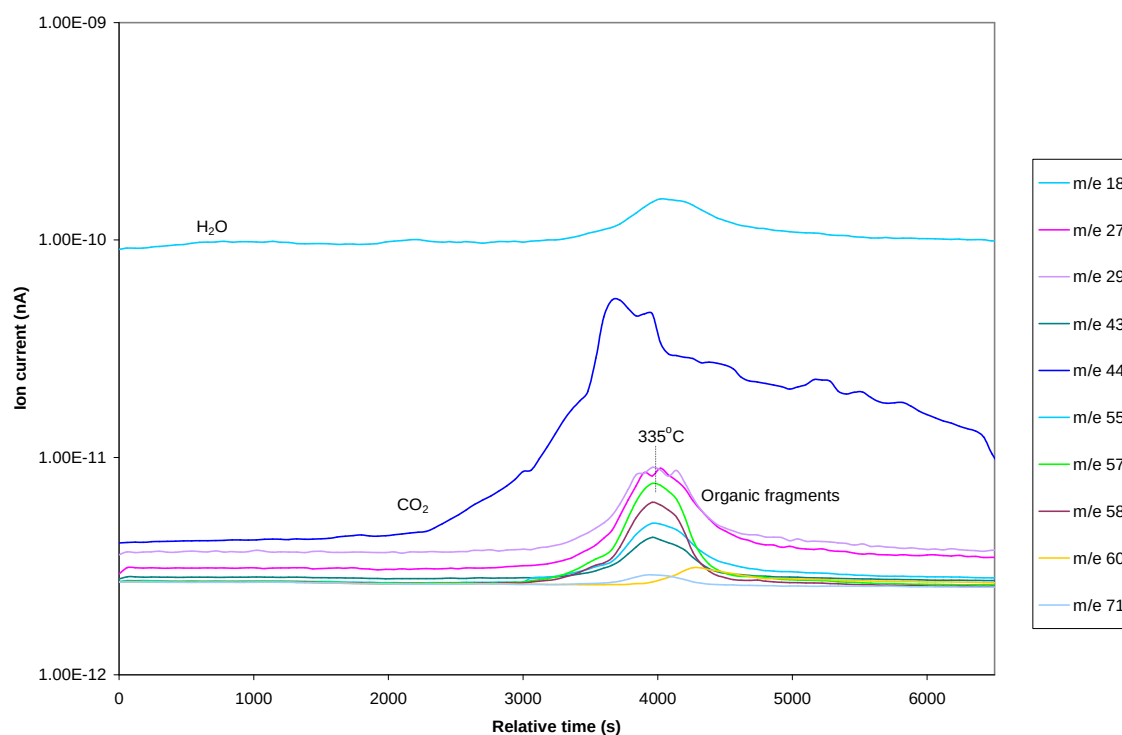


Fig. 4.27 Mass spectrum of cobalt valerate heated at 10°C/min (argon)

(e) Cobalt hexanoate

The TG and DTG profiles for cobalt hexanoate are illustrated in Fig. 4.28.

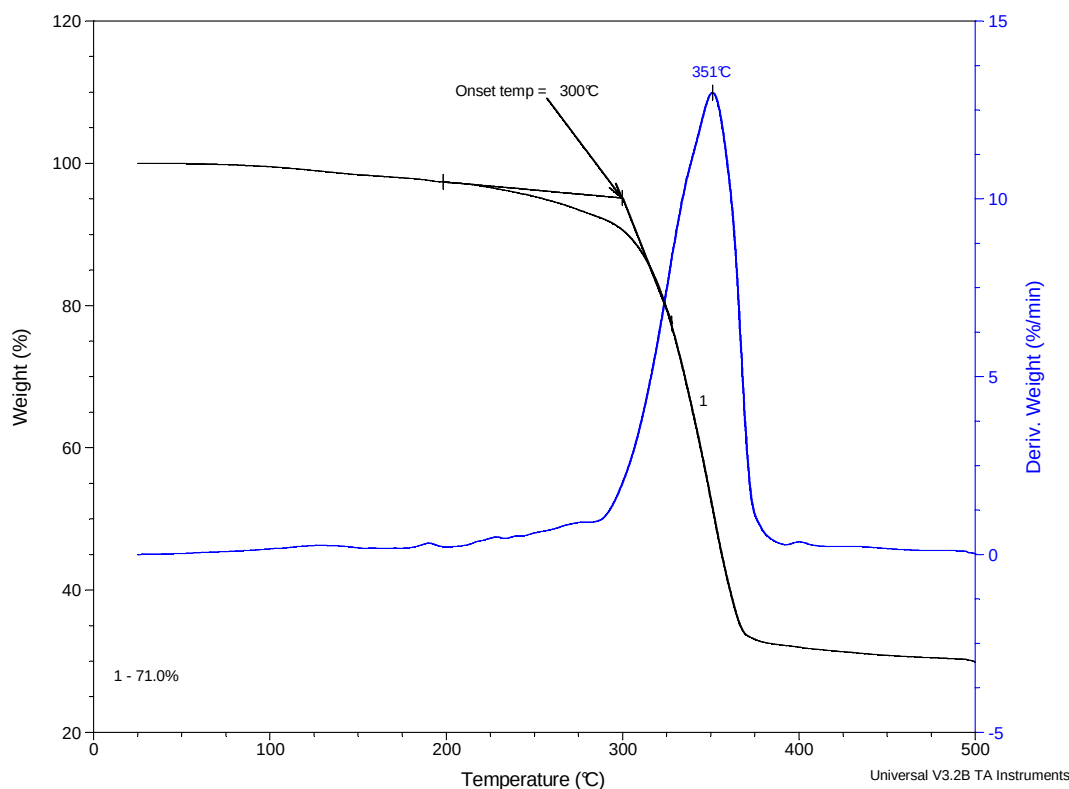


Fig. 4.28 (a) TG and (b) DTG profiles of cobalt hexanoate (argon)

This compound decomposes via a single step and appears to contain no adsorbed moisture or water of crystallization. The mass loss expected when metallic cobalt is formed is 79.6%. Since this value does not correlate with the observed mass loss of 71%, it seems more likely that cobalt hexanoate forms CoO upon decomposition (expected mass loss = 74%). This analysis was repeated in triplicate to verify the findings and all three TG experiments were in good agreement. The average mass loss observed was 71% (as indicated in Fig. 4.28).

The DSC thermogram for cobalt hexanoate is shown in Fig. 4.29.

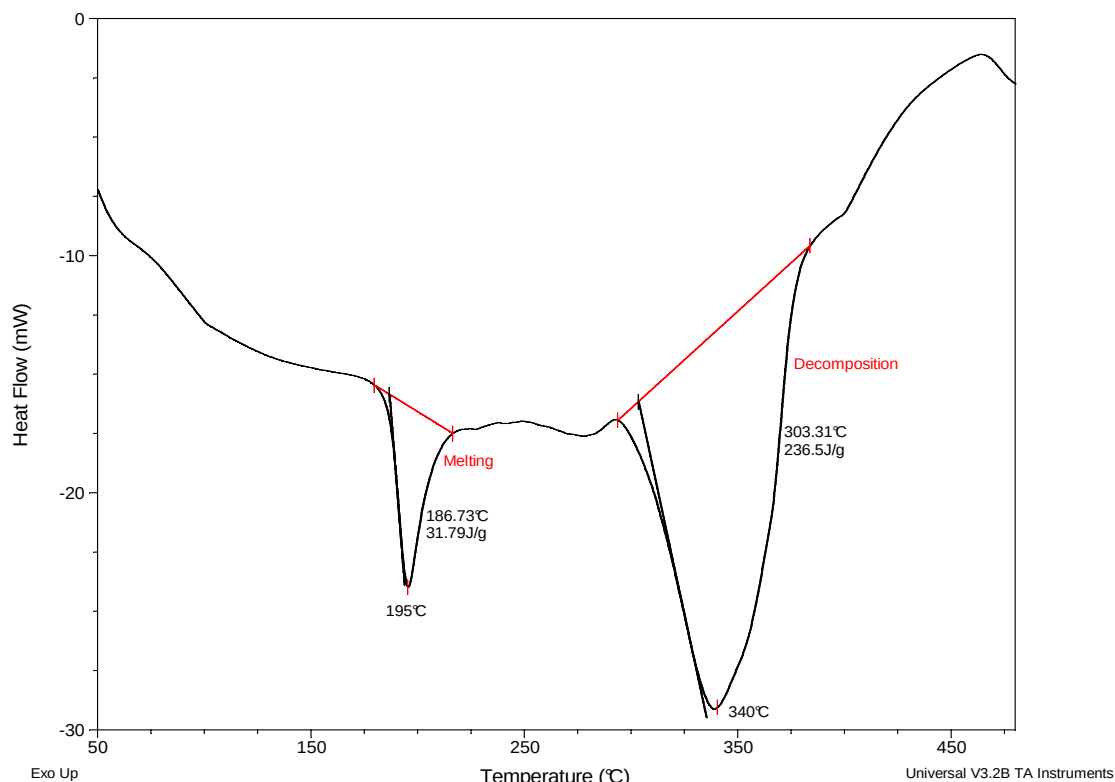


Fig. 4.29 DSC thermogram of cobalt hexanoate (argon)

The DSC thermogram of cobalt hexanoate (Fig. 4.29) shows two endothermic events. The first thermal event at 195°C corresponds to the melting point of this compound, as revealed via separate melting point measurements (~201°C). The second thermal event at 340°C corresponds to the observed mass loss in the TG profile (see Fig. 4.28a), confirming that this is the decomposition endotherm.

(f) Cobalt heptanoate

The TG and DTG profiles of cobalt heptanoate are shown in Fig. 4.30.

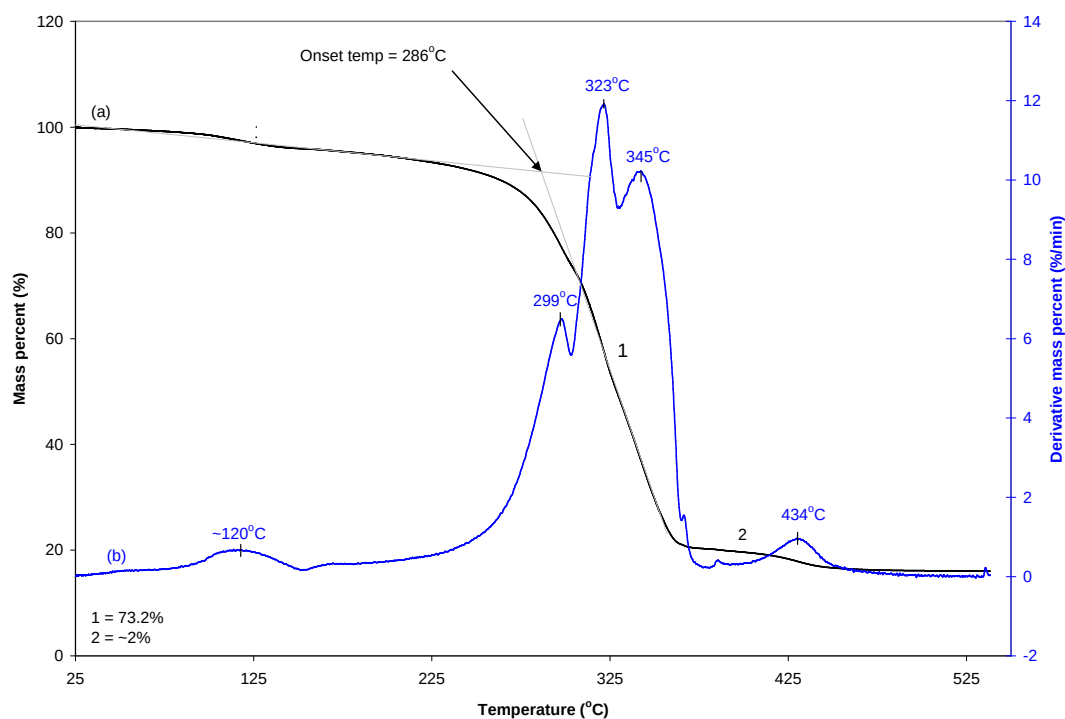


Fig. 4.30 (a) TG and (b) DTG profiles of cobalt heptanoate (argon)

The TG profile of this compound (Fig. 4.30a) reveals a small mass loss of $\sim 2\%$ upon heating which corresponds to a small peak in the DTG profile (Fig. 4.30b) at 120°C . This could be attributed to some residual moisture in the sample. Two mass loss steps are observed: 73.2% commencing at 286°C and $\sim 2\%$ at 434°C . The total mass loss observed is 77.2% . According to gravimetric calculations this mass loss correlates with the mass loss expected to accompany CoO formation (76.4%).

The DTG curve of this compound (Fig. 4.30b) displays multiple peaks. This information suggests that a number of intermediate species may be formed during the decomposition process. Alternatively these spikes in the DTG profile could result from the release of gaseous decomposition products from the bubbling melt that forms as the sample is heated¹⁸. A third possibility, as discussed previously, is caking of the sample¹⁵ and if in fact the TG experiments

are stopped at various intervals during the heating cycle, the sample reveals that clumps of solid material are mixed with the melt. This observation supports the idea that caking occurs in these samples.

The DSC thermogram of cobalt heptanoate is shown in Fig. 4.31.

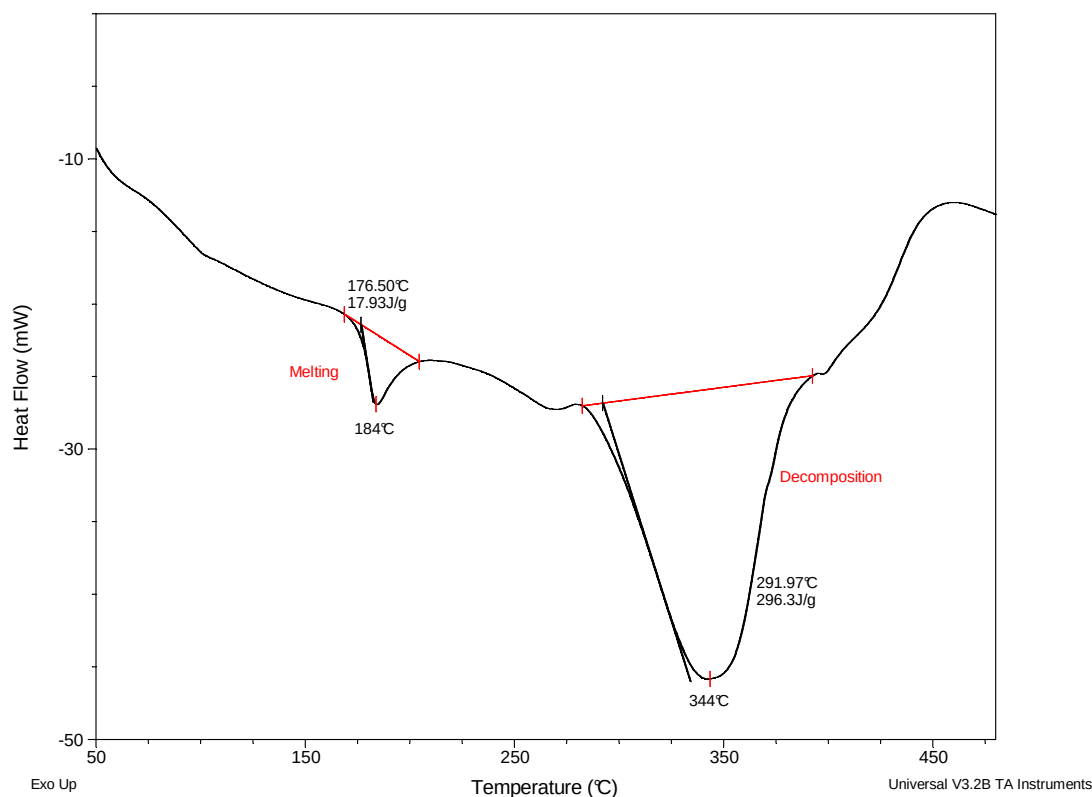


Fig. 4.31 DSC thermogram of cobalt heptanoate (argon)

Two endotherms are observed in the DSC thermogram of cobalt heptanoate (Fig. 4.31). The first endotherm at 184°C most likely corresponds to the melting point of the sample but has not been confirmed by separate melting point measurements. The second endotherm at 344°C corresponds to the mass loss observed in the TG profile (Fig. 4.30a) and corresponds to decomposition. This peak is very broad and most likely consists of a number of smaller peaks that overlap.

(g) Cobalt octanoate

Fig. 4.32 shows the TG and DTG profiles of cobalt octanoate.

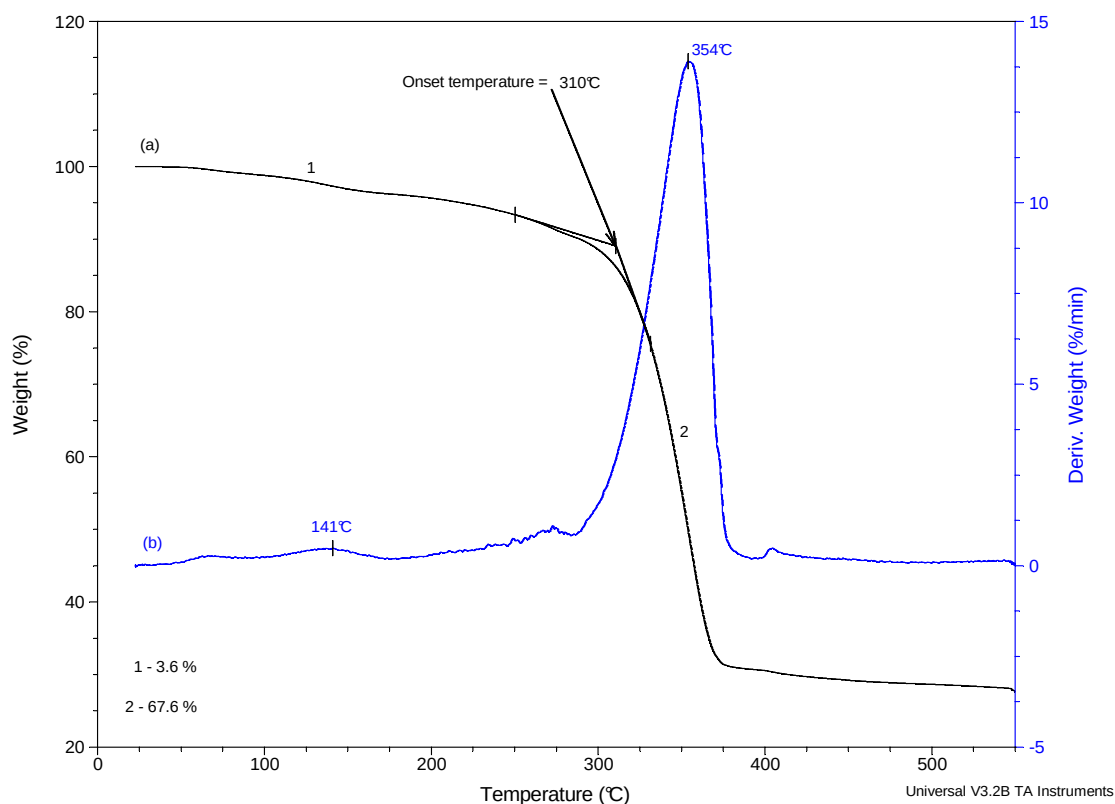


Fig. 4.32 (a) TG and (b) DTG profiles of cobalt octanoate (argon)

The TG profile of cobalt octanoate shows a gradual mass loss of ~4% as heating is commenced. This mass loss is attributed to one mole of water. A further mass loss of 68% is observed, commencing at 310°C. For pure cobalt octanoate a mass loss of 78.3% corresponds to CoO formation. Thus the total mass loss of ~72% observed for this sample could suggest that a minor impurity is present in the sample. Since no traces of residual acid were evident from the infrared spectrum of the sample, the impurity is most likely CoCO_3 . It is however tricky to assign the principal band for CoCO_3 definitively as it occurs in the same region as the symmetrical COO^- stretch.

Fig. 4.33 illustrates the DSC thermogram for cobalt octanoate.

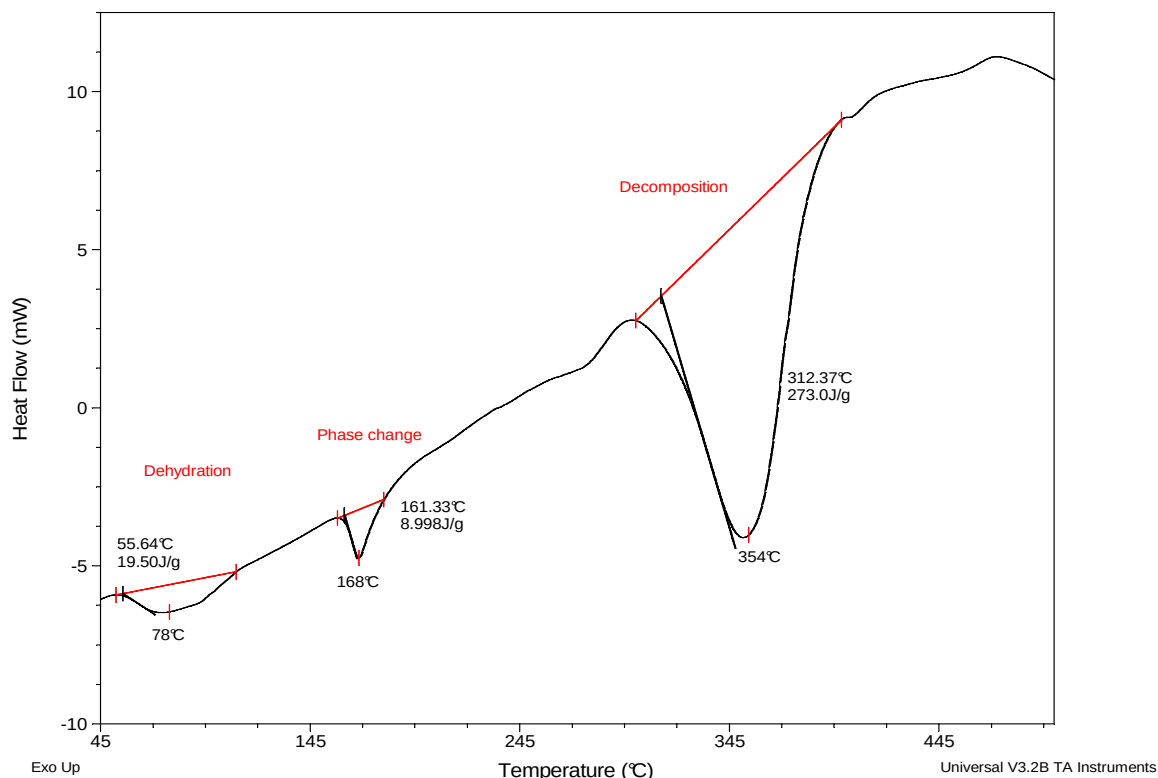


Fig. 4.33 DSC thermogram of cobalt octanoate (argon)

The DSC profile of cobalt octanoate (Fig. 4.33) reveals three endothermic peaks. The first peak at 78°C is associated with the dehydration of the sample. The second at 168°C most likely corresponds to a phase change, possibly the melting point and the largest endotherm at 354°C corresponds to the mass loss step observed in the TG profile (Fig. 4.32a) and is associated with decomposition.

(h) Cobalt nonanoate

The TG and DTG profiles of cobalt nonanoate are shown in Fig. 4.34.

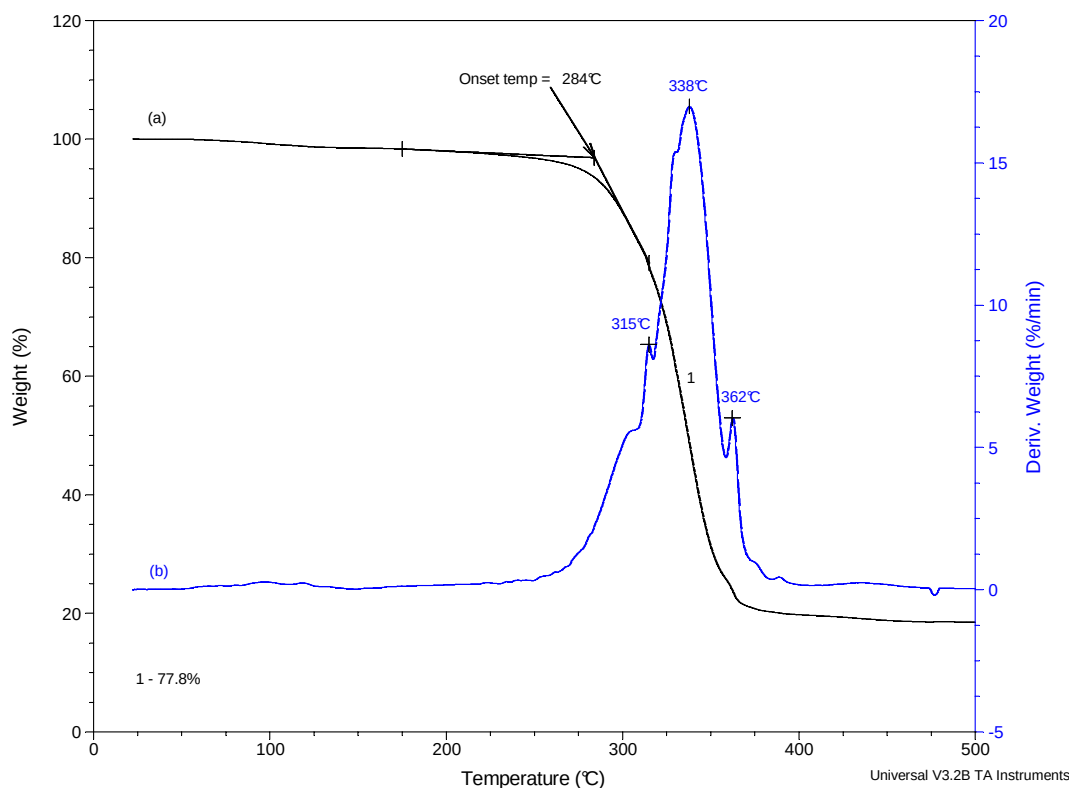


Fig. 4.34 (a) TG and (b) DTG profiles of cobalt nonanoate (argon)

The TG profile for the nonanoate (Fig. 4.34a) reveals that a small amount ($\sim 2\%$) of surface adsorbed water was removed upon heating. A mass loss of 77.8% is observed between 284 and 400°C. For the pure compound, the expected mass loss for CoO formation is 79.9% versus 84.2% for metallic cobalt formation. Therefore the corresponding mass loss of 78% is an indication that CoO is the final decomposition product.

The DTG curve (Fig. 4.34b) once again shows multiple peaks. These peaks may indicate the formation of intermediates during decomposition or could be the result of physical processes such as caking¹⁵ or rapid evolution of gases from the melted sample¹⁸.

The DSC profile for cobalt nonanoate is shown in Fig. 4.35.

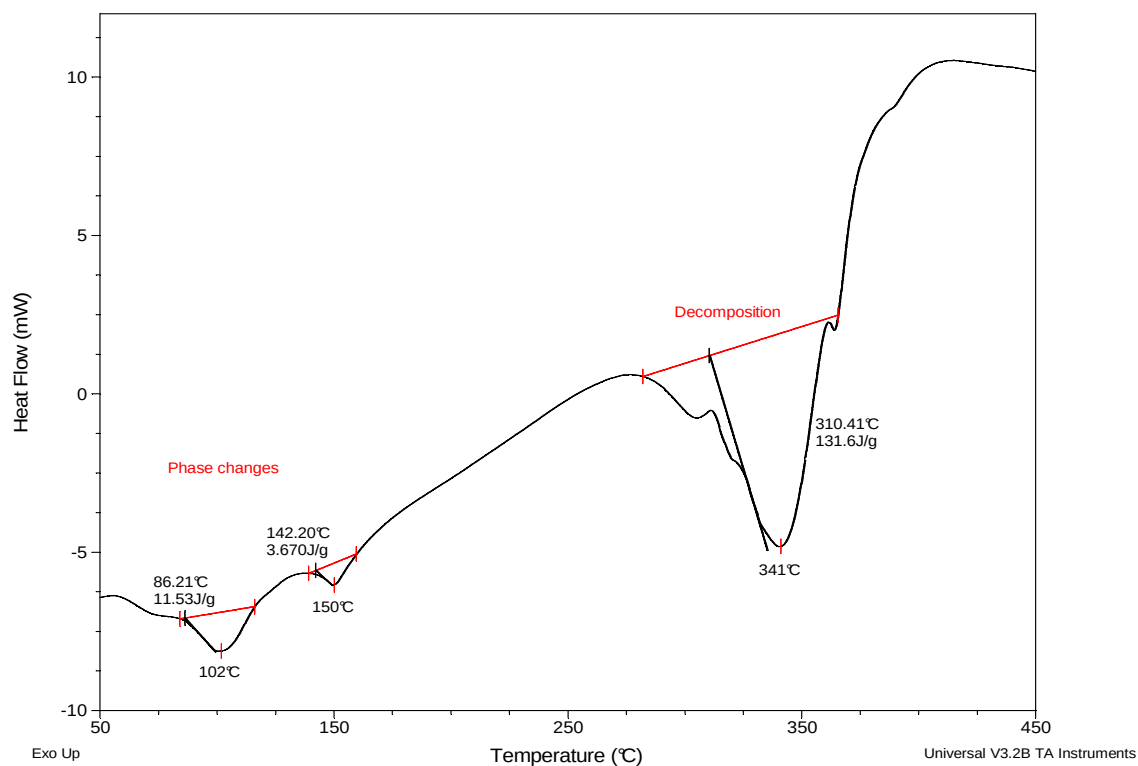


Fig. 4.35 DSC thermogram of cobalt nonanoate (argon)

Three endotherms are observed. The first two smaller endotherms do not correspond to any measurable mass loss in the TG profile (Fig. 4.34a) and most likely correspond to phase changes. The first process at 102°C could also be associated with the desorption of surface moisture. No additional melting point data was collected to confirm whether the second endotherm is the sample's melting point. This is unlikely though since the temperature is somewhat lower than would be anticipated for a compound containing such long hydrocarbon chains and more likely represents a solid-solid phase change⁷. The third large endotherm at 341°C corresponds to decomposition of the compound.

(i) Cobalt decanoate

The TG and DTG profiles of cobalt decanoate are shown in Fig. 4.36.

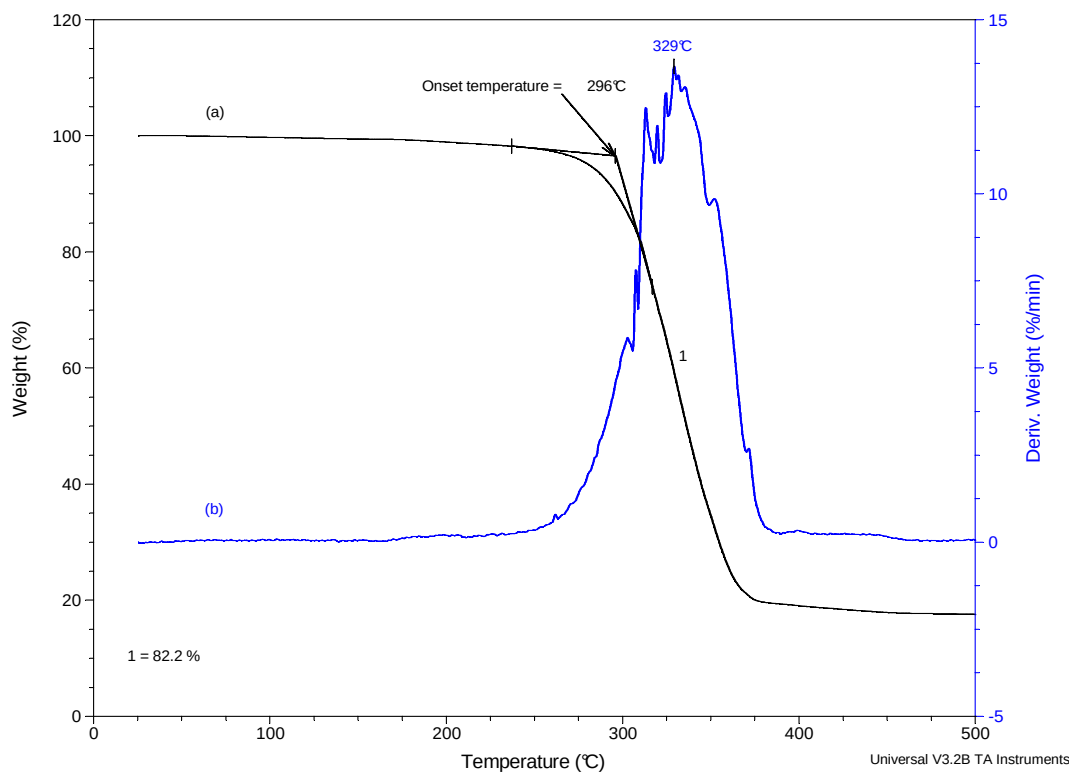


Fig. 4.36 (a) TG and (b) DTG profiles of cobalt decanoate (argon)

The TG profile of cobalt decanoate (Fig. 4.36a) reveals an 82.2% mass loss. Gravimetric calculations reveal that for pure cobalt decanoate, metallic cobalt formation is expected to be accompanied by an 85.3% mass loss and 81.3% mass loss is expected for CoO formation. A total mass loss of 82.2% thus suggests that this compound most likely decomposes to CoO.

The spikes observed in the DTG profile (Fig. 4.36b) may arise as gaseous decomposition products are released from the sample in the melt form¹⁸.

Additional experiments were completed on cobalt decanoate using heating rates of 2, 5, 15 and 20°C/min. The TG profiles for these experiments can be seen in Fig. 4.37. In all instances the mass loss observed was consistent, averaging

82.6%. The DTG profiles for these experiments are consistent with the DTG profile shown in Fig. 4.36b i.e. spikes are observed for all heating rates. As expected, the spikes become larger and more prominent as the heating rate is increased because the rate of decomposition and gas evolution increases as the heating rate is increased.

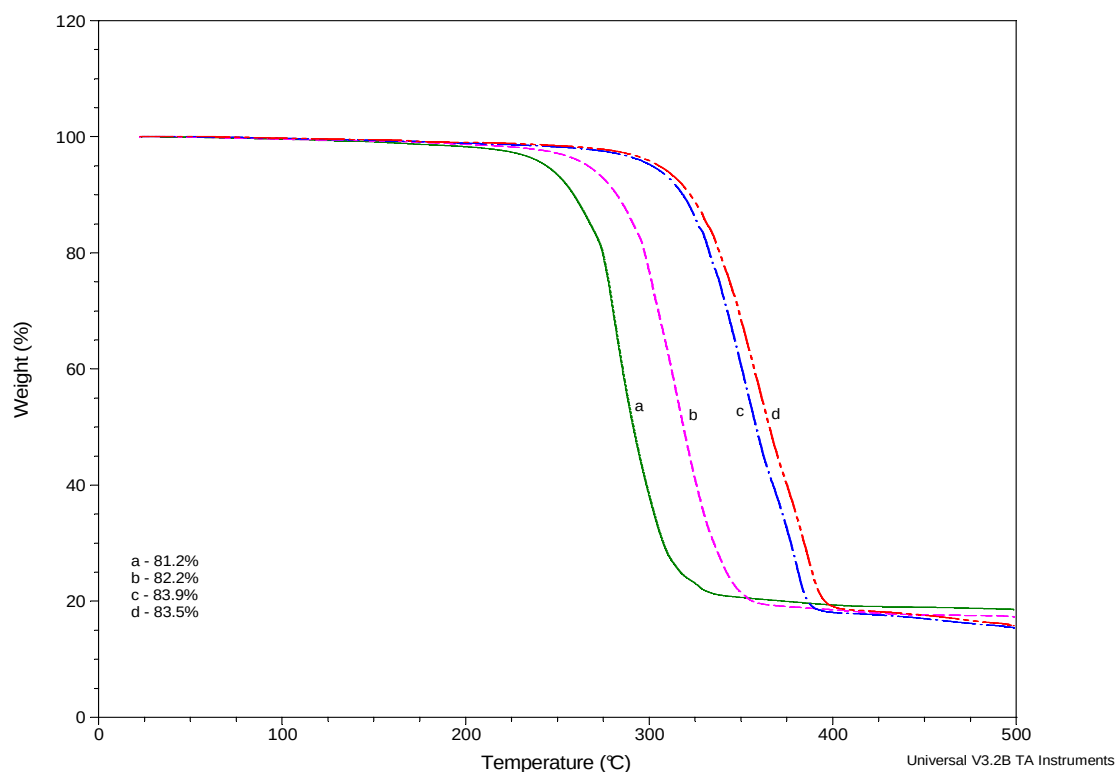


Fig. 4.37 TG profiles of cobalt decanoate heated at (a) 2°C/min, (b) 5°C/min, (c) 15°C/min and (d) 20°C/min (argon)

The data obtained from the five TG experiments was used to estimate the activation energy for the decomposition of this compound using the Kissinger method, as discussed in more detail earlier in chapter 4. Table 4.16 summarises the data for our thermal experiments and the corresponding kinetic plot is illustrated in Fig. 4.38.

Table 4.16 Data for non-isothermal TG experiments of cobalt decanoate

β (K/min)	$T_{\max}$ (K)	$1/T_{\max}$ (K ⁻¹)	$\ln(\beta/T_{\max}^2)$
2	552	1.81×10^{-3}	- 11.93
5	574	1.74×10^{-3}	- 11.10
10	602	1.66×10^{-3}	- 10.50
15	628	1.59×10^{-3}	-10.18
20	636	1.57×10^{-3}	- 9.91

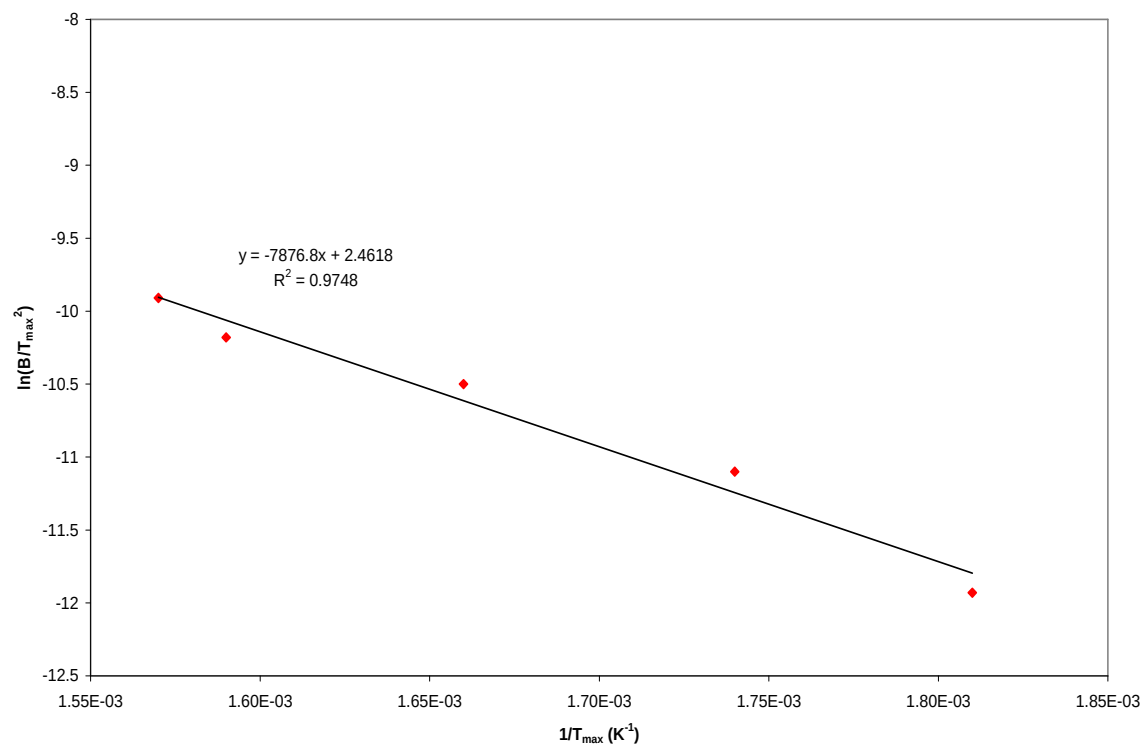


Fig. 4.38 Kinetic plot for the decomposition of cobalt decanoate

As per the Kissinger equation¹⁶:

$$E_a \beta (RT_{\max}^2) = Ae^{-E_a/RT_{\max}} \quad (1)$$

Where: A = Frequency factor

β = Heating rate (K/min)

E_a = Activation energy (J.mol⁻¹)

R = Gas constant (8.315 J.K⁻¹.mol⁻¹)

T_{max} = Corresponding temperature at DTG peak maxima (See Fig 4.34b)

Taking the natural logarithm of equation (1):

$$\ln (\beta/T_{max}^2) = -\ln (AR/E_a) + E_a/RT_{max} \quad (2)$$

Thus activation energy, E_a , can be obtained by plotting $\ln (\beta/T_{max}^2)$ against $1/T_{max}$, where the slope of the straight line is equal to $-E_a/R$.

Thus: $E_a = - (\text{Slope} \times R)$

$$E_a = - (-7876.8 \text{ K} \times 8.315 \text{ J.K}^{-1}.\text{mol}^{-1})$$

$$E_a = 6.550 \times 10^4 \text{ J.mol}^{-1} \equiv 65.5 \text{ kJ.mol}^{-1}$$

The activation energy for the decomposition of cobalt decanoate is 65.5 kJ.mol⁻¹.

This value is significantly lower than the activation energy determined for the decanoate's shorter chain counter part, cobalt propionate. A possible explanation is steric effects. The shorter propionate chains may be able to adopt a much more tightly packed configuration around the central cobalt atom as there will be less steric interaction between the chains. The longer decanoate chains cannot pack as tightly around the cobalt atom as they are much larger, resulting in increased interaction (i.e. repulsion) between the chains. These repulsive forces between the chains decrease the overall stability of the molecule, lowering the activation energy required for decomposition.

The DSC profile of cobalt decanoate is shown in Fig. 4.39.

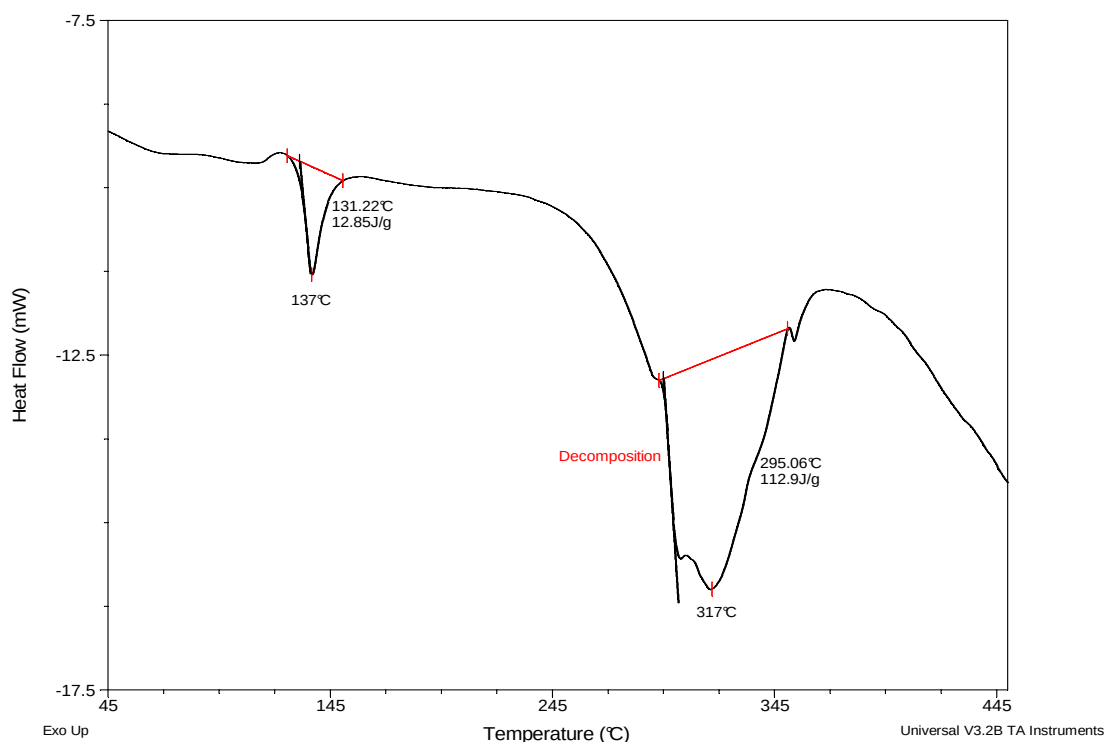


Fig. 4.39 DSC thermogram of cobalt decanoate (argon)

Two endotherms are observed. The first endotherm does not correspond to any measurable mass loss and is most likely associated with a phase change. Since the temperature is relatively low (137°C), it may be a solid-solid phase change which is not uncommon amongst carboxylates⁷. This hypothesis could be confirmed by examination of the sample under a hot stage microscope. The second endotherm corresponds to mass losses observed in the TG profile (Fig. 4.38a) and represents decomposition.

Thermal data for the cobalt carboxylates is summarised in Table 4.17. Observed mass losses are compared to mass losses determined from gravimetric calculations and used to determine which residues were formed during decomposition. The onset temperature for each decomposition reaction can be defined as the temperature at which decomposition commences and was

determined mathematically by finding the point of intersection formed by two lines drawn tangentially to the TG profiles, one vertical and one horizontal. $T_{\max}$ values are the peak maxima values on the DTG profiles and indicate the point at which decomposition proceeds most rapidly for each reaction.

Table 4.17 TGA data for cobalt carboxylates

Compound	Observed mass loss (%) [*]	Residue(s)	Onset temp. (°C)	$T_{\max}$ (°C)
Acetate	64.2 (64.8)	CoO	101 263 350	124 275 361
Propionate	72.4 (71.2)	Co	269	304
Butyrate	77.1 (74.1)	Co	282	328
Valerate	75.3 (77.4)	CoO	296	335, 355
Hexanoate	71.0 (74.1)	CoO	300	351
Heptanoate	75.2 (76.4)	CoO	286	323, 345
Octanoate	71.2 (78.3)	CoO	310	354
Nonanoate	77.8 (79.9)	CoO	284	338
Decanoate	82.2 (81.3)	CoO	298	329

^{*} Expected values in brackets

From Table 4.17 it becomes clear that in the lower carboxylates there is a gradual increase in thermal stability as the length of the carboxylate chain is increased i.e. increases in the decomposition onset temperatures are observed. Interestingly though, from the valerate (C_5) upwards it would seem that carboxylates that contain an even number of carbon atoms in their carboxylate chains (hereafter referred to as even members) have a higher thermal stability than their counterparts containing an odd number of carbon atoms in their carboxylate chains (hereafter referred to as odd members), since their onset

temperatures of decomposition are higher. The trends described above are illustrated in Fig. 4.40.

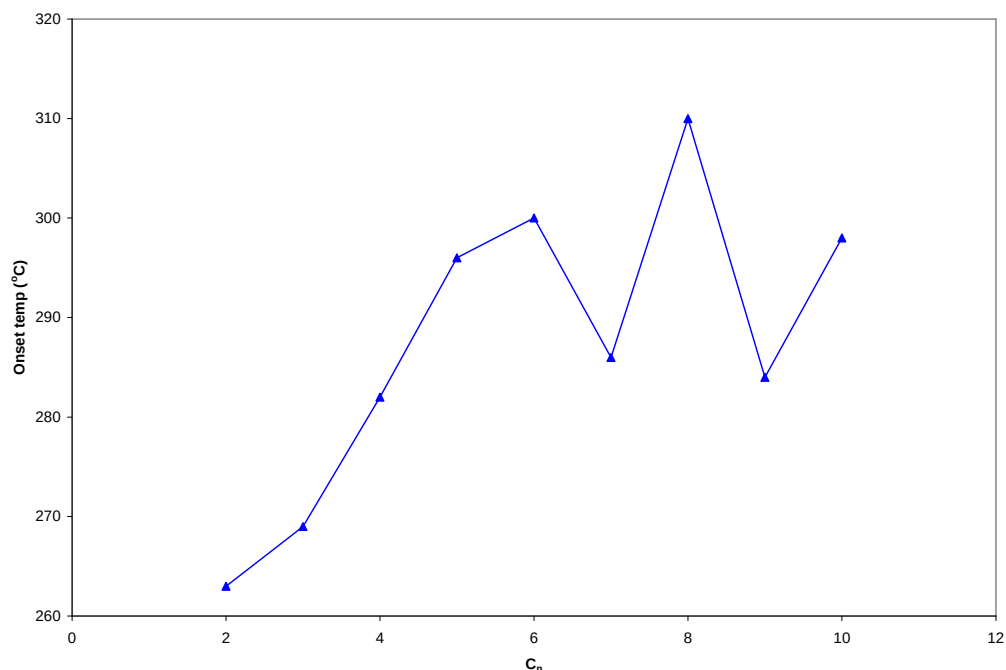


Fig. 4.40 Variation in decomposition onset temperature with increasing number of carbon atoms (C_n) for cobalt carboxylates

Although the exact reason for this observation is unclear, the most plausible explanation is based on differences in “packing effects” between odd members and their even counterparts¹⁹. Boese and co-workers determined that for the heavier analogues (C_n≥5) in a series of *n*-alkanes, the odd members cannot pack as closely as the even members, or they are forced to take up torsional strain due to their geometry and therefore have lower melting points²⁰. They developed a geometrical model to illustrate odd-even effects in these heavier analogues. The model is based on molecular symmetry and shape and requires that: (i) molecules are arranged into layers, (ii) –CH₂ groups of successive molecules are interlinked to form columnar stacks and (iii) end groups can only interact with other end groups²⁰. The model does not apply to lower members since there is

significant interference between the end groups and $-\text{CH}_2$ groups of adjacent molecules resulting in entirely different structures.

Their model showed that the intermolecular distances between the end groups, i.e. $-\text{CH}_3$ groups, are responsible for the differences observed in the melting points of *n*-alkanes. Odd members cannot approach as closely as even members making them less dense and lowering their melting points¹⁹. Fig. 4.41 reveals a simplified geometrical description (in planar 2-D view) to explain this finding.

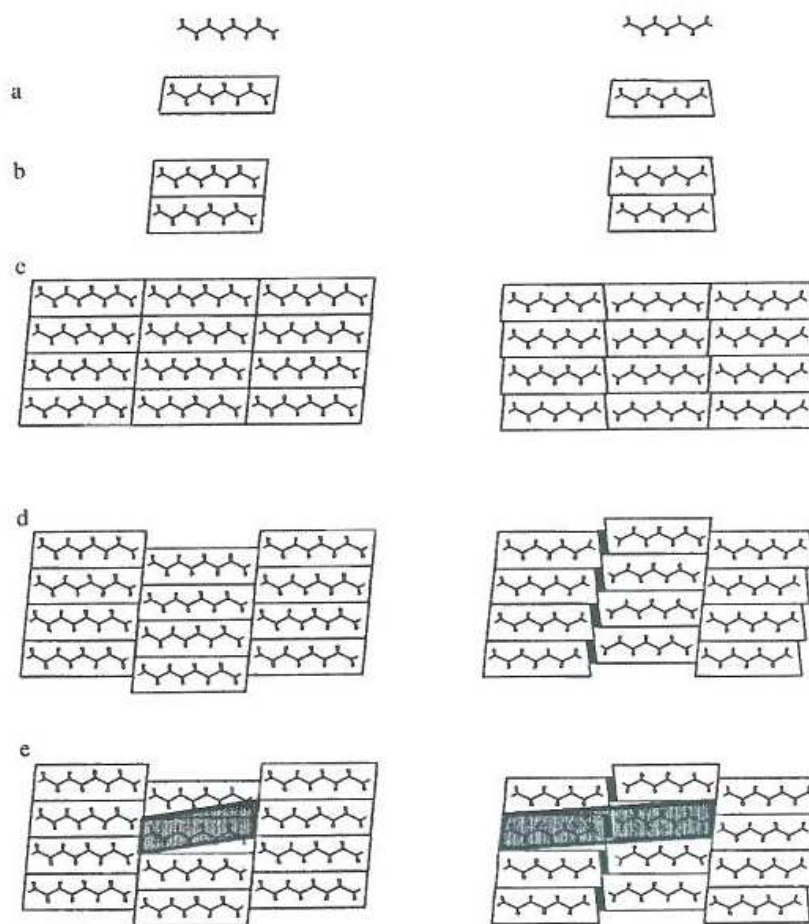


Fig. 4.41 Schematic representation of the packing of even-numbered (left) and odd-numbered (right) *n*-alkanes¹⁹

The shape of an even member can be described in the plane of the carbon skeleton as a parallelogram, that of an odd member as a trapezoid (Fig. 4.41a). If close packing of parallelograms is required, a pattern may result as shown in Fig. 4.41b. However an analogous packing is also possible for the trapezoids (Fig. 4.41c).

If the main axis of the molecules is increased i.e. an additional -CH_2 group is added to the chain, it is expected that the area (or in 3-D case the volume) increases by similar proportions (Fig. 4.41c). Such a packing would lead to a monotonic increase in the density because a parallelogram and a trapezoid have the same area with the same length of the centre line and height. However the -CH_3 groups situated opposite each other try to adopt a staggered conformation (as seen in Fig. 4.41b). Thus the columns of the parallelograms have to be shifted with respect to each other so as to achieve the staggered arrangement of -CH_3 groups (Fig. 4.41d left). A similar shift is possible for the trapezoid pattern only on one side, on the other side the shift results in very long distances and the -CH_3 groups are not really situated opposite each other (Fig. 4.41d right). This arrangement has large gaps (shaded in black), compared to the right and centre layer.

Thus even-numbered alkanes have optimal intermolecular contacts at both ends whereas the odd members possess these at one end only and at the other end the distances are longer. This leads to a less dense packing for the odd members and as a consequence lower melting points¹⁹.

Similar studies have been conducted on a series of *n*-alkyl carboxylic acids²¹. Alternating melting points can be rationalised using a similar 2-D model, however molecules form hydrogen-bonded dimers that are arranged into bilayers. The packing density within bilayers is comparable between different acids and it is

believed that differences in the packing densities between bilayers gives rise to the trends observed in the melting points of the acids²¹.

The information in Table 4.17 also reveals that the cobalt carboxylates considered in this project are stable below 200°C. Decomposition occurs in the range 265 - 400°C and proceeds rapidly to yield CoO. This observation was expected since there are numerous accounts describing this result^{2,8,11,12,15}. In the case of the propionate and butyrate where metallic cobalt was formed, it is possible that H₂ is generated as a gas product during the decomposition process which may then facilitate the reduction of CoO to metallic cobalt as a secondary process¹³.

Due to the relatively high thermal stability of the cobalt carboxylates, cobalt may not necessarily be a suitable candidate to pursue as a commercial decarbonylation catalyst. Since the majority of these compounds only decompose above 300°C, it would be expensive to utilize them on the plant. To elaborate on this statement, two primary methods of supplying energy for plant processes are discussed briefly.

Steam heaters are commonly used to supply the energy required for plant processes. These units generate superheated steam in large quantities which supplies energy for process-heating²². Since steam has a definite pressure for each fixed boiling or condensing temperature, the desired temperature for a process can be controlled by choosing the steam pressure²³. When higher temperatures are needed, the higher corresponding steam pressure becomes important in the design of the process equipment and both economic and safety considerations become critical. The use of steam heating is thus usually limited to pressures ≤ 2.2 MPa or $\sim 180^\circ\text{C}$ ²³. When temperatures in excess of 180 – 205°C are needed, other heating media are preferred.

Much of the energy required in petrochemical industries is introduced into the process through fired heaters or furnaces²⁴. The energy input for a process results from the heat liberated by the combustion of fuel within an internally insulated chamber of the fired heater. Higher temperatures can be maintained in these units however their operation is far more energy intensive²⁴. Satisfactory combustion requires adequate mixing of the fuel source with air and careful consideration must be given to the design of the system as well as the stoichiometry of the components put into the system²⁴. CO₂ emissions from fired heater units are substantial.

Therefore the use of steam heaters over fired heaters is advantageous for two reasons: (i) economically they are less expensive to operate than fired heaters and (ii) environmentally they pose less risk as opposed to fired heaters which generate large amounts of the greenhouse gas CO₂.

4.4 Conclusions

In summary, the data revealed that the physical and chemical properties of the cobalt carboxylates are very similar and it would appear that the difference in chain length of the carboxylate moiety has only a limited effect on the behaviour of these compounds.

IR data revealed that the compounds were of a sufficient purity for investigation. The two characteristic bands typical of carboxylate ions were observed for all the compounds and the separation of these two bands ($\Delta\nu$) was determined for each compound and used to make inferences about the possible carboxylate bonding mode in each case. However, this method of assigning structures based on the $\Delta\nu$ values was originally developed using a series of metal acetates only and we have extended this method to the longer chain carboxylates. Unfortunately no crystals

suitable for X-ray diffraction analysis could be obtained and the proposed structures could not be confirmed.

Examination of the thermal data shows that the cobalt carboxylates considered in this project are stable below 200°C. Decomposition occurs in the range 265 - 400°C and proceeds rapidly to yield CoO. Metallic cobalt formation is suspected in some cases and the reason for this observation could be H₂ facilitated reduction of CoO to Co as a secondary process during decomposition¹³.

An interesting feature observed in the DTG profiles of some compounds is the occurrence of multiple peaks observed over the mass loss step. This would seem to imply that the compounds exhibit more complex decomposition behaviour than the single step in the TG profiles suggest. The possibility that the compounds decompose via multiple reactions to yield unstable intermediates that immediately decompose further can not be ruled out. However there are literature reports that suggest that cobalt carboxylates tend to "cake" when heated¹⁵ i.e. fusion occurs forming a crust or diffusional layer that results in apparent discontinuities in the decomposition process. If TG experiments are stopped at various intervals during the heating cycle, examination of the samples reveal that clumps of solid material are formed in the melt. It is thus probable that the cobalt carboxylates are subject to physical rather than chemical effects when heated.

More intensive examination of the thermal data reveals that cobalt carboxylates containing an even number of carbon atoms in the carboxylate chain appear to be thermally more stable than their odd carbon counterparts, as their onset of decompositions are at higher temperatures. This result is not unexpected since it is a well documented fact that differences exist in the packing of odd-numbered and even-numbered alkanes and alkane derivatives^{19,20}. The geometry that can

be achieved in even-numbered derivatives is conducive to much more efficient close packing of molecules leading to increased densities and hence higher thermal stabilities than their odd-numbered analogues.

Cobalt carboxylates exhibit relatively high thermal stability and decompose between 265 – 400°C. They are not necessarily good candidates to be used as commercial decarbonylation catalysts as the higher temperatures required to decompose these compounds would result in the need for fired heaters on the plant. Fired heaters are expensive and have a larger environmental footprint.

4.5 References

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