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THERMAL STUDIES OF HEAVY METAL CARBOXYLATES.
III. METAL DODECANOATE–CARBOXYLIC ACID MIXTURES

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ABSTRACT

The tendency of chromium, copper, nickel and zinc dodecanoates to complex with dodecanoic and octadecanoic acids is investigated by analysis of the thermogravimetric curves. Complexing appears to occur only with the chromium dodecanoate, and in mixtures of copper, nickel and zinc dodecanoates with octadecanoic acid the dodecanoate chain is replaced by octadecanoate.

INTRODUCTION

In an earlier publication [1] a thermogravimetric study of chromium octadecanoate–octadecanoic acid mixtures was reported and evidence was presented that chromium octadecanoate (probably $Cr(OH)(OOCC_{17}H_{35})_2$ [2]) forms a complex with octadecanoic acid and the acid is released from such mixtures in two distinct stages. That study has been extended to the dodecanoates of Cr(III), Cu(II), Ni(II) and Zn(II) mixed with dodecanoic and octadecanoic acid separately and some of the findings are described below.

EXPERIMENTAL

Dodecanoate preparation

Full details of the preparation, purification and analysis of the dodecanoates of Cr(III), Cu(II), Ni(II) and Zn(II) have been given earlier [3].

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Thermogravimetry

Samples (1–3 mg) were investigated in a Stanton–Redcroft TG750 thermobalance using a heating rate of 10 or 20 °C min^{-1}. Platinum crucibles and white-spot nitrogen (dried with molecular sieves and flowing at 25 cm^3 min^{-1}) were used.

Mixtures were constituted by simply adding both components separately to the crucible.

RESULTS

Chromium(III) dodecanoate–dodecanoic acid

The behaviour of this system is similar (Figs. 1 and 2) to that of the octadecanoate–octadecanoic acid mixture [1]. Two extra peaks are observed in the DTG curve of chromium(III) dodecanoate as dodecanoic acid is added. The mass loss associated with one (attributable to complexed acid) reaches a maximum and constant value (peak 2); the other (free acid) increases throughout (peak 1). The mass losses for peaks 3 and 4, owing to

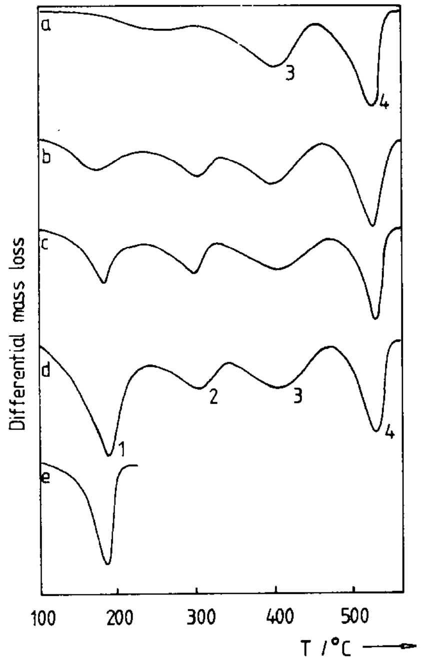

Fig. 1. DTG curves for (a) chromium(III) dodecanoate, (b–d) chromium(III) dodecanoate–dodecanoic acid mixtures of increasing acid content, and (e) dodecanoic acid.

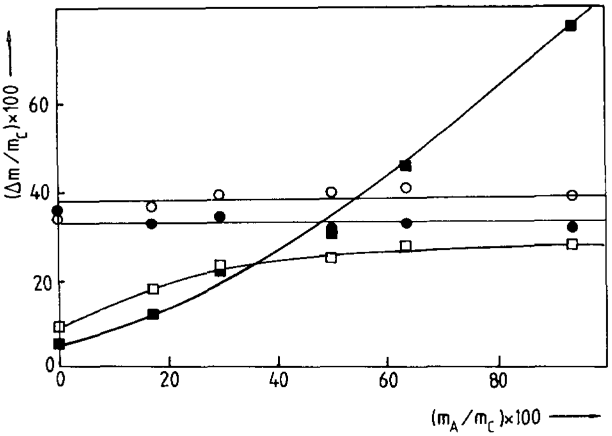

Fig. 2. Mass losses for chromium(III) dodecanoate–dodecanoic acid mixtures (Δm, mass loss; m_c, mass of chromium(III) dodecanoate; m_A, mass of dodecanoic acid): ■, peak 1 (25–233° C); □, peak 2 (233–326° C); ○, peak 3 (326–456° C); ●, peak 4 (456–582° C).

the decomposition of the dodecanoate, remain constant throughout. The molar ratio of soap to complexed acid is close to 2 : 1 as for the octadecanoate.

Copper(II), nickel(II), zinc(II) dodecanoates–dodecanoic acid

The TG behaviour of copper dodecanoate–dodecanoic acid, nickel dodecanoate–dodecanoic acid and zinc dodecanoate–dodecanoic acid mixtures

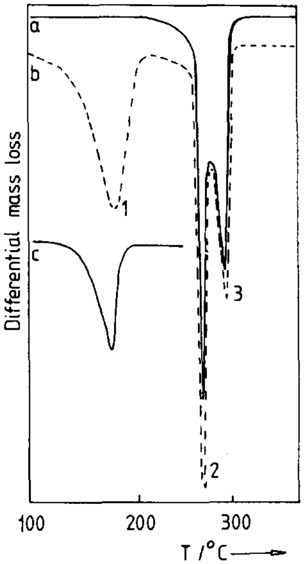

Fig. 3. DTG curves for (a) copper(II) dodecanoate, (b) copper(II) dodecanoate–dodecanoic acid mixture, and (c) dodecanoic acid.

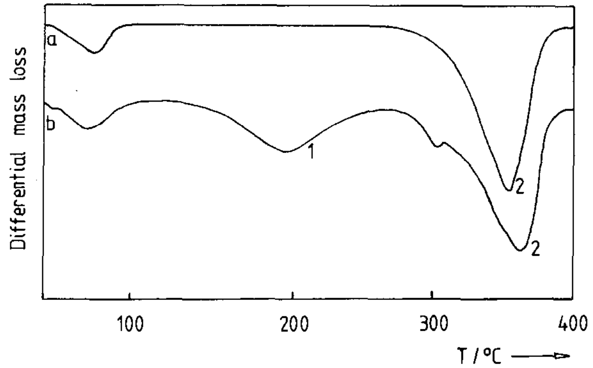

Fig. 4. DTG curves for (a) nickel(II) dodecanoate and (b) nickel(II) dodecanoate–dodecanoic acid mixture.

is shown in Figs. 3–5. There is no evidence in these traces for two peaks corresponding to acid release in two stages. The peak temperature of the one extra peak matches that for pure dodecanoic acid and the mass loss for this peak is close to that expected on the basis of added acid (not less than 95% of the added acid is accounted for). Consequently complexing between the dodecanoates of Cu(II), Ni(II) and Zn(II) appears to be absent.

(It is noted that for the nickel(II) dodecanoate mixtures a small shoulder develops on the low temperature side of the major dodecanoate peak as acid is added and the peak associated with the release of water of hydration becomes structured. The reasons for this remain to be investigated. Despite this, quantitative analysis of the nickel mixture curves shows that not less than 95% of the added acid is accounted for in peak 1).

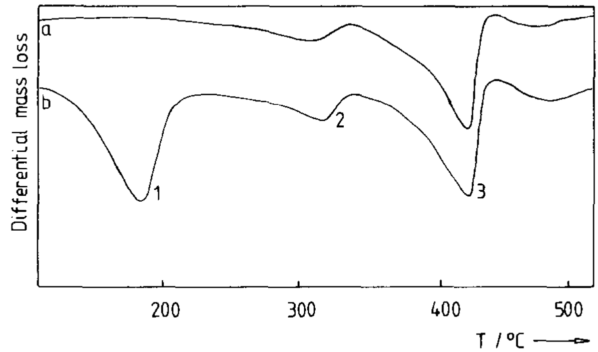

Fig. 5. DTG curves for (a) zinc(II) dodecanoate and (b) zinc(II) dodecanoate–dodecanoic acid mixture.

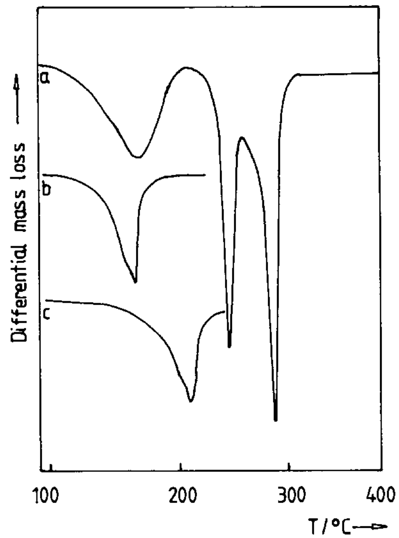

Fig. 6. DTG curves for (a) copper(II) dodecanoate–octadecanoic acid mixture, (b) dodecanoic acid and (c) octadecanoic acid .

Copper(II), nickel(II), zinc(II) dodecanoates–octadecanoic acid

Figure 6 shows the result of adding octadecanoic acid to copper dodecanoate. There is one extra peak corresponding to the release of acid before the carboxylate begins to decompose, and so, as with the copper dodecanoate–dodecanoic acid mixture there appears to be no complexing. However, analysis of the mass loss associated with this extra peak for seven different mixtures of carboxylate to acid, molar ratios from 1 : 072 to 1 : 1.53, shows it to correspond to only 0.72 (± 0.02) of the added octadecanoic acid. If the reaction

$$Cu(OOCC_{11}H_{23})_2 + 2HOOCC_{17}H_{35} \rightarrow Cu(OOCC_{17}H_{35})_2 + 2HOOCC_{11}H_{23} \tag{1}$$

took place and all the octadecanoic acid exchanged with the dodecanoate, the ratio of the mass loss observed to the mass loss expected for no exchange would be equal to the ratio of the relative molar masses of the acids, i.e. $200 : 284 = 0.704$. Thus it is concluded that the exchange reaction (1) goes to completion.

The same behaviour was observed for Zn(II) and Ni(II) with results corresponding to complete exchange being obtained.

Chromium(III) dodecanoate–octadecanoic acid

Figure 7 shows the DTG curves obtained for a series of chromium dodecanoate–octadecanoic acid mixtures of varying carboxylate to acid

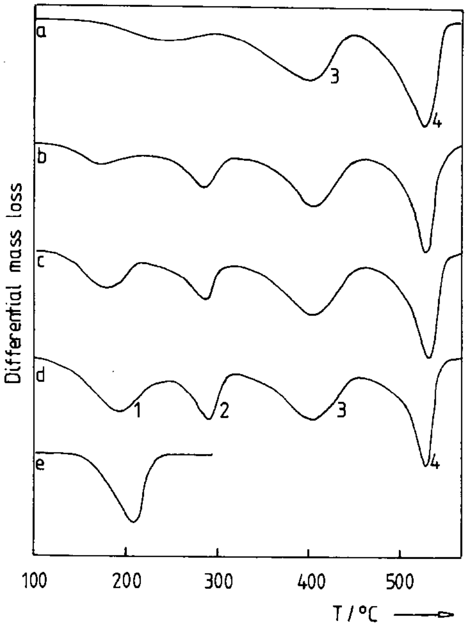

Fig. 7. DTG curves for (a) chromium(III) dodecanoate, (b)–(d) chromium(III) dodecanoate–octadecanoic acid mixtures of increasing acid content and (e) octadecanoic acid.

ratio. These curves, on superficial examination, appear to be very similar to those shown in Fig. 1 for the dodecanoate–dodecanoic acid system. However, a more quantitative analysis shows that, unlike in the latter system, the percentage mass loss for peak 2 does not reach a maximum value and that, for peaks 3 and 4, it does not remain constant as the amount of acid added increases (Fig. 8). These observations can be explained on the basis of an interchange reaction of the type shown by the copper(II), nickel(II), zinc(II) dodecanoate–octadecanoic acid mixtures, each further addition of acid allowing more interchange to occur and so producing steadily increasing contributions to peaks 3 and 4 over the range of compositions studied. A further complication exists in this case as the complexing demonstrated with the chromium(III) dodecanoate–dodecanoic acid may result in complexes between chromium(III) dodecanoate and either or both dodecanoic acid and octadecanoic acid, and between the chromium octadecanoate formed and either or both of the two acids present.

CONCLUSIONS

The chromium salt of dodecanoic acid forms a complex with dodecanoic acid of stoichiometry close to 2 : 1 (soap : acid) whereas the copper, nickel and zinc dodecanoates do not.

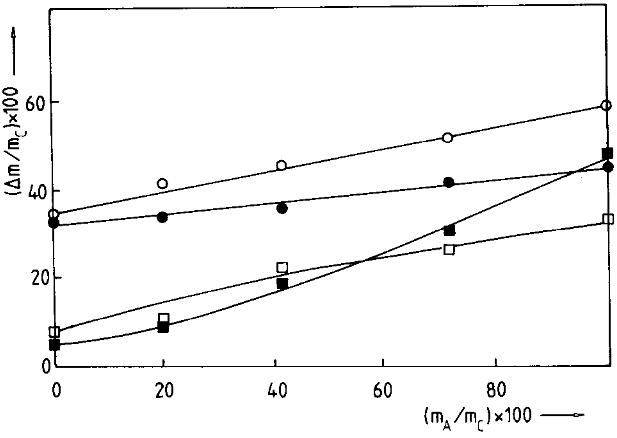

Fig. 8. Mass losses for chromium(III) dodecanoate–octadecanoic acid mixtures (Δm, mass loss, m_c, mass of chromium(III) dodecanoate, m_A, mass of octadecanoic acid): ■, peak 1 (25–232° C); □, peak 2 (232–316° C); ○, peak 3 (316–460° C); ●, peak 4 (460–585° C).

When copper(II), nickel(II) and zinc(II) dodecanoates are heated with octadecanoic acid the corresponding metal octadecanoate and dodecanoic acid are formed. This is shown by the quantitative analysis of the DTG curves. Supporting evidence is to be found in the following observations.

(i) When copper(II) dodecanoate and octadecanoic acid (1 : 1 molar ratio) were heated in a vitreous silica crucible at 473 K under a flowing dried white-spot nitrogen atmosphere a solid collected in an acetone/CO_2 trap. The melting point and IR spectrum of the solid showed it to be dodecanoic acid.

(ii) The peak temperature of the first peak in the DTG trace for copper(II) dodecanoate–octadecanoic acid mixture lies closer to the peak temperature of pure dodecanoic acid than that of pure octadecanoic acid.

(iii) Nickel(II) octadecanoate loses its water of hydration at a higher temperature than nickel(II) dodecanoate and mixtures of various molar ratios of nickel(II) dodecanoate and octadecanoic acid show mass losses attributable to water of hydration, at both lower and higher temperatures indicating the presence of both nickel(II) dodecanoate and nickel(II) octadecanoate. (This also indicates that the interchange of acid radicals must occur at a temperature as low as 350 K.)

ACKNOWLEDGEMENTS

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