XI.—*The Sub-acetate and Sub-sulphate of Lead.*

By Henry George Denham.

In recent papers the author has shown how lead sub-oxide may be converted into the sub-haloid salts by the action of alkyl haloid vapour (T., 1917, **111**, 29; 1918, **113**, 249); in the present paper a somewhat similar method has been used for the preparation of lead sub-acetate and sub-sulphate.

In all these experiments, the lead sub-oxide was prepared by the decomposition of pure lead oxalate according to the method previously described (*loc. cit.*). The same precautions have been followed in order to secure thorough preliminary heating of the reacting gases, the vapour being passed through a capillary spiral tube contained in the oven before it came in contact with the sub-oxide. The only modification necessary in the distillation has been that no drying agent was used in the apparatus, and it was necessary to heat electrically all the leading tubes in order to prevent undesired condensation and to secure a steady rate of distillation.

Preparation of Lead Sub-acetate.

Preliminary experiments were carried out with methyl acetate. About 10 c.c. of a carefully dried sample of this substance were distilled through about 0·75 gram of lead sub-oxide, the duration of the experiment being approximately ninety minutes. Analysis of the product indicated that at 310° the sub-acetate decomposes completely, metallic lead being formed, whilst at temperatures much below this, the reaction proceeded too slowly to appear promising. Ethyl acetate behaved similarly, and an experiment was then carried out with acetic anhydride.

Lead sub-oxide mixed with about four times its weight of powdered glass was prepared in two bulbs (for details, see T., 1917, **111**, 29), and the apparatus filled with oxygen-free nitrogen. About 8 c.c. of carefully fractionated acetic anhydride were distilled through the bulbs at 195°, as recorded on a standardised platinum thermometer. This slow distillation generally lasted about eighty to ninety minutes. The oven was then cooled to about 180°, and the apparatus was exhausted by means of a Sprengel pump. The bulbs were then sealed off and were available for analysis. By this procedure, any trace of acetic anhydride could be removed from the bulb without causing any decomposition of the sub-acetate.

One difficulty still remained. Traces of water were found to be retained most tenaciously by the sub-acetate. A few samples which were quite free from moisture were prepared, but in general, although the ratio of lead to acetate in the compound agreed with the theoretical ratio for lead sub-acetate, from 1 to 3 per cent. of water was also present. The presence of the water was repeatedly verified by the action of heat, a liquid which rendered anhydrous copper sulphate blue being fairly readily expelled.

Traces of acetic acid were generally present in nearly all the samples of acetic anhydride used, and this probably accounted for the presence of water in the sub-acetate. However, as the anhydrous and the hydrated sub-acetate showed no difference in solubility and general properties, anhydrous acetic anhydride was used only in certain control experiments.

Found: Pb = 77·6, 77·9, 77·9; $C_2H_3O_2 = 22·3$, 22·0, 22·2.

$CH_3·CO_2Pb$ requires Pb = 77·82; $C_2H_3O_2 = 22·18$ per cent.

In seven experiments made with acetic anhydride containing traces of acetic acid, the average of the analyses was Pb = 75·8; $C_2H_3O_2 = 21·5$. There is a possible hydrate of the formula $(CH_3·CO_2Pb)_2,H_2O$ which contains Pb = 75·3 per cent., and it appears probable that where acetic anhydride containing traces of acetic acid is used, the product is the hydrate, containing more or less of the anhydrous sub-acetate. Thus in two experiments, in which the same sample of acetic anhydride was used, after a distillation lasting ninety minutes, the percentage of lead was: (*a*) bulb 1, 75·4, bulb 2, 75·2; (*b*) bulb 1, 75·1, bulb 2, 75·2.

Properties of the Sub-acetate.

In order to obtain evidence of the existence of the sub-acetate, determinations of the conductivity of a saturated solution of the substance and of the normal dehydrated acetate were carried out in absolute alcohol at 25°. The apparatus and method previously described (*loc. cit.*) were again used in order that traces of oxygen might be excluded when the sub-acetate was used. The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of the normal acetate was 4100 ohms, and of the sub-acetate, (*a*) 6100, (*b*) 6400, (*c*) 6000 ohms.

As further evidence of the existence of a definite sub-acetate of lead, experiments on the decomposition of the normal acetate and the sub-acetate were undertaken. A sample of the anhydrous normal acetate was heated in a vacuum and the temperature slowly raised. At 200°, a very slow evolution of gas occurred, becoming rather brisker at 240°. The temperature was then kept constant and the pump kept in action for nineteen hours. Gas was still very slowly evolved, and it was found that the acetate had scarcely changed colour, and there was a considerable crop of long, white, needle-like crystals which had volatilised out of the bulb into the relatively cooler leading tube within the oven.

A sample of the sub-acetate was then similarly treated. At 200°, gas was slowly evolved, the evolution becoming brisker at 240°. After seven hours at 240°, gas was still being evolved slowly, and a small, volatilised band of white, amorphous, basic material was found outside the furnace, whilst the material in the bulb had undergone a marked change. It was now full of long, needle-like, greyish crystals. This change, from a finely crystalline, bluish-grey substance into a mass of grey, needle-like crystals, was very marked, as, too, was the entire absence of the volatilised, white, needle-like crystals obtained in the decomposition of the normal acetate. The behaviour on heating the different acetates in a vacuum is so different that it would be difficult to maintain the view that the sub-acetate is a heterogeneous mixture of metal and normal acetate, and these results, coupled with the different conductivity of the saturated solutions, must rather be held to confirm the view of the chemical individuality of the sub-acetate. The sub-acetate exhibits the same behaviour towards acids as other sub-salts of lead, namely, it is rapidly decomposed into metal and normal salt.

Lead Sub-sulphate.

Methyl sulphate was distilled through lead sub-oxide at 280° for about seventy-five minutes, the manipulation being similar to that already described for the sub-haloid salts of lead (*loc. cit.*). No difference in behaviour or in appearance was detected in the products prepared from lead sub-oxide or from the sub-oxide diluted with four times its weight of silica. On the other hand, when the distillation was carried out at 310°, and the silica omitted, the resulting grey mass was seen under the microscope to contain clusters of white crystals in a dark background, and was clearly heterogeneous.

In the sub-sulphate prepared according to the above method, the lead was estimated by conversion into lead sulphate, and the sulphate by treating the sub-salt with dilute nitric acid, evaporating to dryness, washing out the lead nitrate, and weighing the residue in a Gooch crucible as lead sulphate. Owing to the presence of traces of carbonaceous matter, the precipitate was generally faintly grey until after gentle ignition.

Found: Pb = 81·25, 81·62, 81·30, 81·29; SO_4 = 18·65, 18·56, 18·80, 18·62.

$PbSO_4$ requires Pb = 81·18; SO_4 = 18·82 per cent.

Properties of the Sub-sulphate.

The action of acids on the sub-sulphate is similar to their action on the sub-haloid salts. A solution of ammonium acetate when boiled with the substance leaves a deposit of spongy lead. In order to test the chemical individuality of a saturated solution of the salt, determinations of the conductivity in water and alcohol at 18° were made. The resistance of the water was 27,000 ohms, whilst that of a saturated solution of lead sulphate was 3030 ohms, and that of the sub-sulphate was (*a*) in air, 3100 ohms, and (*b*) in a vacuum, 3200 ohms.

The difference is so slight that it appears highly probable that there is decomposition into lead and lead sulphate, although no visible change occurred in the appearance of the residue.

The resistance of the alcohol was 90,000 ohms, whilst that of a saturated solution of lead sulphate was 93,000 ohms, and of the sub-sulphate 75,000 ohms.

Although a much more marked difference was obtained, the evidence afforded by the conductivity method was still so inconclusive that further evidence as to the individuality of the salt was sought by investigating the influence of temperature on the sub-sulphate. Were the substance a heterogeneous mixture of lead and lead sulphate, a rise in temperature above the melting point of lead would be expected to cause a pronounced change in the appearance of the finely divided lead. Before heating the sample, some of it was carefully observed under the microscope, and no sign whatever of heterogeneity was noticed, but the whole appeared a uniform iron-grey. The temperature was raised 120° above the melting point of lead for a period of four hours. On cooling, the microscope failed to reveal any change whatsoever in the appearance of the salt. The entire absence of anything in the nature of minute globules of lead certainly supports the contention that this greyish substance is definitely lead sub-sulphate.

Conclusion.

(1) Lead sub-acetate has been obtained by the action of acetic anhydride on lead sub-oxide at 195°.

(2) The substance is bluish-grey, and behaves similarly to other sub-salts of lead.

(3) Its solubility in alcohol differs slightly from that of the normal acetate, but the behaviour of the two acetates on heating in a vacuum supports the view of the chemical individuality of the sub-acetate.

(4) The sub-sulphate has been prepared by the action of methyl sulphate vapour on the sub-oxide at 280°.

(5) The substance is dark grey; conductivity experiments indicate that it decomposes on solution in water, but it appears more soluble in alcohol than does the normal sulphate.

(6) On heating the substance 120° above the melting point of lead, no change in its appearance could be detected or any sign of globules of lead.

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