

## KINETICS AND REACTION MECHANISM FOR THE THERMAL DECOMPOSITION OF SOME EVEN CHAIN LEAD(II) CARBOXYLATES

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### ABSTRACT

The kinetics of the thermal decomposition of lead(II) dodecanoate, tetradecanoate and octadecanoate have been studied thermogravimetrically in the temperature range 298–1073 K by the modified method of Freeman and Carroll. The thermogravimetric curves show that while the octadecanoate decomposes in one single step to lead oxide, the dodecanoate and tetradecanoate decompose in two stages to lead oxide. The kinetic results show all the reactions, except the second step breakdown of dodecanoate (which is nearly unity), to be of zero order. Activation energy values are presented for the desorption of carbon dioxide and the diffusion controlled rate of formation of a degradative intermediate identified as a ketone. Tentative mechanisms are advanced to explain the degradative route of these compounds.

### INTRODUCTION

Many of the early studies on the thermal behaviour of long chain metal carboxylates have tended to concentrate on structural and physical changes up to and beyond the melting temperature but well before the onset of decomposition [1–5]. A survey of the literature reveals that not much information on the kinetics and decomposition mechanism has been reported so far. However, the thermal decomposition and decomposition kinetics of several metal acetates have been extensively studied and reported [6–8]. These studies have shown that even in these simple acetates, the decomposition mechanisms are very complicated. Thus, Judd et al. [6] have found that the thermal decomposition reaction changed depending on whether the final product of decomposition was a metal or metal oxide. If the metal oxide was the final product, acetone was the major organic intermediate, whilst acetic acid was found when the metal alone was produced. In addition, very early work [9–11] on the thermal decomposition of some metal carboxylates has shown that these compounds decomposed at temperatures in excess of 200°C to yield a ketone as the major organic product. Indeed, the action of heat on calcium laurate has long been used to prepare 12-tricosanone.

In this work, the thermal decomposition kinetics of dodecanoate, tetradecanoate and octadecanoate of lead(II) have been studied and suggestions made on the mechanisms of decomposition and the likely side reactions that may occur.

## EXPERIMENTAL

### *Materials*

The dodecanoate, tetradecanoate and octadecanoate of lead(II) were prepared by metathesis in alcohol solution [12–14], recrystallised from hot benzene and characterised as previously described [1,2]. The melting point data and elemental analyses were consistent with those described in the literature.

### *Thermogravimetry*

Thermogravimetric experiments were carried out on a Stanton-Redcroft TG 750 thermobalance on carboxylate samples in the weight range 3–7 mg at a heating rate of  $20^{\circ}\text{C min}^{-1}$  in dry nitrogen at a flow rate between 20 and  $25\text{ cm}^3\text{ min}^{-1}$ . Changes in sample weight were recorded as a permanent trace on a Servoscribe 2s RE 571 X–Y recorder which recorded weight as a function of temperature at a recorder sensitivity of 10 mV and chart speed of  $30\text{ mm min}^{-1}$ . The temperature was simultaneously recorded by means of a Pt/Pt–13% Rh thermocouple situated in the microfurnace assembly. The samples, contained in shallow platinum crucibles provided by the manufacturers of the thermobalance, were heated from ambient to 1073 K.

### *$^1\text{HNMR}$ spectra*

Spectra were measured on a Perkin-Elmer R10 spectrometer at 60 MHz. Solutions in deuterated chloroform were used with tetramethylsilane as internal standard.

### *IR spectra*

A Pye Unicam SP 3-300 spectrometer calibrated with polystyrene was used to obtain spectra of degraded intermediates in deuterated chloroform.

## RESULTS AND DISCUSSION

The continuous % weight loss curves for the thermal decomposition of the lead(II) soaps from 298 to 1073 K are shown in Fig. 1. Decomposition was observed to begin at approximately 513 K and became very rapid between 690 and 730 K. In the cases of the lead(II) dodecanoate ( $\text{PbC}_{12}$ ) and tetradecanoate ( $\text{PbC}_{14}$ ), decomposition occurred in two stages. The first stage was complete after ~30% weight loss for  $\text{PbC}_{12}$  at ~682 K and 51–53% weight loss at approximately 729 K for  $\text{PbC}_{14}$ , and stage two after 62% ( $\text{PbC}_{12}$ ) and 65% ( $\text{PbC}_{14}$ ). The octadecanoate decomposed in one single step resulting in a 71% loss in weight. These results indicated that the final product of decomposition was lead oxide where 38%, 35% and 29% weight remaining for  $\text{PbC}_{12}$ ,  $\text{PbC}_{14}$ , and  $\text{PbC}_{18}$ , respectively, were in good agreement

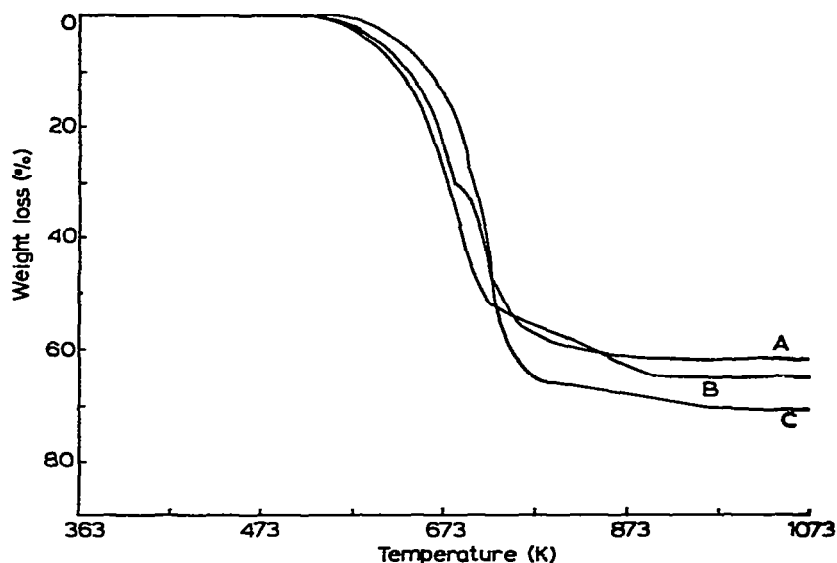


Fig. 1. Thermogravimetric curves for the decomposition of  $\text{PbC}_{12}$  (A);  $\text{PbC}_{14}$  (B), and  $\text{PbC}_{18}$  (C).

with the theoretical weight remaining for the formation of lead oxide of 36.9%, 33.8% and 28.9%.

Kinetic information on the decomposition was obtained from these curves by the modified method of Freeman and Carroll [15], which is based on the expression

$$\Delta \log(dw/dt) = n \Delta \log W_r - (\Delta E/2.303 R) \Delta (1/T) \quad (1)$$

where  $dw/dt$  is the rate of reaction, determined from tangents to the weight loss curves;  $n$  is the order of reaction;  $\Delta E$  is the activation energy;  $R$  is the gas constant; and  $T$  is the absolute temperature.

$$W_r = \Delta W_c - \Delta W$$

where,  $\Delta W_c$  is the total weight loss associated with a given reaction; and  $\Delta W$  is the weight loss at the point where  $dw/dt$  is taken. The order of reaction and activation energy can be obtained from eqn. (1) by plotting  $\Delta \log(dw/dt)$  vs.  $\Delta \log W_r$  at constant  $\Delta (1/T)$ . The order of reaction is determined from the slope and the activation energy from the intercept at  $\Delta \log W_r = 0$ . The rate of reaction and  $W_r$  at constant  $\Delta (1/T)$  were determined from the plot of the first derivative of the thermogravimetric curve and the corresponding  $W_r$  as a function of the reciprocal of absolute temperature. A typical plot is shown in Fig. 2. The values of  $dw/dt$  and  $W_r$  were taken at equal intervals of  $1/T$  of  $2.0 \times 10^{-5} \text{ K}^{-1}$ . Typical values obtained for the various parameters are tabulated in Table 1. Modified Freeman and Carroll data were similarly obtained for  $\text{PbC}_{12}$  and  $\text{PbC}_{14}$  decompositions.

The kinetic plots for the first stage decomposition of  $\text{PbC}_{12}$  and  $\text{PbC}_{14}$  and the single step decomposition of  $\text{PbC}_{18}$  are shown in Fig. 3. The points representing approximately 30% up to  $\sim 682 \text{ K}$  and  $\sim 52\%$  up to  $\sim 729 \text{ K}$  of the reaction for  $\text{PbC}_{12}$  and  $\text{PbC}_{14}$ , respectively, and 71% of reaction in the case

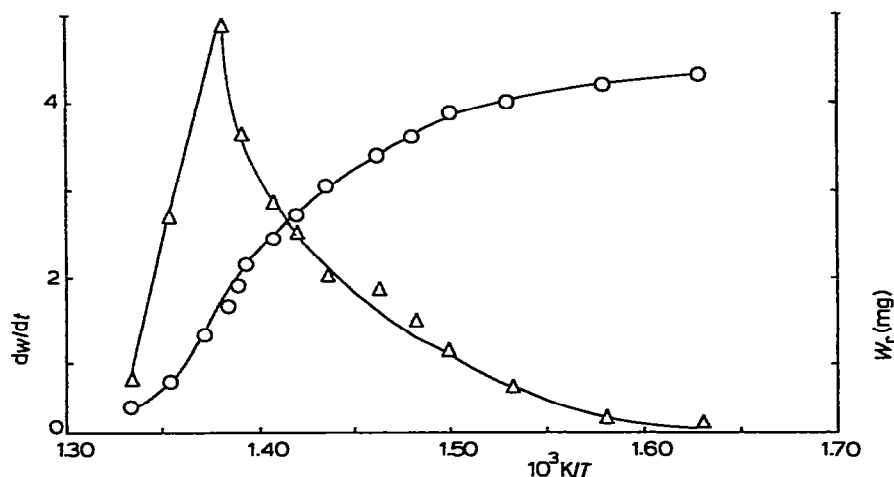


Fig. 2. Plot of  $dw/dt$  ( $\Delta$ ) and  $W_r$  ( $\circ$ ) as a function of temperature for the decomposition of  $PbC_{18}$ .

of  $PbC_{18}$ , do not fall on a straight line. The Arrhenius plots (Fig. 4) indicate zero order kinetics up to this stage of decomposition. In addition, the plots show that in each case there are two activation processes; the first occurring over the first 5–8% of reaction and the other over the next 8–30% ( $PbC_{12}$ ) and 6–52% ( $PbC_{14}$ ) of reaction. In the case of  $PbC_{18}$ , the second activation process occurs over the range 6–63% of reaction. The second stage decomposition data were similarly analysed and the kinetic data so obtained for all the soaps, together with the least squares estimated limits of error, are collected in Table 2.

The Table shows that with the exception of the second stage decomposition of  $PbC_{12}$ , where  $n$  is nearly unity, all the decomposition reactions are of

TABLE 1  
TG data for lead(II) octadecanoate

$dw/dt$	$W_r$ (mg)	$\log$ $dw/dt$	$\log$ $W_r$	$\Delta \log$ $dw/dt$	$\Delta \log$ $W_r$
0.28	4.28	-0.553	0.631	-0.030	0.005
0.30	4.23	-0.523	0.626	-0.114	0.004
0.39	4.19	-0.409	0.622	-0.117	0.005
0.51	4.14	-0.292	0.617	-0.119	0.006
0.67	4.08	-0.174	0.611	-0.098	0.011
0.84	3.98	-0.076	0.600	-0.042	0.016
1.08	3.84	-0.033	0.584	-0.154	0.024
1.32	3.63	0.121	0.560	-0.094	0.034
1.64	3.36	0.215	0.526	-0.095	0.038
2.04	3.08	0.310	0.489	-0.092	0.054
2.52	2.72	0.401	0.435	-0.104	0.069
3.20	2.32	0.505	0.366	-0.180	0.140
4.84	1.68	0.685	0.225	0.143	0.243
3.48	0.96	0.542	-0.018	0.360	0.234
1.52	0.56	0.182	-0.252		

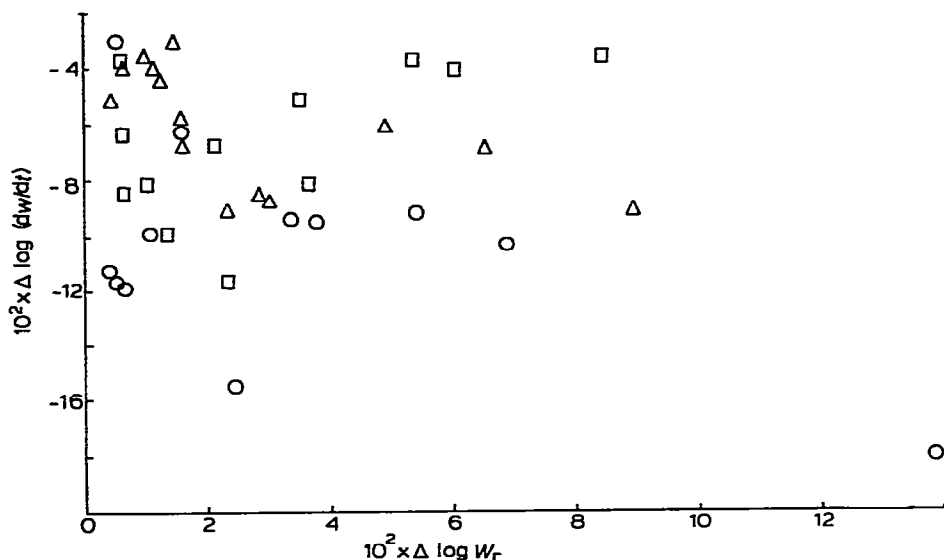


Fig. 3. Kinetic plots for the decomposition of  $\text{PbC}_{12}$  ( $\Delta$ );  $\text{PbC}_{14}$  ( $\square$ ); and  $\text{PbC}_{18}$  ( $\circ$ ).

zero order. Moreover, the octadecanoate result presented here supports that obtained by Rasheed and Bhole [16] for the thermal decomposition of zinc(II) octadecanoate ( $\text{ZnC}_{18}$ ), where zero order kinetics was also found for that single step process. However, the activation energy value found by those workers for  $\text{ZnC}_{18}$  is different from the value found here for  $\text{PbC}_{18}$  decomposition. Rasheed and Bhole [16] presented a value for the overall decomposition which, in view of similar values presented by other workers [7] on like systems, is not unreasonable; the result here indicates that two processes of different energy values are involved.

It should be borne in mind that these lead(II) carboxylates all melt [17] before the onset of decomposition and that the decomposition products are some gas plus a solid ( $\text{PbO}$ ). The reactions are therefore heterogeneous.

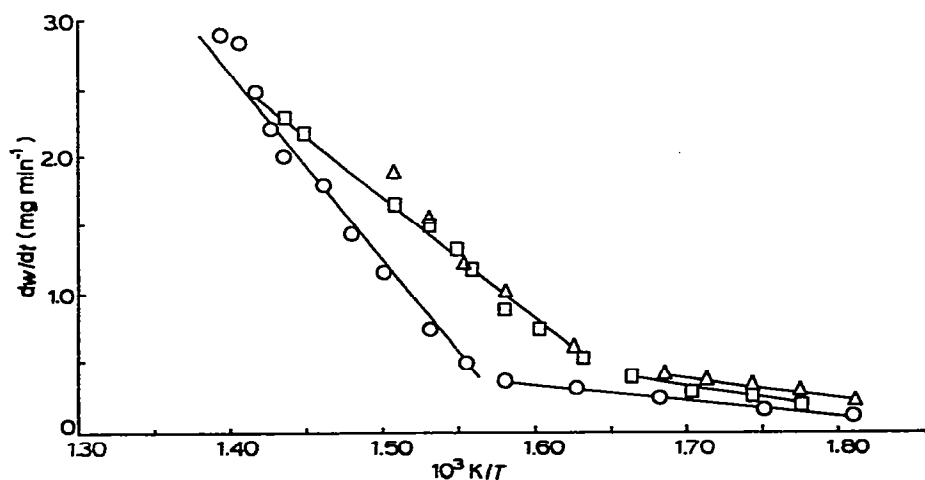


Fig. 4. Arrhenius decomposition plots of  $\text{PbC}_{12}$  ( $\Delta$ ),  $\text{PbC}_{14}$  ( $\square$ ); and  $\text{PbC}_{18}$  ( $\circ$ ).

TABLE 2  
Kinetic data

Compound	<i>n</i>	<i>E</i> (kJ mole <sup>-1</sup> )	Temp. range (K)
PbC <sub>12</sub>	0 <sup>a</sup>	12.45 <sup>a</sup> ± 1	542–623
		76.16 <sup>a</sup> ± 4	623–682
	0.8 <sup>b</sup>	539.95 <sup>b</sup> ± 11	682–848
PbC <sub>14</sub>	0 <sup>a</sup>	13.63 <sup>a</sup> ± 2	519–614
		74.91 <sup>a</sup> ± 2	614–711
	0 <sup>b</sup>	15.30 <sup>b</sup> ± 3	711–887
PbC <sub>18</sub>	0	11.31 ± 1	510–643
		128.00 ± 6	643–748

<sup>a</sup> first stage decomposition.

<sup>b</sup> second stage decomposition.

Therefore, zero order kinetics indicate that the reactions are independent of initial carboxylate concentration, and the surface of the molten soap remains covered by gaseous product throughout the reaction. The activation energy values accounting for the first 5–8% weight loss is most probably representative of the desorption of a gaseous product from the surface of the molten soap. Clearly, this term must be dependent on the surface area and surface tension of the molten soap. Since surface area can be assumed to vary only slightly, it is envisaged that surface tension is the most important term here. Unfortunately, this area of molten carboxylate chemistry has not been researched, but, in the case of *n*-octane where the total surface energy is approximately 12 kJ mole<sup>-1</sup> at 20°C [18], the activation energy values reported here of between 11–14 kJ mole<sup>-1</sup> are not unreasonable for this type of process.

An initial weight loss of 5–8% is indicative of the loss of 1 mole of carbon dioxide from one mole of carboxylate. That carbon dioxide was indeed the gaseous fraction lost, has been confirmed by standard chemical tests in separate decompositions carried out in a pyrex heating tube under a stream of dry nitrogen. The amounts produced over this temperature range were also estimated by titration of the gas dissolved in an excess of standard barium hydroxide solution. The results obtained were, in all cases, in very good agreement with the TG weight loss data. Separate decompositions were also carried out on the PbC<sub>12</sub> and PbC<sub>14</sub> in the temperature range 573–663 K in an attempt to identify the partially decomposed intermediate. Differential thermogravimetry indicated that in this temperature range the most stable intermediates were formed. Thus, each partially decomposed sample was worked up in ether and the purity of the product ascertained by thin layer chromatography (TLC) in several solvent systems. The TLC results indicated that each degraded product was a single compound. Typical IR and NMR spectra of the degraded intermediate obtained from PbC<sub>12</sub> are shown in Figs. 5 and 6, respectively.

The IR spectrum is that for a typical carbonyl compound where the band at 1745 cm<sup>-1</sup> seems likely to be due to the presence of carbonyl groups.

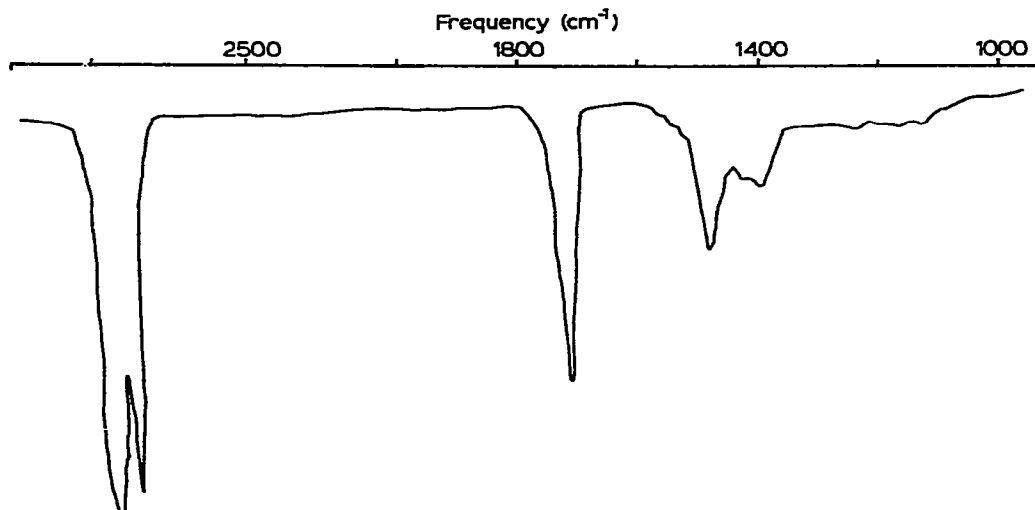


Fig. 5. IR spectrum of degraded  $\text{PbC}_{12}$  intermediate.

Absorptions in the region  $1410\text{--}1440\text{ cm}^{-1}$  could be tentatively assigned to  $\text{—CH}_2\text{—CO—}$ . The absence of any absorptions in the region  $2700\text{--}2900\text{ cm}^{-1}$  indicates that the compound is not an aldehyde. Further confirmation of this tentative assignment as a ketone is provided by the NMR spectrum. The typical aldehydic chemical shifts in the region  $9.5\text{--}10.1\text{ ppm}$  are absent. The spectrum shows the typical methyl group protons attached to an adjacent carbon atom at  $0.82\text{ ppm}$  and methyl group protons attached to a carbonyl group at  $2.35\text{ ppm}$ . A tentative structure (I) for the compound is now proposed

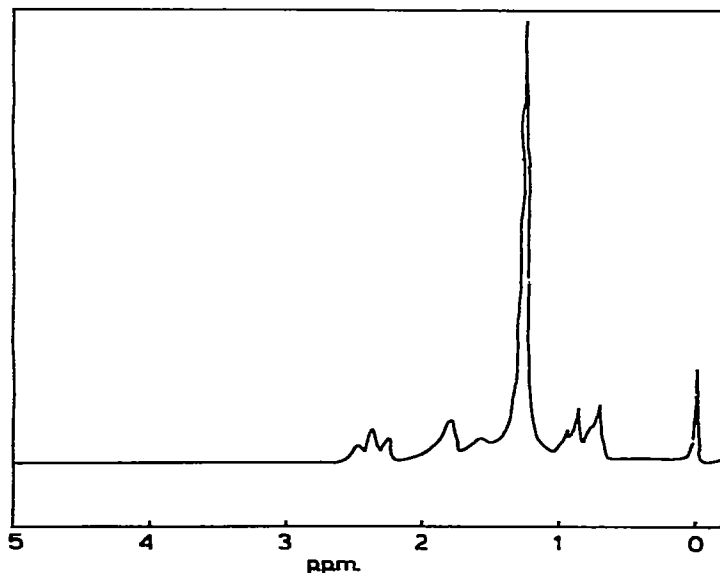
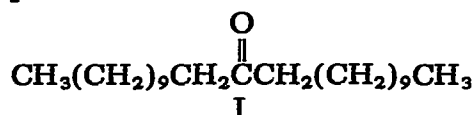


Fig. 6. NMR spectrum of degraded  $\text{PbC}_{12}$  intermediate.







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