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CONTRIBUTIONS

TO

THE HISTORY

OF THE

PHOSPHORUS-BASES.

BY
AUGUSTUS WILLIAM HOFMANN.

PARTS I. II. AND III.

LONDON:
PRINTED BY TAYLOR AND FRANCIS, RED LION COURT, FLEET STREET.
1861.

CONTRIBUTIONS

TO

THE HISTORY

OF THE

PHOSPHORUS-BASES.

BY

AUGUSTUS WILLIAM HOFMANN, F.R.S.,

PRESIDENT OF THE CHEMICAL SOCIETY OF LONDON,

CORR. MEMBER OF THE INSTITUTE OF FRANCE, ETC.

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1861.

From the PHILOSOPHICAL TRANSACTIONS.—PART II. 1860.

CONTRIBUTIONS

TO

THE HISTORY OF THE PHOSPHORUS-BASES.

By AUGUSTUS WILLIAM HOFMANN, F.R.S.

FIRST MEMOIR.

In a paper* published a few years ago by M. Cahours and myself, the remarkable phosphorus-compounds, whose existence was first pointed out by the experiments of M. Paul Thénard, were subjected to a more complete examination than they had previously received.

The discovery of a better mode of preparation enabled us to gain a clearer view of the nature of this group of substances, and to throw additional light on their relations to the nitrogen-bases; but, owing to the overwhelming number of reactions which presented themselves, we were unable to submit the behaviour of the phosphorus-bases with other groups of bodies to a detailed examination.

In continuation of former experiments, I have lately been much engaged in the investigation of the polyatomic ammonias, the study of which was naturally suggested by the beautiful researches which have been published on the polyatomic alcohols. In the course of these experiments, I frequently had occasion to return to the phosphorus-bases, the employment of triethylphosphine in particular having in many instances led to results which would not easily have been obtained in any other way. The possibility of preparing this body in a state of perfect purity and in considerable quantity, by a series of processes, which, if not quite simple, are at least definite and certain, its position in the system of organic compounds, its conveniently situated boiling-point, the energy and precision of its reactions, and lastly, the simplicity which characterizes these reactions, in consequence of the absence of unreplaced hydrogen in triethylphosphine, —whereby the formation of a large number of compounds of subordinate theoretical interest is excluded,—all these conditions tend strongly to invite us to the study of a body, in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness.

It was originally my intention to put together—in one frame, as it were—the various facts which I have collected relating to the phosphorus-bases; but the material lies scattered in so many directions, that I deem it more advisable to publish these observations in a number of shorter memoirs, which, from the nature of the subject, must be more or less fragmentary.

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* Philosophical Transactions, vol. cxlvii. p. 575.

2

Preparation of Triethylphosphine.

The whole of the material used in my experiments was prepared by the process formerly described in detail by Cahours and myself. The only alteration, which has been found advisable, relates to the separation of the triethylphosphine from the chloride-of-zinc-compound, which is produced by the action of trichloride of phosphorus on zinc-ethyl. It was formerly our practice to throw solid hydrate of potassium into the viscid mass of this salt, and then to dissolve the potassa by gradually dropping water into the retort, the heat resulting from the reaction being sufficient to carry over the base nearly anhydrous. It is better, however, to mix the double salt at once with water, and then decompose it in a retort filled with hydrogen, by allowing strong potassa-solution slowly to flow into it. On subsequently distilling the mixture on a sand-bath in a continuous but very slow stream of hydrogen, the triethylphosphine passes over with the aqueous vapour and floats on the top of the condensed water in the receiver. By adopting this mode of proceeding, the reaction is more under the command of the operator, and as the phosphorus-base is not sensibly soluble in water, the quantity of the product is not thereby diminished.

By exact adherence to the prescribed conditions, it is by no means difficult to prepare considerable quantities of pure triethylphosphine; nevertheless the amount obtained is always less than it should be in proportion to the weight of the materials used. This loss is mainly due to the formation of secondary products, which cannot be wholly avoided even when the zinc-ethyl is carefully prepared, and to partial decomposition of the latter substance during distillation: for it is scarcely possible to imagine a more elegant reaction than that which takes place between trichloride of phosphorus and ready-formed zinc-ethyl. Under these circumstances, many attempts were naturally made to obtain the phosphorus-base in other ways; I have always, however, returned to our original process.

Totally unsuccessful was the attempt to obtain triethylphosphine, without previous preparation of zinc-ethyl, by exposing a mixture of 1 equiv. of trichloride of phosphorus and 3 equivs. of iodide of ethyl with excess of zinc in sealed tubes to a temperature of 150° C. The bodies react under these circumstances; but as only traces of triethylphosphine are produced, I have not thought it worth while to pursue this reaction further. A more favourable result was obtained by heating a mixture of zinc and phosphorus with anhydrous iodide of ethyl to between 150° and 160°. After several hours' digestion, the tubes were found to be coated with white crystals, and a considerable portion of the phosphorus had passed into the red modification. Powerful escape of gas always took place on opening the tubes, and in several instances they were shattered, even when their points were softened in the lamp-flame to diminish the violence of the concussion. Besides zinc-ethyl, the presence of which is indicated by the abundant evolution of hydride of ethyl which is observed on treating the contents of the tube with water, the chief products of this reaction are three phosphorus-compounds, which are formed in proportions varying according to the temperature and the duration of the action.

On extracting the brown residue in the tubes with warm water, and evaporating the clear solution, an oily substance separates which covers the bottom of the dish, and on cooling solidifies into a mass of hard crystals. By repeatedly crystallizing this substance from boiling water and from alcohol, large crystals are obtained, which give off triethylphosphine when treated with potassa even in the cold, and are found to consist of a compound of iodide of zinc with iodide of triethylphosphonium.

I. 0·3721 grm. of the compound dried at 100°, when burnt with a mixture of chromate of lead and oxide of copper[*], gave 0·2435 grm. of carbonic acid and 0·1320 grm. of water.

II. 0·3274 grm. of substance gave 0·3789 grm. of iodide of silver.

III. 0·3800 grm. of substance gave 0·4370 grm. of iodide of silver.

These experiments lead to the formula

$$C_6\,H_{16}\,P\,Zn\,I_2 = [(C_2\,H_5)_3\,H\,P]\,I,\ Zn\,I$$[†].

	Theory.		Experiment.		
			I.	II.	III.
C_6	72	17·75	17·85	——	——
H_{16}	16	3·95	3·94	——	——
P	31	7·65	——	——	——
Zn	32·5	8·01	——	——	——
I_2	254	62·64	——	62·52	62·13
	405·5	100·00			

A solution of iodide of triethylphosphonium mixed with iodide of zinc immediately gives a crystalline compound of exactly similar characters.

The mother-liquor of the double salt yields, when further evaporated, another crystalline body which is more difficult to purify. After three or four crystallizations, however, well-developed crystals are obtained, which do not yield triethylphosphine when treated with potash, either in the cold or with aid of heat. The analysis, to be given further on, shows that this crystalline substance is a compound of iodide of zinc and oxide of triethylphosphine,

$$C_6\,H_{15}\,P\,O,\ Zn\,I = (C_2\,H_5)_3\,P\,O,\ Zn\,I.$$

The third compound, which remains in the mother-liquor after the two former have crystallized out, and separates, on further evaporation, in beautiful needle-shaped crystals, may be recognized without difficulty as iodide of tetrethylphosphonium. The crystals are insoluble in cold potassa-solution, and give off triethylphosphine only when heated with solid hydrate of potassium.

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[*] The combustion of the phosphorus-compounds is not very easily effected. The experiment succeeds best with a mixture of chromate of lead and oxide of copper. All the carbon-determinations quoted in the following pages have been made with this mixture, unless another mode of proceeding is specially stated. All the substances analysed were dried at 100°, except in a few cases, when the mode of drying is also specially mentioned.

[†] H=1; O=16; S=32; C=12.

This iodide likewise unites with iodide of zinc; and as this latter salt is always present in the mother-liquor in considerable quantity, the double salt is generally obtained together with the simple iodide.

The mode of formation of these compounds is represented by the following equations:—

$$8C_2H_5I + P_2 + 3Zn_2 = 2([(C_2H_5)_3HP]I, ZnI) + 4ZnI + 2C_2H_4.$$
$$8C_2H_5I + P_2 + 3Zn_2 = 2([(C_2H_5)_4P]I, ZnI) + 4ZnI.$$

The compound containing oxide of triethylphosphine is evidently formed at the expense of the air in the tube:—

$$2[(C_2H_5)_3P] + O_2 + 2ZnI = 2[(C_2H_5)_3PO, ZnI].$$

The above zinc-iodide-compounds of triethyl- and tetrethyl-phosphonium possess interest only in so far as they may serve for the preparation of the phosphorus-base. The mixture evaporated to dryness and distilled with hydrate of potassium in an atmosphere of hydrogen, does indeed yield appreciable quantities of triethylphosphine: the action of iodide of ethyl upon a mixture of zinc and phosphorus may therefore be recommended when it is desired to prepare a sample of this remarkable compound without specially arranged apparatus; but it is not adapted for the preparation of the phosphorus-base on the large scale.

I have endeavoured to prepare by this process *triamylphosphine* and *triallylphosphine*, but the results were not such as to encourage me to continue the experiments.

Cahours has recently made similar experiments, but with a difference in the mode of conducting them, which cannot fail to influence the result. Instead of subjecting iodide of ethyl to the action of a mechanical mixture of zinc and phosphorus, he has caused the compound Zn_3P to act upon iodide of ethyl at a high temperature. The reaction will doubtless proceed more regularly under these conditions; but the advantage which may perhaps be gained by avoiding the preparation of the zinc-ethyl is compromised, at least in part, by the time and trouble expended in the somewhat complicated preparation of trizincophosphide.

Oxide of Triethylphosphine.

The formation of the compound of this oxide with iodide of zinc to which I have alluded, induced me to subject to a careful examination the beautifully crystallized body produced from the phosphorus-base by exposure to the air. In our former experiments, Cahours and myself had often observed this substance, but we did not succeed in obtaining it in a state of purity fit for analysis. Nevertheless, founding our conclusion on the composition of the corresponding sulphur-compound, and having regard to the analogies presented by the bodies of the arsenic- and antimony-series, we regarded this body as the oxide of the phosphorus-base

$$(C_2H_5)_3PO.$$

I have since confirmed this formula by analysis.

The difficulties which in our experiments opposed the preparation of this compound in the pure state, arose entirely from the comparatively small quantity of material with which we had to work. Nothing is easier than to obtain this oxide in a state of purity, provided the available quantity of material is sufficient for distillation. In the course of a number of preparations of triethylphosphine for the new experiments, a considerable quantity of the oxide had accumulated in the residues left after distilling the zinc-chloride-compound with potassa. On subjecting these residues to distillation in a copper retort, a large portion of the oxide passed over with the aqueous vapours, and a further quantity was obtained as a tolerably anhydrous but strongly coloured liquid, by dry distillation of the solid cake of salts which remained after all the water had passed over. The watery distillate, with or without addition of hydrochloric acid, was evaporated on the water-bath as far as practicable, and the concentrated solution was mixed with solid hydrate of potassium, which immediately separated the oxide in the form of an oily layer floating on the surface of the potash. The united products were then left in contact with solid potash for twenty-four hours, and again distilled. The first portion of the distillate still contained traces of water, a thin layer of triethylphosphine floating upon the surface. As soon as the distillate solidified, the receiver was changed, and the remaining portion (about nine-tenths) collected apart as the pure product. To prevent absorption of water, the quantity required for analysis was collected during the distillation.

0·2589 grm. of oxide of triethylphosphine gave 0·5098 grm. of carbonic acid and 0·2660 grm. of water.

The formula

$$C_6H_{15}PO=(C_2H_5)_3PO$$

requires the following values:—

	Theory.		Experiment.
C_6	72	53·73	53·70
H_{15}	15	11·20	11·41
P	31	23·13	——
O	16	11·94	——
	134	100·00	

With reference to the properties of oxide of triethylphosphine, I may add the following statements to the description formerly given*. This substance crystallizes in beautiful delicate needles, which, if an appreciable quantity of the fused compound be allowed to cool slowly, frequently attain the length of several inches. I have been unable to obtain well-formed crystals; as yet I have not found a solvent from which this substance can be crystallized. It is soluble in all proportions, both in water and alcohol, and separates from these solvents on evaporation in the liquid condition, and solidifies only after every trace of water or alcohol is expelled. Addition of ether to the alcoholic solution precipitates this body likewise as a liquid. The melting point of oxide

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* Philosophical Transactions, 1857, p. 586.

of triethylphosphine is 44°; the point of solidification at the same temperature. It boils at 240° C. (corrected).

As no determination of the vapour-density of any member of the group of compounds to which the oxide of triethylphosphine belongs has yet been made, it appeared to me of some interest to perform this experiment with the oxide in question. Since the determination by DUMAS' method could not have been performed without sacrificing a considerable amount of material, and GAY-LUSSAC's was inapplicable on account of the high boiling-point of the compound, I adopted a modification of the latter, consisting essentially in generating the vapour in the closed arm of a U-shaped tube filled with mercury and immersed in a copper vessel containing heated paraffin, and calculating its volume from the weight of the mercury driven out of the other arm. As I intend to publish a full description of this method, which promises to be very useful in certain cases, I shall here content myself with stating the results obtained in one of the experiments.

Substance	0·150 grm.
Volume of vapour	49·1 cub. cent.
Thermometer (corrected)	266°·6 C.
Barometer at 0° C.	0·7670 metre.
Additional mercury column at 0° C. . .	0·1056 metre.

These numbers prove the vapour-density of oxide of triethylphosphine to be 66·30, referred to hydrogen as unity, or 4·60 referred to atmospheric air. Assuming that the molecule of oxide of triethylphosphine corresponds to 2 vols. of vapour*, the calculated specific gravity of its vapour $=\frac{134}{2}=67$, when referred to hydrogen, and 4·63 when referred to air. Hence we may conclude that in oxide of triethylphosphine, the elements are condensed in the same manner as in the majority of thoroughly investigated organic compounds.

From the facility with which triethylphosphine is converted into the oxide by exposure to the air, even at ordinary temperatures, and from the very high boiling-point of the resulting compound, in consequence of which its vapour can exert but a very slight tension at ordinary temperatures, I am induced to think that the phosphorus-base may be used in many cases for the volumetric estimation of oxygen. When a paper ball soaked in triethylphosphine is passed up into a portion of air confined over mercury, the mercury immediately begins to rise, and continues to do so for about two hours, after which the volume becomes constant, the diminution corresponding very nearly to the proportion of oxygen in the air. To obtain very exact results, however, it would probably be necessary in every case to remove the residual vapour of triethylphosphine by means of a ball saturated with sulphuric acid.

Oxide of triethylphosphine exhibits in general but small tendency to unite with other bodies; nevertheless it forms crystalline compounds with iodide and bromide of zinc. I have examined more particularly the zinc-iodide-compound already mentioned.

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* $H_2O=2$ vols. of vapour.

Oxide of Triethylphosphine and Iodide of Zinc.

On mixing the solutions of the two bodies, the compound separates, either as a crystalline precipitate or in oily drops, which soon solidify with crystalline structure. It is easily purified by recrystallization from alcohol.

I. 0·6535 grm. of the double salt gave 0·5884 grm. of carbonic acid and 0·3070 grm. of water.

II. 0·3685 grm. of the double salt gave 0·3299 grm. of carbonic acid and 0·1757 grm. of water.

III. 0·5985 grm. of the salt obtained in the same preparation gave 0·4782 grm. of iodide of silver.

IV. 1·1680 grm. of another preparation gave 0·9420 grm. of iodide of silver.

V. 0·3060 grm. of the double salt gave 0·2466 grm. of iodide of silver. The crystals used in this analysis had been obtained by the action of zinc and phosphorus on iodide of ethyl.

VI. 0·5456 grm. of substance gave 0·4333 grm. of iodide of silver.

VII. 1·1600 grm. of substance gave 0·9340 grm. of iodide of silver.

The salt employed in analyses VI. and VII. had been prepared by precipitating the hydrochloric solution of the oxide with iodide of zinc.

These analytical results establish the formula

$$C_6 H_{15} P O, Zn I = (C_2 H_5)_3 P O, Zn I.$$

Theory.			Experiment.						
			I.	II.	III.	IV.	V.	VI.	VII.
C_6	72	24·53	24·55	24·39	——	——	——	——	——
H_{15}	15	5·12	5·22	5·29	——	——	——	——	——
P	31	10·56	——	——	——	——	——	——	——
O	16	5·45	——	——	——	——	——	——	——
Zn	32·5	11·08	——	——	——	——	——	——	——
I	127	43·26	——	——	43·17	43·53	43·55	42·92	43·51
	293·5	100·00							

It is remarkable that this compound is formed in presence of a large excess of hydriodic and even of hydrochloric acid.

The crystals melt at 99°; they readily dissolve in warm water, and even more easily in alcohol. From the alcoholic solution well-formed crystals are frequently obtained.

My friend Quintino Sella has examined these crystals. This examination, as well as all the other crystallographical researches given in these papers, are parts of inquiries to which the celebrated crystallographer of Turin is devoting such leisure as is left to him by numerous professorial avocations and the onerous duties of an active parliamentary life. To his kindness I am indebted for the following description:—

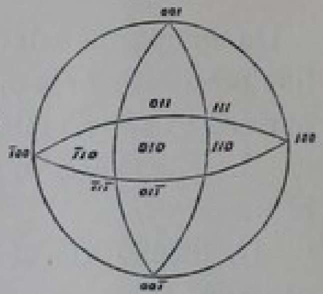
"System monoclinic:—

100, 101=34° 25′; 101, 001=48° 48′; 111, 010=50° 16′.

Forms observed:—

100, 010, 001, 110, 011, 111 (Fig. 1).

Fig. 1.



Angles.		Calculated.	Observed.	
			In hemitropic crystals.	In simple crystals.
		° ′	° ′	° ′
100, 010	=	90	——	——
100, 001	=	83 13	82 57	83 23
100, 110	=	47 39	47 48	47 42
100, 011	=	86 10	86 10	——
100, 111	=	50 37	50 21	——
010, 001	=	90	——	——
010, 110	=	42 21	——	42 19
010, 011	=	34 24	——	——
010, 111	=	50 16	——	——
001, 110	=	85 26	85 18	85 23
001, 011	=	55 36	55 44	——
001, 111	=	59 34	59 39	——
110, 1̄10	=	84 42	84 29	84 38
110, 011	=	52 45	——	——
110, 011̄	=	61 55	——	——
110, 111	=	25 52	25 30	——
110, 1̄11̄	=	87 49	——	——
011, 011̄	=	68 48	68 32	——
011, 111	=	35 33	35 44	——
011, 1̄11̄	=	76 3	——	——
111, 1̄11̄	=	100 32	100 37	——

According to Naumann:—

$$a:b:c=1·3312:1:0·9052;\quad \gamma=83°\ 13'.$$

Forms observed:—

$$\infty\bar{P}\infty,\ \infty\grave{P}\infty,\ 0P,\ \infty P,\ \bar{P}\infty,\ -P.$$

According to Weiss:—

$$a:b:c=1:0·9052:1·3312;\quad a\,o\,c=96°\ 47'.$$

Forms observed:—

$a:\infty b:\infty c$; $\infty a:b:\infty c$; $\infty a:\infty b:c$; $a:b:\infty c$; $\infty a:b:c$; $a:b:c$.

According to LEVY:—

M M=84° 42′; M P=94° 34′; $b:h=1:0{\cdot}9869$.

Forms observed:—

h', g', P, M, $e' d^{\frac{1}{2}}$.

Combinations observed:—

110, 001 (Fig. 2).
110, 001; 100 (Figs. 3 & 4).
110, 001; 100, 010 (Fig. 5).
001, 100, 110, 111.
001, 100, 110, 111; 011.
001, 100, 110, 111; 011, 010 (Fig. 6).

Fig. 2.

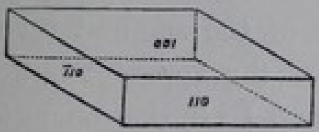


Fig. 3.

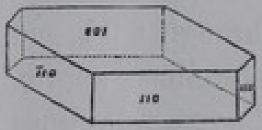


Fig. 4.

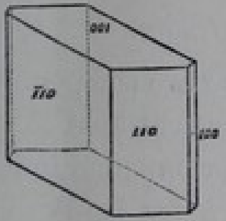


Fig. 5.

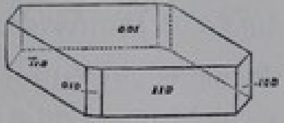
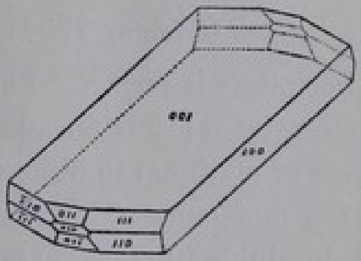


Fig. 6.



Hemitropic crystals with the axis of hemitropy [1 0 0], with the face of hemitropy 0 0 1=0 P (NAUMANN)=$\infty a:\infty b:c$ (WEISS)=P (LEVY).

Fig. 7.

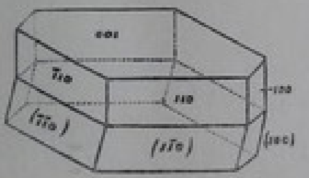


Fig. 8.

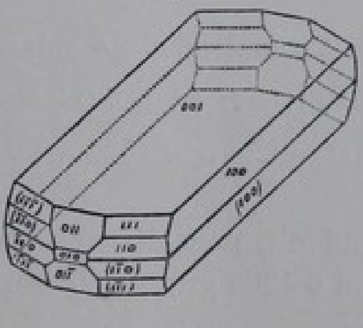
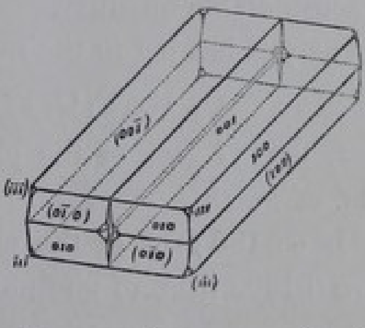


Fig. 9.



The hemitropic crystals are sometimes simple, as in Fig. 7; sometimes complicated, as in Fig. 8. It is then difficult to distinguish them from trimetric crystals; they become, however, intelligible by assuming that they result from four hemitropic crystals grouped round [1 0 0], as in Fig. 9. It is found sometimes that several crystals, like those of Fig. 8, are associated by 0 0 1.

It deserves to be noticed that the crystals (Figs. 2, 3, 4, 5 and 7) were formed in the presence of hydrochloric acid, and that in the absence of this acid, only crystals of Fig. 8 are obtained, which, without the study of the cleavage and the optical characters, could not be distinguished from trimetric crystals.

Cleavages 0 0 1 and 1 1 0 distinct and easily obtained. The cleavage 1 1 0 of the hemitropic crystals (Fig. 8) exhibits re-entering angles.

Lustre vitreous on the fracture, fatty on the faces.

Hardness somewhat greater than that of gypsum.

The crystals are optically positive; the line of symmetry [0 1 0] is their principal medium line. The coloured rings are visible through the faces of the cleavage 1 1 0, and the plane of the optical axes appears to be perpendicular to the axis of the prism 1 1 0. Through the cleavage 1 1 0 of the hemitropic crystals (Fig. 7), two systems of rings are seen.

The angle of the optical axes, seen through the faces 1 1 0 and $\bar{1}$ 1 0, is 74°. By rough measurement through 0 0 1 and 0 1 $\bar{1}$, the value of the smallest index of refraction $\gamma = 1{\cdot}58$ was determined approximately; and since the apparent optical axes deviate only by a few degrees from lines normal to 1 1 0 and $\bar{1}$ 1 0, the conclusion is admissible that the internal angle of the optical axes differs but little from 78°[*]."

Oxide of Triethylphosphine and Dichloride of Platinum.

No precipitate is formed on mixing the aqueous solutions of the two compounds, however concentrated; but on adding the anhydrous oxide to a concentrated solution of dichloride of platinum in absolute alcohol, a crystalline platinum-compound is deposited after a few moments. This compound is exceedingly soluble in water, easily soluble in alcohol, insoluble in ether. On adding ether to the alcoholic solution, the salt is precipitated, although with difficulty, in the crystalline state. The alcoholic solution, when evaporating spontaneously, yields beautiful hexagonal plates, frequently of rather large dimensions. On account of its extreme solubility, it is not quite easy to obtain this salt in considerable quantity.

Analysis has led to the somewhat complicated formula

$$C_{24}H_{60}P_4O_3Pt_2Cl_6 = 3[(C_2H_5)_3PO], (C_2H_5)_3PCl_2, 2PtCl_2.$$

I. 0·4187 grm. of the platinum-salt gave 0·4632 grm. of carbonic acid, and 0·2545 grm. of water.

II. 0·5185 grm. of the platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1092 grm. of platinum, and 0·4808 grm. of chloride of silver.

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[*] Some of Sella's crystallographical researches were received whilst this paper was passing through the press. These researches will be published in detail in *Memorie della Reale Accademia delle Scienze di Torino*, Serie 2. tom. xx. under the title: *Sulle Forme Cristalline di alcuni Sali derivati dall' Ammoniaca per* Quintino Sella, *Deputato al Parlamento Italiano.*

The above formula requires:—

	Theory.		Experiment.	
			I.	II.
C_{24}	288	30·95	30·17	——
H_{60}	60	6·45	6·75	——
P_4	124	13·33	——	——
O_3	48	5·16	——	——
Pt_2	197·4	21·21	——	21·06
Cl_6	213	22·90	——	22·93
	930·4	100·00		

The platinum-salt has likewise been examined by QUINTINO SELLA.

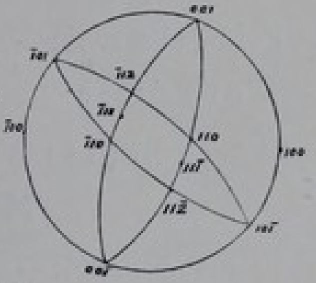
"System monoclinic:—

100, 101=27° 19′; 101, 001=46° 23′; 010, 111=41° 4′.

Forms observed:—

100, 001, 110, 1̄01, 1̄11, 1̄12 (Fig. 10).

Fig. 10.



Angles.		Calculated.	Observed.
100, 001	=	73° 42′	73° 30′
100, 110	=	56 41	——
100, 1̄01	=	143 30	——
100, 1̄11	=	116 36	——
100, 1̄12	=	108 9	——
001, 110	=	81 8	81 8
001, 1̄01	=	69 48	69 48
001, 1̄11	=	78 55	78 51
001, 1̄12	=	61 10	61 14
110, 1̄10	=	66 38	66 38
110, 1̄01	=	116 12	116 23
110, 1̄11	=	63 22	——
110, 111̄	=	19 57	——
110, 1̄12	=	63 19	——
110, 112̄	=	37 42	——
1̄01, 1̄11	=	56 9	——
1̄01, 1̄12	=	52 53	52 32

Angles.		Calculated.
$\bar{1}11, 11\bar{1}$	=	67° 42′
$\bar{1}11, \bar{1}12$	=	17 44
$\bar{1}11, 11\bar{2}$	=	73 43
$\bar{1}12, 11\bar{2}$	=	84 11

According to NAUMANN:—

$$a:b:c=1{\cdot}5776:1:0{,}6308;\quad \gamma=73°\ 42'.$$

Forms observed:—

$$\infty \not{\mathrm{P}} \infty,\quad 0\,\mathrm{P},\quad \infty \mathrm{P},\quad \not{\mathrm{P}} \infty,\quad \mathrm{P},\quad \tfrac{1}{2}\mathrm{P}.$$

According to WEISS:—

$$a:b:c=1:0{\cdot}6308:1{\cdot}5776;\quad a\,o\,c=106°\ 28'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c;\quad -a:\infty b:c;\quad -a:b:c;\quad -a:b:\tfrac{1}{2}c.$$

According to LEVY:—

$$\mathrm{M\,M}=66°\ 38';\quad \mathrm{M\,P}=98°\ 52';\quad b:h=1:1{\cdot}3343.$$

Forms observed:—

$$h',\quad \mathrm{P},\quad \mathrm{M},\quad a',\quad b^{\frac{1}{2}},\quad b'.$$

Combinations observed:—

0 0 1, 1 0 0, 1 1 0 (Fig. 11).
0 0 1, 1 1 0, $\bar{1}$ 1 2, $\bar{1}$ 0 1.
0 0 1, 1 1 0, $\bar{1}$ 1 2, $\bar{1}$ 0 1, 1 0 0, $\bar{1}$ 1 1 (Fig. 12).

Fig. 11.

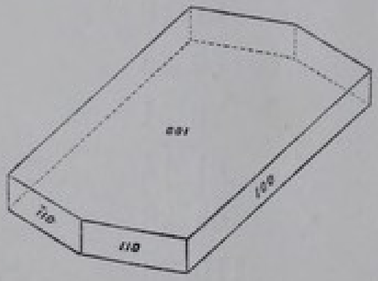
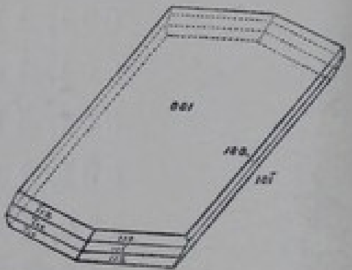


Fig. 12.



Cleavages $\bar{1}01$ and 110 distinct and easily obtained.

Colour orange-red.

The optical axes are situated in 0 1 0, *i. e.* in the plane of symmetry. They are seen through the faces 0 0 1 and the cleavages $\bar{1}$ 0 1, and they make an apparent angle of about 64°."

On mixing a concentrated solution of the oxide of triethylphosphine with *trichloride* *of gold*, a deep-yellow oil is separated, which crystallizes with difficulty after considerable standing. This compound is exceedingly soluble in water and in alcohol. When the aqueous solution is heated, the gold is reduced; the transformation which the oxide of triethylphosphine undergoes in this reaction has not been examined.

Chloride of Tin forms likewise an oily compound with the oxide: I have not succeeded in crystallizing this compound.

Chloride of Mercury is without any action on oxide of triethylphosphine.

Oxychloride of Triethylphosphine.

On passing a current of dry hydrochloric acid through a layer of oxide of triethylphosphine which is fused in a U-shaped tube surrounded by boiling water, brilliant crystals are soon formed. These crystals, however, rapidly disappear, the compound formed in the commencement of the reaction uniting with an excess of hydrochloric acid. The viscous liquid, which ultimately remains behind, loses, when heated, the excess of hydrochloric acid, leaving an exceedingly deliquescent crystalline mass, very soluble in alcohol, insoluble in ether.

For analysis, the new compound was washed with absolute ether, and dried over sulphuric acid *in vacuo*, either at the common temperature or at 40°. Three chlorine-determinations in specimens of different preparations yielded the following results:—

I. 0·8845 grm. of substance gave 0·6920 grm. of chloride of silver.
II. 0·3548 grm. of substance gave 0·2918 grm. of chloride of silver.
III. 0·3557 grm. of substance gave 0·2979 grm. of chloride of silver.

The chlorine-percentages corresponding to these numbers exhibit far greater discrepancies than are generally observed in experiments of this description; this result is obviously due to the extremely deliquescent character of the crystals. It cannot, however, be doubted that the compound examined is an oxychloride of triethylphosphine represented by the formula

$$C_{12}H_{30}P_2OCl_2=(C_2H_5)_3PO+(C_2H_5)_3PCl_2.$$

	Theory.		Experiment.		
			I.	II.	III.
2 equivs. Triethylphosphine .	236	73·07	——	——	——
1 equiv. Oxygen	16	4·95	——	——	——
2 equivs. Chlorine	71	21·98	19·35	20·35	20·72
1 equiv. Double Compound .	323	100·00			

The dichloride of triethylphosphine cannot be formed by the action of hydrochloric acid upon the oxide.

The oxychloride exhibits with other compounds the deportment of the oxide. It furnishes with dichloride of platinum the same platinum-salt which is obtained with the oxide. In a similar manner, it gives with iodide of zinc the iodide-of-zinc-compound of the oxide previously described. Only once—under conditions not sharply enough observed at the time, and which I was afterwards unable to reproduce in repeated experiments—a compound of the oxychloride with iodide of zinc was formed. This substance, readily soluble in water and alcohol, crystallized from the latter solvent in beautiful colourless transparent octohedra, which, on analysis, gave the following result:—

0·2093 grm. of salt, precipitated by nitrate of silver, gave 0·2474 grm. of a mixture of iodide and chloride of silver.

With the probable assumption that the compound contains 1 equiv. of chlorine for 1 equiv. of iodine, this result corresponds to 50·74 per cent. of chlorine and iodine.

Accordingly the octohedra would be a double compound of the iodide-of-zinc-salts of the oxide and of the chloride of triethylphosphine.

The formula

$$C_{12}\,H_{30}\,P_2\,O\,Cl_2\,Zn_2\,I_2=(C_2\,H_5)_3\,P\,O,\ Zn\,I+(C_2\,H_5)_3\,P\,Cl_2,\ Zn\,I$$

requires 50·62 per cent. of chlorine and iodine.

Behaviour of Triethylphosphine with Sulphur-compounds.

The remarkable tendency of the phosphorus-base to unite with sulphur has already been mentioned in the previous memoir; the combination of the two bodies is attended with evolution of heat, the result being a beautifully crystalline substance,

$$C_6\,H_{15}\,P\,S=(C_2\,H_5)_3\,P\,S,$$

corresponding to the oxide of triethylphosphine.

This behaviour has induced me to study the action of several sulphur-compounds on the phosphorus-base. In the cases which I have examined, the ultimate product is almost invariably the sulphide of triethylphosphine, already mentioned as resulting from the direct combination of the phosphorus-base with sulphur; but the conditions under which this sulphide is produced vary considerably, and in the majority of cases it occurs only as a secondary product of the decomposition of other more direct compounds, some of which appeared to me sufficiently interesting to deserve more minute investigation.

In the course of the experiments which I am going to describe, I have prepared considerable quantities of the sulphide of triethylphosphine. This compound, although remarkable for the facility with which it crystallizes, is not easily procured in well-formed crystals. It was only once or twice that I obtained crystals with good faces. They were examined by QUINTINO SELLA, who communicates to me the following results:—

"System rhombohedric:—

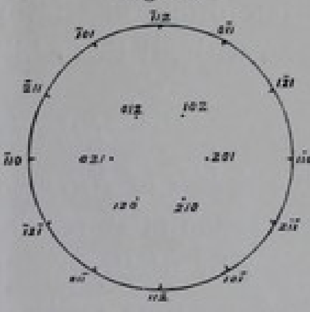
$$1\,0\,0,\ 1\,1\,1=54°\ 35'.$$

Forms observed:—

$$1\,0\,\bar{1},\ 2\,\bar{1}\,\bar{1},\ 2\,1\,0\ \text{(Fig. 13)}.$$

Angles.		Calculated.	Observed.
$10\bar{1}, 01\bar{1}$	=	60° 0′	60° 1′
$10\bar{1}, 2\bar{1}\bar{1}$	=	30 0	29 59
$10\bar{1}, 210$	=	50 56	51 0
$10\bar{1}, 120$	=	71 38	71 34
$2\bar{1}\bar{1}, 210$	=	56 55	——
$2\bar{1}\bar{1}, 120$	=	90 0	——
$210, 120$	=	36 44	36 50
$210, 021$	=	66 10	66 20
$210, 012$	=	78 9	——

Fig. 13.



According to Naumann:—

$$R=90^\circ\ 13'.$$

Forms observed:—

$$\infty P\,2,\ \infty R,\ \tfrac{2}{3}P\,2.$$

According to Weiss:—

$$a=0{\cdot}8211.$$

Forms observed:—

$$a:\tfrac{1}{2}a:a:\infty c;\quad \infty a:a:a:\infty c;\quad a:\tfrac{1}{2}a:a:\tfrac{1}{3}c.$$

According to Levy:—

$$P\,P=90^\circ\ 13'.$$

Forms observed:—

$$d',\ e^2,\ b^2.$$

Combinations observed:—

$10\bar{1}, 210$ (Fig. 14).

$10\bar{1}, 210;\ 2\bar{1}\bar{1}$.

Fig. 14.

The summit of the hexagonal prisms is almost always badly terminated, since they are frequently hollow: bright faces 2 1 0 are but rarely met with. In one single case $2\bar{1}\bar{1}$ could be distinctly traced. The general habitus of the crystals is that of thin, long, hexagonal needles. At summer heat, the crystals are very soft and flexible; they may be bent 180° without breaking. At lower temperatures, they are harder and much less flexible.

The crystals are optically positive. It is possible to measure the deviation through the faces of the hexagonal prism, whence it may be inferred that the index of refraction for the extraordinary ray $\epsilon=1{\cdot}65$, and for the ordinary ray $\omega=1{\cdot}59$."

Behaviour of Triethylphosphine with Sulphuretted Hydrogen.

The phosphorus-base has no action on *sulphuretted hydrogen*. When it is brought in contact with hydrosulphuric acid over mercury, the gas does not exhibit any alteration. No sulphide of triethylphosphine is formed even in presence of air, as might indeed have been expected. The attraction of the phosphorus-base for oxygen prevents the oxidation of the sulphuretted hydrogen; a solution of this gas in water, when mixed with a few drops of triethylphosphine, may be preserved in air-filled vessels much longer than without this addition.

Behaviour of Triethylphosphine with Sulphide of Nitrogen.

Sulphide of Nitrogen, $N_2 S_2$ (?), prepared as recommended by FORDOS and GELIS, viz. by the action of ammonia on chloride of sulphur dissolved in disulphide of carbon, is decomposed by triethylphosphine, with evolution of light and heat. Gas is evolved, and at the same time a yellowish liquid is produced, which, on cooling, solidifies into a fibrous mass of crystals of the sulphide.

Behaviour of Triethylphosphine with Mercaptan.

When these two bodies are mixed together in an atmosphere of carbonic acid, no alteration takes place even if they are left in contact for some time, or if they are heated to 100° in sealed tubes for twenty-four hours. But if the mixture be poured into an air-filled flask, crystals of sulphide of triethylphosphine make their appearance in a few hours. The crystals increase if the air has free access to the mixture; but if the flask be corked, the crystallization is interrupted. On opening the flask, the entry of the air may be recognized by the light cloud which the phosphorus-base, diffused through the atmosphere of the vessel, forms with the oxygen. When a mixture containing excess of mercaptan was left for a few days in an open flask, every trace of phosphorus-base had disappeared, and the remaining colourless liquid was filled with crystals of the sulphide. On mixing this liquid with water, it separated into two layers, the upper of which quickly solidified, especially on exposure to the air, to an imperfectly crystalline mass, easily recognized as a mixture of sulphide of triethylphosphine with excess of mercaptan. The impure crystals were exposed for a while to the air and then recrystallized from boiling water.

0·3703 grm. of the crystals, dried over sulphuric acid *in vacuo*, gave 0·6485 grm. carbonic acid and 0·3304 water.

The formula

$$C_6 H_{15} P S = (C_2 H_5)_3 P S$$

requires—

	Theory.		Experiment.
C_6	72	48·00	47·76
H_{15}	15	10·00	9·91
P	31	20·67	——
S	32	21·33	——
	150	100·00	

The lower stratum of liquid is aqueous alcohol containing small quantities of oxide of triethylphosphine and mercaptan. To remove the latter, the liquid was shaken up with recently precipitated mercuric oxide and distilled. The distillate, rectified several times over lime, yielded a clear liquid, which burnt with a colourless flame and exhibited all the characters of alcohol.

The interpretation of this result appears at the first glance exceedingly simple; the sulphide of triethylphosphine cannot be formed directly from the phosphorus-base, but owes its origin to the oxide first produced by the action of air, this oxide being decomposed by the mercaptan and yielding sulphide of triethylphosphine and alcohol:

$$(C_2H_5)_3PO+\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S=\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O+(C_2H_5)_3PS.$$

Experiment shows, however, that this equation illustrates only the final result of the reaction. Oxide of triethylphosphine and mercaptan, brought together under the most various conditions at ordinary temperatures and under pressure, do not yield a trace of sulphide of triethylphosphine; and we have to suppose, therefore, that the mercaptan interchanges its sulphur with the oxygen of the oxide of triethylphosphine, only at the instant of formation of the latter, or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

In connexion with this subject, various attempts were made to replace the oxygen in oxide of triethylphosphine by sulphur. But neither by treatment with sulphide of ammonium, nor by continued boiling with the higher sulphides of potassium, could the oxide be converted into the corresponding sulphide, whereas the conversion of the sulphide into the oxide takes place without any difficulty. This, however, is not more than might have been expected from the behaviour of the oxide with hydrochloric acid, mentioned in one of the preceding paragraphs. The different degrees of stability which characterize the oxide and the sulphide of triethylphosphine may also be strikingly seen in the behaviour of these compounds with sodium, the sulphide being reduced, with the greatest facility, to free triethylphosphine, even below the melting-point of the sodium, whereas the oxide may be distilled from sodium without experiencing the slightest alteration*. Ebullition with ordinary concentrated nitric acid likewise converts the sulphide into the oxide, the sulphur being at the same time transformed into sulphuric acid. The liquid filtered off from the precipitate obtained by barium-salts, when evaporated to dryness and fused with nitrate of potassium, yields no further trace of sulphur.

Behaviour of Triethylphosphine with Disulphide of Carbon.

These two bodies, when mixed in the anhydrous state, act upon one another with considerable force, amounting frequently to explosive violence, and unite into a red crystalline mass. The compound is best prepared by mixing the solutions of its constituents in alcohol or ether: the new body then instantly separates in beautiful red crystalline laminæ.

---

* In the previous memoir, it is stated that the phosphorus-base is reproduced from the oxide by the action of metallic sodium. Probably the oxide used in the former experiments contained a small quantity of free triethylphosphine, and thus led to an erroneous statement.

Several times recrystallized from alcohol and dried over sulphuric acid, the new body has furnished the following results on analysis:—

I. 0·3610 grm. of the disulphide-of-carbon-compound gave 0·5750 grm. of carbonic acid and 0·2490 grm. of water.

II. 0·3595 grm. of a new preparation gave 0·5790 grm. of carbonic acid and 0·2481 grm. of water.

III. 0·4180 grm. of a third preparation gave 0·6680 grm. of carbonic acid and 0·3027 grm. of water.

IV. 0·3505 grm. of substance, heated with a mixture of carbonate and chlorate of potassium, gave 0·8355 grm. of sulphate of barium.

These numbers lead to the formula

$$C_7 H_{15} P S_2 = (C_2 H_5)_3 P + C S_2.$$

Theory.			Experiment.			
			I.	II.	III.	IV.
C_7	84	43·30	43·43	43·92	43·58	——
H_{15}	15	7·73	7·66	7·67	8·04	——
P	31	15·98	——	——	——	——
S_2	64	32·99	——	——	——	32·72
	194	100·00				

The red crystals are not the only product of the action of disulphide of carbon on triethylphosphine. A second beautifully crystallized compound is deposited after some time from the mother-liquor. This substance, probably a secondary product of the action of the air, is formed in extremely minute quantity; its nature is not yet established.

The compound of triethylphosphine with disulphide of carbon is insoluble in water, sparingly soluble in ether, moderately soluble in disulphide of carbon, and somewhat more soluble in alcohol, especially when heated. The solution has no action on vegetable colours. From the boiling alcoholic solution, it separates on cooling in red needles, somewhat resembling the crystals of chromic acid, which are formed by the action of strong sulphuric acid in a solution of chromate of potassium. The ethereal solution, left to evaporate in an open cylinder, deposits finely developed, deep-red crystals of considerable size. QUINTINO SELLA has examined these crystals with the following results.

"System monoclniic:—

100, 101=29° 41½′; 010, 111=74° 4′; 101, 001=27° 7½′.

Forms observed:—

100, 010, 001, 110, $\bar{1}01$ (Fig. 15).

Combinations observed:—

100, 110, 001, $\bar{1}01$ (Fig. 16).

100, 110, 001, $\bar{1}01$, 010 (Fig. 17).

Fig. 15.

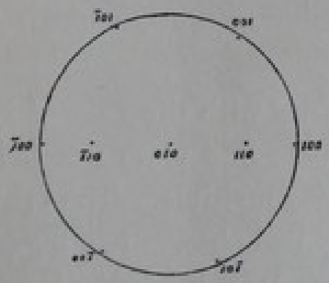


Fig. 16.

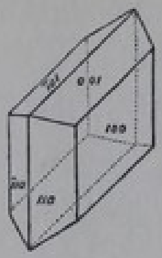
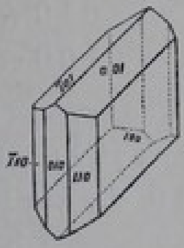


Fig. 17.



Angles.		Calculated.		Observed.	
		°	′	°	′
100, 010	=	90		90	5
100, 001	=	56	49	56	49
100, 110	=	27	39	27	39
100, $\bar{1}$01	=	114	2	114	2
010, 001	=	90		90	6
010, 110	=	62	21	62	21
010, $\bar{1}$01	=	90		90	
001, 110	=	61		60	55
001, $\bar{1}$01	=	57	13	57	13
110, $\bar{1}$01	=	111	9	110	55
110, $\bar{1}$10	=	124	41	124	42

According to Naumann:

$$a : b : c = 0{\cdot}9205 : 1 : 1{\cdot}5970 ; \quad a\,o\,b = \gamma = 56^\circ\ 49'.$$

Forms observed:—

∞ P ∞, ∞ P̶ ∞, 0 P, ∞ P, P̶ ∞.

According to Weiss:—

$$a : b : c = 1 : 1{\cdot}5970 : 0{\cdot}9205 ; \quad a\,o\,c = 123^\circ\ 11'.$$

Forms observed:—

$$a : \infty b : \infty c ; \quad \infty a : b : \infty c ; \quad \infty a : \infty b : c ; \quad a : b : \infty c ; \quad -a : \infty b : c.$$

According to Levy:—

$$\text{M M} = 124^\circ\ 41' ; \quad \text{M P} = 119^\circ ; \quad b : h = 1 : 0{\cdot}4885.$$

Forms observed:—

h', g', P, M, a'.

The faces are all bright, with the exception of $\bar{1}$ 0 1, which is frequently dull, and which, on account of this difference of lustre, may be easily distinguished from 0 0 1. The faces 1 0 0 and 1 1 0 exhibit delicate striæ parallel to the edge of intersection.

Cleavages:—

0 1 0 very distinct and easily obtained, although sometimes slightly curved.
1 0 0 easily obtained and fibrous.

The crystals are optically positive: the medium-line coincides with the axis of symmetry [0 1 0], and the angle of the optical axes is considerable; in a plate parallel to 0 1 0, the beginning of the rings may be seen, their centres being invisible. The centres may be seen, however, with the aid of a glass prism; and from this observation, together with the fact that the indices of refraction are not very far from 1·75, it may be inferred that the interior angle of the optical axes is not very different from 70°. The plane of the optical axes is nearly parallel to the face 0 0 1; it deviates only by a few degrees, exhibiting a tendency to approach the plane perpendicular to 1 0 0. The axis of symmetry, or of smallest elasticity, exhibits a violet-red colour, which even in very thin layers is very intense. The axis nearly parallel to [1 0 0], or the axis of greatest elasticity, exhibits a similar but much lighter red tint; the axis of mean elasticity shows in thin layers a straw-yellow, in thicker layers an orange-yellow. In polarized light one of the most beautiful examples of polychroism is observed by looking across the faces 0 1 0, the colour passing in the case of thin layers from a pure yellow to a deep red. But even in ordinary light the polychroism is perceptible; for the light passes with a violet-red through the faces 1 0 0, and with an orange-red colour of far less intensity through the faces 0 1 0.

Hardness less than that of gypsum."

The red crystals appear to possess the character of a weak base. They dissolve in strong hydrochloric acid, forming a colourless liquid, from which potassa or ammonia throws down the compound in its original state, though somewhat lighter in colour, on account of its minute state of division. The acid solution forms with dichloride of platinum a light yellow amorphous salt, insoluble in alcohol and ether, which changes colour and somewhat decomposes on drying. It darkens in colour, even when dried at the common temperature *in vacuo*, hydrochloric acid fumes being evolved. The analysis of two different preparations gave the following results:—

0·7263 grm. platinum salt, treated with carbonate of sodium, &c., gave 0·1885 grm. =25·95 per cent. of platinum, and 0·7450 grm. of chloride of silver =25·37 per cent. of chlorine.

In a second determination, 0·1900 grm. of platinum-salt, analysed in the same manner, gave 0·200 grm. of chloride of silver =26·04 per cent. of chlorine.

The formula

$$(C_2H_5)_3P, CS_2, HCl, PtCl_2$$

requires 24·66 per cent. of platinum and 26·61 per cent. of chlorine.

The gold-salt is obtained like the platinum-salt, and exhibits similar properties. This salt is not better adapted for analysis.

It is not very easy to form a clear notion of the constitution of the red crystals. According to the formula, the compound is the primary triethylphosphonium-salt of sulphocarbonic acid *minus* 1 equiv. of sulphuretted hydrogen, and corresponds therefore to sulphocarbamic acid, the ammonium salt of which, as is well known, is produced by the action of ammonia on disulphide of carbon. There is, however, no analogy in the constitution of the two substances.

The new compound exhibits a remarkable tendency to pass into the sulphide of triethylphosphine. On mixing its alcoholic solution with oxide or nitrate of silver, carbonic acid is evolved, sulphide of silver and metallic silver are separated, and the filtered solution, when evaporated, deposits crystals of the sulphide:

$$(C_2H_5)_3P, CS_2 + 2Ag_2O = Ag_2S + Ag_2 + CO_2 + (C_2H_5)_3PS.$$

The disulphide-of-carbon-compound undergoes a similar change, even under the influence of moisture. Crystals, not dried with sufficient care, when kept in corked tubes, were changed after a few months into a yellowish white semifluid mass, of peculiar odour, which, by recrystallization from boiling water, furnished a considerable quantity of pure sulphide of triethylphosphine. To establish this transformation by numbers, the purified crystals were identified by analysis.

I. 0·5345 grm. of the sulphide gave 0·9440 grm. of carbonic acid and 0·4915 grm. of water.

II. 0·2460 grm. of the sulphide, oxidized with nitric acid, gave 0·3810 of sulphate of barium.

The formula

$$C_6H_{15}PS = (C_2H_5)_3PS$$

requires—

	Theory.		Experiment.	
			I.	II.
C_6	72	48·00	48·16	——
H_{15}	15	10·00	10·21	——
P	31	20·67	——	——
S	32	21·33	——	21·27
	150	100·00		

It is obvious that the transformation of the red crystals into the sulphide involves the co-operation of the elements of water. Perfectly dry crystals were preserved in sealed tubes for many months without the slightest alteration. The crystals fuse at 95° and volatilize at 100°; in the absence of moisture, they may be heated under pressure to 150° without undergoing any decomposition. The phenomena are very different in the presence of water. When exposed for some days in sealed tubes with water to a temperature of 100°, the red crystals are gradually transformed into white needles, which are easily recognized as sulphide of triethylphosphine. The transformation is independent of atmospheric air; for it takes place with equal facility in vessels filled with air, or carbonic acid, or *in vacuo*.

The products which accompany the sulphide formed in this reaction vary according to the time during which the red crystals are digested with water. If the tubes be allowed to cool after one or two days' digestion, the liquid generally becomes filled with white needles, which are, however, still intermixed with red prisms, showing that the transformation is not yet complete. Scarcely any gas escapes when the tubes are opened, but when gently heated, the liquid yields abundance of disulphide of carbon. On the other hand, when the tubes are heated until the transformation of the red compound is accomplished,—which generally takes place after three or four days' digestion,—a large volume of gas escapes on opening, and the tubes are occasionally shattered. The gas which is thus evolved consists of sulphuretted hydrogen and carbonic acid, which are obviously secondary products of the reaction, arising from the protracted action of the water upon the disulphide of carbon which is separated in the first stage of the process. The liquid, from which the crystals of the sulphide have been deposited, has a distinctly alkaline reaction, belonging neither to the sulphide nor to the red crystals from which the sulphide arises, both these compounds being without action on vegetable colours. To seize the basic substance, the liquid was evaporated on the water-bath, till the sulphide had been as far as possible expelled, and then precipitated with iodide of zinc, which does not combine with the sulphide, traces of this body, which might have remained, being in this manner eliminated. The iodide-of-zinc-precipitate was semi-solid, and slowly became crystalline on treatment with alcohol; it did not, however, exhibit a sufficiently definite appearance to warrant its analysis. The bases were therefore at once liberated again by digesting the precipitate with oxide of silver; the powerfully alkaline liquid thus obtained gave, on addition of hydrochloric acid and dichloride of platinum, a difficultly soluble platinum-salt, crystallizing, after the necessary purification, from boiling water in splendid octohedra, which on analysis proved to be the methyl-triethylphosphonium-compound.

0·3799 grm. platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1110 grm. =29·21 per cent. of platinum.

The formula

$$[(CH_3)(C_2H_5)_3P]Cl, PtCl_2$$

requires 29·18 per cent. of platinum.

The solution filtered off from the octohedral salt gave, on evaporation, the extremely soluble six-sided tables of the platinum-salt of oxide of triethylphosphine, which I have mentioned in the commencement of this paper.

The products of the action of water upon the red crystals, then, are sulphide of triethylphosphine—the principal product,—oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide-of-carbon-compound and two molecules of water contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon.

$$4[(C_2H_5)_3P, CS_2]+2\left[\left.\begin{matrix}H\\H\end{matrix}\right\}O\right]=2[(C_2H_5)_3PS]+(C_2H_5)_3PO+\left.\begin{matrix}[(CH_3)(C_2H_5)_3P]\\H\end{matrix}\right\}O+3CS_2.$$

Whilst engaged with the experiments involved in the elucidation of this subject, I observed occasionally small, well-defined yellow crystals disseminated among the mixture of white and red needles, which are deposited when the digestion-tubes are allowed to cool, before the transformation is terminated. The yellow crystals appeared in greater quantity towards the close of the operation, and were found to be a secondary product formed by the action of the sulphuretted hydrogen, which is generated in the last stage of the process. I have since learnt to prepare the yellow crystals by a simpler and more definite method. This remarkable compound has become the starting-point of a new inquiry, the result of which I reserve for a later communication.

The formation of the red crystals by the union of triethylphosphine and disulphide of carbon takes place so rapidly, and with such facility, that ever since for the first time I observed this phenomenon, I have used the disulphide of carbon as a reagent for the detection of the phosphorus-bases; for trimethylphosphine exhibits a deportment perfectly similar to that of the ethyl-body. The minutest quantities of these bases may thus be readily and safely recognized. The reaction is best observed by pouring the liquid to be examined upon a watch-glass, and allowing the vapour of the disulphide of carbon to flow from an inclined bottle upon the liquid. Immediately the watch-glass is coated with a beautiful net-work of the red crystals. It requires scarcely to be mentioned that the crystals are not formed when the phosphorus-bases are combined with acids. They appear, however, readily on adding to a mixture of their salts and disulphide of carbon, a drop of potash, which liberates the bases.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance, which in delicacy could be compared with it. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas may, as I have shown already in another place*, be recognized without any difficulty. When the gas is passed through a bulb-apparatus containing ether to which a few drops of triethylphosphine are added, the liquid soon assumes a reddish tint, which gradually increases in intensity, until, when the ether is evaporated, the interior of the apparatus appears coated with a delicate efflorescence of the red crystals. Scarcely more than half a cubic foot of the present London coal-gas is required for this experiment.

In order to satisfy myself that disulphide of carbon may be employed with safety as a test for the phosphorus-bases, it was necessary to examine the deportment of this compound with the *arsines* and *stibines*. Disulphide of carbon exhibits no reaction with *triethylarsine* and *triethylstibine*. I have left mixtures of these bases with the disulphide in contact for a considerable length of time, both at the common temperature and at 100°, without being able to observe the slightest alteration. I have also satisfied myself that disulphide of carbon, at all events at the common temperature, is without action upon *phosphoretted hydrogen*.

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* Quarterly Journal of the Chemical Society, vol. xiii. p. 87.

On examining somewhat minutely into the deportment of triethylphosphine with sulphur-compounds, the organic sulphocyanates could not be left unnoticed. My attention was in the first place fixed by the sulphocyanate of phenyl, which I had just discovered at the time I was engaged in the study of these reactions. I owe to the kindness of Dr. LEIBIUS a very considerable quantity of this somewhat difficultly obtainable sulphocyanate, the full description of which will be found in a paper on phenyl-derivatives shortly to be published. The deportment of this compound with triethylphosphine, however, is here given in connexion with the phosphorus-bases.

Action of Sulphocyanate of Phenyl upon Triethylphosphine.

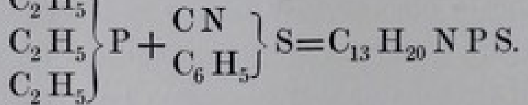
The reaction between the two substances in the anhydrous state is very violent, and frequently causes the inflammation of the phosphorus-base. The mixture assumes a deep-yellow colour, and on cooling deposits sometimes splendid uranium-yellow needles; often, however, it remains liquid for hours, and even for days, but suddenly solidifies, when touched with a glass rod, into a hard yellow crystalline mass. The new compound is most conveniently prepared by allowing the sulphocyanate to act upon the triethylphosphine in the presence of a considerable volume of ether. The product of the reaction, being difficultly soluble in cold ether, often separates in the crystalline state, more frequently as an oil, which solidifies after some time. In order to ensure perfect purity, it is only necessary to crystallize the compound once or twice from boiling ether.

I. 0·2160 grm. of the yellow crystals, dried *in vacuo* over sulphuric acid, gave 0·4923 grm. of carbonic acid and 0·1585 grm. of water.

II. 0·2242 grm. of crystals of a second preparation gave 0·5110 grm. of carbonic acid and 0·1675 grm. of water.

III. 0·3491 grm. of substance, burnt with carbonate of sodium and oxide of mercury, gave 0·3250 grm. of sulphate of barium*.

These numbers characterize the new body as a combination of one molecule of triethylphosphine with one molecule of sulphocyanate of phenyl:



$$\left.\begin{matrix}C_2H_5\\C_2H_5\\C_2H_5\end{matrix}\right\}P+\left.\begin{matrix}CN\\C_6H_5\end{matrix}\right\}S=C_{13}H_{20}NPS.$$

	Theory.		Experiment.		
			I.	II.	III.
C_{13}	156	61·66	62·16	62·16	——
H_{20}	20	7·90	8·14	8·30	——
N	14	5·54	——	——	——
P	31	12·25	——	——	——
S	32	12·65	——	——	12·79
	253	100·00			

---

* When attempting to determine the sulphur as sulphide of silver, I found that on ebullition of the

The above formula is fully corroborated by the analysis of several well-defined salts, which will be mentioned presently.

The yellow crystals are insoluble in water. Alcohol, both cold and hot, dissolves them in almost every proportion The best crystals were obtained by the spontaneous evaporation of the ethereal solution in a high open cylinder. Some of these crystals were so well developed, that QUINTINO SELLA was enabled to submit them to a detailed crystallographic examination, which I here insert.

"System monoclinic:—

100, 001=61° 2′; 010, 110=44° 27′.

Forms observed:—

100, 010, 001, 110 (Fig. 18).

Combinations observed:—

110, 001 (Fig. 19).

110, 100, 001 (Fig. 20).

110, 001; 100, 010 (Fig. 21).

Fig. 18.

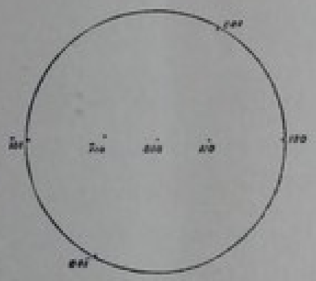


Fig. 19.

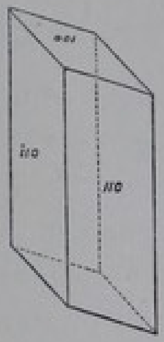


Fig. 20.

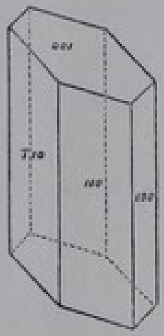
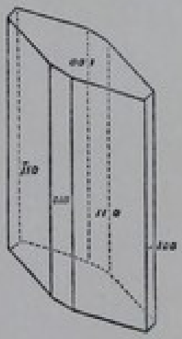


Fig. 21.



Angles.		Calculated.		Observed.	
		°	′	°	′
100, 010	=	90	0	90	0
100, 001	=	61	2	60	53
100, 110	=	45	33	45	33
010, 001	=	90	0	——	
010, 110	=	44	27	44	27
001, 110	=	70	10	70	24
110, $\bar{1}$10	=	88	54	88	54

---

alcoholic solution with nitrate of silver not more than about one-half of the sulphur was separated as sulphide of silver. 0·3180 grm. of substance gave 0·1491 grm. of sulphide of silver=6·05 per cent. of sulphur. In the presence of ammonia the whole amount of sulphur is precipitated as sulphide of silver.

According to NAUMANN:—

$$b:c=1:0{\cdot}8583;\quad \gamma=61^\circ\ 2'.$$

Forms observed:—

$$\infty\bar{\mathrm{P}}\infty,\ \infty\grave{\mathrm{P}}\infty,\ 0\mathrm{P},\ \infty\mathrm{P}.$$

According to WEISS:—

$$a:b=1:0{\cdot}8583;\quad a\,o\,c=118^\circ\ 58'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c.$$

According to LEVY:—

$$\mathrm{M\ M}=88^\circ\ 54';\quad \mathrm{M\ P}=109^\circ\ 50'.$$

Forms observed:—

$$h', g', \mathrm{P}, \mathrm{M}.$$

The faces 0 0 1 present less lustre than the others, which are very brilliant, when the crystals are taken from a tube which contains a number of the crystals. In contact with the air they become opaque, and the faces lose their lustre, but they become again transparent when returned to the tube containing the other crystals.

Cleavage 1 0 0 easily obtained; cleavage 1 1 0 fibrous.

Hardness nearly that of gypsum.

The plane of the optical axes is parallel to [0 1 0], or to the axis of symmetry.

Colour light yellow, with a tint of green."

If we endeavour to associate this compound with well-known bodies, in order to obtain some insight into the probable arrangement of its proximate constituents, both its formation and its deportment point to *urea*. Urea is generated by the combination of ammonia and cyanic acid: the yellow crystals are formed by the union of two compounds derived respectively from ammonia and cyanic acid; in urea the faculty possessed by ammonia of combining with acids has been preserved; the new compound likewise exhibits the sharply-defined characters of a monacid base. Whatever constitution be attributed to urea, must also be claimed for the new base. If urea be viewed as a monacid diamine,

$$\mathrm{C\,H_4\,N_2\,O} = \left.\begin{matrix}(\mathrm{C\,O})''\\ \mathrm{H_2}\\ \mathrm{H_2}\end{matrix}\right\}\mathrm{N_2},$$

the yellow crystals present themselves as

$$\mathrm{C_{13}\,H_{20}\,N\,P\,S} = \left.\begin{matrix}(\mathrm{C\,S})''\\ (\mathrm{C_2\,H_5})_2\\ (\mathrm{C_2\,H_5})\,(\mathrm{C_6\,H_5})\end{matrix}\right\}\mathrm{N\,P}.$$

The new compound accordingly belongs to the type urea: it may be viewed as ordinary urea, the oxygen of which is replaced by sulphur, for the hydrogen of which ethyl and phenyl have been substituted, whilst phosphorus has taken the place of half the nitrogen. Regarded from this point of view, the formation of the new compound presents considerable interest; it offers the first example of the perfect substitution of the hydrogen in urea, which had remained doubtful hitherto, and illustrates in a remarkable manner the persistence of the type urea under the influence of an almost overwhelming substitution. At the same time it deserves to be noticed that the corresponding oxygenated urea remains to be discovered.

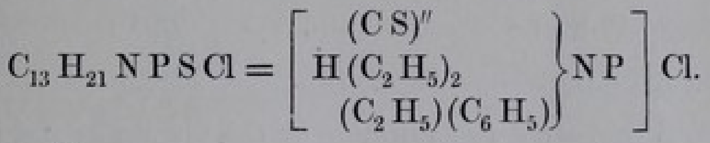
The new compound, as already mentioned, possesses the properties of a well-defined organic base. Insoluble in water, it dissolves with the greatest facility even in very diluted acids, giving rise in many cases to easily-crystallizable salts which are capable of double decomposition, and from which the base may be reprecipitated by the careful addition of potassa or ammonia.

Chloride.—The solution of the phenyl-compound in warm concentrated hydrochloric acid solidifies on cooling to a crystalline mass, which, when recrystallized from moderately warm water, furnishes splendid cadmium-yellow crystals, frequently an inch in length. Boiling water has to be avoided, since it decomposes the substance. Even the dry crystals are altered at 100°; they must therefore, like all the other salts of the base, be dried *in vacuo* over sulphuric acid.

I. 0·1953 grm. of substance gave 0·3850 grm. of carbonic acid and 0·1293 grm. of water.

II. 0·5635 grm. of substance gave 0·2850 grm. of chloride of silver.

These numbers correspond to the formula



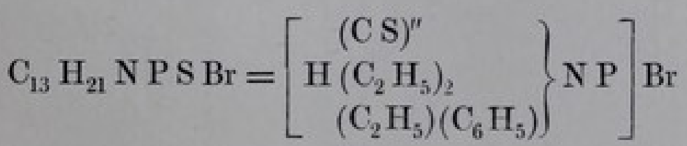
$$C_{13}H_{21}NPSCl = \left[\left.\begin{array}{c}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{array}\right\}NP\right]Cl.$$

	Theory.		Experiment.	
			I.	II.
C_{13}	156	53·88	53·76	——
H_{21}	21	7·25	7·36	——
N	14	4·84	——	——
P	31	10·71	——	——
S	32	11·06	——	——
Cl	35·5	12·26	——	12·51
	289·5	100·00		

Bromide.—Both in preparation and properties, precisely similar to the salt previously mentioned.

0·2835 grm. of bromide gave 0·1620 grm. of bromide of silver.

The formula



$$C_{13}H_{21}NPSBr = \left[\left.\begin{array}{c}(CS)''\\ H(C_2H_5)_2\\ (C_2H_5)(C_6H_5)\end{array}\right\}NP\right]Br$$

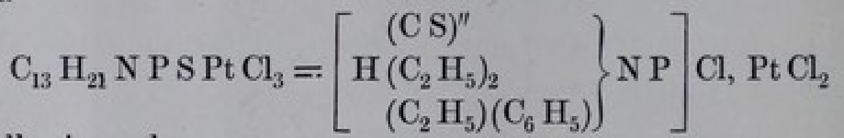
requires the following values:—

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	75·76	——
1 equiv. of Hydrogen	1	0·29	——
1 equiv. of Bromine	80	23·95	24·31
1 equiv. of Bromide	334	100·00	

Platinum-salt.—The solution of the chloride furnishes with dichloride of platinum a light-yellow crystalline precipitate. Dilute solutions slowly deposit this salt in somewhat better-formed crystals, which are frequently grouped in lily-shaped aggregations.

0·4690 grm. of platinum-salt, heated with carbonate of sodium, gave 0·0995 grm. of platinum and 0·4505 grm. of chloride of silver.

The formula



$$C_{13}H_{21}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)'' \\ H(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right]Cl,\ PtCl_2$$

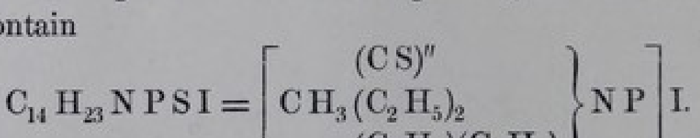
requires the following values:—

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	55·11	——
1 equiv. of Hydrogen . . .	1	0·21	——
1 equiv. of Platinum . . .	98·7	21·49	21·22
3 equivs. of Chlorine . . .	106·5	23·19	23·75
1 equiv. of Platinum-salt . .	459·2	100·00	

I did not succeed in preparing the sulphate or the nitrate of the base. The phenyl-compound is rapidly decomposed under the influence of these acids; it forms, however, beautifully crystallized salts with the iodides of methyl and ethyl. I have examined only the former of these compounds.

Iodide-of-Methyl-compound.—When iodide of methyl is poured into an ethereal solution of the urea, the new compound is at once separated as a heavy oil which rapidly solidifies into a crystalline mass. The crystals dissolve in boiling water which on cooling deposits the iodide in splendid needles of a golden-yellow colour.

These crystals contain



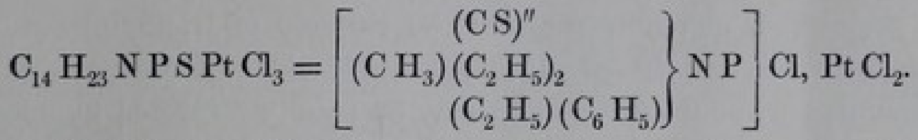
$$C_{14}H_{23}NPSI = \left[\left.\begin{matrix}(CS)'' \\ CH_3(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right]I.$$

0·3885 grm. of iodide gave 0·2300 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	64·06	——
1 equiv. of Methyl	15	3·79	——
1 equiv. of Iodine	127	32·15	31·97
1 equiv. of Iodide	395	100·00	

Platinum-salt of the Methyl-compound.

The chloride obtained by treating the iodide with chloride of silver, yields upon addition of dichloride of platinum, an acicular platinum-salt, which may be recrystallized without decomposition from boiling water. Its composition corresponds to that of the iodide:

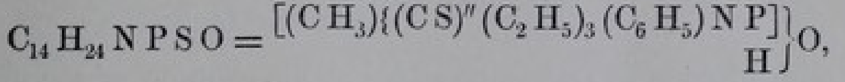


$$C_{14}H_{23}NPSPtCl_3 = \left[\left.\begin{matrix}(CS)'' \\ (CH_3)(C_2H_5)_2 \\ (C_2H_5)(C_6H_5)\end{matrix}\right\} NP\right] Cl,\ PtCl_2.$$

0·3395 grm. of platinum-salt, treated with carbonate of sodium, gave 0·0700 grm. of platinum and 0·3095 grm. of chloride of silver.

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	53·47	——
1 equiv. of Methyl	15	3·16	——
1 equiv. of Platinum . . .	98·7	20·86	20·62
3 equivs. of Chlorine . . .	106·5	22·51	22·55
1 equiv. of Platinum-salt . .	473·2	100·00	

The iodide, when treated with oxide of silver, furnishes, together with iodide of silver, a very caustic liquid containing the corresponding hydrate. The presence in this liquid of the compound



$$C_{14}H_{24}NPSO = \left.\begin{matrix}[(CH_3)\{(CS)''(C_2H_5)_3(C_6H_5)NP] \\ H\end{matrix}\right\} O,$$

is proved by the fact of the characteristic needle-shaped platinum-salt being immediately reproduced when it is saturated with hydrochloric acid and mixed with dichloride of platinum. The free base is, however, readily decomposed. On boiling, the odour of sulphocyanate of phenyl becomes at once perceptible; if ebullition be continued until the odour has disappeared, addition of hydrochloric acid and dichloride of platinum no longer furnishes the difficultly soluble needles. In their place, large well-developed orange-yellow octohedra are deposited on evaporation, which by analysis were found to be the platinum-salt of methyl-triethylphosphonium.

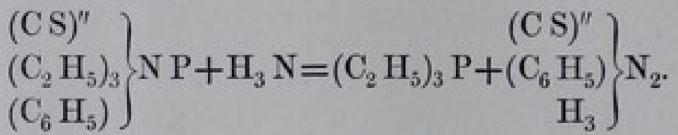
0·2210 grm. of platinum-salt, precipitated by sulphuretted hydrogen, &c., gave 0·0640 grm.=28·96 per cent. of platinum.

The formula

$$[(CH_3)(C_2H_5)_3P]Cl,\ PtCl_2$$

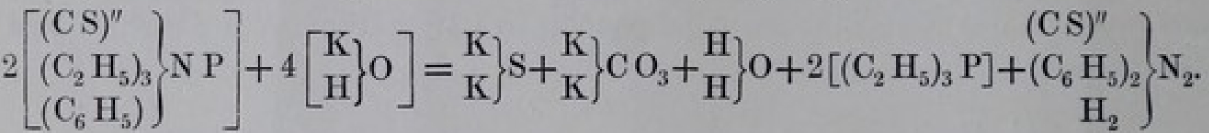
requires 29·18 per cent. of platinum.

The free methylated phenyl-base then simply splits by ebullition into sulphocyanate of phenyl and oxide of methyl-triethylphosphonium. When the solution is boiled by itself, the sulphocyanate is separated as such; when it is boiled in the presence of oxide of silver, the sulphocyanate is, partly at least, destroyed, the alkaline solution becoming acid and exhibiting the presence of considerable quantities of sulphuric acid. This transformation clearly shows how feebly the proximate constituents are held together in the urea. The same instability is perceptible in the general deportment of the compound. Even extremely dilute nitric acid liberates the sulphocyanate of phenyl, whilst the phosphorus-base is converted into the oxide. The chloride is one of the more stable salts of the urea, but it is likewise readily altered; on addition of a large quantity of water, the solution of the salt becomes milky, the sulphocyanate of phenyl being separated in oily globules, and now contains the chloride of triethylphosphonium. On adding ammonia to the *concentrated* solution of the chloride, the urea, as has been already stated, is separated without change, and may be readily recovered by taking up with ether and crystallizing. If, on the other hand, the *dilute* solution be boiled with ammonia, the turbidity perceptible in the commencement disappears again, and after a few moments beautiful crystals of *phenyl-sulphocarbamide* are deposited, triethylphosphine being simultaneously liberated:



$$\left.\begin{matrix}(C\,S)''\\(C_2H_5)_3\\(C_6H_5)\end{matrix}\right\}N\,P+H_3N=(C_2H_5)_3P+\left.\begin{matrix}(C\,S)''\\(C_6H_5)\\H_3\end{matrix}\right\}N_2.$$

On treating the chloride with potassa, phenomena exactly analogous are observed; the crystals which are separated, are, however, *diphenyl-sulphocarbamide*:



$$2\left[\left.\begin{matrix}(C\,S)''\\(C_2H_5)_3\\(C_6H_5)\end{matrix}\right\}N\,P\right]+4\left[\left.\begin{matrix}K\\H\end{matrix}\right\}O\right]=\left.\begin{matrix}K\\K\end{matrix}\right\}S+\left.\begin{matrix}K\\K\end{matrix}\right\}C\,O_3+\left.\begin{matrix}H\\H\end{matrix}\right\}O+2[(C_2H_5)_3P]+\left.\begin{matrix}(C\,S)''\\(C_6H_5)_2\\H_2\end{matrix}\right\}N_2.$$

If a few drops of disulphide of carbon be added to the solution of the urea, the liquid, when gently heated, assumes a deep red colour, and deposits on cooling the beautiful ruby-red crystals $(C_2H_5)_3P, CS_2$, which I have mentioned in a previous paragraph of this paper. The mother-liquor of these crystals furnishes on evaporation oily droplets of sulphocyanate of phenyl. The urea, even when perfectly pure and dry, cannot be preserved without undergoing a gradual alteration. If the crystals be left under a bell-jar containing atmospheric air, they become dull, and at last moist and sticky, whilst a peculiar extremely disagreeable odour, distantly resembling that of hydrocyanic acid, becomes perceptible; at the same time, a delicate net-work of fine needles begins to appear on the glass, easily recognized as sulphide of triethylphosphine. The crystals of the urea fuse at 57°·5, forming a yellow liquid, which, in consequence of incipient decomposition, resolidifies but slowly and imperfectly. At 100° the phenomena just mentioned are much more distinctly observed, and especially the smelling body is unmistakeably perceived. The peculiar-smelling body is likewise almost overwhelmingly produced on evaporating the ethereal mother-liquor of the compound. As yet I have not been able to lay hold of the possessor of this remarkable odour. The ethereal mother-liquor, when evaporated, leaves a brown syrup, which after some time deposits large crystals of sulphide of triethylphosphine. Submitted to distillation, this residue yields, together with other products, an additional quantity of the crystallized sulphur-compound.

Transformations precisely similar are observed when the crystals of the urea, in sealed tubes, are exposed to a temperature of from 150° to 160°. The brown fused mass which is thus formed, solidifies on cooling with crystalline structure; the crystals, however, are no longer the original compound, but sulphide of triethylphosphine, which is surrounded by another substance. The examination of this reaction has not yet been completed. The nature of the final products of the metamorphosis may, however, be anticipated in some measure by the results obtained in studying the deportment of triethylphosphine with *sulphocyanate of ethyl* and *sulphocyanate of ethylene*, which will be briefly mentioned in some of the following paragraphs.

Action of Sulphocyanate of Allyl upon Triethylphosphine.

To generalize the relations established in the preceding paragraph, I was induced to examine the deportment of the phosphorus-base with oil of mustard. The two bodies act upon each other with extraordinary violence; the mixture turns brown, but does not solidify either by cooling or by agitation. After some days, however, the syrup yields brown crystals which are difficult to purify. The purification of the compound succeeds, however, without any difficulty when the reaction is allowed to take place in ether. In this manner a crystalline mass is easily obtained, which requires only to be washed with cold ether, and then once recrystallized from boiling ether.

0·3623 grm. of the substance, dried over sulphuric acid *in vacuo*, gave 0·7368 grm. of carbonic acid and 0·3040 grm. of water.

The formula

$$C_{10}H_{20}NPS = \left.\begin{array}{l}(CS)''\\(C_2H_5)_2\\(C_2H_5)(C_3H_5)\end{array}\right\}NP$$

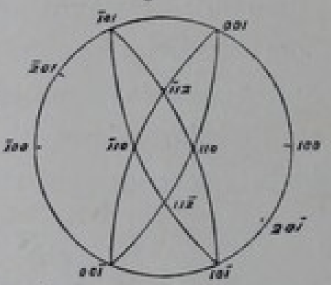
requires the following values:—

Theory.			Experiment.
C_{10}	120	55·30	55·46
H_{20}	20	9·21	9·32
N	14	6·45	——
P	31	14·29	——
S	32	14·75	——
	217	100·00	

The allyl-compound behaves in all respects like the phenyl-compound. It is insoluble in water, but easily soluble in alcohol; the solution has a faintly alkaline reaction. It fuses at 68° and solidifies at 61°. At a higher temperature, it is decomposed exactly like the phenyl-compound. In this case also, a peculiar, and if possible, still more repulsive odour is evolved, while crystals of sulphide of triethylphosphine separate in large quantity.

The allyl-compound crystallizes with extraordinary facility. There is no difficulty in obtaining it in colourless transparent crystals half an inch in length, and perfectly developed on all sides. I scarcely remember any other organic compound that crystallizes so readily. The crystals, as appears from the measurements of QUINTINO SELLA, are isomorphous with those of the corresponding phenyl-compound*. SELLA has communicated to me the following details respecting his examination.

Fig. 22.



"System monoclinic:—

100, 101=35° 42′; 001, 101=29° 3′; 010, 111=39° 22′.

Forms observed:—

100, 001, 110, $\bar{1}01$, $\bar{2}01$, $\bar{1}12$ (Fig. 22).

Angles.		Calculated.	Observed.
100, 001	=	64° 45′	64° 45′
100, 110	=	66 14	66 14
100, $\bar{1}01$	=	114 9	114 9
100, $\bar{2}01$	=	143 51	143 54
100, $\bar{1}12$	=	89 32	89 13
001, 110	=	80 15	80 10
001, $\bar{1}01$	=	49 24	49 25
001, $\bar{2}01$	=	79 6	79 7
001, $\bar{1}12$	=	51 8	51 17
110, $\bar{1}10$	=	47 33	47 31
110, $\bar{1}01$	=	99 30	99 30
110, $\bar{2}01$	=	109 0	108 54
110, $\bar{1}12$	=	48 23	48 41
110, $11\bar{2}$	=	48 37	48 34
$\bar{1}01$, $\bar{2}01$	=	29 41	29 38
$\bar{1}01$, $\bar{1}12$	=	51 7	51 2
$\bar{2}01$, $\bar{1}12$	=	66 20	67 5
$\bar{1}12$, $11\bar{2}$	=	87 31	87 55

According to NAUMANN:—

$$a:b:c=0{\cdot}8321:1:0{\cdot}3984;\quad \gamma=64^\circ\ 45'.$$

Forms observed:—

$$\infty\text{Ᵽ}\infty;\ 0\text{P},\ \infty\text{P},\ \text{Ᵽ}\infty,\ 2\text{P}\infty,\ \tfrac{1}{2}\text{P}.$$

---

* Both substances are isomorphous with thiosinamine or sulphallyl-urea,

$$\left.\begin{array}{c}(CS)''\\(C_3H_5)\,H\\H_2\end{array}\right\}N_2,$$

the crystalline form of which has been determined by SCHABUS.

According to WEISS:—

$$a:b:c=1:0·3984:0·8321;\quad aoc=115°\ 15'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:\infty b:c;\quad a:b:\infty c;\quad -a:\infty b:c;\quad -\tfrac{1}{2}a:\infty b:c;\quad -a:b:\tfrac{1}{2}c.$$

According to LEVY:—

$$MM=47°\ 33';\quad MP=99°\ 45';\quad b:h=1:0·7730.$$

Forms observed:—

$$h',\ P,\ M,\ a',\ a^{\frac{1}{2}},\ b'.$$

Combinations observed:—

001, 100, 110 (Fig. 23).
001, $\bar{1}01$, 110 (Fig. 24).
100, 001, $\bar{1}01$, 110 (Fig. 25).
100, 001, $\bar{1}01$, 110; $\bar{1}12$ (Fig. 26).
100, 001, $\bar{1}01$, 110, $\bar{2}01$, $\bar{1}12$ (Fig. 27).

Fig. 23.

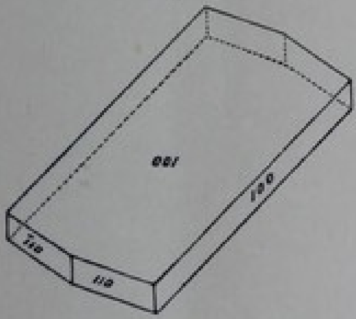


Fig. 24.

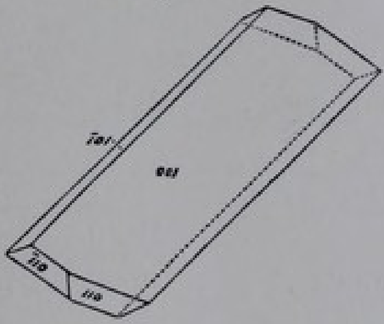
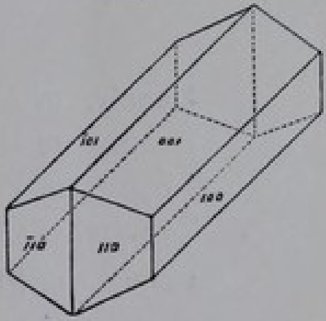


Fig. 25.



The crystals sometimes present the appearance of trimetric crystals (Fig. 25), sometimes they are flattened parallel with 001, and considerably elongated in the direction [010] (Figs. 23, 24). The faces $\bar{1}12$ are rounded off and cannot be well measured, although it is possible to verify the zones to which they belong: some of these faces are occasionally wanting, and many of the crystals present only two of these faces (Fig. 27).

Cleavages 100 and 001 distinct, and easily obtained.

Fig. 26.

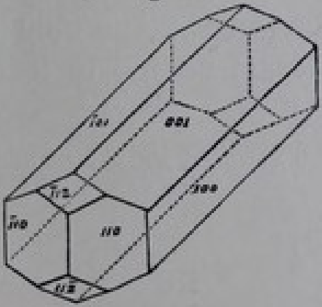
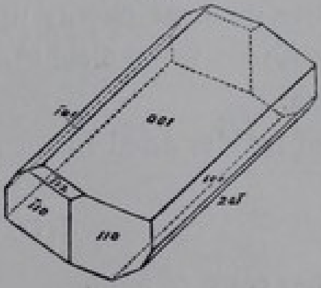


Fig. 27.



The optical axes are situated in the plane of symmetry, viz. 010. The bisecting line is not very far from normal to $\bar{1}01$. A system of rings is observed both through the faces 1 0 0 and through the faces $2\,0\,\bar{1}$; another system is seen through the faces 0 0 1. The apparent angle of the optical axes is about 38°, if the first system of rings be observed through 1 0 0, and about 68½° if this system be seen through $2\,0\,\bar{1}$. The mean index of refraction, *i. e.* of that which corresponds to a ray lying in a plane parallel to 0 1 0 and polarized in that plane, is $\beta=1{\cdot}657$. Hence it follows that the internal angle of the optical axes is about 72½°.

Hardness less than that of gypsum."

Platinum-salt.—I have contented myself with verifying the formula of the allyl-urea by the analysis of the platinum-salt. The allyl-compound dissolves readily in hydrochloric acid, and the solution, when mixed with dichloride of platinum, yields a light-yellow scaly precipitate having a silky lustre, which fuses to a yellow oil in boiling water.

0·5605 grm. of the crystals, dried over sulphuric acid, precipitated by sulphuretted hydrogen, &c., gave 0·1282 grm. of platinum.

The formula

$$C_{10}H_{21}NPSPtCl_3 = \left[\left.\begin{array}{l}(C\,S)''\\ H\,(C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{array}\right\}NP\right]Cl,\,PtCl_2$$

requires

	Theory.		Experiment.
1 equiv. of Allyl-compound . .	217	51·28	——
1 equiv. of Hydrogen	1	0·23	——
1 equiv. of Platinum	98·7	23·32	22·87
3 equivs. of Chlorine	106·5	25·17	——
1 equiv. of Platinum-salt . . .	423·2	100·00	

The allyl-base described in the preceding pages has the composition of sulphocyanate of triethyl-allylphosphonium:

$$\left.\begin{array}{l}(C\,S)''\\ (C_2H_5)_2\\ (C_2H_5)(C_3H_5)\end{array}\right\}N\,P = \left.\begin{array}{c}C\,N\\ {[(C_2H_5)_3(C_3H_5)\,P]}\end{array}\right\}S.$$

I felt some interest in comparing the latter compound with the allyl-base. Iodide of allyl acts with the greatest energy upon triethylphosphine. The solid product of the reaction, recrystallized from alcohol, furnishes splendid needles of iodide of triethyl-allylphosphonium.

0·6740 grm. of iodide, dried *in vacuo*, gave 0·5535 grm. of iodide of silver=44·38 per cent. of iodine.

The formula $[(C_2H_5)_3(C_3H_5)\,P]\,I$

requires 44·40 per cent. of iodine.

Treatment with chloride and oxide of silver yields the corresponding chloride and hydrate. They resemble in every respect the tetrethylphosphonium-compounds. The chloride gives with dichloride of platinum an easily crystallizable octohedral platinum-salt.

The hydrate of triethyl-allylphosphonium forms with hydrosulphocyanic acid a difficultly crystallizable salt which is easily soluble in water, and differs, as might have been expected, entirely from the allyl-base, which has the same composition.

Behaviour of Triethylphosphine with the Sulphocyanates of Ethyl and Ethylene.

I have in vain endeavoured to produce, by the action of triethylphosphine on the sulphocyanates of methyl, ethyl, and amyl, compound ureas analogous to the allyl- and phenyl-bodies. It is true that these substances act upon triethylphosphine even at ordinary temperatures; in the case of sulphocyanate of methyl, indeed, the action is very brisk, but I did not succeed in obtaining definite compounds. Sulphocyanate of ethyl remained for months in contact with triethylphosphine without depositing any crystalline compound. The non-production of these ureas cannot, however, excite surprise, if we remember in how many respects, and especially in their relation to ammonia, the sulphocyanogen-compounds of ethyl and its homologues differ from those of allyl and phenyl.

When a mixture of triethylphosphine and one of the above-mentioned sulphocyanates is heated for some hours in a sealed tube to 100°, an abundant crop of crystals of sulphide of triethylphosphine is deposited from the liquid after cooling. These crystals are surrounded by a brown viscid substance, soluble to a certain extent in water, easily soluble with green colour in alcohol. In order to disentangle from this mixture the complementary product of the reaction, the semicrystalline mass, obtained by the action of sulphocyanate of ethyl, was shaken with ether to separate the sulphide, evaporated with an excess of hydrochloric acid, and the residue redissolved in water, when a quantity of the brown impurities remained insoluble. The filtered solution gave with trichloride of gold a dingy yellow precipitate, which by treatment with sulphuretted hydrogen, reprecipitation of the separated chloride by trichloride of gold, &c., ultimately assumed the characters of the pure gold-salt of *tetrethylphosphonium*.

0·2240 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·0910 grm. =40·62 per cent. of gold.

The formula

$$[(C_2H_5)_4P]Cl, AuCl_3$$

requires 40·53 per cent. of gold.

The chloride, prepared from the gold-salt, gave with dichloride of platinum beautiful octohedra of the platinum-salt of tetrethylphosphonium.

0·6300 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1784 grm. =28·31 per. cent. of platinum.

The formula

$$[(C_2H_5)_4P]Cl, PtCl_2$$

requires 28·02 per cent. of platinum.

The action of sulphocyanate of ethyl upon triethylphosphine may be accordingly represented by the equation

$$\left.\begin{matrix}C\,N\\C_2H_5\end{matrix}\right\}S + 2\,[(C_2H_5)_3P] + \left.\begin{matrix}H\\H\end{matrix}\right\}O = (C_2H_5)_3PS + \left.\begin{matrix}[(C_2H_5)_4P]\\H\end{matrix}\right\}O + H\,C\,N.$$

I have not been able to trace directly the hydrocyanic acid which figures in this equation, but this acid appears unmistakeably in its products of decomposition. The brown substance which accompanies the sulphide of triethylphosphine and the hydrate of tetrethylphosphonium is rich in nitrogen; boiled for some time with hydrochloric acid, it yields abundance of chloride of ammonium. In fact, it was on account of the presence of ammonia among the products of the reaction, that it became necessary to precipitate the tetrethylphosphonium in the first place in the form of the gold-compound.

I have likewise examined the behaviour of disulphocyanate of ethylene with triethylphosphine. The reaction takes place with energy at ordinary temperatures. When triethylphosphine is poured into a concentrated alcoholic solution of sulphocyanate of ethylene, the liquid immediately solidifies to a dazzling white crystalline mass of sulphide of triethylphosphine. It deserves to be noticed that the same decomposition takes place also when the substances are allowed to react in the presence of anhydrous ether. The transformation which the sulphocyanate of ethylene undergoes under the influence of triethylphosphine is perfectly analogous to the change of the ethyl-compound when submitted to the same agent. Instead of a derivative of tetrethylphosphonium, the sulphocyanate of ethylene produces the cyanide of a diatomic metal, of *ethylene-hexethyl-diphosphonium.*

$$\underbrace{\left.\begin{matrix}(C\,N)_2\\(C_2H_4)''\end{matrix}\right\}S_2}_{\substack{\text{Sulphocyanate}\\\text{of ethylene.}}} + 4\,\underbrace{[(C_2H_5)_3P]}_{\substack{\text{Triethylphos-}\\\text{phine.}}} = 2\,\underbrace{[(C_2H_5)_3PS]}_{\substack{\text{Sulphide of}\\\text{triethylphos-}\\\text{phine.}}} + \underbrace{\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''(C\,N)_2}_{\substack{\text{Dicyanide of ethylene-hex-}\\\text{ethyl-diphosphonium.}}}.$$

Owing to the low temperature at which the reaction is accomplished, the hydrocyanic acid is not changed in this case, and may be recognized without difficulty by the ordinary reagents. The diphosphonium, which is simultaneously formed, was traced as platinum-salt, exactly in the same manner as the tetrethylphosphonium in the process previously mentioned. The product of the reaction, freed as far as possible from the sulphide by repeated evaporation and ultimately by treatment with ether, was precipitated by dichloride of platinum. The dingy platinum-salt was purified by treatment with sulphuretted hydrogen and reprecipitation. Repeatedly treated in this manner, it assumed the character of a pure compound.

0·2745 grm. of this salt gave 0·0804 grm. =29·29 per cent. of platinum.

The formula

$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2, 2\,Pt\,Cl_2$$

requires 29·27 per cent. of platinum. Since I shall have to give a detailed account of the diphosphonium-compounds in one of the following sections of this inquiry, I need not for the present enter into further particulars regarding this reaction.

In concluding this paragraph, I may append a few remarks upon the deportment of sulphocyanate of triethylphosphonium under the influence of heat. This salt is readily procured by dissolving triethylphosphine in hydrosulphocyanic acid. Submitted to the action of heat, it is partly volatilized without decomposition; the greater portion, however, is decomposed, the sulphide and the disulphide-of-carbon-compound of triethylphosphine, together with free disulphide of carbon, appearing among the volatile products of the reaction; while a brown ill-defined substance remains in the retort, yielding, when treated with an alkali, an appreciable quantity of ammonia. I have not examined this change in detail, but it is obvious that one of the direct products of the reaction is sulphocyanate of ammonium, the further decomposition of which explains the appearance of the disulphide of carbon, as well as the other products observed. The residue, of course, must contain the varied compounds generated by the action of heat on sulphocyanate of ammonium.

Behaviour of the Arsines and Stibines with the Sulphocyanates of Phenyl and Allyl.

The facility with which the compound ureas containing nitrogen and phosphorus are formed, induced me to attempt the production of analogous compounds with arsenic or antimony in place of phosphorus. I therefore treated sulphocyanate of phenyl and oil of mustard successively with triethylarsine and triethylstibine, first at ordinary and then at gradually increasing temperatures in sealed tubes. But not one of these experiments led to the expected result. The arsines and stibines differ, indeed, in their chemical characters much more from ammonia than the phosphines. Their incapability of forming saline compounds with acids is alone sufficient to render the formation of ureas containing arsenic and antimony somewhat improbable. When mixtures of triethylarsine with sulphocyanate of phenyl on the one hand, and sulphocyanate of allyl on the other, were left to stand for some time at ordinary temperatures, the liquid in both cases was found to be traversed by a small quantity of beautiful needle-shaped crystals. The crystals from both mixtures were found to be the same; they were readily identified with the white needles which are gradually formed in triethylarsine when left in contact with atmospheric air.

Behaviour of Triethylphosphine with Cyanates.

The formation of sulphuretted ureas containing phosphorus and nitrogen led me to try whether the corresponding oxygen-compounds could likewise be produced.

When *cyanate of phenyl* is mixed with the phosphorus-base, great heat is evolved, indicating a marked chemical reaction. The mixture on cooling solidifies into a mass of shining crystals which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty even in boiling alcohol. By recrystallization from the last-mentioned solvent, the new body is easily obtained pure. The further examination of the resulting crystals proved, however, that they by no means consisted of the compound urea of which I was in search. From the analysis, which I intend to give in connexion with other researches, it appeared that the crystals still possessed the composition of cyanate of phenyl, that, indeed, they were *cyanurate of phenyl*. The triethylphosphine in this case appears to induce nothing more than a new molecular disposition of the elements in cyanate of phenyl. The peculiar character of this metamorphosis may be perceived in the most beautiful manner by dipping a glass rod moistened with triethylphosphine into a considerable quantity of cyanate of phenyl. The liquid immediately becomes hot, and solidifies after a few seconds into a shining crystalline mass of the cyanurate.

Similar results were obtained by the action of the phosphorus-base on *cyanate of ethyl*. The two bodies may be mixed without evolution of heat, and the mixture does not solidify; but the transformation is soon indicated by the diminution of the penetrating odour of the cyanate. If, as soon as the odour has disappeared, the liquid be mixed with dilute hydrochloric acid which removes the free phosphorus-base, the oil which floats on the surface quickly solidifies into a solid crystalline mass exhibiting, when recrystallized from boiling water, all the properties of *cyanurate of ethyl*.—When a stream of *cyanic acid* gas is passed through triethylphosphine, the odour of the acid disappears, while the phosphorus-base becomes turbid, and yields a white deposit of *cyanuric acid*.

In connexion with these experiments, I have had occasion to convince myself that *cyanic acid* gas and *phosphoretted hydrogen* do not act upon one another, at least at ordinary temperatures.—I was naturally anxious to ascertain whether the peculiar action of the phosphorus-base on the cyanates extended likewise to the cyanides. I found, however, that *cyanide of methyl* (acetonitrile) or *cyanide of phenyl* (benzonitrile) may be left for days in contact with the phosphorus-base at temperatures varying from 100° to 150°, without experiencing the slightest alteration. Had these substances been changed under the above conditions, like the cyanates, their transformation into methyl- and phenyl-compounds corresponding to cyanethine might have been expected.

Experiments in the Methyl-series.

The information which I have collected with reference to the phosphorus-compounds, has been almost exclusively obtained by the study of triethylphosphine. In exceptional cases only have I worked in the methyl-series. Trimethylphosphine, on account of its volatility, is much less easily prepared than the ethyl-compound, and especially much more difficult to preserve. This body is oxidized with such rapidity, that it disappears from the hands of the operator during manipulation. Its odour, moreover, is insupportable for any length of time.

Nevertheless, I have made a few experiments with the methyl-compound, a slight sketch of which may form the conclusion of this paper.

The phosphorus-derivatives of the methyl-series exhibit the most perfect analogy with the corresponding ethyl-compounds.

Oxide of trimethylphosphine produces with iodide of zinc, with dichloride of platinum, and with trichloride of gold, the homologues of the several compounds obtained from oxide of triethylphosphine.

When trimethylphosphine, either pure or dissolved in alcohol and ether, is submitted to the action of disulphide of carbon, all the phenomena are reproduced which I have mentioned at some length in describing the corresponding ethyl-base. The red crystals which are formed are somewhat paler, much more volatile, and much more readily altered. The disulphide-of-carbon-compounds of the methyl- and ethyl-series exhibit in their properties the same relation which obtains between the sulphides of the two series.

0·2586 grm. of the disulphide-of-carbon-compound gave 0·3030 grm. of carbonic acid and 0·1415 grm. of water.

The formula

$$C_4 H_9 P S_2 = (C H_3)_3 P, C S_2$$

requires the following values:—

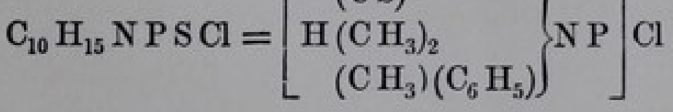
Theory.			Experiment.
C_4	48	31·58	31·95
H_9	9	5·92	6·08
P	31	20·39	——
S_2	64	42·11	——
	152	100·00	

The red crystals are changed with the utmost facility into sulphide of trimethylphosphine. In the hope of forming fine crystals, similar to those obtained with the ethyl-compound, a solution of the red crystals in warm ether was allowed to cool in a tall open cylinder. When the solution was examined next morning it had become colourless, leaving, upon spontaneous evaporation, the beautiful crystals of the sulphur-compound.

The sulphocyanates of phenyl and allyl readily combine with trimethylphosphine. The reaction is even more powerful than with the ethyl-base. The urea-body which trimethylphosphine produces with sulphocyanate of phenyl is a liquid which I have not been able to obtain in the solid state. Directly prepared from the constituents, or separated from one of its crystalline salts, it forms a slightly coloured oily liquid, soluble in water, difficultly soluble in ether, readily soluble in alcohol. On adding concentrated hydrochloric acid to the oil, it gradually solidifies to a crystalline mass of sulphur-yellow delicate, hair-like needles, which may be recrystallized both from water and from alcohol. I have fixed the composition of this phosphoretted urea by a chlorine-determination in the chloride.

0·2718 grm. gave 0·1540 grm. chloride of silver.

The formula

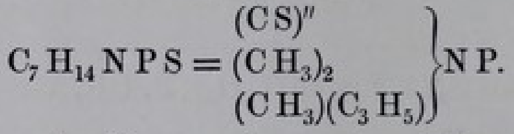


$$C_{10} H_{15} N P S Cl = \left[\left. \begin{matrix} (C S)'' \\ H (C H_3)_2 \\ (C H_3)(C_6 H_5) \end{matrix} \right\} N P \right] Cl$$

requires

	Theory.		Experiment.
1 equiv. of Urea-compound . . .	211	85·25	——
1 equiv. of Hydrogen	1	0·41	——
1 equiv. of Chlorine	35·5	14·34	14·02
1 equiv. of Chloride	247·5	100·00	

The brown liquid which is formed, with considerable evolution of heat, when trimethylphosphine is brought in contact with mustard oil, gradually deposits well-formed transparent colourless prisms, the habitus of which resembles that of the corresponding ethyl-compound. The crystals were not analysed, but there can be no doubt that they were the methylated phosphorus-urea of the allyl-series



$$C_7 H_{14} N P S = \left.\begin{array}{l}(C S)''\\(C H_3)_2\\(C H_3)(C_3 H_5)\end{array}\right\} N P.$$

Phosphoretted hydrogen is without action on the sulphocyanates of phenyl and allyl.

In conclusion, I beg to thank Drs. A. Leibius and M. Holzmann for their assistance in some of the experiments connected with this inquiry.

SECOND MEMOIR.

THEORY OF DIATOMIC BASES.—DIPHOSPHONIUM-COMPOUNDS.

In surveying the rich harvest of discoveries which of late years have rewarded the exertions of chemists, with reference to their general effect on the progress of the science, we cannot avoid recognizing as one of the most valuable amongst their acquisitions, the development of the theory of polyatomic compounds. Seldom has a theory diffused a clearer light on previously established facts, or exerted a more fructifying and inspiring influence on the labours of chemists. First coming into notice in the classical researches of Graham and Liebig on the polybasic acids, and afterwards extended and generalized by the experiments of Gerhardt and Williamson, it has acquired in Berthelot's beautiful investigation of Glycerin, a new field of discovery, the active cultivation of which has already brought to maturity a great variety of fruits. An important step in the development of these ideas was made by H. L. Buff, in showing that dibromide of ethylene can be converted into a corresponding sulphocyanate, and in the conclusions which he drew from this observation, until, in the brilliant experimental researches of Wurtz on the diatomic alcohols, the doctrine of polyatomic compounds has received its clearest and most elegant expression.

Considering the untiring activity with which chemists have devoted themselves to the study of the polybasic acids and, within the last few years, of the polyatomic alcohols, it cannot but appear remarkable that so little attention should hitherto have been bestowed on the polyacid bases. It is true that we are already in possession of many valuable observations relating to these bodies; but they are isolated, and the facts which they have established can scarcely be looked upon as more than accidental acquisitions. Regarded in the scientific sense as a class, and in their relations to other groups of bodies, the polyatomic bases have hitherto been left without examination.

Respecting the constitution of these compounds, and the conditions under which they would be produced, no doubt could be entertained. For, as from a single molecule of water, a monatomic alcohol, a monobasic acid, or a monacid base can be produced, according to the nature of the monatomic radical by which the hydrogen is replaced, so likewise must it be possible, by a proper selection of polyatomic radicals, to link two or more molecules of water, so as to form one molecule of a polyacid base, just as the introduction of other polyatomic radicals gives rise to the formation of polyatomic alcohols or polybasic acids. It remained only to submit these ideas to the test of experiment.

Material for building up this group of bodies appeared to present itself unmistakeably in the chlorine-, bromine-, and iodine-compounds of ethylene and its homologues. As some years ago I had succeeded in converting the corresponding ethyl-compounds by the action of ammonia into the monacid ethyl-bases, I was justified in expecting that, by treating the ethylene-compounds with ammonia, diacid bases might be formed. Respecting some of the bodies which are produced in these reactions, investigations had already been published by CLOËZ*, and more recently by NATANSON†, whose results appeared at first sight to give but little encouragement to any such attempt. But a careful examination of these researches soon convinced me that, when viewed by the light which the progress of science has since thrown upon this subject, the results elicited are far from unfavourable to my theoretical conceptions.

I have once more studied these reactions, and have obtained experimental confirmation of the correctness of my anticipations. But the action of ammonia on the chloride, bromide, and iodide of ethylene presents unexpected complications, quite independent of those indicated by theory, and for which I was not altogether prepared.

Consider for a moment the manner in which the reaction between ammonia and a diatomic bromide—dibromide of ethylene for instance—may take place. Just as bromide of ethyl, acting, as it does, on a single molecule of ammonia, gives rise to the formation of the four bromides,

$$\begin{aligned} &[(C_2H_5)\ H_3N]\,Br^{\ddagger},\\ &[(C_2H_5)_2\,H_2N]\,Br,\\ &[(C_2H_5)_3\,H\ N]\,Br,\\ \text{and } &[(C_2H_5)_4\quad N]\,Br, \end{aligned}$$

so likewise may dibromide of ethylene, acting on two molecules of ammonia, be expected to produce four diatomic bromides, viz.—

$$\begin{aligned} &[(C_2H_4)''\,H_6N_2]''\,Br_2,\\ &[(C_2H_4)''_2\,H_4N_2]''\,Br_2,\\ &[(C_2H_4)''_3\,H_2N_2]''\,Br_2,\\ \text{and } &[(C_2H_4)''_4\quad N_2]''\,Br_2. \end{aligned}$$

These, however, are by no means the only compounds which, in accordance with our present conception of diatomic compounds, may be formed in this reaction.

It appears from the researches of WURTZ, that dibromide of ethylene does not pass into ethylene-alcohol at a single bound, but that there exists an intermediate member of the series still containing half the bromine,

$$\underbrace{(C_2H_4)''\left\{\begin{matrix}Br\\Br\end{matrix}\right.}_{\substack{\text{Dibromide of}\\\text{Ethylene.}}}\qquad\qquad \underbrace{(C_2H_4)''\left\{\begin{matrix}Br\\HO\end{matrix}\right.}_{\substack{\text{Intermediate}\\\text{Bromide.}}}\qquad\qquad \underbrace{(C_2H_4)''\left\{\begin{matrix}HO\\HO.\end{matrix}\right.}_{\substack{\text{Ethylene-}\\\text{alcohol.}}}$$

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* Instit. 1853, p. 213.

† Ann. Chem. Pharm. xcii. 48. and xcviii. 291.

‡ H=1; O=16; S=32; C=12, &c.

There could, therefore, be no doubt that dibromide of ethylene would, under certain conditions, likewise react with ammonia as a monatomic compound, giving rise to another series of bodies in which the hydrogen would be more or less replaced by the monatomic radical C_2H_4Br, viz.—

$$[(C_2H_4Br)\ H_3N]Br,$$
$$[(C_2H_4Br)_2H_2N]Br,$$
$$[(C_2H_4Br)_3H\ N]Br,$$
$$\text{and } [(C_2H_4Br)_4\ \ N]Br.$$

Further, if the reaction took place in presence of water, it was to be expected that the bromine, wholly or partially eliminated as hydrobromic acid, would be replaced by the molecular residue of the water; and thus, independently of any mixed compounds containing bromine *and* oxygen, a series of salts might be looked for, in which a molecule $C_2H_4HO=C_2H_5O$ would enter monatomically, viz.—

$$[(C_2H_5O)\ H_3N]Br,$$
$$[(C_2H_5O)_2H_2N]Br,$$
$$[(C_2H_5O)_3H\ N]Br,$$
$$\text{and } [(C_2H_5O)_4\ \ N]Br.$$

Lastly, remembering the tendency exhibited by ethylene-compounds to resolve themselves, in presence of alkalies, into vinyl-compounds, it appeared not improbable that a fourth series of bodies would likewise be formed, viz.—

$$[(C_2H_3)\ H_3N]Br,$$
$$[(C_2H_3)_2H_2N]Br,$$
$$[(C_2H_3)_3H\ N]Br,$$
$$\text{and } [(C_2H_3)_4\ \ N]Br;$$

and thus was presented the not very inviting problem of separating from a great mass of bromide of ammonium, no fewer than sixteen different bases.

In the experiments on the action of dibromide of ethylene on ammonia and its homologues, which I hope to lay before the Royal Society in a special paper, I have indeed by no means met with the whole of these compounds; but in place of the deficient members of the groups, new products have made their appearance, whose formation in the present state of our knowledge could scarcely have been predicted. Without entering into details respecting these products, I will merely observe that I was induced, by the complication of this reaction, to subject dibromide of ethylene to the action of ethylamine, diethylamine, and finally of triethylamine instead of ammonia; for it could not be doubted that with the progressive substitution of ethyl for the hydrogen in ammonia, the process would be simplified, the number of possible products of reaction being considerably diminished. Ammonia indeed—omitting secondary products—is capable of producing not less than *sixteen* compounds, whereas ethylamine cannot yield more than *twelve*, diethylamine not more than *eight*, and, lastly, in the reaction between triethylamine and dibromide of ethylene the number of compounds possible under the most favourable circumstances is limited to *four*. Experiment has verified this anticipation; in the same proportion as the substitution advances in the ammonia submitted to the action, the number of products generated diminishes; nevertheless, the experiment with triethylamine, from which I had expected the simplest and clearest solution of my problem, did not entirely satisfy me, inasmuch as I did not succeed in obtaining more than *three* of the compounds out of the *four* which are indicated by theory. It was not indeed till I repeated the experiment in the phosphorus-series, using, instead of triethylamine, the corresponding phosphorus-base, that I succeeded in obtaining *all* the compounds, and that the results appeared as the pure expression of theory, undisturbed by accidental products. In its reaction with dibromide of ethylene, the sharply defined characters of triethylphosphine exhibit themselves with welcome distinctness; and in the products resulting from the action, the peculiar relations between monatomic and diatomic bases become perceptible with a degree of clearness and generality such as I have never observed in any similar reaction among bodies of the nitrogen-series. It is the smoothness of these reactions which renders it desirable to commence an account of a more general investigation of the diatomic bases with a description of the bodies belonging to the phosphorus-series.

ETHYLENE-GROUP.

Action of Dibromide of Ethylene on Triethylphosphine.

When these two bodies are brought together in quantities not too large, the liquid becomes turbid, but no rise of temperature takes place to indicate the occurrence of chemical action. The mixture, after being left to itself for a few hours, deposits white crystals, the formation of which continues till the entire liquid is converted into a white saline mass. If the mixture be even gently heated, the crystallization takes place instantaneously, and a violent reaction sets in, which is very apt to project a portion of the resulting salt from the vessel. In operating on rather a large scale in vessels filled with air, the heat evolved on agitation, in consequence of the oxidation of the phosphorus-base, is often sufficient to start the reaction.

In preparing considerable quantities of the white crystals, I have therefore found it convenient to add to the triethylphosphine twice its volume of ether, to mix the ethereal solution with the dibromide of ethylene in a flask filled with carbonic acid gas, and to heat the mixture in a water-bath, the flask being provided with an inverted cooling apparatus, so that the vapours which escape may be condensed and returned. Or, the mixture of triethylphosphine, dibromide of ethylene and ether may be introduced into long tubes previously drawn out, and the tubes, after sealing, be immersed for some hours in boiling water. As the value of dibromide of ethylene is trifling in comparison with that of triethylphosphine, I always used, in commencing the study of this reaction, the former substance in excess. The triethylphosphine is quickly fixed by the dibromide of ethylene, and the action may be considered as terminated when the presence of the free phosphorus-base in the mixture is no longer indicated by disulphide of carbon. As soon as this point is attained, the crystalline bromides may be thrown on a filter, the ether allowed to run off, and the crystals freed from excess of bromide of ethylene by washing them for a while with anhydrous ether, in which they are quite insoluble.

The crystals thus obtained dissolve with great facility in water and in ordinary alcohol, somewhat less readily in boiling absolute alcohol. This solution on cooling deposits well-developed crystals, which sustain a heat of 100° without decomposition, but show a slight tendency to deliquesce in the air. The analysis of these crystals, and their behaviour with reagents, showed unmistakeably that, in the action of dibromide of ethylene on triethylphosphine, two bromides at least are formed. The determination of the bromine by means of nitrate of silver in the products of different preparations, purified by successive crystallizations from alcohol, gave the following percentages of bromine:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Bromine . .	32·10	29·58	28·30	28·05	27·46	27·30	27·15	26·85	25·94.

On again repeating the crystallization, the amount of bromine precipitated by nitrate of silver did not exhibit any further diminution.

The complete analysis of the crystals, purified by a great number of crystallizations from alcohol, which will be given in a subsequent paragraph of the paper, has led me to the simple expression

$$C_8\,H_{19}\,P\,Br_2 = C_6\,H_{15}\,P + C_2\,H_4\,Br_2,$$

whence it appears that the body is produced by the combination of one molecule of triethylphosphine with one molecule of the bromine-compound.

The purification of the second substance, yielding with nitrate of silver a larger proportion of bromine, which remains in the mother-liquor of the compound just described, is somewhat complicated. As I shall have to return to this body in the description of the individual compounds, I content myself in this place with just setting forth the general character of the reaction by quoting the formula deduced from its examination. The analysis of this bromine-compound, together with those of a whole series of bodies derived from it, has led to the formula

$$C_{14}\,H_{34}\,P_2\,Br_2 = 2\,C_6\,H_{15}\,P + C_2\,H_4\,Br_2,$$

showing that the body is a compound of two molecules of triethylphosphine and one molecule of dibromide of ethylene.

These observations are sufficient to establish the peculiar nature of the reaction in question. There are clearly two successive phases to be distinguished, according as the bromide of ethylene lays hold of one or two molecules of triethylphosphine; secondary products may likewise be formed, which for the present may be left out of consideration, as I shall have to allude to them in the course of the memoir. It is, however, worth while to mention in this place that, when the experiment is made with pure substances, and under the conditions above mentioned, the two bromides described are almost the only products of the reaction.

These two bodies have become the starting-points of two extensive groups of compounds, which may even now be distinguished as the *series of monatomic compounds*, and the *series of diatomic compounds.*

I now proceed to the detailed description of the individual members of these series.

SERIES OF MONATOMIC COMPOUNDS. MONOPHOSPHONIUM COMPOUNDS.

Salts of Bromethyl-triethylphosphonium.

Bromide of Bromethyl-triethylphosphonium.—By this long name I designate the crystalline substance which is produced by the union of one molecule of dibromide of ethylene and one molecule of triethylphosphine. The preparation of this compound has already been given in the preceding paragraph. It is the chief product of the reaction when the dibromide of ethylene is in excess.

The equation

$$C_2 H_4 Br_2 + C_6 H_{15} P = C_8 H_{19} P Br_2$$

requires about 1 vol. of dibromide of ethylene to 1·5 vol. of triethylphosphine; but even when a larger quantity of the bromine-compound is *heated* with the phosphorus-base, both in presence or absence of ether or alcohol, we always obtain an appreciable quantity of the second bromide. It is only by allowing an *immense* excess of dibromide to act at the *common temperature* upon triethylphosphine, either in presence or absence of ether, that the formation of the second bromide is altogether avoided. In this reaction, which is not complete in less than twenty-four hours, a considerable quantity of gas is evolved, which does *not* appear when the substances are heated together.

To purify a product, which contains appreciable quantities of the second bromide, it is necessary to crystallize it at least three or four times from absolute alcohol; in the last crystallization it is desirable to mix the alcoholic solution with a moderate quantity of ether. The solution, if left to itself, frequently deposits separate well-defined crystals, which may be dried without decomposition at 100°, and which melt at about 235° with partial decomposition, hydrobromic acid being abundantly evolved. The bromide, purified in the manner just described, gave on analysis the following numbers:—

I. 0·5630 grm. of bromide gave 0·6521 grm. of carbonic acid and 0·3173 grm. of water.

II. 0·4926 grm. of bromide, precipitated by nitrate of silver, gave 0·3004 grm. of bromide of silver.

A simple experiment showed that nitrate of silver precipitates from this compound only part of the bromine. When the liquid filtered from the precipitated bromide of silver was mixed with carbonate of sodium, to remove the excess of silver, and evaporated, the residue, when ignited with lime and dissolved in nitric acid, gave, on addition of nitrate of silver, a fresh quantity of bromide of silver. I therefore endeavoured to obtain the entire quantity of bromine by means of recently precipitated oxide of silver, a process which I had previously found serviceable in similar cases. The result confirmed my anticipation. Digestion with oxide of silver removes the whole of the bromine, and shows that the quantity precipitated by nitrate of silver is only half the total amount.

III. 1·8445 grm. of bromide digested with oxide of silver, gave, after the removal of the excess of oxide of silver by nitric acid, 2·2635 grm. of bromide of silver.

These numbers lead to the formula

$$C_8\,H_{19}\,P\,Br_2,$$

as seen from the following comparison:—

	Theory.			Experiment.		
				I.	II.	III.
C_8	96	31·37		31·59	——	——
H_{19}	19	6·21		6·26	——	——
P	31	10·14		——	——	——
Br	80	26·14	52·28	——	25·94	52·22
Br	80	26·14		——	——	
	306	100·00				

The interpretation of these results presents no difficulty. The crystals are evidently the bromide of a monophosphonium in which 3 equivs. of ethyl are substituted for 3 equivs. of hydrogen, the last equivalent of hydrogen being replaced by a secondary radical, $C_2\,H_4\,Br$, which for the present I will call monobrominated ethyl or bromethyl.

The molecular formula

$$[(C_2\,H_4\,Br)\,(C_2\,H_5)_3\,P]\,Br$$

represents the constitution of this salt.

I have already observed that this bromide is occasionally obtained in well-defined crystals. They were examined by Quintino Sella, who has sent me the following description:—

"System monometric (regular).

The crystals exhibit the form of the rhombic dodecahedron 1 1 0 (Fig. 28). They are sometimes elongated so as to present the aspect of dimetric crystals, as in Fig. 29. Sometimes it even happens that one of the faces $\bar{1}\,1\,0$ is much more developed than the parallel face $1\,\bar{1}\,0$ (Fig. 30), so that scarcely more than half the crystal (Fig. 29) appears to exist. Sometimes the faces exhibit striæ parallel to the adjacent edges of the rhombic dodecahedron.

Fig. 28.

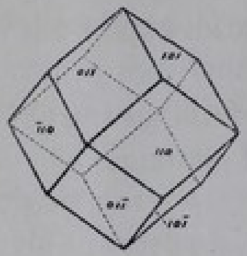


Fig. 29.

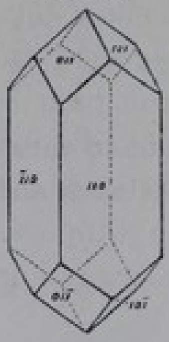
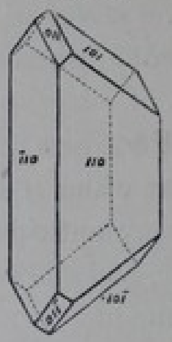


Fig. 30.



Lustre fatty.

Hardness inferior to that of gypsum.

The crystals have no action on polarized light."

By treating the bromide with silver-salts *in the cold*, the bromine external to the phosphonium-metal is replaced by the acid-radical united with the silver, while the bromine belonging to the phosphonium remains untouched. In this manner we obtain the salts of the new metal, which exhibit an inclination to unite with excess of the silver-salt, in the form of double compounds. The *chloride* and the *nitrate* prepared from the bromide by the action of chloride and nitrate of silver are extremely soluble in water and alcohol, and crystallize indistinctly. The *sulphate* forms long white crystalline needles, likewise very soluble in water and alcohol. It is very easily obtained by the action of sulphuretted hydrogen on the double salt which is formed by treating the bromide with sulphate of silver; on adding alcohol and ether to the concentrated liquid containing free sulphuric acid, it is precipitated in crystals. The sulphate, treated with iodide of barium, yields the *iodide*, a salt which dissolves sparingly in water, and crystallizes in scales of a pearly lustre.

I have not examined these salts more particularly, as they scarcely present any theoretical interest, and as the composition of the bromide, which forms the starting-point of the series, is sufficiently corroborated by the analysis of the platinum- and gold-salts.

Platinum-salt.—The chloride obtained by digesting the bromide with excess of chloride of silver is mixed with dichloride of platinum, when the platinum-salt is deposited on cooling in light orange-yellow prisms, frequently an inch in length. This salt is somewhat sparingly soluble in cold, more readily in boiling water, and may be crystallized without decomposition. During the recrystallizations, this salt, under circumstances not yet clearly made out, is occasionally obtained in crystals of an octohedral habitus.

This platinum-salt, though somewhat sparingly soluble, is nevertheless essentially different from the platinum-salt of the diphosphonium to be described hereafter, which accompanies the bromethyl-triethylphosphonium. The latter is nearly insoluble in water, and is precipitated from the most dilute solutions. This character forms a means of testing the purity of the monophosphonium-bromide in the succession of crystallizations to which it has to be submitted for the sake of purification. The salt is pure when the dilute solution, after being treated with chloride of silver, no longer gives a precipitate with dichloride of platinum.

I. 0·4593 grm. of platinum-salt gave 0·3854 grm. of carbonic acid and 0·1880 grm. of water.

II. 0·5397 grm. of platinum-salt gave 0·4515 grm. of carbonic acid and 0·2157 grm. of water.

III. 0·549 grm. of platinum-salt, fused with carbonate of sodium, gave 0·785 grm. of a mixture of bromide and chloride of silver and 0·1253 grm. of platinum.

These numbers fix the formula

$$C_8 H_{19} Br P Pt Cl_3 = [(C_2 H_4 Br)(C_2 H_5)_3 P] Cl, Pt Cl_2.$$

Theory.				Experiment.		
				I.	II.	III.
C_8	96	22·26		22·88	22·81	——
H_{19}	19	4·41		4·55	4·44	——
P	31	7·19		——	——	——
Br	80	18·55	43·25	——	——	43·11*
Cl_3	106·5	24·70		——	——	
Pt	98·7	22·89		——	——	22·82
	431·2	100·00				

As I have already mentioned, this platinum-salt can easily be obtained in fine long needles; they exhibit, however, but rarely well-formed terminal faces. Only once I succeeded in getting them somewhat better developed. These crystals were examined by Quintino Sella with the following results:—

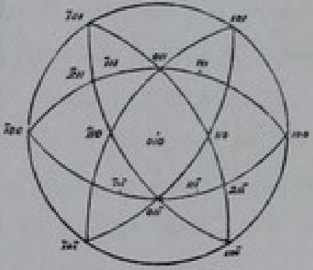
"System monoclinic:—

100, 101=55° 59′; 001, 101=33° 3′; 010, 111=60° 37′.

Forms observed:—

100, 010, 110, 101, $\bar{1}01$, 011, 111, $\bar{1}11$, $\bar{2}11$ (Fig. 31).

Fig. 31.



Angles.		Calculated.	Observed.
100, 010	=	90° 0′	—
100, 110	=	45 55	45 57
100, 101	=	55 59	55 51
100, $\bar{1}01$	=	122 40	122 40
100, 011	=	89 12	89 12
100, 111	=	60 50	61 1
100, $\bar{1}11$	=	117 56	117 50
100, $\bar{2}11$	=	137 4	136 54

---

* With the admissible assumption that the compound contains 3 equivs. of chlorine for 1 equiv. of bromine.

Angles.		Calculated.	Observed.
$010, 110$	=	44° 5′	° ′ ——
$010, 101$	=	90 0	——
$010, \bar{1}01$	=	90 0	——
$010, 011$	=	55 49	55 49
$010, 111$	=	60 37	——
$010, \bar{1}11$	=	60 14	——
$010, \bar{2}11$	=	67 30	——
$110, \bar{1}10$	=	88 11	88 7
$110, 101$	=	67 6	67 8
$110, \bar{1}01$	=	112 3	111 53
$110, 011$	=	65 35	65 29
$110, 01\bar{1}$	=	66 48	66 50
$110, 111$	=	46 15	46 6
$110, \bar{1}1\bar{1}$	=	89 14	——
$110, \bar{1}11$	=	88 15	——
$110, 11\bar{1}$	=	46 57	——
$110, \bar{2}11$	=	103 33	——
$110, 21\bar{1}$	=	38 21	——
$101, \bar{1}01$	=	66 41	66 49
$101, 011$	=	46 6	46 2
$101, 111$	=	29 23	29 18
$101, \bar{1}11$	=	69 54	——
$101, \bar{2}11$	=	86 42	——
$\bar{1}01, 011$	=	46 28	46 24
$\bar{1}01, 111$	=	69 49	——
$\bar{1}01, \bar{1}11$	=	29 46	——
$\bar{1}01, \bar{2}11$	=	29 36	——
$011, 01\bar{1}$	=	111 38	111 37
$011, 111$	=	28 22	28 11
$011, \bar{1}1\bar{1}$	=	109 11	——
$011, \bar{1}11$	=	28 44	28 36
$011, 11\bar{1}$	=	108 36	——
$011, \bar{2}11$	=	47 52	47 42

Angles.		Calculated.	Observed.
		° ′	° ′
$011, 21\bar{1}$	=	103 56	——
$111, \bar{1}1\bar{1}$	=	121 14	121 23
$111, \bar{1}11$	=	57 7	56 49
$111, 11\bar{1}$	=	93 12	——
$111, \bar{2}11$	=	76 14	75 53
$111, 21\bar{1}$	=	82 5	——
$\bar{1}11, 11\bar{1}$	=	120 28	——
$\bar{1}11, \bar{2}11$	=	19 7	19 4
$\bar{1}11, 21\bar{1}$	=	124 23	——
$\bar{2}11, 21\bar{1}$	=	134 59	——

According to NAUMANN:—

$$a:b:c=0{\cdot}6580:1:0{\cdot}9685; \quad \gamma=89^\circ\ 2'.$$

Forms observed:—

$\infty\bar{P}\infty$, $\infty\grave{P}\infty$, ∞P, $\bar{P}\infty$, $-\bar{P}\infty$, $\grave{P}\infty$, P, $-P$, $2\bar{P}2$.

According to WEISS:—

$$a:b:c=1:0{\cdot}9685:0{\cdot}6580; \quad a\,o\,c=90^\circ\ 58'.$$

Forms observed:—

$a:\infty b:\infty c$; $\infty a:b:\infty c$; $a:b:\infty c$; $a:\infty b:c$; $-a:\infty b:c$; $\infty a:b:c$; $a:b:c$; $-a:b:c$; $-\frac{1}{2}a:b:c$.

According to LEVY:—

$$\mathrm{M\,M}=88^\circ\ 11'; \quad \mathrm{M\,P}=90^\circ\ 40; \quad b:h=1:0{\cdot}4726.$$

Forms observed:—

h', g', M, o', a', e', $d^{\frac{1}{2}}$, $b^{\frac{1}{2}}$, a_3.

Fig. 32.

Fig. 33.

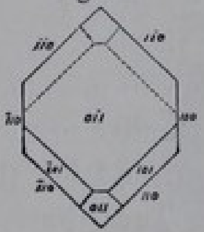
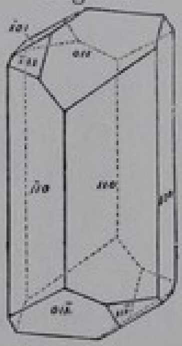


Fig. 34.



Combinations observed:—

$1 1 0, 0 1 1, 1 0 0;\ \ 1 0 1, \bar{1} 0 1$ (Figs. 32, 33).
$1 1 0, 0 1 1;\ \ 1 0 0, \bar{1} 1 1, \bar{1} 0 1$ (Fig. 34).
$1 1 0, 0 1 1;\ \ 1 0 0, \bar{1} 1 1, \bar{1} 0 1, \bar{2} 1 1$ (Fig. 35).
$1 1 0, \bar{1} 1 1;\ \ 1 0 0, \bar{1} 0 1, 0 1 1, 1 1 1$ (Fig. 36).
$1 1 0, 0 1 1;\ \ 1 0 0, 1 1 1; 1 0 1, \bar{1} 1 1, \bar{2} 1 1$ (Fig. 37).
$1 1 0, 0 1 1, 1 0 0;\ \ 0 1 0, 0 1 1, \bar{1} 0 1, \bar{2} 1 1$ (Figs. 38, 39).

Fig. 35.

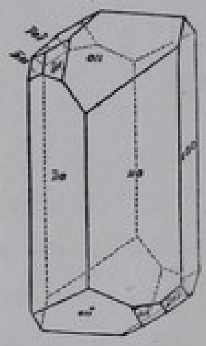
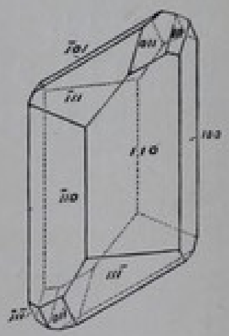


Fig. 36.



The faces $0 1 1$ are often very unequally developed, as seen in Figs. 32 and 33, and in Figs. 38 and 39; under these circumstances some of the faces of the forms $1 1 1$, $\bar{1} 1 1$, $\bar{2} 1 1$ are apt to disappear, as may be seen in Figs. 38 and 39.

Fig. 37.

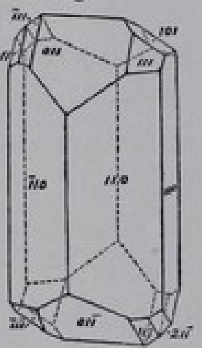
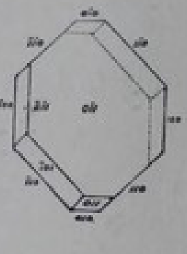


Fig. 38.

Fig. 39.



Cleavages: $1 0 0$, $1 1 0$. Lustre: vitreous.

Colour: orange with a tint of yellow in minute, and of red in larger, crystals.

The plane of the optical axes is parallel to the axis of symmetry [0 1 0], for rings are observed across the faces of the prism $1 1 0$, the centres of which are disposed symmetrically with regard to [0 1 0]. The principal medium-line is perpendicular to [0 1 0]."

Gold-salt.—Light yellow needles, difficultly soluble in cold water, recrystallizable from boiling water.

0·2394 grm. of gold-salt left on ignition 0·0841 grm. of gold.

The formula

$$C_8H_{19}BrPAuCl_4 = [(C_2H_4Br)(C_2H_5)_3P]Cl, AuCl_3$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	226	40·00	——
4 equivs. of Chlorine	142	25·13	——
1 equiv. of Gold	197	34·87	35·12
1 equiv. of Gold-salt	565	100·00	

I have in vain endeavoured to prepare the hydrate

$$C_8H_{20}BrPO = \left.\begin{matrix}[(C_2H_4Br)(C_2H_5)_3P] \\ H\end{matrix}\right\}O$$

belonging to these salts.

In quoting the analysis of the bromide, I have already mentioned that this salt, when treated with oxide of silver, gives up the whole of its bromine. On mixing the caustic liquid filtered from the silver-salt with hydrochloric acid and dichloride of platinum, we no longer obtain the sparingly soluble platinum-salt crystallizing in the characteristic needles; but the liquid, after being considerably concentrated by evaporation, yields well-defined, reddish-yellow octohedra belonging to another base. An exactly similar result is obtained on attempting to separate the base from the sulphate by means of baryta. After filtering off the sulphate of barium, there remains a strongly alkaline liquid, which likewise yields only the octohedral platinum-salt, while the presence of bromide of barium in the solution indicates the transformation of the original molecular system. The elimination of the second equivalent of bromine by silver-salts, which takes place instantly and completely in alkaline liquids, may likewise be effected by continual ebullition in neutral and even in acid solutions, though always slowly and incompletely. If the bromide be precipitated by excess of nitrate of silver, the filtered liquid, on being boiled and evaporated, deposits a fresh quantity of bromide of silver; but in most cases, even after long-continued boiling, a considerable quantity of bromine remains latent, and may be immediately recognized by again filtering the liquid and slightly supersaturating it with ammonia, the whole of the remaining bromine being then precipitated as bromide of silver. This deportment furnishes in fact a characteristic distinction of the bromethylated bromide, by which this substance may often be conveniently recognized. It deserves to be remarked that the fixed caustic alkalies exert but a slight action on the bromethylated bromide; the compound is precipitated by the alkalies from its cold aqueous solution in the crystalline state and without decomposition, and it is only after some time that alterations take place, probably affecting its intimate constitution. The nature of these alterations has not yet been made out. The crystals may be boiled for some time with alcoholic solution of potassa without decomposition. The bromide likewise suffers no alteration by continued digestion with water or alcohol at 100°.

SALTS OF OXETHYL-TRIETHYLPHOSPHONIUM.

Iodide.—When the caustic liquid produced by treating the bromide of bromethyl-triethylphosphonium with oxide of silver is neutralized with hydriodic acid and the solution evaporated, an iodide is obtained which crystallizes in needles, and dissolves very readily in water and alcohol. The finest crystals are obtained by mixing the alcoholic solution with ether till it becomes opalescent, and then allowing it to crystallize. If too much ether has been added, the new iodide is precipitated as an oil, which solidifies but slowly to a crystalline mass. The salt becomes coloured at 100°, and must therefore be dried *in vacuo.*

I. 0·3003 grm. of iodide gave 0·3615 grm. of carbonic acid and 0·1890 grm. of water.
II. 0·4665 grm. of iodide gave 0·5760 grm. of carbonic acid and 0·2832 grm. of water.
III. 0·3705 grm. of iodide gave 0·2990 grm. of iodide of silver.
IV. 0·2970 grm. of iodide gave 0·2427 grm. of iodide of silver.
V. 0·4080 grm. of iodide gave 0·3344 grm. of iodide of silver.

These numbers lead to the formula

$$C_8H_{20}OPI = [(C_2H_5O)(C_2H_5)_3P]I,$$

which requires the following values:—

Theory.			Experiment.				
			I.	II.	III.	IV.	V.
C_8	96	33·10	32·84	33·67	——	——	——
H_{20}	20	6·90	6·99	6·74	——	——	——
O	16	5·51	——	——	——	——	——
P	31	10·69	——	——	——	——	——
I	127	43·80	——	——	43·62	44·16	44·28
	290	100·00					

The transformation of the bromethylated phosphonium takes place, therefore, exactly as might be expected from analogy, the bromine being eliminated as bromide of silver, and its place being taken by the molecular residue of the water:—

$$[(C_2H_4Br)(C_2H_5)_3P]Br + Ag_2O + H_2O = 2AgBr + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O.$$

Hydrate.—The caustic solution of the oxide exhibits the usual characteristic properties of this class of bodies. Over sulphuric acid, the solution thickens to a syrupy, extremely deliquescent mass, from which the base separates in oily drops on addition of potassa. Its decomposition by heat is characteristic; at a rather high temperature, it is resolved into oxide of triethylphosphine, ethylene, and water:—

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O = (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The oxide of triethylphosphine was identified by the preparation of its platinum-salt; the ethylene, by converting it into the bromide.

The above equation represents the final result of the action of heat; this final result, however, is preceded by several intermediate changes, to which I shall return in a subsequent chapter of this paper.

Bromide.—Extremely soluble. Dries up over sulphuric acid to an indistinct crystalline mass.

Chloride.—This compound resembles the bromide in every respect. Both these salts readily form double compounds with iodide and bromide of zinc. The chloride, under the influence of pentabromide and pentachloride of phosphorus, undergoes remarkable transformations, to which I shall presently recur.

Perchlorate.—Laminæ somewhat sparingly soluble in cold water.

I have not analysed any of these salts, inasmuch as the composition of this series of compounds is sufficiently established by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—The alkaline solution, from which the iodide was obtained, yields, when saturated with hydrochloric acid, mixed with dichloride of platinum, and evaporated, the above-mentioned platinum-salt, crystallizing in well-developed octohedra, the measurements of which I subjoin. It is easily soluble in hot water, and may be recrystallized without decomposition.

Its composition is

$$C_8H_{20}OPPtCl_3 = [(C_2H_5O)(C_2H_5)_3P]Cl, PtCl_2,$$

as appears from the following analysis:—

I. 0·4626 grm. of platinum-salt gave 0·4510 grm. of carbonic acid and 0·2217 grm. of water.

II. 0·5278 grm. of platinum-salt, when fused with carbonate of sodium, gave 0·1408 grm. of platinum and 0·6175 grm. of chloride of silver.

III. 0·5195 grm. of platinum-salt gave 0·1405 grm. of platinum and 0·6110 grm. of chloride of silver.

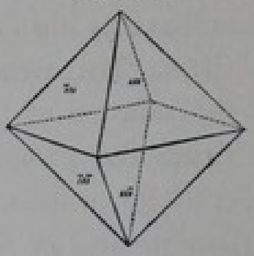
IV. 1·3105 grm. of platinum-salt, precipitated with hydrosulphuric acid, gave 0·3522 grm. of platinum.

The several salts analysed were of different preparations. The specimen submitted to analysis IV. was obtained under particular conditions, to which I shall return hereafter.

Theory.			Experiment.			
			I.	II.	III.	IV.
C_8	96	26·07	26·58	——	——	——
H_{20}	20	5·43	5·32	——	——	——
O	16	4·35	——	——	——	——
P	31	8·42	——	——	——	——
Pt	98·7	26·81	——	26·68	27·04	26·87
Cl_3	106·5	28·92	——	28·94	29·08	——
	368·2	100·00				

The following are the details of QUINTINO SELLA's measurements:—

Fig. 40.



"System monometric:—

Forms observed:—

111 (Fig. 40).

Angles.		Calculated.	Observed.
$111, 11\bar{1}$	=	70° 32′	70° 7′
$11\bar{1}, \bar{1}1\bar{1}$	=	70 32	70 33
$\bar{1}1\bar{1}, \bar{1}11$	=	70 32	70 16
$\bar{1}11, 111$	=	70 32	71 4
$111, \bar{1}1\bar{1}$	=	109 28	109 32
$\bar{1}11, 11\bar{1}$	=	109 28	109 44

The octohedra are generally very minute. The crystals have no sensible influence on polarized light. Colour orange."

Gold-salt.—Golden-yellow needles, sparingly soluble in cold, readily in boiling water; in a quantity of boiling water not sufficient to dissolve them, they fuse to a transparent yellow oil. Not decomposed by recrystallization. Precipitated by trichloride of gold from a moderately concentrated solution of the chloride.

0·630 grm. of gold-salt, precipitated with hydrosulphuric acid, &c., gave 0·2475 grm. of gold.

The formula

$$C_8 H_{20} O P Au Cl_4 = [(C_2 H_5 O)(C_2 H_5)_3 P] Cl, Au Cl_3$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium .	163	32·48	——
4 equivs. of Chlorine	142	28·28	——
1 equiv. of Gold	197	39·24	39·28
1 equiv. of Gold-salt	502	100·00	

I have already alluded to the decomposition which the chloride of the oxethylated phosphonium undergoes under the influence of pentabromide of phosphorus. The two bodies act upon one another with great violence; oxybromide of phosphorus and hydrobromic acid are evolved, and the residue is found to contain the chloride of the bromethylated phosphonium from which the oxethylated compound was originally produced.

$$[(C_2 H_5 O)(C_2 H_5)_3 P] Cl + P Br_5 = P O Br_3 + H Br + [(C_2 H_4 Br)(C_2 H_5)_3 P] Cl.$$

Nothing is easier than to obtain experimental proof of this transformation, which is of considerable theoretical interest. After the oxybromide and the excess of pentabromide have been removed as completely as possible by evaporation, the remaining liquid yields, on addition of dichloride of platinum, a sparingly soluble, still impure platinum-salt, which, after washing, may be decomposed by sulphuretted hydrogen and thereby purified. If the chloride thus formed be precipitated with excess of nitrate of silver, and the nitrate of the base, filtered from the chloride of silver, be mixed with ammonia and gently heated, a copious precipitate is immediately formed, consisting of bromide of silver. This reaction is characteristic of the bromethylated body. Moreover, on mixing the solution of the nitrate freed from silver with dichloride of platinum, and recrystallizing the platinum-precipitate from boiling water, the liquid yields on cooling the splendid needles of the platinum-salt of the bromethylated triethylphosphonium. The analysis of this salt was omitted, partly because no doubt could be entertained respecting its nature, and partly because I had occasion to establish by a number—as will be noticed hereafter—the nature of the precisely similar reaction between chloride of oxethyl-triethylphosphonium and pentachloride of phosphorus.

Thus it is seen that the molecular group C_2H_5O, which is supposed to replace the hydrogen in the salt, suffers, under the influence of pentabromide of phosphorus, alterations exactly similar to those which it would have undergone under similar circumstances when conceived as a constituent of alcohol.

If we consider the facility with which the bromethylated phosphonium is converted into the oxethylated compound by the action of oxide of silver, and the simple re-formation of the first-mentioned body by means of pentabromide of phosphorus, a great variety of new experiments suggest themselves. In reviewing the relations which obtain between the bromethylated and oxethylated phosphoniums, who could fail to perceive that the two hydrogen-replacing radicals, which constitute the difference between these two organic metals, stand to one another in the same relation as bromide of ethyl and alcohol, or bromide of acetyl and acetic acid? But if this be so, what a number of new bodies does this consideration bring into view, even if we limit our calculation to the transformations of which the molecular group C_2H_5O in alcohol is susceptible! As yet I have scarcely penetrated into this new field of inquiry, and I must be satisfied to quote a single experiment, which exhibits the above-mentioned bodies in a new light. The salts of bromethylated and oxethylated triethylphosphonium may be regarded as tetrethylphosphonium salts, in which an atom of hydrogen is replaced by bromine and the radical HO respectively:

Bromide of tetrethylphosphonium	$[(C_2H_4H)(C_2H_5)_3P]Br$,
Bromide of bromethylated triethylphosphonium .	$[(C_2H_4Br)(C_2H_5)_3P]Br$,
Bromide of oxethylated triethylphosphonium . .	$[(C_2H_4HO)(C_2H_5)_3P]Br$;

and the question arose whether the bromethylated salt might not be converted by a simple process into the tetrethylphosphonium-compound. This transformation may indeed be effected without the slightest difficulty. On acidulating the solution of the bromethylated bromide with sulphuric acid, and digesting it with granulated zinc, the bromine is eliminated in the form of hydrobromic acid, its place being filled up by one equivalent of hydrogen:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + H_2 = HBr + [(C_2H_5)_4P]Br.$$

By decanting the liquid from the excess of zinc and treating it with oxide of silver, oxide of zinc, bromine and sulphuric acid are removed, and a solution of oxide of tetrethylphosphonium is obtained, which, when mixed with hydrochloric acid and dichloride of platinum, yields well-developed octohedra of the platinum-salt of tetrethylphosphonium.

0·444 grm. of this salt, decomposed by hydrosulphuric acid, yielded &c., 0·1240 grm. of platinum.

The formula

$$C_8H_{20}PPtCl_3 = [(C_2H_5)_4P]Cl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Tetrethylphosphonium	147·0	41·75	——
1 equiv. of Platinum	98·7	28·02	27·93
3 equivs. of Chlorine	106·5	30·23	——
1 equiv. of Platinum-salt	352·2	100·00	

The chloride obtained in the analysis was converted, by successive treatment with oxide of silver and hydriodic acid, into the corresponding iodide. This characteristic salt appeared on careful comparison exactly similar to the iodide of tetrethylphosphonium prepared in the ordinary way.

Here, then, we have an instance of the direct reproduction of an ethyl-compound from a body of the ethylene-group by a simple process of reduction. Similar transformations would doubtless succeed in many other cases, and this is perhaps a fitting opportunity of directing attention to the interest which the employment of this reaction would have in connexion with the intermediate hydrochloric glycol-ether discovered by WURTZ. Probably this compound, when subjected to the action of nascent hydrogen, would be directly converted into alcohol:

$$(C_2H_4)''\left\{\begin{matrix}HO\\Cl\end{matrix}\right. = C_2H_5ClO,$$

$$(C_2H_4)''\left\{\begin{matrix}HO\\H\end{matrix}\right. = C_2H_6O;$$

and when considered with reference to this decomposition, would appear as monochlorinated alcohol.

It was chiefly the facility with which a tetrethylphosphonium-compound may be obtained from the bromethylated bromide that induced me to designate the hydrogen-replacing molecules C_2H_4Br and C_2H_5O, which we meet in the compounds above described, as *bromethyl* and *oxethyl*. I was anxious to submit the ideas which guided me in the selection of these terms to the test of experiment. We know from the experiments of REGNAULT, that dichloride of ethylene and monochlorinated chloride of ethyl are essentially different bodies; and not less distinct are dibromide of ethylene and monobrominated bromide of ethyl, which I have obtained in the course of these experiments by the action of bromine on bromide of ethyl. But, on the other hand, the allied members of these two pairs of bodies are so closely related to each other, that, under the influence of powerful reagents, they not unfrequently yield exactly the same products of transformation. I may here refer especially to an interesting experiment of Beilstein, who has shown that dichloride of ethylene and monochlorinated chloride of ethyl, when treated with alcoholic potassa, undergo the same decomposition: both these compounds give up hydrochloric acid, being converted into chloride of vinyl.

The denomination, *bromethyl-triethylphosphonium*, which I have adopted for the metal produced by the action of dibromide of ethylene on triethylphosphine, involves to a certain extent the assumption that this body might also, under favourable circumstances, be produced by the mutual action of triethylphosphine and monobrominated bromide of ethyl. In a subsequent chapter of this inquiry I shall have an opportunity of showing how far this assumption is established by experiment.

Salts of Vinyl-triethylphosphonium.

In tracing the history of the salts of bromethyl-triethylphosphonium, I have mentioned that these substances lose their latent bromine, though slowly, when boiled with silver-salts. I was curious to ascertain whether this reaction involves the same metamorphosis which the bromethylated body undergoes under the influence of oxide of silver.

In the anhydrous condition, the bromethylated bromide acts but slowly on acetate of silver. In the presence of alcohol or water, the reaction is soon accomplished at 100° C. The liquid filtered from the bromide of silver yields no further precipitate on addition of ammonia, showing that the whole of the bromine is eliminated. When evaporated with hydrochloric acid, the liquid abundantly evolves acetic acid. After sufficient concentration, it yields with dichloride of platinum a fine octohedral salt, which may be purified by crystallization.

I. 0·4222 grm. of platinum-salt gave 0·4203 grm. of carbonic acid and 0·2017 grm. of water.

II. 0·4215 grm. of platinum-salt of a new preparation gave 0·4267 grm. of carbonic acid and 0·1990 grm. of water.

III. 0·9430 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·2660 grm. of platinum.

IV. 0·7115 grm. of platinum-salt gave 0·2015 grm. of platinum.

V. 0·3625 grm. of platinum-salt gave 0·1020 grm. of platinum.

VI. 0·6354 grm. of platinum-salt gave 0·1785 grm. of platinum.

VII. 0·5585 grm. of platinum-salt gave 0·1590 grm. of platinum.

VIII. 0·3675 grm. of platinum-salt gave 0·1025 grm. of platinum and 0·451 grm. of chloride of silver.

The percentages derived from these experiments characterize the compound

$$C_8 H_{18} P Pt Cl_3 = [(C_2 H_3)(C_2 H_5)_3 P] Cl, Pt Cl_2,$$

which requires the following values:—

Theory.			Experiment.							
			I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C_8	96	27·41	27·15	27·61	——	——	——	——	——	——
H_{18}	18	5·14	5·30	5·24	——	——	——	——	——	——
P	31	8·85	——	——	——	——	——	——	——	——
Pt	98·7	28·19	——	——	28·20	28·33	28·13	28·09	28·47	27·89
Cl_3	106·5	30·41	——	——	——	——	——	——	——	30·39
	350·2	100·00								

It is thus seen that the action of silver-salts—at all events of acetate of silver—upon the bromethylated bromide differs from that of oxide of silver. While the latter gives rise to the formation of an oxethylated phosphonium, the former produces a phosphoretted metal in which three atoms of ethyl are associated with one atom of the radical C_2H_3, which may be termed vinyl. The product, then, which is formed by the action of acetate of silver upon the bromethylated bromide is the acetate of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + 2\left(\left.\begin{matrix}C_2H_3O\\Ag\end{matrix}\right\}O\right) = 2AgBr + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O + \left.\begin{matrix}C_2H_3O\\ [(C_2H_3)(C_2H_5)_3P]\end{matrix}\right\}$$

I have been satisfied to establish the formation and composition of the vinyl-compound by a careful and frequently repeated analysis of the platinum-salt, which had been obtained from the products of four different operations. The salts of vinyl-triethylphosphonium resemble the oxethylated compounds. I have prepared the iodide, which crystallizes, but is extremely soluble even in absolute alcohol.

I have observed the formation of vinyl-compounds in several other processes, which may here be briefly mentioned, although I must state at once that the experimental evidence on which these observations are based is less conclusive.

The oxethylated compound differing from the vinyl-triethylphosphonium-salt simply by the elements of one molecule of water, which the latter contains less, the question naturally suggested itself whether, under the influence of heat, the oxethylated compound might not be converted into the vinyl-body. The results of two experiments appear to answer this question in the affirmative. In one case the bromide of bromethyltriethylphosphonium had been boiled for a considerable time with oxide of silver. The product of the reaction, converted into a platinum-salt, gave the following numbers:—

I. 0·6956 grm. of platinum-salt, ignited with carbonate of sodium, gave 0·1985 grm. of platinum and 0·8528 grm. of chloride of silver.

In another experiment, performed chiefly with the view of studying the action of heat upon the oxethylated base, a concentrated solution of the latter was evaporated in a capsule over an open flame until a very appreciable quantity was entirely decomposed. The residue was saturated with hydrochloric acid and precipitated with dichloride of platinum. A difficultly soluble amorphous platinum-salt was thrown down, at which I shall glance again in a subsequent chapter of this paper, and the mother-liquor furnished an octohedral platinum-salt, which was crystallized from boiling water and submitted to analysis.

II. 0·4180 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1180 grm. of platinum.

These numbers characterize the vinyl-compound.

	Vinyl-compound.	Oxethyl-compound.	Experiment.	
			I.	II.
Platinum	28·19	26·81	28·53	28·23
Chlorine	30·41	28·92	30·33	——

I must, however, add at once, that I failed to reproduce this result in repeating the experiment in a somewhat different manner. Oxide of oxethyl-triethylphosphonium was evaporated in a retort until a considerable quantity of the difficultly soluble amorphous platinum-salt was obtained on addition of dichloride of platinum. The mother-liquor of this salt furnished on evaporation well-formed octohedra.

0·3592 grm. of this platinum-salt gave 0·3447 grm. of carbonic acid and 0·1752 grm. of water.

This result shows that the oxethylated compound had not been changed.

	Vinyl-compound.	Oxethyl-compound.	Experiment.
Carbon	27·41	26·07	26·17
Hydrogen . . .	5·14	5·43	5·42

The temperature in this experiment had never risen above 150° C., which may account for the stability of the oxethylated body under the circumstances.

The vinyl-compound appears to be formed also by the action of heat upon the bromethylated bromide:

$$[(C_2H_4Br)(C_2H_5)_3P]Br = [(C_2H_3)(C_2H_5)_3P]Br + HBr$$

Torrents of hydrobromic acid are evolved, and the residue yields, after treatment with chloride of silver, on addition of dichloride, an octohedral platinum-salt. The decomposition is, however, completed only with difficulty. The evolution of hydrobromic acid continues for hours, even when the salt is kept at a temperature (between 235° and 250°), at which considerable quantities are entirely decomposed. I have thus been prevented from procuring an amount of the salt sufficient for its identification with the vinyl-compound obtained by the action of acetate of silver.

Vinyl-triethylphosphonium-salts are formed in one or two other reactions, which will be noticed in subsequent paragraphs of this inquiry.

SERIES OF DIATOMIC COMPOUNDS. DIPHOSPHONIUM COMPOUNDS.

SALTS OF ETHYLENE-HEXETHYL-DIPHOSPHONIUM.

Dibromide.—The occurrence of this salt among the products of the action of dibromide of ethylene on triethylphosphine has already been mentioned in the introduction to the experimental part of the memoir. On bringing together the materials in the proportions indicated by the equation

$$C_2H_4Br_2 + 2C_6H_{15}P = C_{14}H_{34}P_2Br_2,$$

that is to say, one volume of dibromide of ethylene and three volumes of the phosphorus-base, the diatomic compound is obtained, nearly in the theoretical quantity. It is distinguished from the monatomic product of the same reaction by its much greater solubility even in absolute alcohol, from which it separates, only after almost complete evaporation, in needles which are permanent in the air. In ether this salt is insoluble, as are in fact most of the bromides of the phosphorus-bases, both monatomic and diatomic. The dibromide obtained by the direct action of dibromide of ethylene on triethylphosphine always contains a small quantity of the monatomic bromide, from which it can only be purified with great difficulty. And further, if the dibromide of ethylene has not been carefully purified from adhering hydrobromic acid, the resulting salt is likewise contaminated with traces of the extremely soluble hydrobromate of the phosphorus-base, the presence of which likewise interferes very much with the purification of the product. Lastly, the formation of oxide of triethylphosphine can never be entirely avoided, even when the operation is conducted in an atmosphere of carbonic acid. To obviate these inconveniences, the compound submitted to analysis was prepared by saturating the hydrate, to be presently described, with hydrobromic acid.

I. 0·4837 grm. of bromide gave 0·7091 grm. of carbonic acid and 0·3543 grm. of water.
II. 0·4850 grm. of bromide gave 0·4300 grm. of bromide of silver.

The simplest expression of these results is the formula

$$C_7H_{17}PBr;$$

the formation of the compound, however, and its deportment, fully to be discussed in the following paragraphs, prove unmistakeably that this expression must be doubled, and that the weight and composition of the molecule of this body is represented by the formula

$$C_{14}H_{34}P_2Br_2.$$

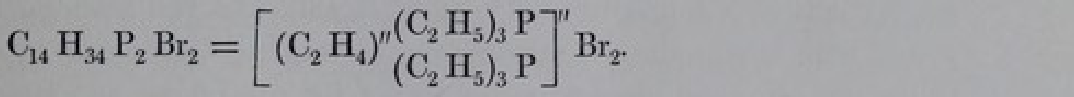
	Theory.		Experiment. I.	Experiment. II.
C_{14}	168	39·62	39·98	——
H_{34}	34	8·02	8·13	——
P_2	62	14·62	——	——
Br_2	160	37·74	——	37·71
	424	100·00		

On comparing the composition of the two bromides which are formed from dibromide of ethylene by the fixation of one or two molecules of triethylphosphine, it could scarcely be doubted that the monatomic compound, even when already formed, must still be in a condition to take up the second molecule of triethylphosphine, and thus to pass into the diatomic bromide. The correctness of this supposition is easily established by experiment. The monatomic bromide acts strongly, even at ordinary temperatures, on a fresh quantity of the phosphorus-base, being transformed, with evolution of heat, into the diatomic compound

$$C_8 H_{19} P Br_2 + C_6 H_{15} P = C_{14} H_{34} P_2 Br_2.$$

In presence of alcohol and at 100°, the reaction is completed in a few seconds. With lively interest have I followed up the result of this simple experiment; for its success obviously pointed to a source from which an almost incalculable number of diatomic compounds of the most varied composition might be obtained. For this reason I have not omitted to establish by numbers the conversion of the monatomic into the diatomic bromide, and in the following sections I shall have frequent occasion to cite analytical results, which leave no doubt as to the facility of this transformation.

The molecular constitution of the new bromide is satisfactorily represented by the formula



$$C_{14} H_{34} P_2 Br_2 = \left[(C_2 H_4)'' \begin{matrix} (C_2 H_5)_3 P \\ (C_2 H_5)_3 P \end{matrix} \right]'' Br_2.$$

The salt is derived from a diatomic metal, a diphosphonium, in which 6 equivs. of hydrogen are replaced by 6 equivs. of ethyl, and the remaining 2 equivs. of hydrogen by the radical ethylene indivisible under the given circumstances. It is the diatomic character of the ethylene that links together the two molecules of triethylphosphine, and gives to the new molecular system the necessary stability.

The dibromide is very easily attacked by silver-compounds, and in this manner an extensive series of very sharply characterized diphosphonium-salts may be obtained, many of which crystallize remarkably well. In these reactions, however, a tendency towards the formation of double compounds is frequently observed, and hence it is for the most part better to prepare the salts by treating the free base with the corresponding acids.

In examining the dibromide, I have made some observations which I may take an opportunity of pursuing further by and by. When the aqueous solution of this salt is mixed with bromine-water, very beautiful yellow needles are immediately separated, consisting of a polybromide. These needles may be recrystallized from boiling water, but, it appears, not without decomposition. They have but an ephemeral stability. On boiling the compound, bromine continues to be evolved, and ultimately the original bromide is left behind. Polybromides, of exactly similar character, are formed by the action of bromine on the bromides of all the ammonium- and phosphonium-bases that I have examined.

I have already pointed out that, in fixing one molecule of triethylphosphine to form the compound

$$[(C_2H_4Br)(C_2H_5)_3P]Br,$$

dibromide of ethylene exhibits a deportment which might have been expected from bromide of bromethyl, with which it is isomeric. It was of some interest to examine, experimentally, the behaviour of triethylphosphine with monobrominated bromide of ethyl. This substance had never been prepared. I have obtained it, together with the dibrominated bromide of ethyl $(C_2H_3Br_2)Br$, by submitting bromide of ethyl to the action of dry bromine under pressure at a temperature of 180° C. Brominated bromide of ethyl is a heavy aromatic oil, boiling at 110° C., and consequently differing altogether from dibromide of ethylene, which boils at 130° C., and with which it is isomeric. The brominated bromide attacks the phosphorus-base much more slowly than the dibromide; the final result, however, is exactly the same, the bromide of the bromethylated monophosphonium and the dibromide of the ethylene-diphosphonium being produced. The former of these salts is obtained in comparatively small quantity, and I was therefore unable to identify the compound in question with the bromethylated bromide formed by means of the ethylene-compound, otherwise than by the characteristic reaction with silver-salts, mentioned in an earlier paragraph of this paper. The diphosphonium-compound, on the other hand, is easily produced from brominated bromide of ethyl in sufficiently large quantity. I had no difficulty in establishing the absolute identity of this compound with the product obtained from dibromide of ethylene, by a careful comparison of the chemical and physical properties of the substances, and moreover by the analysis of a di-iodide and a platinum-salt prepared by means of the bromide-of-ethyl-derivative. These analyses are given among the analytical details establishing the composition of these salts.

Dihydrate.—The free base is easily obtained by the action of oxide of silver on the dibromide, or better on the di-iodide, which latter is, of all the diphosphonium-compounds of this class, the easiest to obtain in the pure state. If the alcoholic solution of the crude dibromide be used in this experiment, the first portions of oxide of silver added to the liquid are completely dissolved, and the solution, which has already become alkaline, deposits a white crystallized double compound of the dibromide with bromide of silver, which, however, is completely decomposed by further addition of oxide of silver and dilution with water. In this manner there is produced an extremely caustic, nearly odourless liquid, having a strongly alkaline taste, and exhibiting the same bitterness which is so often observed in the analogous bodies of the nitrogen-series. In other respects, the base exhibits the properties which characterize the hydrates of tetrethylphosphonium* and tetrethylammonium†. The solution, when evaporated in an open vessel, rapidly absorbs carbonic acid, and ultimately yields a semi-crystalline mixture of dihydrate and carbonate. When evaporated *in vacuo* over sulphuric acid, the caustic solution gradually dries up to a syrupy, extremely deliquescent mass, which exhibits no traces of crystallization. On mixing the highly concentrated solution of the dihydrate

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* Philosophical Transactions, 1857, Part II. p. 583.

† Ibid. 1851, Part II. p. 357.

with solution of potassa, the base is separated from the liquid in oily drops, which are, however, readily dissolved on addition of water. The free base, like the corresponding monophosphonium- and even monammonium-compounds, cannot therefore be obtained in a state fit for analysis; its formation, however, as well as its conversion into a series of well-defined salts corresponding to the dibromide, characterize it as an oxide derived from the type,

$$\left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2,$$

as the hydrated dioxide of ethylene-hexethyl-diphosphonium:

$$C_{14}H_{36}P_2O_2=\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]''\\H_2\end{matrix}\right\}O_2.$$

Complicated as the construction of this compound must appear, the body is remarkable for its stability. Its solution may be boiled and considerably concentrated upon the water-bath without decomposition, and remains unchanged even when exposed for some time under pressure to a temperature of 150°; indeed the decomposition of the hydrate does not begin till the liquid is evaporated to dryness. The changes which this compound suffers under the influence of higher temperatures are not without interest. They are rather intricate, and I propose therefore to devote a special paragraph to their study.

In its deportment with metallic salts, the hydrate of the diphosphonium closely resembles the fixed alkalies, as may be seen from the following Table:—

Deportment of the Hydrate of the Diphosphonium with reagents.

Barium-salts Strontium-salts Calcium-salts Magnesium-salts	White precipitates of the hydrates.
Aluminium-salts	White precipitate of hydrate of aluminium, soluble in excess of the precipitant.
Chromium-salts	Green precipitate of hydrate of chromium, soluble in an excess of the precipitant, and reprecipitated on ebullition.
Nickel-salts	Apple-green precipitate of the hydrate.
Cobalt-salts	Blue precipitate of the hydrate.
Iron-salts:—	
Ferrosum	Greenish precipitate of the hydrate.
Ferricum	Reddish-brown precipitate of the hydrate.
Zinc-salts	White gelatinous precipitate of the hydrate, insoluble in excess.
Lead-salts	White amorphous precipitate of hydrate of lead, soluble in excess.
Silver-salts	Black-brown precipitate of oxide of silver.
Mercury-salts:—	
Mercurosum	Black precipitate of the suboxide.
Mercuricum	Yellow precipitate of the oxide.

Copper-salts	Light blue precipitate of the hydrate, insoluble in excess: in presence of sugar, the precipitate dissolves in excess, forming an azure-blue solution, from which, if glucose has been employed, a red precipitate of suboxide of copper separates on ebullition.
Cadmium-salts Bismuth-salts	White precipitates of the hydrates.
Tin-salts:—	
Stannosum:—	
Chloride, containing free hydrochloric acid	White acicular precipitate of a double compound.
Stannicum:—	
Chloride	White gelatinous precipitate, extremely soluble in excess.
Antimony-salts:—	
Trichloride	White acicular precipitate of a double compound.
Gold-salts:—	
Trichloride	Golden-yellow crystalline precipitate of a double compound.
Platinum-salts:—	
Dichloride	Pale-yellow, slightly crystalline precipitate of a double compound.

These are, with few exceptions, the reactions of a solution of potassa. It is scarcely necessary to add that the hydrate of the diphosphonium expels, even at the common temperature, ammonia, phenylamine, triethylphosphine, and a considerable number of other amines and phosphines from their saline combinations.

The free base exhibits the deportment of caustic potassa also towards iodine and sulphur. It dissolves crystals of *iodine* with facility; the colourless solution is neutral, and yields on evaporation a syrup-like half-crystalline mass, easily recognized as a mixture of the di-iodide with the di-iodate. Treatment with alcohol separates the crystals of the more difficultly soluble iodide from the gummy iodate. On adding concentrated hydrochloric acid to the liquid obtained by dissolving iodine in the free base, a dark-coloured substance (iodine or a periodide) is separated; after a few seconds, however, the liquid is decolorized and solidifies to a mass of beautiful lemon-yellow crystals. The diphosphonium-salts are thus seen to exhibit phenomena exactly similar to those which were observed by Weltzien in the case of the compounds of tetramethyl- and tetrethyl-ammonium. I hope to find an opportunity of returning to a more minute examination of the yellow compound, which, by recrystallization from boiling alcohol, may be obtained in splendid needles, and which will probably be found to be a compound of the di-iodide with chloride of iodine. For the present I may remark that similar compounds are formed by all the bases of the type ammonium and diammonium which I have examined, provided they belong to that class in which the substitution is complete. A variety of monophosphonium- and monarsonium-salts, and lastly of compounds of phosphammoniums and phospharsoniums, submitted to the same process, have furnished perfectly similar results. Hydrochloric acid occasionally produces crystalline precipitates in the concentrated solutions of the iodates, even of bases containing unreplaced hydrogen; these precipitates disappear, however, on addition of water, or on gently warming, and are essentially different from the compounds previously mentioned. *Sulphur* dissolves in a concentrated solution of the dihydrate, although with difficulty, to a yellow liquid, which precipitates the black sulphide from lead-solutions, and is decomposed by acids, with separation of sulphur and evolution of sulphuretted hydrogen. *Phosphorus* is not attacked by the solution of the hydrate, not a trace of phosphoretted hydrogen being evolved even by protracted ebullition.

Disulphhydrate.—The solution of the base saturated with hydrosulphuric acid, when allowed to remain for some time over sulphuric acid *in vacuo*, dries up to a gummy mass, which exhibits as little inclination to crystallize as the dihydrate itself. When evaporated on the water-bath in contact with the air, the disulphhydrate is decomposed, the sulphur being oxidized; ultimately an imperfect crystallization of the sulphate remains behind.

Dichloride.—This salt is easily obtained by treating the dibromide or the di-iodide with chloride of silver, and also by saturating the free base with hydrochloric acid; it is extremely soluble in water and in alcohol, insoluble in ether. The concentrated solution solidifies over sulphuric acid into a mass of large and highly deliquescent crystalline plates of a pearly lustre, which may be exposed to a very high temperature (290° to 300°) without the slightest alteration. The salt is precipitated unchanged from its aqueous solution by potassa. For analysis, the salt was dried *in vacuo* over sulphuric acid.

0·4325 grm. of dichloride gave 0·3670 grm. of chloride of silver.

The chloride accordingly contains

$$C_{14}\,H_{34}\,P_2\,Cl_2=\left[(C_2\,H_4)''\begin{matrix}(C_2\,H_5)_3\,P\\(C_2\,H_5)_3\,P\end{matrix}\right]''Cl_2.$$

	Theory.		Experiment.
1 equiv. of Diphosphonium .	264	78·81	——
2 equivs. of Chlorine	71	21·19	20·99
1 equiv. of Dichloride	335	100·00	

The dichloride forms with metallic chlorides numerous well-crystallized double compounds, some of which will be more particularly described hereafter.

The dichloride of the ethylene-diphosphonium is likewise produced by the action of monochlorinated chloride of ethyl, prepared in accordance with Regnault's indications, by the action of chlorine upon chloride of ethyl. The chlorinated compound acts but slowly upon triethylphosphine at 100° C. By digesting the mixture for twenty-four hours at 120°, a considerable proportion solidified to a white fibrous crystalline mass, which proved to be exclusively the dichloride of the diphosphonium. It was identified by conversion into the characteristic platinum-salt, and subsequently into the iodide, both of which were analysed. The details are given under the head of the di-iodide and platinum-salt of the diphosphonium.

Di-iodide.—This salt is perhaps the most characteristic of the diphosphonium-compounds. Crystallizing with peculiar readiness,—being easily soluble in hot, but sparingly soluble in cold water,—slightly soluble also in alcohol, and insoluble in ether, —it possesses all the properties which can facilitate the preparation of a pure and definite substance. It has therefore, for the most part, served as the starting-point of the diphosphonium-compounds.

I have already remarked that, in the preparation of the monatomic bromide, the formation of the dibromide can scarcely ever be entirely prevented. The mother-liquors, remaining after numerous preparations of the monatomic bromide, were therefore united and treated with oxide of silver, whereby a caustic liquid was obtained containing the hydrate of the diphosphonium, contaminated with the hydrate of the oxethylated monophosphonium arising from the decomposition of the bromethylated compound. These hydrates were converted, by saturation with hydriodic acid, into the corresponding iodides, the separation of which presented no further difficulty, inasmuch as the iodide of the oxethylated monophosphonium is extremely soluble in water and in alcohol. The sparingly soluble di-iodide was easily obtained in a state of perfect purity by several crystallizations. The crystals are anhydrous. Any hygroscopic moisture that may adhere to them is most conveniently removed by drying them over sulphuric acid, since the salt begins to turn slightly brown at 100°.

I. 0·5690 grm. of iodide gave 0·6742 grm. of carbonic acid and 0·3403 grm. of water.
II. 0·2270 grm. of iodide gave 0·2055 grm. of iodide of silver.
III. 0·3245 grm. of iodide gave 0·2935 grm. of iodide of silver.

The salt which served for analysis III. had been prepared from a dibromide obtained by submitting the pure bromide of the bromethylated triethylphosphonium to the action of triethylphosphine.

IV. 0·3970 grm. of iodide gave 0·3607 grm. of iodide of silver. The salt used for this determination had been prepared by submitting triethylphosphine to the action of *bromethylated bromide of ethyl* (see the paragraph on the dibromide of ethylene-diphosphonium), converting the dibromide formed into the corresponding chloride, into the platinum-salt, and ultimately into the iodide.

V. 0·4090 grm. of iodide gave 0·3700 grm. of iodide of silver. The specimen used for analysis had been prepared by treating triethylphosphine with *chlorinated chloride of ethyl*, precipitation of the product of the reaction as platinum-salt, and transformation of the latter into the iodide.

The formula

$$C_{14}H_{34}P_2I_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

requires

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
C_{14}	168	32·43	32·31	——	——	——	——
H_{34}	34	6·57	6·64	——	——	——	——
P_2	62	11·97	——	——	——	——	——
I_2	254	49·03	——	48·92	48·88	49·10	48·88
	518	100·00					

The di-iodide crystallizes from boiling water in needle-shaped crystals, which often attain a considerable size. Quintino Sella has communicated to me the following results, which he has obtained on examining these crystals:—

"System trimetric:—

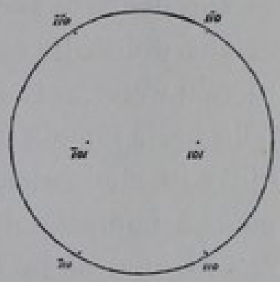
0 0 1, 1 0 1=45° 9′

1 0 0, 1 1 0=60° 18′.

Forms observed:—

1 1 0, 1 0 1 (Fig. 41).

Fig. 41.



Angles.		Calculated.	Observed.
1 1 0, $\bar{1}$ 1 0	=	59° 24′	59° 22′
1 0 1, $\bar{1}$ 0 1	=	90 18	90 16
1 1 0, 1 0 1	=	69 26	69 21

According to Naumann:—

$a:b:c=1{\cdot}0052:1:0{\cdot}5704.$

Forms observed:—

∞P, $\breve{\text{P}}\,\infty$.

According to Weiss:—

$a:b:c=1:0{\cdot}5704:1{\cdot}0052.$

Forms observed:—

$a:b:\infty c;\quad a:\infty b:c.$

According to Levy:—

M M=120° 36′; $b:h=1:0{\cdot}8732.$

Forms observed:—

M, e^1.

Combinations observed:—

1 1 0, 1 0 1 (Figs. 42, 43).

1 1 0, 1 0 1 with other faces, too much rounded to admit of correct determination (Fig. 44).

Fig. 42.

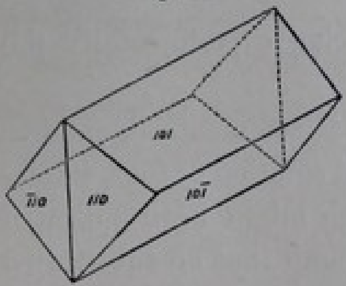


Fig. 43.

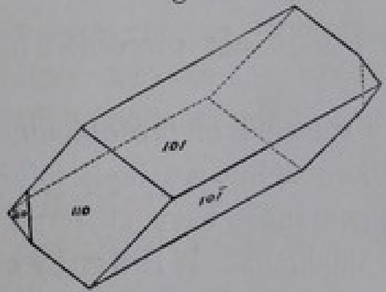
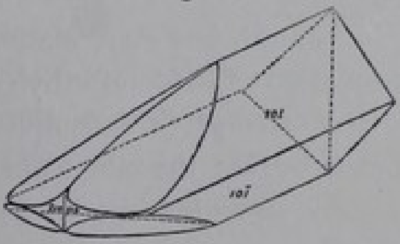


Fig. 44.



Cleavages 1 1 0 and 1 0 1 distinct and easily obtained.

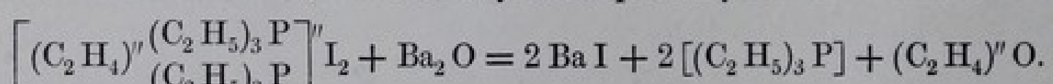
The crystals are long needles; the faces $\bar{1}\,1\,0$ are often but little developed (Fig. 43); the crystals have then a monoclinic aspect; but the measurement of the angles $1\,1\,0$, $1\,0\,1$ and $\bar{1}\,1\,0$, $\bar{1}\,0\,1$ has furnished nearly the same result; and moreover, on examining the crystals with the polarizing microscope, the line $[0\,1\,0]$ is found to be nearly one of the axes of elasticity.

The angle $1\,0\,1$, $\bar{1}\,0\,1$ is so near to 90°, that there might appear some reason for regarding the crystals as dimetric hemihedrals. I am not, however, of this opinion, for I have observed only two cleavages, $1\,1\,0$, $\bar{1}\,1\,0$, instead of the four corresponding to the dimetric system; moreover the angle $1\,0\,1$, $\bar{1}\,0\,1$ has *always* been found a little greater than 90°.

The needles, when small, are transparent; the larger ones are rather milky, and hollow inside.

The lustre of the faces $1\,0\,1$ is slightly nacreous; that of the faces $1\,1\,0$ is vitreous."

The di-iodide, as already observed, is very much more soluble in boiling water than in cold water. 100 parts of boiling water dissolve 458·3 parts of the salt, of which only 3·08 parts remain in solution at 12°. A remarkable character of the salt is its insolubility in moderately concentrated solution of potassa; the dilute solution mixed with potassa immediately yields a crystalline precipitate; the same property is exhibited, as is well known, by the iodides of tetrethylammonium and of the other ammonium- and phosphonium-metals. The solution of the di-iodide, like those of the diphosphonium-salts in general, is perfectly neutral; it is colourless when first prepared, but on exposure to light, soon acquires a tint of yellow, and finally turns brown; at the same time depositing a reddish compound, doubtless analogous to the periodides, which, as I observed some time ago, are formed under similar circumstances from the iodides of tetramethyl- and tetrethyl-ammonium, and which have since been so successfully studied by WELTZIEN. This red compound is immediately precipitated on adding a solution of iodine to the colourless solution. The di-iodide, like most diphosphonium-compounds, exhibits great stability. It melts, without the slightest decomposition, at 231°, and solidifies, with crystalline structure, a few degrees lower. When more strongly heated over an open flame, it is decomposed, with formation of a red-brown substance, which I have not examined. On distilling the di-iodide with excess of caustic baryta in an atmosphere of hydrogen, triethylphosphine passes over; no gaseous product is formed in this reaction. Together with iodide of barium which remains behind, and triethylphosphine which distils over, oxide of ethylene is probably formed in this reaction.



$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2 + Ba_2O = 2\,BaI + 2\,[(C_2H_5)_3P] + (C_2H_4)''O.$$

I should, however, state that I have not succeeded in tracing experimentally the formation of oxide of ethylene.

An attempt to decompose the solution of the di-iodide with sodium-amalgam was unsuccessful; the salt, which is likewise but sparingly soluble in solution of soda, immediately separated out, and no appearances were observed which might have indicated the formation of the ammonium-amalgam. It is worthy of remark that no substituted ammonium-amalgam has yet been produced.

The di-iodide forms, with various metallic salts, crystalline double compounds, among which I have more particularly examined the zinc-salt; its analysis will be given further on.

Difluoride.—The solution of the hydrate, neutralized with hydrofluoric acid and dried over sulphuric acid, leaves a colourless transparent syrup, which does not crystallize, even after standing for a considerable length of time in air or *in vacuo.* The fluorine-compound, like the other diphosphonium-salts, is soluble in alcohol but insoluble in ether.

Silico-fluoride.—The solution, neutralized with hydrofluosilicic acid, likewise failed to yield crystals by evaporation.

Dicyanide.—The solution of the hydrate, mixed with excess of hydrocyanic acid, retains its alkaline reaction; when evaporated on the water-bath, it gives off every trace of hydrocyanic acid. On digesting a solution of the di-iodide with excess of cyanide of silver, a double compound dissolves, which crystallizes in splendid needles, but is likewise decomposed by evaporation, with evolution of hydrocyanic acid and separation of cyanide of silver.

Disulphocyanate.—When a solution of the di-iodide is boiled with excess of recently precipitated sulphocyanate of silver, a solution of the disulphocyanate is obtained, perfectly free from silver, and solidifying by evaporation on the water-bath into a crystalline mass. The salt dissolves readily in water and in alcohol, and is precipitated therefrom by ether. The aqueous solution is likewise precipitated by potassa, the oily drops thus separated gradually solidifying into crystalline rosettes.

Dinitrate.—This salt, prepared by saturating the base with nitric acid, forms laminar crystals, permanent in the air, extremely soluble in water, less soluble in alcohol, and precipitated from the alcoholic solution by ether, as an oil which gradually solidifies. The solution forms with mercuric chloride a precipitate which crystallizes in needles.

Diperchlorate.—This salt is perhaps the most beautiful of the diphosphonium-compounds. On mixing moderately concentrated solutions of the hydrate and perchloric acid, the liquid is soon traversed by delicate crystalline needles, often an inch long. They may be recrystallized from boiling water and dried at 100° without decomposition. At a higher temperature, they are decomposed, with slight detonation.

In the analysis of the perchlorate, the diphosphonium was weighed in the form of the nearly insoluble platinum-salt.

0·3130 grm. of diperchlorate, evaporated to dryness with an excess of dichloride of platinum, gave, after treatment with alcohol, 0·4535 grm. of the diphosphonium-platinum-salt.

$$C_{14}\,H_{34}\,P_2\,Cl_2\,O_8=\left[\,(C_2\,H_4)''\begin{matrix}(C_2\,H_5)_3\,P\\(C_2\,H_5)_3\,P\end{matrix}\right]''Cl_2\,O_8.$$

	Theory.		Experiment.
1 equiv. of Diphosphonium . .	264	57·02	56·71
2 equivs. of Chlorine . . .	71	15·33	——
8 equivs. of Oxygen	128	27·65	——
1 equiv. of Diperchlorate. . .	463	100·00	

Di-iodate.—The base, neutralized with iodic acid and evaporated over sulphuric acid, yields an extremely deliquescent syrup which crystallizes but gradually. Solution of potassa separates the hydrate from the concentrated solution, in oily drops, sparingly soluble crystalline iodate of potassium being at the same time precipitated. The solution, mixed with hydrochloric acid, yields the lemon-yellow crystalline compound already mentioned.

Carbonate.—The solution of the oxide remains alkaline, even after saturation with carbonic acid; on evaporation, it leaves a mass having a slightly crystalline structure.

Sulphate.—Radio-crystalline, extremely deliquescent salt. Repeated attempts to produce diphosphonium-alums by mixing the solution with the sulphates of aluminium and chromium were unsuccessful.

Chromate.—The solution of the free base, neutralized with pure chromic acid, deposits, when in an atmosphere dried by sulphuric acid, extremely soluble needles arranged in stellated groups. With excess of chromic acid, nothing but an uncrystallizable syrup is obtained.

Oxalate.—Both the acid and the neutral solution of the base in oxalic acid dries up to a slightly crystalline mass.

Phosphate.—The di-iodide, boiled with excess of phosphate of silver, yields a neutral solution of the phosphate of the diphosphonium, which remains as a slightly crystalline mass when the solution is evaporated. Crystallization is not promoted by addition either of free phosphoric acid or of the hydrate.

Tartrate.—Extremely soluble; difficult to crystallize.

Dipicrate.—The aqueous solution of picric acid, added to a moderately concentrated solution of the hydrate, instantly produces a yellow crystalline precipitate, which separates from the boiling alkaline solution in long needles.

The diphosphonium-salts form a long series of double compounds, most of which crystallize splendidly.

Platinum-salt.—The solution of the dichloride, even when extremely dilute, yields with dichloride of platinum a pale-yellow precipitate, which appears amorphous to ordinary observation, but when examined under a microscope of rather high power, resolves itself into small prisms. This salt is nearly insoluble in cold and even in boiling water, so that, as already observed, the diphosphonium may be quantitatively estimated in this form. The precipitate dissolves, though with difficulty, in concentrated hydrochloric acid, and crystallizes from the solution, by slow cooling, in small but well-defined crystals of a bright orange-red colour.

QUINTINO SELLA has examined these crystals, and obtained the following results:—

" System monoclinic:—

100, 001=82° 36′.

Forms observed:—

100, 010, 001 (Fig. 45).

Fig. 45.

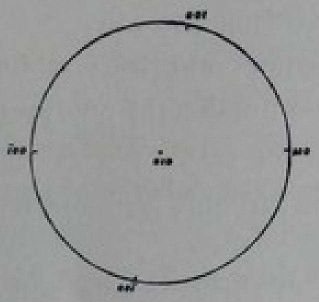
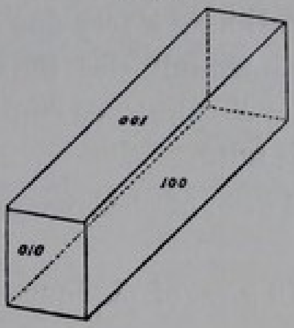


Fig. 46.



Angles.		Calculated.	Observed.
		° ′	° ′
100, 010	=	90 0	90 3
100, 001	=	82 36	82 36
010, 001	=	90 0	89 57

According to NAUMANN:—

γ=82° 36′.

Forms observed:—

∞P̄∞, ∞P̀∞, 0P.

According to WEISS:—

a o c=97° 24′.

Forms observed:—

$a:\infty b:\infty c$; $\infty a:b:\infty c$; $\infty a:\infty b:c$.

According to LEVY:—

h^1P=97° 24′.

Forms observed:—

h^1, g^1, P.

Combinations observed:—

100, 010, 001 (Fig. 46).

Cleavages 100, 010, 001 distinct and easily obtained, more especially 010.

The crystals are elongated in the direction of the axis of symmetry, and often hollowed out for a great part of their length when rather thick, that is to say, when their sides attain the width of half a millimetre. The hollow has the form of a pyramid having its base on the face 010 and its apex towards the centre of the crystal The face 010 is often reduced to a very narrow rectangular rim. The opposite apex of the crystal is irregular, as if it had adhered to the side of the vessel. The face 001 is in general rather more developed than 100.

The crystals are optically negative. The plane of the optical axes is parallel to the line of symmetry [010]; the principal medium-line is perpendicular to the latter, and forms an angle of about 30° with a line normal on face 0 0 1. In fact, a plate parallel to 0 1 0 stops the passage of a ray of polarized light in that direction. Moreover, rings are observed through the faces 0 0 1, and in a plane parallel to the line of symmetry 0 1 0, and rather inclined towards a line normal on such face. The angle of the optical axes, seen in this manner through the faces 0 0 1, appears to be very nearly 110°.

The crystals have a very fine orange-colour and a vitreous lustre."

This platinum-salt was the first diphosphonium-compound with which I became acquainted, a circumstance explaining the considerable number of analyses which were made of this salt.

I. 0·6534 grm. of platinum-salt gave 0·5938 grm. of carbonic acid and 0·2995 grm. of water.

II. 0·7179 grm. of platinum-salt gave 0·6545 grm. of carbonic acid and 0·3135 grm. of water.

III. 0·3568 grm. of platinum-salt gave 0·3289 grm. of carbonic acid and 0·1585 grm. of water.

IV. 0·3250 grm. of platinum-salt gave 0·3009 grm. of carbonic acid and 0·1480 grm. of water.

V. 0·5809 grm. of platinum-salt gave 0·5228 grm. of carbonic acid and 0·2670 grm. of water. This compound had been prepared from a diphosphonium-salt obtained by the action of brominated bromide of ethyl upon triethylphosphine.

VI. 0·7200 grm. of platinum-salt, when fused with carbonate of sodium, gave 0·2120 grm. of platinum and 0·9120 grm. of chloride of silver.

VII. 0·4075 grm. of platinum-salt gave 0·1205 grm. of platinum and 0·5235 grm. of chloride of silver.

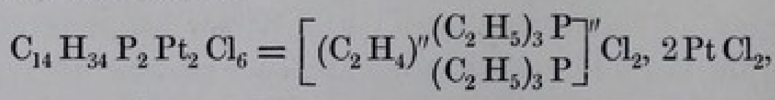
VIII. 0·3470 grm. of platinum-salt gave 0·1030 grm. of platinum and 0·4428 grm. of chloride of silver.

IX. 0·4615 grm. of platinum-salt gave 0·1355 grm. of platinum.

X. 0·4105 grm. of platinum-salt gave 0·1210 grm. of platinum. This salt had been obtained by the action of chlorinated chloride of ethyl upon triethylphosphine. The mother-liquor furnished by the analysis of the iodide (V.) had served for its preparation.

XI. 0·6158 grm. of platinum-salt gave 0·7778 grm. of chloride of silver.

These numbers fix the formula



$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2,$$

the theoretical values of which I place in juxtaposition with the experimental percentages:

	Theory.	
C_{14}	168	24·91
H_{34}	34	5·05
P_2	62	9·19
Pt_2	197·4	29·27
Cl_6	213	31·58
	674·4	100·00

Experiment.										
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
24·78	24·86	25·14	25·25	24·54	——	——	——	——	——	——
5·09	4·85	4·94	5·06	5·10	——	——	——	——	——	——
——	——	——	——	——	——	——	——	——	——	——
——	——	——	——	——	29·44	29·57	29·68	29·36	29·11	——
——	——	——	——	——	31·33	31·78	31·57	——	——	31·24

Palladium-salt.—A dilute solution of the dichloride is not precipitated by chloride of palladium. On concentrating the mixture and allowing it to cool slowly, reddish-yellow prisms make their appearance: by rapid evaporation a brick-red crystalline powder is obtained. Alcohol added to the aqueous solution of the two salts throws down the double salt as a chocolate-coloured crystalline magma composed of small interlaced needles. I have not analysed this compound.

Gold-salt.—Beautiful golden-yellow needles, difficultly soluble in cold, easily soluble in boiling water, and containing

$$C_{14}H_{34}P_2Au_2Cl_8 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2,\ 2AuCl_3,$$

as shown by the following analyses:—

I. 0·6200 grm. of gold-salt gave 0·4159 grm. of carbonic acid and 0·2032 grm. of water.

II. 0·3540 grm. of gold-salt gave 0·1490 grm. of gold.

	Theory.		Experiment.	
			I.	II.
C_{14}	168	17·83	18·29	——
H_{34}	34	3·61	3·64	——
P_2	62	6·58	——	——
Au_2	394	41·83	——	42·09
Cl_8	284	30·15	——	——
	942	100·00		

Mercury-salt.—Delicate crystalline needles or laminæ, sparingly soluble in water and in alcohol, obtained by mixing the chloride of the diphosphonium with mercuric chloride.

I. 0·2660 grm. of mercury-salt gave 0·2390 grm. of the diphosphonium-platinum-salt and 0·1255 grm. of sulphide of mercury.

II. 0·5650 grm. of mercury-salt gave 0·2670 grm. of sulphide of mercury and 0·5515 grm. of chloride of silver.

These analyses lead to the formula

$$C_{14}H_{34}P_2Hg_3Cl_5 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2,\ 3\,HgCl,$$

as seen from the following comparison:—

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diphosphonium .	264·0	35·60	35·18	——
3 equivs. of Mercury	300·0	40·46	40·64	40·73
5 equivs. of Chlorine	177·5	23·94	——	24·14
1 equiv. of Mercury-salt . .	741·5	100·00		

Tin-salt.—This salt, which is prepared like the mercury-compound, crystallizes from water in large well-formed prismatic crystals. According to some determinations, which, however, gave only approximate results, the tin-salt appears to have the composition

$$\left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Cl_2,\ 4\,SnCl.$$

Di-iodide and Iodide of Zinc.—On mixing the two solutions, a crystalline precipitate is obtained, which separates in long needles when recrystallized from boiling water. The salt, which is apt to assume a yellowish coloration, contains

$$C_{14}H_{34}P_2Zn_2I_4 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' I_2,\ 2\,ZnI.$$

0·5735 grm. of zinc-salt gave 0·6401 grm. of iodide of silver.

The above formula requires the following values:—

	Theory.		Experiment.
1 equiv. of Diphosphonium . .	264	31·54	——
2 equivs. of Zinc	65	7·77	——
4 equivs. of Iodine	508	60·69	60·31
1 equiv. of Zinc-salt	837	100·00	

Dibromide and Bromide of Silver.—I have mentioned this salt already when describing the preparation of the hydrate from the dibromide. When oxide of silver, which should not be mixed with too much water, is added in small portions to a boiling concentrated solution of the dibromide in alcohol as long as it dissolves, the filtered solution deposits on cooling white crystals, which contain

$$C_{14}H_{34}P_2AgBr_3 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' Br_2,\ AgBr.$$

Analysis has furnished the following numbers:—

I. 0·4465 grm. of double salt, fused with carbonate of sodium, left, after removal of the bromide of sodium, a silver-residue, which, when treated with nitric and hydrochloric acid, gave 0·1042 grm. of chloride of silver.

II. 0·6442 grm. of double salt gave, on boiling with water, a residue of 0·2710 grm. of bromide of silver; the filtrate yielded with nitrate of silver an additional amount of 0·3220 grm. of bromide of silver; the total amount of bromide of silver obtained being therefore 0·5930 grm.

III. 0·7065 grm. of double salt gave by treatment with nitrate of silver 0·6538 grm. of bromide of silver.

	Theory.		Experiment.		
			I.	II.	III.
C_{14}	168	27·45	——	——	——
H_{34}	34	5·56	——	——	——
P_2	62	10·13	——	——	——
Ag	108	17·65	17·56	——	——
Br_3	240	39·21	——	39·17	39·37
	612	100·00			

The salt crystallizes, but not readily, from boiling alcohol. It is immediately decomposed by water, bromide of silver being separated, and the bromide of the diphosphonium passing into the solution.

In describing the general character of the action of dibromide of ethylene upon triethylphosphine, I have mentioned that, in addition to the monatomic and diatomic bromides, which are the principal products of the reaction, secondary compounds may be formed, but always in comparatively small quantities. The mother-liquors generally contain oxide of triethylphosphine, formed by the action of the atmosphere; they contain, moreover, bromide of triethylphosphonium, if the dibromide had not been carefully deprived of hydrobromic acid. The bromide of triethylphosphonium, however, under certain conditions, arises from the scission of dibromide of ethylene into hydrobromic acid and bromide of vinyl, the latter producing in this case the bromide of vinyl-triethylphosphonium. I had an opportunity of establishing this fact experimentally, when preparing a considerable quantity of the dibromide of the diphosphonium. The phosphorus-base having been employed in excess in this operation, not a trace of the bromethylated monophosphonium had been formed, the absence of which was carefully proved by a special experiment. The bromides were then transformed into chlorides and the latter precipitated by dichloride of platinum; the mother-liquor filtered off from the copious precipitate of the diphosphonium-salt was considerably evaporated, when, on cooling, well-formed octohedra were deposited, which were recrystallized from water.

0·4835 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1365 grm.=28·23 per cent. of platinum.

The theoretical platinum percentage of the compound

$$[(C_2H_3)(C_2H_5)_3P]Cl, PtCl_2$$

is 28·19. The formation of the vinyl-compound under these circumstances is easily explained.

$$C_2H_4Br_2 + 2[(C_2H_5)_3P] = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HP]Br.$$

The amount of vinyl-compound produced is but very small in proportion to that of the other salts which are formed in the mutual action between triethylphosphine and dibromide of ethylene.

ACTION OF HEAT UPON THE HYDRATE OF THE DIPHOSPHONIUM.

The hydrate, when submitted to the action of heat, undergoes a series of remarkable changes, which I have studied with lively interest. The decomposition commences at 160°; on raising the temperature gradually to 250°, the whole of the hydrate passes over in the form of liquid and gaseous products. The liquid product consists of triethylphosphine and oxide of triethylphosphine; the gas contains a considerable proportion of ethylene, which is readily characterized by its deportment with bromine. This transformation may be represented by the following equation:—

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3P + (C_2H_5)_3PO + C_2H_4 + H_2O.$$

The succession of changes, however, through which the hydrate runs before it is broken up, shows unmistakeably that this equation can represent but one phase, even of the final transformation of the diphosphonium-compound. The study of the intermediate changes presents unusual difficulties, and I confess at once that I have failed to solve the problem to my entire satisfaction.

The experiments performed with a view of disentangling the intricacies of these reactions, will perhaps be better understood if I commence with setting forth the ideas which I have ultimately formed of these metamorphoses, and then state the analytical results which have assisted me in forming them.

Under the influence of heat, the hydrate of the diphosphonium undergoes two principal transformations, which are accomplished side by side. A portion of this compound gives rise to the formation of oxide of triethylphosphine and hydrate of tetrethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3PO + \left.\begin{matrix}[(C_2H_5)_4P] \\ H\end{matrix}\right\}O,$$

the latter splitting ultimately into oxide of triethylphosphine and hydride of ethyl,

$$\left.\begin{matrix}[(C_2H_5)_4P] \\ H\end{matrix}\right\}O = (C_2H_5)_3PO + (C_2H_5)H;$$

a second portion is resolved into triethylphosphine and hydrate of oxethyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\}O_2 = (C_2H_5)_3P + \left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\}O;$$

the latter may undergo, at a high temperature, a further transformation, separating, partially at least, into water and hydrate of vinyl-triethylphosphonium,

$$\left.\begin{matrix}[(C_2\,H_5\,O)\,(C_2\,H_5)_3\,P]\\ H\end{matrix}\right\}O = \left.\begin{matrix}H\\ H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2\,H_3)\,(C_2\,H_5)_3\,P]\\ H\end{matrix}\right\}O,$$

the vinyl-compound yielding, in the last stage of the reaction, oxide of triethylphosphine and ethylene,

$$\left.\begin{matrix}[(C_2\,H_3)\,(C_2\,H_5)_3\,P]\\ H\end{matrix}\right\}O = (C_2\,H_5)_3\,P\,O + C_2\,H_4.$$

The separation of the triethylphosphine and its oxide by the action of heat upon the hydrated diphosphonium requires no special experimental demonstration. To individualize the other compounds, the following experiments were made:—A considerable quantity of the dihydrate was evaporated in a retort in an atmosphere of hydrogen. As soon as the phosphorus-base began to distil freely—at about 190° C.—the operation was interrupted, and the residuary alkaline liquid saturated with hydrochloric acid and precipitated with dichloride of platinum. A dingy yellow amorphous precipitate was thrown down, insoluble in cold water, and the mother-liquor, on evaporation, furnished a mass of deep orange-red octohedra, which were transformed into the corresponding iodine-compound. The salt thus obtained proved unmistakeably a mixture of two compounds of different solubility. The less soluble was obtained in beautiful crystals, exhibiting all the characters of iodide of tetrethylphosphonium. The salt was identified by analysis.

I. 0·7480 grm. of iodide gave 0·6360 grm. of iodide of silver.

II. 0·3215 grm. of iodide, once more recrystallized, gave 0·2760 grm. of iodide of silver.

	Theory of the iodide of			Experiment.	
	Oxethylated triethyl-phosphonium.	Vinyl-triethyl-phosphonium.	Tetrethyl-phosphonium.	I.	II.
Iodine . .	43·80	46·69	46·35	45·94	46·38

The platinum-salt corresponding to the difficultly soluble iodide gave, on analysis, the following results:—

I. 0·4727 grm. of platinum-salt gave 0·4723 grm. of carbonic acid and 0·2470 grm. of water.

II. 0·4478 grm. of platinum-salt gave 0·4442 grm. of carbonic acid and 0·2305 grm. of water.

III. 0·5430 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1510 grm. of platinum.

IV. 0·4097 grm. of platinum-salt gave 0·1145 grm. of platinum.

V. 0·6140 grm. of platinum-salt gave 0·1728 grm. of platinum.

I place the percentages deduced from these analyses in juxtaposition with the theoretical values corresponding to the platinum-salts of vinyl-triethyl- and tetrethyl-phosphonium.

	Theory.		Experiment.				
	Vinyl-compound.	Tetrethyl-compound.	I.	II.	III.	IV.	V.
Carbon . .	27·41	27·26	27·25	27·05	——	——	——
Hydrogen . .	5·14	5·68	5·80	5·71	——	——	——
Platinum . .	28·19	28·02	——	——	27·81	27·94	28·14

The hydrogen-determinations prove unequivocally that the compound is the platinum-salt of the tetrethylphosphonium. The formation of the tetrethylphosphonium-compound is moreover demonstrated by the analysis of the corresponding gold-salt.

I. 0·5783 grm. of gold-salt gave 0·4158 grm. of carbonic acid and 0·2200 grm. of water.

II. 0·5795 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·2352 grm. of gold.

	Theory.		Experiment.	
	Vinyl-triethyl-phosphonium-salt.	Tetrethyl-phosphonium-salt.	I.	II.
Carbon . .	19·83	19·75	19·61	——
Hydrogen . .	3·71	4·11	4·22	——
Gold . . .	40·70	40·53	——	40·59

Here likewise the hydrogen-determination is characteristic of the tetrethylphosphonium-compound. The result of analysis is most satisfactorily confirmed by the crystallographical examination of the salts under consideration. Q. SELLA has compared the crystals of the iodide above-mentioned with crystals of iodide of tetrethylphosphonium obtained in the usual way. I have appended at the conclusion of this paper the elaborate investigation of this beautiful salt, with which my friend has furnished me.

Far less conclusive is the experimental evidence which I am enabled to offer in support of the opinion, that the hydrate of tetrethylphosphonium formed by the action of heat on the hydrated diphosphonium is accompanied by the oxethylated triethylphosphonium-compound. The principal argument in favour of this view is the abundant evolution of triethylphosphine, which cannot be understood unless we assume the simultaneous formation of the oxethylated, or the vinyl-compound. I have failed in my endeavours to prepare the more soluble iodide which accompanies the tetrethylphosphonium-compound in a state of purity. Nor was the attempt to separate the two compounds in the form of platinum-salts rewarded by better success. Both platinum-salts crystallize in octohedra which differ but slightly in solubility. Nevertheless the following determinations leave but little doubt as to the presence of the oxethylated phosphonium among the products resulting from the decomposition of the hydrate of diphosphonium under the influence of heat.

I. 0·320 grm. of platinum-salt gave 0·3091 grm. of carbonic acid and 0·1625 grm. of water.

II. 0·4675 grm. of platinum-salt gave 0·4573 grm. of carbonic acid and 0·2352 grm. of water.

III. 0·3250 grm. of platinum-salt of the same preparation, treated with sulphuretted hydrogen, &c., gave 0·0890 grm. of platinum.

	Theory.		Experiment.		
	Tetrethylphosphonium-salt.	Oxethyl-triethylphosphonium-salt.	I.	II.	III.
Carbon . .	27·26	26·07	26·34	26·67	——
Hydrogen .	5·68	5·43	5·64	5·59	——
Platinum . .	28·02	26·81	——	——	27·38

The experimental numbers characterize a mechanical mixture of the two platinum-salts.

The action of heat upon the hydrate of the diphosphonium induces yet another transformation, to which I have already alluded when mentioning the dingy yellow insoluble precipitate which is formed on addition of dichloride of platinum to the product of the action of heat upon the hydrate, neutralized with hydrochloric acid.

The following paragraph contains the fragmentary information which I have collected in studying these changes.

PARADIPHOSPHONIUM-COMPOUNDS.

The basic compound which yields the amorphous yellow platinum-salt repeatedly mentioned, is a transient product of the action of heat on the hydrated diphosphonium. If during distillation, the alkaline residue in the retort be tested from time to time with dichloride of platinum, a point is soon reached, when instead of the slightly crystalline precipitate, perfectly insoluble in dilute hydrochloric acid, which appears at the commencement of the operation, an amorphous, generally dingy yellow precipitate is obtained, immediately dissolving on addition of a few drops of dilute hydrochloric acid. If the distillation be now interrupted and the residue neutralized with hydrochloric acid, and mixed with a few drops of dichloride of platinum, a discoloured precipitate is thrown down, the filtrate from which, on addition of a further quantity of platinum-solution, yields the amorphous salt, of a light yellow colour, and in a state of purity. This salt exhibits no trace of crystalline structure, even when examined under the most powerful microscope: in the perfectly dry state it is remarkably electrical, flying about in all directions during trituration.

The same substance is obtained when the hydrated oxethyl-triethylphosphonium is submitted to the action of heat. By interrupting the process at a convenient time, and adding dichloride of platinum to the neutralized residue, phenomena identical with those just mentioned are observed.

The compound which produces the amorphous yellow precipitate was lastly obtained, under the following circumstances.

While engaged with the study of the vinyl-compounds, the examination of which I have described in one of the previous paragraphs of this paper, the idea suggested itself that the bromide of vinyl-triethylphosphonium might also be formed by the action of bromide of vinyl (C_2H_3Br) on triethylphosphine:

$$(C_2H_5)_3P + C_2H_3Br = [(C_2H_3)(C_2H_5)_3P]Br.$$

In performing the experiment, I had an opportunity of observing the sluggishness of action of this bromide, often previously noticed in experimenting in the ammonium-series. When gaseous bromide of vinyl is passed through triethylphosphine, not a trace of it is fixed by the phosphorus-base. Triethylphosphine may be distilled in an atmosphere of the bromine-compound without undergoing any alteration. Bromide of vinyl, freed from every trace of adhering dibromide of ethylene by repeated distillation at a low temperature, and subsequent washing with lukewarm water, was therefore enclosed, together with triethylphosphine, in a strong glass tube. No change was perceptible after two days' digestion at 100°; and it was only on the third day that a thin layer of viscid matter began to separate at the bottom of the tube. The digestion was then continued at a higher temperature; and after the mixture had been exposed for three days longer to a temperature varying from 160° to 180°, about half the fluid was found to be converted into a solid mass, while a limpid liquid floated on the top. On opening the tube, cooling it well at the time, the liquid effervesced strongly, and a gas escaped which burned with a green-edged flame, and appeared to consist, partly at all events, of the vapour of unaltered bromide of vinyl. In subsequent repetitions of the experiment, it frequently happened that the tubes were shattered by the sudden expansion of the compressed gas; hence probably permanent gases are formed in the reaction. The liquid decanted from the solid proved to be a mixture of undecomposed bromide of vinyl with free phosphorus-base; the solid mass was found to consist of several bodies. On dissolving it in water, a rather small quantity of a sparingly soluble, beautifully crystalline, nacreous salt separated out, the composition of which is at present undetermined. By treatment of the filtered solution with oxide of silver, a strongly alkaline liquid was produced, which, when neutralized with hydrochloric acid and precipitated with dichloride of platinum, gave at once the amorphous yellow platinum-salt easily soluble in dilute hydrochloric acid.

On analysis, this platinum-salt furnished the following results. Analyses I. and II. were made with the salt obtained by the action of bromide of vinyl on triethylphosphine. The platinum-determination III. refers to a salt prepared with the product of the action of heat on the hydrated diphosphonium.

I. 0·5717 grm. of platinum-salt gave 0·5211 grm. of carbonic acid and 0·2538 grm. of water.

II. 0·7623 grm. of platinum-salt, decomposed with hydrosulphuric acid, &c., gave 0·2228 grm. of platinum.

III. 0·6531 grm. of platinum-salt, analysed in the same manner, gave 0·1895 grm. of platinum.

The percentages corresponding to these analytical numbers are exactly those of the platinum-salt of the ethylene-diphosphonium.

$$C_{14}H_{34}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2, 2PtCl_2.$$

	Theory.		Experiment. I.	II.	III.
C_{14}	168	24·91	24·85	——	——
H_{34}	34	5·05	4·93	——	——
P_2	62	9·19	——	——	——
Pt_2	197·4	29·27	——	29·23	29·01
Cl_6	213	31·58	——	——	——
	674·4	100·00			

Nevertheless the two substances are not identical. In addition to the difference in the physical properties and in the behaviour with dilute hydrochloric acid, the two salts exhibit other well-defined marks of distinction. The crystalline salt is perfectly insoluble in water, even when boiling. The amorphous salt dissolves readily, and is deposited again on cooling in the same amorphous condition. In designating this peculiar molecular variety as paradiphosphonium-compound, I simply wish to distinguish it from the salt of the ordinary diphosphonium, without giving any opinion respecting the nature of the difference. The existence of the diphosphonium-compounds in the crystalline and in the amorphous condition, reminds us of the behaviour of some of the native organic bases under the influence of heat. It is well known that several of these substances, which are remarkable for their powers of crystallization, are rendered perfectly amorphous when heated for some time above their melting-point.

As might have been expected, the paradiphosphonium-compounds are slowly and gradually reconverted into the ordinary diphosphonium-salts *.

The hydrated paradiphosphonium, when separated from the platinum-compound by successive treatment with sulphuretted hydrogen and oxide of silver, yields with hydriodic acid a gummy mass which only gradually assumes the crystalline form. By a considerable number of recrystallizations, the characteristic di-iodide was ultimately obtained with all its properties; when converted, by treatment with chloride of silver, into the dichloride, and precipitated by dichloride of platinum, it immediately yielded the well-known crystalline precipitate so frequently mentioned in this paper. In order to fix by numbers this transition, and more especially the formation of diphosphonium-compounds by the action of bromide of vinyl upon triethylphosphine, the soluble bromide obtained in the reaction between the two last-named bodies was successively treated with oxide of silver and hydriodic acid. The iodide, after numerous crystallizations from alcohol, gave on analysis the following numbers:—

---

* In several experiments, the reaction between bromide of vinyl and triethylphosphine gave rise to the formation of a mixture of the amorphous and crystalline diphosphonium-compounds.

I. 0·3388 grm. of iodide, having a slightly yellowish tint, gave 0·4017 grm. of carbonic acid and 0·2077 grm. of water.

II. 0·2470 grm. of iodide gave 0·2255 grm. of iodide of silver.

The formula

$$C_{14}H_{34}P_2I_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]'' I_2$$

requires

	Theory.		Experiment. I.	Experiment. II.
C_{14}	168	32·43	32·34	——
H_{34}	34	6·57	6·81	——
P_2	62	11·97	——	——
I_2	254	49·03	——	49·33
	518	100·00		

This result was unequivocally confirmed by the analysis of the corresponding crystalline platinum-salt.

0·3550 grm. of the salt gave 0·3297 grm. of carbonic acid and 0·1650 grm. of water, representing 25·33 per cent. of carbon and 5·16 per cent. of hydrogen. The theoretical percentages are 24·91 of carbon and 5·05 of hydrogen.

The transition of a diphosphonium-compound from the crystalline to the amorphous, and from the amorphous to the crystalline condition, appears intelligible enough *. The transformation of the oxethylated monophosphonium, however, into a diphosphonium-compound, and the formation of the latter by the action of bromide of vinyl upon triethylphosphine, claims our attention for a moment.

The conversion of the hydrate of oxethyl-triethylphosphonium † into the hydrated diphosphonium is readily understood, if we remember that two molecules of the former contain the elements of one molecule of the latter and of one molecule of ethylene-alcohol:

$$2\left[\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\H\end{matrix}\right\}O\right] = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]\\H_2\end{matrix}\right\}O_2 + C_2H_6O_2.$$

I am unable to say whether the group $C_2H_6O_2$ actually separates as ethylene-alcohol, or, which is more probable, in the form of water and oxide of ethylene, or even of aldehyde. Material and patience began to fail when I had reached this point, and I must reserve the decision of this question to later experiments ‡.

---

* The diphosphonium-salt, which is formed by the action of sulphocyanate of ethylene upon triethylphosphine (see page 36), likewise, in the first place, yields the amorphous platinum-salt when precipitated by dichloride of platinum.

† I need scarcely mention that the purity of the compound used in my experiments had been established by a special analysis. When prepared from imperfectly purified bromethylated bromide, the oxethylated base is apt to contain minute quantities of the hydrate of the diphosphonium.

‡ The convertibility of the oxethylated triethylphosphonium-salts into diatomic compounds has induced

The same remark applies to the final elucidation of the reaction between triethylphosphine and bromide of vinyl, which, as I have pointed out, likewise gives rise to the formation of diphosphonium-compounds. Two molecules of triethylphosphine and two molecules of bromide of vinyl contain the elements of one molecule of dibromide of the ethylene-diphosphonium and one molecule of acetylene:

$$2[(C_2H_5)_3P] + 2C_2H_3Br = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right]'' Br_2 + C_2H_2;$$

and experiment proves that a considerable amount of permanent gas is generated in this reaction; but there are other products formed, and it would be idle to dwell any longer on the interpretation of these unfinished observations.

In conclusion, I append Q. SELLA's crystallographical examination of the iodide of tetrethylphosphonium, to which I have alluded in the latter portion of this paper, and also the results obtained by him in measuring the corresponding platinum-salt.

Crystalline Form of Iodide of Tetrethylphosphonium.

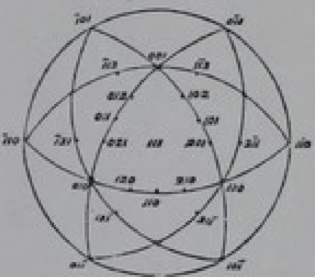
"System rhombohedric:—

$$111, 100 = 59° 32'.$$

Forms observed:—

$$111, 10\bar{1}, 100, 110, 210, 31\bar{1} \text{ (Fig. 47).}$$

Fig. 47.



Angles.	Calculated.	Observed.
	° ′	° ′
$111, 10\bar{1}$ =	90 0	89 29
$111, 100$ =	59 32	——
$111, 110$ =	40 22	40 22
$111, 210$ =	44 28	44 28
$111, 31\bar{1}$ =	63 0	63 2
$10\bar{1}, 01\bar{1}$ =	60 0	60 7
$10\bar{1}, 100$ =	41 43	41 44
$10\bar{1}, 010$ =	90 0	90 2
$10\bar{1}, 110$ =	55 53	55 58
$10\bar{1}, 101$ =	90 0	89 59
$10\bar{1}, 210$ =	45 32	45 30

---

me to try whether the action of triethylphosphine upon them would accomplish this transformation:

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P] \\ H\end{matrix}\right\} O + (C_2H_5)_3P = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6P_2]'' \\ H_2\end{matrix}\right\} O_2.$$

But even when heated up to 150°, the two bodies remain unaltered; nor is there any action when the oxide is replaced by the bromide of oxethyl-triethylphosphonium.

Angles.		Calculated.	Observed.
$10\bar{1}, 120$	=	69° 30′	69° 33′
$10\bar{1}, 31\bar{1}$	=	27 0	26 58
$10\bar{1}, 13\bar{1}$	=	63 33	63 33
$100, 010$	=	96 34	96 31
$100, 110$	=	48 17	48 15
$100, 011$	=	99 54	——
$100, 210$	=	27 47	27 48
$100, 120$	=	68 47	68 42
$100, 021$	=	99 16	——
$100, 31\bar{1}$	=	26 27	26 26
$100, 13\bar{1}$	=	76 42	76 5
$100, \bar{1}31$	=	115 47	——
$110, 101$	=	68 14	68 3
$110, 210$	=	20 30	20 27
$110, 201$	=	57 3	——
$110, 102$	=	81 19	——
$110, 31\bar{1}$	=	32 16	——
$110, 3\bar{1}1$	=	69 46	——
$110, 1\bar{1}3$	=	98 51	——
$210, 120$	=	41 0	40 54
$210, 201$	=	41 0	——
$210, 021$	=	74 41	——
$210, 012$	=	88 56	——
$210, 31\bar{1}$	=	18 32	18 34
$210, 13\bar{1}$	=	50 30	——
$210, \bar{1}31$	=	89 20	——
$31\bar{1}, 13\bar{1}$	=	52 55	52 52
$31\bar{1}, 3\bar{1}1$	=	52 55	52 59
$31\bar{1}, \bar{1}31$	=	101 0	101 2
$31\bar{1}, \bar{1}13$	=	126 0	126 4

According to NAUMANN:—

$R = 83° \ 26'$

Forms observed:—

$0R;\ \infty P2;\ R;\ -\frac{1}{2}R;\ \frac{2}{3}P2;\ \frac{4}{3}P2.$

According to WEISS:—

$$a=0{\cdot}6793$$

Forms observed:—

$$\infty a:\infty a:\infty a:c;\quad a:\tfrac{1}{2}a:a:\infty c;\quad \infty a:a:a:c;\quad \infty a':a':a':\tfrac{1}{2}c;$$

$$a:\tfrac{1}{2}a:a:\tfrac{1}{3}c;\quad a:\tfrac{1}{2}a:a:\tfrac{2}{3}c.$$

According to LEVY:—

$$\mathrm{P\,P}=83^\circ\ 26'.$$

Forms observed:—

$$a',\ d',\ \mathrm{P},\ b',\ b^2,\ e_3.$$

Fig. 48.

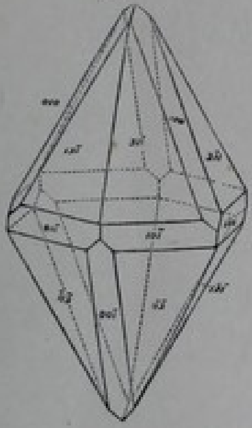


Fig. 49.

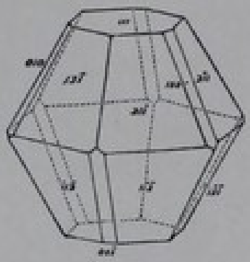
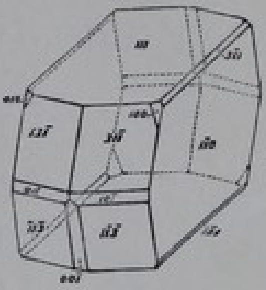


Fig. 50.



Combinations observed:—

$3\,1\,\bar{1};\ 1\,0\,0,\ 1\,0\,\bar{1}$ (Fig. 48).

$3\,1\,\bar{1},\ 1\,1\,1,\ 1\,0\,0$ (Fig. 49).

$3\,1\,\bar{1},\ 1\,1\,1,\ 1\,0\,\bar{1};\ 1\,0\,0$ (Fig. 50).

$3\,1\,\bar{1},\ 1\,1\,0,\ 1\,0\,0;\ 1\,0\,\bar{1},\ 2\,1\,0$ (Figs. 51 and 52).

$3\,1\,\bar{1},\ 1\,0\,0,\ 1\,1\,0;\ 1\,0\,\bar{1},\ 2\,1\,0,\ 1\,1\,1.$

The crystals prepared by treating triethylphosphine with iodide of ethyl exhibit the forms Figs. 51 and 52.

Fig. 51.

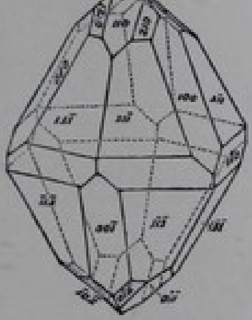
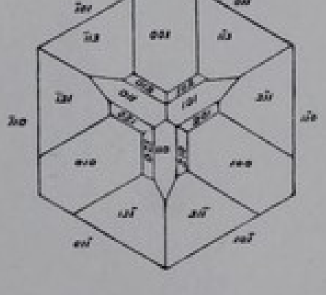


Fig. 52.



The crystals obtained by submitting the hydrated diphosphonium to the action of heat, and neutralizing the alkaline residuary product with hydriodic acid, have the form Fig. 48, when rather large and slightly yellow, and the forms Figs. 49 and 50, when minute and perfectly white.

The crystals of the form Fig. 50 are most frequent; they seem to have adhered to the vessel with one of the larger faces of the prism $1\,0\,\bar{1}$.

Crystals distinct. Lustre on the faces, except 1 1 1, very great.

Crystals optically positive. The indices of refraction are for the ordinary ray $\omega=1{\cdot}660$, for the extraordinary ray $\epsilon=1{\cdot}668$.

The crystals of iodide of tetrethylphosphonium are isomorphous with those of iodide of silver. In the latter substance, 1 1 1, 1 0 0=58° 27′, instead of 59° 32′, found in the tetrethylphosphonium-salt. Both salts have the same hexagonal habitus, and both are optically positive."

Crystalline Form of the Platinum-salt of Tetrethylphosphonium.

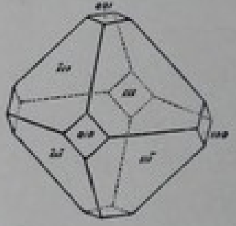
"System monometric:—

Forms observed:—

1 0 0, 1 1 1 (Fig. 53).

Angles.		Calculated.	Observed.
0 0 1, 1 1 1	=	54° 44′	54° 40′
1 1 1, $1\,1\,\bar{1}$	=	70 32	70 36

Fig. 53.



The faces of the cube 1 0 0 are very brilliant; those of the octohedron 1 1 1 are often hollow.

No influence on polarized light.

Colour orange-red."

THIRD MEMOIR.

PHOSPHAMMONIUM AND PHOSPHARSONIUM-, DIARSONIUM- AND ARSAMMONIUM-COMPOUNDS.

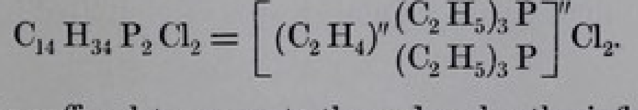
In the former section of this inquiry, I have endeavoured to trace the history of the bodies which are generated by the mutual action of triethylphosphine and dibromide of ethylene. I have endeavoured, as far as possible, to fix with precision the several phases of this reaction, and carefully studied its principal products, the history of which appears to open the clearest perception of the nature of the polyatomic ammonias, and more especially of their connexion with the monatomic bases. The four saline compounds which, in accordance with the indications of theory, are formed by the action of dibromide of ethylene upon triethylphosphine, the bromides of the bromethylated, oxethylated, and vinylated monophosphonium, and of ethylene-diphosphonium represent, in the phosphorus-series, as well as in the nitrogen- and arsenic-series, four classes of salts, the individual terms of which admit of being constructed in unlimited number and endless variety.

The following pages are devoted to the consideration of several compounds belonging to these four principal groups. The examination of the mixed diatomic bases of the phosphorus-nitrogen, phosphorus-arsenic- and arsenic-nitrogen-series, have more especially fixed my attention. Before, however, proceeding to a detailed account of these substances, which form more particularly the subject of this paper, a few experiments may still be briefly mentioned which are even more closely connected with the observations recorded in the previous memoir.

Action of Dichloride of Ethylene on Triethylphosphine.

It is precisely analogous to that of dibromide of ethylene, giving rise to the two compounds—

$$C_8 H_{19} P Cl_2 = [(C_2 H_4 Cl)(C_2 H_5)_3 P] Cl, \text{ and}$$



$$C_{14} H_{34} P_2 Cl_2 = \left[(C_2 H_4)'' \begin{matrix} (C_2 H_5)_3 P \\ (C_2 H_5)_3 P \end{matrix} \right]'' Cl_2.$$

If the reaction be suffered to go on to the end under the influence of heat, the resulting white crystalline mass consists almost entirely of the diphosphonium-compound; no matter in what proportions the two bodies may be mixed, or whether they act upon one another in absence or in presence of alcohol or ether. To obtain the monatomic compound, a mixture of triethylphosphine with a very large excess of chloride of ethylene must be left to itself for some days. The white crystalline needles, which the liquid deposits, are mixed even then with a considerable quantity of the diphosphonium-compound; but on treating their solution with dichloride of platinum, and leaving the pale-yellow precipitate, which exhibits an unmistakeable diphosphonic character, at rest for some hours, it becomes traversed by a number of deep orange-yellow crystalline stars, which may easily be separated from the yellow powder by mechanical rinsing. By boiling the yellow powder with water, an additional quantity of this orange-yellow salt is obtained, which may be purified, together with the first portion, by recrystallization. This salt resembles in most respects the platinum-salt of bromethylated triethylphosphonium; it is, however, somewhat more soluble, and exhibits a more decided tendency to assume the octohedral character. As the properties of this body plainly show that it is the platinum-salt of chlorethylated triethylphosphonium,

$$C_8\,H_{19}\,P\,Pt\,Cl_4 = [(C_2\,H_4\,Cl)(C_2\,H_5)_3\,P]\,Cl,\,Pt\,Cl_2,$$

I have contented myself with determining the amount of platinum contained in it.

0·3470 grm. of platinum-salt, decomposed with hydrosulphuric acid, &c., gave 0·089 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	181·5	46·94	——
1 equiv. of Platinum	98·7	25·52	25·64
3 equivs. of Chlorine	106·5	27·54	——
1 equiv. of Platinum-salt . . .	386·7	100·00	

The chloride prepared from the needle-shaped platinum-salt by sulphuretted hydrogen yielded, when treated with oxide of silver, a caustic liquid, which, after addition of hydrochloric acid and dichloride of platinum, deposited the well-known octohedra of the oxethylated phosphonium-salt:

$$[(C_2\,H_5\,O)(C_2\,H_5)_3\,P]\,Cl,\,Pt\,Cl_2.$$

No doubt could exist respecting the nature of the sparingly soluble diphosphonium-platinum-salt. It was nevertheless recrystallized from boiling hydrochloric acid and identified by analysis.

I. 0·5005 grm. of platinum-salt gave 0·4617 grm. of carbonic acid and 0·2139 grm. of water.

II. 0·5240 grm. of platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1525 grm. of platinum.

The formula

$$C_{14}\,H_{34}\,P_2\,Pt_2\,Cl_6 = \left[\,(C_2\,H_4)''\begin{matrix}(C_2\,H_5)_3\,P\\(C_2\,H_5)_3\,P\end{matrix}\right]''Cl_2,\,2\,Pt\,Cl_2$$

requires the following numbers:—

Theory.			Experiment.	
			I.	II.
C_{14}	168	24·91	25·16	——
H_{34}	34	5·05	4·74	——
P_2	62	9·19	——	——
Pt_2	197·4	29·27	——	29·10
Cl_6	213	31·58	——	——
	674·4	100·00		

The compounds of chlorethylated triethylphosphonium are likewise formed under conditions similar to those which have already been mentioned as leading to the reproduction of the bromethylated from the oxethylated salt. On subjecting the chloride of oxethylated triethylphosphonium to the influence of pentachloride of phosphorus, a violent reaction takes place, attended with evolution of vapours of oxychloride of phosphorus. If the chloride of phosphorus be added by small portions till no further action is perceptible, and the mixture be then digested till the hydrochloric acid, the oxychloride, and any excess of pentachloride are driven off, the chloride of the chlorethylated compound remains in the retort.

$$[(C_2H_5O)(C_2H_5)_3P]Cl + PCl_5 = POCl_3 + [(C_2H_4Cl)(C_2H_5)_3P]Cl + HCl.$$

To fix the nature of this reaction by a number, the solution of the residual chloride was precipitated with dichloride of platinum. On recrystallizing the platinum-precipitate from boiling water, the beautiful needles characteristic of the chlorethylated compound immediately made their appearance.

By analysis,

0·4122 grm. of platinum-salt gave 0·1065 grm. = 25·83 per cent. of platinum.

The formula

$$[(C_2H_4Cl)(C_2H_5)_3P]Cl,\ PtCl_2$$

requires 25·52 per cent. of platinum.

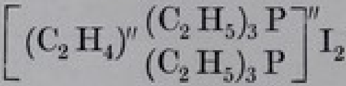
Monochlorinated chloride of ethyl acts on triethylphosphine like dichloride of ethylene. At the common temperature, and with a large excess of the chlorinated compound, the chloride of chlorethyl-triethylphosphonium is produced, which was easily identified by the reaction with excess of nitrate of silver and ammonia, repeatedly mentioned in the previous memoir. At the temperature of 100°, and with a considerable excess of triethylphosphine, crystals of the dichloride of ethylene-diphosphonium are soon deposited. The nature of the latter was fixed by the preparation of the characteristic platinum-salt, and of the beautifully crystallized di-iodide.

ACTION OF DI-IODIDE OF ETHYLENE ON TRIETHYLPHOSPHINE.

The two bodies, in the absence of solvents, act upon one another with explosive violence. The heat evolved causes the iodide of ethylene to resolve itself into ethylene and iodine, which unites directly with the phosphorus-base. If the violence of the action be diminished by admixture of alcohol, a white crystalline mass is obtained consisting almost entirely of the hydriodate of the phosphorus-base.

If the compounds

$$[(C_2H_4I)(C_2H_5)_3P]I \text{ and}$$



$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''I_2$$

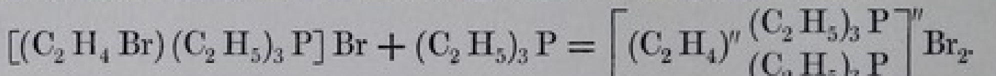
are likewise formed, they must be present in extremely small quantities only. The crystals, dissolved in water and decomposed by baryta, left, after the triethylphosphine had been removed by ether, the iodine by oxide of silver, and the baryta by means of carbonic acid, scarcely traces of an organic compound. The triethylphosphine evidently acts upon iodide of ethylene just like an alcoholic solution of potassa, the chief phase of the reaction doubtless consisting in the transformation,

$$(C_2H_5)_3P + (C_2H_4)''I_2 = [(C_2H_5)_3HP]I + C_2H_3I.$$

I should not omit to mention, however, that the production of iodide of vinyl (C_2H_3I) was not demonstrated by a special experiment. There was some probability of an iodethylated triethylphosphonium-compound being formed by the action of iodide of phosphorus on the chloride or iodide of the oxethylated metal; but these bodies do not act on one another.

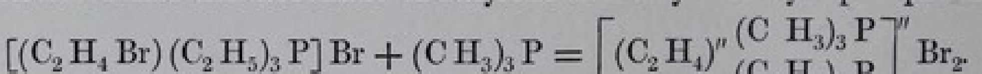
HYBRIDS OF ETHYLENE-DIPHOSPHONIUM.

In a former paragraph, I mentioned as a fact of peculiar interest, the formation of the dibromide of hexethylated ethylene-diphosphonium by the reaction



$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3P = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

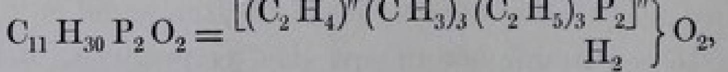
The study of this reaction naturally led me to try that of trimethylphosphine on the bromide of bromethylated triethylphosphonium, which I had a right to expect would thus be converted into the dibromide of ethylene-trimethyl-triethyldiphosphonium:



$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3P = \left[(C_2H_4)''\begin{matrix}(C\ H_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$$

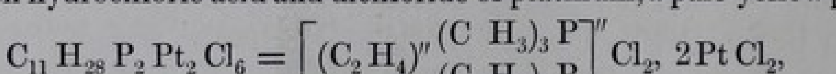
ACTION OF TRIMETHYLPHOSPHINE ON BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

These two bodies act upon each other with the greatest energy, and moreover exactly in the manner indicated by theory. The resulting compound was, of course, examined only as far as necessary to establish the character of the reaction. The bromide of the hybrid diphosphonium is more soluble than the similar diphosphonium-compound previously described, which in other respects it greatly resembles. Oxide of silver eliminates the extremely caustic base,



$$C_{11}H_{30}P_2O_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)_3(C_2H_5)_3P_2]''\\H_2\end{matrix}\right\}O_2,$$

which yields with hydrochloric acid and dichloride of platinum, a pale-yellow platinum-salt,



$$C_{11}H_{28}P_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C\ H_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2,\ 2PtCl_2,$$

crystallizing in scales from boiling water. I have contented myself with determining the amount of platinum in this salt.

0·4794 grm. of platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0·1502 grm. of platinum.

	Theory.		Experiment.
1 equiv. of Diphosphonium	222·0	35·10	——
2 equivs. of Platinum . .	197·4	31·22	31·33
6 equivs. of Chlorine . .	213·0	33·68	——
1 equiv. of Platinum-salt .	632·4	100·00	

The salts of the hybrid diphosphonium crystallize like those of the corresponding hexethylated compound, but, as far as they have been examined, are somewhat more soluble; this remark applies especially to the di-iodide.

It seemed worth while to try whether the bromide of bromethylated triethylphosphonium was capable of fixing a molecule of *phosphoretted hydrogen*. I found, however, that the two bodies do not act upon one another. Phosphoretted hydrogen gas, passed through the alcoholic solution of the bromide, either cold or boiling, did not seem to affect it in any way.

Action of Dibromide of Ethylene on Trimethylphosphine.

This reaction exhibits a repetition of all the phenomena observed in that which takes place between the dibromide and triethylphosphine. The process is completed, if possible, even sooner than in the ethyl-series. The lower boiling-point and overpowering odour of the trimethylphosphine, render it advisable to mix the materials with considerable quantities of alcohol or ether; moreover, on account of the extreme oxidability of the phosphorus-compound, it is necessary to operate in vessels filled with carbonic acid and immediately sealed before the blowpipe. After digestion for a short time at 100°, the mixture of the two liquids solidifies to a hard, dazzling white, crystalline mass, containing the two bromides,

$$C_5H_{13}PBr_2 = [(C_2H_4Br)(CH_3)_3P]Br, \text{ and}$$

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)'' \begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]'' Br_2,$$

one or the other predominating, according to the proportions in which the two bodies were allowed to act upon one another.

It is not difficult to establish by numbers the formation of these two bodies.

Bromide of Bromethyl-trimethylphosphonium.—When a solution of trimethylphosphine in absolute alcohol, mixed with a very large excess of dibromide of ethylene, is exposed for some hours to a temperature of from 50° to 60°, the liquid on cooling deposits well-formed crystals. It is desirable not to pass this temperature; at the boiling-point of water the mixture turns brown, in consequence of secondary reactions. One or two crystallizations from absolute alcohol render the crystals perfectly pure; they exhibit in this state the chemical and physical characters of the corresponding ethylated body, possessing, however, a different crystalline form. I have fixed the composition of this substance by the determination of the bromine accessible to silver-salts.

0·3980 grm. of bromide, precipitated by nitrate of silver, gave 0·2820 grm. of bromide of silver.

The formula

$$C_5\,H_{13}\,P\,Br_2=[(C_2\,H_4\,Br)\,(C\,H_3)_3\,P]\,Br,$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium	184	69·70	——
1 equiv. of Bromine . .	80	30·30	30·16
1 equiv. of Bromide . .	264	100·00	

This result was confirmed by several analyses of the corresponding

Platinum-salt.—This is easily formed by treating the bromide with chloride of silver, when a crystallizable chloride is produced, which yields with dichloride of platinum splendid orange-yellow needles, containing

$$C_5\,H_{13}\,P\,Br\,Pt\,Cl_3=[(C_2\,H_4\,Br)\,(C\,H_3)_3\,P],\ Pt\,Cl_2.$$

I. 0·5440 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1390 grm. of platinum.

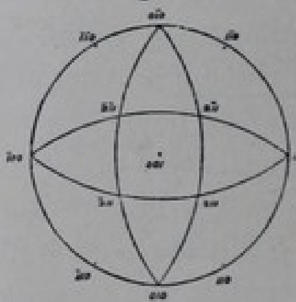
II. 0·495 grm. of platinum-salt, analysed in the same manner, gave 0·126 grm. of platinum.

III. 0·304 grm. of platinum-salt gave 0·077 grm. of platinum.

	Theory.		Experiment.		
			I.	II.	III.
1 equiv. of Phosphonium . .	184·0	47·27	——	——	——
1 equiv. of Platinum . . .	98·7	25·36	25·55	25·45	25 33
3 equivs. of Chlorine . . .	106·5	27·37	——	——	——
1 equiv. of Platinum-salt . .	389·2	100·00			

I have already mentioned that the bromide of bromethyl-trimethylphosphonium crystallizes differently from the bromide of the ethylated body. Whilst the latter is obtained in rhombic dodecahedrons, the methylated bromide affects forms belonging to the trimetric system. QUINTINO SELLA has made the following examination of this compound:—

Fig. 54.



"System trimetric:—

100, 110 = 60° 24′;

001, 101 = 22° 9′.

Forms observed:—

100, 010, 001, 110, 211 (Fig. 54).

Angles.		Calculated.	Observed.
		° ′	° ′
100, 010	=	90 0	90 2
100, 001	=	90 0	89 58
100, 110	=	60 24	60 26
100, 211	=	56 30	56 27
010, 001	=	90 0	90 6
010, 110	=	29 36	29 36
010, 211	=	60 56	60 55
001, 110	=	90 0	89 55
001, 211	=	47 19	47 17
110, $\bar{1}$10	=	59 12	59 12
110, 211	=	45 59	45 45
110, $\bar{2}$11	=	81 23	81 21
211, $\bar{2}$11	=	67 0	67 6
211, 2$\bar{1}$1	=	58 7	58 10
211, $\bar{2}\bar{1}$1	=	94 39	94 34

According to Naumann:—

$$a : b : c = 0{\cdot}4071 : 1 : 0{\cdot}5681.$$

Forms observed:—

$$\infty \breve{P} \infty,\ \infty \bar{P} \infty,\ 0\,P,\ \infty\,P,\ 2\,\breve{P}\,2.$$

According to Weiss:—

$$a : b : c = 1 : 0{\cdot}5681 : 0{\cdot}4071.$$

Forms observed:—

$$a : \infty b : \infty c;\quad \infty a : b : \infty c;\quad \infty a : \infty b : c;\quad a : b : \infty c;\quad \tfrac{1}{2} a : b : c.$$

According to Levy:—

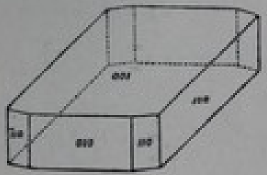
$$\text{M M} = 120^\circ\ 48';\quad b : h = 1 : 0{\cdot}3539.$$

Forms observed:—

$$g', h', \text{P}, \text{M}, e_3.$$

Combinations observed:—

Fig. 55.



100, 010, 001; 110 (Fig. 55).
100, 010, 001; 110, 211 (Fig. 56).
110, 001; 100 (Fig. 57).
110, 001; 100, 010, 211 (Fig. 58).
001, 010, 211 (Fig. 59).

Fig. 56.

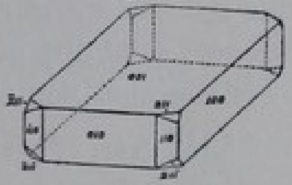


Fig. 57.

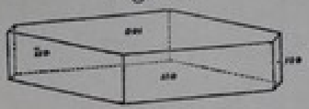


Fig. 58.

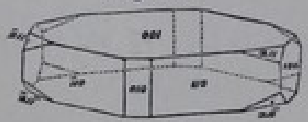
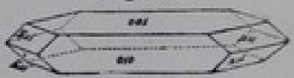


Fig. 59.



The crystals are generally tabular, as in the above figures; sometimes, however, they are elongated in the direction [0 0 1], and then the faces are most unequally developed. Figs. 60 and 61, and, again, Figs. 62 and 63 exhibit two very remarkable crystals of this kind.

The faces of the form 2 1 1 are generally very unequally developed, and some are actually wanting. In the crystals Figs. 60 and 61, and, again, Figs. 62 and 63, only two out of the eight faces 2 1 1 were well developed. The six others were wanting, or could but just be traced.

Fig. 60.

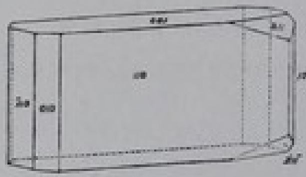


Fig. 61.

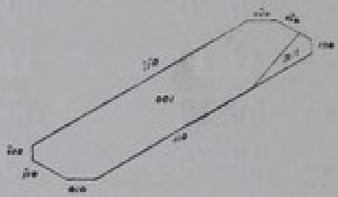


Fig. 62.

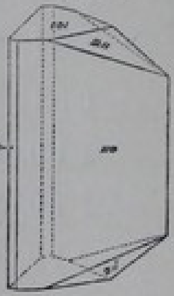
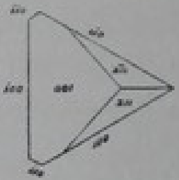


Fig. 63.



The lustre of the faces 0 0 1 is glassy, or even pearly. The lustre of the other faces is less marked, and more fatty.

Cleavages 0 0 1 easily obtained and rather perfect; 1 1 0 easily obtained, but fibrous.

The axes of optical elasticity, in the order of magnitude, are [0 0 1], [1 0 0], [0 1 0]."

Compounds of Oxethyl-trimethylphosphonium.

The liquid filtered from the sulphide of platinum in the three analyses of the platinum-salt of bromethyl-trimethylphosphonium above given, yielded by evaporation the extremely soluble and deliquescent chloride. This salt has not been analysed; but I have transformed it, by oxide of silver, into the corresponding oxethylated compound,

$$C_5H_{15}PO_2 = \left.\begin{matrix}[(C_2H_5O)(CH_3)_3P]\\ H\end{matrix}\right\}O.$$

The caustic liquid is converted by hydrochloric acid into the easily soluble chloride corresponding to the hydrate; this chloride, treated with dichloride of platinum, yields the platinum-salt of oxethylated trimethylphosphonium, which crystallizes in octohedra, like the corresponding ethyl-compound, but is distinguished from the latter by its extraordinary solubility in water.

The composition of this salt was fixed by a platinum-determination.

0·3383 grm. of platinum-salt, precipitated with hydrosulphuric acid, &c., gave 0·1010 grm. of platinum.

The formula

$$C_5H_{14}POPtCl_3 = [(C_2H_5O)(CH_3)_3P]Cl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . . .	121	37·09	——
1 equiv. of Platinum	98·7	30·26	29·86
3 equivs. of Chlorine	106·5	32·65	——
1 equiv. of Platinum-salt . . .	326·2	100·00	

SALTS OF ETHYLENE-HEXMETHYL-DIPHOSPHONIUM.

Dibromide.—This salt is formed when dibromide of ethylene is treated with an excess of trimethylphosphine. The reaction is rapidly accomplished at the temperature of boiling water. The salt resembles the dibromide of the ethyl-series in its properties. It is extremely soluble, and was only once obtained in well-defined crystals, which were analysed and determined. Many efforts were made to produce these well-formed crystals a second time, but without success.

0·2940 grm. of dibromide gave 0·3246 grm. of bromide of silver, corresponding to the formula

$$C_8H_{22}P_2Br_2 = \left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2,$$

as seen by the following comparison of the theoretical and experimental percentages of bromine:—

	Theory.		Experiment.
1 equiv. of Diphosphonium . . .	180	52·94	——
2 equivs. of Bromine	160	47·06	47·00
1 equiv. of Dibromide	340	100·00	

The following are the details of SELLA's crystallographical determination:—

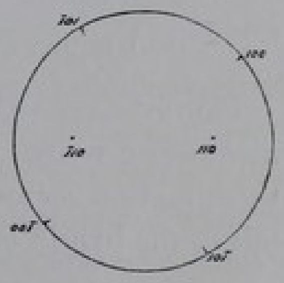
"System monoclinic:—

$$100,\ 101 = 17°\ 45'; \quad 101,\ 001 = 20°\ 4'; \quad 010,\ 111 = 57°\ 47'.$$

Forms observed:—

$$001,\ 110,\ \bar{1}01 \text{ (Fig. 64).}$$

Fig. 64.



Angles.	Calculated.	Observed.
$110,\ 001$ =	58° 22′	58° 22′
$001,\ \bar{1}01$ =	80 52	80 50
$110,\ \bar{1}10$ =	83 13	83 12
$110,\ \bar{1}01$ =	108 35	108 33

According to NAUMANN:—

$$a : b : c = 1{\cdot}1255 : 1 : 0{\cdot}5445; \quad \gamma = 37°\ 49'.$$

Forms observed:—

$$0P,\quad \infty P,\quad P\infty.$$

According to WEISS:—

$$a : b : c = 1 : 0{\cdot}5445 : 1{\cdot}1255; \quad a\,o\,c = 142^\circ\ 11'.$$

Forms observed:—

$$\infty a : \infty b : c; \quad a : b : \infty c; \quad -a : \infty b : c.$$

According to LEVY;—

$$\mathrm{M\,M} = 83^\circ\ 13'; \quad \mathrm{M\,P} = 121^\circ\ 38'; \quad b : h = 1 : 0{\cdot}9884.$$

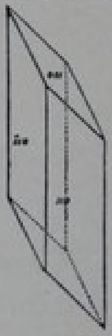
Forms observed:—

P, M, a'.

Combinations observed:—

0 0 1, 1 1 0 (Fig. 65).

Fig. 65.



The face $\bar{1}\,0\,1$ has not been directly observed, but was found to be a cleavage. There is also another cleavage 0 0 1, as distinct and easily obtained as $\bar{1}\,0\,1$."

The dibromide of hexmethylated ethylene-diphosphonium, treated with oxide of silver, yields the corresponding hydrate,

$$C_8\,H_{24}\,P_2\,O_2 = \left.\begin{matrix}[(C_2\,H_4)''(C\,H_3)_6\,P_2]'' \\ H_2\end{matrix}\right\}O_2,$$

which forms with acids a series of salts resembling the corresponding ethyl-compounds. Of these I have briefly examined the di-iodide and the platinum-salt.

Di-iodide.—The base neutralized with hydriodic acid furnishes a salt crystallized in difficultly soluble needles, surpassing in beauty the corresponding body in the ethyl-series.

0·3515 grm. of salt gave 0·3775 grm. of iodide of silver, leading to the formula

$$C_8\,H_{22}\,P_2\,I_2 = \left[(C_2\,H_4)''\begin{matrix}(C\,H_3)_3\,P \\ (C\,H_3)_3\,P\end{matrix}\right]''I_2,$$

which requires

	Theory.		Experiment.
1 equiv. of Diphosphonium . . .	180	41·43	——
2 equivs. of Iodine	254	58·57	57·92
1 equiv. of Di-iodide	434	100·00	

Platinum-salt.—This is an apparently amorphous precipitate, which is nearly insoluble in water, dissolves with extreme slowness in boiling hydrochloric acid, and separates therefrom on cooling in golden-yellow laminæ, very much like those of the platinum-salt of the hybrid ethylene-trimethyl-triethyl-diphosphonium. It consists of

$$C_8\,H_{22}\,P_2\,Pt_2\,Cl_6 = \left[(C_2\,H_4)''\begin{matrix}(C\,H_3)_3\,P \\ (C\,H_3)_3\,P\end{matrix}\right]''Cl_2,\,2\,Pt\,Cl_2.$$

I. 0·4940 grm. of platinum-salt gave, when precipitated by sulphuretted hydrogen, &c., 0·1650 grm. of platinum.

II. 0·5730 grm. of platinum-salt gave 0·1900 grm. of platinum.

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diphosphonium .	180·0	30·49	——	——
2 equivs. of Platinum . . .	197·4	33·43	33·40	33·16
6 equivs. of Chlorine . . .	213·0	36·08	——	——
1 equiv. of Platinum-salt . .	590·4	100·00		

SERIES OF MIXED DIATOMIC BASES.

The investigation of the intimate relation which unites the bromethylated monophosphonium with the ethylene-diphosphonium-compounds, together with the establishment of the easy transition from the monatomic to the diatomic series, naturally suggested the idea of subjecting the bromethylated bromide, which forms the starting-point of the whole investigation, to the action of *monamines*, *monarsines*, and *monostibines*, in the expectation that diatomic bases would be formed containing nitrogen, arsenic, and antimony, side by side with phosphorus, and equivalent to it in chemical value and character. How far this expectation has been realized may be seen from the following experiments.

PHOSPHAMMONIUM-COMPOUNDS.

Action of Ammonia on Bromide of Bromethyl-triethylphosphonium.

In alcoholic solution, these two bodies act upon one another at ordinary temperatures, the reaction being indicated by considerable evolution of heat. To ensure complete transformation, the mixture is digested at 100° for half an hour in sealed tubes. On evaporating the alcohol and the excess of ammonia, there remains an extremely deliquescent saline mass, which crystallizes with difficulty. To remove small quantities of ammonia which may be present in the form of bromide of ammonium, the solution of the saline residue is treated with excess of oxide of silver, whereby a strongly alkaline liquid is set free, which may be digested on the water-bath without decomposition, so that traces of ammonia are easily driven off. Further investigation showed the presence in the caustic alkaline liquid of a base containing both phosphorus and nitrogen, viz. the hydrate of ethylene-triethylphosphammonium,

$$C_8H_{24}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3PN]'' \\ \quad\quad\quad\quad\quad\quad H_2\end{matrix}\right\}O_2.$$

The reaction between the bromethylated monophosphonium and ammonia had therefore taken place exactly as might have been expected from the behaviour of the former compound with the monophosphines:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + H_3N = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ H_3N\end{matrix}\right]''Br_2.$$

I have fixed the composition of the nitrophosphoretted base by the analysis of the platinum-salt and of the gold-salt.

Platinum-salt.—On saturating the alkaline hydrate with hydrochloric acid and adding dichloride of platinum, a very voluminous, pale-yellow, slightly crystalline precipitate is obtained, which is difficultly soluble in boiling water, and also in boiling concentrated hydrochloric acid. The acid solution deposits well-formed prismatic crystals. The crystallization from concentrated hydrochloric acid is necessary to ensure the purity of the product; it appears that the direct precipitate contains an admixture which remains dissolved in the acid. Specimens of different preparation gave on analysis the following results:—

I. 0·6817 grm. of platinum-salt gave 0·4220 grm. of carbonic acid and 0·2256 grm. of water.

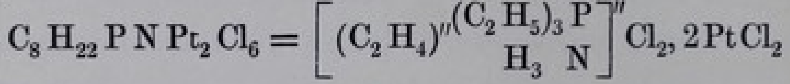
II. 0·8285 grm. of platinum-salt gave 0·5195 grm. of carbonic acid and 0·2890 grm. of water.

III. 0·3658 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1257 grm. of platinum.

IV. 0·5005 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1716 grm. of platinum.

V. 0·8835 grm. of platinum-salt, treated in the same manner, gave 0·3069 grm. of platinum.

The formula



$$C_8H_{22}PNPt_2Cl_6=\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\ \ N\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires

Theory.			Experiment.				
			I.	II.	III.	IV.	V.
C_8	96	16·74	16·88	17·10	——	——	——
H_{22}	22	3·84	3·67	3·87	——	——	——
P	31	5·41	——	——	——	——	——
N	14	2·44	——	——	——	——	——
Pt_2	197·4	34·43	——	——	34·28	34·36	34·73
Cl_6	213	37·14	——	——	——	——	——
	573·4	100·00					

Some of the crystals, obtained on slowly cooling a boiling solution in concentrated hydrochloric acid, were sufficiently well-formed to enable Q. SELLA to examine them crystallographically. He has communicated to me the following description:—

"System trimetric:—

100, 110 = 59° 50′; 001, 101 = 70° 38′.

Forms observed:—

100, 110, 101, 010 (Fig. 66).

Angles.		Calculated.	Observed.
100, 010	=	90° 0′	89° 40′
100, 110	=	59 50	59 55

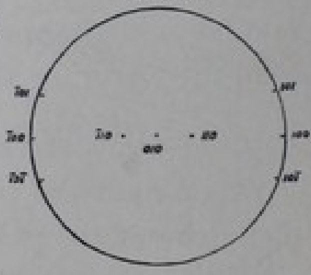


Fig. 66.

Angles.		Calculated.	Observed.
100, 101	=	19° 22′	19° 27′
010, 110	=	30 10	——
010, 101	=	90 0	——
110, $\bar{1}$10	=	60 20	60 10
110, 101	=	61 42	61 37
101, $\bar{1}$01	=	38 44	38 54

According to Naumann:—

$$a:b:c=2{\cdot}8449:1:0{\cdot}5812.$$

Forms observed:—

$$\infty\breve{P}\infty,\ \infty\bar{P}\infty,\ \infty P,\ \breve{P}\infty.$$

According to Weiss:—

$$a:b:c=1:0{\cdot}5812:2{\cdot}8449.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad a:b:\infty c;\quad a:\infty b:c.$$

According to Levy:—

$$\mathrm{M\,M}=119°\,40';\quad b:h=1:2{\cdot}4596.$$

Forms observed:—

g', h', M, e'.

Combinations observed:—

100, 110, 101 (Fig. 67).

100, 110, 101; 010 (Fig. 68).

Fig. 67.

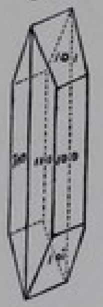
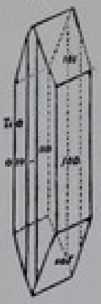


Fig. 68.



Cleavage 0 1 0 imperfect.

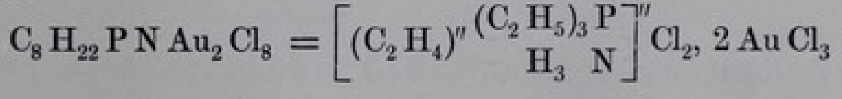
The faces 1 0 1 are dull, the others brilliant. The crystals are optically negative. The medium line is perpendicular to 1 0 0, and the plane of the optical axes is parallel to 0 0 1. The external angle of the optical axes appears to be about 60°.

Hardness greater than that of gypsum."

Gold-salt.—The solution of the dichloride, which is obtained by treating the crystallized platinum-salt with hydrosulphuric acid, yields with trichloride of gold a golden-yellow precipitate consisting of fine needles, which are difficultly soluble in water.

0·3845 grm. of gold-salt, precipitated by hydrosulphuric acid, &c., gave 0·1800 grm. of gold.

The formula



$$C_8H_{22}PNAu_2Cl_8=\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\ H_3\quad N\end{matrix}\right]''Cl_2,\ 2\,AuCl_3$$

requires

	Theory.		Experiment.
1 equiv. of Phosphammonium	163	19·38	——
2 equivs. of Gold	394	46·85	46·81
8 equivs. of Chlorine	284	33·77	——
1 equiv. of Gold-salt	841	100·00	

The analysis of the platinum-salt and of the gold-salt sufficiently fixes the composition of the series of diatomic phosphammonium-compounds. I have prepared some of the simple salts of this nitrophosphoretted metal, especially the dichloride, the dibromide, and the di-iodide. They all crystallize pretty well, although they are in general more soluble and less stable than the diphosphonium-salts. The diperchlorate is rather difficultly soluble, and crystallizes with facility. These salts have not been analysed. The free base likewise resembles the hydrate of the diphosphonium. Its solution is powerfully alkaline, and precipitates from most metallic salts the hydrates of the metals. The solution of the base may be concentrated on the water-bath without losing ammonia; addition of potassa to the residuary liquid separates the hydrate in oily drops, which redissolve when mixed with water.

The peculiar construction of this body induced me to examine its deportment under the influence of heat. The substitution being limited to 5 equivs. of hydrogen, the question arose whether the hydrate could be distilled in the form of a phosphamine of the formula

$$\left.\begin{array}{l}(C_2H_4)''\\(C_2H_5)_2\\(C_2H_5)H\end{array}\right\}PN.$$

Experiment showed, however, that the base cannot be volatilized without entire decomposition; the product of distillation no longer contains a trace of the original body. Ammonia is abundantly evolved during the distillation, and at a certain stage of the process the residue contains the hydrate of vinylated triethylphosphonium,

$$\left.\begin{array}{r}[(C_2H_4)''(C_2H_5)_3H_3PN]''\\H_2\end{array}\right\}O_2 = H_3N + H_2O + \left.\begin{array}{r}[(C_2H_3)(C_2H_5)_3P]\\H\end{array}\right\}O.$$

I infer this from the analysis of an iodide obtained by neutralizing with hydriodic acid the mixed base which had been heated for some time. This salt was exceedingly soluble in water, and even in absolute alcohol, and was precipitated from the latter by addition of ether.

0·4865 grm. of iodide gave 0·416 grm. of iodide of silver.

The formula

$$C_8H_{18}PI = [(C_2H_3)(C_2H_5)_3P]I$$

requires the following values:—

	Theory.		Experiment.
1 equiv. of Phosphonium . .	145	53·31	——
1 equiv. of Iodine	127	46·69	46·4
1 equiv. of Iodide	272	100·00	

The mother-liquor of this salt was freed from excess of silver and precipitated by trichloride of gold. The yellow needles were analysed.

0·6580 grm. of gold-salt gave 0·2615 grm. =39·68 per cent. of gold.

The formula

$$C_8H_{18}PAuCl_4 = [(C_2H_3)(C_2H_5)_3P]Cl, AuCl_3$$

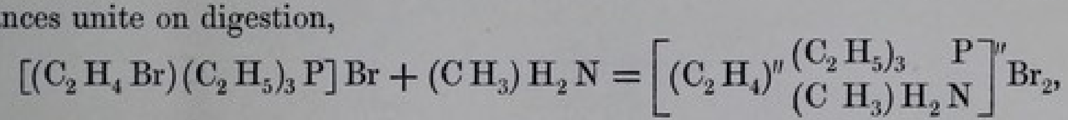
requires 39·24 per cent. of gold.

The deportment of the bromethylated bromide under the influence of ammonia, opens an almost unlimited series of diatomic nitrophosphoretted metals. It is only necessary to replace in the above reaction the ammonia by a monamine, in order to obtain a new metal of almost any composition which could be desired. I have produced a few bodies of this description, in order to establish experimentally the relations, which theory, resting on the observations in the ammonia-reaction, sufficiently suggests.

Action of Methylamine on the Bromide of Bromethyl-triethylphosphonium.

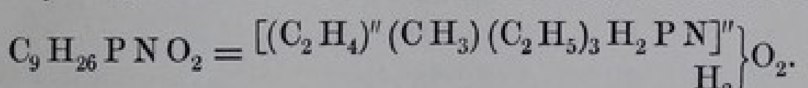
Compounds of Ethylene-methyl-triethylphosphammonium.

Repetition of all the phenomena observed in the experiment with ammonia. Both substances unite on digestion,



$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)H_2N = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C\ H_3)H_2N\end{matrix}\right]'' Br_2,$$

and the compound yields, on treatment with oxide of silver, the caustic base

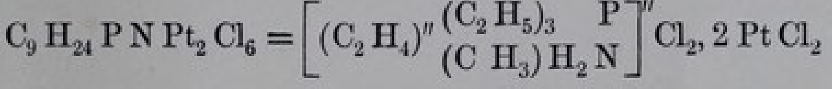


$$C_9H_{26}PNO_2 = \left.\begin{matrix}[(C_2H_4)''(CH_3)(C_2H_5)_3H_2PN]''\\ H_2\end{matrix}\right\}O_2.$$

I have been satisfied to fix the composition of this body by the analysis of a rather difficultly soluble platinum-compound, crystallizing from boiling water in splendid needles, frequently an inch in length. I did not succeed, however, in obtaining, either from boiling water or from boiling hydrochloric acid, crystals which could have been determined. For analysis the salt was recrystallized from boiling water.

0·3734 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1250 grm. of platinum.

The formula



$$C_9H_{24}PNPt_2Cl_6 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C\ H_3)H_2N\end{matrix}\right]'' Cl_2, 2PtCl_2$$

requires

	Theory.		Experiment.
1 equiv. of Phosphammonium . . .	177	30·13	——
2 equivs. of Platinum	197·4	33·60	33·48
6 equivs. of Chlorine	213	36·27	——
1 equiv. of Platinum-salt	587·4	100·00	

Action of Ethylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-tetrethylphosphammonium.

The two bodies unite with evolution of heat. Since the salts of the new phosphammonium crystallize very beautifully, I have not been able to resist the temptation of examining several of them somewhat more minutely.

Platinum-salt.—The crude product of the reaction, purified with oxide of silver and saturated with hydrochloric acid, furnishes, on addition of dichloride of platinum, an orange-yellow platinum-compound, crystallizing in needles very similar to those of the methyl-compound above-described. The salt, recrystallized from boiling water, gave on analysis the following numbers:—

I. 0·7544 grm. of platinum-salt gave 0·5565 grm. of carbonic acid and 0·3023 grm. of water.

II. 0·6056 grm. of platinum-salt, when treated with sulphuretted hydrogen, &c., gave 0·1964 grm. of platinum.

The formula

$$C_{10}H_{26}PNPt_2Cl_6 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]'' Cl_2, 2\,PtCl_2$$

requires

	Theory.		Experiment.	
			I.	II.
C_{10}	120	19·96	20·12	——
H_{26}	26	4·32	4·45	——
P	31	5·15	——	——
N	14	2·33	——	——
Pt_2	197·4	32·82	——	32·43
Cl_6	213	35·42	——	——
	601·4	100·00		

Q. SELLA has determined the crystalline form of this beautiful salt.

"System monoclinic:—

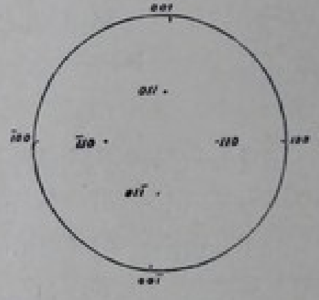
100, 101 = 43° 35′; 101, 001 = 43° 17′; 111, 010 = 55° 36′.

Forms observed:—

100, 001, 110, 011 (Fig. 69).

Angles.		Calculated.	Observed.
100, 001	=	86° 52′	86° 52′
100, 110	=	44 55	45 8
100, 011	=	87 47	87 38
001, 110	=	87 47	87 53
001, 011	=	44 46	44 47
110, $\bar{1}$10	=	90 10	90 10
110, 011	=	58 21	58 5
110, 01$\bar{1}$	=	61 59	62 11
011, 01$\bar{1}$	=	90 29	90 29

Fig. 69.



According to NAUMANN:—

$$a:b:c = 0{\cdot}9945:1:1{\cdot}0013; \quad \gamma = 86^\circ\ 52'.$$

Forms observed:—

$$\infty \bar{P} \infty, \quad 0\,P, \quad \infty P, \quad \not{P} \infty.$$

According to WEISS:—

$$a:b:c = 1:1{\cdot}0013:0{\cdot}9945; \quad aoc = 93^\circ\ 8'.$$

Forms observed:—

$$a:\infty b:\infty c; \quad \infty a:\infty b:c; \quad a:b:\infty c; \quad \infty a:b:c.$$

According to LEVY:—

$$MM = 90^\circ\ 10'; \quad MP = 92^\circ\ 13; \quad b:h = 1:0{\cdot}7027.$$

Forms observed:—

$$h', \quad P, \quad M, \quad e'.$$

Combinations observed:—

1 1 0, 0 1 1 (Fig. 70).
1 1 0, 0 1 1, 0 0 1 (Fig. 71).
1 1 0, 0 1 1, 0 0 1, 1 0 0 (Figs. 72, 73).

Fig. 70.

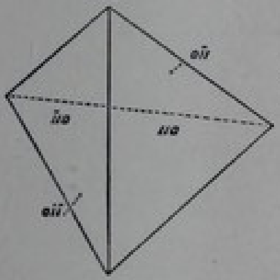


Fig. 71.

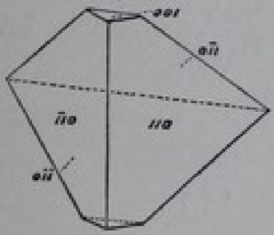


Fig. 72.

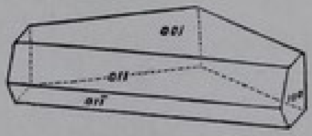
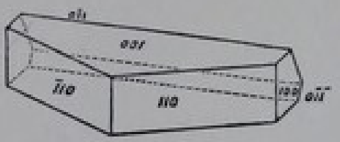


Fig. 73.



The crystals are hemihedral: the faces 0 0 1 and 1 0 0 have their parallels, but of the four faces of the forms 1 1 0 and 0 1 1 only two were observed with their corresponding parallels.

All the crystals examined exhibit the faces 1 1 0, $\bar{1}\,1\,0$, and the faces $0\,\bar{1}\,1$, $0\,\bar{1}\,\bar{1}$ (Figs. 70, 71, and 73). In a single crystal (Fig. 72) the faces $\bar{1}\,\bar{1}\,0$, $1\,\bar{1}\,0$, and the faces 0 1 1, $0\,1\,\bar{1}$ were observed. It is evident that the crystals Figs. 72 and 73 are symmetrical but not superposable.

The crystals frequently exhibit the habitus of triangular tables (Figs. 72 and 73); sometimes they are tetrahedrons (Fig. 70), or beveled tetrahedrons (Fig. 71).

The faces are very brilliant but very often rounded, so that they are apt to yield many images and a great difference in the angles.

The observed angles given in the above table are the mean of the results obtained in the measurement of six crystals.

Another difficulty in the determination of these crystals is the minute difference of the angles of the zones [0 0 1] and [1 0 0]. The results of observation are $1\,1\,0, \bar{1}\,1\,0 = 90^\circ\,10'$; $0\,1\,1, 0\,1\,\bar{1} = 90^\circ\,29'$; but I cannot affirm that the second angle is greater than the first. For distinguishing the two zones I had at my disposal only one criterion, which is of comparatively little value. The faces designated as $1\,1\,0$, $\bar{1}\,1\,0$ are in general equally developed, but of the two others, $0\,\bar{1}\,1$ is much larger than $0\,\bar{1}\,\bar{1}$, as seen in Fig. 73. I took it for granted that the two equally developed faces belonged to the zone $[0\,0\,1]$, and the unequally developed faces to the zone $[1\,0\,0]$.

The plane of polarization is not altered if the light passes through the faces $0\,0\,1$, $0\,0\,\bar{1}$ and the faces $1\,0\,0$, $\bar{1}\,0\,0$ in the direction $[0\,1\,0]$.

Colour orange-red.

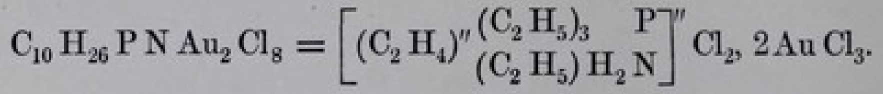
The minuteness of the crystals, and the difficulty of fixing them on account of their hemihedral form, has prevented me from finding their cleavages."

Gold-salt.—Golden-yellow, difficultly soluble needles, which may be recrystallized from boiling water without decomposition.

I. 0·6325 grm. of gold-salt gave 0·3285 grm. of carbonic acid and 0·1788 grm. of water.

II. 0·6963 grm. of gold-salt left after ignition 0·3160 grm. of gold. The residue of gold retained with great pertinacity a small quantity of carbon, from which it could be separated only by solution in *aqua regia*, filtration, and re-evaporation.

The analyses lead to the formula



$$C_{10}H_{26}PNAu_2Cl_8 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P \\ (C_2H_5)\,H_2 & N\end{matrix}\right]'' Cl_2,\ 2\,AuCl_3.$$

	Theory.		Experiment.	
			I.	II.
C_{10}	120	13·81	14·16	——
H_{26}	26	2·99	3·14	——
P	31	3·57	——	——
N	14	1·61	——	——
Au_2	394	45·34	——	45·38
Cl_8	284	32·68	——	——
	869	100·00		

Di-iodide.—It was prepared from the recrystallized platinum-salt by treatment with sulphuretted hydrogen, decomposition of the resulting dichloride by oxide of silver, and neutralization of the liberated base with hydriodic acid. White acicular crystals, extremely soluble in water, but not deliquescent, likewise very soluble in spirit of wine, difficultly soluble in absolute alcohol, insoluble in ether. From the alcoholic liquid, the salt is precipitated by ether in the crystalline state. From the aqueous solution, the iodide separates, on addition of potassa, in the form of oily globules, which gradually solidify with crystalline structure.

Since the examination of the phosphammonium-compounds could not have been legitimately concluded without a nitrogen-determination, the nitrogen was taken in this iodide.

I. 0·6663 grm. of di-iodide, dried *in vacuo* over sulphuric acid, gave 0·3335 grm. of ammonio-chloride of platinum.

II. 0·4680 grm. of di-iodide gave 0·4891 grm. of iodide of silver.

The formula is accordingly

$$C_{10}H_{26}PNI_2 = \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3 & P\\ (C_2H_5)H_2 & N\end{matrix}\right]'' I_2.$$

Theory.			Experiment.	
			I.	II.
C_{10}	120	26·97	——	——
H_{26}	26	5·84	——	——
P	31	6·97	——	——
N	14	3·14	3·14	——
I_2	254	57·08	——	56·48
	445	100·00		

The caustic base, which corresponds to the iodide, is readily obtained by oxide of silver. It presents considerable stability, and may be evaporated on the water-bath until it separates in heavy oily globules. Here again the action of heat might have given rise to the formation of a volatile phosphamine,

$$\left.\begin{matrix}(C_2H_4)''\\ (C_2H_5)_2\\ (C_2H_5)_2\end{matrix}\right\} PN,$$

capable of reproducing the salts from which it was derived. But, exactly as in the case of the compound formed by the coalescence of triethylphosphine and ammonia, distillation destroys the base. The deportment of this substance under the influence of heat is characteristic; its study cannot fail to assist in the general elucidation of the constitution of this class of bodies. I may, in a subsequent inquiry, find an opportunity of returning to this question.

Both methylamine and ethylamine being primary monamines, I have, in conclusion, submitted the bromethylated bromide to the action of a secondary base, viz. diethylamine, and lastly, of some tertiary bases, viz. trimethylamine and triethylamine.

Action of Diethylamine on the Bromide of Bromethyl-triethylphosphonium.

Compounds of Ethylene-pentethylphosphammonium.

The reaction is similar to that of ethylamine; the resulting product, conveniently treated, yields a splendid platinum-salt crystallizing in rectangular plates.

Two platinum-determinations furnished the following results:—

I. 0·4900 grm. of platinum-salt, treated with hydrosulphuric acid, &c., gave 0·1557 grm. of platinum.

II. 0·6280 grm. of platinum-salt, analysed in the same manner, gave 0·1990 grm. of platinum.

These numbers correspond to the formula

$$C_{12}H_{30}PNPt_2Cl_6=\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Cl_2,\ 2PtCl_2.$$

	Theory.		Experiment.	
			I.	II.
1 equiv. of Phosphammonium	219·0	34·79	——	——
2 equivs. of Platinum . . .	197·4	31·37	31·77	31·68
6 equivs. of Chlorine . . .	213·0	33·84	——	——
1 equiv. of Platinum-salt . .	629·4	100·00		

ACTION OF TRIMETHYLAMINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

ETHYLENE-TRIMETHYL-TRIETHYLPHOSPHAMMONIUM-COMPOUNDS.

As to the preparation and properties, I may refer to the preceding paragraphs. It is only necessary to quote the analysis of the platinum-salt, which crystallizes in beautiful needles.

I. 0·4758 grm. of platinum-salt gave 0·3715 grm. of carbonic acid and 0·1907 grm. of water.

II. 0·7485 grm. of platinum-salt, when fused with carbonate of sodium, &c., gave 0·2415 grm. of platinum and 1·0580 grm. of chloride of silver.

The formula

$$C_{11}H_{28}PNPt_2Cl_6=\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)_3N\end{matrix}\right]''Cl_2,\ 2PtCl_2$$

requires

	Theory.		Experiment.	
			I.	II.
C_{11}	132	21·45	21·29	——
H_{28}	28	4·55	4·45	——
P	31	5·04	——	——
N	14	2·27	——	——
Pt_2	197·4	32·08	——	32·26
Cl_6	213	34·61	——	34·96
	615·4	100·00		

The examination of this compound has induced me to perform an experiment which may here be briefly mentioned. The action of trimethylamine on dibromide of ethylene gives rise to the formation of a beautifully crystallized salt, the bromide of bromethyl-trimethylammonium, of which I have already given a fugitive sketch in the 'Proceedings of the Royal Society'*. I was curious to ascertain whether the dibromide, generated by the union of *trimethylamine* with the bromide of bromethyl-*triethyl-phosphonium*, could likewise be formed by submitting the bromide of bromethyl-*trimethyl-*

---

* Proceedings of the Royal Society, vol. ix. p. 293.

ammonium to the action of *triethylphosphine*:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (CH_3)_3N = [(C_2H_4Br)(CH_3)_3N]Br + (C_2H_5)_3P$$
$$= \left[(C_2H_4)'' \begin{matrix}(C_2H_5)_3\,P\\(CH_3)_3\,N\end{matrix}\right]'' Br_2.$$

The bromide of bromethylated trimethylammonium is indeed readily attacked by triethylphosphine, but the change is very different from what I had expected. I intend in another paper to return to the products of this reaction.

Before leaving the history of the phosphammonium-compounds, I have briefly to allude to a peculiar deportment of the bromethylated bromide. When treating this compound with triethylamine instead of trimethylamine, expecting, of course, to observe a repetition of the phenomena so frequently witnessed, I was surprised to find that these substances, although acting with considerable energy, fail to produce the anticipated phosphammonium-compound. This unforeseen result induced me to examine this reaction repeatedly and with particular care. The result remained the same. On evaporating the alcoholic product of the reaction, and treating the concentrated solution with oxide of silver, a powerfully alkaline liquid remained, even after the expulsion of the triethylamine, considerable quantities of which were liberated. This residuary alkaline liquid, saturated with hydrochloric acid, yielded, on addition of dichloride of platinum, the beautiful octohedra of the oxethylated triethylphosphonium-platinum-salt, which was identified by analysis. The specimen which was employed in analysis IV., mentioned in the description of the oxethylated platinum-salt, had been prepared by the action of triethylamine on the bromethylated bromide:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N + H_2O = [(C_2H_5O)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

This equation involves the intervention of water in the reaction, which was obviously furnished by the imperfectly de-hydrated alcohol used in the experiments. In the anhydrous state, the bromethylated bromide and triethylamine scarcely act at 100°; between 120° and 130°, a reaction takes place, among the products of which, as yet very imperfectly examined, I was likewise unable to trace the presence of a phosphammonium-like compound. It can scarcely be doubted that this reaction gives rise to the formation of bromide of vinyl-triethylphosphonium:

$$[(C_2H_4Br)(C_2H_5)_3P]Br + (C_2H_5)_3N = [(C_2H_3)(C_2H_5)_3P]Br + [(C_2H_5)_3HN]Br.$$

Experimentally the question remains undecided.

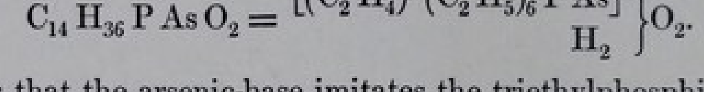
The elegance and precision with which the bromethylated bromide fixes the elements of ammonia and of the monamines, very naturally suggested the idea of examining the deportment of this body under the influence of diamines and triamines. The results obtained in these experiments do not belong to this part of the inquiry. Suffice it to say for the present, that these substances attack the bromide with the utmost energy, giving rise to an almost unlimited number of polyatomic bases of a higher order, the constitution of which, though complicated, is traceable in advance by the experience acquired in the simpler forms of reaction.

PHOSPHARSONIUM-COMPOUNDS.

There was no necessity for entering into a detailed examination of this class of compounds. I have in fact been satisfied to establish, by a few characteristic numbers, the existence of the phospharsonium-group.

ACTION OF TRIETHYLARSINE ON THE BROMIDE OF BROMETHYL-TRIETHYLPHOSPHONIUM.

On digesting the two substances in sealed tubes, the usual phenomena are observed. The saline mass which is formed yields, by treatment with oxide of silver *in the cold*, a powerfully alkaline solution containing the dihydrate of ethylene-hexethylphospharsonium,



$$C_{14}H_{36}PAsO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]'' \\ H_2\end{matrix}\right\}O_2.$$

It is thus obvious that the arsenic-base imitates the triethylphosphine in its deportment with the bromethylated bromide. The two substances simply combine to form the dibromide of the phospharsonium.

The alkaline solution of the hydrate of the phospharsonium exhibits the leading characters of this class of bases; I may therefore refer to the detailed account which I have given of the hydrate of the diphosphonium. The saline compounds likewise resemble those of the diphosphonium. The dichloride and the di-iodide were obtained in beautiful crystalline needles, exhibiting a marked tendency to form well-crystallized double salts. I have prepared the compounds of the dichloride with chloride of tin, bromide of zinc, trichloride of gold, and lastly, with dichloride of platinum. The latter compound was analysed in order to fix the composition of the series.

Platinum-salt.—The product of the reaction of triethylarsine upon the bromethylated bromide is treated with oxide of silver *in the cold*, and the alkaline solution thus obtained is saturated with hydrochloric acid, and precipitated with dichloride of platinum. An exceedingly pale yellowish, apparently amorphous precipitate of marked diphosphonic appearance is thrown down, almost insoluble in water, but dissolving in boiling concentrated hydrochloric acid. The hydrochloric solution deposits, on cooling, beautiful orange-red prisms, resembling the crystals of the corresponding diphosphonium-platinum-salt.

I. 0·4668 grm. of platinum-salt gave 0·3914 grm. of carbonic acid and 0·2003 grm. of water.

II. 0·4585 grm. of platinum-salt, fused with carbonate of sodium, gave 0·5460 grm. of chloride of silver. The platinum separated in this experiment was contaminated with arsenic.

The formula

$$C_{14}H_{34}PAsPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3As\end{matrix}\right]''Cl_2, 2PtCl_2$$

requires

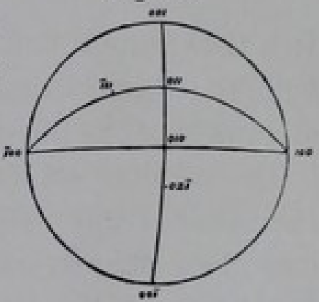
Theory.			Experiment.	
			I.	II.
C_{14}	168	23·38	22·87	——
H_{34}	34	4·73	4·77	——
P	31	4·32	——	——
As	75	10·44	——	——
Pt_2	197·4	27·48	——	——
Cl_6	213	29·65	——	29·46
	718·4	100·00		

Quintino Sella has examined the crystals of the phospharsonium-platinum-salt. I append the results of his observations.

"System triclinic:—

100, 010 = 81° 52′; 100, 001 = 88° 14′;
010, 001 = 89 9; 100, $\bar{1}$11 = 120 18;
010, $\bar{1}$11 = 64 4.

Fig. 74.



Forms observed:—

100, 001, 010, 011, $\bar{1}$11, 02$\bar{1}$ (Fig. 74).

Angles.		Calculated.	Observed.
100, 010	=	81° 52′	81° 52′
100, 001	=	88 14	88 14
100, 011	=	83 48	83 52
100, 02$\bar{1}$	=	84 14	——
100, $\bar{1}$11	=	120 18	120 18
010, 001	=	89 9	89 9
010, 011	=	53 3	——
010, 02$\bar{1}$	=	34 25	34 28
010, $\bar{1}$11	=	64 4	63 53
001, 011	=	36 6	——
001, 02$\bar{1}$	=	123 34	123 38
001, $\bar{1}$11	=	46 54	46 37
011, 02$\bar{1}$	=	87 29	——
011, $\bar{1}$11	=	36 30	——
02$\bar{1}$, $\bar{1}$11	=	91 15	——

According to NAUMANN:—

$$a:b:c = 0{\cdot}8533:1{\cdot}1689:1;\quad \alpha = 81^\circ\ 53';\quad \beta = 88^\circ\ 20';\quad \gamma = 90^\circ\ 36'.$$

Forms observed:—

$$\infty\bar{P}\infty;\quad \infty\breve{P}\infty;\quad 0P;\quad \breve{P}'\infty;\quad 2\breve{P}_{,}\infty;\quad P'.$$

According to WEISS:—

$$a:b:c = 1:1{\cdot}1689:0{\cdot}8533;\quad aob = 98^\circ\ 7';\quad boc = 90^\circ\ 36';\quad coa = 91^\circ\ 40'.$$

Forms observed:—

$$a:\infty b:\infty c;\quad \infty a:b:\infty c;\quad \infty a:\infty b:c;\quad \infty a:b:c;\quad -a:b:c;\quad \infty a:b:-2c.$$

According to LEVY:—

$$MT = 98^\circ\ 8';\quad TP = 91^\circ\ 46';\quad PM = 90^\circ\ 51'.$$

$$H:F:D = 0{\cdot}8533:1{\cdot}1689:1.$$

Forms observed:—

$$M, T, P, d', e', c^{\frac{1}{2}}.$$

Combinations:—

$100,\ 010,\ 001$ (Fig. 75).
$100,\ 010,\ 001;\ \bar{1}11$ (Fig. 76).
$100,\ 010,\ 001;\ \bar{1}11,\ 02\bar{1}$
$100,\ 010,\ 001;\ \bar{1}11,\ 02\bar{1},\ 011$ (Fig. 77).

Fig. 75.

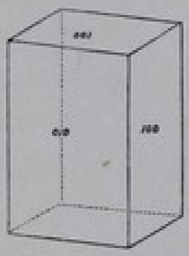


Fig. 76.

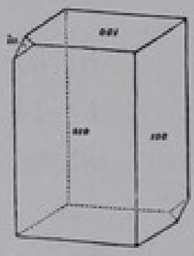


Fig. 77.

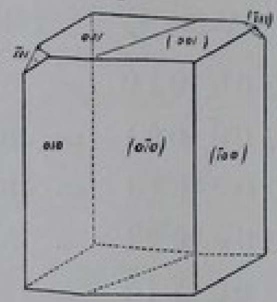
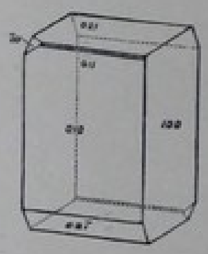


Fig. 78.



Cleavages 1 0 0 and 0 0 1: distinct and easily obtained. The cleavage is occasionally observed to take place during measuring, probably in consequence of the heat emanating from the face, which has to be brought close on account of the minuteness of the crystals.

Hemitropic crystals with the axis of hemitropy [0 0 1] (Fig. 78). It was possible to verify by measurement that the axis of hemitropy is really [0 0 1], and not a line perpendicular to one of the faces of the crystal."

The phospharsonium-compounds, and more especially the hydrate of the series, are far less stable than the corresponding terms of the diphosphonium-series.

If the product of the action of triethylarsine on the bromethylated monophosphonium be *boiled* with oxide of silver, instead of being treated in the cold, not a trace of the phospharsonium-compound is obtained. The caustic solution which is formed, yields, when saturated with hydrochloric acid and precipitated with dichloride of platinum, only the rather soluble octohedral crystals of the oxethylated triethylphosphonium.

The nature of this transformation is clearly exhibited when a solution of the hydrate of the phospharsonium, filtered off *in the cold* from the excess of oxide of silver, is submitted to ebullition. Immediately the clear liquid is rendered turbid from separated triethylarsine which becomes perceptible, moreover, by its powerful odour; the solution now contains the hydrate of oxethylated triethylphosphonium.

$$\left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6PAs]''\\ H_2\end{matrix}\right\}O_2=(C_2H_5)_3As+\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\}O.$$

When the dibromide is boiled with the oxide of silver, a beautiful silver mirror is formed on the sides of the vessel, obviously in consequence of a partial oxidation of the liberated triethylarsine.

Some experiments were made to produce a diatomic compound containing phosphorus and antimony. I expected to form this body, the dibromide of a phosphostibonium, by the action of triethylstibine on the bromethylated bromide, so frequently mentioned in this paper. The two bodies react upon one another, but only after protracted digestion or exposure to a rather high temperature. The product of the reaction is complex, yielding a comparatively small quantity of a difficultly soluble platinum-salt of diatomic appearance. I have repeatedly modified the reaction, and analysed the products in the form of platinum-salts: I omit to quote the detail of these experiments, since they have failed to disentangle the difficulties of the reaction.

Some experiments upon the deportment of dibromide of ethylene with triethylarsine were more successful. The reaction between these two bodies had been selected as a subject of inquiry by Mr. W. Valentin, to whom I am indebted for valuable assistance at the earlier stages of these researches. Circumstances have subsequently prevented Mr. Valentin from carrying out his plan, and I have therefore to take upon myself the responsibility for the following statements. The results obtained in the examination of the arsenic-compounds are by no means absolutely connected with the study of the phosphorus-bases, nevertheless I may be permitted to lay them before the Society, together with the account of the corresponding reaction in the phosphorus-series.

MONARSONIUM-COMPOUNDS.

Action of Dibromide of Ethylene upon Triethylarsine.

The experience gathered during the examination of the phosphorus-bodies enabled me to establish the nature of this reaction by a comparatively small number of platinum-determinations.

Bromide of Bromethyl-triethylarsonium.—To avoid, as far as possible, the formation of the second product, a mixture of triethylarsine with a very large excess of dibromide of ethylene was digested in sealed tubes, at a temperature not exceeding 50° C. Notwithstanding this low temperature, the tubes invariably contained compressed gases. The product of the reaction was treated with water, which extracted a soluble bromide from the ethylene-compound unacted upon. On evaporation, a beautiful bromide was left, which, being copiously soluble in boiling, and sparingly soluble in cold alcohol, could be readily recrystallized from absolute and even from common alcohol. In water this substance is excessively soluble; it is therefore scarcely crystallizable from an aqueous solution.

Analysis, as might have been expected, proved this salt to be the analogue of the bromethylated triethylphosphonium-salt. It contains

$$C_8H_{19}AsBr_2 = [(C_2H_4Br)(C_2H_5)_3As]Br.$$

The bromide of bromethyl-triethylarsonium, the composition of which is sufficiently established by the analysis of the corresponding platinum-salt (see below), can be obtained in beautiful crystals. Their form—the rhombic dodecahedron—is identical with that of the corresponding bromethyl-triethylphosphonium-compound, which the crystals resemble also in their general habitus. I quote the following from SELLA'S examination:—

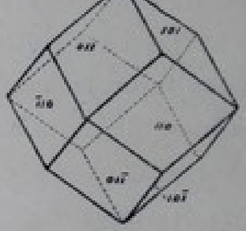
"System monometric.

Forms observed:—

110 (Fig. 79).

Angles.	Calculated.	Observed.
110, $\bar{1}$10	= 90° 0′	90° 3′
110, 101	= 60 0	60 0
110, 01$\bar{1}$	= 60 0	60 8

Fig. 79.



No influence on polarized light."

Platinum-salt.—The solution of the previous salt, converted by treatment with chloride of silver into the corresponding chloride, yields with dichloride of platinum splendid needles of a double salt, difficultly soluble in cold and even in boiling water.

I. 0·9695 grm. of salt, treated with sulphuretted hydrogen, &c., gave 0·2040 grm. of platinum.

II. 1·2175 grm. of salt of a new preparation, analysed in the same manner, gave 0·2545 grm. of platinum.

III. 1·2815 grm. of salt of the last preparation gave 0·2715 grm. of platinum.

The formula

$$C_8H_{19}BrAsPtCl_3 = [(C_2H_4Br)(C_2H_5)_3As]Cl, PtCl_2$$

requires the following values:—

	Theory.		Experiment.		
			I.	II.	III.
1 equiv. of Arsonium	270·0	56·82	——	——	——
1 equiv. of Platinum	98·7	20·77	21·04	20·90	21·18
3 equivs. of Chlorine	106·5	22·41	——	——	——
1 equiv. of Platinum-salt . .	475·2	100·00			

Compounds of Vinyl-triethylarsonium.

The bromide of bromethyl-triethylarsonium, like the corresponding phosphorus-compound, loses its latent bromine under the influence of oxide of silver. If the solution of the bromide be precipitated by an excess of nitrate of silver, one-half of the bromine separates as bromide of silver; the clear filtrate, mixed with ammonia, yields the second half of the bromine in the form of a dense precipitate. Nevertheless the reaction differs from that observed in the phosphorus-series. The bromide of the bromethylated phosphonium, as has been pointed out in a former part of this inquiry, is almost invariably converted into an oxethylated body, its transformation into a vinyl-compound being altogether exceptional. The bromide of the bromethylated arsonium, on the other hand, yields, as a rule, the vinyl-body of the series, the formation of an oxethylated compound taking place only under particular circumstances; in fact so rarely as to leave some doubt regarding the existence of this term of the series. The bromide of the bromethylated arsonium, treated with an excess of oxide of silver, yields a powerfully alkaline solution, the nature of which was determined by the analysis of the corresponding platinum-salt. Transformed into the chloride, and precipitated with dichloride of platinum, this solution yielded beautiful rather soluble octohedra.

I. 0·6312 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1570 grm. of platinum.

II. 0·6338 grm. of platinum-salt, analysed in the same manner, gave 0·1571 grm. of platinum.

III. 0·4345 grm. of platinum-salt gave 0·1093 grm. of platinum.

IV. 0·4135 grm. of platinum-salt gave 0·1025 grm. of platinum and 0·4525 grm. of chloride of silver.

V. 0·3370 grm. of platinum-salt gave 0·0843 grm. of platinum.

These numbers lead to the percentages of a vinyl-triethylarsonium-compound. The formula

$$C_8\,H_{18}\,As\,Pt\,Cl_3 = [(C_2\,H_3)\,(C_2\,H_5)_3\,As]\,Cl,\ Pt\,Cl_2$$

requires the following values:—

	Theory.		Experiment.				
			I.	II.	III.	IV.	V.
1 equiv. of Arsonium . .	189·0	47·94	——	——	——	——	——
1 equiv. of Platinum . .	98·7	25·05	24·87	24·79	25·15	24·78	25·02
3 equivs. of Chlorine . .	106·5	27·01	——	——	——	27·07	——
1 equiv. of Platinum-salt .	394·2	100·00					

Analyses I. and II. were made with the same specimen; analysis III. with a salt obtained in a new preparation; analysis IV. with a salt procured by precipitating the chloride left after the separation of the platinum in the form of sulphide in the previous analysis. For the first three experiments, the solution of the bromethylated arsonium-compound was gently heated with oxide of silver; for experiment V. the digestion had taken place in the cold.

The above numbers show that the transformation of the bromethylated compound ensues according to the following equation:—

$$[(C_2H_4Br)(C_2H_5)_3As]Br + \left.\begin{matrix}Ag\\Ag\end{matrix}\right\}O = 2\,AgBr + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3As]\\H\end{matrix}\right\}O.$$

The idea suggested itself that the vinyl-compound obtained in this reaction might be a secondary product resulting from the decomposition of an oxethylated compound of limited stability formed in the first instance:

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3As]\\H\end{matrix}\right\}O = \left.\begin{matrix}H\\H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3As]\\H\end{matrix}\right\}O.$$

It was with the view of avoiding this decomposition, that the digestion was accomplished at the common temperature for experiment V.; the result, however, showed that even in this case the vinyl-compound was obtained.

Nevertheless the oxethylated body appears to exist. Under circumstances which were not sufficiently well observed at the time, the action of oxide of silver upon the bromide of the bromethylated triethylarsonium yielded an octohedral platinum-salt with the platinum percentage of the oxethylated compound.

0·6103 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1448 grm.=23·72 per cent. of platinum.

The formula

$$[(C_2H_5O)(C_2H_5)_3As]Cl,\ PtCl_2$$

requires 23·94 per cent. of platinum. I have not been able to reproduce this substance.

DIARSONIUM-COMPOUNDS.

Dibromide of Ethylene-hexethyl-diarsonium.—The bromide or chloride of the bromethylated arsonium is but slowly acted upon by triethylarsine at 100° C. Two days' digestion at that temperature had produced but a slight impression; at 150° the reaction is accomplished in two hours. The phenomena now to be recorded presented themselves in the succession repeatedly observed in the phosphorus-series. The dibromide

$$C_{14}H_{34}As_2Br_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2$$

yielded, when debrominated, the powerful alkali

$$C_{14}H_{36}As_2O_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_6As_2]''\\H_2\end{matrix}\right\}O_2.$$

Treated with acids, this alkali produces a series of fine salts, amongst which the di-iodide deserves to be mentioned; it equals in beauty the corresponding diphosphonium-compound. I have fixed the composition of the series by the analysis of the platinum-salt and gold-salt.

Platinum-salt.—Pale yellow crystalline precipitate, similar to the diphosphonium-compound, difficultly soluble in water, soluble in boiling concentrated hydrochloric acid, from which it crystallizes on cooling.

I. 0·8610 grm. of platinum-salt (not recrystallized), treated with sulphuretted hydrogen, &c., gave 0·2220 grm. of platinum.

II. 0·4885 grm. of platinum-salt (crystallized from hydrochloric acid), analysed in the same manner, gave 0·1265 grm. of platinum.

The formula

$$C_{14}H_{34}As_2Pt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]Cl_2, 2PtCl_2$$

requires the following values:—

	Theory.		Experiment.	
			I.	II.
1 equiv. of Diarsonium	352·0	46·17	——	——
2 equivs. of Platinum	197·4	25·89	25·78	25·89
6 equivs. of Chlorine	213·0	27·94	——	——
1 equiv. of Platinum-salt . .	762·4	100·00		

Gold-salt.—The dichloride obtained after separating the platinum in the two preceding analyses by means of sulphuretted hydrogen, was precipitated by trichloride of gold. Yellow slightly crystalline precipitate, soluble in hydrochloric acid, from which it separates in golden-coloured plates.

0·5859 grm. of the salt, treated with sulphuretted hydrogen, &c., gave 0·2220 grm. of gold.

The formula

$$C_{14}H_{34}As_2Au_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]Cl_2, 2AuCl_3$$

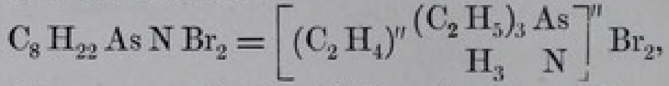
requires

	Theory.		Experiment.
1 equiv. of Diarsonium . .	352	34·18	——
2 equivs. of Gold	394	38·25	37·89
8 equivs. of Chlorine . . .	284	27·57	——
1 equiv. of Gold-salt . . .	1030	100·00	

ARSAMMONIUM-COMPOUNDS.

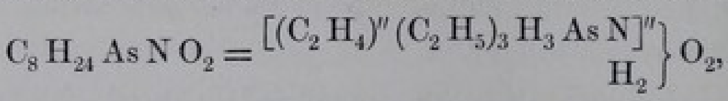
Bromide of bromethylated triethylarsonium, as might have been expected, is capable of fixing ammonia and the monamines, giving rise to the formation of a series of compounds not less numerous than the bodies mentioned in the phosphammonium-series. I have been satisfied to study the action of ammonia upon the bromide.

Dibromide of Ethylene-triethylarsammonium.—Reaction complete in two hours at 100°. The product contains the bromide



$$C_8H_{22}AsNBr_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\ H_3 & N\end{matrix}\right]''Br_2,$$

which was converted, by means of oxide of silver, into the stable caustic base



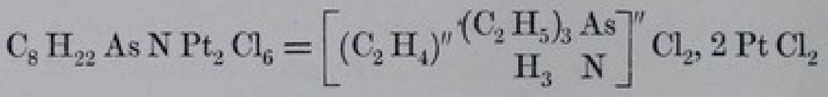
$$C_8H_{24}AsNO_2 = \left.\begin{matrix}[(C_2H_4)''(C_2H_5)_3H_3AsN]''\\ H_2\end{matrix}\right\}O_2,$$

the composition of which was determined by the analysis of the platinum- and gold-salts.

Platinum-salt.—Needles difficultly soluble in boiling water, soluble in boiling concentrated hydrochloric acid, from which well-formed crystals are deposited.

0·4650 grm. of platinum-salt, treated with sulphuretted hydrogen, gave 0·1475 grm. of platinum.

The formula



$$C_8H_{22}AsNPt_2Cl_6 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\ H_3 & N\end{matrix}\right]''Cl_2, 2\,PtCl_2$$

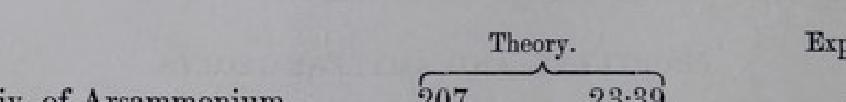
requires

	Theory.		Experiment.
1 equiv. of Arsammonium	207·0	33·53	——
2 equivs. of Platinum	197·4	31·97	31·72
6 equivs. of Chlorine	213·0	34·50	——
1 equiv. of Platinum-salt	617·4	100·00	

Gold-salt.—Yellow compound precipitated from the dichloride obtained in the previous platinum-determination, on adding a solution of trichloride of gold. Soluble in hydrochloric acid, deposited from this solution in golden-yellow plates.

0·3505 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0·1550 grm. of gold.

The values corresponding to the formula



$$C_8H_{22}AsNAu_2Cl_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3 & As\\ H_3 & N\end{matrix}\right]''Cl_2, 2\,AuCl_3$$

are

	Theory.		Experiment.
1 equiv. of Arsammonium . .	207	23·39	——
2 equivs. of Gold	394	44·52	44·22
8 equivs. of Chlorine	284	32·09	——
1 equiv. of Gold-salt	885	100·00	

I have also made a few experiments on the action of dibromide of ethylene upon triethylstibine. The reaction is slow, and required long-continued digestion at temperatures higher than that of boiling water. The tubes invariably contained much gas, and the product of the reaction proved to be an inattractively complex mixture of several compounds, many of them secondary, which by no means invited me to a more minute examination of this process. I omit to quote the few platinum- and chlorine-determinations which were made, since they do not admit of a simple interpretation.

In performing the experiments on the arsenic-bases I have been most ably assisted by my nephew, Dr. P. W. Hofmann, to whom I express my best thanks for his active cooperation in this part of my inquiries.

The experiments carried out in the ethylene-series, develope clearly enough the nature of the diatomic bases, and their relation to the monatomic compounds. I have worked with predilection in this series because the accessibility and manageableness of the material greatly facilitate the unravelling of the often complicated reactions. There could be no doubt that the phenomena observed in the ethylene-series would likewise be reproduced in other homologous series. But as a general view of the nature of this group of bodies had been gained from the observations recorded in the preceding paragraphs, it appeared scarcely necessary to corroborate the results already obtained, by many further experiments, which would have been more or less mere repetitions of the former. Nevertheless I have, in certain cases, likewise drawn other groups into the circle of my observations. Some of the fragmentary results at which I thus arrived I will here briefly communicate.

METHYLENE-GROUP.

In another place* I have mentioned an experiment I had made in the hope of converting iodoform into iodide of carbon, which, however, had yielded nothing but the di-iodide of methylene, discovered not long previously by Boutlerow. As a considerable quantity of this interesting compound (the result of these experiments) was still at my disposal, I took the opportunity of examining more particularly its behaviour to triethylphosphine and the ammonias in general.

The methylenated derivatives of the phosphorus-bases will be more conveniently examined in connexion with another class of compounds, to which a special chapter of this inquiry must be devoted. I will therefore only briefly mention in this place, that I have succeeded in producing several of the bases belonging to the methylene-group. The members of this series present some peculiarities, distinguishing them in a marked manner from the corresponding ethylene-compounds.

PROPYLENE- AND AMYLENE-GROUPS.

The experiments in the propylene- and amylene-groups were instituted almost at the beginning of this investigation, at a time when the reaction between triethylphosphine and dibromide of ethylene had not yet been sufficiently disentangled. The removal of

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* Journal of the Chemical Society, vol. xiii. p. 65.

the difficulties in the ethylene series has naturally cooled my interest in the corresponding reactions of the propylene- and amylene-series, and hence this part of the investigation has been left incomplete.

Triethylphosphine is briskly attacked by the dibromides, both of propylene and amylene; the reactions, however, do not exhibit the welcome simplicity and smoothness which characterize those in the ethylene-series. Even in the propylene-compound, whether it be prepared from amylic alcohol or from iodide of allyl, we miss with regret the sharply defined characters of the corresponding ethylene-body; and in the butylene-, and still more in the amylene-series, these features become fainter and fainter.

When submitted to the action of the dibromides of propylene and amylene, triethylphosphine appears to undergo simultaneously two different sets of changes; the substances formed being partly direct products of the reaction, partly, and perhaps chiefly, indirect products. The diphosphonium-compounds of the propylene- and amylene-series are less stable than the ethylene-diphosphoniums, and are therefore always mixed with such products of decomposition as are formed in the ethylene-group only under the protracted influence of high temperatures. Under all circumstances, however, these dibromides give up the elements of hydrobromic acid, so that we have to eliminate a painfully small quantity of the searched-for products from an unprofitable mass of bromide of triethylphosphonium. In such cases the ordinary methods of separation no longer suffice, and we are compelled to resort to treatment with baryta, the real examination of the products beginning only after the liberated phosphorus-base has been removed by ether, and the bromide of barium decomposed by means of oxide of silver and carbonic acid. By this treatment, beautiful iodides and platinum-salts are obtained, which, however, have as yet been but partially and imperfectly investigated.

PHENYLENE-GROUP.

Unfortunately nothing but fruitless experiments. I had hoped to find in triethylphosphine a bridge between the phenyl- and the phenylene-series, but my expectations have not been realized. The analogy between the salts of bromethylated triethylphosphonium and of bromophenylated ammonium,

$$\begin{array}{l}[(C_2H_4Br)(C_2H_5)_3P]Br,\\ [(C_6H_4Br)\quad H_3\quad N]Br,\end{array}$$

is unmistakeable, and it remained to be seen whether triethylphosphine would attack the salts of bromophenylammonium according to the equation

$$[(C_6H_4Br)H_3N]Br+(C_2H_5)_3P=\left[(C_6H_4)''\begin{matrix}(C_2H_5)_3P\\ H_3\quad N\end{matrix}\right]''Br_2.$$

Unfortunately the mixture of the two bodies is not changed even after being heated for some time to 160°. No better result was obtained by substituting for the bromophenylamine, the corresponding iodinated base. A mixture of triethylphosphine and iodophenylamine, which had been kept for a day at 160°, yielded, on opening the tube, an appreciable quantity of iodine, recognizable by silver-salts, but the decomposition was by no means complete. Hydriodic acid separated from the mixture an iodide which crystallized in long needles, and was found by analysis* to consist of iodide of iodophenylammonium. In the products of transformation of the phosphorus-base I was unable to trace the simple relations pointed out by theory.

BENZYLENE-GROUP.

In conclusion, I will mention a few experiments upon the mutual reaction between triethylphosphine and dichloride of benzylene. By this latter name I denote the compound, discovered by Cahours, which is produced by the action of pentachloride of phosphorus on bitter almond oil.

At ordinary temperatures, and even at 100°, the two compounds react but slowly upon each other; between 120° and 130°, however, especially in presence of alcohol, the change takes place with facility. The resulting crystalline mass, like that obtained in the corresponding experiments in the propylene- and amylene-series, consists chiefly of chloride of triethylphosphonium. After removing the phosphorus-base as completely as possible from the solution of the crystals, by the successive treatment with baryta, oxide of silver, and carbonic acid, there remained a strongly alkaline liquid, the nature of which I endeavoured to determine by the preparation of the iodide and platinum-salt. The liquid, saturated with hydriodic acid, yielded a well-crystallized iodide, which, however, was so soluble and deliquescent that no constant results could be obtained by its analysis. On the other hand, the somewhat sparingly soluble platinum-salt, which is precipitated in small laminæ on treating the solution of the chloride with dichloride of platinum, and which may be recrystallized without alteration from boiling water, yielded results agreeing with one another, although the products of different preparations were submitted to analysis.

I. 0·5979 grm. of platinum-salt gave 0·8166 grm. of carbonic acid and 0·2863 grm. of water.

II. 0·4580 grm. of platinum-salt gave 0·6290 grm. of carbonic acid and 0·2212 grm. of water.

III. 0·2413 grm. of platinum-salt gave 0·3310 grm. of carbonic acid and 0·1160 grm. of water.

IV. 0·6955 grm. of platinum-salt, decomposed by hydrosulphuric acid, &c., gave 0·1670 grm. of platinum.

V. 0·7594 grm. of platinum-salt, fused with carbonate of sodium, &c., gave 0·1810 grm. of platinum and 0·7875 grm. of chloride of silver.

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* 0·2634 grm. of iodide, precipitated by nitrate of silver, gave 0·1778 grm. of iodide of silver =36·48 per cent. of iodine.

The iodide of iodophenylammonium,

$$[(C_6H_4I)H_3N]I,$$

contains 36·60 per cent. of iodine, precipitable by nitrate of silver.

These numbers lead to the formula

$$C_{13}H_{22}PPtCl_3 = [(C_2H_5)_3(C_7H_7)P]Cl, PtCl_2,$$

which represents the platinum-salt of a phosphonium in which the fourth equivalent of hydrogen is replaced by the molecule C_7H_7 (probably benzyl, the radical of benzyl-alcohol).

Theory.			Experiment.				
			I.	II.	III.	IV.	V.
C_{13}	156	37·66	37·25	37·46	37·41	——	——
H_{22}	22	5·31	5·32	5·36	5·34	——	——
P	31	7·49	——	——	——	——	——
Pt	98·7	23·83	——	——	——	23·87	23·83
Cl_3	106·5	25·71	——	——	——	——	25·65
	414·2	100·00					

The transformation of triethylphosphine under the influence of dichloride of benzylene, evidently takes place according to the following equation:

$$3[(C_2H_5)_3P] + C_7H_6Cl_2 + H_2O = [(C_2H_5)_3HP]Cl + [(C_2H_5)_3(C_7H_7)P]Cl + (C_2H_5)_3PO.$$

It may be that the formation of the triethyl-benzylphosphonium-compound is preceded by the production of an ephemeral diatomic base containing the radical C_7H_6,

$$2[(C_2H_5)_3P] + C_7H_6Cl_2 = \left[(C_7H_6)'' \begin{matrix}(C_2H_5)_3P \\ (C_2H_5)_3P\end{matrix}\right]'' Cl_2,$$

which is subsequently decomposed under the joint influence of water and an excess of triethylphosphine. I have not, however, been able, experimentally, to trace this base. Moreover, a difference in the deportment of triethylphosphine with the compounds of ethylene and benzylene is readily intelligible, if we recollect that they are far from being analogous, bichloride of benzylene representing in the benzyl-group the diatomic derivatives which have been obtained from ethylic aldehyde.

The analysis of the benzyl-triethylphosphonium-platinum-salt concludes the experimental part of this section of my researches. The following Table gives at a glance the several groups of bodies examined in Parts II. and III. of this inquiry.

MONATOMIC COMPOUNDS.

PHOSPHORUS-GROUP.

MONOPHOSPHONIUM-SALTS.

Ethyl-series.

Salt of Tetrethylphosphonium	$[(C_2H_5)_4P]Br.$
Salt of Bromethyl-triethylphosphonium	$[(C_2H_4Br)(C_2H_5)_3P]Br.$
Salt of Chlorethyl-triethylphosphonium	$[(C_2H_4Cl)(C_2H_5)_3P]Br.$
Salt of Oxethyl-triethylphosphonium	$[(C_2H_4HO)(C_2H_5)_3P]Br.$
Salt of Vinyl-triethylphosphonium	$[(C_2H_3)(C_2H_5)_3P]Br.$

Ethyl-methyl-series.

Salt of Ethyl-trimethylphosphonium	$[(C_2H_5)(CH_3)_3P]Br.$
Salt of Bromethyl-trimethylphosphonium	$[(C_2H_4Br)(CH_3)_3P]Br.$
Salt of Oxethyl-trimethylphosphonium	$[(C_2H_4HO)(CH_3)_3P]Br.$

Ethyl-benzyl-series.

Salt of Triethyl-benzylphosphonium	$[(C_2H_5)_3(C_7H_7)P]Br.$

ARSENIC-GROUP.

MONARSONIUM-SALTS.

Ethyl-series.

Salt of Tetrethylarsonium	$[(C_2H_5)_4As]Br.$
Salt of Bromethyl-triethylarsonium	$[(C_2H_4Br)(C_2H_5)_3As]Br.$
Salt of Vinyl-triethylarsonium	$[(C_2H_3)(C_2H_5)_3As]Br.$

DIATOMIC COMPOUNDS.

PHOSPHORUS-GROUP.

DIPHOSPHONIUM-SALTS.

Salt of Ethylene-hexethyldiphosphonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$
Salt of Ethylene-trimethyl-triethyldiphosphonium	$\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3P\end{matrix}\right]''Br_2.$
Salt of Ethylene-hexmethyldiphosphonium	$\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(CH_3)_3P\end{matrix}\right]''Br_2.$

ARSENIC-GROUP.

DIARSONIUM-SALTS.

Salt of Ethylene-hexethyldiarsonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3As\\(C_2H_5)_3As\end{matrix}\right]''Br_2.$

PHOSPHORUS-NITROGEN-GROUP.

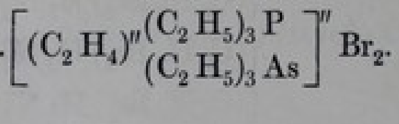
PHOSPHAMMONIUM-SALTS.

Salt of Ethylene-triethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\H_3\ N\end{matrix}\right]''Br_2.$
Salt of Ethylene-methyl-triethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(CH_3)H_2N\end{matrix}\right]''Br_2.$
Salt of Ethylene-tetrethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)H_2N\end{matrix}\right]''Br_2.$
Salt of Ethylene-pentethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_2HN\end{matrix}\right]''Br_2.$
Salt of Ethylene-trimethyl-triethylphosphammonium	$\left[(C_2H_4)''\begin{matrix}(CH_3)_3P\\(C_2H_5)_3N\end{matrix}\right]''Br_2.$

PHOSPHORUS-ARSENIC-GROUP.

Phospharsonium-salts.

Salt of Ethylene-hexethylphospharsonium . . . . . .

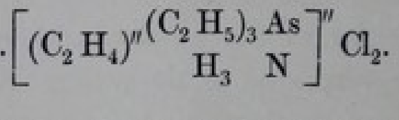


$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\,P\\(C_2H_5)_3\,As\end{matrix}\right]''Br_2.$$

ARSENIC-NITROGEN-GROUP.

Arsammonium-salts.

Salt of Ethylene-triethylarsammonium . . . . . .



$$\left[(C_2H_4)''\begin{matrix}(C_2H_5)_3\,As\\H_3\;\;N\end{matrix}\right]''Cl_2.$$

The experiments described in the preceding pages refer almost exclusively to the study of compounds belonging either to the phosphorus-series or to the phosphorus-nitrogen-series. Numerous analogous terms of the nitrogen-series, monatomic as well as diatomic, with which I have become acquainted in the course of my researches, have been left unnoticed in this memoir. I propose to examine the nitrogen-bodies in a special memoir; and I may here only remark that these substances, although differing in several points, nevertheless so closely imitate, in their general deportment, the corresponding terms of the phosphorus-series, that the picture which in the preceding pages I have endeavoured to delineate of the phosphorus-compounds, illustrates, in a great measure, the deportment of the nitrogen-bodies. We meet here with the peculiar case of the study of the phosphorus-group being in advance of that of the nitrogen-series, whilst generally the investigation of the phosphorus-compounds was taken in hand only after inquiries in the nitrogen-series had furnished the prototypes to be copied.

In conclusion, a few words about the further development of which the experiments described appear to be capable, and about the direction in which I propose to pursue the opened track.

Conceived in its simplest form, the transition from the series of monatomic to that of diatomic bases may be referred to the introduction of a monochlorinated or monobrominated alcohol-radical into the ammonium-nucleus, the chlorine or bromine thus inserted furnishing the point of attack for a second molecule of ammonia. If in bromide of ethylammonium we imagine 1 equiv. of hydrogen in ethyl replaced by bromine, we arrive at the bromide of bromethyl-ammonium, which is capable of fixing a second molecule of ammonia, and of being thus converted into the dibromide of ethylene-diammonium, the latent bromine becoming accessible to silver-salts,

$$[(C_2H_4Br)H_3N]Br+H_3N=[(C_2H_4)''H_6N_2]''Br_2.$$

The further elaboration of this reaction suggests two different methods for the construction of polyatomic bases of a higher order. In the first place, the number of ammonia-molecules to be incorporated in the new system may be increased by the gradually advancing bromination of the radical. By the further bromination of ethyl in bromide of bromethyl-ammonium and the action of ammonia on the bodies thus produced, the following compounds might be generated:—

$$[(C_2H_3Br_2)H_3N]Br+2H_3N=[(C_2H_3)'''\ H_9\ N_3]'''\ Br_3.$$
$$[(C_2H_2Br_3)H_3N]Br+3H_3N=[(C_2H_2)''''\ H_{12}N_4]''''\ Br_4.$$
$$[(C_2H\ Br_4)H_3N]Br+4H_3N=[(C_2H\ )'''''\ H_{15}N_5]'''''\ Br_5.$$
$$[(C_2Br_5)\quad H_3N]Br+5H_3N=[(C_2\quad)''''''\ H_{18}N_6]''''''\ Br_6.$$

Again, the fixation of the ammonia-molecules might be attempted, not by the progressive bromination of the ethyl, but by the accumulation of monobrominated ethyl-molecules in the ammonium-nucleus. The bromide of the di-bromethylammonium, when submitted to the action of ammonia, would thus yield the tribromide of a triammonium, the bromide of tri-bromethylammonium, the tetrabromide of a tetrammonium, and, lastly, the bromide of tetra-bromethylammonium, the pentabromide of a pentammonium.

$$[(C_2H_4Br)_2H_2N]Br+2H_3N=[(C_2H_4)''_2H_8\ N_3]'''\ Br_3.$$
$$[(C_2H_4Br)_3H\ \ N]Br+3H_3N=[(C_2H_4)''_3H_{10}N_4]''''\ Br_4.$$
$$[(C_2H_4Br)_4\quad N]Br+4H_3N=[(C_2H_4)''_4H_{12}N_5]'''''\ Br_5.$$

As yet the bromination of the alcohol-bases presents some difficulty; appropriately selected reactions, however, will doubtless furnish these bodies. They will probably be obtained by indirect means, similar to those by which, years ago, I succeeded in preparing the chlorinated and brominated derivatives of phenylamine; or these substances may be generated by the action of pentachloride and pentabromide of phosphorus upon the oxethylated bases, a process which, from the few experiments recorded in this memoir, promises a rich harvest of results.

I have but faint hope that I may be able to trace these new paths to their goal; inexorable experiment follows but slowly the flight of light-winged theory. The commencement is nevertheless made, and even now the triammonium- and tetrammonium-compounds begin to unfold themselves in unexpected variety.

I conclude this memoir with the expression of my best thanks for the untiring patience with which Mr. PETER GRIESS has assisted me in the performance of my experiments on the phosphorus-bases. The truly philosophical spirit in which this talented chemist has accompanied me throughout the varying fortunes of this inquiry, will always be one of my most pleasing recollections.

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