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Comparison of the thermal behaviour of the metal salts of simple and polymeric carboxylates

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Abstract

The thermal decomposition of several metal polyacrylates and poly(meta)acrylates is compared with the TG of simple carboxylates. The applicability of a general scheme of decomposition is discussed.

INTRODUCTION

Several reports have been published on the thermal decomposition (TD) of polyacrylic acids [1–5], of partially neutralized polyacrylate films [6] and of alkaline and transition metal polyacrylates [7–10]. In particular, Skupinska et al. [9] studied the thermal behaviour of several metal polyacrylates and found that the decomposition of iron(III) polyacrylate starts at a lower temperature and spans a wider range than that of the nickel(II), cobalt(II) and manganese(II) salts. The authors attributed these features to a higher degree of cross-linking in the salt of the trivalent iron(III) than in the divalent M(II) salts. The thermolyses of simple metal carboxylates have also attracted the attention of a number of workers [11], in particular the salts of copper(II) [12–14] and iron(III) [15–17]. Earlier, we reported that metal carboxylates have several decomposition pathways [18]; in the case of iron(III) salts, the presence of OH^- in the basic salt and the possibility of electron transfer from the carboxylate moiety to the metal centre gives rise to a clearly differentiated behaviour compared with divalent metal (other than copper) carboxylates.

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In the present paper we explore the TD of several metal polyacrylates and poly(meta)acrylates. Their comparison enables an assessment to be made of the effect of chain rigidity without the ambiguities implicit in the interpretation of the behaviour of iron(III) salts. The applicability of the general scheme of TD of metal carboxylates derived earlier to salts of polycarboxylates is also discussed.

EXPERIMENTAL

Preparations and chemical analyses

Polyacrylic (PA) salts were prepared by diluting about 5 g of polyacrylic acid (molecular weight 5000) (Aldrich), supplied as 50 wt.%, to 200 ml of water and slowly adding dropwise with stirring 17.35 ml of 2 N NaOH solution (final pH 11.6); an equivalent amount of the metal in the form of a soluble salt was then added. The pH of the final solution was in the range 5–6, except in the case of the iron(III) salt where a twofold excess was used and the final pH was 1.6. The solids obtained were centrifuged and washed several times with doubly distilled water and dried under vacuum over $CaCl_2$. Poly(meta)acrylic (PMA) salts were prepared in a similar way. Metal contents were determined on a Varian Techtrom A-A5R atomic absorption spectrometer.

Spectral characterization

X-ray diffraction data were recorded using a Philips X-ray Generator PW 1130 and IR spectra of solids and gases were measured using Perkin–Elmer 580 B and Beckman 4260 spectrometers. For solids, samples were prepared in the form of KBr disks.

DTA–TGA

Thermogravimetric experiments were performed using a Rigaku Denki CV 8002 L2 thermobalance with samples of about 20 mg under an N_2 atmosphere in the temperature range 25–500 °C at a heating rate of 10 °C min^{-1}.

The identification of the evolved products was performed qualitatively by IR spectroscopy of gases released under isothermal conditions in a tubular furnace.

RESULTS AND DISCUSSION

Nature of the solids

Table 1 shows the extent of hydrogen substitution by the metal ions in the solids. The ratio RCOO(H)/M is in all cases close to three. In the case of divalent metal ions, the ratio implies that one third of the carboxylic acid groups is unionized. In the case of iron(III), several pieces of evidence suggest that iron is bound to one OH^- ion, and therefore behaves as a divalent cation, $FeOH^{2+}$; the fraction of the free carboxylic acid groups is therefore similar to that for the other salts. The following observations provide evidence for this.

(a) The thermolysis of iron(III) indicates the existence of chemically bound water; it is reasonable to assume that the water corresponds to protons bound to $RCOO^-$, and OH^- bound to iron.

(b) Iron(III) forms a series of well-characterized basic carboxylates, i.e. it is well established that in the course of precipitation, hydrolysis competes effectively with the formation of carboxylate–Fe bonds under many experimental conditions.

(c) The IR spectra of the solids show a peak at around 1720 cm^{-1} which corresponds to protonated carboxylate groups.

As the total carboxylate/total iron ratio is about three for each protonated carboxylate, there must be one OH^- group bound to iron(III). In principle, it is expected that the extent of hydrolysis of iron ions in the solids is dependent on the experimental conditions, and comparisons with other reports in the literature must take this fact into account. However, as our solids were prepared at pH 1.6, it seems unlikely that unhydrolised iron polyacrylates may be prepared by straightforward mixing techniques.

TABLE 1

Chemical analyses

Salt	Metal content (%)	RCOO(H)/M
CuPA	19.19	2.96
NiPA	15.04	2.97
FePA	15.26	3.00
CoPA	16.15	2.99
CuPMA	17.92	2.93
NiPMA	18.17	3.06
FePMA	13.53	2.98
CoPMA	18.19	3.08

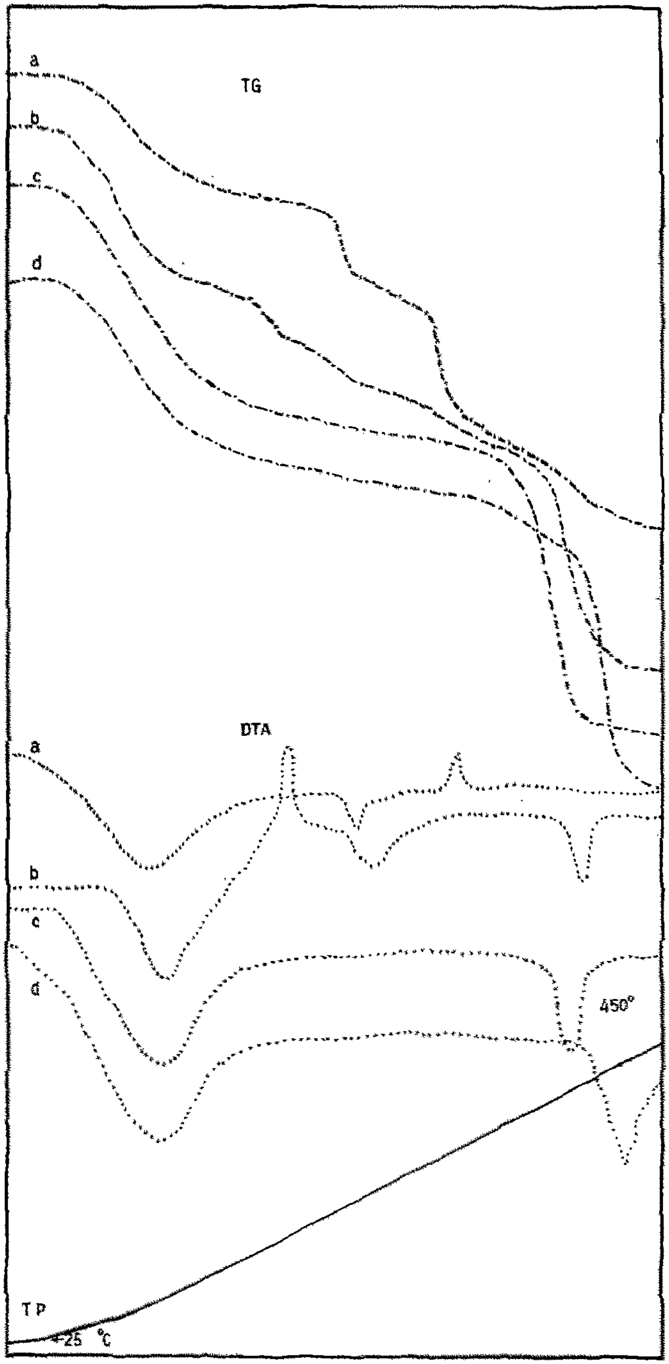


Fig. 1. TG (·—·—·) and DTA (······) curves for the different polyacrylates: curve a, copper(II); curve b, iron(III); curve c, nickel(II); and curve d, cobalt(II) salts. Linear heating is also shown.

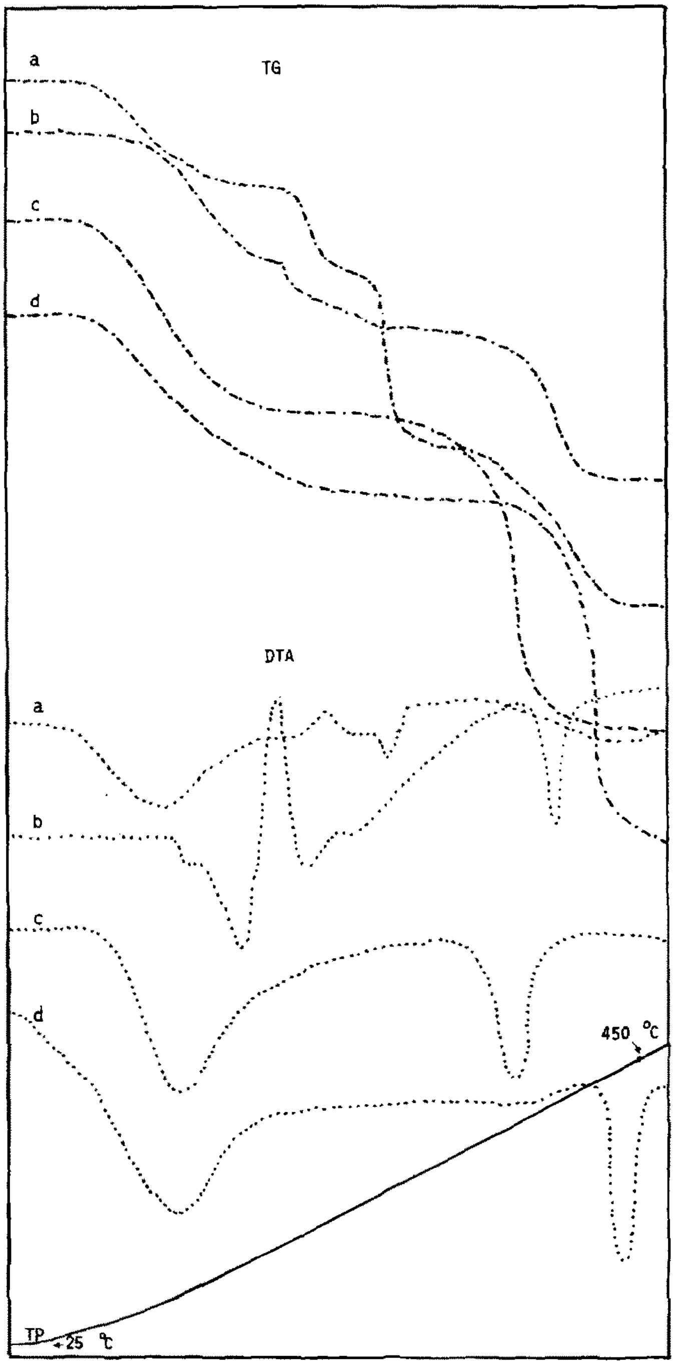


Fig. 2. TG (·—·—·) and DTA (······) curves for the different poly(meta)acrylates: curve a, copper(II); curve b, iron(III); curve c, nickel(II); and curve d, cobalt(II) salts. Linear heating is also shown.

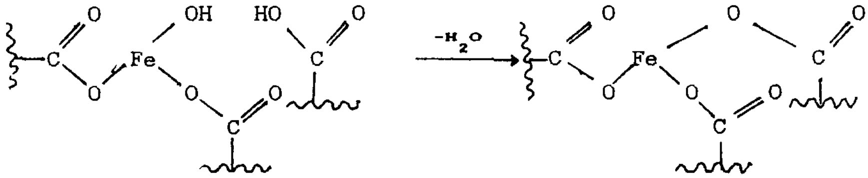
Thermal decomposition

Figures 1 and 2 show the thermograms of the cobalt(II), nickel(II), copper(II) and iron(III) polyacrylates and poly(meta)acrylates respectively. In all cases, the first stage is the release of water (90–115 °C). In the iron salts, the second stage, at 200 °C and 174 °C for PA and PMA respectively, corresponds mainly to a second dehydration. There is some overlap with the decomposition of the organic moiety, and the gaseous products are mainly water and carbon dioxide.

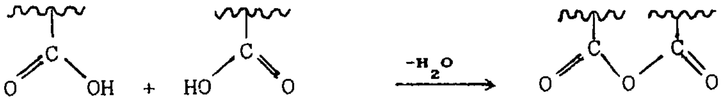
The dehydration is typical of basic iron carboxylates and involves the formation of oxobonds from OH^- groups:

$$R_2FeOH + HOFeR_2 \xrightarrow{-H_2O} R_2Fe\text{–}O\text{–}FeR_2 \qquad (1)$$

In the present systems, substantial fractions of free acid groups are present, and two additional reactions may contribute to the formation of water:



(2)



(3)

TABLE 2

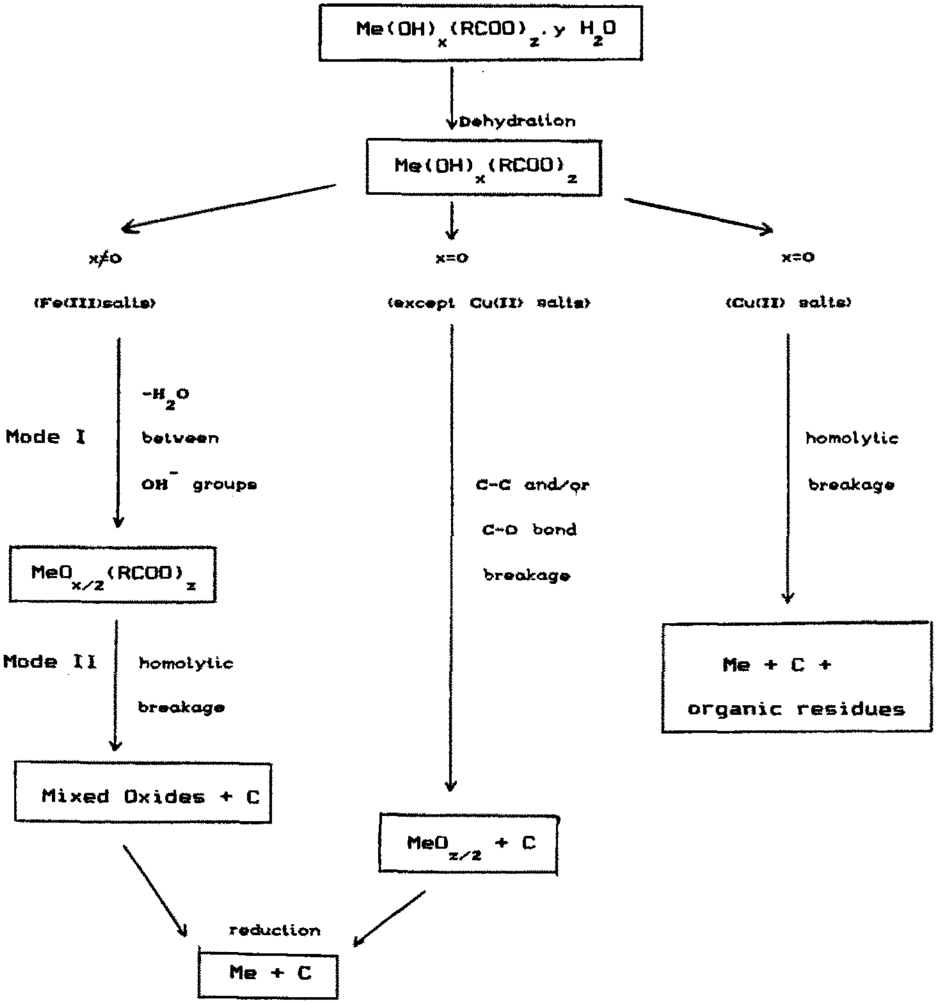
DTA peak temperature data (°C) for the different polymers

	PA salts	PMA salts
Cobalt(II)	102	96
	454	426
Nickel(II)	110	110
	409	376
Copper(II)	96	90
	236	200
	330	264
Iron(III)	115	114
	200	174
	260	250
	414	380

In agreement with the above reaction scheme, the IR spectra of the residual solids indicate the presence of metal carboxylate groups ($\nu = 1640$ and 1390 cm^{-1}) and anhydride groups ($\nu = 1800\ \mathrm{cm}^{-1}$). The presence of oxobonds cannot be probed by this technique.

The third stage in the case of the the iron(III) salts, and the second stage in the other salts, corresponds to loss of weight due to the release of decomposition products from the anionic moiety.

Table 2 gives the decomposition temperatures of the polyacrylates and poly(meta)acrylates studied. The values follow the sequence iron(III) mode I < copper(II) < iron(III) mode II < nickel(II) < cobalt(II), that is, the opposite to the general stability sequence for metal chelates: cobalt(II) < nickel(II) < copper(II) < iron(III).



Scheme 1. The thermal decomposition mechanism of metal carboxylates and polyacrylates. Only solid products are indicated; the temperature increases downward.

The main gaseous products detected were CO_2, CO and lower hydrocarbons; hydrogen was not investigated. The residual metals obtained at high temperatures result in all cases (except copper) from the reduction of the oxides formed at lower temperatures. The reduction takes place below 600 ° C for cobalt and nickel oxides and above 600 ° C for Fe_3O_4. Carbon is most certainly present and is responsible for the reduction of the oxides. In the case of copper, the second peak in the thermogram (centred at 200 and 236 ° C) results in the formation of metallic copper (detected by X-ray diffraction). The weight loss associated with the third peak (264 and 330 ° C) is due to the release of gases from non-volatile organic residues formed in the second stage. The behaviour is totally consistent with that of simple carboxylates, and the sequence of decomposition temperatures is determined by the redox chemistry of the metal centre. In the cases of iron(III) and copper(II), homolytic O–M bond breakage is relatively easy, whilst in nickel(II) and cobalt(II) it requires higher temperatures. In the case of cobalt(II) and nickel(II), C–O bond breakage prevails over O–M bond breakage.

The importance of chain rigidity and cross-linking can be assessed by comparing the behaviour of the polyacrylates and the poly(meta)acrylates (see Table 2). It may be concluded that the effect is only slight.

In summary, the general decomposition scheme given earlier and shown above suffices to describe the behaviour of the polymeric acrylates. This paper, together with our previous publications [14,17,18], provides reasonably complete information about the chemistry involved in the decomposition of metal carboxylates. The diversity of the chemistry involved should be taken into account in any attempt to describe the kinetics of the corresponding isothermal decompositions, as has been pointed out clearly by Galwey [19].

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