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THE THERMAL BEHAVIOUR OF BASIC LEAD(II) DODECYLSULPHATE

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ABSTRACT

The product formed from the reaction between aqueous lead acetate solution and sodium dodecylsulphate is identified as basic lead(II) dodecylsulphate. This decomposes thermally in a single stage process over the temperature range 450–625 K to yield lead sulphate and 1-dodecanol as major products. The kinetics have been studied thermogravimetrically using the modified method of Freeman and Carroll. Below the decomposition temperature, complex phase changes are observed on heating basic lead(II) dodecylsulphate in studies using DTA and hot stage microscopy.

INTRODUCTION

The thermal behaviour, including both phase changes [1–3] and thermal decomposition [4,5], of a variety of long chain lead(II) carboxylates has been extensively studied in this laboratory. It has been noted [6] that sodium dodecylsulphate forms a sparingly soluble salt with lead(II) ions in aqueous solutions. It is of interest to characterize this salt and to study its thermal behaviour to evaluate the effect of changing from a carboxylate to a sulphate head group in these systems. In this paper we report the identification of this salt as basic lead(II) dodecylsulphate, and describe its thermal behaviour.

EXPERIMENTAL

Materials

Sodium dodecylsulphate was B.D.H. 'specially pure' grade, whilst other reagents were of 'Analar' grade. These were all used without further purification.

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Synthesis and characterization of basic lead(II) dodecylsulphate

Sodium dodecylsulphate (0.1 mole) was dissolved in the minimum volume of warm water (ca. 100 cm^3), and the stoichiometric amount of aqueous lead(II) acetate solution was added slowly, with stirring. Upon leaving overnight, a white, fluffy solid precipitated. This was filtered off, and successively washed with distilled water and acetone. The crude product was recrystallized from ethanol, and was characterized by elemental analysis and IR spectroscopy. The lead content of the recrystallized product was determined gravimetrically as lead chromate [7]. An attempt to determine lead by EDTA titration using Eriochrome Black T as indicator was unsuccessful as the endpoint was difficult to determine. A similar problem was encountered in the volumetric determination of copper(II) octadecanoate [8], and may result from the complexing of the indicator with the surfactant anion.

The IR spectrum (CsI pellets, or Nujol mull) showed absorptions at 2950(sh), 2915(s), 2850(m), 1520(m) and 1467(m) cm^{-1}, attributed to C–H stretch and bend vibrations [9], and further bands at 1415(m), 1245(m) and 1220(br) cm^{-1}, characteristic of organic sulphate groups [10,11]. Similar bands are present in the spectrum of sodium dodecylsulphate [10]. However, the elemental analysis results (Table 1) were not consistent with this compound being lead(II) dodecylsulphate, but agreed instead with the result expected for basic lead(II) dodecylsulphate, $Pb(OH)(CH_3(CH_2)_{11}SO_4)$. The IR spectrum did not possess any significant absorption in the region of 3600 cm^{-1}, where the hydroxide stretch vibration might be expected [12]. However, it is probable that hydroxyl hydrogen in this salt would be extensively hydrogen bonded, and such hydrogen bonding is known to broaden O–H stretch vibrations and to shift them to lower frequencies, where they may be hidden under other more intense bands [9]. It is worth noting that in the IR spectra of various basic inorganic salts, the O–H stretch vibrations are often fairly weak, or are missing [13]. The IR spectrum also showed a band at 585

TABLE 1

Elemental analysis of the product from reaction of lead(II) acetate with sodium dodecylsulphate

Element	Percentage		
	Found	Expected for $Pb(C_{12}H_{25}SO_4)(OH)$	Expected for $Pb(C_{12}H_{25}SO_4)_2$
C	30.48	29.44	39.06
H	5.14	5.35	6.83
Pb	41.74	42.32	28.10
S	5.85	6.55	8.69

cm^{-1}, which is the region where M–OH vibrations are suggested to absorb [14]. In addition, a number of other bands were observed between 1155 and 280 cm^{-1} which were not assigned.

From both the IR spectrum and elemental analyses the product appears to be basic lead(II) dodecylsulphate. The thermal degradation products support this assignment.

Physical measurements

Thermogravimetric studies were performed under nitrogen on a Stanton-Redcroft TG-750 thermobalance, whilst DTA measurements were made on a Mettler TA 2000 analyzer. Full details are given elsewhere [1,4,5]. Thermal degradation studies were carried out under nitrogen on ca. 1 g samples of the compound in glass tubes in a furnace. Liquid products were trapped at room temperature. The thermal behaviour was also observed on an improvised hot-stage microscope, fitted with crossed polars.

RESULTS AND DISCUSSION

Decomposition of basic lead(II) dodecylsulphate was shown by thermogravimetry to occur in a single stage, which began at approximately 450 K, and was complete at ca. 625 K after a weight loss of 39.8%. The weight loss is consistent with the loss of $C_{12}H_{26}O$, and the formation of lead(II) sulphate as solid residue (weight loss expected for $PbSO_4$ formation is 38%). Typical thermogravimetric and differential thermogravimetric curves are shown in Fig. 1.

To further characterize the thermal degradation, samples of basic lead(II) dodecylsulphate were heated in an electric furnace under an atmosphere of nitrogen. Decomposition started around 470 K, and at 520 K a colourless liquid started to distil over. The percentage weight loss on heating to 625 K for 1 h (39.4%) was close to that observed by TG. The greyish white solid residue was virtually insoluble in water, but was soluble in hot ammonium acetate solution. Qualitative tests on the solution confirmed the presence of Pb^{2+} (yellow precipitate with potassium chromate solution; white precipitate with concentrated HCl, which was soluble in hot water), and SO_4^{2-} (white precipitate with barium chloride solution). Sulphide ions were not present in the residue (no sulphur precipitated on addition of dilute nitric acid; no H_2S evolved when the residue was heated with concentrated HCl). The qualitative tests [15], and the observed weight loss strongly suggest that the solid product is lead(II) sulphate. This was confirmed by the IR spectrum of the residue (Nujol mull) which was identical to that of authentic lead(II) sulphate. The liquid product was shown by thin layer chromatography (3:1 benzene/ethyl acetate eluent) to possess a single component with R_F 0.80,

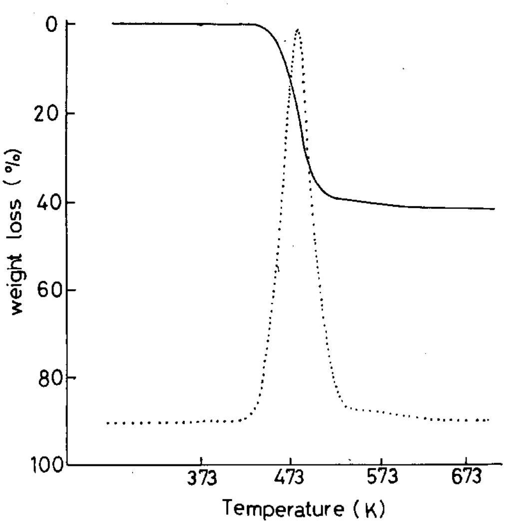

Fig. 1. Thermogravimetric (———) and differential thermogravimetric (······) curves for the decomposition of basic lead(II) dodecylsulphate.

identical to that of dodecan-1-ol. This assignment was confirmed by the NMR spectrum of the liquid (CCl_4 solution) being identical to that of authentic dodecan-1-ol. Further, it can be noted that the temperature at which the liquid distilled over was very close to the boiling point of dodecan-1-ol (259°C [16]). From the above, it would appear that the thermal decomposition of basic lead(II) dodecylsulphate occurs according to the reaction

$$Pb(OH)(CH_3(CH_2)_{11}SO_4) \rightarrow PbSO_4 + CH_3(CH_2)_{11}OH \qquad (1)$$

It is possible that there are other minor organic components formed. However, our method does not permit detection of these.

Kinetic information on the decomposition was obtained from the thermogravimetric curves by the modified method of Freeman and Carroll [4,17,18]. From the slope and intercept [4] of the plot of $\Delta \log(\mathrm{d}w/\mathrm{d}t)$ vs. $\Delta \log W_r$ at constant $\Delta(1/T)$, the decomposition reaction had an order, n, of 1.55 ± 0.2, and an activation energy of 160 ± 25 kJ $mole^{-1}$. The order of this reaction can be contrasted with the case of the thermal decompositions of lead(II) soaps, which all show zero order decomposition under similar conditions [4,5]. At higher temperatures, however, lead(II) dodecanoate does show a first order decomposition step. Further, the activation energy for the decomposition in the basic lead(II) dodecylsulphate is considerably higher than the values reported for the initial decomposition of the lead soaps [4,5]. For example, lead(II) decanoate decomposes in two stages, with an overall activation energy of 52 ± 5 kJ $mole^{-1}$. In that case, the decomposition is suggested to be controlled by diffusion of gaseous products from the surface of the molten soap system [5], such that the activation energy for the decarboxylation step may be even lower.

The big difference in behaviour between basic lead(II) dodecylsulphate and the lead(II) carboxylates may result both from the nature of the bonds being broken, and the physical state of the compound. With lead(II) carboxylates, decomposition of molten phases is occurring. To obtain further information on the processes occurring with basic lead(II) sulphate, the thermal behaviour was studied using an improvised hot-stage microscope. At about 380 K the sample changed from solid to a mechanically deformable phase. This was found to be birefringent when viewed through crossed polars, and appears to be a liquid crystalline phase. The birefringence started to disappear at ca. 470 K, and this phase was replaced by a mixture of solid and liquid. The birefringence did not reappear on cooling. Attempts to obtain further information by DTA showed that the thermal behaviour depended on the rate of heating. The DTA curve at a heating rate of 2 K min^{-1} showed three endothermic peaks around 370 K. At a slower heating rate only a single endotherm at 380 K was observed. In addition, further endotherms were observed around 450–470 K, probably due to the decomposition reaction.

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