

Review

The thermal behaviour of divalent and higher valent metal soaps: a review

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Abstract

The thermal behaviour of di-, tri- and tetravalent metal soaps (carboxylates) is reviewed, with reference to both the phase behaviour and thermal decomposition. General methods of preparation and purification are considered, and results on the structures of the solid phase obtained by techniques such as X-ray diffraction, NMR and vibrational spectroscopy are discussed. The general phase behaviour of these systems is reviewed, and the effects of metal ion, unsaturation and chain branching on this is considered. Transport and other physical properties of molten metal carboxylates, both as pure systems and mixtures, are discussed. Both the products of thermal decomposition and the proposed reaction mechanisms for the degradation of these compounds are considered, and the literature on the kinetics of these reactions is reviewed. Although this literature survey demonstrates that a considerable amount is already known about the thermal behaviour of these systems, it is clear that there is still much to be learnt.

INTRODUCTION

The long-chain carboxylates, or soaps, of polyvalent metal ions are substances of considerable commercial importance, and find applications in areas such as driers in paints or inks, components of lubricating greases, stabilizers for plastics, fungicides, catalysts, waterproofing agents, fuel additives, etc. [1, 2]. The soaps of di- and trivalent metal ions are those most commonly used. They are generally water insoluble, but may be soluble in various organic solvents, in which they commonly show Krafft-type behaviour, with solubilities increasing dramatically above a particular temperature [3–6]. The origin of this increase in solubility is not yet clear, but it is generally agreed that the solutions contain small aggregates of the metal soaps [3, 6].

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Though the soaps of unsaturated or branched-chain carboxylic acids may be fairly soluble in such solvents at room temperature [7–9], the solution temperatures of soaps of the saturated acids are usually rather higher [5]. Solutions of metal decanoates, naphthenates, ethylhexanoates and cyclohexylbutyrates are frequently used in analytical chemistry as standards for the determination of metal content in organic systems by atomic absorption spectroscopy [10, 11]. In addition, long-chain metal carboxylates are also important species in several solvent extraction processes [12].

In addition to the above applications, a number of other uses of polyvalent metal soaps has been suggested. Current interest in low-dimensional compounds has led to a number of investigations on the potential application of metal soaps in this area, particularly as Langmuir–Blodgett (LB) multilayers [13–19]. For example, manganese(II) stearate shows highly two-dimensional magnetic properties, either as a powder or LB film [13–17]. In addition, LB multilayers of lead(II) soaps, such as the myristate, are valuable as soft X-ray crystal analysers [18, 19]¹. Furthermore many of the metal carboxylates exhibit one or more thermotropic liquid crystalline phases, and there is currently increasing interest in the potential applications of such metallic mesogens (metal-containing liquid crystals) [21]. Attention has also been focussed on the polymers formed by divalent metal ions with α, ω -dicarboxylates (halatopolymers), which may find useful materials applications [22–24].

In many of these applications, the thermal behaviour of the metal soaps is of great importance. In this review, we will attempt to give a general picture of such behaviour, both in terms of phase transitions and decomposition processes. For earlier reviews in this area, readers are referred to refs. 25–30. Previous brief reviews of some of the authors' work in this area are presented in ref. 31.

PREPARATION AND PURITY OF POLYVALENT METAL CARBOXYLATES

Literature on the properties of these systems, particularly in some of the early articles, frequently contains conflicting data. Thus, nickel(II) stearate has been reported as melting at 100°C with decomposition, at 155°C without decomposition, and at 80–86°C [27]. The main causes for such discrepancies are differences in purity, and assignment of the melting point to different phase transitions as a consequence of mesophase formation. The values commonly quoted, for example, for the melting points of copper(II) soaps (110–125°C [32]), in fact correspond to the formation of a columnar mesophase [33]. Formation of the isotropic liquid occurs at much higher temperatures [34, 35].

¹ Both trivial and systematic names are commonly used for the fatty acid moiety; their equivalence is given in ref. 20.

Differences in purity can be attributed to various factors. Many of the fatty acids used in the earlier syntheses were actually mixtures of acids of different chain lengths, and considerable caution needs to be exercised in using phase transition temperatures reported in these studies. A similar caveat applies to many commercially available samples. Furthermore, though the polyvalent metal soaps have the formula $(\text{RCO}_2)_n\text{M}$, many commercial products have an excess of acid of metal and only approximate this structure. In some cases, the products may even be the basic $(\text{M}(\text{OH})_x(\text{RCO}_2)_y)$ or acidic $((\text{RCO}_2)_n\text{M} \cdot \text{RCO}_2\text{H})$ soaps. In many cases, soap hydrates may be obtained rather than the anhydrous metal carboxylates [36]. Preparation of soaps of many tri- and higher valent metal ions appears to be particularly difficult, as can be seen with the aluminium(III) carboxylates [37–50], where, for a long time, there was conflicting opinion about the existence of aluminium tri-soaps, until it was shown that they could be prepared under anhydrous conditions [44–48]. Similar problems have been noted with chromium(III) “stearate”, where the normal product of this description has been shown to be a mixture of basic soaps and excess acid [51]. In contrast, the soaps of trivalent lanthanide ions can be readily prepared, even in aqueous solution [52].

General methods of preparation of the carboxylates of polyvalent metal ions are given elsewhere [1, 27, 30, 46–170]. These include precipitation from solutions of sodium or potassium carboxylates by addition of solutions of appropriate salts of the polyvalent metal, ligand exchange between the metal chloride or acetate and the long-chain fatty acid in an aprotic solvent, fusion of metal oxides, hydroxides or carbonates with the fatty acids, and direct reaction of the metal with the molten fatty acid. For pure compounds, the first two processes are generally preferred. The precipitation route is particularly simple, and whilst the earliest studies generally involved reactions in aqueous solutions [171–173], it is usually better to use alcohols or alcohol–water mixtures as solvents. Precipitation is usually rapid, and vigorous stirring is recommended to minimize adsorption of metal salts on the product. For calcium(II) laurate, the kinetics of precipitation have been studied using stopped-flow techniques [174]. In cases where there is a strong tendency to form basic soaps, the use of anhydrous alcohol [48, 49] or aprotic solvents [58] may be necessary. With systems such as manganese(II) carboxylates [15], it may be necessary to perform the reaction under an inert atmosphere to avoid oxidation of the metal ion. This procedure is probably also useful with the synthesis of soaps of unsaturated carboxylic acids. The ligand exchange method, using metal acetates, has been shown to be particularly valuable in the synthesis of the carboxylates of rhodium(II) [63–65] and ruthenium(II) [65, 66]. The acetic acid produced stays in solution. The synthesis of mixed-valent ruthenium(II/III) carboxylates has recently been reported [67], as have the preparations of soaps of some transition metal complexes [68, 175]. Syntheses have been described of soaps of unsatur-

ated [55, 56, 69, 70], branched-chain [71], and hydroxy [72–75] monocarboxylic acids, and of dicarboxylic acids [22–24]. Also, the preparation of some polynuclear mixed carboxylates of nickel(II) [59] and copper(II) [60] have been reported.

Soaps can usually be purified by recrystallization from organic solvents such as benzene or toluene, or from neat fatty acids. However, in some cases, such as the metal 9,10-dihydroxyoctadecanoates [74, 75], complications can arise from gel formation. In addition, with certain branched-chain carboxylates, such as tetrakis(μ (2,2-(dioctyl(acetato)))*-O,O'*-bis(copper(II))) [71], the product may be liquid crystalline at room temperature.

STRUCTURES OF SOLID PHASE OF METAL SOAPS

At room temperature, virtually all pure, saturated, straight-chain metal soaps so far reported are solids. The only example we have been able to find of a metal soap of a straight-chain acid of reasonable purity which appears to be a liquid at room temperature is beryllium(II) laurate [176]. A knowledge of the structure of the solid state is a prerequisite to understanding the phase behaviour of these systems. It is convenient to consider the structure in terms of the coordination of the carboxylate group with the metal ion, the conformation of the hydrocarbon chains, and the packing of the chains within the crystal lattice. The geometry in the polar region of the metal soaps is dominated by the coordination behaviour of the metal ion. The possible modes of bonding of metal ions to carboxylates have been discussed elsewhere [30, 177–179]. These include monodentate coordination, with formation of a single metal–oxygen bond, and different bidentate structures, with the carboxylate either chelating a single metal ion, or bridging between two metal ions. The coordination in the polyvalent metal soaps may well be similar to that in the corresponding short chain carboxylates, and it is suggested with lead(II) soaps [180] that the metal has a coordination number of eight, as is observed in anhydrous lead(II) formate [181]. In common with most lipid systems, such as the pure alkanes [182] or fatty acids [183], the hydrocarbon chains in the solid phase normally have an all-trans conformation, and are packed in the crystal lattice within orthorhombic, monoclinic or triclinic sub-shells. At higher temperatures, a hexagonal form may occur. In some cases [106, 107], polymorphism is observed, with different crystalline modifications being formed on crystallization from solution and on cooling from a melt. As with the alkanes [182, 184], impurities may have a dramatic effect on the chain packing.

Various techniques have been employed to elucidate the structure of the solid phase of metal soaps. Low symmetry, and difficulties in the isolation of pure single crystals of these substances makes complete

structural analysis difficult. Strontium(II) laurate was one of the first divalent metal soaps to be analysed as a single crystal by X-ray diffraction [185]. The stable A-form gave monoclinic crystals, with four soap molecules per unit cell, and an average distance between alternate carbon atoms close to that found in potassium caproate; for the structure of the A form of potassium caproate, see ref. 186. The structure of strontium(II) caprylate hydrate [187] appears to be quite different from that of the anhydrous laurate. Single-crystal X-ray diffraction studies of a number of copper(II) carboxylates have been reported [138, 188, 189], and indicate the presence of binuclear copper(II) complexes, with each metal ion approximately coordinated by one copper atom, four oxygen atoms from the same cell, and one oxygen atom from a neighbouring cell. The small Cu–Cu distance in the dimer is very similar to that in copper(II) acetate monohydrate [190]. Copper-K edge EXAFS spectroscopy of copper(II) stearate [191], in addition to magnetic measurements [112–116, 140], vibrational [116, 129, 142] and UV/visible [129] spectroscopy of various copper(II) soaps support the presence of copper–copper interactions arising from dimeric $((\text{RCO}_2)_2\text{Cu})_2$ units in the crystalline state. One of the hydrocarbon chains in each dimer has the normal all-trans conformation, whilst the other is distorted by formation of a gauche conformation by rotation about the bonds near the carboxylate group. The carboxylate chains are packed into a triclinic sub-shell [188, 189]. Single-crystal X-ray diffraction studies have also been reported for rhodium(II) butyrate [145], and palladium(II) propionate [146]. In both cases, polynuclear metal carboxylates are present. EXAFS spectroscopy has also been applied to the solid phase of rhodium(II) heptanoate [65], and shows the presence of rhodium–rhodium bonds.

Where formation of single crystals has not been achieved, valuable structural information has been obtained from X-ray diffraction patterns of powder samples. Methods for the detailed analyses of these in soap systems have been presented elsewhere [192–195]. The long spacings observed in these cases correspond to reflections from planes containing the metal atoms. A particularly well-studied case is presented by the even-chain-length lead(II) carboxylates [76, 103–105, 196–198]. Because the lead ions are both strong absorbers and scatterers of X-rays, the observed diffraction patterns are dominated by these. Several orders of reflection are observed, and indicate a lamellar layering, with the carboxylate chains arranged orthogonal to planes containing lead atoms. Model calculations [105] indicate that the hydrocarbon chains are in the fully extended all-trans configuration. Plots of lamellar spacings as a function of chain length [107] support this. From both infrared [107] and high-resolution ^{13}C -NMR [180] spectroscopy, it is suggested that there is either an orthorhombic or monoclinic structure. Electron diffraction studies on multilayers of lead(II) stearate [199] lead to similar conclusions.

It has been suggested [197] that the shorter chain-length lead(II) carboxylates have a bilayer arrangement of hydrocarbon chains, whilst homologues with more than twelve carbon atoms have a monolayer organization with respect to the metal planes. These structures are similar to the Y- and X-type multilayers observed with LB films [200], and both types of structures have been suggested with lead(II) soap multilayers [198, 201]. However, results from X-ray diffraction [107, 198], high resolution ^{207}Pb -NMR [202] and ^{13}C -NMR [180] spectroscopic studies indicate that this is not generally true with the solid phase of the lead(II) soaps, and support the idea that all the compounds have the same Y-type structure. As noted earlier, polymorphism is observed in some of these cases. This shows up in differences in the X-ray powder diffraction patterns between pre-melted and recrystallized samples of lead(II) decanoate [198].

X-ray powder diffraction studies have been reported for a large number of soaps of other metal ions, including those of main group elements [24, 44, 48, 78, 82–87, 98, 99, 105–107, 147, 151, 152, 155, 203–208], transition metals [33, 78, 116, 119, 209], lanthanides [162] and actinides [168], and suggest similar lamellar layered structures. In some cases, such as calcium [99], copper(II) [116] and lanthanum soaps [162], it has been suggested that there may be some tilting of the hydrocarbon chains with respect to the planes containing the metal atoms.

High-resolution NMR spectroscopy of solids using high-power-decoupling, cross-polarization and magic-angle-spinning is another powerful technique for determining the structure of solids. High-resolution ^{207}Pb -NMR spectra of lead(II) decanoate and tetradecanoate [202] indicate a single coordination site for the metal ion in both cases. The chemical shift anisotropy, although rather modest, does suggest that the coordination around the metal ion is not completely symmetric. This idea is supported by studies on the luminescence spectrum of lead(II) decanoate, where a large Stokes shift, consistent with an asymmetric environment for the Pb nucleus, is observed [210, 211]. High-resolution ^{13}C -NMR spectra of solid lead(II) decanoate and octadecanoate [180] reveal splittings of the signals attributed to the carboxylate and adjacent methylene groups, suggesting different environments for the carboxylate chains. Similar differences in coordination of carboxylate groups to lead(II) have been reported in diffraction studies on lead(II) formate single crystals [181] and in lead(II) stearate multilayers [199]. As with the copper(II) carboxylates [188, 189], the two chains may differ in the conformations of the methylene groups adjacent to the carboxylate. ^1H -NMR spin-lattice and relaxation measurements on these samples [180] showed that there is a small, but detectable, amorphous region within the crystal. Similar behaviour has been detected for fatty acids using infrared spectroscopy [212], and is probably common to most long-chain aliphatic

compounds. This may be associated with anisotropy in expansion of the crystal lattice, as suggested for related systems [213, 214].

Other magnetic properties have also been employed to study the solid phase of metal soaps. Diamagnetic susceptibilities have been determined for a variety of divalent metal soaps [215], and although these are not particularly informative structurally, they show that the compounds could be divided into two groups of chemically related elements: Mg, Zn and Cd; and Ca, Sr and Ba. Paramagnetic susceptibilities are much more informative, and results have been presented for the carboxylates of iron(III) [113], cobalt(II) [113, 216], nickel(II) [59, 113], copper(II) [60, 65, 112–116, 140], ruthenium(II) [65, 66] and various trivalent lanthanides [160, 164]. Anhydrous iron(III) laurate and stearate have been shown to have high-spin Fe(III) coordinated to the carboxylate [113]. However, from the low magnetic moments and high magnetic field constants, it is suggested that there may be exchange interactions between neighbouring iron atoms. Magnetic measurements on various anhydrous carboxylates of cobalt(II) [113, 216, 217] and nickel(II) [113] suggest tetrahedral coordination of the metal ion. With mixed carboxylate complexes of nickel(II), however, the magnetic moments have been interpreted in terms of an octahedral geometry for the metal ion [59]. In contrast to the anhydrous soaps, it is suggested that the hydrated cobalt(II) soaps have a coordination number of 6 [113, 216]. The colours of the complexes are consistent with this. A number of studies have been carried out on the magnetic susceptibilities of copper(II) soaps [60, 65, 112–116, 140, 218]. Both the low magnetic moment at room temperature and the temperature dependence of the magnetic susceptibility indicate intramolecular anti-ferromagnetic copper–copper interactions. The magnetic moments are independent of the alkyl chain length of the soaps [115], which suggests that the metal coordination environments are very similar in all the compounds. With ruthenium(II) carboxylates [65, 66], the magnetic moments indicate the presence of binuclear ruthenium(II,II) species, with a double metal–metal bond. The soaps have a singlet ground state, and a thermally accessible triplet excited state.

Vibrational spectroscopy is a powerful method for studying such structural aspects as metal carboxylate coordination, metal–metal interactions, chain conformations and chain packing, and a number of infrared and Raman spectral studies have been reported on solid metal soaps. General aspects of the infrared spectra of aliphatic hydrocarbon systems [219–223] and metal carboxylates [28, 177, 224, 225] have been discussed elsewhere. Infrared spectra have been presented for the group-II soaps [23, 79, 81, 93, 94, 99, 226, 227]. Studies on the carboxylate stretch vibrations of calcium [81, 99] and beryllium [93] carboxylates suggest that the metal to oxygen bonds have considerable ionic character. For the phenylstearates, the anti-symmetric carboxylate stretch shows a linear

dependence upon the electronegativity of the metal ion [81]. As with the results of infrared studies on alkaline earth soap monolayers [227], this may reflect an increase in covalent character of the metal–oxygen bond on ascending the group from barium to beryllium. The metal–oxygen stretch vibrations have been reported for Be–O at 822 cm^{-1} [116] and 810 cm^{-1} [93], and for Mg–O at 675 cm^{-1} [116].

With all metal soaps, a series of bands are observed in the $1380\text{--}1170\text{ cm}^{-1}$ region [77, 226] which are directly related to the length of the hydrocarbon chain. These are mainly due to the wagging vibrations of the methylene group, with a smaller contribution from twisting-rocking vibrations, and support the idea that in the solid the chains are predominantly in the fully extended, all-trans configuration. Infrared [79, 107, 154] and Raman [106, 107, 228, 229] spectra have been reported for a number of lead(II) soaps. Infrared studies of the carboxylate stretch vibrations [154] have been interpreted in terms of the carboxylate binding to the metal through chelating or bridging bidentate structures. In agreement with the X-ray diffraction studies mentioned earlier, the progression in the $1350\text{--}1150\text{ cm}^{-1}$ region suggests that the hydrocarbon chains are in their all-trans conformation [79, 154]. This is supported by Raman spectral studies on the in-phase C–C stretching mode at approx. 1128 cm^{-1} [106, 107]. The CH_2 rocking mode in the $680\text{--}750\text{ cm}^{-1}$ region of the infrared spectrum of aliphatic hydrocarbons is very strongly dependent upon the crystallographic packing [220], and the splitting observed with this band in lead(II) soaps [79, 107] suggests that the structure is orthorhombic or monoclinic. C–H stretch modes in the Raman spectra can give information on lateral chain packing, and studies on lead(II) dodecanoate [228] suggest similar ordering to other dodecane derivatives. Low-frequency longitudinal acoustic modes in Raman spectra of aliphatic hydrocarbon derivatives can also give valuable information on chain length and disordering [230, 231]. Studies on Pb soaps [229] suggest that the all-trans chain length of lead(II) carboxylates is somewhat shorter than that of the corresponding alkanes. A number of vibrational spectral studies have been reported on long-chain carboxylates of copper(II) [60, 116, 129, 142, 232]. In a particularly detailed study, using isotopic substitution for band assignments, Strommen et al. measured infrared and Raman spectra for a number of straight-chain copper(II) soaps [142]. This work permits correction of a number of previous misassignments of bands [116, 129]. In the infrared spectra, the carboxylate stretch vibrations are consistent with the presence of bridging carboxylate groups, whilst data for both methylene wagging and in-phase rocking modes support results of X-ray studies [188, 189] that the hydrocarbon chains are not equivalent, and that gauche conformations are present in the chain at room temperature. The Cu–O stretching mode is in the $380\text{--}420\text{ cm}^{-1}$ region, and not, as previously suggested [116], at 670 cm^{-1} . Infrared [142] and

Raman [64, 65] spectra have been reported for rhodium(II) carboxylates. Of particular interest is the observation of a Rh–Rh stretching vibration, confirming the existence of metal–metal single bonds in these compounds. This is supported by results of EXAFS studies [65]. Infrared spectral data have been reported for various other metal carboxylates, including those of Al(III) [44, 50], Zn(II) [94, 154, 208], Cd(II) [154], transition metals [59, 216], lanthanides [162] and actinides [168].

UV/visible absorption spectra can also provide valuable information on metal coordination with transition metal, lanthanide and actinide soaps. With cobalt(II) soaps, it has long been known that the colour is strongly dependent on the method of preparation, and that pink, blue, red and purple compounds can be prepared [118, 126]. The colour appears to depend both on the presence of any coordinated solvent, e.g. water [118], and oxygen [126]. Reflectance spectra of anhydrous cobalt(II) stearate [233] show a broad absorption at 580–590 nm and a weaker band at 400 nm. Whilst detailed assignment of these transitions has not been made, they are consistent with tetrahedrally coordinated cobalt(II). Detailed analyses have been made of the reflectance spectra of various nickel(II) carboxylates [59]. In contrast to the results of the magnetic measurements of Herron and Pink [113], these have been interpreted in terms of an octahedral coordination of the metal. The relatively low values of the Racah B parameters indicate considerable covalency for the metal–ligand bonds in these complexes.

UV/visible spectra of copper(II) soaps have been determined as films, solid mulls and solutions [60, 114, 129, 234]. Broad, asymmetric d–d transitions are observed around 700 nm, suggesting an octahedral geometry, with considerable tetragonal distortion around the metal. In addition, a weaker band is observed at 375 nm, which is associated with a binuclear copper(II) carboxylate configuration. This is further supported by studies on optical dichroism [234], as well as results from other techniques described earlier.

PHASE BEHAVIOUR

Whilst the metal soaps are normally solid at room temperature, one or more phase transitions may be observed over the temperature range up to the onset of thermal decomposition. The phase behaviour depends upon both the metal and the carboxylate chain, and early studies by Lawrence [235], Hattiangdi et al. [236] and Koga and Matsuura [28] showed that liquid crystalline phases are formed in many cases. However, assignment of these mesophases is often controversial, and certain of the proposed structures must be treated with caution. The transitions are normally first order, although second-order transitions have been suggested for calcium(II) [203] and barium(II) stearates [237]. Though the soaps

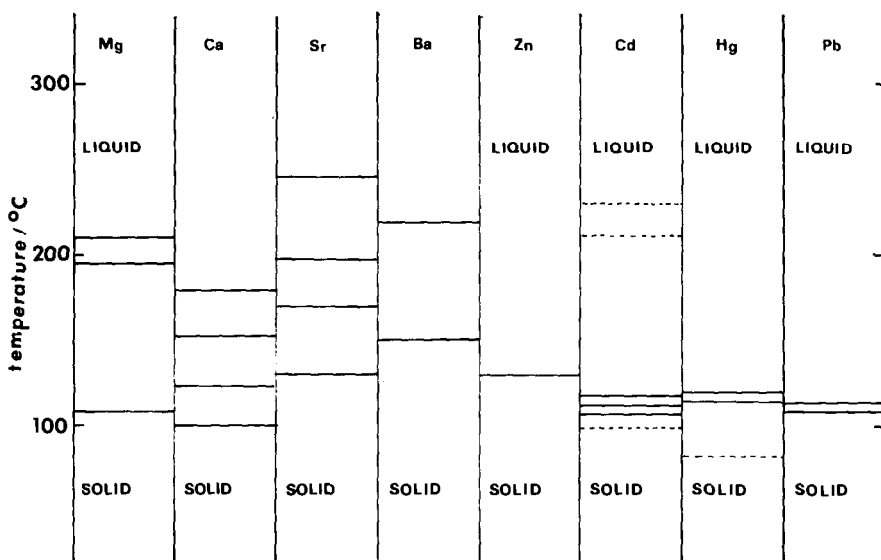


Fig. 1. Reported phase transition temperatures for the octadecanoates of Mg(II), Ca(II), Sr(II), Ba(II) [240], Zn(II) [149], Cd(II) (solid line ref. 149, dotted line ref. 151), Hg(II) (solid line ref. 155, dotted line ref. 153) and Pb(II) [103].

normally decompose at temperatures below their boiling points, distillation of copper(II) laurate [112] and zinc(II) stearate [238] under high vacuum has been reported. The phase behaviour of the alkaline earth soaps has been extensively studied using X-ray diffraction [82–87, 239–241], dilatometry [84], and DTA and DSC [203, 206, 236, 237]. Results of the X-ray studies have been reviewed elsewhere [242, 243] and reveal the presence of various intermediate mesophases between the solid and isotropic liquid. Structures proposed for these include lamellae, discs, rods and ribbons in various one-, two- and three-dimensional arrangements. Results for the stearates are summarized in Fig. 1. It should be noted that assignment of these structures based purely on results of X-ray studies has been questioned [243], and it has been suggested [206] that these do not represent liquid crystalline phases in the classical sense. Raman spectral studies on calcium(II) stearate [242] indicate the onset of conformational disordering occurs above 130°C. The evolution of thermal diffusivity and the heat capacity of various alkaline earth soaps has been measured in the solid and mesophases [245]. Rheological measurements have also been made on calcium(II) stearate as a function of temperature [246], and show marked changes in yield stress, elastic moduli and viscosity around 125°C, confirming transition from a solid to a fluid mesophase. The phase behaviour of the alkaline earth hydroxystearates has also been studied by DTA [247]. A number of transitions are observed on first heating. However, on cooling or reheating, the number of transitions is reduced. The temperature of formation of the isotropic liquid phase increases on

going from magnesium to barium. The dicarboxylate calcium(II) sebacate has been studied by DTA [23], and shows melting transitions around 300°C. Studies on the melt flow suggest the presence of polymeric species of finite length, with rapid association–dissociation of the calcium–carboxylate bond.

The zinc(II) soaps normally appear to pass directly from solid to liquid phases, without forming any mesophases [149, 208, 236, 248]. However, formation of a liquid crystalline phase has been suggested on cooling zinc(II) stearate [147]. In one report, the presence of various solid–solid phase transitions has been suggested for the shorter chain-length zinc(II) carboxylates [149]. However, it has been suggested that this may be due to the presence of impurities [248]. Infrared spectral studies [147, 154] indicate that melting is accompanied by chain disordering. In addition, it is suggested that changes in the coordination of the metal to carboxylate occur on melting. The unsaturated zinc(II) *cis*- and *trans*-9-octadecenoates and 9,12-octadecadienoates have been studied by DTA [69]. For all three compounds, as with zinc(II) stearate [149], only a single peak is observed corresponding to a solid–liquid transition. As with other aliphatic systems, the *cis* isomer shows a lower melting point than the *trans* one, whilst introduction of the second double bond decreases the melting point still further.

The even chain-length cadmium(II) soaps have been studied by X-ray diffraction [78, 151], dilatometry [151] and DTA [149, 150, 236]. From X-ray diffraction studies, it was suggested that an intermediate mesophase, consisting of infinite cylindrical micelles, formed around 100°C, and that the liquid phase was formed at approx. 230°C [151]. However, this has been questioned [149], and results of a DTA study suggest that the observed phase behaviour was due to the presence of impurities. It was suggested instead that the cadmium(II) carboxylates from the dodecanoate to octadecanoate form a single mesophase at around 10–20°C below the melting point, and that they form the liquid phase at around 100–120°C. The liquid phase is highly viscous, and it is suggested that long cylindrical aggregates are present, similar to those proposed for the mesophase in the X-ray diffraction studies. It is worthy of note, however, that the overall enthalpy change from the solid to this highly viscous phase is very much less than the overall melting enthalpies observed with the corresponding lead(II) and zinc(II) carboxylates [149], which suggests that the cadmium(II) compounds are not completely “melted”. Infrared spectral studies on cadmium(II) dodecanoate [154] show loss of structure at around 105°C, suggesting onset of conformational disordering. Cadmium(II) soaps have also been studied as LB films by DSC [249], FTIR [250] and Raman [251] spectroscopy, and show onset of disordering of the hydrocarbon chains at around 110°C. Electron diffraction measurements suggest that some disordering occurs below this

temperature [252]. The observed phase behaviour is very strongly influenced by the presence of traces of water [249].

Mercury(II) soaps have been studied by X-ray diffraction [78, 155], DTA [153, 235] and DSC [155]. It was initially suggested [153] that the decanoate and octadecanoate pass through a solid–solid phase transition before melting, whereas the tetradecanoate and hexadecanoate form a smectic mesophase. However, subsequent studies indicate the even chain-length soaps from the octanoate to tetradecanoate pass directly from solid to isotropic liquid, whilst solid–solid phase transitions are observed before melting in the hexadecanoate and octadecanoate [155]. Results for the phase transitions of the octadecanoates of Zn(II), Cd(II) and Hg(II), and of Pb(II), are also included in Fig. 1. It is of interest that though the low-temperature phase transition temperature in the alkaline earth soaps show a progressive increase on going from magnesium(II) to barium(II), those of Zn(II), Cd(II), Hg(II) and Pb(II) stearates are relatively independent of the cation, probably as a result of the rather more covalent metal–carboxylate bonds in the latter case.

The phase behaviour of some aluminium(III) soaps has been studied by DTA [253]. Normally two or three phase transitions are observed between 100 and 165°C. However, most of the samples studied were probably basic soaps, and not the anhydrous aluminium(III) tricarboxylates. A large number of studies have been reported on the phase behaviour of the long-chain carboxylates of lead(II) [78, 103–107, 198, 236]. For the shorter chain members (up to the dodecanoate), two intermediate phases are observed between the solid and liquid, whilst for longer chain soaps, there is only one mesophase [103–107]. Normally, considerable supercooling is observed in going from mesophase to solid. Low-temperature DSC measurements [254] indicate that there are no solid–solid phase transitions at temperatures down to 180 K. Although differences exist in the assignment of the phases [103–107], it is now generally agreed that the low-temperature mesophase for the short chain homologues, which is the only intermediate phase for the longer soaps, has a fairly rigid structure, intermediate between a solid and liquid crystal. It has been suggested that the structure may be similar to the gel phase observed with phospholipid dispersions [255]. The high-temperature mesophase with the short-chain soaps has a lamellar structure, for which both Smectic A [106] and Smectic C [105] structures have been proposed. These differ by having the hydrocarbon chains either orthogonal or tilted with respect to the planes containing metal atoms. If there is any chain tilting, it is likely to be fairly modest. The kinetics of phase transitions have been studied by isothermal calorimetry [256]. Dilatometric measurements have been made on lead(II) decanoate [107], and show volume changes at the transition temperatures observed by DSC. They confirm that the high-temperature mesophase has a disordered smectic structure, and from the coefficients of thermal

expansion, show that the first mesophase has a character intermediate between solid and liquid crystal. Results of ^{207}Pb -NMR studies [106, 107, 202] suggest that there is no significant change in the lead(II) carboxylate coordination on going from solid to liquid. Fairly sharp isotropic signals are observed in the liquid and L_α phases, suggesting that the metal ion has a fairly rapid motion on the NMR time-scale. In the low-temperature mesophase, a very broad ^{207}Pb signal is observed, with linewidth comparable to that for the solid phase. These results, coupled with a.c. impedance data [257], indicate that the motion of the cation is still highly restricted in this phase. From studies on ^1H -NMR line shape, and longitudinal and transverse relaxation of lead(II) decanoate as a function of temperature [180], it is suggested that there is a small percentage of a fairly mobile amorphous component in the solid phase, even at room temperature, and that the fraction of this increases with temperature, although no disorder is introduced into the overall structure until the first phase transition. On forming the low-temperature mesophase, changes in the overall dynamics are observed, and there is onset of considerable rotational motion within the chain. However, marked chain disordering only occurs on forming the high-temperature mesophase. From ^{13}C -NMR spectra and longitudinal relaxation, the terminal methyl group is seen to have very different dynamics from the rest of the chain, and to possess considerable mobility, even at room temperature. From Raman [106, 107], infrared [154] and ^{13}C -NMR [180] spectral studies, it can be shown that the transition to the high-temperature mesophase or liquid is accompanied by conformational disordering within the hydrocarbon chain. For the decanoate, about two gauche bonds are introduced per chain. This is in good agreement with theoretical predictions [106]. The overall enthalpy changes for the solid–liquid transition have been analysed in terms of contributions from conformational disordering, van der Waals interactions, etc., and calculated enthalpy changes are in excellent agreement with experiment [107]. The entropy change accompanying the mesophase I–II transition in lead(II) decanoate has also been analysed using results of molecular dynamics calculations [106], and again good agreement with experiment is observed. Studies of transition temperatures as a function of chain length [31, 103–107] show a progressive increase towards a plateau for the longest chain members.

This is typical of the behaviour of other aliphatic systems. Odd–even variations are observed in both the solid–low-temperature mesophase and the mesophase I–II or mesophase–liquid transitions [104]. Transition temperatures and enthalpies are given in Table 1. Transition temperatures are expected to be lowered by chain branching, and this has been confirmed experimentally for lead(II) cyclohexyl butyrate [31]. Unsaturation is also expected to lower transition temperatures. In contrast to the phase behaviour of lead(II) stearate [103, 105], lead(II) elaidate melts

TABLE 1

Transition temperatures and enthalpies reported for lead(II) carboxylates

Carbon chain length	Solid→mesophase I		Mesophase I→II or mesophase→liquid		Mesophase II→liquid		Ref.
	<i>T</i> (K)	ΔH (kJ mol ⁻¹)	<i>T</i> (K)	ΔH (kJ mol ⁻¹)	<i>T</i> (K)	ΔH (kJ mol ⁻¹)	
6	335.9	6.02	338.5	15.8	350.2	1.3	103
	337.6	1.02	343.3	23.25	352.6	1.24	105
7	336.6	17.1	356.8 ^a	8.5	374.7	1.4	104
8	352.5	30	356.2	7.9	381.2	1.2	103
	353.8	24.21	353.8 ^b	8.54	382.8	1.03	105
9	348.9	32.2	367.4	16.4	384.8	1.3	104
10	354.9	32.7	367.4	20.0	385.2	1.0	103
	359.0	38.53	371.4	18.11	384.2	0.80	105
	357.1	40.6	369.5	20.1	386.7	1.1	106
11	360.9	50.7	377.0	27.5	383.7	1.1	104
12	365.2	48.3	377.2	29.8	381.2	0.9	103
	369.2	47.55	378.4	28.64	378.4 ^b	0.10	105
13	368.7	58.4	381.5	38.8			104
14	372.7	59.1	382.7	41.6			103
	376.9	52.12	384.1	38.79			105
15	374.7	64.1	384.6	48.1			104
16	373.4 ^c	55	384.2	46.4			103
	380.8	52.69	386.8	45.40			105
17	378.7	68.0	387.4	55.1			104
18	381.2	62.6	387.2	56.9			103
	381.9	55.80	388.1	53.90			105
19	383.8	75.9	389.1	64.3			104

^a An extra phase change occurs at 361.3 K.^b Values observed on cooling.^c Second transition at 380.6 K.

directly from solid to isotropic liquid without formation of any mesophase [69]. The melting point in the unsaturated compound is, as expected, lower than that of the fully saturated derivative. Various lead(II) alkadiynoates have been studied, with particular reference to their potential polymerization to poly(diacetylene) systems [70]. These appear to give fairly ordered smectic mesophases at room temperature, although the textures observed by polarizing microscopy are somewhat ill-defined. There may be a second-order phase transition at around 330 K, and the compounds clear to form an isotropic liquid phase in the 355–387 K region. The phase behaviour of racemic and meso lead(II) 9,10-dihydroxystearates have been studied by DSC [74]. Differences are observed between the behaviour of recrystallized and premelted samples. For example, the racemic compound gives two transitions on first heating but only one on subsequent heating. If the compound is recrystallized, the two transitions are restored. The meso compound appears to show both solid–solid and solid–mesophase transitions before melting to the isotro-

pic liquid phase. The melting points of these compounds are higher than that of lead(II) stearate, possibly as a result of hydrogen bonding.

The even-chain-length manganese(II) carboxylates have been studied by X-ray diffraction [78] and DTA [131, 236]. The octanoate to hexadecanoate soaps appear to form one intermediate mesophase, but the octadecanoate forms two. From studies of the thermodynamic parameters, it is suggested that the phase behaviour is similar to that of the cadmium(II) carboxylates, and DTA and electrical conductivity data suggest that the liquid phase contains the soaps as cylindrical micelles.

Endothermic peaks in the DTA of iron(III) laurate [121] and stearate [236] between 55 and 105°C indicate the presence of a phase transition. However, no phase assignments have been made.

Hattiangdi et al. have studied some cobalt(II) and nickel(II) soaps by DTA [236] and X-ray diffraction [78]. However, the phases were not identified. Kambe et al. [258] studied anhydrous and hydrated cobalt(II) stearate by DTA. On first heating, two peaks were observed at 99 and 108°C in the anhydrous compound. On cooling and subsequent heating, a new low-temperature transition was observed at 44–54°C. It is suggested that on first heating there is a transition from a solid to a plastic mesomorphic phase, which then melts to the liquid. On cooling, the presence of two mesomorphic phases has been suggested. From the colour of the melt and magnetic susceptibility measurements, it is suggested that there is a change in coordination of the metal on going from the solid to the liquid phase.

The phase behaviour of even chain-length copper(II) carboxylates has been studied using optical microscopy, X-ray diffraction [33, 65, 141], DTA and DSC [33, 129], viscosity measurements [35], dilatometry [175], infrared [142], EXAFS [65, 191] and ¹H-NMR spectroscopy [34], and magnetic susceptibility measurements [140]. It has been shown [33, 65, 141] that these compounds show a phase transition from a lamellar crystalline phase to a hexagonal columnar mesophase at around 110–120°C, and that transition to the isotropic liquid occurs above 200°C. However, melting appears to be accompanied by the onset of thermal decomposition. In some cases, there appear to be small pre-transitions prior to formation of the mesophase [33, 129]. The carboxylates exist as binuclear $(\text{Cu}(\text{O}_2\text{CR})_2)_2$ species in the solid and columnar phases [33], and EXAFS studies [65, 191] indicate that the copper–oxygen and copper–copper distances are identical in the two phases. The drop in magnetic susceptibility observed on this transition [140] has been attributed [65] to a change in the bond angle in the binuclear copper complex. FTIR studies of copper(II) docosanoate [142] showed a shift in the CH₂ asymmetric stretch vibration as the temperature was increased from room temperature to 140°C, indicating that onset of conformational disordering occurs in the columnar phase. However, from dilatometry measurement [175], it is

suggested that although the aliphatic chains are in a disordered state in this phase, they are not completely fused. This is supported by the low transition enthalpy observed on going from solid to mesophase [33]. From the observed line widths in proton magnetic resonance studies [34], it is suggested that the hydrocarbon chains are free to rotate in the mesophase, but are not free to diffuse through the lattice. Chain branching is expected to lower transition temperatures, and the copper complex of $(n\text{-C}_9\text{H}_{19})_2\text{CHCH}_2\text{CO}_2\text{H}$ forms the columnar mesophase at 348 K (140). With tetrakis($\mu(2,2\text{-}(\text{dioctyl}(\text{acetato})))\text{-}O, O'\text{-bis}(\text{copper}(\text{II})))$, it is suggested that the compound is present as a liquid crystalline phase at room temperature [71]. Rhodium(II) [63–65] and ruthenium(II) [65, 66] carboxylates show similar behaviour to the copper(II) ones, forming columnar liquid crystalline phases involving binuclear metal carboxylate complexes. EXAFS studies on the rhodium(II) complexes [65] indicate that there are no significant changes in interatomic distances within the binuclear rhodium core on the solid–mesophase transition. Raman spectral studies [64] on rhodium(II) carboxylates show changes both in the frequency and band half-width of the Rh–Rh vibration on going from solid to mesophase, indicating a weakening of the metal–metal bond.

A non-reversible endothermic peak has been observed in DSC studies of soaps of $\text{Co}(\text{en})_3^{3+}$, $\text{Ir}(\text{en})_3^{3+}$ and $\text{Rh}(\text{en})_3^{3+}$ between 350 and 400 K [259]. However, no phase assignments were made.

Studies have been reported on the phase behaviour of various binary mixtures of divalent metal carboxylates [85, 87, 260, 261], as well as of mixtures of soaps with other compounds [149, 153, 198, 262–264].

TRANSPORT PROPERTIES OF MOLTEN METAL CARBOXYLATES

A number of studies have been reported on the transport properties of the liquid phase of various metal carboxylates. The temperature dependences of the electrical conductivities, viscosities and molar volumes of even-chain lead(II) [102, 265], zinc(II) [102, 265] and cadmium(II) [148] carboxylates containing six to eighteen carbon atoms have been studied from their melting points to just below the decomposition temperatures. The studies have been extended to unsaturated molten metal carboxylates [69] and to some binary mixtures [266–268]. The conductivity measurements [102] revealed that for the zinc carboxylates, the specific conductivities decreased with increase in chain length. The plots of the logarithm of specific conductivity against inverse temperature were linear ($\log k = \log Q - \Delta H/2.303RT$, where k is the specific conductivity, Q is a constant and ΔH is the activation energy for conductance). The activation energies are insensitive to carboxylate chain length, suggesting that the current carriers must be the same in each case. A model has been presented in which conductivity has been attributed almost entirely to metal ions

resulting from the ionization equilibria in the melt



where A is the carboxylate group.

With the lead(II) soaps [102], the Arrhenius plots show curvature. This has been explained in terms of a dissociation equilibrium, which reaches completion in the high-temperature region. Similar behaviour is observed with cadmium(II) carboxylates [148]. However, the activation energies are much higher than with the corresponding lead soaps. Fogg and Pink [80] had earlier studied the conductivities of a number of molten metal carboxylates. The reported conductivities were very low in comparison with most fused salts, and this was explained in terms of the existence of aggregates, such as micelles, in the melts. They presented a model for conductance in which the main current carrier is the micelle, with only small contributions to the conductance from free ions. However, only a limited range of soaps was studied, which did not permit systematic investigation of the effect of carboxylate chain length or metal ion on the conductivity. Furthermore, the temperature range observed was too narrow to detect possible curvature in the activation energy plots. There is agreement between the studies of Sime and co-workers and Adeosun and co-workers [102, 148, 265–268] and of Ubbelohde and coworkers [269–273] on the mechanism of charge conduction in molten soaps. These latter workers studied the conductivity of the liquid phase of sodium and potassium soaps, and reported that the transport of electricity is by ion migration only, and that the mobility of the alkali cation is much greater than that of the bulky anions. These cations are viewed as wandering through a hindering maze of negatively charged organic molecules. The free volume around each cation is assumed to be playing a critical role in the motion of the ions. Data have been presented to show that the hindrance to cation migration becomes larger as anion size increases. In a.c. impedance studies on some molten lead(II) carboxylates [257], it was found that the effect of frequency on conductance is small, but that there is a considerable effect on capacitance.

The electrical conductivity of some molten manganese(II) carboxylates has been reported [131]. Specific conductances are higher than those of the zinc soaps, but smaller than the corresponding lead(II) or cadmium(II) carboxylates. Plots of specific conductance against inverse temperature show curvature, which was interpreted in terms of a simple dissociation equilibrium.

The effects of unsaturation on the conductivity of some molten soaps has been studied, and measurements have been carried out on lead(II) and zinc(II) soaps of *cis*- and *trans*-9-octadecenoic acid and 9,12-octadecadienoic acids [69]. The activation energies for conductance in these unsaturated soaps are similar to those of the corresponding

octadecanoates, suggesting that the metal ions are the main charge carriers in the melt.

Studies have been extended to some binary mixtures of lead(II) dodecanoate/lead(II) acetate [266], lead(II) dodecanoate/dodecanoic acid [267] and lead(II) dodecanoate/lead(II) oxide [268]. The Arrhenius plots for conductance for all the mixtures show similar curvature to that observed with pure lead(II) dodecanoate. For the lead(II) dodecanoate/lead(II) acetate mixtures, the activation energies for conductance in the low-temperature region are independent of composition, suggesting that the major current carrier is the Pb^{2+} ion. Increase in conductance of the mixture with concentration of lead acetate is attributed to increasing Pb^{2+} concentration. For lead(II) dodecanoate/dodecanoic acid and lead(II) dodecanoate/lead(II) oxide mixtures, the activation energies for conductance in the low-temperature region show a steady decrease with increasing concentration of the second component, which has been suggested to arise from the increased mobility of the charge carriers in the presence of these additives.

Electrical conductances of pure, racemic lead 9,10-dihydroxyoctadecanoate, and its binary mixtures with lead(II) octadecanoate have been measured [75]. The conductance of the dihydroxy soap is lower than that of lead(II) stearate at all temperatures. As with other lead(II) soaps, plots of $\log(\text{conductivity})$ against inverse temperature for mixtures of the dihydroxy soap in lead(II) octadecanoate show curvature for mole fractions less than 0.02. The conductances of the mixtures are reproducible with temperature cycling from 10 K above the melting point to approx. 480 K. For mole fractions of the soap from 0.03 to 1.00, the Arrhenius plots display a maximum, with conductances being reversible with increasing temperature up to this maximum, and beyond showing a permanent decrease. A model in which lead(II) ions react with hydroxy groups at high temperatures has been presented to explain this maximum.

Data have been presented for the electrical conductances of mixtures of different metal soaps [274]. Whilst the activation energies for mixtures of different lead(II) soaps are concentration independent, supporting the model of the major charge carrier being the free metal cation, results for mixtures of lead(II) and zinc(II) or cadmium(II) soaps show deviations from ideal behaviour, suggesting that entropies and enthalpies of mixing may be important.

The electrical conductances of mixtures of molten zinc(II), lead(II) and cadmium(II) octadecanoates with cetyl trimethylammonium bromide have been studied [275]. In some cases, deviations from ideality were observed, probably as a result of complexation or ion pair formation.

The viscosities of molten lead(II) [265], zinc(II) [265] and cadmium(II) [148] *n*-alkanoates have been studied. Plots of $\log \eta$ against inverse temperature are linear for all the compounds, with the slopes giving the

activation energy for viscous flow. Plots of ΔH_f against carbon chain length gave 6 kJ mol^{-1} per C atom for lead(II) soaps, 4 kJ mol^{-1} per C atom for zinc(II) soaps and approx. 1 kJ mol^{-1} per C atom for cadmium(II) soaps. From this, it is suggested that while the unit of flow may be a single carboxylate moiety in cadmium carboxylates, aggregates of 3–5 molecules are involved in the viscous flow of zinc and lead carboxylates. Results of ^1H - and ^{13}C -NMR spectral studies [276] support the idea that aggregates are present in these systems. The activation energies for viscous flow depend upon the carbon-chain length of the metal carboxylates, in contrast to those of electrical conductance. This shows that the anions are involved in the mechanism of viscous flow, and also supports the dissociation model for conductance, where the organic anions do not contribute significantly to the transport of current. Studies on pyrene excimer formation in the liquid and L_α mesophase of lead(III) decanoate [276] indicate a local viscosity of the probe which is about an order of magnitude less than the bulk viscosity.

Viscosity measurements have also been made on the unsaturated lead(II) and zinc(II) soaps of oleic, elaidic and linoleic acids [69]. The activation energies for the flow of the unsaturated salts were much smaller than those of the corresponding saturated carboxylates, the stearates, indicating that the structure of the anion is very crucial in determining viscous flow. This trend is very similar to that observed by Kaufmann and Funke [278] on the viscosity of stearic, oleic and linoleic acids, where viscosity decreases with an increase in the number of isolated double bonds. The viscosity of the trans-isomers are reported to be higher than the corresponding cis ones [69], although, within experimental error, the activation energies for viscous flow are the same. Furthermore, conjugation increases viscosity, although the magnitude of this effect is difficult to determine accurately because a slight amount of polymerization in the compounds could produce a substantial increase in viscosity. One possible reason why the viscosities of the unsaturated soaps are often found to be lower than the corresponding saturated ones is that the double bond imposes some degree of rigidity on the soap molecules, thereby preventing close packing upon aggregation in the melt.

Investigations have been extended to the viscosities of binary mixtures of lead(II) dodecanoate/lead(II) acetate [266], lead dodecanoate/dodecanoic acid [267] and lead(II) dodecanoate/lead(II) oxide [268]. Within the composition range studied, the activation energies for the mixtures lead dodecanoate/lead acetate and lead dodecanoate/dodecanoic acid are similar to that of the pure lead dodecanoate. The unit of viscous flow in the lead soap/acetate mixture is suggested to be the same as in the pure soap. To gain insight into the unit of flow in the soap/acid mixtures, the viscosities of lead(II) carboxylate/carboxylic acid mixtures (0.1 mole fraction) have been investigated as a function of

temperature for the even-chain compounds C_{10} to C_{18} . Information on the unit of flow can readily be obtained from the rate of increase of ΔH_f with carbon chain length. A plot of ΔH_f against chain length for these systems is linear, with the slope being 2.4 kJ mol^{-1} per C atom. This is markedly lower than the slopes of 4.2 and 4.0 kJ mol^{-1} per C atom obtained for the systems lead alkanoate/lead acetate (0.1 mole fraction) [266] and pure lead *n*-alkanoate [265] respectively, suggesting that addition of the carboxylic acid causes a slight decrease in the size of the unit of flow. It can be noted that with the pure *n*-alkanoic acids [279], the slope of the corresponding plot is 0.8 kJ mol^{-1} per C atom, suggesting that in this case the mobile units are the simple acid monomers. On increasing the acid concentration there is probably a continuous decrease in the size of the unit of flow from about 3–5 molecules in the pure soap to 1 molecule in the acid. As with the soap/acid mixtures, addition of lead(II) oxide to pure lead(II) carboxylates was observed to cause a slight decrease in the unit of viscous flow [268]. However, in contrast to the behaviour of the systems lead dodecanoate/lead acetate and lead dodecanoate/dodecanoic acid, the activation energy for viscous flow shows a dramatic increase on adding small amounts of PbO. From results of optical observations on a polarizing microscope, coupled with DTA studies, it has been suggested that the structure of the liquid phase changes from small, essentially spherical, micelles in the pure lead dodecanoate to long cylindrical micelles with the addition of PbO [262], and the sharp increase in the activation energy to flow is attributed to these structural changes [268].

A number of studies have been reported on the densities and molar volumes of metal soaps using dilatometry. It is of interest to compare the behaviour of these with the alkali metal soaps. The eutectic temperature in sodium laurate/lauric acid has been established by this technique [280]. Dilatometry has also been used to study the phase behaviour of metal salts of some straight-chain fatty acids containing an even number (8–22) of carbon atoms [281, 282]. The phase transitions in these systems were regarded as successive stages of melting. Skoda and Brouwer have examined the molar volumes as a function of temperature of a number of anhydrous soaps consisting of straight and branched carbon chains [383, 384]. The results indicate the existence of different modes of hydrocarbon chain packing in the crystalline and mesomorphic phases of anhydrous sodium and lithium soaps. The magnitude of the molar melting dilation in the soaps was found to decrease with increase in the size of the cation, and is lower than that of the corresponding hydrocarbons. As a complementary technique to DTA or DSC, dilatometry has been used to reveal the intermolecular association in the molten state of sodium stea- rates–stearic acid mixtures. Dilatometric studies on intermediate phases in calcium(II) [84], cadmium(II) [151], lead(II) [107] and copper(II) [175] soaps have already been discussed.

The molar volumes of zinc(II) [102], lead(II) [102] and cadmium(II) [148] carboxylates, as well as those of binary mixtures [266–268, 285], have been examined. At low temperatures (below 476 K), the plots of molar volume against temperature for lead, zinc and cadmium carboxylates are linear. For all of the zinc soaps, there is a slight curvature towards higher molar volume and higher temperatures. For lead decanoate and dodecanoate, deviations from linearity at high temperatures are slightly non-random, with the molar volume of the decanoate being concave and that of the dodecanoate being convex towards the temperature axis. The molar volumes of lead, zinc and cadmium soaps are linear functions of chain length in the temperature range studied. The relationships, at one particular temperature (450 K), are as follows: lead soaps, $V_{450} = 53.01 + 36.53n \text{ cm}^3 \text{ mol}^{-1}$; zinc soaps, $V_{450} = 56.97 + 36.45n \text{ cm}^3 \text{ mol}^{-1}$; cadmium soaps, $V_{450} = 25.70 + 37.70n \text{ cm}^3 \text{ mol}^{-1}$, where n is the number of carbon atoms in the fatty acid chains, and the total number of carbon atoms per molecule of soap is $2n$. From these relationships, the increase in volume per methylene group for lead, zinc and cadmium carboxylates are 18.3, 18.3 and $18.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ respectively. It is suggested that the higher value obtained for cadmium carboxylates indicates greater disorder of the aliphatic chains in the melt. The volume occupied by the head groups are found to be 89.5×10^{-6} , 93.4×10^{-6} and $63.4 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for lead, zinc and cadmium carboxylates respectively, suggesting a more tight packing of the ionic group in the aggregates in the cadmium soaps.

The molar volumes of the lead and zinc salts of *cis*-9-octadecenoic, *trans*-9-octadecenoic and 9,12-octadecadienoic acids have been measured [69]. The molar volumes of both the lead and zinc salts only differ by about 3% from each other and from those of the corresponding octadecanoates, suggesting that unsaturation of the hydrocarbon chains does not significantly affect molar volumes, and that the length of the aliphatic chain is a much more important factor. The configuration of the geometric isomers also does not seem to have any effect, because the molar volumes of the oleates and elaidates were essentially the same.

The molar volumes of some binary mixtures have also been determined. Over the concentration range of the additive studied (0.00–0.20 mole fraction), the plots of molar volume against concentration for the systems lead(II) dodecanoate/dodecanoic acid [267], lead(II) dodecanoate/lead(II) oxide [268] and lead(II) dodecanoate/lead(II) acetate [266] are linear. This suggests that, within the limitations of the experiments, there is no significant deviation from ideal behaviour within this concentration range. To obtain more information on the liquid phase of these mixtures, the molar volumes have been studied for the system lead(II) dodecanoate/dodecanoic acid over the complete composition range from pure soap to pure acid [285]. The liquid phases of the two

components are stable over similar temperature ranges and appear, from optical observations to be completely miscible. At any particular temperature, the molar volumes show a steady decrease with increasing mole fraction of the acid. While mixtures at low or high acid mole fraction show the expected linear plots of molar volume against temperature, at an acid mole fraction of approx. 0.5 these plots show curvature at high temperatures. Similar curvatures are observed in the plots of molar volumes against temperature for equimolar mixtures of lead(II) hexadecanoate/hexadecanoic acid and lead(II) octadecanoate/octadecanoic acid. This behaviour demonstrates the presence of a slight excess volume of mixing in these mixtures, especially at high temperatures. Deviations from ideal behaviour in these systems were suggested to arise from changes in the nature of the aggregates present in the melt. This view is strengthened by viscosity data [267] which show a decrease in the size of the units of flow of lead(II) carboxylates upon the addition of the corresponding carboxylic acid. Further support for changes in the nature of the aggregates comes from the work of Fendler [286], who reported that the presence of additives causes a reduction in the tendency of soap molecules to micellize as a consequence of a resistance to mixing. With the lead(II) carboxylate/carboxylic acid mixtures, it has been suggested that the deviations observed at high temperature are a result of the monomer–dimer equilibrium of the acid, and that the monomeric acid species tend to disturb the structures of the soap aggregates more than the hydrogen bonded dimers [285].

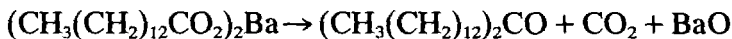
Surface tensions have been measured of the liquid phase of a number of lead(II), zinc(II) and cadmium(II) carboxylates [287]. The magnitudes of the surface tensions are much lower than those of molten inorganic salts, but are comparable with those of short chain-length aliphatic hydrocarbons. They appear to increase slightly with chain length, and with unsaturation. Surface tensions of the cadmium soaps are somewhat lower than those for the lead and zinc soaps, possibly as a result of different aggregates present in the melts. Parachors have also been calculated, and are lower than predicted by atomic parachor parameters. Differences between lead and zinc soaps have been interpreted in terms of the more covalent character of Zn(II) soaps.

The general surface and interfacial properties of films of metal soaps have been reviewed [288]. These results have practical relevance to the tribology of Langmuir–Blodgett multilayers, which have also been studied by direct measurements [289].

PRODUCTS OF THERMAL DECOMPOSITION

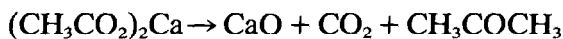
It has long been established that salts of carboxylic acids decompose thermally to yield symmetrical ketones as the major product [290–292].

For example, barium tetradecanoate when heated to temperatures in excess of 200°C produces heptacosan-14-one in good yields [292]

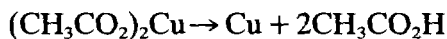


In addition, ketones have been prepared in good yields as pyrolysis products from mixed salts of organic acids [293, 294]. Though these reactions are well known, their decomposition mechanisms are complicated. In this section, the products obtained from thermal decomposition of a few selected types of metal carboxylates will be considered, with only brief reference to mechanisms. Further details of the thermal decomposition of metal carboxylates are given in an excellent review [295]. More detailed considerations of the kinetics and mechanisms of these reactions will be deferred to the next section.

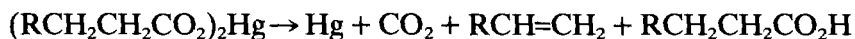
Judd et al. [296] found that acetone is the major product formed on pyrolysing calcium acetate



However, on pyrolysing copper(II) acetate, formation of metallic copper and acetic acid was observed.



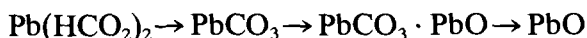
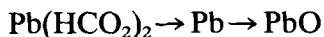
Similar behaviour was observed with silver(I) acetate, and it was suggested that when the residue was a metal oxide, acetone was the main organic product, but when the residue was a metal, acetic acid was the product. Metallic copper has also been observed in the thermal decomposition of various short-chain copper(II) carboxylates in an inert atmosphere [297], whilst in the presence of oxygen the oxide was formed. Evidence has been presented for formation of intermediate copper(I) species on thermal decomposition of copper(II) carboxylates [298, 299]. Care must be exercised in extrapolating results for pyrolysis of short-chain-length carboxylates, where the compound is normally present as a solid, to metal soaps, where decomposition occurs in the melt. However, with copper(II) [130] and mercury(II) soaps [300], thermal decomposition has also been shown to produce the metal and carboxylic acid. In addition, there is evidence for formation of the α -olefin.



Alkene formation here is strongly reminiscent of the formation of this species on one-electron oxidation of carboxylic acids in Kolbe electrosynthesis [301].

Baraldi [302] studied the thermal decomposition of lead(II) formate using an infrared emission spectrometer, and obtained evidence for complex behaviour. On heating in air, a phase transition occurred at 115°C, following which decomposition took place which led directly to

metal and oxide, or to carbonate, which decomposed to the oxide



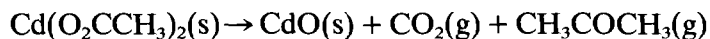
Under vacuum, the same transformations occurred at higher temperatures and led to formation of the metal. With soaps in general, it is also observed that decomposition occurs at lower temperatures in air than in inert atmospheres [303]. The thermal decomposition of the intermediate lead(II) carbonate has been discussed in detail elsewhere [304, 305].

McAdie and Jervis worked on the thermal decomposition of barium, strontium, magnesium, cadmium and zinc acetates [306]. The thermal decomposition of anhydrous barium acetate has been reported to yield barium carbonate with the evolution of acetone [307–309]. Formation of barium oxide is prohibited thermodynamically [310] at the decomposition temperature of the acetate, which has been variously reported to have values between 241 and 480°C



Similarly, the thermal decomposition of strontium acetate yielded strontium carbonate and acetone.

The thermal decomposition of cadmium acetate dihydrate produces the loss of both molecules of water below 150°C, and the decomposition continues at a reasonable rate to produce an amorphous form of CdCO_3 , which readily decomposes to CdO and CO_2 [310]. Only under conditions where the rate of decomposition of cadmium acetate is slow can evidence for its formation be obtained, which probably accounts for the reported lack of evidence for the carbonate from several workers [309, 311, 312]. The decomposition mechanism has been suggested to be similar to that for barium acetate [310], with the exception that the carbonate is metastable and decomposes directly to the oxide. Thermodynamically, the overall decomposition process is endothermic [313]



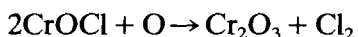
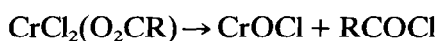
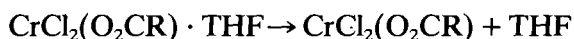
The thermal decomposition of magnesium acetate tetrahydrate causes a loss of water from this salt between 100 and 200°C, producing the anhydrous acetate, which subsequently decomposes with the evolution of acetone at 330°C to give magnesium oxide. Yakerson et al. [314] argued that magnesium carbonate is the decomposition product of anhydrous magnesium acetate, and that the MgO results only from the secondary decomposition of this. This may occur through a hydroxycarbonate if water vapour is present [315]. Further studies on the decomposition of the Group-II metal acetates at temperatures up to 500°C by McAdie [316] confirmed that carbonates were produced in the cases of barium and strontium, and oxides in the cases of magnesium, cadmium and zinc.

These latter materials also appear to decompose, at least partially, from the molten state, involving formation of crystalline intermediates, possibly the mixed acetate–oxide or oxyacetate type. Studies on the thermal degradation of beryllium [93] and magnesium [394] soaps show metal oxide, ketone and carbon dioxide as main products, whilst the solid residue appears to be the carbonate with calcium [317] and barium [318] soaps.

With zinc(II) soaps, pyrolysis has been reported to produce ketones and carbon dioxide, with a mixture of zinc carbonate and oxide as solid residue [152, 319]. Production of ketone, metal oxide and carbon dioxide has also been indicated with aluminium(III) [101], cobalt(III) [258] and lanthanide(III) [52, 162] soaps. Formation of metal oxide has also been suggested on thermal decomposition of some complex rhodium(III) carboxylates [259, 320].

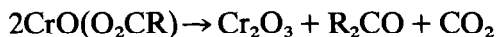
Although these studies show that thermal decomposition of metal carboxylates normally yields ketones as the main organic products, use of more sophisticated analytical techniques indicate the presence of a number of minor components. Thus, Ellis and Okoh [321] showed in the thermal decomposition of lead(II) decanoate that whilst the ketone nonadecan-10-one was the major product, lower ketones, alkanes, alkenes, CO₂ and CO are also produced. Complex decomposition routes have been observed with Zn(II), Mn(II) [322] and Fe(II) [323] carboxylates, with the formation of CO, CO₂, H₂O, H₂ and metal oxide. In the case of the iron(III) compounds, formaldehyde and iron(II) formate were also observed. Mossbauer spectroscopy has shown that thermal degradation of iron(III) propionate and butyrate tetrahydrates also produces intermediate iron(II) species [324].

Rai and Parashar [62] studied the thermal decomposition of a number of carboxylate derivatives of chromium(III). Chromium dichloride monocarboxylate monotetrahydrofuran adducts are found to be thermally stable up to 120°C, above which a slow decomposition starts, and continues to approx. 250°C, involving the loss of THF. The decomposition of chromium dichloride monocarboxylate begins around 240°C and becomes rapid by 400°C. The inorganic residue is the chromium oxychloride, which itself starts decomposing between 400 and 500°C to give chromium(III) oxide. The overall reaction sequence is

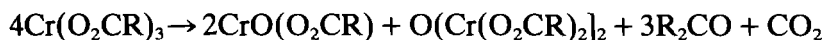


Chromium(III) monochloride dicarboxylates follow a different route of decomposition. They are stable up to 180°C, above which the following

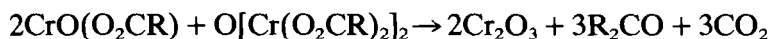
reactions occur



Corresponding acyl halides and ketones undergo rapid decomposition at about 480°C. The mode of decomposition of chromium tricarboxylates is found to be different from that of the aluminium or lanthanide tricarboxylates [52, 101, 162]. In that case, all indications suggest a two-step decomposition, with the compounds being stable up to 210°C, and then showing liberation of carbon dioxide. Decomposition of the corresponding ketones is also observed in this process. Chromium oxycarboxylates formed in the decomposition process remain stable up to 350°C. The first mode of decomposition may be represented as



This may be followed by the decomposition of the ketone. Chromium oxycarboxylates undergo further decomposition above 380°C with the formation of chromium trioxide and the corresponding ketones. It is suggested that these ketones undergo decomposition at such high temperatures in the presence of air



Wood and Seddon have studied the thermal decomposition of various transition metal carboxylates, both alone and as mixtures with acids, alcohols, esters and amines [317, 325, 326]. Decomposition of the pure soaps generally produces the metal oxide, carbon dioxide and ketone.

A study has been reported of the thermal degradation of various commercial metal octadecanoates using TG, DTG, TG-MS and high pressure DTA [327]. With the calcium soap, CaCO_3 was obtained, which releases CO_2 on further heating to give the oxide. Carbon monoxide also appears to have been produced as a major product at the temperature of loss of the organic component. With Zn(II), Pb(II), Sn(II), Mg(II) and Fe(III) stearates, the inorganic residues are the metal oxides.

In certain cases [328], decomposition of metal carboxylates has been used to produce organometallic compounds.

As long ago as 1893, Wislicenus [329] showed that thermal decomposition of barium adipate produced cyclopentanone as the inorganic residue. It was not specified if barium oxide or carbonate was obtained. The thermal decomposition of a number of other dicarboxylates has also been reported [330–338]. With the short chain-length members, the cyclic ketones are generally formed.

Biader Ceipidor and co-workers [335–337] studied the thermal decomposition of the following potassium chromium(III) dicarboxylates: malonate, monomethylmalonate, dimethylmalonate, oxalate, maleate, succinate

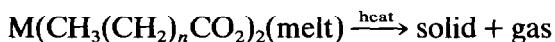
and phthalate. Studies on closely related systems were also carried out by Wendlandt et al. [338]. $K_3Cr(Ox)_3$ was found to be thermally stable up to 300°C, with a slow decomposition, involving decarboxylation occurring above this temperature, and continuing until 530°C. This gave a mixture of K_2CrO_4 and potassium carbonate [338]. For $K_3Cr(\text{malonate})_3$, thermal decomposition of the anhydrous salt started at 150°C and continued until 325°C, when a mixture of chromium and potassium carbonate-oxide ($CrK_3(CO_3)_{3/2}O_{3/2}$) was observed. At 600°C, the decomposition became rapid and the product left was a mixture of chromium and potassium oxides, stoichiometrically corresponding to CrK_3O_3 . $K_3Cr(\text{succinate})_3$ was found to be thermally stable up to 80°C, above which temperature the anhydrous salt started decomposing up to 400°C, with formation of a chromium and potassium mixed oxide/carbonate system. Increasing the temperature to 700°C, yielded a mixture of chromium and potassium oxides.

$K_3Cr(\text{maleate})_3$ started decomposing at 180°C, and was converted to a mixture of chromium and potassium oxides at 700°C. With the mixed phthalate, decomposition started at 110°C, with decarboxylation beginning at around 530°C to give a mixture of chromium and potassium carbonates and oxides, while the corresponding oxides were formed at 800°C. The effect of methyl substitution was studied with the malonates. The thermal decomposition of the malonate, monomethylmalonate and dimethylmalonate follow a common reaction sequence to give a mixture of oxides and carbonates, which at higher temperatures gives a residue consisting of just the metal oxides. The monomethylmalonate complex starts melting at 110°C. At 320°C, demethylation and decarboxylation has occurred, whilst above 600°C, the mixture of oxides is obtained. With the dimethylmalonate complex, melting started at 90°C, and the demethylation and decarboxylation reactions starts at 280°C, whilst metal oxide formation occurs above 400°C.

KINETICS

The literature on the thermal decomposition kinetics of di- and higher valent metal carboxylates is vast and, in many respects, gives a confused picture of the thermal behaviour of these compounds. For example, Mehrotra and coworkers [136, 339] have investigated the isothermal decomposition of some even-chain manganese(II) carboxylates as a function of temperature and time, and concluded that the kinetics are most adequately expressed by the Prout–Tomkins equation [340] using two different rate constants. Unfortunately, these authors give little information on the physical state of the compounds just prior to decomposition. A thorough appreciation of the physical changes in the salts under investigation before decomposition is necessary if misleading

kinetic information is to be avoided. For example, several of these compounds melt before decomposition leading to heterogeneous decomposition reactions [306, 321, 341, 342].



Clearly, the application of solid state kinetic equations to what are, essentially, decompositions from the melt could be misleading. Thus, Barnes et al. [343] were able to conclude, for the thermal decomposition of calcium octadecanoate, that changes from the molten to the solid state occurred with attendant complications of thermal behaviour. Nevertheless, useful kinetic information can be obtained if there is a clear understanding of the heterogeneous nature of such metal carboxylate decomposition reactions. For instance, Rubinshtein and Yakerson [344] have used conventional kinetic analysis to obtain data from the thermal decomposition reactions of several acetates, reasoning that the physical state of the melt during decomposition is analogous to that of a liquid undergoing thermal decomposition. For other carboxylates, more sophisticated interpretations of kinetic data have been proposed. For example, Terez and Gyula [345] have studied the thermal decomposition of several calcium salts in air and found orders of reaction varying between 0.2 and 0.7. This variation in reaction order was attributed to the formation of calcium carbonate, with a loosened crystal structure, as the end product. Similarly, Brown [346] attributed the different kinetic behaviour observed in the thermal decomposition of lead citrate, prepared in two different ways, to differences in structural order of the starting material. Electron micrographs showed that nucleation occurs randomly on the surface of the more ordered particles, and nuclei grow rapidly to form spheres of lead metal, one of the end products of decomposition. In the case of several nickel(II) carboxylates, Wheeler and Galwey [347] were able to obtain kinetic equations characteristic of a degradation mechanism involving nucleation and growth of particles of a solid product. In addition, they showed that the rate-controlling process in the isothermal decomposition reaction in oxygen is determined by the product (nickel oxide) surface and defect properties. However, identifying the factors which control the kinetic behaviour has not been easy, and some hypotheses have been the subject of controversy. For instance, there is some disagreement in the literature concerning the thermal decomposition reaction of manganese(II) oxalate [348–351]. Conclusive proof for a contracting sphere mechanism [352] for $0.3 < \alpha < 0.9$ has been obtained by Brown et al. [353] from a kinetic analysis of reduced time data. In addition, they showed that the rates of reaction in oxygen and in vacuo are influenced by

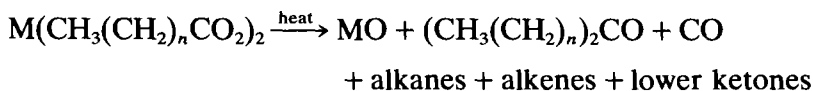
the method of salt dehydration prior to decomposition. This means that the generation and advance of the reactant/product interface is influenced by the reactant structures developed during dehydration. Nevertheless, there is still some uncertainty over the description of the precise rate-limiting step. Kinetic results from decomposition of other divalent metal oxalates and formates, where similar mechanisms have been proposed, have been widely reported [295, 354–359].

The decomposition kinetics of the corresponding hydrated salts have also been widely documented. Mikhail et al. [360] have, from TG data, interpreted the decomposition reaction of zinc oxalate dihydrate as occurring in two stages, the first of which involves dehydration in a pseudo-first-order reaction, which is dependent upon the ambient atmosphere. At low water-vapour pressures, dehydration is activated by diffusion, which changes, predominantly, to a reaction activated by desorption at higher water concentrations. The second stage of decomposition is unaffected by the surrounding atmosphere. Isothermal data obtained by Galwey and Brown [361] for nickel formate dihydrate confirms the importance of access of water vapour in the decomposition reaction of hydrated salts. Decomposition rates are sensitive to vapour pressures in the vicinity of reactant crystallites leading, most probably, to variations in the reported kinetic behaviour of these salts. Whilst Bassi and Kalsi [362] did not discuss the effect of water vapour on the decomposition reaction of cupric acetate monohydrate, they were able to conclude, from isothermal data, that dehydration and subsequent decomposition of the dehydrated acetate both follow an Avrami–Erofeev [363] equation, with an activation energy or both events in the region of 30 kJ mol^{-1} . Similar results were obtained by Tanaka and Tokumitsu [364] from isothermal and rising temperature experiments for thermal dehydration of manganese oxalate dihydrate. They found that dehydration was regulated by one of the Avrami–Erofeev equations. Although these results are in conflict with the earlier results of Dollimore et al. [365], and Mourad and Nashed [366], Tanaka and Tokumitsu pointed out that differences in the results might be ascribed to differences in sample and measuring conditions. It is not surprising, then, that much of the work on the thermal dehydration reactions of oxalates is still the subject of active discussion. For example, Shkarin et al. [367] concluded, from the similarities they found in the kinetics of dehydration of some transition metal oxalates (all first-order processes with $E_a \approx 100 \text{ kJ mol}^{-1}$), that the mechanisms of the reaction are probably identical. Later work by various groups has suggested that the decomposition mechanisms are dissimilar in some cases, notably the copper(II) [362] and nickel(II) [368] salts. The complexities of kinetic behaviour observed with simple carboxylates are not always observed with the longer chain-length salts. Rising temperature kinetic studies on the higher, even chain-length divalent metal carboxy-

lates, such as the octanoate to octadecanoate, have shown, in most cases, zero-order decomposition kinetics [319, 321, 365–373], with activation energies for the overall decomposition reaction to products of around 30–50 kJ mol⁻¹. These are remarkably consistent, particularly in view of the different methods of kinetic analysis employed. Moreover, because zero-order kinetics are consistent with a diffusion mechanism as the rate-controlling step, these results indicate that the reactions are independent of initial carboxylate concentration, and the surface of the molten salt remains covered by gaseous product(s) throughout the reaction. Conversely, the isothermal decomposition data have tended to yield higher values for activation energy [347, 374, 375], and orders of reaction other than zero.

MECHANISMS OF THERMAL DECOMPOSITION OF CARBOXYLATES

It is well known that salts of many carboxylic acids decompose thermally to yield ketones as the major product [290–292, 296, 370]. The reaction scheme for thermal decomposition in various atmospheres is usually given as



In some reported cases, an anhydride is cited as the primary product of decomposition instead of ketone [376–380]. As discussed, this may arise via the acid, produced in a Kolbe-type reaction involving one-electron oxidation of the carboxylate. Competition between this reaction pathway, and ketone formation must depend strongly upon the lifetimes of any intermediate species.

Recent results [381, 382] have allowed the direct determination of the lifetimes of RCO₂· radicals, which are the probable intermediates in these processes. Further studies in this area are likely to help predict whether ketone or acid formation will be the predominant process. In some cases, metal carbonate is the intermediate [321, 383] or end product [306–309, 384, 385], instead of the more commonly observed metal oxide or metal.

Decomposition reactions are sensitive to the type of metal ion present in the salt, and the effect of possible product accumulation. The function of the metal ion is still somewhat obscure. For example, we have already indicated that acetone formation occurs with acetates of cations, such as calcium(II), which do not readily undergo redox processes. In contrast, carboxylates of copper(II), silver(I) and mercury(II), which all have energetically accessible zero, mono- and divalent oxidation states, all seem to produce carboxylic acids, and probably olefins as major products [130, 296, 300]. Several mechanisms have been proposed to explain the degradation route of metal carboxylates [308, 344, 386–391]. With the use

of more sensitive instrumentation to analyse and identify reaction products, such as GC–MS, it is now becoming clear that the decomposition reactions are far more complex than reported in the early literature, and many more products than anticipated have been identified [321, 391]. For example GC analysis of the decomposition products of lead(II) decanoate at 390°C showed formation of appreciable amounts of alkanes, alkenes, decanone, undecan-6-one, dodecanone and tridecanone, in addition to the parent ketone, nonadecan-10-one [321]. Furthermore, the high temperatures generally required for rapid reaction, and the non-integral reaction orders [359, 392] obtained from decomposition kinetic studies on many di- and higher valent metal carboxylates, support a chain mechanism initiated by free radicals. Indeed, free radicals have been strongly implicated in the thermal decomposition reactions of some acetates [306], calcium butanoate [393], and calcium [391] and lead(II) [321] decanoates. However, although a radical mechanism is most plausible in many of these decompositions, an unambiguous interpretation of the mechanism of these reactions is still a matter of dispute, and much work still remains to be done in this area.

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NOTE ADDED IN PROOF

Since submission of this article, we have become aware of the following relevant papers.

Alkyl chain motions of dicopper-tetraalkanoates in the crystalline and columnar phases. A quasielastic neutron scattering study, A.M. Giroud-Godquin, P. Maldivi, J.C. Marchon, M. Bée and L. Carpentier, *Mol. Phys.*, 68 (1989) 1353.

Alkyl chain motions in columnar mesophases. A quasielastic neutron scattering study of dicopper tetrapalmitate, L. Carpentier, M. Bée, A.M. Giroud-Godquin, J. Maldivi and J.C. Marchon, *Mol. Phys.*, 68 (1989) 1367.

Multiple bonds between metal atoms in ordered assemblies: liquid crystals containing Mo–Mo quadruple bonds, R.H. Cayton, M.H. Chisholm and F.D. Darrington, *Angew. Chem. Int. Ed.*, 29 (1990) 1481.

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Structural study of crystalline and columnar copper(II) soaps, M. Ibn-Elhaj, D. Guillon, A. Skoulios, A.M. Giroud-Godquin and P. Maldivi, *Liquid Crystals*, 11 (1992) 731.