XXIII. *Contributions to the History of the Phosphorus-Bases.*

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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,

$$[(C_2H_5)\ H_3N]Br‡,$$
$$[(C_2H_5)_2H_2N]Br,$$
$$[(C_2H_5)_3H\ N]Br,$$
$$\text{and } [(C_2H_5)_4\quad N]Br,$$

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

$$[(C_2H_4)''H_6N_2]''Br_2,$$
$$[(C_2H_4)''_2H_4N_2]''Br_2,$$
$$[(C_2H_4)''_3H_2N_2]''Br_2,$$
$$\text{and } [(C_2H_4)''_4\quad N_2]''Br_2.$$

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,

$(C_2H_4)''\{^{Br}_{Br}$	$(C_2H_4)''\{^{Br}_{HO}$	$(C_2H_4)''\{^{HO}_{HO.}$
Dibromide of Ethylene.	Intermediate Bromide.	Ethylene-alcohol.

* 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.—

$$[(C_2H_4Br)\ H_3N]Br,$$
$$[(C_2H_4Br)_2\ H_2N]Br,$$
$$[(C_2H_4Br)_3\ H\ N]Br,$$
$$\text{and } [(C_2H_4Br)_4\ N]Br.$$

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.—

$$[(C_2H_5O)\ H_3N]Br,$$
$$[(C_2H_5O)_2\ H_2N]Br,$$
$$[(C_2H_5O)_3\ H\ N]Br,$$
$$\text{and } [(C_2H_5O)_4\ N]Br.$$

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.—

$$[(C_2H_3)\ H_3N]Br,$$
$$[(C_2H_3)_2\ H_2N]Br,$$
$$[(C_2H_3)_3\ H\ N]Br,$$
$$\text{and } [(C_2H_3)_4\ N]Br;$$

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

$$C_2H_4Br_2 + C_6H_{15}P = C_8H_{19}PBr_2$$

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.

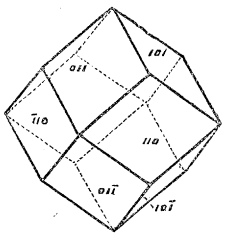


Fig. 29.

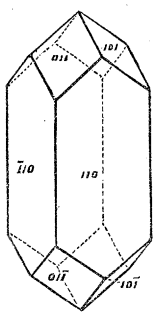
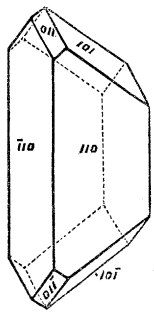


Fig. 30.



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:—

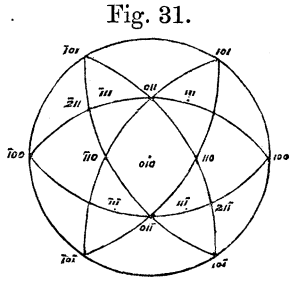
"System monoclinic:—

1 0 0, 1 0 1 = 55° 59′; 0 0 1, 1 0 1 = 33° 3′; 0 1 0, 1 1 1 = 60° 37′.

Forms observed:—

1 0 0, 0 1 0, 1 1 0, 1 0 1, $\bar{1}$ 0 1, 0 1 1, 1 1 1, $\bar{1}$ 1 1, $\bar{2}$ 1 1 (Fig. 31).

Fig. 31.



Angles.		Calculated.	Observed.
		° ′	° ′
1 0 0, 0 1 0	=	90 0	——
1 0 0, 1 1 0	=	45 55	45 57
1 0 0, 1 0 1	=	55 59	55 51
1 0 0, $\bar{1}$ 0 1	=	122 40	122 40
1 0 0, 0 1 1	=	89 12	89 12
1 0 0, 1 1 1	=	60 50	61 1
1 0 0, $\bar{1}$ 1 1	=	117 56	117 50
1 0 0, $\bar{2}$ 1 1	=	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:—

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

Forms observed:—

$$\infty P\,\infty,\ \infty P\infty,\ \infty P,\ P\infty,\ -P\infty,\ P\infty,\ P,\ -P,\ 2P2.$$

According to WEISS:—

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

Forms observed:—

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

According to LEVY:—

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

Forms observed:—

$$h',\ g',\ M,\ o',\ a',\ e',\ d^{\frac{1}{3}},\ b^{\frac{1}{2}},\ a_3.$$

Fig. 32.

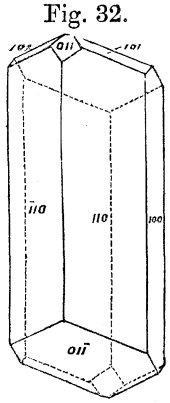


Fig. 33.

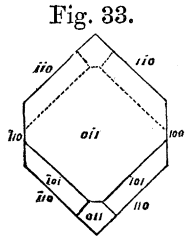
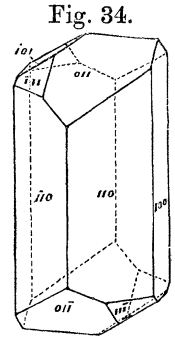


Fig. 34.



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.

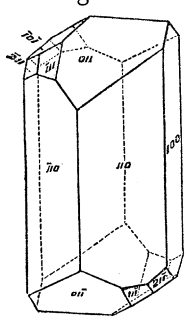
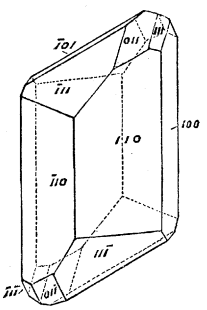


Fig. 36.



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.

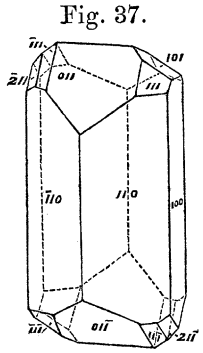


Fig. 38.

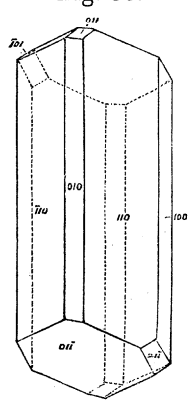
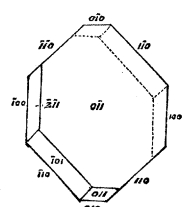


Fig. 39.



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

$$C_8 H_{19} Br P Au Cl_4 = [(C_2 H_4 Br)(C_2 H_5)_3 P] Cl, Au Cl_3$$

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

$$C_8 H_{20} Br P O = \left.\begin{matrix}[(C_2 H_4 Br)(C_2 H_5)_3 P] \\ H\end{matrix}\right\} O$$

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

$$C_8 H_{20} O P I = [(C_2 H_5 O)(C_2 H_5)_3 P] I,$$

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:—

$$[(C_2 H_4 Br)(C_2 H_5)_3 P] Br + Ag_2 O + H_2 O = 2 Ag Br + \left.\begin{matrix}[(C_2 H_5 O)(C_2 H_5)_3 P] \\ H\end{matrix}\right\} O.$$

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:—

$$\left.\begin{matrix}[(C_2 H_5 O)(C_2 H_5)_3 P] \\ H\end{matrix}\right\} O = (C_2 H_5)_3 P O + C_2 H_4 + H_2 O.$$

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

$$C_8 H_{20} O P Pt Cl_3 = [(C_2 H_5 O)(C_2 H_5)_3 P] Cl, Pt Cl_2,$$

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.

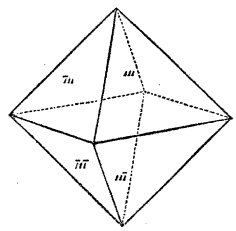
The several salts analysed were of different preparations. The specimen submitted to analysis IV. was obtained under particular conditions, to which I shall return hereafter.

	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:—

"System monometric:—

Fig. 40.



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

$$C_8 H_{20} P Pt Cl_3 = [(C_2 H_5)_4 P] Cl, Pt Cl_2$$

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:

$$(C_2 H_4)'' \left\{ \begin{matrix} H\,O \\ Cl \end{matrix} \right. = C_2 H_5 Cl O,$$

$$(C_2 H_4)'' \left\{ \begin{matrix} H\,O \\ H \end{matrix} \right. = C_2 H_6 O;$$

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 $C_2 H_4 Br$ and $C_2 H_5 O$, 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 experi-

ments 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-triethyl-phosphonium:

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

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 bromethyl-triethylphosphonium 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.	Experiment. 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.	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

* 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

$$C_{14}H_{34}P_2Cl_2 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2.$$

	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:—

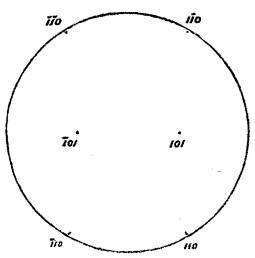
$0\,0\,1,\ 1\,0\,1 = 45°\ 9'$

$1\,0\,0,\ 1\,1\,0 = 60°\ 18'.$

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:—

$a : b : c = 1·0052 : 1 : 0·5704.$

Forms observed:—

$\infty P,\ \breve{P}\infty.$

According to WEISS:—

$a : b : c = 1 : 0·5704 : 1·0052.$

Forms observed:—

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

According to LEVY:—

$M\,M = 120°\ 36';\quad b : h = 1 : 0·8732.$

Forms observed:—

M, e^l.

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.

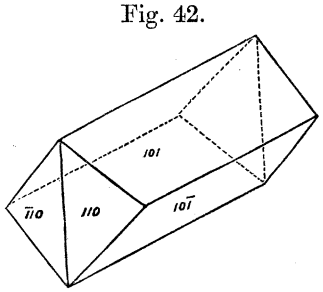


Fig. 43.

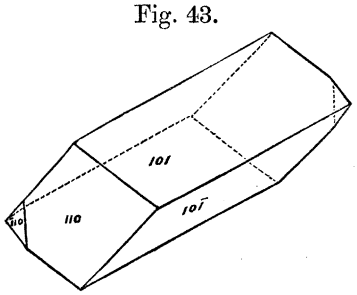
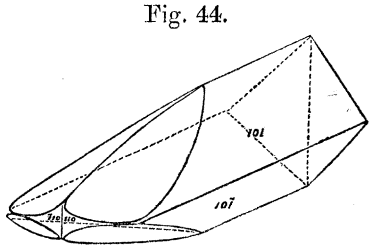


Fig. 44.



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.

$$C_{14}H_{34}P_2Cl_2O_8 = \left[(C_2H_4)''\begin{matrix}(C_2H_5)_3P\\(C_2H_5)_3P\end{matrix}\right]''Cl_2O_8.$$

		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:—

$$1\,0\,0,\ 0\,0\,1 = 82^\circ\ 36'.$$

Forms observed:—

$$1\,0\,0,\ 0\,1\,0,\ 0\,0\,1 \text{ (Fig. 45).}$$

Fig. 45.

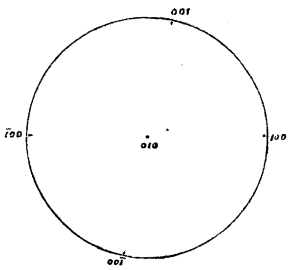
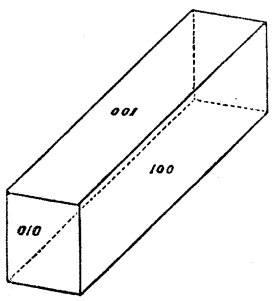


Fig. 46.



Angles.		Calculated.	Observed.
1 0 0, 0 1 0	=	90° 0′	90° 3′
1 0 0, 0 0 1	=	82 36	82 36
0 1 0, 0 0 1	=	90 0	89 57

According to NAUMANN:—

$$\gamma = 82^\circ\ 36'.$$

Forms observed:—

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

According to WEISS:—

$$a\,o\,c = 97^\circ\ 24'.$$

Forms observed:—

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

According to LEVY:—

$$h'\,P = 97^\circ\ 24'.$$

Forms observed:—

$$h', g', P.$$

Combinations observed:—

$$1\,0\,0,\ 0\,1\,0,\ 0\,0\,1 \text{ (Fig. 46).}$$

Cleavages 1 0 0, 0 1 0, 0 0 1 distinct and easily obtained, more especially 0 1 0.

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 0 1 0 and its apex towards the centre of the crystal. The face 0 1 0 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 0 0 1 is in general rather more developed than 1 0 0.

The crystals are optically negative. The plane of the optical axes is parallel to the line of symmetry [0 1 0]; 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 vinyltriethylphosphonium. 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,

$$\left.\begin{matrix}[(C_2H_5O)(C_2H_5)_3P]\\ H\end{matrix}\right\}O = \left.\begin{matrix}H\\ H\end{matrix}\right\}O + \left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\ H\end{matrix}\right\}O,$$

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

$$\left.\begin{matrix}[(C_2H_3)(C_2H_5)_3P]\\ H\end{matrix}\right\}O = (C_2H_5)_3PO + C_2H_4.$$

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.	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:

$$2\left[\left[(C_2H_5O)(C_2H_5)_3P\right]\Big\}O\right] = \left[(C_2H_4)''(C_2H_5)_6P_2\right]\Big\}O_2 + C_2H_6O_2.$$

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.

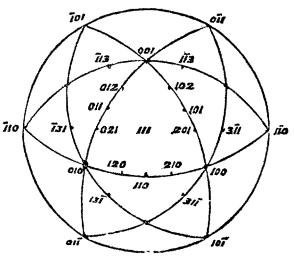
" System rhombohedric:—

$111, 100 = 59° 32'.$

Forms observed:—

$111, 10\bar{1}, 100, 110, 21\bar{1}, 31\bar{1}$ (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.

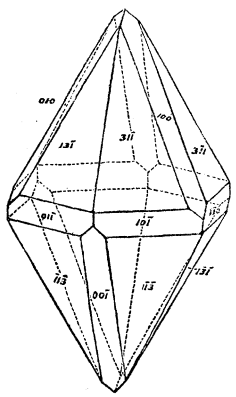


Fig. 49.

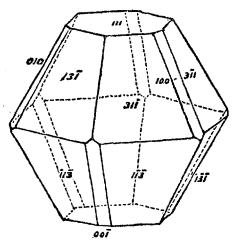
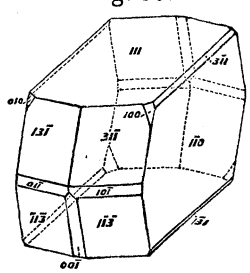


Fig. 50.



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.

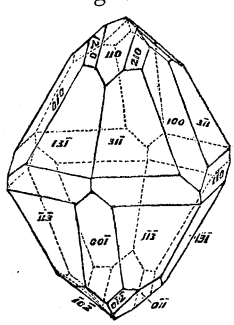
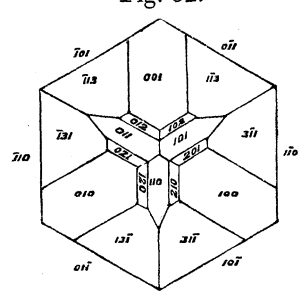


Fig. 52.



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 $\epsilon = 1{\cdot}668$.

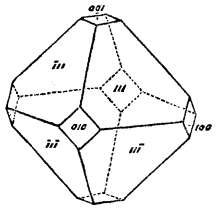
The crystals of iodide of tetrethylphosphonium are isomorphous with those of iodide of silver. In the latter substance, 1 1 1, 1 0 0 = 58° 27′, instead of 59° 32′, found in the tetrethylphosphonium-salt. Both salts have the same hexagonal habitus, and both are optically positive."

Crystalline Form of the Platinum-salt of Tetrethylphosphonium.

"System monometric:—

Forms observed:—

Fig. 53.



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

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."