XVIII.—*Action of Bromine and Chlorine on the Salts of Tetrethylphosphonium.*

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THE action of the halogens on trimethylsulphine salts formed the subject of a paper communicated to the Society by Dobbin and one of us (Trans., 1885, 56), and in a subsequent communication the action of the halogens on tetramethylammonium salts was described by the same authors (Trans., 1886, 846). In these papers, it was shown that the haloïd salts of these bases can combine directly with iodine, bromine, chlorine, or iodine monochloride, to form compounds of the general formula RX_3 (where R is the basic radicle and X is I, Br, or Cl); that those members of the series which contain not less than one atom of iodine in the molecule are fairly stable crystalline solids of a characteristic black, red, or yellow colour; that the other members, containing only bromine or chlorine, or both, are red or yellow liquids, stable only in an atmosphere of the halogen from which they have been formed; that some of these unstable compounds have a sufficiently definite composition (corresponding to the general formula RX_3) as proved by synthetic experiments; but that

others have a tendency to absorb a large excess of halogen without very great alteration of properties, particularly where bromine is the halogen added. It was also shown that this formation of perhaloid compounds is an action of wider application than, at first, would seem probable; for not only may the nature of the organic basic radicles be varied very considerably, but qualitative experiments with the sulphates of trimethylsulphine and tetramethylammonium showed that these, as well as the haloïd salts, can combine directly with bromine and chlorine. The striking resemblance between the behaviour, in this respect, of the sulphates and the chlorides led the authors to reject that view of the constitution of the perhaloid compounds which is represented by the formula $R'X < \frac{X}{X}$; and the option was left of regarding them all as molecular compounds of the formula $R'X, X_3$, or of regarding the central atom of the basic radicle (S or N) as capable of directly attaching to itself the additional halogen atoms ($R'''X_3$). Quantitative data, however, were required to fully prove the similarity of the action of the sulphates and chlorides or bromides. It was thought that more stable compounds might be obtained from the salts of a phosphorus base, and a preliminary experiment with tetrethylphosphonium iodide showed that at any rate this salt is capable of yielding perhaloid compounds resembling those already studied. The investigation was then interrupted, and has only lately been resumed by the present authors. Tetrethylphosphonium salts have been used on account of the greater ease with which they may be prepared as compared with the methyl compounds. The iodide was prepared by Hofmann's method from phosphonium iodide and absolute alcohol, and was proved by analysis to be of sufficient purity.

	P.	C.	H.	I.
Found (per cent.)	—	34·79	7·39	45·68
Calculated (per cent.).....	11·31	35·03	7·29	46·35

In any future experiments, however, we should prefer the method of preparation described by us in the next paper (p. 138), on account of its greater simplicity and economy.

Action of Bromine on Tetrethylphosphonium Iodide.

When bromine is added to this salt, combination occurs, accompanied by the development of much heat, the whole phenomena

being similar to those observed in the cases of the iodides of trimethylsulphine and tetramethylammonium. When the resulting heavy red liquid is freed from excess of bromine by evaporation and by washing with anhydrous ether, a bright red solid remains, which dissolves in warm alcohol, and on evaporation may be obtained in orange-red crystals. The appearance and properties of these leave no room for doubting that they are *tetraphosphonium dibromiodide*,

this was confirmed by analysis.

*I. 0.1809 gram gave 0.1450 gram CO_2 and 0.0880 gram H_2O ; or 0.03955 gram C and 0.00798 gram H.

II. 0.1970 gram gave, after reduction with sulphurous acid, 0.2800 gram of the mixed silver salts AgBr and AgI . Assuming this mixture to be in the proportion $2\text{AgBr} : \text{AgI}$, it contains 0.07332 gram Br and 0.05820 gram I.

	Calculated for $\text{P}(\text{C}_2\text{H}_5)_4\text{IBr}_2$.	Found.	
		I.	II.
P	7.14	—	—
C	22.12	21.86	—
H	4.61	5.40	—
I	29.26	—	29.54
Br	36.87	—	37.22
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This dibromiodide, like those previously described, yields a black explosive substance when treated with aqueous ammonia; and forms an additive compound of the formula $\text{P}(\text{C}_2\text{H}_5)_4\text{IBr}_2 + 2\text{NH}_3$, when subjected to the action of a current of dry ammonia. This compound is black in colour. When left exposed to the air it loses ammonia, and leaves the dibromiodide as a red powder.

0.1470 gram of the dibromiodide yielded 0.1582 gram of the black ammonia compound.

* This dibromiodide, the corresponding dichloriodide, and the tribromide, were found to present unusual difficulties when submitted to combustion—difficulties not met with in the case of tetraphosphonium iodide on the one hand, or of the perhaloid compounds of trimethylsulphine and tetramethylammonium on the other. An open tube was employed with oxide of copper and chromate of lead, with silver at the exit end. The combustions had to be conducted with extreme slowness to avoid loss of phosphine-smelling volatile matter (which spoilt the first experiments), and in every case a refractory black residue remained which yielded only to prolonged heating in the oxygen current. This may account for the high percentages of hydrogen found, though all the usual precautions were employed for drying the gas.

	Percentage increase of weight.
Calculated for $P(C_2H_5)_4IBr_2 + 2NH_3 \dots$	7.26
Found	7.47

A synthetic experiment was made in order to ascertain whether, by bromination of the iodide, any compound could be obtained containing more bromine than the dibromiodide. 0.3087 gram of the dry iodide was exposed for three-quarters of an hour at the ordinary temperature to a current of dry air laden with bromine vapour. The iodide was contained in a porcelain boat placed in a glass tube, and the boat and tube, together with the glass stopper, were tared at the commencement. After clearing out the tube with a rapid current of dry air, it was found that there was an increase of weight equivalent to a gain of 3.4 atoms of Br by each molecule of $P(C_2H_5)_4I$. The product was a dark-red liquid. The tube was now placed in an air-bath, and kept at 110° for two hours, whilst the bromine current was kept up, and the increase of weight was again ascertained, and found to be equivalent to a gain of 5.2 atoms of bromine by each molecule of $P(C_2H_5)_4I$, though there was not much change in the appearance of the liquid product. This was then subjected to a current of pure dry air at the ordinary temperature, and weighed from time to time. It was soon converted into a bright-red solid substance, and this continued to lose bromine slowly, but after three hours still retained what was equivalent to 3.6 atoms for each molecule of the iodide.

Bromine passed.	Dry air passed.	Weight found.	Increase per cent.	Atoms of Br per mol.	Nature of product.
$\frac{3}{4}$ hour, cold.	—	0.6172	99.9	3.4	Liquid.
2 hours at $110^\circ \dots$ }	—	0.7827	153.0	5.2	Liquid.
—	3 hours	0.6320	104.7	3.6	Solid.

Weight of iodide used, 0.3087 gram.

There is, then, a marked tendency for $P(C_2H_5)_4I$ to take up more than Br_2 , but if a definite higher compound exists, it is of an unstable nature. It will be seen that the behaviour of the iodide towards chlorine favours, by analogy, the supposition that an unstable *tetra-bromiodide*, $P(C_2H_5)_4IBr_4$, may exist.

Action of Chlorine on Tetrethylphosphonium Iodide.

The absorption of chlorine by the dry salt is attended by development of heat and the formation of a substance which, at first brown,

becomes yellow as the action proceeds; it is facilitated by keeping the salt at a temperature of about 70° , in which case a red liquid is obtained that solidifies to a darkish yellow, crystalline mass on cooling in an atmosphere of chlorine. Its composition was ascertained by the following synthetic experiment, which was conducted in a manner similar to that already described:—

Weight of iodide taken	1.011 gram.
Chlorine passed at 70°	1 hour.
Weight of product (solid)	1.520 gram.
Percentage increase of weight.	50.3 per cent.
Percentage increase calculated for formation of $P(C_2H_5)_4ICl_4$	51.8 per cent.

This *tetrachloriodide* very slowly loses chlorine in dry air, but decomposes with loss of chlorine when treated with water or alcohol.

Its alcoholic solution, on evaporation, yields yellow crystals of the *dichloriodide*, $P(C_2H_5)_4ICl_2$, a substance closely resembling the dichloriodides previously described, both in appearance and in its reactions with ammonia, &c. On analysis it gave the following results:—

- I. 0.1233 gram gave 0.1255 gram CO_2 and 0.075 gram H_2O , equivalent to 0.03423 gram C and 0.00833 gram H.
- II. 0.1586 gram, after reduction with sulphuric acid, gave 0.2368 gram of mixed silver salts. On the assumption that this contains iodide and chloride in the proportions of $AgI:2AgCl$, it is equivalent to 0.0576 gram I and 0.0322 gram Cl.

	Calculated for $P(C_2H_5)_4ICl_2$.	Found.	
		I.	II.
P	8.98	—	—
C	27.83	27.75	—
H	5.80	6.74	—
I	36.81	—	36.32
Cl	20.58	—	20.30
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100.00			

Action of Bromine on Tetrethylphosphonium Bromide.

The bromide employed was made from the iodide by shaking its solution with recently precipitated silver bromide. An estimation of the bromine showed it to be of sufficient purity.

	Br per cent.
Found	34.79
Calculated for	35.24

A synthetic experiment with this salt showed that when subjected to the action of bromine-vapour at 110° it absorbs it to form a dark-red liquid, which at the ordinary temperature is converted into a scarlet, crystalline solid having the composition indicated by the formula $P(C_2H_5)_4Br_7$, that is, the bromide is converted into the *heptabromide* by addition of six atoms of bromine. The details of the experiment are given in the following table :—

Weight of bromide taken	0.1472 gram.
Bromine current at 110°	1 hour.
Weight of product (solid)	0.4554 gram.
Increase of weight	209.4 per cent.
Increase calculated for $P(C_2H_5)_4Br_7$	211.4 per cent.

This heptabromide, like the higher compounds derived from the iodide, is not stable in air and also loses part of its bromine when treated with absolute alcohol. The alcoholic solution yields red crystals of the *tribromide*, $P(C_2H_5)_4Br_3$. This compound closely resembles the dibromiodide, but does not form an addition product with ammonia and is dissolved by ammonia solution. No solid tribromides were obtained from trimethylsulphine or tetramethylammonium, but only unstable red liquids. The difference in behaviour in the present instance may be wholly attributable to the presence of ethyl in place of methyl radicles, rather than to the presence of phosphorus in place of sulphur or nitrogen; for Marquardt (*J. pr. Chem.* **1**, 429) obtained a solid tribromide of tetrethylammonium. The following were the results obtained by analysis :—

- I. 0.2046 gram gave 0.1860 gram CO_2 and 0.1022 gram H_2O , equivalent to 0.05073 gram C and 0.01135 gram H.
- II. 0.2645 gram gave 0.2380 gram CO_2 and 0.1362 gram H_2O , equivalent to 0.06491 gram C and 0.01513 gram H.
- III. 0.1808 gram, after reduction with sulphuric acid, gave 0.2640 gram $AgBr$, equivalent to 0.11234 gram Br.

	Calculated for $P(C_2H_5)_4Br_3$.	Found.		
		I.	II.	III.
P	8.01	—	—	—
C	24.80	24.79	24.54	—
H.....	5.18	5.54	5.72	—
Br	62.01	—	—	62.14
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100.00				

Action of Chlorine on Tetrethylphosphonium Chloride.

The chloride employed was prepared by shaking a solution of the iodide with recently precipitated silver chloride, and was thoroughly dried by heating in a current of dry air at 110° . The salt absorbs chlorine and turns yellow at the ordinary temperature, but the action goes better at $105\text{--}110^{\circ}$. Under these conditions, a yellow liquid is obtained which, on cooling, solidifies to a yellow, crystalline mass. A quantitative experiment showed this to consist of the *trichloride*, $\text{P}(\text{C}_2\text{H}_5)_3\text{Cl}_3$.

Weight of chloride taken.....	0.1172 gram.
Chlorine passed in the cold.....	$2\frac{1}{2}$ hours.
Chlorine passed at $105\text{--}110^{\circ}$	$1\frac{1}{2}$ „
Weight of product (solid).....	0.1608 gram.
Increase of weight.....	37.2 per cent.
Calculated increase for $\text{P}(\text{C}_2\text{H}_5)_3\text{Cl}\cdot\text{Cl}_2$	38.9 per cent.

The trichloride is a yellow, crystalline substance which deliquesces in the air and is decomposed by water and alcohol with reformation of the chloride. Like other perhaloid compounds it is insoluble in anhydrous ether. There appears to be no tendency to form a higher addition product than the trichloride.

Action of Bromine on Tetrethylphosphonium Sulphate.

The sulphate was prepared from the iodide by means of silver sulphate. In order to thoroughly dry the salt obtained by evaporation of the solution, it was found necessary to heat it for some hours at a temperature ranging from 100° to 170° in a Sprengel vacuum. It was then submitted to the action of bromine vapour in the same manner as the bromide, the increase of weight being observed first after bromination at 110° , and subsequently after further bromination at the ordinary temperature. It was found that the sulphate has the power of taking up a large quantity of bromine, but that the amount absorbed and the character of the product vary considerably according to the temperature. The product formed at 110° is, when cold, a red solid; and the increase of weight in this case corresponds to the formation of $[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{SO}_4\text{Br}_{12}$; and this, it may be remarked, is analogous to the highest brominated derivative of the bromide, $\text{P}(\text{C}_2\text{H}_5)_3\text{Br}_6$, which it closely resembles in its general properties—appearance, instability in air, decomposition by alcohol, &c. The product formed at the ordinary temperature differs from this, being a dark red liquid and containing a still larger amount of bromine. In the two experiments made, details of which are given below, the

increase of weight at the ordinary temperature corresponded closely with that required for the formation of $[P(C_2H_5)_4]_2SO_4, Br_{22}$; but it is doubtful whether this really marks the formation of a distinct compound or the extreme limit of bromine absorption. When this highly brominated liquid is left in a desiccator over solid potash, or when it is treated with a current of dry air, it quickly loses bromine and assumes the solid state; but the decomposition does not stop here, and we have not succeeded in obtaining any brominated sulphate of stability equal to that of the tribromide or the dibromodide.

Experiment.	I.	II.
Weight of sulphate used, in grams ..	0.2678	0.2192
Bromine passed at 110°	1 hour	1 hour
Weight of product (solid)	0.9206	0.7552
Percentage gain of weight	243.8	244.5
Bromine subsequently passed in cold..	2 hours	1 hour
Weight of product (liquid)	1.4848	1.2207
Percentage gain of weight	454.4	456.9
Percentage gain calculated for $[P(C_2H_5)_4]_2SO_4, Br_{22}$	451.3	
Percentage gain calculated for $[P(C_2H_5)_4]_2SO_4, Br_{12}$	246.2	

The solid brominated sulphate dissolves in alcohol and red crystals are formed in quantity when the solution is partly evaporated; but a study of these and estimations of the bromine proved them to consist of tetrethylphosphonium tribromide. It was proved that the crystals contained no sulphuric acid, but the mother-liquor was found to be strongly acid. The alcohol, therefore, produces decomposition, and it is interesting to note that the phosphorus radicle retains the bromine in preference to the sulphuric acid group.

I. 0.1196 gram, after reduction with sulphurous acid, gave 0.176 gram AgBr, equivalent to 0.07489 gram Br.

II. 0.0492 gram gave 0.072 gram AgBr, equivalent to 0.03064 gram Br.

	Calculated for for $P(C_2H_5)_4Br_3$.	Found.	
		I.	II.
Br per cent.....	62.01	62.62	62.27

Action of Chlorine on Tetrethylphosphonium Sulphate.

The thoroughly dried sulphate combines with chlorine, but less readily and (as in other cases) to a less extent than with bromine. The salt turns yellow, and, if the temperature be raised to 130° while the chlorine is passing, fuses to a yellow liquid, which solidifies on cooling in the chlorine atmosphere. In the two experiments made, it

was found that the increase of weight corresponded to the formation of the compound $[P(C_2H_5)_4]_2SO_4Cl_4$; and this, it may be noted, is analogous to the formation of the chlorinated chloride $P(C_2H_5)_4Cl_2$, already described. The sulphate, therefore, appears to resemble the bromide in its action towards bromine and the chloride in its action towards chlorine, both as to the composition and as to the appearance and properties of the products formed. This is in accordance with the previously recorded qualitative observations on the sulphates of trimethylsulphine and tetramethylammonium.

Experiment.	I.	II.
Weight of sulphate used, in grams....	0.2172	0.2018
Chlorine passed at 130°.....	1½ hours	1½ hours
Weight of product.....	0.2964	0.2790
Percentage gain of weight	36.4	38.2
Percentage gain calculated for $[P(C_2H_5)_4]_2SO_4Cl_4$	36.4	

This chlorinated sulphate dissolves in water with effervescence, due to escape of chlorine, deliquesces when exposed to the atmosphere, and slowly evolves chlorine when subjected to a current of dry air.

The following table contains a list of the polyhaloid-derivatives described in this paper, together with a summary of the methods of forming them and of their properties. In some cases the formulæ given are doubtfully indicative of definite compounds.

No.	Compound formed.	Method of formation.	Temp. of formation.	Characters of the compound.
1..	$P(C_2H_5)_4IBr_4$ (?)	Bromine on iodide.	cold	Bright red cryst. solid, unstable in air.
2..	$P(C_2H_5)_4IBr_2$	Alcohol on 1.....	—	Orange crystals: stable.
3..	$P(C_2H_5)_4ICl_4$	Chlorine on iodide.	70°	Dark yellow cryst. mass: unstable.
4..	$P(C_2H_5)_4ICl_2$	Alcohol on 3.....	—	Yellow crystals, stable.
5..	$P(C_2H_5)_4Br_7$	Bromine on bromide	110°	Scarlet cryst. mass: unstable.
6..	$P(C_2H_5)_4Br_3$	Alcohol on 5 or 9..	—	Red crystals: stable.
7..	$P(C_2H_5)_4Cl_3$	Chlorine on chloride	110°	Yellow cryst. mass: unstable.
8..	$[P(C_2H_5)_4]_2SO_4Br_{22}$ (?) .	Bromine on sulphate	cold	Red liquid: unstable.
9..	$[P(C_2H_5)_4]_2SO_4Br_{12}$...	Bromine on sulphate	110°	Red solid: unstable.
10..	$[P(C_2H_5)_4]_2SO_4Cl_4$	Chlorine on sulphate	130	Yellow solid: unstable.