XXIX.—*The Sub-bromide and Sub-chloride of Lead.*

By Henry George Denham.

In a recent paper (T., 1917, **111**, 29), the author has described a method for the preparation of lead sub-iodide by the action of methyl iodide vapour on lead sub-oxide. As indicated in that paper, the method appears of a somewhat general nature, applicable at least to the preparation of other sub-salts of lead. In the present paper, the method has been used to prepare lead sub-bromide and sub-chloride, the only radical alteration being in the replacement of the methyl haloid by the ethyl compound, owing to the more convenient boiling point of the higher homologue.

Lead Sub-bromide.

The apparatus already described in the previous paper (*loc. cit.*) has, with a few minor alterations, proved quite suitable. The lead sub-oxide was prepared from lead oxalate (Found: Pb = 70·17. Calc.: Pb = 70·18 per cent.) precipitated from an acid solution of lead acetate by the addition of oxalic acid, the actual decomposition of the oxalate into the sub-oxide being carried out precisely as described in the former paper. The alterations in the apparatus to be noted were the replacement of phosphoric oxide as a drying agent by anhydrous calcium chloride, and the introduction of a contriction in the glass tubing leading from the oven to the condenser. The former was a matter of necessity, owing to a temporary shortage of the phosphoric oxide, the latter was devised to facilitate the control of the distillation. Shortly after the ethyl bromide* had been introduced into the apparatus, a little distillate collected at the constriction and formed a most convenient gauge for noting the velocity of distillation. This is a very

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* *Purification of the Ethyl Bromide.*—The ethyl bromide was prepared from chemically pure potassium bromide, ethyl alcohol, and sulphuric acid. The distillate was treated with dilute sodium carbonate solution, several times with water, then shaken at least four or five times with concentrated sulphuric acid, and finally with water (owing to a tendency to emulsify, it was often found necessary to wash several times with dilute sodium hydroxide solution before the final washing with water). The bromide was dried over calcium chloride, and fractionated from phosphoric oxide, the fraction of constant boiling point alone being used. This method of purification had to be rigidly followed, otherwise samples of ethyl bromide were obtained that contained traces of some reactive impurity in sufficient quantity to cause appreciable errors when a relatively large amount of the bromide was distilled through the sub-oxide.

essential point, for the ethyl bromide appears to react much less vigorously with lead sub-oxide than does methyl iodide. Thus, in the preparation of lead sub-iodide, about fifty minutes' distillation sufficed to convert the sub-oxide into the sub-haloid, whilst in the present case at least 150 minutes' distillation was required to secure complete reaction. The need for a preliminary heating of the vapour before it enters the reaction bulb is even more necessary than in the case of lead sub-iodide. This was again obtained by passing the vapour through a capillary spiral. The extreme slowness of the reaction naturally leads one to search closely for the temperature at which the ethyl bromide just escaped decomposition. By the process of "bracketing," it was found that the distillation can be safely carried through at 261°, but not higher. At temperatures much lower than this, the last traces of sub-oxide react very sluggishly; for example, at 258°; analysis indicated the presence of 74·1 per cent. of lead (PbBr requires Pb=72·16 per cent.), although, by the prolonged absence of the evolution of gas, the reaction appeared quite complete. At 262° gas was evolved until the end of the experiment, the product was much lighter than that obtained in experiments carried out at 261°, and analysis gave Pb=70·2 per cent. Undoubtedly there had been incipient decomposition of the bromide vapour, with liberation of bromine and subsequent oxidation of the lead sub-bromide to the normal bromide. Indeed, it may be safely asserted that whenever this evolution of gas continues throughout the experiment, one invariably obtains a product contaminated by more or less lead bromide. After the distillation was completed, the receiver containing the distillate was cooled with liquid ammonia, the apparatus partly exhausted, the receiver sealed off, and the exhaustion continued until the pressure had fallen to about 1 mm. It was found to be unnecessary to continue the exhaustion longer as several experiments showed no trace of a volatile product, such as occurred in the preparation of lead subiodide. On the other hand, the amount of non-volatile carbonaceous matter was sufficiently high to necessitate estimation, generally amounting to from 0·3 to 0·5 per cent. of the weight of the lead sub-bromide.

Method of Analysis.—The mixture of lead sub-bromide, carbonaceous matter, and silica was digested with concentrated acetic acid, then extracted with water; after four extractions the residue was treated with a little hot, very dilute nitric acid, as it was found that the carbonaceous matter otherwise tended to coagulate and retain traces of lead bromide. Two washings with the dilute nitric acid sufficed to remove the whole of the dissolved bromide. The bromine was then weighed as silver bromide; the silica and carbon were weighed in a Gooch crucible, and after ignition in a muffle the weight of carbon was obtained by difference.

The analytical details of the accompanying experiment will make clear the use to which the knowledge of the percentage of carbon was put in arriving at the percentage of lead in the sample.

Typical Experiment.

Two bulbs each containing about 5 grams of lead oxalate intimately mixed with 2 to 3 grams of powdered silica.

Decomposition took place at a maximum temperature of 340° and maximum pressure of 5 cm. Ethyl bromide: about 15 c.c. Temperature of distillation, 261°. *Remarks.*—Five c.c. of distillate had collected in sixty-five minutes. No gas evolution for the last forty minutes. Duration of distillation, one hundred and thirty-five minutes.

Estimation of Lead:—

Weight of bulb and contents .... = 8·6648
,, ,, ,, ... = 3·7758

,, ,, carbon, silica, bromide .... = 4·8890
Corrected for air displacement .... = 4·8910
Weight of silica .... = 4·4039
,, ,, carbon (calculated from Br analysis) ...... = 0·0017

,, ,, bromide used.................................... = 0·4854

,, ,, lead sulphate.................................... = 0·5148
Percentage of Pb .... = 72·46

Estimation of Bromine:—

Weight of bulb and contents .... = 8·6020
,, ,, ,, ... = 3·4394

,, ,, carbon, silica, bromide .... = 5·1626
Corrected for air displacement .... = 5·1644
,, carbon and silica .... = 4·4927
,, substance .... = 0·6717
,, AgBr found .... = 0·4424
Percentage of Br.. = 28·03

Synopsis of Results.

Experiment.	Duration of distillation.	Absence of gas evolution for	Pb. Per cent.	Br. Per cent.
1	135 min.	40 min.	72·5	28·0
2	122 ,,	20 ,,	71·7	28·4
3	140 ,,	25 ,,	71·6	27·5
4	180 ,,	60 ,,	72·5	27·3
5	180 ,,	20 ,,	72·5	28·4
6	175 ,,	20 ,,	71·7	28·2
7	135 ,,	50 ,,	71·8	28·0
8	135 ,,	65 ,,	72·6	28·0
9	155 ,,	90 ,,	71·9	27·9
		Mean	72·09	27·97
		Calc.	72·16	27·84

The slight fluctuations about the mean undoubtedly arise from the extreme difficulty in (*a*) securing complete absence of oxygen, not only in preparing the sub-oxide, but in the introduction of the ethyl bromide and in the distillation, for example, 0·1 c.c. of oxygen let into the apparatus would cause an error of nearly 0·2 per cent. in the estimation of bromine; (*b*) maintaining the temperature of the oven just below that of incipient decomposition during distillation; and (*c*) securing sufficiently slow velocity of distillation to secure thorough heating of the vapour throughout a lengthy experiment.

Properties of Lead Sub-bromide.—The substance oxidises very slowly, more rapidly if the air is moist. After boiling with water in the air and filtering, very little evidence is obtained in the filtrate either of lead or of bromine, whilst if a saturated solution of the sub-bromide is prepared in the absence of air, there is obtained with hydrogen sulphide a darkening in the colour of the solution, but no precipitate separates; under similar conditions lead bromide gives a heavy, black precipitate. A saturated solution prepared in a vacuum gives with silver nitrate only a faint opalescence.

The colour of the sub-bromide appears to be a distinct gray, and although the presence of 0·3 to 0·5 per cent. of carbonaceous matter must necessarily darken the colour, there is little doubt that the grayish appearance is characteristic of the sub-bromide for the following reasons: (*a*) Whenever analysis gives a higher percentage of bromine than 27·9, that is, whenever oxidation has occurred through the temperature being sufficiently high to liberate bromine from the ethyl bromide with consequent oxidation of the sub-bromide to the normal bromide, the colour changes to a much paler one, the substance becoming at times nearly white.

After a rapid distillation carried out at 300° the product was found to be a pale gray, although the percentage of bromine did not exceed 30·6.

Moreover, such a pale coloured product gives, on extraction with hot water, a copious precipitate with a solution of silver nitrate, a reaction which totally fails when the gray product is used.

(*b*) On heating gray lead sub-bromide in a vacuum for two hours at 370°, the colour becomes distinctly paler, and a rapid extraction with hot water reveals the presence of a considerable amount of lead bromide.

The sub-bromide slowly decolorises bromine water, rapidly on warming to about 50°. The sub-bromide, on treatment with acetic acid, nitric acid, etc., immediately decomposes into lead and lead bromide, and after diluting and boiling, complete solution takes place, except for a small quantity of carbonaceous matter.

Determination of Solubility.—As a further proof of the individuality of the compound, the determination of the solubility of the salt in a vacuum by the conductivity method was used. The apparatus already figured (*loc. cit.*) was again used. Small bulbs of thin glass containing silica and about 0·1 gram of lead sub-bromide were prepared by the usual method, and the purity of the samples was controlled by the analysis of the contents of larger bulbs. The actual procedure already described (*loc. cit.*) was closely followed.

The resistance of a saturated solution of carefully prepared lead bromide at 25° was found to be 22 ohms, remaining constant for two hours.

The mean of two closely agreeing experiments with lead sub-bromide gave the following results:

Resistance of the water before breaking the bulb...... = 26000 ohms.
After breaking the bulb...................................... = 1860 „

this remaining unchanged for several hours.

If the ionic mobilities of the bromine and the lead ions (whether Pb^+ or Pb_2^{++}) are assumed to be the same as in the case of the normal bromide (76·6 and 71·8 respectively), and if complete dissociation takes place, the solubility of the sub-bromide is 0·4 milli-equivalent per litre. This value is about the same as that for the subiodide already recorded (0·35 milli-equivalent per litre), but in both cases it must be emphasised that the values obtained for the solubility are probably a little high, due to unavoidable traces of the normal salt. Such traces are almost certain to be formed through the action of heat on the sub-salt during the sealing of the bulb, whilst the carbonaceous matter, too, may exert an influence on the solubility.

Lead Sub-chloride.

When the lead oxalate has been completely decomposed into sub-oxide about 10 grams of ethyl chloride thoroughly cooled by liquid ammonia were introduced into the distillation flask. By this means any desired quantity could be rapidly introduced from the tubes. The distillation of the chloride could be rapidly regulated by adjusting the temperature of the water-bath, but owing to the low boiling point of the chloride no effort was made to collect the distillate. The reaction between the sub-oxide and the vapour of the ethyl chloride was very slow, and it was soon found that approximately three hours were required for the distillation and a temperature as high as 311° (as recorded by a standardised thermometer). This is shown in the following table.

TABLE I.

Experiment.	Temperature.	Duration.	Cl. Per cent.
1	261°	85 min.	4·2
2	275	135 ,,	7·4
3	300	165 ,,	11·1
4	310–11	165 ,,	14·4
5	312	160 ,,	15·0
6	315	180 ,,	17·2
		Theoretical ...	14·6

The highest temperature at which the distillation may be carried out appears to be 311°, and the duration of the experiment in the neighbourhood of three hours. The slowness of reaction suggested that it might be possible to carry through the experiment without having silica present, as was the case with the sub-iodide. In two experiments it was impossible to detect any difference between samples prepared in the presence and in the absence of silica, and in the majority of the experiments tabulated in table II silica was not used as diluent. The only other change in the procedure was that phosphoric oxide was again used as a drying agent, in order to eliminate any traces of ammonia absorbed by the ethyl chloride when it was being introduced into the apparatus.

Method of Analysis.—A slight modification in the method of estimating lead was necessary owing to the high percentage of carbonaceous matter retained in the reaction bulbs. As a rule the estimation of chlorine revealed the presence of about 2 per cent. by weight of carbonaceous matter. The low value at first found by the old method in the estimation of lead under conditions when the estimation of chlorine led one to expect that a pure sample of sub-chloride had been obtained, suggested that this carbonaceous matter, impregnated as it would be with lead sulphate, might be exercising a reducing action with a consequent slight loss of lead. Thus in one experiment the percentage of chlorine found was exactly correct, whilst the percentage of lead was 84·4 (calc., 85·4). Two bulbs were then prepared, the lead in one being estimated by the method already described; in the other the sub-chloride was extracted five times with hot dilute nitric acid, the filtrate concentrated in a weighed silica crucible, and finally evaporated with excess of sulphuric acid. The results by the old and the new methods were respectively 83·6 and 85·1 per cent., a duplicate experiment giving identical results. The results recorded in table II were obtained by the modified method for estimating lead, the percentage of chlorine being obtained in a manner similar to that described for the bromide, except that no estimation of silica was necessary.

The analytical results are given in table II.

TABLE II.

Experiment.	Duration of distillation.	Pb. Per cent.	Cl. Per cent.
10	190 min.	85·14	14·24
11	205 ,,	85·30	14·85
12	165 ,,	85·53	14·90
13	210 ,,	85·11	14·60
14	210 ,,	85·17	14·04
15	180 ,,	85·94	14·91
	Mean	85·36	14·59
	Theoretical ...	85·39	14·61

Properties of Lead Sub-chloride.—The colour of the sub-chloride is closely similar to the gray colour of the sub-bromide. It must again be emphasised that the gray appearance does not arise from the presence of the carbonaceous matter, for if the sub-chloride is heated in a vacuum above 400°, it becomes nearly white owing to the reaction:

$$2PbCl \longrightarrow PbCl_2 + Pb,$$

the whiteness of the normal chloride more than compensating for the darkness arising from the presence of an equivalent quantity of lead. The sub-chloride is fairly stable in air, but rapidly decolorises bromine water and permanganate solution.

A saturated aqueous solution of lead sub chloride prepared in a vacuum gives a faint precipitate with silver nitrate as well as with hydrogen sulphide, strongly contrasting in this respect with the less readily soluble sub-bromide and sub-iodide. The sub-salt is also readily decomposed by acids.

Determination of Solubility.—As a quantitative proof that the gray substance is not an intimate mixture of lead and lead chloride in molecular quantities, a comparison of its solubility with that of the normal chloride has been made by the conductivity method already described.

Resistance of a solution of lead chloride, three times recrystallised, at 25° = 15·9 ohms, a second determination giving the same result.

A small bulb containing 0·1 gram of lead sub-chloride was broken in a vacuum.

Resistance before the bulb was broken .... = 21000 ohms.
,, after ,, ,, ,, ,, ... = 340 ,,

If one assumes the ionic mobilities of the lead and chlorine ions to be the same as for the normal chloride (71·8 and 75·5 respectively) and that complete dissociation takes place (highly probable if the constitution of the salt is represented by the formula $PbCl$, but subject to correction if the formula should prove to be Pb_2Cl_2), the solubility is found to be 2·2 milli-equivalents per litre.

Summary.

1. Lead sub-chloride and lead sub-bromide have been prepared by the action of ethyl chloride or bromide vapour at 311° and 261° respectively on lead sub-oxide.

2. Both compounds are grey, sparingly soluble, fairly stable in air, but readily oxidised by bromine water.

3. The sub-chloride has a solubility of about 2·2 milli-equivalents per litre, the sub-bromide 0·4 milli-equivalent per litre.

4. The sub-salts are readily decomposed by acid into the normal salt and metal.

Further work on the sub-salts of lead, etc., is still in progress. The author desires to record his appreciation of the facilities placed at his disposal by the Walter and Eliza Hall Trust for the prosecution of this research.

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