XXVIII. *Researches on the Phosphorus-Bases.*

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In a note on the action of chloride of methyl upon phosphide of calcium, communicated more than ten years ago to the Institute of France*, M. Paul Thénard pointed out the existence of a series of bodies which correspond to the compounds of phosphorus with hydrogen, which may, in fact, be viewed as hydrides of phosphorus, the hydrogen of which is replaced by an equivalent quantity of methyl.

One of these bodies, a liquid possessing a most offensive odour, spontaneously inflammable and explosive in the highest degree, corresponds to the liquid phosphoretted hydrogen, and appears to occupy, in the phosphorus-series, the same position which belongs to kakodyle among the arsenic-compounds. It is a colourless, somewhat viscid liquid which boils at about 250° C. Exposed to the slow action of the atmosphere this liquid is converted into a compound which is strongly acid and easily crystallizes. This acid is probably analogous to kakodylic acid.

In addition to this liquid body, two solid substances are formed by the action of chloride of methyl upon phosphide of calcium. One of these, according to M. Paul Thénard, corresponds to the solid phosphoretted hydrogen, whilst the other, which is the principal product of the reaction, constitutes the hydrochlorate of a very volatile phosphoretted base. From its composition this body may be viewed as ammonia, in which the nitrogen is replaced by phosphorus, whilst methyl is substituted for the hydrogen. When repeating these experiments in the ethyl-series Paul Thénard arrived at similar results, to which he however only briefly alludes.

At the time when these experiments were first made, the ammonia-bases had not been discovered, and the subject presented obstacles so numerous and varied that the researches of this chemist remained unfinished. Nobody will be surprised at this, who has made himself acquainted with the difficulty of effecting the above-mentioned reactions, and who from his own experience knows the danger which attends the preparation of these compounds, and the horrible odour which some of them possess.

Paul Thénard's remarkable researches did not excite, at the time of their publication, that degree of interest which they really deserved. There were but few facts known, at that period, with which his results could naturally be connected; indeed, until after the ammonia-bases were discovered, the importance of the experiments on these phosphorus-bodies could scarcely be recognized; then it was that M. Paul Thénard's investigations

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* Comptes Rendus, t. xxi. p. 144, and t. xxv. p. 892.

attracted that attention to which they were entitled; then it was that the remarkable parallelism of the compounds of phosphorus and nitrogen, more and more distinctly exhibited by these discoveries, began to become an object of general interest to chemists.

It is now many years since M. PAUL THÉNARD abandoned the study of the phosphorus-compounds, for the first knowledge of which we are indebted to him. The unfinished state in which these researches remained, and the rich and abundant harvest collected since that period in all the neighbouring fields of science, necessitated a revision of the subject. The discovery of methylamine, dimethylamine, and trimethylamine, and of the corresponding terms in the ethyl- and amyl-series, had shown that the hydrogen in ammonia may be replaced by binary molecules, such as methyl, ethyl, amyl and phenyl, the newly-formed compounds retaining the basic character of the original ammonia-molecule; whilst the production of triethylstibine and triethylarsine had furnished the proof that the total replacement of the hydrogen in the indifferent antimonietted and arsenietted hydrogen exalts the chemical character of these compounds in a most remarkable manner, the methylated and ethylated bodies exhibiting basic characters scarcely inferior to those of ammonia itself. It remained therefore to be investigated whether phosphorus, which, by its chemical tendencies, stands between nitrogen and arsenic, would exhibit a similar deportment. It remained to be ascertained in what manner the gradual entrance of binary molecules in the place of the hydrogen in phosphoretted hydrogen would change the character of the original compound. The discovery of the tetrethylated ammonium-bases had also opened a new field of research, in which the corresponding terms of the antimony- and arsenic-series were rapidly brought to light. It was indeed possible to predict with certainty, that an appropriately selected method would lead to the production of the analogous derivatives of phosphoretted hydrogen. The time for resuming the study of the phosphorus-bases had in fact arrived.

We have been engaged for a considerable time in the investigation of this subject, and now beg to offer to the Royal Society in the following pages an account of our experiments.

In the first place, we have endeavoured to obtain the bases corresponding to phosphoretted hydrogen, by a method analogous to that followed by M. PAUL THÉNARD.

Recent experience suggested at once the replacement of the gaseous chloride of methyl by the liquid iodide, which is so much more convenient for experiment; and also the substitution, for the phosphide of calcium, of the compound of phosphorus and sodium obtained by the direct union of the elements. On the application of heat, these substances act on one another with great energy, producing combustible and detonating compounds, so that the experiment is not without danger. Often the product of the operation is lost; and if the reaction has taken place without explosion, the separation of the constituents of the very complicated mixture which results can be effected only with the greatest difficulty.

We have convinced ourselves that the product of the action of iodide of methyl upon phosphide of sodium consists chiefly of three different substances, viz. of a liquid which probably is Me_2P, and corresponds to kakodyl; of a second liquid, Me_3P, corresponding to trimethylstibine and trimethylarsine; and lastly, of a beautiful crystalline solid body, Me_4PI, which is the analogue in the phosphorus-series of iodide of tetramethylammonium.

We abstain from a minute description of the experiments made in this direction, since in the further course of the inquiry we have forsaken this method altogether. Indeed this mode of preparation is very uncertain, and the separation of the products formed is attended with almost insurmountable obstacles, not to speak of the difficulty of obtaining pure phosphide of sodium fit for the reaction. The question resolved itself into the discovery of a method which would yield us the desired substances conveniently, without danger, in considerable quantity, and in a state of absolute purity.

It appeared to us that the action of terchloride of phosphorus on zinc-methyl, zinc-ethyl, &c. would enable us to attain the desired result. Experiment has fully confirmed this anticipation.

Dr. FRANKLAND's remarkable observations on the action of zinc upon iodide of methyl and iodide of ethyl at high temperatures are still fresh in the memory of chemists. Besides the hydrocarbons methyl and ethyl, zinc-methyl and zinc-ethyl are formed in this reaction, which exhibit the deportment of true organic metals, comparable in the intensity of their combining powers with the most electro-positive elements. In the action of a chloride upon such a compound metal, the chlorine was sure to seize upon the zinc, and it was extremely probable that, together with chloride of zinc, methyl- or ethyl-compounds would be formed in definite proportions. In the action of terchloride of phosphorus, the formation of a methyl- or ethyl-compound of phosphorus, corresponding in composition to the terchloride of phosphorus, might be with certainty expected:

$$PCl_3+3MeZn=3ZnCl+Me_3P.$$

These anticipations were in fact fulfilled. The products of these reactions, the bases Me_3P and E_3P, which we propose to call respectively trimethylphosphine and triethylphosphine, remain united with chloride of zinc, and a simple distillation with an alkali alone is necessary to liberate them.

$$3ZnCl, Me_3P+6KO=3KCl+3(KO, ZnO)+PMe_3$$
$$3ZnCl, E_3P+6KO=3KCl+3(KO, ZnO)+PE_3.$$

They are obtained in this way as volatile oils, with a peculiar and strongly-marked odour, and possessing distinctly basic properties.

We found no difficulty in procuring the bodies in question by this method in a state of perfect purity, so as to examine their properties with accuracy.

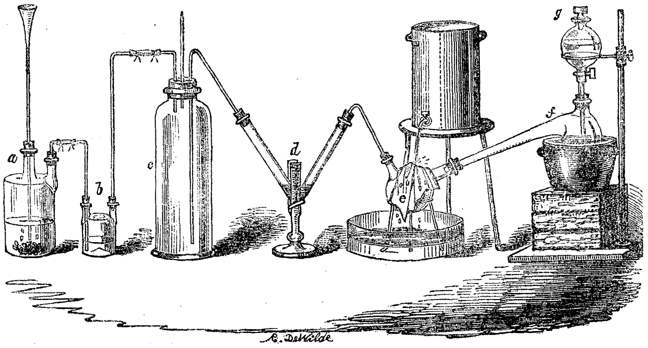
From the outline which we intend to give, it will be obvious that this group of bodies exhibits the most striking analogies with the ammonia-bases; so much so, in fact, that frequently it will only be necessary to repeat the observations, which were published by one of us about eight years ago, regarding the methylated and ethylated derivatives of ammonia*.

The experiments which we have to communicate refer chiefly to the methyl- and ethyl-compounds; though here and there we have used amyl as material. Since we have preferred working in the ethyl-series, we begin with the description of the ethyl-compounds.

EXPERIMENTS IN THE ETHYL-SERIES.

ACTION OF TERCHLORIDE OF PHOSPHORUS ON ZINC-ETHYL.

The reaction between these two bodies is very violent, and readily gives rise to dangerous explosions, if the necessary precautions are neglected. We have generally adopted the following arrangement. A tubulated retort is joined to a receiver which in its turn is connected with a wide glass tube bent at an angle of about 130°, and acts like a second receiver. The angle of this tube is filled with terchloride of phosphorus, and the tube is connected with a large cylinder which is supplied by a suitable apparatus with dry carbonic acid. As soon as the carbonic acid has expelled the air from the reservoir, tube, receiver, and retort, an exit-tube from the reservoir, up to that time closed by a caoutchouc cap, is opened to let out the carbonic acid, the evolution of which is maintained during the whole operation. The tubulature of the retort is now connected with the copper digester in which the zinc-ethyl has been prepared; and as soon as the retort has received a charge of the ethereal solution of zinc-ethyl, there is fixed into the same tubulature a little dropping apparatus, consisting of a glass globe, with a tubulature and stopper at the top, and terminating below in a glass tube in which a stopcock is fitted. This apparatus is filled with terchloride of phosphorus, and by appropriately adjusting the stopcock and opening or closing the stopper of the glass globe, any desired flow of the fluid can be maintained with the greatest nicety.



a. Apparatus for generating carbonic acid. *b.* Wash-bottle containing sulphuric acid. *c.* Reservoir of carbonic acid. *d.* Bent tube containing terchloride of phosphorus. *e.* Receiver. *f.* Retort containing zinc-ethyl. *g.* Dropping apparatus filled with terchloride of phosphorus.

However slowly the action may be accomplished, and however well, moreover, the retort

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* Philosophical Transactions, 1850, p. 93; 1851, p. 357.

and receiver may be cooled by water or ice, the action is nevertheless invariably so violent, that all the ether, and with it a large quantity of the zinc-ethyl, passes over into the receiver. By the powerful ebullition which periodically ensues, a portion of the vapour is driven even into the bent tube, and a considerable loss of zinc-ethyl is incurred unless this tube be filled with terchloride of phosphorus, which greedily absorbs every trace of the former compound. This fluid valve, ascending and descending in the tube, in accordance with the progress of the reaction, regulates the function of the apparatus so perfectly, that the operation, which always takes several hours, when once begun continues by itself. Sometimes the absorption is so violent that the terchloride of phosphorus in the tube is sucked back into the receiver, but even then no loss is to be feared, since the tube is connected with the reservoir filled with carbonic acid.

The first drops of terchloride of phosphorus which fall into the solution of zinc-ethyl, hiss like water when coming in contact with red-hot iron. The action becomes by-and-by less violent, and as soon as an evolution of heat is no longer perceptible, the operation is terminated. There remain in the retort, in the receiver, in the bent tube, and sometimes even in the carbonic acid reservoir, two liquid layers,—the one a heavy pale straw-coloured thick fluid, the other a transparent colourless mobile fluid floating on the former.

The heavy fluid, a compound of the phosphorus-base with chloride of zinc, nearly solidifies on cooling, but the viscid transparent mass exhibits no trace of crystalline structure. The light fluid is a mixture of ether with an excess of the terchloride of phosphorus; after disconnecting the apparatus, it is poured off from the viscous fluid, and may be used, after distillation, in a second operation.

In order to liberate the phosphorus-base from its combination with zinc, nothing more than a distillation with potassa is required. To prevent the destruction of the retort, to which the zinc-compound adheres with pertinacity, and the loss of so precious a material, this operation is conveniently performed in the following manner. Solid hydrate of potassa is placed on the hard resinous cake attached to the bottom of the retort, and a slow current of water allowed to flow in by the dropping apparatus, after the air in the retort has been carefully displaced by hydrogen: the heat evolved during the reaction is quite sufficient to volatilize the base with the vapour of the water; it may be condensed by an ordinary cooler. The base, which is now floating on the water of the distillate, is removed by means of a separating funnel; it is allowed to stand for a day over hydrate of potassa, and finally rectified in a current of dry hydrogen gas.

Triethylphosphine.

Thus obtained, triethylphosphine is a colourless, transparent, mobile liquid, which strongly refracts light. The compound is lighter than water, its specific gravity being found to be 0·812 at 15°·5 C.; it is perfectly insoluble in water, but soluble in every proportion in alcohol and ether. Its odour is penetrating, almost benumbing, but still not disagreeable. The intolerable smell which renders it so unpleasant to work with these phosphorus-compounds generally, arises from other products, which make their appearance in considerable quantities, especially in preparing the phosphorus-base by means of phosphide of sodium and iodide of ethyl. In a diluted state, the odour of the pure triethylphosphine has the greatest similarity to that of the hyacinth*. Long-continued working with this substance causes headache and sleeplessness.

The boiling-point of the triethylphosphine is 127°·5 C., under the barometric pressure of 0·744 m. The determination was made with an ounce of the pure substance. The distillation of the phosphorus-base must be performed in a stream of dry hydrogen, for it attracts oxygen with great energy, especially at high temperatures. It is impossible to pour the liquid from one vessel into another without its becoming perceptibly warm. The product of oxidation formed in this way becomes evident in the last stage of the distillation. When the larger quantity of the base has distilled over, the mercury in the thermometer begins suddenly to rise, and before the temperature has become again stationary, the neck of the retort is found to be coated with a network of beautiful crystals, which are even drawn over into the receiver. These crystals are permanent as long as they are protected from the action of the moist air. After disconnecting the apparatus, it is vain to attempt to collect the crystals, the most minute quantity of water causing them to liquefy to a heavy oil, soluble in water. From these remarks, it is obvious that triethylphosphine must be almost always contaminated with a small quantity of this substance; in fact a bottle containing the base cannot be opened without its being formed. When the phosphorus-base is brought in contact with oxygen, vapours are immediately formed; the liquid frequently becomes so hot that it inflames, and the body is burnt with evolution of dense white fumes of phosphoric acid. If a strip of paper, moistened with triethylphosphine, be introduced into a test-tube containing oxygen and immersed into hot water, the vapour of the phosphorus-base produces with the oxygen an explosive mixture, which detonates after a few moments with considerable violence. When poured into a flask filled with chlorine gas, every drop is inflamed with disengagement of pentachloride of phosphorus and hydrochloric acid, and separation of carbon. Triethylphosphine unites with bromine and iodine, evolving considerable heat, which may give rise to inflammation; but if the action be moderated, crystalline compounds are produced. In cyanogen gas the phosphorus-base is converted into a brown resinous mass. If a piece of sulphur be thrown into a test-tube containing

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* There is nothing new in the fact that the odour of a substance may be considerably changed by dilution. Several years ago, when occupied in the preparation of different ethers, which have found numerous applications in perfumery, I had frequent opportunities of observing how the desired aroma, which was absent in the pure substance, was brought out by dilution with alcohol. The hyacinth smell of the dilute phosphorus-base is so characteristic, that one morning I found in my laboratory a large basket filled with hyacinths, the present of a lady friend of mine, who, interested in my labours, had a strong impression that triethylphosphine must be present in the hyacinth. In the interest of science, the entire floral adornment of the garden had been unmercifully sacrificed! It would have been ungrateful not to distil them, but I regret to say, that the anticipation of the amiable donor, who wished to enrich me with so interesting a discovery, proved unfounded. The hyacinth does not contain any phosphorus-base.—A. W. H.

triethylphosphine, it becomes so hot as to fuse the sulphur, which then floats on the liquid base in the form of globules, as sodium does on water, and at last entirely disappears. The clear liquid thus obtained, solidifies on cooling to a magnificent crystalline mass. The experiment must be made with caution, since the vapour of the phosphorus-compound, which rises during the reaction, generally explodes on coming in contact with the air contained in the vessel. Selenium gives rise to similar but less powerful phenomena.

Although triethylphosphine, in its relations to other bodies, possesses all the characters of a well-defined base, it does not exhibit an alkaline reaction. When freshly prepared, it is without action on vegetable colours, but when exposed only for a few moments to the influence of the air, it begins to show a constantly increasing acid reaction. Triethylphosphine unites with acids slowly, but with considerable evolution of heat; with concentrated acid the temperature frequently rises to such a degree as to give rise to inflammation of the liquid. Most of its salts are crystalline compounds, but are very soluble and deliquescent.

The composition of triethylphosphine was sufficiently established in theory, both by its mode of formation and by numerous analogies. Nevertheless we have made an experimental determination.

When freshly prepared and burnt with chromate of lead, 0·369 grm. of triethylphosphine furnished 0·8106 grm. of carbonic acid and 0·4212 grm. of water.

The formula

$$C_{12}H_{15}P = \left.\begin{matrix}E\\E\\E\end{matrix}\right\}P$$

leads to the following numbers:—

	Theory.		Experiment.
12 equivs. of Carbon	72	61·01	60·00
15 equivs. of Hydrogen	15	12·71	12·68
1 equiv. of Phosphorus	31	26·28	——
1 equiv. of Triethylphosphine . . .	118	100·00	

The combustion shows a small loss of carbon; but if it be recollected with what avidity this base attracts oxygen, and that the previous manipulations were performed in atmospheric air, this is easily accounted for. It would have been loss of time to repeat this experiment, especially since we shall have to mention in the following pages many analytical determinations, which, although referring to other substances, enable us to infer with equal certainty the composition of the phosphorus-base.

Triethylphosphine forms crystalline compounds with the hydrogen-acids of chlorine, bromine, and iodine, with sulphuric and nitric acids; but all these salts, which can be obtained in the dry state only by the aid of the exsiccator, are but little suitable for analysis. The solution in hydrochloric acid affords a crystalline platinum-salt, which is insoluble in cold water, in alcohol and ether, but which, on account of the facility with which it decomposes at 100° C., must be dried in the exsiccator. In the water-bath it fuses and is altogether decomposed. The determination of the platinum in the phosphorus-compounds presents considerable difficulties. The platinum in these substances cannot be determined in the ordinary way by simple ignition, because a considerable quantity of platinum is carried off with the phosphorus-vapour, however slowly and carefully the process may be carried out. We unfortunately did not find this out, until a great number of unsuccessful analyses had been made. By heating with a considerable excess of carbonate of sodium in a porcelain crucible on a sand-bath, the temperature of which is gradually raised, the determination succeeds without difficulty. After removal of the portion soluble in water, the platinum-residue, which is always contaminated with silicic acid, is dissolved in nitrohydrochloric acid, the solution evaporated to dryness, and the residue again dissolved in acid: the careful evaporation of this solution furnishes a perfectly accurate result. This method is somewhat tedious, but there is some compensation for this increased complexity by the simultaneous determination of the chlorine.

The analysis of the platinum-salt of triethylphosphine has furnished the following results:—

0·2795 grm. of platinum-salt gave 0·3725 grm. of chloride of silver and 0·0855 grm. of platinum, corresponding to the formula

$$C_{12}H_{15}P, HCl, PtCl_2=E_3P, HCl, PtCl_2.$$

	Theory.		Experiment.
12 equivs. of Carbon	72	22·21	——
16 equivs. of Hydrogen . . .	16	4·94	——
1 equiv. of Phosphorus . . .	31	9·56	——
3 equivs. of Chlorine	106·5	32·85	32·96
1 equiv. of Platinum	98·7	30·44	30·59
1 equiv. of Platinum-salt . .	324·2	100·00	

The preceding experiments sufficiently fix the composition of triethylphosphine. This compound is in fact triethylamine, in which the nitrogen is replaced by an equivalent quantity of phosphorus. The perfect analogy with triethylamine is also shown by the deportment of the phosphorus-base with the iodides of ethyl, methyl and amyl. Triethylphosphine combines with these substances, forming well-crystallized and highly characteristic salts, which may be regarded as iodide of ammonium, in which the nitrogen is replaced by phosphorus and the hydrogen by the radicals of the alcohols.

Iodide of Tetrethylphosphonium.

On mixing triethylphosphine with iodide of ethyl, a violent action ensues after a few moments; the liquid effervesces with almost explosive violence, and then solidifies to a white crystalline mass. If, instead of the pure base, an ethereal solution be employed, the crystals are formed more slowly. This new compound is extremely soluble in water, less so in alcohol, and insoluble in ether. The aqueous solution crystallizes on addition of potassa-solution, in which this compound, like the iodides of tetramethylammonium and tetrethylammonium, is but slightly soluble. From the alcoholic solution the salt falls, on addition of ether, as a crystalline powder. If ether be added to a cold alcoholic solution, as long as the precipitate first produced is dissolved by boiling, well-formed crystals of the iodide are deposited on cooling.

The mode of formation and analysis leave no doubt respecting the nature of these crystals. They contain the elements of 1 equiv. of triethylphosphine and 1 equiv. of iodide of ethyl.

$$\underbrace{C_{12}H_{15}P}_{\substack{\text{Triethyl-}\\\text{phosphine.}}} + \underbrace{C_4H_5I}_{\substack{\text{Iodide of}\\\text{ethyl.}}} = \underbrace{C_{16}H_{20}PI.}_{\text{New compound.}}$$

The following are the results of analyses:—

I. 0·743 grm. of the iodide yielded 0·630 grm. of iodide of silver.
II. 0·648 grm. of the iodide gave 0·555 grm. of iodide of silver.
III. 0·412 grm. of the iodide gave 0·3555 grm. of iodide of silver.

Percentage of iodine:—

I.	II.	III.	Mean.
45·82	46·30	46·62	46·25

The formula

$$C_{16}H_{20}PI = \left.\begin{matrix}E\\E\\E\\E\end{matrix}\right\}PI$$

requires

	Theory.		Experiment.
1 equiv. of the Phosphorus-body . . .	147	53·65	——
1 equiv. of Iodine	127	46·35	46·25
1 equiv. of the Iodine-compound . . .	274	100·00	

Notwithstanding the transparency of the constitution of these compounds, we feel some embarrassment in fixing their nomenclature. We propose to designate the hypothetical compound of one equivalent of phosphorus and four equivalents of ethyl by the name "Tetrethylphosphonium." This term is long, but it leaves no doubt regarding the composition of the body, and marks at the same time its analogy with tetrethylammonium. The iodine-compound is accordingly the iodide of tetrethylphosphonium.

Hydrated Oxide of Tetrethylphosphonium.

The separation of the iodine from the before-mentioned compound presents no difficulties. Oxide of silver removes this element even at the common temperature. A strongly alkaline solution is obtained which retains a small quantity of silver in solution. This liquid, which is almost without odour, and has a bitter and phosphoric taste, when placed over sulphuric acid, dries up into a crystalline extremely deliquescent mass, the silver separating at the same time in the form of a black powder, or as a brilliant metallic mirror. The mass, when redissolved in water, furnishes a colourless liquid free from silver, but generally containing some carbonic acid. The avidity with which the oxide of tetrethylphosphonium attracts both water and carbonic acid, has prevented us from analysing this body, but its formation, the composition of the corresponding iodide, and the analysis of a platinum- and gold-salt, hereafter to be mentioned, sufficiently warrant the formula

$$C_{16}H_{21}PO_2=E_4PO, HO.$$

In its deportment with other substances the body in question resembles the oxide of tetrethylammonium; we refer therefore to the detailed description which one of us has given of this compound in a former memoir*. The solution of the oxide of tetrethylphosphonium shows in fact all the reactions of a solution of potassa; the precipitates, such as alumina and protoxide of zinc, dissolve, however, less readily in excess of the phosphorus-compound. The action of heat upon this body gives rise to a peculiar transformation, to which we shall return hereafter.

Tetrethylphosphonium produces crystallizable salts with hydrochloric, nitric, and sulphuric acids. All these compounds exhibit the deliquescent character of the oxide. Like the latter, they are also soluble in alcohol; in ether they are for the most part insoluble. The hydrochloric solution furnishes, with bichloride of platinum and terchloride of gold, difficultly soluble precipitates, which are well adapted for analysis.

Chloride of Tetrethylphosphonium and Bichloride of Platinum.

The pale orange-yellow precipitate which falls on addition of bichloride of platinum to a moderately dilute solution of the chloride, dissolves with difficulty, but without decomposition, in boiling water; it is insoluble in alcohol and in ether. It can be dried at 100° C.

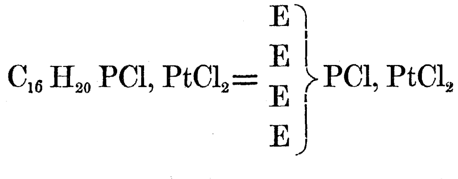
I. 0·1108 grm. of the platinum-salt, when fused with carbonate of sodium, gave 0·135 grm. of chloride of silver and 0·0305 grm. of platinum.

II. 0·5510 grm. of the platinum-salt, treated in a similar way, gave 0·6710 grm. of chloride of silver.

III. 0·5535 grm. of platinum-salt gave 0·1547 grm. of platinum.

IV. 0·3180 grm. of platinum-salt gave 0·089 grm. of platinum.

The formula



$$C_{16}H_{20}PCl, PtCl_2=\left.\begin{matrix}E\\E\\E\\E\end{matrix}\right\}PCl, PtCl_2$$

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* Philosophical Transactions, 1851, p. 357.

requires

	Theory.		Experiment.			
			I.	II.	III.	IV.
1 equiv. of Tetrethylphosphonium	147	41·75	——	——	——	——
3 equivs. of Chlorine	106·5	30·23	30·14	30·12	——	——
1 equiv. of Platinum	98·7	28·02	27·53	——	27·95	27·98
	352·2	100·00				

Chloride of Tetrethylphosphonium and Terchloride of Gold.

The crystalline precipitate, obtained by mixing the two solutions, separates from boiling water in brilliant golden-yellow needles.

0·317 grm. of the gold-salt, dried at 100° C., furnished, after ignition, 0·1275 grm. of gold.

This determination leads to the formula

$$C_{16}H_{20}PCl, AuCl_3 = \left.\begin{matrix}E\\E\\E\\E\end{matrix}\right\}PCl, AuCl_3,$$

as is seen by the following comparison:—

	Theory.		Experiment.
1 equiv. of Tetrethylphosphonium .	147	30·25	——
4 equivs. of Chlorine	142	29·22	——
1 equiv. of Gold	197	40·53	40·22
1 equiv. of Gold-salt	486	100·00	

ACTION OF HEAT UPON OXIDE OF TETRETHYLPHOSPHONIUM.

The change which oxide of tetrethylammonium undergoes by the action of heat is well known; this body splits into olefiant gas, water, and triethylamine.

$$E_4NO, HO = C_4H_4 + 2HO + E_3N.$$

We expected an analogous transformation of oxide of tetrethylphosphonium, but experiment has proved that this body suffers a different decomposition. On submitting freshly-prepared oxide of tetrethylphosphonium to distillation, water only passes over in the first instance, but as soon as the solution has attained a certain state of concentration, it suddenly effervesces with evolution of an inflammable gas which may be collected over water. This gas contains carbon and hydrogen, but no phosphorus; it may be left in contact with bromine-water without experiencing the slightest absorption. This experiment shows that the gas cannot contain any ethylene, and with almost the same certainty we may infer the absence in it of all the hydrocarbons of the formula $C_n H_n$. The evolution of gas ceases long before the whole amount of the liquid contained in the retort has distilled over. On the contrary, it is observed that immediately after the evolution of gas has ceased, the distillation nearly stops, and commences again only when the temperature has reached 200°; a viscid, nearly inodorous liquid now distils over, the temperature slowly rising, until at about 240° a constant boiling-point is attained: what now distils, generally solidifies to a radiated crystalline mass in the neck of the retort. On fusing this mass with a spirit-lamp, and collecting the liquid in a receiver, it frequently resolidifies instantaneously on cooling; often, however, it remains liquid for months. This body is extremely deliquescent: a crystal exposed to the air only for a few seconds liquefies entirely. It is soluble in water in every proportion, also in alcohol, less so in ether. The aqueous solution is precipitated by potassa; the dissolved body separates in this case in colourless oily drops, which remain liquid even after much concentration, and rapidly dissolve again on diluting the potassa solution with a comparatively small quantity of water. Acids dissolve the oil likewise with facility.

It is obvious at a glance, that the body in question is identical with the product formed by the action of air upon triethylphosphine. A careful comparison of the properties of the two substances places their identity beyond any doubt. It is, moreover, easily proved that the body is a product of oxidation. On boiling triethylphosphine with moderately strong nitric acid, and adding potassa to the highly concentrated liquid, the characteristic oily drops are immediately separated, and disappear again upon addition of water. At the common temperature, oxide of mercury is without action upon triethylphosphine, but on gently warming the mixture, a considerable evolution of heat takes place, metallic mercury is separated, and an oily substance produced which has all the characters of the new compound, and often sublimes in radiated crystals, coating the colder part of the vessel. With oxide of silver exactly the same phenomena are observed. On the other hand, the oily body, when submitted to the action of potassium, instantaneously reproduces triethylphosphine.

It is difficult to obtain this body in a state fit for analysis. It is not affected by solid hydrate of potassa, but on distilling the two substances together, the distillate is nevertheless found to contain a certain amount of moisture, the hydrate of potassa losing a certain quantity of water at the temperature of distillation. If the crystalline mass be separated from the potassa before distillation, it attracts so much water during manipulation, that even now it becomes but imperfectly crystalline after distillation. Distillation with anhydrous phosphoric acid furnishes the compound perfectly dry and solid; unfortunately, however, a portion of the substance is thus decomposed with separation of free phosphorus which contaminates the distillate. Nor have we succeeded in uniting this substance to crystalline combinations; nitrate of silver, bichloride of platinum, and several other reagents were tried in vain.

It is obvious that the preparation of this body in a state of purity is attended with unusual difficulties. These difficulties might certainly have been surmounted, but we believe that the deportment of triethylphosphine with sulphur and selenium, which will be more minutely described hereafter, enables us to infer retrospectively the composition of the oxide with a degree of certainty scarcely inferior to that furnished by analysis itself. The examination of well-defined sulphur- and selenium-compounds of the composition respectively

$$C_{12}H_{15}PS_2 = E_3PS_2 \text{ and}$$
$$C_{12}H_{15}PSe_2 = E_3PSe_2,$$

sufficiently proves that the body in question is the corresponding oxide, that it is in fact a combination of triethylphosphine with 2 equivalents of oxygen, $C_{12}H_{15}PO_2 = E_3PO_2$; an inference which is moreover supported by the existence of analogous and similarly formed combinations in the antimony- and arsenic-series, viz.

$$C_{12}H_{15}SbO_2 = E_3SbO_2, \text{ and}$$
$$C_{12}H_{15}AsO_2 = E_3AsO_2.$$

The formation of such a binoxide by the distillation of the hydrated oxide of tetrethylphosphonium, is readily intelligible, if we assume that the hydrocarbon simultaneously disengaged consists of hydride of ethyl, an assumption which is in accordance with the general characters of this gas.

$$\underbrace{E_4PO, HO}_{\substack{\text{Hydrated oxide of}\\ \text{tetrethylphosphonium.}}} = \underbrace{E_3PO_2}_{\substack{\text{Binoxide of}\\ \text{triethylphosphine.}}} + \underbrace{EH}_{\substack{\text{Hydride of}\\ \text{ethyl.}}}$$

We should have liked to establish this equation by some analytical numbers, but after some fruitless trials to prepare the substance in a state of purity, we were obliged to desist from the attempt. Even the preparation of a considerable quantity of oxide of tetrethylphosphonium is a long, laborious and expensive operation; but to these numerous impediments a further difficulty is added, which at the first glance appeared altogether inexplicable. Under certain conditions the distillation of oxide of tetrethylphosphonium furnishes either no inflammable gas at all, or only traces; at the same time the formation of the crystalline binoxide either entirely ceases, or takes place only in very minute quantities. We have convinced ourselves that this invariably occurs when the alkaline solution, by exposure to the air, has attracted a considerable quantity of carbonic acid. Instead of hydride of ethyl and binoxide of triethylphosphine, the phosphorus-base itself is obtained in this case, together with another liquid body which contains no phosphorus. By dissolving the distillate in ether, fixing the triethylphosphine by sulphur, and then evaporating the ether, an inflammable aromatic liquid remains, which floats on water. We had not more than a few drops of this oil at our disposal, which precluded the idea of an analysis, but we have no doubt that this liquid is carbonate of ethyl.

$$\underbrace{E_4P, CO_3}_{\substack{\text{Carbonate of}\\ \text{tetrethylphosphonium.}}} = \underbrace{E_3P}_{\substack{\text{Triethyl-}\\ \text{phosphine.}}} + \underbrace{ECO_3.}_{\substack{\text{Carbonate}\\ \text{of ethyl.}}}$$

Chloride, Bromide, and Iodide of Triethylphosphine.

Binoxide of triethylphosphine, when treated with hydrochloric, hydrobromic and hydriodic acids, is converted into the corresponding chloride, bromide, and iodide, which closely resemble the oxide in their general properties. They are liquids which gradually solidify in the exsiccator; the crystals fuse at 100° and begin to volatilize, although their boiling-point is very high. The compounds of triethylphosphine with chlorine, bromine, and iodine may also be obtained by the action of these elements in aqueous or alcoholic solutions upon the phosphorus-base itself. Both methods, however, furnish products which are with difficulty purified.

These compounds, as well as the saline compounds which the oxide of triethylphosphine produces with sulphuric and nitric acids, and which in the exsiccator gradually solidify into semi-crystalline masses, have but slightly occupied our attention, because the formation of beautiful sulphur- and selenium-compounds enabled us to gain a sufficiently precise idea regarding the chemical characters of these substances in general.

Bisulphide of Triethylphosphine.

The remarkable phenomena which attend the combination of triethylphosphine with sulphur have been already described. The compound is likewise obtained by distilling triethylphosphine with cinnabar, which in this reaction is reduced to subsulphide or to metallic mercury. Treatment of the oxide with sulphuretted hydrogen or with sulphide of ammonium does not furnish the compound.

The best mode of preparing this beautiful body is the following. Flowers of sulphur are gradually introduced into a dilute solution of the phosphorus-base in ether. The liquid effervesces upon each addition, and the sulphur disappears. As soon as sulphur remaining undissolved indicates the completion of the reaction, the ether is volatilized, and the residuary mixture of free sulphur and bisulphide of triethylphosphine separated by boiling water. On cooling, the liquid deposits the compound in crystals of perfect purity. This sulphur-compound is one of the finest products with which we have become acquainted in the course of our inquiries. Its crystallizing power is such, that by slowly cooling the solution most beautiful crystals may be obtained, even in a test-tube, the liquid column being traversed by an aggregate of thin vertical needles, often five or six inches in length. The difference of the solubility of the compound in cold and boiling water is very great; indeed, but a minute quantity remains in solution at the common temperature. On adding an alkali to the cold solution the mixture becomes turbid, and deposits, after a few moments, small crystals. The sulphur-compound in this respect resembles the corresponding oxide, which is likewise less soluble in alkalies than in pure water. This phenomenon is most strikingly observed by adding potassa to a boiling saturated aqueous solution of the bisulphide; it instantaneously separates in clear oily drops, which rapidly solidify into spherical aggregates of crystals as the liquid cools. The compound is even more readily soluble in alcohol and ether, and also crystallizes from these liquids, but less beautifully. The solubility in bisulphide of carbon is almost unlimited; from this solvent it crystallizes imperfectly.

The fusing-point of the bisulphide of triethylphosphine is 94° C.; it resolidifies at 88°. When heated beyond 100° C. the bisulphide is volatilized, with diffusion of a white vapour of a disagreeable sulphur-odour, which is but slightly perceptible at the common temperature. When heated with a quantity of water insufficient for its solution, the sulphur-compound rises to the surface as a clear transparent oil, which is copiously volatilized with the vapour of water.

The solution of the bisulphide is without action on vegetable colours. The compound nevertheless appears to possess faintly basic properties. It dissolves more readily in hydrochloric acid, especially when concentrated, than in water, and the solution furnishes with bichloride of platinum a yellow precipitate, which however rapidly cakes into a resinous mass, giving indications of decomposition by the separation of bisulphide of platinum, so that it was not adapted for analysis. The sulphur-compound also dissolves in dilute sulphuric and nitric acids; concentrated nitric acid decomposes it; the fuming acid gives rise to a sort of detonation. The aqueous solution of the bisulphide is not affected by acetate of lead, nitrate of silver, or protoxide of mercury, even at the boiling temperature; the alcoholic solution, on the other hand, is instantaneously decomposed with separation of the sulphide of lead, silver or mercury. The liquid filtered off from the precipitates now contains the oxide of triethylphosphine, either free or in the form of acetate or nitrate, and may be readily separated by the addition of an alkali to the solution. The action of potassium upon this compound instantaneously reproduces the phosphorus-base.

The bisulphide of triethylphosphine has the composition

$$C_{12} H_{15} PS_2 = E_3 PS_2.$$

I. 0·1355 grm. of the substance, burnt in a glass tube with a mixture of common salt and chlorate of potassium, gave 0·2190 grm. of sulphate of barium.

II. 0·4007 grm. of the substance yielded 0·623 grm. of sulphate of barium.

	Theory.		Experiment.		
			I.	II.	Mean.
1 equiv. of Triethylphosphine	118	78·67	——	——	——
2 equivs. of Sulphur	32	21·33	22·14	21·35	21·74
1 equiv. of Bisulphide of triethylphosphine	150	100·00			

The formation of the bisulphide takes place with such facility, and the properties of the compound are so characteristic, that we have frequently used flowers of sulphur as a reagent for triethylphosphine.

Biselenide of Triethylphosphine.

In the action of selenium upon triethylphosphine, the phenomena described in the preceding paragraphs are repeated. The reaction, however, as might have been expected, is less powerful.

The selenium-compound crystallizes from water with the same facility as the sulphur-compound, but the solution is apt to undergo partial decomposition when exposed to the atmosphere. Even the dry crystals are slowly reddened in the air. The fusing-point of the selenide is 112° C.; it is easily volatilized, undergoing partial decomposition. It contains

$$C_{12}H_{15}PSe_2 = E_3PSe_2.$$

In analysing this body, we have availed ourselves of the ready decomposition which it undergoes by nitrate of silver, when dissolved in alcohol.

0·378 grm. of the substance gave 0·557 grm. of selenide of silver.

	Theory.		Experiment.
1 equiv. of Triethylphosphine	118	59·9	——
2 equivs. of Selenium	79	40·1	39·45
1 equiv. of Biselenide of triethylphosphine	197	100·0	

In order to give more completely the history of the phosphorus-bases, we have also examined the compounds which are formed by the action of the iodides of methyl and amyl upon triethylphosphine; but since the products of these reactions resemble in every respect the corresponding ethyl-compounds, we have only to mention the analytical results.

Iodide of Methyltriethylphosphonium.

In treating triethylphosphine with iodide of methyl, all the phenomena mentioned in the case of the analogous experiment with iodide of ethyl are repeated. The action is even still more violent and rapid; and if no ether be added, a portion of the product is readily lost by the explosive effervescence of the liquid. The crystals thus obtained contain

$$C_{14}H_{18}PI = (MeE_3)PI.$$

0·544 grm. of the compound, dried at 100° C., gave 0·491 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. Methyltriethylphosphonium . .	133	51·15	——
1 equiv. of Iodine	127	48·85	48·77
1 equiv. of the Iodide	260	100·00	

On treating the solution of this compound, which essentially resembles the simple ethyl-compound, with oxide of silver, a strongly alkaline solution of oxide of methyltriethylphosphonium is obtained. The solution, when saturated with hydrochloric acid and mixed with bichloride of platinum, furnishes a beautiful orange-yellow platinum-salt, crystallizing in well-defined cubes, truncated by the planes of the octahedron. This salt, which is insoluble in alcohol and ether, may be recrystallized from boiling water without decomposition; it contains

$$C_{14}H_{18}PCl, PtCl_2=(MeE_3)PCl, PtCl_2.$$

0·4297 grm. of the platinum-salt, fused with carbonate of sodium, gave 0·551 grm. of chloride of silver and 0·127 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Methyltriethylphosphonium .	133	39·20	——
3 equivs. of Chlorine	106·5	31·49	31·72
1 equiv. of Platinum	98·7	29·31	29·55
1 equiv. of the Platinum-salt	338·2	100·00	

Iodide of Triethylamylphosphonium.

Iodide of amyl acts but slowly on the phosphorus-base. From a mixture of the two substances in ether, beautiful crystals are deposited after a few days, which may be purified by solution in alcohol and precipitation by ether; they contain

$$C_{22}H_{26}PI=(E_3Ayl)PI.$$

0·577 grm. of the substance gave 0·432 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. of Triethylamylphosphonium .	189	59·80	——
1 equiv. of Iodine	127	40·20	40·45
1 equiv. of the Iodide	316	100·00	

Treatment of this compound with oxide of silver furnishes the free oxide of triethylamylphosphonium, with all the properties characteristic of the class. The corresponding chloride deposits, on addition of bichloride of platinum, a beautiful platinum-salt, crystallizing in prisms, with flat terminal planes. It is insoluble in alcohol and ether, but rather soluble in water. The platinum-salt has the composition

$$C_{22}H_{26}PCl, PtCl_2=(E_3Ayl)PCl, PtCl_2.$$

0·3494 grm. of the platinum-salt gave 0·3873 grm. of chloride of silver and 0·0880 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Triethylamylphosphonium .	189	47·94	——
3 equivs. of Chlorine	106·5	27·02	27·42
1 equiv. of Platinum	98·7	25·04	25·18
1 equiv. of the Platinum-salt	394·2	100·00	

Action of Heat upon the Hydrated Oxide of Triethylamylphosphonium.

On heating this oxide a small quantity of an inflammable gas is evolved, a liquid being formed at the same time, which boils at about 280° C., and obviously corresponds to the binoxide of triethylphosphine. Two distinct changes may occur in this case. Since the oxide contains several radicals, it is possible that either ethyl or amyl may be eliminated in this decomposition, and the liquid simultaneously generated must therefore contain either

$$(E_2\,Ayl)\,PO_2,\ \text{or}\ E_3\,PO_2.$$

The higher boiling-point of the compound, and the deportment of the corresponding nitrogen-term (the oxide of triethylamylammonium), which on distillation furnishes diethylamylamine together with water and olefiant gas, are in favour of the first assumption. Accordingly, the inflammable gas would also in this case be hydride of ethyl, and the transformation of the oxide of triethylamylphosphonium under the influence of heat would be represented by the equation

$$\underbrace{(E_3\,Ayl)PO,\ HO}_{\substack{\text{Oxide of triethylamyl-}\\ \text{phosphonium.}}} = \underbrace{(E_2\,Ayl)O_2}_{\substack{\text{Binoxide of diethyl-}\\ \text{amylphosphine.}}} + \underbrace{EH}_{\substack{\text{Hydride}\\ \text{of ethyl.}}}$$

Experimentally the question remains undecided.

EXPERIMENTS IN THE METHYL-SERIES.

The results recorded in the preceding sections afford a tolerably complete view of the phosphorus-bases. We may therefore be brief in describing the experiments which we have made with the methyl-compounds.

Trimethylphosphine.

This remarkable body is obtained by the same process which we have minutely described for the preparation of the corresponding ethyl-base. Zinc-methyl and terchloride of phosphorus furnish the compound of chloride of zinc and trimethylphosphine, from which the base may be expelled by the action of potassa. All the precautions which have been mentioned as necessary in the preparation of the ethyl-base, are required in a higher degree for the methylated body. Since zinc-methyl attracts oxygen even with greater avidity than zinc-ethyl, the current of carbonic acid must be continuously maintained for a long period. The intensity with which zinc-methyl decomposes terchloride of phosphorus, is not inferior to the violent reaction between caustic baryta and anhydrous sulphuric acid. The mixing cannot, therefore, be too slowly effected. In expelling trimethylphosphine from its zinc-compound, refrigeration by ice is absolutely necessary, since this body is far more volatile than the ethyl-base. The distillation must be made in hydrogen gas, and the current of gas must moreover flow very slowly, otherwise, however perfect and careful may be the arrangements for cooling, a considerable quantity of the body will evaporate in the hydrogen and be lost, not to speak of the diffusion of the almost intolerable odour of the methyl-base in the atmosphere of the laboratory.

Trimethylphosphine is a colourless, transparent, very mobile liquid of an indescribable odour, powerfully refracting light, lighter than water, in which menstruum it is insoluble. The boiling-point of the liquid lies between 40° and 42° C., which agrees with PAUL THÉNARD's observations. Trimethylphosphine has even a more powerful attraction for oxygen than the corresponding ethyl-base. In contact with the air, it fumes and is apt to be inflamed. On distilling even the freshly prepared methyl-base, the neck of the retort becomes coated in the last stage of the operation with a network of beautiful crystals, perfectly similar to those which are observed with the ethyl-base. These crystals may be readily obtained in larger quantity by exposing the methyl-base to a slow current of dry atmospheric air. It is scarcely necessary to mention that these crystals are the binoxide of trimethylphosphine.

In its deportment with chlorine, bromine, iodine, sulphur and selenium, and finally with the acids, the methyl-base exactly imitates the ethylated body. The reactions are however more rapid and energetic.

We have been satisfied to identify trimethylphosphine, prepared by means of zinc-methyl, by the analysis of a platinum-salt.

Hydrochlorate of Trimethylphosphine and Bichloride of Platinum.

The solution of the methyl-base in hydrochloric acid, furnishes with bichloride of platinum, an orange-yellow, indistinctly crystalline precipitate, which, like the corresponding ethyl-compound, is readily decomposed by exposure to 100° C. For analysis it was dried in the exsiccator over sulphuric acid. It contains

$$C_6 H_9 P, HCl, PtCl_2 = Me_3 P, HCl, PtCl_2.$$

0·4021 grm. of the platinum-salt gave 0·1402 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Trimethylphosphine	76·0	26·94	——
1 equiv. of Hydrochloric acid .	36·5	12·93	——
2 equivs. of Chlorine	71·0	25·16	——
1 equiv. of Platinum	98·7	34·97	34·86
1 equiv. of the Platinum-salt .	282·2	100·00	

Iodide of Tetramethylphosphonium.

The iodide is a white crystalline mass, obtained by the action of iodide of methyl upon an ethereal solution of triethylphosphine. This compound, which may be readily recrystallized from alcohol, is the finest product of the series. Freshly prepared, it exhibits the silvery lustre of sublimed naphthalin. In contact with the atmosphere it assumes a slightly reddish colour.

The composition of this compound is represented by the formula

$$C_8H_{12}PI = M_4PI.$$

On analysis, 0·5455 grm. of the iodide gave 0·5870 grm. iodide of silver.

	Theory.		Experiment.
1 equiv. of Tetramethylphosphonium . . .	91	41·75	——
1 equiv. of Iodine	127	58·25	58·14
1 equiv. of Iodide of tetramethylphosphonium	218	100·00	

On treating the solution of the iodide with oxide of silver, a very caustic solution of the oxide is obtained.

Chloride of Tetramethylphosphonium and Bichloride of Platinum.

The solution of this oxide, mixed with hydrochloric acid and bichloride of platinum, furnishes a platinum-salt which is insoluble in alcohol and ether, but crystallizes from water in beautiful octahedra. It contains

$$C_8H_{12}PCl, PtCl_2 = Me_4PCl, PtCl_2.$$

By analysis, 0·6365 grm. of the platinum-salt gave 0·2120 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Tetramethylphosphonium	91	30·73	——
3 equivs. of Chlorine	106·5	35·95	——
1 equiv. of Platinum	98·7	33·32	33·30
1 equiv. of the Platinum-salt . . .	296·2	100·00	

Chloride of Tetramethylphosphonium and Terchloride of Gold.

The method of preparation, and the properties of the gold-salt of chloride of tetramethylphosphonium, are perfectly similar to those of the corresponding ethyl-body.

When dried at 100° C., 0·3545 grm. left, after ignition, 0·1630 grm. of gold.

The formula

$$C_8H_{12}PCl, AuCl_3 = Me_4PCl, AuCl_3$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Tetramethylphosphonium	91	21·17	——
4 equivs. of Chlorine	142	33·02	——
1 equiv. of Gold	197	45·81	45·98
1 equiv. of the Gold-salt	430	100·00	

ACTION OF HEAT UPON THE HYDRATED OXIDE OF TETRAMETHYLPHOSPHONIUM.

Binoxide of Trimethylphosphine.

Precisely similar phenomena as in the ethyl-series: formation of binoxide of trimethylphospine and hydride of methyl (marsh-gas).

$$\underbrace{Me_4PO,HO}_{\substack{\text{Hydrated oxide of}\\ \text{tetramethylphosphonium.}}} \quad = \quad \underbrace{Me_3PO_2}_{\substack{\text{Binoxide of tri-}\\ \text{methylphosphine.}}} \quad + \quad \underbrace{MeH}_{\substack{\text{Hydride of methyl}\\ \text{(marsh-gas).}}}$$

The direct formation of the binoxide by the action of oxygen upon trimethylphosphine has been already mentioned.

Bisulphide and Biselenide of Trimethylphosphine.

These bodies likewise resemble the corresponding members of the ethyl-series; they are, however, more soluble and more volatile. The sulphur-compound crystallizes from a highly concentrated aqueous solution in masses of well-formed four-sided prisms, which fuse at 105° C.

The selenium-compound crystallizes exactly like the ethyl-body; its fusing-point is 84° C. In contact with the air this compound blackens with separation of selenium. In this decomposition the characteristic odour of mesitilene is very perceptibly evolved. Even without an analysis we may assign to these compounds the formulæ

$$C_6H_9PS_2 = Me_3PS_2 \text{ and}$$

$$C_6H_9PSe_2 = Me_3PSe_2.$$

In conclusion, the action of the iodides of ethyl and amyl upon trimethylphosphine may be briefly mentioned.

Iodide of Trimethylethylphosphonium.

This substance is rapidly formed by the action of iodide of ethyl upon the ethereal solution of the methyl-base. The compound, which crystallizes perfectly well from boiling alcohol, contains

$$C_{10}H_{14}PI = (Me_3E)PI.$$

0·4435 grm. of substance gave 0·4403 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. of Trimethylethylphosphonium	105	45·24	——
1 equiv. of Iodine	127	54·76	53·67
1 equiv. of the Iodide	232	100·00	

Chloride of Trimethylethylphosphonium and Bichloride of Platinum.

By treating the iodide with oxide of silver, the caustic oxide is obtained, which gives, with hydrochloric acid and bichloride of platinum, a yellow platinum-salt, insoluble in alcohol and ether, but rather soluble in water. From the boiling solution it is deposited in magnificent octahedra.

0·5095 grm. of the platinum-salt gave 0·700 grm. of chloride of silver and 1616 grm. of platinum.

The formula $C_{10}H_{14}PCl, PtCl_2=(Me_3E)Cl, PtCl_2$

requires the following numbers:—

	Theory.		Experiment.
1 equiv. of Trimethylethylphosphonium	105·0	33·86	——
3 equivs. of Chlorine	106·5	34·33	33·95
1 equiv. of Platinum	98·7	31·81	31·72
1 equiv. of Platinum-salt	310·2	100·00	

Iodide of Trimethylamylphosphonium.

The ethereal solution of the constituents slowly deposits this compound. It is extremely soluble in water, and hence, if the ethereal solution of the iodide of ethyl contain the most minute trace of water, the salt separates in the form of a syrup, which only gradually solidifies. It crystallizes in needles, although with difficulty, from absolute alcohol. Its composition is

$$C_{16}H_{20}PI=Me_3AylPI.$$

0·5495 grm. of the substance gave 0·4700 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. of Trimethylamylphosphonium	147	53·65	——
1 equiv. of Iodine	127	46·35	46·22
1 equiv. of the Iodide	274	100·00	

Chloride of Trimethylamylphosphonium and Bichloride of Platinum.

The oxide liberated from the iodide by means of oxide of silver, furnishes, with hydrochloric acid and bichloride of platinum, a very soluble platinum-salt, which crystallizes from boiling water in splendid needles, aggregated in spherules.

I. 0·8275 grm. of this platinum-salt gave 1·009 grm. of chloride of silver and 0·231 grm. of platinum.

II. 0·2455 grm. gave 0·3010 grm. of chloride of silver.

These numbers lead to the formula

$$C_{16}H_{20}PCl, PtCl_2=(Me_3Ayl)PCl, PtCl_2,$$

as is seen by the following comparison:—

	Theory.		Experiment.	
			I.	II.
1 equiv. of Trimethylamylphosphonium	147·0	41·74	——	——
3 equivs. of Chlorine	106·5	30·24	30·16	30·33
1 equiv. of Platinum	98·7	28·02	27·91	——
1 equiv. of the Platinum-salt	352·2	100·00		

The analysis of this platinum-salt concludes the experimental part of our inquiry; for clearness and comparison we subjoin the following synopsis of the compounds which we have investigated.

α. METHYL-SERIES.

Trimethylphosphine	$Me_3 P$.
Platino-chloride of trimethylphosphine	$Me_3 P, HCl, PtCl_2$.
Binoxide of trimethylphosphine	$Me_3 PO_2$.
Bisulphide of trimethylphosphine	$Me_3 PS_2$.
Biselenide of trimethylphosphine	$Me_3 PSe_2$.
Iodide of tetramethylphosphonium	$Me_4 PI$.
Platino-chloride of tetramethylphosphonium	$Me_4 PCl, PtCl_2$.
Auro-chloride of tetramethylphosphonium	$Me_4 PCl, AuCl_3$.
Iodide of trimethylethylphosphonium	$(Me_3 E) PI$.
Platino-chloride of trimethylethylphosphonium	$(Me_3 E) PCl, PtCl_2$.
Iodide of trimethylamylphosphonium	$(Me_3 Ayl) PI$.
Platino-chloride of trimethylamylphosphonium	$(Me_3 Ayl) PCl, PtCl_2$.

β. ETHYL-SERIES.

Triethylphosphine	$E_3 P$.
Platino-chloride of triethylphosphine	$E_3 PCl, PtCl_2$.
Binoxide of triethylphosphine	$E_3 PO_2$.
Bisulphide of triethylphosphine	$E_3 PS_2$.
Biselenide of triethylphosphine	$E_3 PSe_2$.
Iodide of tetrethylphosphonium	$E_4 PI$.
Platino-chloride of tetrethylphosphonium	$E_4 PCl, PtCl_2$.
Auro-chloride of tetrethylphosphonium	$E_4 PCl, AuCl_3$.
Iodide of methyltriethylphosphonium	$(MeE_3) PI$.
Platino-chloride of methyltriethylphosphonium	$(MeE_3) PCl, PtCl_2$.
Iodide of triethylamylphosphonium	$(Ayl E_3) PI$.
Platino-chloride of triethylamylphosphonium	$(Ayl E_3) PCl, PtCl_2$.

On glancing once more over the phosphorus-compounds described in the preceding memoir, a comparison of these substances with the corresponding terms of the nitrogen-, arsenic-, and antimony-series is unavoidably forced upon us. Whether we consider the composition, or whether we review the properties of these groups, the most striking analogies, indeed an almost perfect parallelism, cannot be mistaken; the same formulæ, the same mode of combination, the same decompositions.

This analogy is particularly manifest in the compounds belonging to the ammonium-type. In these remarkable bodies, nitrogen, phosphorus, arsenic, and antimony appear to play absolutely the same part. It is more especially in the oxides of these compound metals that analogy of composition induces a perfect identity in properties, and, indeed, of very salient properties, which may be traced in almost every direction. If we were satisfied with the study of the reactions of these bodies, we should never suspect, in compounds exhibiting such a close similarity of properties, the presence of elements so dissimilar as nitrogen, phosphorus, arsenic, and antimony; they might, moreover, be confounded with potassa and soda, by which they are scarcely surpassed in alkaline power. Only the deportment of the hydrated oxides, under the influence of heat, distinguishes the derivatives of nitrogen from the corresponding terms of the phosphorus-, arsenic-, and antimony-series.

If we regard, on the other hand, the compounds belonging to the ammonia-type, we observe that the electro-positive character of the substances gradually rises in intensity from the nitrogen- to the antimony-compounds.

Thus, trimethylamine and triethylamine are not capable of uniting with oxygen, chlorine, bromine, and iodine; a power which the corresponding terms of the phosphorus-, arsenic-, and antimony-series possess in a high degree.

Triethylamine unites with the acids producing compounds of the formula

$$\begin{gathered} E_3\,N,\,HCl \\ E_3\,N,\,HSO_4 \\ E_3\,N,\,HNO_6. \end{gathered}$$

The corresponding compounds in the arsenic- and antimony-series do not exist; at all events chemists have not yet succeeded in preparing them. Triethylarsine and triethylstibine only combine *directly* with oxygen, chlorine, sulphur, &c., producing saline bodies, which have the composition respectively—

$$\begin{array}{lcl} E_3\,AsO_2 & \ldots\ldots & E_3\,SbO_2 \\ E_3\,AsCl_2 & \ldots\ldots & E_3\,SbCl_2 \\ E_3\,AsS_2 & \ldots\ldots & E_3\,SbS_2. \end{array}$$

In the phosphorus-series, lastly, the two classes are represented. Triethylphosphine not only forms compounds analogous to the salts of triethylamine, but also the terms corresponding to the binoxides of triethylarsine and triethylstibine. We have in the first place the terms

$$\begin{gathered} E_3\,P,\,HCl \\ E_3\,P,\,HSO_4 \\ E_3\,P,\,HNO_6, \end{gathered}$$

and in the second place compounds of the formulæ

$$\begin{gathered} E_3\,PO_2 \\ E_3\,PCl_2 \\ E_3\,PS_2. \end{gathered}$$

The phosphorus-compounds accordingly hold a position intermediate between the nitrogen-compounds on the one hand, and the arsenic- and antimony-series on the other. It cannot, however, be denied that the phosphorus-compounds stand closer to the arsenic- and antimony-series than to the nitrogen-group.

This cannot surprise us, when we consider the close analogies which phosphorus and arsenic present in many other directions. Both phosphorus and arsenic form well-characterized polybasic acids; the acids of antimony are not yet sufficiently investigated, but the acids of nitrogen, which are better examined, are all found to be essentially monobasic. The equivalent numbers, too, of phosphorus, arsenic, and antimony, present a remarkable connexion, the difference between those of phosphorus and arsenic, and those of arsenic and antimony being virtually the same—

Phosphorus . . .	31	
		difference . . . 44
Arsenic	75	
		difference . . . 45,
Antimony	120	

whilst the equivalent of nitrogen stands altogether apart from the rest.

The same relative position of the elements nitrogen, phosphorus, arsenic and antimony, may also be traced in their hydrides,

$$H_3N \qquad H_3P \qquad H_3As \qquad H_3Sb.$$

Ammonia is a powerful alkali;—phosphoretted hydrogen only unites with hydrobromic and hydriodic acids, whilst in arseniettéd and antimonietted hydrogen, the power of combining with acids has altogether disappeared. In these hydrogen-compounds the gradation of properties is indeed much more marked than in their trimethylated and triethylated derivatives. On comparing the terminal points of the series, ammonia and antimonietted hydrogen, we cannot fail to be struck by the dissimilarity of properties which at the first glance appears to limit the analogy of the two compounds to a mere parallelism of composition.

In the methylated and ethylated derivatives of these compounds, the intensity of the chemical tendencies in general is so much raised, that the gradation is no longer perceptible to the same extent.

We cannot conclude this memoir without thankfully acknowledging the able and untiring assistance we have received, during this lengthened inquiry, from Dr. A. Leibius in the analyses, and from Messrs. W. H. Perkin and C. Hoffmann in the preparation of the numerous compounds which had to be investigated.