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THERMAL ANALYSIS OF OCTADECANOIC ACID AND SOME OF ITS SALTS

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ABSTRACT

Octadecanoic acid was investigated as a model compound for one of the functional groups known to occur in low-rank coals, viz. carboxylate groups. TG, DTG, TG–MS and high pressure DTA were used to elucidate the type of reactions occurring during pyrolysis and hydropyrolysis of octadecanoate salts. The decomposition temperature varied from about 300°C for the tin(II) salt to 500°C for the potassium salt, apparently because of the varying ionic bond strengths involved. Only those salts which decomposed to form metal oxides gave significant amounts of carbon dioxide during the organic decomposition reaction; the others gave mainly carbon monoxide.

INTRODUCTION

The majority of ash-forming constituents of Morwell and Yallourn brown coals (Australia) are present at cations intimately bound to the coal substance via carboxylate groups. Some of the carboxylate groups in brown coal are in the acid form [1]. The proportion of carboxylate salts to carboxylic acid groups varies from one brown coal to another [2]. The amount of metallic cations associated with carboxylate groups has a bearing on the uses to which the coal is to be put. In combustion, for example, the metallic components generally end up in the ash. Some of the inorganic constituents of coal catalyse hydroliquefaction [3–5]. By soaking powdered brown coal in a solution of an appropriate salt, the inherent cations can be exchanged for other ions [6]. This property has been used to advantage by exchanging ions which are known to have useful catalytic activity for hydrogenation, e.g., iron, tin and zinc [7,8]. The behaviour of the inorganic constituents during hydroliquefaction of brown coal has been investigated. Iron carboxylates formed magnetite (Fe_3O_4), calcium carboxylates formed vaterite ($CaCO_3$) [9].

Octadecanoic acid was used in this study as a model for part of the structure of low-rank coals because it contains a carboxylate group attached to a long chain hydrocarbon. The effect of substituting the hydrogen ion by

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various other cations on the reactivity of the group was investigated by thermal analysis.

EXPERIMENTAL

Materials

All the chemicals used were of commercial grade and used without further purification.

Differential thermal analysis (DTA)

A high pressure DTA sample holder (15 BR2) was used with a Stone 200 DTA instrument. The 2–6-mg sample was weighed on a 4-mg aluminium foil dish, and placed on the ring thermocouple (Platinel 2). An empty aluminium dish was placed on the reference thermocouple ring.

The sample chamber was flushed twice with hydrogen at 8 MPa pressure before filling to the operating pressure of 8.0 MPa. The heating rate was set to 10°C min^{-1}, but, because of the absorption of hydrogen by the platinel thermocouples, they had to be recalibrated (using analytical grade KNO_3, $KClO_4$, K_2SO_4 as standards). The actual heating rate varied from 25°C min^{-1} at 100°C to 10°C min^{-1} at 600°C. The same experimental setup was used for DTA experiments in nitrogen at 4 MPa pressure, but with the normal thermocouple calibration.

Thermogravimetry (TG) and derivative thermogravimetry (DTG)

A Mettler thermobalance was used with a flow of 300 cm^3 min^{-1} of nitrogen or dry air. The heating rate was 6°C min^{-1}. The DTG was recorded simultaneously. Sample size was 40–60 mg.

Thermogravimetry–mass spectrometry (TG–MS)

Combined thermogravimetry–mass spectrometry used a Stanton-Redcroft 770 thermobalance interfaced to an Extranuclear quadrupole mass spectrometer via a 1.6-m long PTFE tube [10]. The TG of the 2–10-mg sample was run in helium flowing at 70 cm^3 min^{-1}, at a heating rate of 10°C min^{-1}. The mass numbers were scanned from 10 to 250.

X-ray diffraction (XRD)

Unreacted octadecanoates. The aluminium sample holder was reverse filled to minimize preferred orientation. A Philips diffractometer was used. The scanning conditions were: Cu K_α radiation; scan rate 1.0° 2θ min^{-1}; time constant 1 s; 2000 counts s^{-1} full scale. A carbon monochromator was used to reduce the background due to iron-fluorescence.

Residues after heating. Because of the small amount of sample it was mounted on a glass slide. Other conditions as above.

RESULTS AND DISCUSSION

The DTA curves of the zinc and calcium salts of octadecanoic acid gave a single sharp endothermic peak at about 150°C, indicating a simple phase transition from solid to liquid (Fig. 1). The iron and lead salts gave two low-temperature endothermic peaks. These peaks are reported by Adeosun and Sime [11] (for the lead salt) to be due to phase transitions from solid to a smectic mesophase and from the mesophase to liquid. The DTA curves of sodium and potassium octadecanoates are more complicated. The sodium salt has been reported to undergo six transitions from solid via mesophases to liquid [12]. The tin salt gave a large endotherm corresponding to the free acid impurity, followed by a small shoulder due to melting of the tin salt. After washing with hot acetone to remove the acid, stannous octadecanoate gave only one sharp endotherm at 70°C and a broader one at about 130°C.

Ferloni et al. [13] reported the DTA of potassium octadecanoate in nitrogen at atmospheric pressure. They found peaks at about 500 and 530°C. At the higher pressure used here a complex peak was observed, and the main peak temperature was about 480°C.

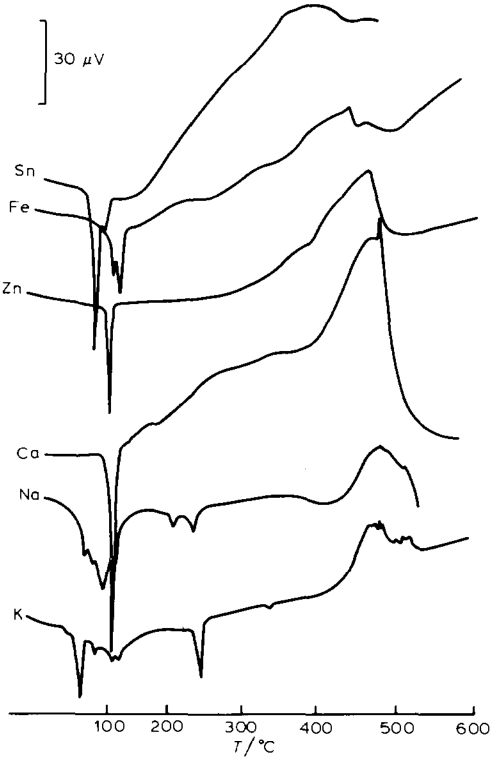

Fig. 1. DTA in nitrogen at 4 MPa pressure of octadecanoates of: Sn (as received), 5.2 mg; Fe, 3.0 mg; Zn, 1.9 mg; Ca, 2.8 mg; Na, 4.1 mg; K, 4.3 mg.

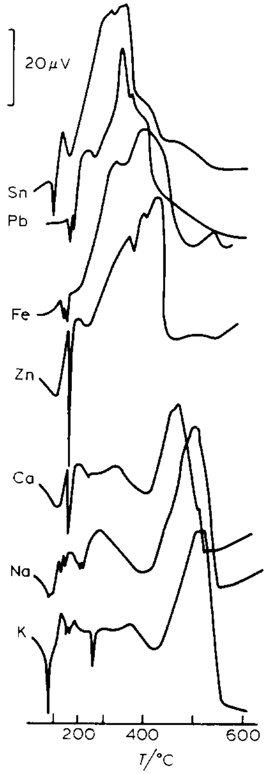

Fig. 2. DTA in hydrogen at 8.0 MPa of octadecanoates of: Sn (washed with hot acetone), 3.6 mg; Pb, 6.3 mg; Fe, 4.2 mg; Zn, 2.8 mg; Ca, 3.4 mg; Na, 3.4 mg; K, 4.7 mg.

All the salts, and the acid itself, gave a large complex exothermic effect in high pressure hydrogen (Fig. 2). This exotherm is caused by the hydropyrolysis of the compounds. The peak temperature of this effect increased in the

TABLE 1

Relationship between the temperature of reaction in hydrogen and the electronegativity of the element

Element	Exotherm T(°C)	Electronegativity (Pauling)
H	250–300	2.1
Sn	300–340	1.8
Pb	340–350	1.8
Fe	300–400	1.8
Zn	350–410	1.6
Mg	375	1.2
Ca	440	1.0
Na	490	0.9
K	500	0.8

order: H < Sn < Pb < Fe < Mg < Zn < Ca < Na < K. In nitrogen a smaller exothermic effect was observed due to pyrolysis, but the order of peak temperatures was much the same (Fig. 1). The electronegativity of these elements increased in the opposite order to their peak temperature (see Table 1). As the electronegativity increases, the ionic character of the bond between the cation and the carboxylate group is expected to become weaker. This appears to be the reason for the variation in the temperature of the decomposition reaction. Cations such as tin, lead and iron do not actually catalyse the initiation of hydrogenation of the carboxylate. The reaction is apparently thermally initiated, as are those of model compounds not containing metal ions [14–17]. Certain metal ions may catalyse subsequent reactions.

Ellis [18] investigated the decomposition of lead octadecanoate in nitrogen by TG. He postulated a sequence of reactions, in which the molten salt formed the ketone $C_{17}H_{35}COC_{17}H_{35}$, carbon dioxide and lead oxide, before the ketone pyrolysed.

The DTG of ferric octadecanoate in nitrogen showed two main stages of reaction (Fig. 3) and TG–MS showed that the first of these (at 310°C) was largely due to loss of carbon dioxide and the second peak was probably due to pyrolysis of the ketone. This implies that the ketone formation is, in this case, separate. If the ketone-forming reaction occurs at a temperature at which the ketone is stable then this stage is observed before the main decomposition reaction. For the more stable salts the decomposition reaction commences at a temperature where the ketone is unstable and the ketone-forming reaction is not observed.

Reaction in hydrogen can result in different products. From thermodynamic data [19], PbO is expected to be reduced by hydrogen to elemental lead ($\Delta G^0 = -39.7$ kJ mol^{-1}, $\Delta H^0 = -22.8$ kJ mol^{-1})

$$PbO + H_2 \rightarrow Pb + H_2O$$

and hematite is expected to be reduced to magnetite ($\Delta G^0 = -33.0$ kJ mol^{-1}, $\Delta H^0 = -6.0$ kJ mol^{-1})

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O$$

In both cases, XRD patterns of the products confirmed the occurrence of reductions of this type. When the thermal analysis of iron octadecanoate was carried out in inert gas or in hydrogen, all the following compounds were detected by XRD of quenched samples: Fe_3O_4, FeO, Fe, Fe_3C. The reduction through this sequence of phases would be caused by the presence of the carbonaceous residue of pyrolysis of the octadecanoate ion. The reduction of lead oxide to lead may account for one of the shoulders on the main exothermic DTA peak of lead octadecanoate in hydrogen (Fig. 2). Tin(II) oxide is expected to disproportionate [20]: $2\ SnO \rightarrow SnO_2 + Sn$ ($\Delta G^0 = -5.90$ kJ mol^{-1}), and tin was observed both visually and by XRD. The other cations (Na, K, Ca, Mg, Zn) are not expected to be reduced and no evidence was found to suggest that this occurred.

Some of the octadecanoates (Ca, Na, K) decomposed to form a carbonate which, if heated sufficiently, released carbon dioxide to form an oxide, whereas with others (Zn, Pb, Sn, Mg) no carbonate was observed in the product. Whether the decarboxylation stops at the metal carbonate or not can be predicted from the thermodynamics of the following reaction

$$(M^{n+})_{2/n}CO_3(s) \rightarrow (M^{n+})_{2/n}O(s) + CO_2(g)$$

Those metals for which ΔG for this reaction at 700 K is negative (Table 2), formed an oxide, whereas those for which ΔG is positive (sodium, potassium and calcium) formed a carbonate. In the case of iron and tin, the reactions are more complicated. There are no thermodynamic data for a carbonate of iron(III), although such a carbonate has been claimed to be formed by the decomposition of iron(III) hexanoate or octanoate [21]. No iron carbonate was observed in this study. In air the tin octadecanoate residue was cassiterite (SnO_2), the SnO having been oxidized by atmospheric oxygen. At about 900°C, the PbO residue began to decompose in hydrogen to lead and water.

The solid inorganic product of DTA of calcium octadecanoate in hydrogen was shown by X-ray diffraction to be calcite. This contrasts with the finding that calcium carboxylates in brown coal gave vaterite, probably because of the presence of other metal ion impurities [9].

Those octadecanoate salts which decompose to form a carbonate (K, Na, Ca) do not, therefore, liberate much carbon dioxide unless heated to the decomposition temperature of the carbonate. This observation is of relevance to the processing of low-rank coals. Some workers have assumed that the evolution of carbon dioxide from coals on heating implies decomposition of all carboxylates in the coal. In principle it is possible that these salts may survive treatment at about 400°C, a typical coal-processing temperature.

TABLE 2

Thermodynamics[a] of decarboxylation reaction at 700 K

Cation	ΔG(kJ mol^{-1})	Equilibrium constant, K	Product in calculation	Product observed
Na	173	1×10^{-13}	Na_2O	Na_2CO_3
Ca	66	1×10^{-5}	CaO	$CaCO_3$
Mg	−4.5	2.2	MgO	MgO
Pb(II)	−15.3	13.8	PbO	PbO
Fe(II)[b]	−44.5	2×10^3	FeO	FeO, etc.
Zn	−50.8	6×10^3	ZnO	ZnO

[a] Data from refs. 19, 22.

[b] No data for iron(III) carbonate, potassium carbonate, or tin carbonate.

TG and DTG

The DTG curves (Fig. 3) show that the sodium, calcium and magnesium salts contained approximately 1 mole of water of crystallization. The DTG peaks associated with the main decomposition were simple and sharp for those salts which decomposed at the highest temperatures (e.g., sodium) but split in the case of salts which decomposed at lower temperatures (e.g., iron). The small peak at about 700°C for the calcium salt is due to the decomposition of calcium carbonate.

TG–MS

The organic pyrolysis products varied with the temperature of decomposition. Tin octadecanoate decomposed at the lowest temperature (300°C) and its products, due to their low volatility, condensed in the outlet tube from the thermobalance and no significant amount reached the mass spectrometer. Samples having higher decomposition temperatures tended to crack more on decomposition, giving volatile products. A large range of masses

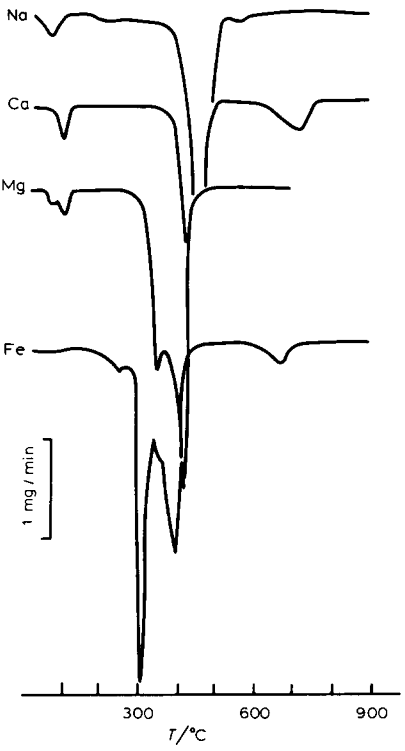

Fig. 3. DTG in flowing nitrogen at 6°C min^{-1} of octadecanoates of: Na, 61.2 mg; Ca, 47.1 mg; Mg, 40.0 mg; Fe, 51.6 mg.

was detected by MS, from 14 to 101, and traces in some cases up to 239 ($C_{17}H_{35}$).

The mass spectra also showed whether carbon monoxide or dioxide was the predominant product. For sodium, potassium and calcium, carbon monoxide ($m/z = 28$) was predominant at the temperature of the main organic decomposition. These are the samples which reacted to form carbonates. On the other hand, zinc and iron octadecanoates gave a large peak for carbon dioxide ($m/z = 44$) at 310°C, but only a very small peak for carbon monoxide. These are salts which reacted to form oxides instead of carbonates.

The main DTG peak for the iron salt was at 310°C and this coincided with the maximum rate of evolution of carbon dioxide ($m/z = 44$) determined by TG–MS. There was a shoulder in the carbon dioxide evolution peak at 260°C. This implies a two-step decomposition process. Bassi et al. [23] postulated that the iron(III) salts of propanoic acid and butanoic acid decompose, in air, via the iron(II) salt to hematite. Mössbauer evidence [24–26] supported the postulated iron(II) phase. Varma and Bhargava [21] postulated that iron(III) hexanoate and pentanoate decompose via iron(III) carbonate and the ketone to hematite. The alleged existence of an iron(III) carbonate was supported only by TG evidence. In the present results the shoulder in the carbon dioxide evolution peak shows that a two-step process occurs. This is consistent with the mechanism proposed by Bassi et al. [23]. In the present study, no evidence was found for an iron (III) carbonate.

CONCLUSIONS

Quantitative TG calculations were not useful due to the formation of pyrolysis char in most samples. However, simultaneous TG–MS enabled the main reaction sequences to be elucidated for a series of metal salts of octadecanoic acid.

The nature of the cation bonded to the octadecanoate ion affects the bond strength and thence the stability of octadecanoate salts. The reaction temperature of the salts with hydrogen varied from about 300°C for tin(II) to about 500°C for potassium. The order of reaction temperature observed was: $Sn < Pb < Fe < Zn < Mg < Ca < Na < K$. The reaction is thermally initiated, but metals such as tin, iron, lead and zinc may catalyse subsequent hydrogen transfer reactions—this was beyond the scope of this study.

The free energy of the hypothetical reaction

$$(M^{n+})_{2/n}CO_3(s) \rightarrow (M^{n+})_{2/n}O(s) + CO_2(g)$$

is the factor which determines whether a particular octadecanoate salt decomposes to a carbonate or directly to an oxide. Those which form a carbonate (K, Na, Ca) do not therefore liberate much carbon dioxide unless heated to the decomposition temperature of the carbonate. This observation is of relevance to the processing of low-rank coals. Some workers have equated evolution of carbon dioxide on heating with decomposition of all carboxylates. The non-carbon dioxide producing carboxylates are also the most stable. In principle it is possible that these salts may survive treatment at about 400°C, a typical coal-processing temperature.

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