

XXXI.—On *Plumbic Tetrethide*.

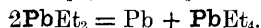
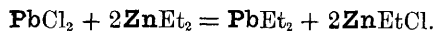
By E. FRANKLAND, F.R.S., and AWBREY LAWRENCE, Esq.

IN the year 1859, Buckton (*Phil. Trans.*, **149**, 431) described the preparation of plumbic tetrethide, established its constitution, and announced its chief properties; but no further study of the reactions of this body having since been made, we beg to submit to the Society the following observations upon its behaviour in contact with various gaseous reagents.

After exposure to an atmosphere of each of the following gases for a period varying from eight to eleven days, we found that no action took place, and that there was no perceptible diminution in the volume of the gas:—Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen. On the other hand, sulphurous anhydride was rapidly absorbed, converting the liquid plumbic tetrethide into a white amorphous solid.

*Action of Sulphurous Anhydride on Plumbic Tetrethide.*

For the preparation of the plumbic tetrethide used in these experiments we employed a modification of Buckton's method. Dry plumbic chloride was added to zinc ethyl so long as any reaction took place. A large quantity of metallic lead in a spongy condition was deposited without any evolution of gas, whence we infer that the dyad compound ( $\text{PbEt}_2$ ) is first formed and then decomposed according to the following equations:—



It has been shown by one of us (*Phil. Trans.*, **142**, 417) that stannous ethide is similarly decomposed, though less readily into stannic ethide and metallic tin:—



and we have recently availed ourselves of this transformation for the preparation of large quantities of stannic ethide (*Jour. Chem. Soc.*, 1879, p. 130).

The initial process in the preparation of plumbic tetrethide is best conducted in a stout glass bottle in which the mixture can be well stirred with a glass rod, and the plumbic chloride should be added until it no longer changes colour. Instead of separating the crude plumbic tetrethide by water, and distilling it *in vacuo* to avoid decomposition as recommended by Buckton, we found the following plan simpler and quite satisfactory.

The product of the reaction was slowly mixed with a large volume of water in a capacious flask or retort, which was then placed in an oil bath and its contents distilled in a current of steam so long as any heavy oily drops passed over. The distillate consisted of water and a heavy layer of plumbic tetrethide which, when separated, was ready for the following reaction. Before adopting this process it was ascertained that plumbic tetrethide suffers no decomposition by distillation with water.

Several ounces of plumbic tetrethide were placed in a Winchester quart bottle filled with dry sulphurous anhydride, which was afterwards supplied as often as necessary. The colourless liquid first changed to a yellowish-green turbid and thick oil, and finally, after forty-eight hours, became a white amorphous solid, refusing to absorb more of the gas. Preliminary experiments showed that this amorphous mass was, to a large extent, soluble in water, the insoluble residue consisting chiefly of plumbic sulphite or sulphate; and that, either dry or dissolved in water, it gave a splendidly crystalline sublimate when heated to  $100^{\circ}$ . Guided by these observations, the white amorphous product was put into a beaker, the mouth of which a second beaker was luted with gummed paper, and a steam heat was then applied to the first beaker for several hours. In this way a considerable bulk of crystals sublimed into the second beaker, although their weight was but small. These crystals possessed the properties of diethyl sulphone ( $\text{SO}_2\text{Et}_2$ ), but they were contaminated with a volatile lead compound, which left a residue of plumbic oxide amounting to about 5 per cent. of their weight when they were burnt in a stream of air and oxygen. As this residue was not materially diminished by recrystallisation from an aqueous solution, the crystals were dissolved in hot and strong nitric acid, some red fumes were evolved, and on evaporation to dryness the residue suddenly solidified to a crystalline mass. This mass was treated with alcohol in which nearly the whole of it dissolved, the solution was filtered and evaporated to crystallisation, the crystals being afterwards redissolved in water and recrystallised. On combustion they now left only 1.5 per cent. of residue.

Submitted to analysis, the purified crystals gave the following results:—

I. 0.1464 gram burnt with cupric oxide in a stream of air and oxygen, gave 0.2120 gram of carbonic anhydride and 0.1114 gram of water.

II. 0.1158 gram, burnt with a mixture of potassic chlorate and sodic carbonate, gave 0.2250 gram of baric sulphate.

These numbers agree closely with those calculated from the formula of diethyl sulphone, as shown by the following comparison:—

		Calculated.		Found.	
		I.	II.		
C <sub>4</sub> . . . . .	48	39.35	39.49	—	
H <sub>10</sub> . . . .	10	8.19	8.44	—	
S . . . . .	32	26.23	—	26.68	
O <sub>2</sub> . . . . .	32	26.23	—	—	
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	122	100.00			

The identity of this body with diethyl sulphone is confirmed by a comparison of their chief properties. They are both unacted upon by strong nitric acid, and both melt at 70° C., and suddenly solidify at 55°.

The substance remaining after the separation of diethyl sulphone was dissolved in water and filtered from an insoluble residue, which consisted chiefly of plumbic sulphate. The filtrate, which obviously contained a lead salt, was divided into two parts, one being devoted to treatment with baric hydrate, and the other to the action of sulphuretted hydrogen with a view to the separation of the free acid.

To the first portion an excess of baric hydrate was added, and the copious precipitate of plumbic hydrate separated by filtration. The strongly alkaline filtrate was then distilled in order to separate, if present, any volatile organo-lead base; but the distillate was neutral. Carbonic anhydride was then passed through the residue in the retort to remove excess of baryta, and the liquid was boiled and filtered. The filtrate was next treated with sulphuretted hydrogen to decompose the last traces of lead compound, the black precipitate filtered off, and the solution boiled with baric carbonate and filtered. The filtrate was evaporated to its crystallising point, and a crop of rhomboidal crystals obtained which, after drying at 100°, gave the following results on analysis, and these, taken in connection with the reaction giving rise to this compound, leave no doubt that it is the barium salt of ethyl sulphinic acid (SOEtHo) containing one molecule of water of crystallisation, as is seen from the following comparison:—

I. 0.1421 gram, burnt with cupric oxide in a stream of oxygen, gave 0.0474 gram of water and 0.0714 gram of carbonic anhydride.

II. 0.1364 gram, burnt with cupric oxide in a stream of oxygen, gave 0.0451 gram of water and 0.0689 gram of carbonic anhydride.

IV. 0.2620 gram, burnt with potassic chlorate and sodic carbonate, gave 0.3480 gram of baric sulphate.

Calculated into percentages, these results give numbers agreeing with the formula  $(\text{SOEt})_2\text{BaO}''$ ,  $\text{OH}_2$ , or  $\text{C}_4\text{H}_{12}\text{BaS}_2\text{O}_5$ :—

Calculated.			Found.			
			I.	II.	III.	IV.
C <sub>4</sub> . . . .	48	14·08	13·70	13·77	—	—
H <sub>12</sub> ..	12	3·52	3·70	3·67	—	—
S <sub>2</sub> . . . .	64	18·77	—	—	—	18·24
Ba . . . .	137	40·17	—	—	39·38	—
O <sub>5</sub> . . . .	80	23·46	—	—	—	—
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An attempt was made to prepare the silver salt of this acid, but the compound underwent decomposition even in the dark.

The barium salt after purification was submitted to analysis with the following results:—

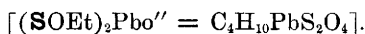
I. 0.1844 gram of the dried substance ignited with concentrated sulphuric acid, gave 0.1207 gram of baric sulphate.

II. 0.1166 gram, burnt with cupric oxide in a stream of oxygen, gave 0.0357 gram of water and 0.0588 gram of carbonic anhydride.

III. 0.2830 gram burnt with potassic chlorate and sodic carbonate, gave 0.3781 gram of baric sulphate.

These results calculated into percentages give numbers agreeing fairly well with those just given for baric ethyl sulphinate, viz., carbon, 13.75; hydrogen, 3.40; barium, 38.49; sulphur, 18.35.

In another experiment this reaction was carried on in an atmosphere of carbonic anhydride with exactly the same results, as the following analyses of the lead salt show :—



I. 0.1687 gram, burnt with cupric oxide in a stream of air and oxygen, gave 0.0738 gram of carbonic anhydride and 0.0413 gram of water.

II. 0.1550 gram, burnt as before, gave 0.0680 gram of carbonic anhydride and 0.0420 gram of water.

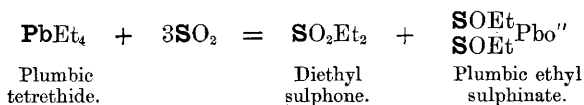
III. 0.1617 gram, burnt with a mixture of sodic carbonate and potassic chlorate, gave 0.1817 gram of baric sulphate.

IV. 0.2243 gram gave, after ignition with sulphuric acid, 0.1705 gram of plumbic sulphate.

V. 0.2496 gram, similarly treated, gave 0.1889 gram plumbic sulphate.

Calculated.				Found.					Mean.
				I.	II.	III.	IV.	V.	
C <sub>4</sub> ..	48	12.21		11.93	11.96	—	—	—	11.95
H <sub>10</sub> ..	10	2.54		2.72	3.01	—	—	—	2.86
S <sub>2</sub> ..	64	16.28		—	—	15.43	—	—	15.43
Pb ..	207	52.67		—	—	—	51.88	51.70	51.79
O <sub>4</sub> ..	64	16.30		—	—	—	—	—	17.97
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	393	100.00							

The formation of diethyl sulphone (sulphuric diethoxide) and plumbic ethyl sulphinate is explained by the following equation:—



Ethylsulphinic acid was discovered by Hobson (*Jour. Chem. Soc.*, **10**, 55), but its formula was first established by Wischin (*Ann. Chem. Pharm.*, **139**, 364). This acid may be considered as derived from sulphurous acid by the substitution of a semi-molecule of ethyl for one of hydroxyl, thus:—



It is also equally true that ethylsulphinic acid is propionic acid, in which one atom of tetrad-sulphur has been substituted for one of carbon, thus:—



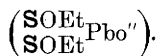
The following is a summary of the results described in the foregoing pages:—

1. Plumbic tetrethide in quantity may be most conveniently obtained by distilling with water the product of the action of zinc-ethyl upon plumbic chloride.

2. Prolonged exposure at ordinary temperatures to the following gases produces no chemical change in plumbic tetrithide:—

Ammonia, carbonic anhydride, carbonic oxide, cyanogen, nitric oxide, oxygen, sulphuretted hydrogen.

3. Plumbic tetrithide rapidly absorbs sulphurous anhydride, and is transformed into a white solid which is composed of diethyl sulphone (sulphuric diethoxide,  $\text{SO}_2\text{Et}_2$ ) and plumbic ethyl sulphinate,



4. No volatile organo-metallic base is formed in this reaction, like that which we have shown to be produced in the corresponding operation with stannic ethide (*Jour. Chem. Soc.*, 1879, 130). In the presence of sulphurous anhydride plumbic tetrithide is at once deprived of the whole of its ethyl, whereas stannic ethide retains three-fourths of it.

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