

PRODUCT ANALYSIS, REACTION MECHANISM AND KINETICS OF THE THERMAL DECOMPOSITION OF SOME EVEN CHAIN-LENGTH MERCURY(II) CARBOXYLATES

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ABSTRACT

The products of the thermal decomposition of some even chain-length mercury(II) carboxylates have been characterized. The products obtained for each soap include liquid mercury, carbon dioxide, a carboxylic acid, and an odd chain-length alkene. The suggestion that the alkene could be converted to an odd chain-length carboxylic acid is discussed. The liquid mercury is shown to come directly from the decomposition of the soaps and not through an intermediate of mercury(II) oxide. A possible mechanism for the degradative route is suggested.

The activation energies for the decomposition of the soaps are independent of the carbon-chain length and correlation between the activation energy for decomposition and activation energy for viscosity cannot be made as was done for lead(II) carboxylates. However, like lead(II) soaps, the desorption of carbon dioxide occurs from the surface of the melts.

INTRODUCTION

Metal carboxylates have high solvent power in a fairly high temperature range (120–425 °C), and good thermal and electrical conductivities [1]. Hence, they are useful as reaction media in specific syntheses such as in fungicide preparation and emulsion polymerisation in paints. The stability of this group of compounds is, without doubt, important for any general study directed at establishing their physical and thermal properties. Previous studies from this laboratory have provided information on the thermal behaviour of some long-chain metal carboxylates [2–11]. Most of these studies have discussed extensively the problems involved in the melting and mesophase formation in some metal carboxylates [2–9]. For example, Adeosun, using differential thermal analysis (DTA), reported the thermodynamic studies of phase transitions in even chain-number mercury(II) carboxylates

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from octanoate to octadecanoate [9]. He observed that there seemed to be no correlation between the chain length and the number or type of phases exhibited by the mercury soaps. Recently, Ellis and Okoh [10,11] using thermogravimetry (TG) and derivative thermogravimetry (DTG) reported the kinetics of the thermal decomposition of some lead(II) carboxylates in the temperature range 298–1073 K. The results showed that the final product of decomposition was lead(II) oxide. Earlier, Judd et al. [12] studied the thermal decomposition and decomposition kinetics of several metal ethanoates. They reported that while propanone was the major organic intermediate when the metal oxide was the solid residue, ethanoic acid was obtained when the solid residue was the metal. Some other workers have established the formation of symmetrical ketones as the major organic products on pyrolysis of salts of carboxylic acids [13–15]. The formation of mixed ketones has also been reported during the thermal decomposition of salts of organic acids [16,17]. Lee, Reed and co-workers proposed different mechanisms to explain the degradative paths of these compounds [18–22].

One notable feature common to all these studies has been the identification of a solid residue as the final decomposition product. The study of the thermal decomposition of mercury(II) carboxylates seems to be of interest because the mode of decomposition is likely to be different from the desorption of carbon dioxide from the surface of a solid reported for most metal carboxylates. It should be noted that Lawrence, during the preparation of some metal carboxylates, observed that mercury(II) carboxylates (laurate, stearate and oleate) decomposed suddenly with a considerable evolution of heat leaving liquid mercury metal as the final decomposition product [23]. The evolved gas was not mentioned and the other decomposition products were not fully analysed.

The present work reports the identification of the decomposition products and the decomposition kinetics of the even chain-length mercury(II) carboxylates from decanoate to hexadecanoate, inclusive. Suggested mechanisms are proposed to explain the degradative route of the systems.

EXPERIMENTAL

Materials

The preparation and purification of mercury(II) carboxylates has been described elsewhere [9]. All the fatty acids employed were “specially pure” grade, B.D.H. products and were stated to be of at least 99% purity by GLC assay. They were used without further purification. Mercuric(II) chloride was AnalaR grade from B.D.H.

Decomposition methods

The decomposition of the mercury(II) soaps was carried out in a pyrolysis apparatus constructed at the University of Ife Workshop. The apparatus consists of a long decomposition tube, made of pyrex glass, with a quick-fit outlet designed to hold a condenser. A "cup" is attached to the base of the condenser for collecting condensed decomposition products. One end of the decomposition tube carries a U-tube containing a drying agent (fused calcium chloride) and attached to the U-tube is a soda lime tube to absorb the evolved carbon dioxide from the decomposition tube. Another U-tube of silica gel is attached to the other end of the soda lime tube to prevent the soda lime from absorbing moisture from the atmosphere.

Thermal decomposition studies were carried out in nitrogen on a weighed quantity of mercury(II) carboxylate. The soda lime tube was weighed before and after the decomposition process to obtain the weight of the evolved CO_2 . IR, TLC, elemental analyses and chemical tests were made to characterise the decomposition products. Decomposition and characterisation were carried out at least twice for each sample using fresh materials.

The degradation for kinetic studies was done in air at a constant temperature in a Gallenkamp muffle furnace. Weighed samples were placed in small glass bottles and introduced into the furnace through an inlet that can be swung open. This technique ensured a temperature variation of about $\pm 3^\circ\text{C}$. Samples were withdrawn from the furnace after 10, 20, 30, 40, 50, 60 and 240 mins, allowed to cool and weighed. Measurements were made in triplicate on each sample at 453, 473 and 493 K and within the limits of experimental conditions fairly consistent results were obtained.

RESULTS AND DISCUSSION

For the pyrolysis analysis, all the soaps were heated beyond their melting points and up to 473 K. The products of decomposition included mercury metal, carbon dioxide and solid organic mixtures. In each analysis, mercury metal remained as the final decomposition product which settled at the bottom of the decomposition tube. The mercury ball is easily identified by its colour and, except that it was poured on the floor to observe it roll, no further test was carried out for its identification.

Two methods were employed for the estimation of carbon dioxide produced from the decomposition of each mercury(II) carboxylate. First, the amount of CO_2 evolved when a weighed quantity of mercury(II) soap was heated was measured by trapping it in soda lime. The weight of CO_2 produced was obtained from the difference in the weights of the soda lime tube before and after the absorption of CO_2 . The results are shown in Table 1. It can be seen from Table 1 that one mole of a soap sample gave one mole

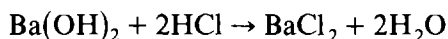
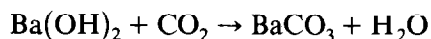
TABLE 1

Data for the formation of CO₂ from the decomposition of mercury(II) carboxylates

Hg(II) soaps	Melting points(K)	Weight of soap decomposed (g)	Weight of CO ₂ produced (g)	Mole ratio CO ₂ /Hg(II) soap
Decanoate	390–391	3.001	0.231	1:1
Dodecanoate	392–394	3.500	0.264	1:1
Tetradecanoate	389–392	1.941	0.132	1:1
Hexadecanoate	389–391	4.864	0.307	1:1

Errors from three runs in the values of CO₂ for each soap are within $\pm 2\%$.

of CO₂ on decomposition. The second method of determining the amount of CO₂ involved bubbling the evolved gas into a jar containing a known volume of standard barium hydroxide solution (0.05 M). The excess Ba(OH)₂ solution was then titrated with hydrochloric acid of known concentration. As shown by the following equations



the quantity of Ba(OH)₂ that reacted with the CO₂ was calculated and, hence, the amount of CO₂ determined. The carbon dioxide/mercury(II) carboxylate mole ratio obtained in this method was also 1:1 and the errors in the determination of the amount of CO₂ agreed within $\pm 3\%$ for triplicate runs. Qualitatively, this second method revealed the evolved gas to be CO₂ by the clear solution of Ba(OH)₂ which turned milky upon passing the evolved gas into it.

The other organic products from the decomposition of each soap are correspondingly similar and so the results obtained for the degradation of mercury(II) dodecanoate are used as an example for the discussion. Two solid organic products were identified after the decomposition of the soap. A white fluffy solid deposited on the cup as well as on the side of the condenser, while a brown solid settled with the mercury balls at the bottom of the decomposition tube. The white fluffy material was labelled DP/C₁₂/1 and was recrystallised from a hot methanol/water mixture. The brown solid product was carefully scraped off and part of it put on a thin layer chromatography (TLC) column and developed in three solvent mixtures of petroleum ether (60–80 °C)/benzene in the ratios 4:1, 2:1 and 1:1. The result showed two compounds when viewed in a jar of iodine. This observation led to further tests. The brown material was dissolved in dilute NaOH solution and extracted with ether. The ether extract was dried over anhydrous sodium sulphate, filtered and evaporated to dryness. The product was named DP/C₁₂/2. The aqueous extract was treated with dilute HCl solution and

extracted with ether. The resulting ethereal solution was also dried over anhydrous Na_2SO_4 , filtered and evaporated to dryness. A fluffy white solid, very similar to DP/C₁₂/1 was obtained, which was labelled DP/C₁₂/3.

The IR spectra of samples DP/C₁₂/1 and DP/C₁₂/3 were recorded and the absorption bands of diagnostic values are listed below.

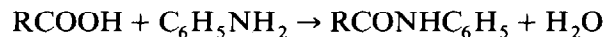
DP/C₁₂/1

1700 cm^{-1} (s) C–O stretch of C=O group, 3100 cm^{-1} (very broad) O–H stretch in hydrogen-bonded acid.

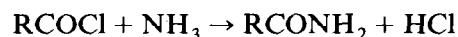
DP/C₁₂/3

1697 cm^{-1} (s) C–O stretch of C=O group, 3050 cm^{-1} (broad) O–H stretch in hydrogen-bonded acid.

Both DP/C₁₂/1 and DP/C₁₂/3 were insoluble in water but soluble in sodium hydroxide and sodium hydrogen carbonate. Since water-insoluble compounds containing acidic functional groups are generally soluble in alkalis, we speculated that DP/C₁₂/1 and DP/C₁₂/3 are probably acids. Because our speculation from the solubility tests was reinforced by the IR data, we proceeded to prepare the most common crystalline derivatives of carboxylic acids, anilides and amides from our samples. The anilides of the samples were prepared by their reaction with aniline [24] following the equation below



The product of the reaction was recrystallised from hot ethanol. The amides were prepared by first reacting the samples with phosphorus pentachloride before reacting the acid chloride produced with concentrated ammonia solution [24] as shown by the following equations



The amides were recrystallised from a hot water/ethanol mixture. The melting points of DP/C_n/1 *, DP/C_n/3 and their derivatives are presented in Table 2 with melting points from the literature [25] of the authentic acid and their anilide and amide derivatives. The correlation in the values of the melting points of our samples and their derivatives with the literature melting points of authentic acids and their derivatives clearly supports our speculation that DP/C_n/1 and DP/C_n/3 are acids. It is our belief that DP/C_n/3 is part of DP/C_n/1 which recondensed at the bottom of the decomposition tube after the source of heat was withdrawn. The DP/C_n/1, or DP/C_n/3 in the case of the degradation of mercury(II) dodecanoate, will be dodecanoic acid.

* C_n is half the number of carbon atoms in the soaps.

TABLE 2
Melting points of DP/C_n/1, DP/C_n/3, authentic acids and their anilide and amide derivatives

Mercury(II)	Acid product expected	Melting points of DP/C _n /1 and their derivatives (°C)		Melting points of DP/C _n /3 and their derivatives (°C)		Literature m.p.s. of authentic acids and their derivatives				
		Acid	Anilide	Amide	Acid	Anilide	Amide	Authentic acid	Anilide	Amide
Decanoate	Decanoic	31	76-77	105-106	30-31	76-78	106-108	29-31	-	108
Dodecanoate	Dodecanoic	45-46	77-78	108-109	44-46	76-78	107-109	43-46	78	110
Tetradecanoate	Tetradecanoic	54-56	83-85	102-104	55-57	84-85	102-105	55-58	-	105-107
Hexadecanoate	Hexadecanoic	61-64	90-93	103-106	60-62	92-94	104-106	60-63	91	106

The percentage of carbon and hydrogen in the other sample, DP/C₁₂/2, was determined and the values obtained are shown in Table 3 with those for DP/C₁₂/1 and DP/C₁₂/3. The values for C and H as shown in Table 3 for DP/C₁₂/2 were close to the theoretical values of 85.71 and 14.29% for C and H, respectively, in an alkene of eleven carbon atoms which can be formed as a result of the decarboxylation of mercury(II) carboxylate. It should be noted that the percentage of C and H in DP/C₁₂/2 is considerably higher than both the values obtained for C and H in DP/C₁₂/1 or DP/C₁₂/3 and the theoretical values of 72.00 and 12.00%, respectively, in pure dodecanoic acid. A solution of DP/C₁₂/2 was found to decolourise a solution of bromine in carbon tetrachloride, suggesting that DP/C₁₂/2 contains unsaturated centre(s). There was no visible reaction when a solution of DP/C₁₂/2 was added to a solution of silver nitrate in alcohol. This shows that the unsaturated centre established with the Br₂/CCl₄ reaction is not due to a triple (C≡C) bond in an alkyne with a terminal hydrogen. Within the range of temperature employed in this work, and from the mechanism of decomposition proposed, it is difficult to see how an alkyne other than one with a terminal hydrogen can be formed. Thus, we concluded that sample DP/C₁₂/2 is an alkene. It is to be noted that DP/C_n/2 from the other soaps, i.e., mercury(II) decanoate, tetradecanoate and hexadecanoate, were subjected to the same tests that were carried out for DP/C₁₂/2 and they all gave the same results suggesting that the DP/C_n/2 are the corresponding alkenes from the decomposition of the soaps.

To further confirm the identity of DP/C₁₂/2, a solution of this compound and one available alkene, dodec-1-ene, were placed on a TLC column and developed separately in three different benzene/petroleum ether mixtures. The R_f value of DP/C₁₂/2 was found to be the same as that of dodec-1-ene. The R_f value of dodec-1-ene, an alkene with twelve carbon atoms, is not expected to be very different from that of an alkene with eleven carbon atoms, thus strengthening our belief that DP/C₁₂/2 is an alkene.

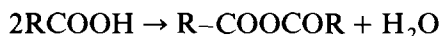
Lawrence [23], during the preparation of some metal carboxylates, mentioned that mercury(II) carboxylates decomposed with the evolution of heat, giving metallic mercury and a mixture of acid and acid anhydride. His decomposition temperature of about 483 K for mercury(II) dodecanoate was quite close to the range of temperature used in the present work. However,

TABLE 3

C and H analysis (%) of the organic products from the decomposition of mercury(II) dodecanoate

Element	DP/C ₁₂ /2	DP/C ₁₂ /1	DP/C ₁₂ /3
C	82.64	70.23	71.02
H	13.74	11.38	11.59

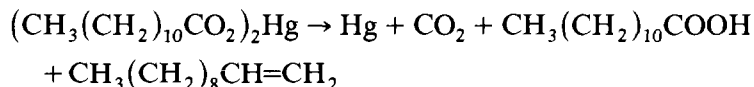
the melting points of all his soaps were lower than these obtained in this study. For example, the melting point of ~ 363 K he reported for mercury(II) dodecanoate was considerably lower than our value of 392–394 K, and lower than that of 394.2 K reported by Adeosun [9] using the DTA method. This probably suggests that Lawrence's soaps might contain some impurities. Pure dodecanoic acid melts at 317 K. It is not unlikely that some excess acid in his soaps was being converted into the acid anhydride as a result of heating according to the equation



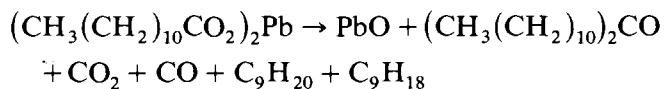
even before the onset of the decomposition of the soaps. Again, the evolved gas was not mentioned in his brief discussion of the decomposition products. This shows clearly that his main objective was to carry out the preparation of metal soaps and any mention of the products of decomposition can thus be viewed as mere observation during the preparation processes.

One significant feature of our analysis is the identification of alkene as one of the products of the degradation of mercury(II) carboxylates. Our mercury(II) soaps were prepared using even-chain aliphatic acids. The present result indicates a possible route for obtaining an odd chain-length alkene from the degradation of an even chain-length mercury(II) soap. It may be feasible to convert such an alkene into an alcohol, which could then be oxidised to produce a more expensive odd chain-length carboxylic acid.

It is clear from our analysis that mercury metal was the final residue upon the pyrolysis of a mercury(II) carboxylate. The equation for the decomposition of mercury(II) dodecanoate based on the products obtained is



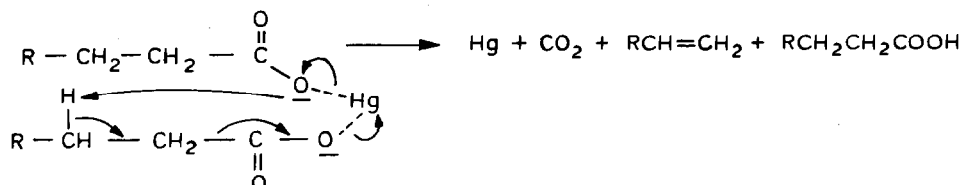
This result agrees with that of the studies on the thermal decomposition of phenylmercury(II) carboxylates in alcohols at 125 and 200 °C in which mercury metal and carboxylic acids were among the products of decomposition [26]. It seemed clear from that study that the solvent molecules may be playing some role in the decomposition process, in contrast to the present case in which reactions occurred in the molten state. However, the identification of mercury metal as a solid residue is a common feature of the two cases. The present result differs from those obtained for the degradation of lead(II) carboxylates in which lead(II) oxide was shown to be the solid residue as the equation for the decomposition of lead(II) dodecanoate indicates [10]



In the case of mercury(II) soaps, mercury was shown to come directly from the decomposition of the soaps by setting up three porcelain boats, which

were heated under identical conditions. One boat contained AnalaR grade B.D.H. mercury(II) oxide; the second contained the same quantity of HgO as in the first boat but with a certain amount of DP/C_n/2 and DP/C_n/3; the third contained a pure sample of mercury(II) carboxylate. The mixture of HgO, DP/C_n/2 and DP/C_n/3 was taken to check the possible effect of material environment on the decomposition of HgO. The result showed that while liquid mercury was observed in the boat containing the mercury(II) carboxylate after decomposition, no visible reaction occurred within our decomposition temperature range, in the other two boats. Only a slight evaporation of the organic product was observed in the case of the boat containing the mixture of HgO, DP/C_n/2 and DP/C_n/3. This suggests, perhaps conclusively, that mercury balls came directly from the decomposition of the soaps, and not through an intermediate of mercury(II) oxide, which could then break down to mercury metal. It is thus clear that the degradative route for mercury(II) soaps is likely to be different from that postulated for lead(II) carboxylates where lead(II) oxide was identified as the final decomposition product.

It seems reasonable, if one takes the results of all the product analyses together, to formulate that a mercury(II) carboxylate decomposed via the dissociation of the O–Hg bond and the simultaneous abstraction of β-hydrogen by the carboxylate anion to release CO₂, mercury metal, an alkene and a carboxylic acid.



If we take mercury(II) dodecanoate as an example, the products of decomposition will be mercury, CO₂, dodecanoic acid and undec-1-ene. This degradative path differs from that proposed for the decomposition of some lead(II) soaps in which the mechanism involved the initiation step that produced free radicals [10,11]. However, it is satisfying to note that the results of the present study, that of lead(II) carboxylates and organomercuric peroxides [27] are in agreement with the work on the decomposition of several metal ethanoates where it was reported that propanone was the usual intermediate product when the metal oxide was the solid residue while ethanoic acid was often obtained as the intermediate when the solid residue was the metal [12]. On the strength of this work and that of lead(II), zinc(II) and other metal carboxylates [10,11,12,29] one is tempted to speculate that the decomposition of metal carboxylates follows the trend of the properties of elements in the electrochemical series, where most inorganic salts of the elements above hydrogen in the series decompose to give the oxide of the

metal while those below it give the metal on heating.

The kinetic measurements were studied isothermally at a temperature range close to that employed for the pyrolysis analysis. At temperatures of 453, 473 and 493 K, weight/weight loss was measured as a function of time. The data obtained were fitted into the equation [28]

$$\partial\alpha/\partial t = K_{(T)}[1 - \alpha]^n$$

where $\partial\alpha/\partial t$ is the instantaneous reaction rate and is obtained at regular intervals by drawing tangents to the curve of the fraction of the sample decomposed against time (Fig. 1); $K_{(T)}$ is the rate constant at a given temperature; n is the order of the reaction; and α is the fraction of the sample decomposed

$$\alpha = \frac{W_0 - W_t}{W_0 - W_\infty}$$

where W_0 is the initial weight; W_t is the weight after heating for time t ; and W_∞ is the weight after heating for 240 min, i.e., at the completion of decomposition. The values of α and the reaction rates, $\partial\alpha/\partial t$, obtained from Fig. 1 at 493 K are presented in Table 4 for mercury(II) dodecanoate as a typical example.

The logarithms of the rates were plotted against $\log(1 - \alpha)$ for each

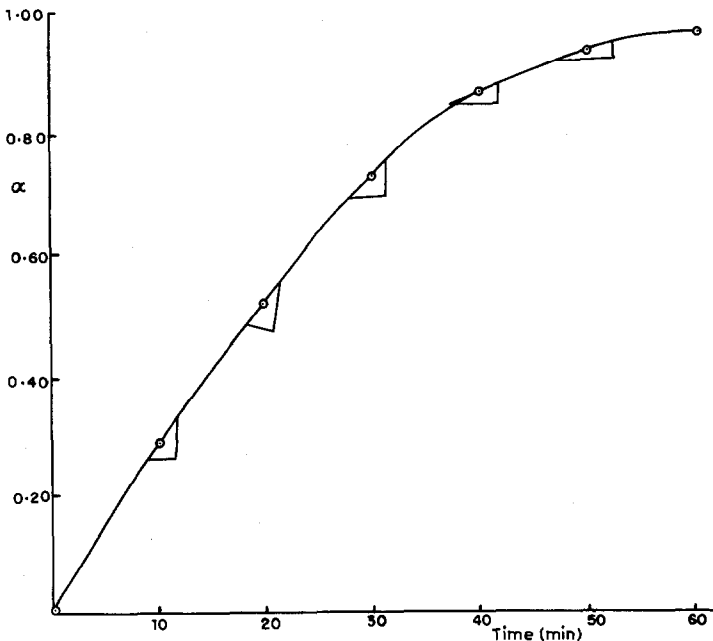


Fig. 1. Plot of fraction of the decomposed sample, α , against time for mercury(II) dodecanoate at 493 K.

TABLE 4

Kinetic data for the decomposition of mercury(II) dodecanoate at 493 K

Time (min)	α	Rate, $\partial\alpha/\partial t \times 10^2$
10	0.282	2.500
20	0.516	2.204
30	0.727	1.833
40	0.867	0.834
50	0.932	0.615
60	—	—

mercury(II) carboxylate at 453, 473 and 493 K. Figure 2, for mercury(II) dodecanoate at 493 K, is a typical plot with a correlation coefficient of 0.9778 and the slope is equal to n , while the intercept is equal to $\log K_{(T)}$. The values of $\log K_{(T)}$ obtained at various temperatures for the soaps are shown in Table 5.

The activation energy, E for decomposition is obtained from the Arrhenius plot, $\log K = \log A - E/2.303RT$ and the values of E are presented in Table 6 together with those reported for the decomposition of some lead(II) carboxylates [10,11] for comparison.

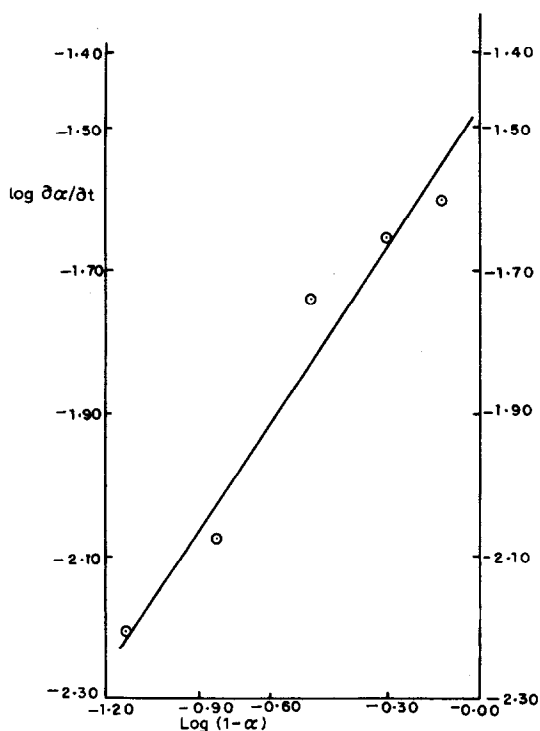


Fig. 2. Plot of $\log \partial\alpha/\partial t$ against $\log(1-\alpha)$ for mercury(II) dodecanoate at 493 K.

TABLE 5

Values of $\log K$ for mercury(II) carboxylates

Mercury(II) carboxylates	$\log K$		
	453 K	473 K	493 K
Decanoate	-1.769	-1.401	-1.276
Dodecanoate	-1.902	-1.561	-1.465
Tetradecanoate	-1.494	-1.117	-1.109
Hexadecanoate	-1.590	-1.223	-1.113

It can be seen from Table 6 that the activation energies for decomposition of mercury(II) carboxylates are independent of chain length. This result contrasts with that obtained for lead(II) soaps where the activation energies for decomposition seemed to be dependent on the number of carbon atoms in the soaps. While the value for the decomposition of mercury(II) decanoate is somewhat similar to that of lead(II) decanoate, the activation energies obtained for mercury(II) dodecanoate and mercury(II) tetradecanoate are considerably lower than those reported for their lead counterparts. However, the present activation energies for the degradation of mercury(II) salts are all close to the value of 41.8 kJ mol^{-1} reported for the decomposition of zinc (II) octadecanoate [29]. It is therefore tempting to speculate that the metal ion plays a significant role in the decomposition process. This speculation is made attractive by the fact that the rupture of the oxygen-metal bond is often the initiation step in the degradative routes of most metal carboxylates.

All the mercury(II) soaps, like the lead salts, melt before the onset of decomposition and from the product analyses, solids, liquids and carbon dioxide gas are found to co-exist in the melt, thereby making the reaction heterogeneous. Thus, the desorption of CO_2 is expected to occur from the surface of the melts. Ellis [10] observed that the contribution to the activation energies for the decomposition of some lead(II) soaps should come from the energy for the desorption of CO_2 from the surface of the melt and that for the diffusion and chemical attack of the species during the decomposition. The former energy term was said to be surface area and surface tension

TABLE 6

Activation energies for the decomposition of some mercury(II) and lead(II) carboxylates

Carboxylates	$E \text{ (kJ mol}^{-1}\text{)}$	
	Mercury	Lead
Decanoate	52.9 ± 4	52.0 ± 5
Dodecanoate	46.8 ± 5	88.6 ± 5
Tetradecanoate	41.7 ± 4	88.5 ± 4
Hexadecanoate	51.2 ± 3	-

dependent while the latter energy was reported to be a function of the viscosity of the molten soap. The trend in the viscosity of molten lead(II) soaps had earlier been studied by Ekpe and Sime [30]. They observed that the carboxylate anion is involved in the mechanism of viscous flow and that the species responsible for flow in lead(II) and zinc(II) soaps are the charged ions, MA^+ and A^- (A^- is the carboxylate group). At any temperature the activation energy for viscous flow was indicated to increase with the carbon-chain length in the melts. Thus, Ellis suggested that the energy for diffusion and attack would be viscosity dependent because diffusion and attack would be more difficult in the case of the salts with longer carbon chains (higher activation energy for viscosity) than in those with shorter chains, since steric effects might be active. While it seemed clear from the data of Ellis that the activation energies for both the viscous flow and the degradation of lead(II) salts follow the same trend of increase with increasing number of carbon atoms in the soaps, it is difficult from the present results to risk the correlation of the activation energy for viscosity to that of decomposition in mercury(II) soaps, particularly since data are not available in the literature on the activation energy for the viscous flow of molten mercury(II) carboxylates.

We have obtained values of n , the order of reaction, ranging between 0.4 and 1.2. It is not clear from this work whether the decomposition of the soaps takes place in a single step or in a series of steps. If the latter is the case, then it is clear that the present method of kinetic decomposition is not suitable for determining the order followed by each stage of decomposition, as was done for lead(II) carboxylates using the TG method [10]. Thus, it is difficult to understand, from the present work, whether or not the n -value obtained for each soap is the sum of the orders for the various stages of decomposition. Whatever the case, we tend to agree with Bohon who reported that the order of reaction obtained from kinetic data fixed into equations often has values that should be interpreted with caution [31].

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