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THERMAL STUDIES OF HEAVY METAL CARBOXYLATES.
II. THERMAL BEHAVIOUR OF DODECANOATES

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ABSTRACT

Mechanisms are proposed for the thermal decomposition of several metal dodecanoates on the basis of experimentally observed mass losses during heating. The tendency of the chromium, copper and sodium dodecanoates to complex with a range of additives is also compared.

INTRODUCTION

Previous studies of thermal behaviour of long chain metal soaps suggest that, in general, they decompose via the corresponding ketone or acid to the carbonate, oxide or metal [1–5]. Evidence has also been presented [6,7] that certain metal carboxylates complex with acid present in admixture. This paper extends those studies. It reports a preliminary thermogravimetric comparison and analysis of pure samples of the dodecanoates of chromium, copper, zinc, nickel, calcium and sodium and of mixtures of chromium, copper and sodium dodecanoates with compounds other than the acid, containing a C_{12} chain, to try to elucidate the means of complex formation.

EXPERIMENTAL

Dodecanoate preparation

Chromium(III). 1.5% w/w aqueous $C_{11}H_{23}COONa$ and 1% w/w aqueous $K_2SO_4Cr_2(SO_4)_3 \cdot 24\ H_2O$ solutions were poured into a third vessel and

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maintained at 293 K for 1 h. The precipitate was filtered, washed with water, air dried and then vacuum dried over P_4O_{10}. $C_{11}H_{23}COOH$ was removed from the product by washing with Analar acetone at 273 K.

Analysis: Cr, 10.82%; calculated for $CrOH(OOCC_{11}H_{23})_2$, 11.12%.

Calcium. An aqueous metathetic reaction, as for Cr, was employed using $CaCl_2$ as the calcium source. The product was washed with Analar ethanol and vacuum dried at 323 K over P_4O_{10}.

Analysis: Ca, 8.72%; calculated for $Ca(OOCC_{11}H_{23})_2 \cdot H_2O$, 8.78%.

Nickel(II). A similar preparation was used for nickel dodecanoate with $NiCl_2 \cdot 6\ H_2O$ as the second solution. The resulting colloidal precipitate was coagulated by adding 10 cm^3 of 10% w/w aqueous $NiCl_2$ solution. The precipitate was dried at room temperature over P_4O_{10} before soxhlet extraction with dried ether. Yield, 95%.

Analysis: Ni, 11.89; C, 56.87; H, 10.25%; calculated for $Ni(OOCC_{11}H_{23})_2 \cdot 2\ H_2O$: Ni, 11.90; C, 58.43; H, 10.22%.

Copper(II). A one-stage method for the preparation of pure Cu and Zn dodecanoate was developed from those described by Oudemans [8] and Mehrotra et al. [9]. Excess 1% w/v $Cu(OOCCH_3)_2$ in hot ethanol (filtered through 0.2μm pore filter) was added to 2.5% w/v ethanolic $C_{11}H_{23}COOH$. A precipitate formed on adding distilled water which was stirred for 1 h before filtration and washing with water, ethanol and acetone. The product was air dried and then vacuum dried at 353 K over P_4O_{10}. Yield, 90%.

Analysis: Cu, 13.66; C, 63.02; H, 10.10%; calculated for $Cu(OOCC_{11}H_{23})_2$: Cu, 13.75; C, 62.37; H, 10.03%.

Zinc. As for copper but using $Zn(OOCCH_3)_2$ and drying at 323 K over P_4O_{10}. Yield, 75%.

Analysis: Zn, 14.06; C, 62.71; H, 10.31%; calculated for $Zn(OOCC_{11}H_{23})_2$: Zn, 14.09; C, 62.13; H, 9.99%.

Thermogravimetry

A Stanton-Redcroft TG750 thermobalance was employed. White spot N_2 dried with molecular sieves was passed at 25 $cm^3\ min^{-1}$ over 1–2 mg of sample contained in a Pt crucible.

RESULTS

Single substances

Chromium dodecanoate

Rai and Parashar [10] have studied the thermal decomposition of $Cr(OOCC_{11}H_{23})_3$ and $CrCl(OOCC_{11}H_{23})_2$ and have suggested decomposition processes.

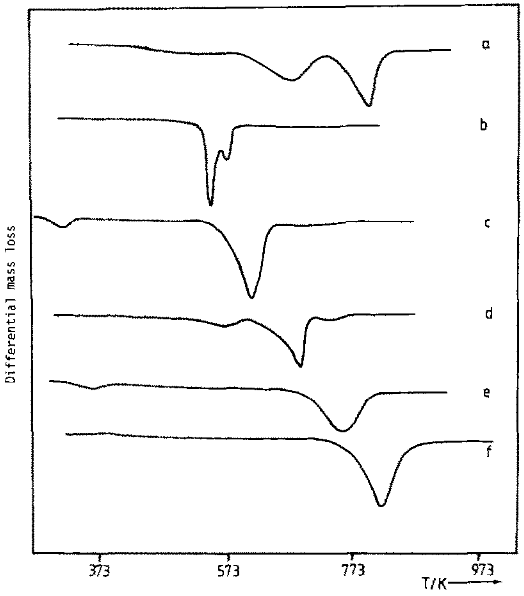

Fig. 1. Differential mass loss versus temperature, *T*, for (a) Cr, (b) Cu, (c) Ni, (d) Zn, (e) Ca and (f) Na dodecanoate (not all to the same scale).

The chromium dodecanoate used in this study was prepared by an aqueous metathetic reaction which is believed to produce mainly $Cr(OH)(OOCC_{11}H_{23})_2$ [11,12] and its thermal behaviour is more likely to follow that of $CrCl(OOCC_{11}H_{23})_2$ than that of $Cr(OOCC_{11}H_{23})_3$.

Rai and Parashar's suggestion was a two-stage decompositon, namely:

$$\text{(i) } CrCl(OOCC_{11}H_{23})_2 \xrightarrow{\sim 473°C} CrO(OOCC_{11}H_{23}) + C_{11}H_{23}COCl$$

$$\text{(ii) } 2\,CrO(OOCC_{11}H_{23}) \xrightarrow{\sim 593°C} Cr_2O_3 + (C_{11}H_{23})_2CO + CO_2$$

Two major peaks are observed on the DTG trace (Fig. 1a) and the

TABLE 1

TGA of Cr(III) dodecanoate

	Mass loss (%)		Residual mass (%)
Experiment	Ambient to 733 K	733–857 K	
	49.0	32.8	18.3
Theory	Reaction A	Reaction B	
	47.5	36.2	16.3

corresponding mass losses are compared with those expected for the following reactions in Table 1.

$$2\,Cr(OH)(OOCC_{11}H_{23})_2 \rightarrow 2\,CrO(OOCC_{11}H_{23}) + (C_{11}H_{23})_2CO + CO_2 + H_2O \qquad (A)$$

$$2\,CrO(OOCC_{11}H_{23}) \rightarrow Cr_2O_3 + (C_{11}H_{23})_2CO + CO_2 \qquad (B)$$

The figures in Table 1 support the proposed mechanism showing reasonable agreement, especially since there may be some residual dodecanoic acid in the sample which is believed to complex with the $Cr(OH)(OOCC_{11}H_{23})_2$ and which would contribute to the mass loss between 470 and 570 K. [7]

Copper dodecanoate

The decomposition of copper decanoate and octadecanoate was suggested by Mehrotra et al. [13] to occur in a single step:

$$Cu(OOCR)_2 \rightarrow R_2CO + CO_2 + CuO$$

Figure 1b, however, shows two peaks separated by ~ 30 K and this difference in TG traces is probably due to a difference in sample size (110 mg [13] and 1.28 mg, this work), the thermal lag within the larger sample reducing resolution of the TG curve.

The mass losses for the following two-stage decomposition are shown in Table 2 along with the losses observed experimentally:

$$2\,Cu(OOCC_{11}H_{23})_2 \rightarrow CuO \cdot Cu(OOCC_{11}H_{23})_2 + (C_{11}H_{23})_2CO + CO_2 \qquad (C)$$

$$CuO \cdot Cu(OOCC_{11}H_{23})_2 \rightarrow 2\,CuO + CO_2 + (C_{11}H_{23})_2CO \qquad (D)$$

The overall decomposition is the same as that proposed by Mehrotra et al., viz.

$$2\,Cu(OOCC_{11}H_{23})_2 \rightarrow 2\,CuO + 2\,CO_2 + (C_{11}H_{23})_2CO$$

The figures in Table 2 support the mechanism proposed, involving an oxide–dodecanoate intermediate containing two copper atoms which is not unreasonable since copper soaps can exhibit dimerism [14,15]. The observed residual mass indicates some decomposition of the CuO to Cu.

TABLE 2

TGA of Cu(II) dodecanoate

	Mass loss (%)		Residual mass (%)
Experiment	Ambient to 550 K	550–1047 K	
	45.6	39.8	14.6
Theory	Reaction C	Reaction B	
	41.4	41.4	17.2 (CuO) 13.7 (Cu)

TABLE 3

TGA of Ni(II) dodecanoate

	Mass loss (%)		Residual mass (%)
Experiment	Ambient to 380 K	380–782 K	
	8.8	77.0	14.2
Theory	Reaction E	Reaction F	
	7.3	77.6	15.2 (NiO) 11.9 (Ni)

Nickel dodecanoate

12-Tricosanone was identified as a decomposition product of nickel dodecanoate in a thermogravimetric study by Mehrotra and Kachhwaha [2] who expressed the thermal decomposition as

$$Ni(OOCC_{11}H_{23})_2 \rightarrow NiO + (C_{11}H_{23})_2CO + CO_2$$

Their residual mass matched that expected on the basis of NiO. The analysis of the trace shown in Fig. 1c agrees with this proposal, the first mass loss being attributed to the loss of two molecules of water. The residual mass given in Table 3 also indicates some decomposition of the NiO.

$$Ni(OOCC_{11}H_{23})_2 \cdot 2\ H_2O \rightarrow Ni(OOCC_{11}H_{23})_2 + 2\ H_2O \qquad (E)$$

$$Ni(OOCC_{11}H_{23})_2 \rightarrow NiO + (C_{11}H_{23})_2CO + CO_2 \qquad (F)$$

Zinc dodecanoate

Zinc dodecanoate appears to decompose in at least three stages (Fig. 1d). The theoretical mass losses corresponding to the following reactions are listed in Table 4 and show good agreement with values obtained from the thermal traces.

$$4\ Zn(OOCC_{11}H_{23})_2 \rightarrow (C_{11}H_{23})_2CO + CO_2 + ZnO + 3\ Zn(OOCC_{11}H_{23})_2 \qquad (G)$$

$$3\ Zn(OOCC_{11}H_{23})_2 \rightarrow 3(C_{11}H_{23})_2CO + 3\ ZnCO_3 \qquad (H)$$

$$3\ ZnCO_3 \rightarrow 3\ ZnO + 3\ CO_2 \qquad (I)$$

Overall

$$Zn(OOCC_{11}H_{23})_2 \rightarrow (C_{11}H_{23})_2CO + ZnO + CO_2$$

The proposed scheme appears to involve a four-centred polymeric unit. Flora and Vâmos [6] have suggested similar intermediates for other metal acetates and octadecanoates.

TABLE 4

TGA of Zn(II) dodecanoate

	Mass loss (%)			Residual mass (%)
Experiment	Ambient to 614 K	614–715 K	715–995 K	
	21.4	53.2	6.0	19.4
Theory	Reaction G	Reaction H	Reaction I	
	20.6	54.7	7.1	17.6

Calcium dodecanoate

Two major peaks are observed on the trace for calcium dodecanoate in the temperature range ambient to 1089 K (Fig. 1e); these, it is suggested, are associated with the following reactions:

$$Ca(OOCC_{11}H_{23})_2 \cdot H_2O \rightarrow Ca(OOCC_{11}H_{23})_2 + H_2O \qquad (J)$$

$$Ca(OOCC_{11}H_{23})_2 \rightarrow CaCO_3 + (C_{11}H_{23})_2CO \qquad (K)$$

Above 1098 K a further 9.7% mass loss is observed attributable to the decomposition of $CaCO_3$;

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (L)$$

The data presented in Table 5 support these suggestions.

Lorant [3] has proposed a similar mechanism for the decomposition of calcium octadecanoate.

Sodium dodecanoate

This dodecanoate appears to decompose in a single stage (Fig. 1f) represented by

$$2\ Na(OOCC_{11}H_{23}) \rightarrow Na_2CO_3 + (C_{11}H_{23})_2CO \qquad (M)$$

The expected and observed mass losses are shown in Table 6. The residue was black indicating contamination of the Na_2CO_3 with C and explaining the high residual mass.

TABLE 5

TGA of Ca(II) dodecanoate

	Mass loss (%)			Residual mass (%)
Experiment	Ambient to 390 K	390–823 K	823–1061 K	
	3.8	71.7	9.7	14.8
Theory	Reaction J	Reaction K	Reaction L	
	4.0	74.1	9.6	12.3

TABLE 6

TGA of Na dodecanoate

	Mass loss (%)	Residual mass (%)
Experiment	373–821 K	
	71.8	28.2
Theory	Reaction M	
	76.2	23.8

Mixtures

The thermal behaviour of chromium, copper and sodium dodecanoates in the presence of various amounts of dodecanol, 1-aminododecane and dodecyl dodecanoate was investigated.

Chromium(III) dodecanoate / dodecanol

The DTG curves obtained by adding increasing amounts of dodecanol to chromium(III) dodecanoate are shown in Fig. 2 and the corresponding mass losses are given in Table 7. Peak 3 (regarded as a doublet) and peak 4 are associated with the chromium soap degradation, and the percentage mass losses for these peaks remain effectively constant throughout the dodecanol

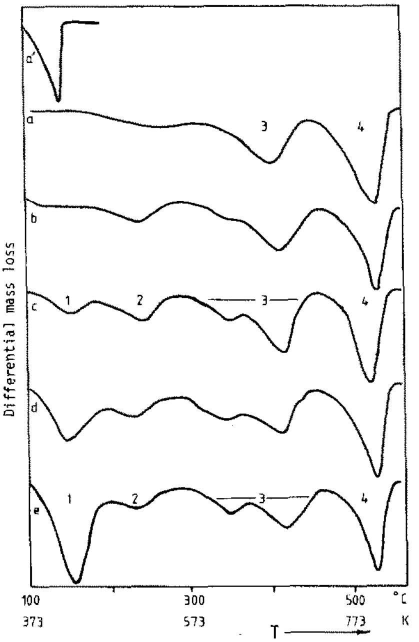

Fig. 2. Differential mass loss versus temperature, T, for chromium(III) dodecanoate/dodecanol mixtures. (a′) Pure dodecanol, (a)–(e) increasing dodecanol content.

TABLE 7

TGA of Cr(III) dodecanoate/dodecanol mixtures

Mass of dodecanol [a]	Mass loss [a]			
	Ambient to 471 K Peak 1	471–557 K Peak 2	557–730 K Peak 3	730–858 K Peak 4
0	2.1	9.0	37.6	33.1
14.4	8.2	14.9	39.1	33.9
27.5	15.4	17.3	40.5	33.5
47.9	38.2	16.7	39.8	31.6
77.0	69.6	17.6	40.0	32.1
117.0	102.0	19.4	43.8	32.4

[a] To enable direct comparison of different runs the mass of the additive and the mass loss are expressed as a percentage of the initial mass of dodecanoate.

addition. Peak 1 steadily increases as the percentage of dodecanol present increases and this is thought to be due to free unbound dodecanol, the peak position corresponding closely to that of pure dodecanol. Peak 2, after initial small increases, reaches a constant value and this is attributed to complexed alcohol, further analysis suggesting a 4 : 1 soap to alcohol molecular ratio. The relative behaviour of these peaks is clearly shown in Fig. 3.

Chromium(III) dodecanoate / 1-aminododecane

This system exhibits very similar behaviour as Fig. 4 and Table 8 show.

Chromium(III) dodecanoate / dodecyl dodecanoate

The DTG curve for this mixture shows only one extra peak as dodecyl dodecanoate is added (Fig. 5) and this peak corresponds closely with the single peak found for the pure dodecyl dodecanoate decomposition.

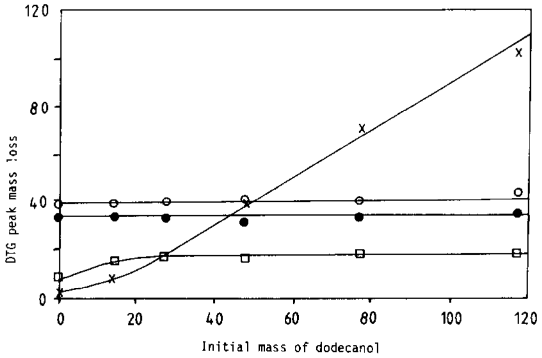

Fig. 3. DTG peak mass loss versus initial mass of dodecanol, (×) Peak 1, (□) peak 2, (○) peak 3, (●) peak 4.

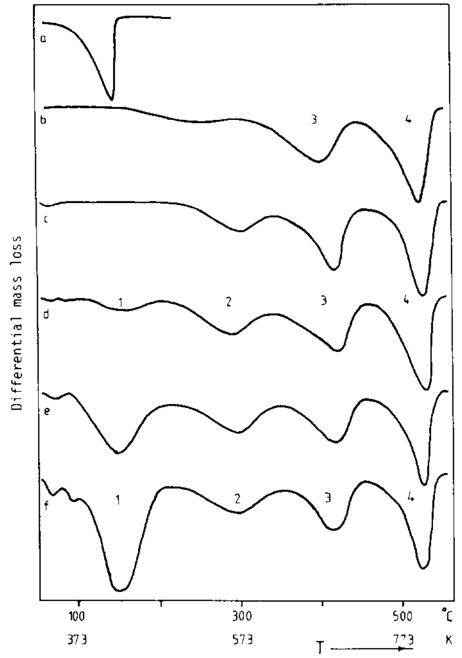

Fig. 4. Differential mass loss versus temperature, T, for chromium(III) dodecanoate/1-aminododecane mixtures. (a) Pure 1-aminododecane, (b)–(f) increasing 1-aminododecane content.

TABLE 8

TGA Cr(III) dodecanoate/1-aminododecane mixtures

Mass of 1-aminododecane [a]	Mass loss [a]			
	346–496 K Peak 1	496–614 K Peak 2	614–729 K Peak 3	729–857K Peak 4
0	2.9	14.2	31.4	33.0
15.8	6.5	23.5	31.4	32.8
34.6	13.2	31.8	31.4	31.0
68.7	55.5	32.3	30.5	31.7
98.6	87.6	29.8	29.4	30.2

[a] See Table 7.

Copper(II) dodecanoate / dodecanol

When a mixture of copper(II) dodecanoate and dodecanol (molar ratio 1 : 0.90) was heated the DTG curve obtained was a simple summation of the corresponding curves for the individual compounds (Fig. 6-I). Analysis indicated that 99.5% of the added dodecanol was released at a temperature close to its normal boiling point.

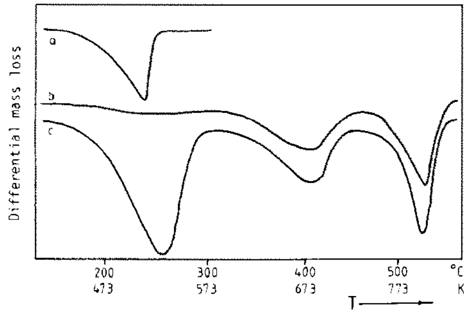

Fig. 5. Differential mass loss versus temperature, *T*, for (a) pure dodecyl dodecanoate, (b) chromium(III) dodecanoate and (c) a mixture of the two components.

Copper(II) dodecanoate / 1-aminododecane

The degradation of this system gave a DTG curve containing two major peaks with the higher temperature one showing a distinct shoulder (Fig. 6-II). This curve resembles neither the curves for the two pure components nor that obtained by superimposition of the pure component curves.

Copper(II) dodecanoate / dodecyl dodecanoate

This mixture produced a DTG curve (Fig. 6-III) which corresponds to the simple summation of the curves obtained for the two pure compounds.

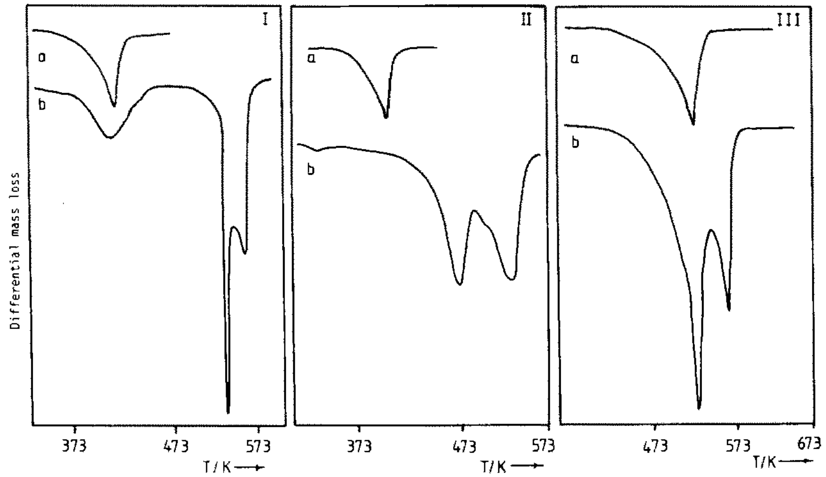

Fig. 6. Differential mass loss versus temperature, *T*: I (a) dodecanol, (b) copper(II) dodecanoate/dodecanol mixture; II (a) 1-aminododecane, (b) copper(II) dodecanoate/1-aminododecane mixture; III (a) dodecyl dodecanoate, (b) copper(II) dodecanoate/dodecyl dodecanoate.

TABLE 9

TGA of Na dodecanoate/additive

Additive	Molar ratio metal salt : additive	T_p of additive's mass loss when pure	T_p of additive's mass loss in the presence of soap	$100 \times \left(\frac{\text{mass lost on heating}}{\text{initial mass of additive in mixture}} \right)$
Dodecanol	1 : 1.04	409	418	96.5
1-Aminododecane	1 : 0.75	407	403	99.6
Dodecyl dodecanoate	1 : 0.54	510	517	95.5

T_p = peak temperature (K).

Sodium dodecanoate / additive

Addition of dodecanol to sodium dodecanoate produced DTG curves which indicated that the loss of neither of the compounds from the mixture was influenced by the presence of the other. The dodecanol was found to be released in close to 100% yield, at a temperature very near to that expected from an inspection of the DTG curve of the pure alcohol.

The same conclusion may be drawn for mixtures of sodium dodecanoate with 1-aminododecane and with dodecyl dodecanoate, data from the analysis of the DTG traces being shown in Table 9.

DISCUSSION

Single substances

In a number of the thermogravimetric traces (e.g. Cr, Cu, Zn) two thermal events overlap and the trace does not return to the baseline between these events. In such cases, in determining the percentage mass losses, it was consistently assumed that the first event ceased and the second event began at that temperature corresponding to the minimum in the derivative (DTG) curve. Allowing for the errors introduced by this assumption the experimental mass losses agree closely with those expected for the proposed simple decomposition mechanisms for the dodecanoates studied.

However, although the thermal traces are simple, consisting of only two or three smooth peaks, and the decomposition stages can be represented by simple chemical reactions, as shown by the data presented here, it is believed that it is a deceptive simplicity and that the decompositions are considerably more complex.

Evolved gas analysis of the volatile products from the thermal decomposition of sodium decanoate is reported to have indicated the presence of not one ketone, as might be expected from a simple mechanism similar to those discussed here, but a number of ketones containing from 3 to 18 carbon atoms [16].

Thus such thermal analysis may correctly indicate the major intermediates and products but the decompositions of these solids, while apparently simple as judged from the smooth thermal traces, are probably more complex.

Mixtures

Several metal carboxylates have been shown to form a complex or addition compound with the parent acid [6,7]. Friberg et al. [17], for the sodium octadecanoate/octadecanoic acid system, proposed a tetrahedral arrangement around the metal atom with hydrogen bonding between the acid –OH group and the alkanoate =O atom.

Such hydrogen bonding would not be possible between sodium and copper dodecanoates and dodecyl dodecanoate, and no evidence in these thermal investigations was found for such complexes.

Similarly sodium dodecanoate/1-aminododecane and sodium dodecanoate/dodecanol mixtures do not appear to interact to form simple molecular complexes when heated together.

The same conclusions can be drawn for mixtures of copper(II) dodecanoate with dodecanol, 1-aminododecane, and dodecyl dodecanoate. With 1-aminododecane, however, there appears to be some interaction but not of the type associated with the acid/alkanoate systems where two distinct peaks can be attributed to free and bound acid. With a mixture containing 1-aminododecane, in considerable excess of that required to form a 1 : 1 complex with copper(II) dodecanoate, there is no evidence of a peak corresponding to free 1-aminododecane and the copper(II) dodecanoate DTG trace is considerably changed. This suggests that a chemical reaction has occurred and the effect is to be further investigated.

The chromium soap showed no interaction with the dodecyl ester of dodecanoic acid but with dodecanol and 1-aminododecane complexing did occur. Two extra peaks in the DTG curve are obtained on addition of the second component indicating that some of the additive does not escape at the expected temperature but is held back in the mixture to be lost at a higher temperature. Hydrogen-bonding may again be responsible for this or, alternatively, lone electron pairs on the nitrogen or oxygen atoms could coordinate with the chromium atom. The absence of such behaviour with the ester is probably due to steric reasons.

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