

XVII.—*Phenyltrimethylammonium Perhaloids.*

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It has been known for a long time that both organic and inorganic haloids combine with one or more molecules of free halogen to give crystalline substances termed perhaloids, of which KI_3 , NMe_4I_3 , NMe_4ICl_2 are typical examples. Comparatively little, however, seems to be known about the chemical structure or the reactions of these substances. The purpose of many investigations in the past would seem to have been directed principally towards establishing whether there exists an upper limit to the combining power of the atoms forming such complexes, in order to test the validity of this or that hypothesis concerning residual valence, partial valence, or the contra-valence of the atoms concerned.

This communication describes experiments carried out with phenyltrimethylammonium haloids in order to establish the following points:

(a) To which atom in a quaternary ammonium salt the capacity for the addition of free halogen is due.

(b) To what extent and under what conditions interconversion of periodides, perbromides, chloro-iodides, and bromo-iodides is possible.

(c) Whether isomeric perhaloids can be prepared containing the same atoms differently arranged, or

(d) Whether from a given set of halogen atoms one favoured arrangement of such atoms always exists.

(e) Whether any trustworthy means of degradation of a perhaloid could be devised in order that the structural arrangement of its atoms could be deduced.*

In an investigation of perbromides derived from aromatic nitrogenous bases, de Vries (*Annalen*, 1905, **343**, 128) concluded that, since nitrogen-free compounds such as the haloid salts of oximes and oxonium bases also give perhaloids, which he considered analogous to the perhaloids of quaternary ammonium salts and of the hydrobromides of primary, secondary, and tertiary amines, the affinity which unites the added halogen atoms to the molecule is *not* dependent on the nitrogen atom but on the halogen atom which is united to the nitrogen. As the validity of this reasoning depends on the similarity in chemical properties between the perhaloids of oxonium bases and those of quaternary ammonium salts, the authors felt that this assumption of de Vries should be placed on firmer ground. Non-halogen salts of a quaternary ammonium base, that is, phenyltrimethylammonium nitrate and sulphate, were treated with chlorine, bromine, and iodine, but in no case have nitrates or sulphates with added halogen been obtained. Very small quantities of QmBr_3 ,[†] QmI_3 , QmI_5 , together with much unchanged nitrate or sulphate, were obtained in each case. These experiments confirmed the view that the necessary condition for obtaining perhaloids is that a halogen atom shall be present as a salt-forming element in the original quaternary ammonium salt, that the affinity which holds the added halogens emanates from the *N*-halogen atom, but not in an indefinite way from the molecule as a whole nor from the nitrogen atom.

It is interesting to notice that, at one time, Masson and Kirkland (T., 1889, **55**, 132) believed that they had evidence of the

* In connexion with the perhaloids the following terms are employed in this communication :

1. *N*-Halogen, by which is meant the halogen atom in a perhaloid which is united directly to the nitrogen atom of the base.

2. Added-halogens, which are those halogen atoms in a perhaloid (intimately associated with the *N*-halogen) which are most easily detached from the molecule. This term does *not* refer to the method of formation; for example, by treatment of quaternary ammonium iodides with chlorine, derivatives of the quaternary ammonium chloride are obtained: $\text{R}_4\text{NI} + \text{Cl}_2 = \text{R}_4\text{NCl, ICl}$. In the perhaloid so obtained, the added halogens are considered to be ICl—not chlorine—and in the same way chlorine and not iodine would be considered the *N*-halogen.

3. Parent quaternary salt, which is the salt resulting from a perhaloid by the elimination of the added halogens.

† $\text{Qm} = \text{NPhMe}_3$ —.

formation of perhaloids of phosphonium compounds derived from tetraethylphosphonium sulphate, for example, $(\text{PEt}_4)_2\text{SO}_4\text{Br}_{22}$ and $(\text{PEt}_4)_2\text{SO}_4\text{Br}_{12}$. These authors, however, found that after crystallisation from alcohol these compounds were free from sulphate.

De Vries regarded perhaloids as molecular compounds which, being unstable, easily break down into relatively stable, simpler compounds, but the term seems misleading as applied to quaternary ammonium perhaloids, for most of these possess considerable stability, definite crystalline form, definite melting point, and can be recrystallised from such a solvent as glacial acetic acid. Emphasis is laid on this point because the so-called instability of quaternary ammonium perhaloids has been much exaggerated in the past. It will be shown later that such perhaloids in the finely powdered, solid state have dissociation pressures at temperatures below 94° which, in most cases, are actually lower than those of the parent quaternary ammonium salts.

To obtain information on points (b), (c), (d), and (e), the quaternary ammonium chloride, bromide, or iodide in glacial acetic acid solution was treated with halogen. The perhaloid thus obtained could then be treated further with halogen, but it soon became evident that the same compounds were being obtained by different methods of preparation and that the constitutions of the compounds could not be deduced from their methods of formation, but would have to be elucidated by the nature of the degradation products.

The first method of degradation consisted in the use of ethyl malonate, which was found to be a very gentle and convenient method of removing halogens. An example of its use is furnished by the degradation of $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}_3$, which on treatment with ethyl malonate yields $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}$.

As a more vigorous means of withdrawing halogens, acetone (dry) at temperatures from 18° to its boiling point was found to be particularly useful.* On treatment with acetone, these perhaloids (except those containing the group I_2 or I_4) lose their added halogens and the parent quaternary ammonium salt is precipitated, for example, $\text{QmCl}\cdot\text{ICl}$ with acetone gave QmCl ; $\text{QmCl}\cdot\text{ICl}_3$ gave QmCl ; $\text{QmBr}\cdot\text{IBr}$ gave QmBr ; $\text{QmBr}\cdot\text{Br}_2$ gave QmBr ; $\text{QmBr}\cdot\text{Cl}_2$ gave QmBr ; and $\text{QmBr}\cdot\text{ICl}$ gave QmBr . Periodides of the types $\text{QmI}\cdot\text{I}_2$ and $\text{QmI}\cdot\text{I}_4$, as also bromodi-iodides, $\text{QmBr}\cdot\text{I}_2$, are not,

* Comparative experiments were carried out at temperatures from 18° to the boiling point of acetone and during periods of time varying from fifteen minutes to sixty hours. In every case identical products were obtained in the same reaction. As is to be expected, the velocity of the reaction is affected by the temperature. On account of their different velocities the reactions with the individual perhaloids were carried out at different temperatures in order that they might be completed within a single day.

however, attacked appreciably by acetone under these conditions. From the fact that the acetone treatment of different perhaloids may give rise to the elimination of chlorine alone, bromine alone, iodine and chlorine, or iodine and bromine the likelihood that acetone may exercise too marked a preferential affinity for one halogen rather than another is small. This acetone treatment, first employed by de Vries and by Hantzsch for the degradation of perbromides and extended by the authors to mixed perhaloids in general, is probably the most trustworthy method for ascertaining the constitution of the parent quaternary ammonium salt. It has the great advantage over all methods using water or other hydroxylic solvents that secondary changes are eliminated.

After degradation had indicated the nature of the parent quaternary salt and of the added halogens, a synthesis from these was attempted either in acetic, hydrobromic, or hydrochloric acid solution, and in every case the identity between the synthetic product and the original perhaloid was complete.

In Table I are summarised the methods of formation of the different perhaloids, their degradation products, products of chlorination, etc.

It is to be noticed that the capacity for the direct addition of halogens by the quaternary ammonium salts (without interchange of reacting elements) is greatest in the case of the quaternary ammonium bromide. This is shown in Table II. Whereas the iodide gives rise to only one type of perhaloid, that is, the periodides, and the chloride only to the chloro-iodochlorides, it is seen that the bromide gives rise to five distinct types, of which QmBr,Cl_2 is the least stable. The most interesting of these types is QmBr,ICl , which contains three atoms of different halogens united together. Its constitution follows from its degradation by the acetone treatment into the quaternary ammonium bromide. Many attempts were made to prepare the isomeric substance QmCl,IBr , but without success. When the chloride was treated with iodine monobromide, QmCl,ICl and QmBr,IBr resulted. It appears as if the arrangement QmCl,IBr is essentially unstable.

Replacement of Halogen Atoms in Perhaloids.

From a study of Table I it is seen that by the action of a halogen on a perhaloid or on a quaternary ammonium salt, an exchange of the *N*-halogen or of the added halogen frequently takes place. The following generalisations have been observed with regard to these replacements :

1. Chlorine invariably replaces the *N*-halogen in the quaternary ammonium iodide or in periodides. It also replaces the *N*-bromine

TABLE I.

Method of formation.	Formula.	Product of acetone treatment.	Product of chlorination.	Product of bromination.	Product of iodination.	Product from IBr or ICl.
$\text{QmCl}_2\text{I}_2 + \text{acetone}$	QmCl	—	unchanged	QmBr_2Br_2 (traces)	QmI_2I_2 (10%)	QmCl_2I_2
$\text{QmBr}_2\text{Br}_2 + \text{acetone}$	QmBr	—	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2I_2	QmBr_2IBr
$\text{NPhMe}_2 + \text{MeI}$	QmI	—	$\text{QmCl}_2\text{I}_2 + \text{QmCl}_2\text{I}_2$	QmBr_2IBr	$\text{QmI}_2\text{I}_2, \text{QmI}_2\text{I}_2$, etc.	QmBr_2IBr
$\text{QmI} + \text{excess Cl}_2$	QmCl_2I_2	QmCl	unchanged	unchanged	—	—
$\text{QmBr}_2\text{IBr} + \text{excess Cl}_2$	QmCl_2I_2	—	$\text{QmCl}_2\text{I}_2 + \text{QmCl}_2\text{I}_2$	—	unchanged	—
$\text{QmCl}_2 + \text{ICl}$	QmCl_2I_2	—	QmCl_2I_2	—	unchanged	—
$\text{QmBr}_2 + \text{ICl}$	QmBr_2I_2	QmBr	QmCl_2I_2	—	—	—
$\text{QmI} + \text{Br}_2$	QmBr_2IBr	—	—	—	—	—
$\text{QmBr}_2 + \text{Cl}_2$	QmBr_2Cl_2	—	—	—	—	—
$\text{QmBr}_2\text{Br}_2 + \text{Cl}_2$	QmBr_2Cl_2	—	unchanged	—	—	—
$\text{QmBr}_2 + \text{Br}_2$	QmBr_2Br_2	—	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2IBr	—
$\text{QmBr}_2 + \text{I}_2$	QmBr_2I_2	unchanged	QmCl_2I_2	QmBr_2IBr	unchanged	—
$\text{QmI} + \text{I}_2$	QmI_2I_2	—	QmCl_2I_2	—	QmI_2I_2 , etc.	—
$\text{QmI} + 2\text{I}_2$	QmI_2I_2	—	$\text{QmCl}_2\text{I}_2 + \text{QmCl}_2\text{I}_2$	—	—	—

TABLE II.

Quat. ammon. salt.	Product when treated with				
	Cl_2	Br_2	I_2	ICl or ICl_3	IBr .
QmCl	—	—	—	QmCl_2I_2 QmCl_2I_2	—
QmBr	QmBr_2Cl_2	QmBr_2Br_2	QmBr_2I_2 QmI_2I_2 QmI_2I_2 QmI_2I_2	QmBr_2IBr	QmBr_2IBr
QmI	—	—	—	—	—

in derivatives of the quaternary ammonium bromide only when iodine is also present in the solution. The chlorine of iodine monochloride replaces the *N*-bromine of QmBr only when at least two atomic proportions of Cl (as ICl) are present. Chlorine replaces the added halogens in QmBr, Br₂ giving QmBr, Cl₂.

2. Bromine causes replacement of the *N*-halogen in the quaternary ammonium iodide and in periodides. Bromine replaces, to a very small extent, the *N*-halogen in the quaternary ammonium chloride, yielding perbromides. Bromine does not react with derivatives of the quaternary ammonium chloride such as QmCl, ICl₃ and QmCl, ICl.

3. Iodine was found to replace *N*-halogens in only one case, and then only to a small extent, that is, QmCl, treated with excess of iodine, gave a small quantity of the periodide. Iodine was found frequently to combine with the added halogens, forming iodine monochloride or monobromide (2 mols.); one molecule combined with the quaternary ammonium salt, forming a mixed perhaloid, so that the final result appeared as though one atom of added halogen had been replaced by iodine : $\text{QmBr, Br}_2 + \text{I}_2 = \text{QmBr, IBr} + \text{IBr}$.

The validity of these generalisations is exemplified by the following experiments :

(a) A hot solution of QmCl, ICl₃ and QmCl, ICl in glacial acetic acid was treated with bromine. The crystals which separated on cooling were found to be identical with the unchanged substance. This result supports generalisation 1, for if a perbromide were formed momentarily, being in presence of chlorine and iodine monochloride, it must reform immediately QmCl, ICl and QmCl, ICl₃.

(b) One molecular proportion of iodine trichloride was dissolved in glacial acetic acid and heated at 40° so as to become dissociated largely into chlorine and iodine monochloride. One molecular proportion of phenyltrimethylammonium bromide, also dissolved in glacial acetic acid, was added to the solution, when crystallisation began in less than a minute, the product being QmCl, ICl and not QmBr, ICl or QmBr, Cl₂.

(c) Acetic acid solutions of varying amounts of iodine monochloride, carefully purified by distillation so as to be free from the trichloride, were added to acetic acid solutions of phenyltrimethylammonium bromide. When one molecular proportion of iodine monochloride was used, the product was found to be QmBr, ICl, but when two or more molecular proportions were used, the product was invariably QmCl, ICl. In the latter case, the product was found to be the same irrespective of whether the bromide solution was added to the iodine monochloride or vice versa, provided at least

two molecular proportions of the monochloride were present before the mixed solutions were cooled and had begun to crystallise.

As perhaloids are in general much less soluble in acetic acid than the parent quaternary ammonium salts, it was considered likely that low solubility might be the determining factor in deciding which compound would result, but investigation showed that such is not a factor of the first order of importance in deciding the course of the reactions. This fact, taken in conjunction with the absence of isomeric forms, suggests that the course of the reaction depends entirely on the inherent stability of certain arrangements or groupings of halogen atoms.

The stability of the perhaloids has been studied from another point of view, namely, that of the dissociation pressure of the finely powdered solid under the influence of rise in temperature. The values obtained are given in the experimental portion. In spite of a few slight discrepancies, the order of these dissociation pressures for the perhaloids is surprisingly small, being less than those of the quaternary ammonium salts themselves up to temperatures of about 90° . Above this temperature, rapid decomposition takes place. This result, although unexpected, is not altogether without a parallel, for somewhat similar behaviour is noticeable in the case of corresponding oxygen compounds, for example, the relative stability of chlorates and hypochlorites.

EXPERIMENTAL.

Analysis has been found necessary only where either a new substance has been encountered or the identification of a compound by means of (a) appearance and crystalline form, (b) melting point, alone or in admixture, has been inconclusive. In general, much more reliance can be placed on these two simple methods than had been anticipated, although it will be appreciated that with such reactive substances as perhaloids the melting point of a mixture did not always give definite results owing to mutual interaction.

Analysis.—The halogen estimations were all done in sealed tubes at 240° . The mixed silver haloids were weighed and then converted into silver chloride by heating in a stream of chlorine at 200° .

Methods of Degradation.—(a) By means of Ethyl Malonate. As an example of this method, the degradation of $\text{NPhMe}_3\text{Cl}_3$ may be described. The perhaloid was dissolved in about ten times its weight of ethyl malonate and warmed quickly to 40° , when evolution of hydrogen chloride began. The solution was then transferred to a desiccator and the latter evacuated. On the addition of ether to the solution the lower perhaloid was

precipitated in a pure condition, the yield being 97 per cent. of the theoretical. (b) By means of Acetone. For this method, absolutely dry acetone must be used. The best temperatures were found to be between 18° and the boiling point, and at the end of the reaction the quaternary ammonium salt usually crystallised from the reaction mixture or was precipitated by the addition of dry ether.

Action of Halogens on Phenyltrimethylammonium Iodide.—Chlorine in glacial acetic acid at 20–80° gave a mixture of $\text{NPhMe}_3\text{Cl}_2\text{I}$ (2 mols.) and $\text{NPhMe}_3\text{Cl}_2\text{I}_2$ (1 mol.). Bromine at 80° in glacial acetic acid yielded $\text{NPhMe}_3\text{Br}_2\text{I}$, whilst iodine at 80° yielded the di-, tetra-, and hexa-iodides. Iodine monochloride at 100° in glacial acetic acid gave NPhMe_3I_4 (60 per cent. yield).

Phenyltrimethylammonium Bromide, NPhMe_3Br .—This was prepared by a modification of the method employed by Vorländer and Siebert (*Ber.*, 1919, 52, 284) and by Tapel and Brendler (*Ber.*, 1898, 31, 1349). Fifty grams of $\text{NPhMe}_3\text{Br}_2$, prepared from the sulphate by the addition of bromine, were dissolved in 150 c.c. of dry acetone and shaken. After five minutes, the solution became colourless and precipitation of the quaternary bromide took place. This was recrystallised from a mixture of dry alcohol and dry ether. The yield was 32 grams.

With chlorine at 60° in glacial acetic acid, the quaternary ammonium bromide gave $\text{NPhMe}_3\text{Br}_2\text{Cl}_2$ (Found : C = 37·7; H = 5·0; Br = 27·8; Cl = 24·1. $\text{C}_9\text{H}_{14}\text{NCl}_2\text{Br}$ requires C = 37·7; H = 4·9; Br = 27·85; Cl = 24·7 per cent.); with bromine, it gave $\text{NPhMe}_3\text{Br}_2$, with iodine, $\text{NPhMe}_3\text{Br}_2\text{I}_2$, with iodine monobromide $\text{NPhMe}_3\text{Br}_2\text{I}$, with iodine monochloride (1 mol.), $\text{NPhMe}_3\text{Br}_2\text{Cl}$, and with iodine trichloride or the monochloride (2 mols.), there resulted $\text{NPhMe}_3\text{Cl}_2\text{I}$.

Phenyltrimethylammonium Chloride, NPhMe_3Cl .—This could not be isolated in the solid form, but was obtained as an oil when the hydroxide and hydrochloric acid were concentrated to a syrup, the syrup dissolved in absolute alcohol, and the chloride precipitated by ether. For identification purposes, the double salt with mercuric chloride, $\text{NPhMe}_3\text{Cl}_2\text{HgCl}_2$, melting at 184°, was employed. Chlorine, dissolved in hydrochloric acid, in alcohol, or in glacial acetic acid, had no action on this compound; bromine gave a 10 per cent. yield of $\text{NPhMe}_3\text{Br}_2$; iodine in acetic acid gave a 10 per cent. yield of the tetra-iodide, NPhMe_3I_4 (m. p. 84°); whilst iodine monochloride gave a nearly quantitative yield of $\text{NPhMe}_3\text{Cl}_2\text{I}$.

Action of Halogens on Phenyltrimethylammonium Iodide Di-iodide and on the Tetra-iodide.—The di-iodide, NPhMe_3I_2 , when treated

with chlorine in glacial acetic acid at 45° , gave $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}_3$, melting at 144° , whilst bromine at 80° gave $\text{NPhMe}_3\text{Br}\cdot\text{IBr}$, melting at 120° ; iodine gave the tetra-iodide, $\text{NPhMe}_3\text{I}\cdot\text{I}_4$.

The tetra-iodide with chlorine at 100° gave a mixture of $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}$ and $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}_3$.

Phenyltrimethylammonium Bromide Dichloride, $\text{NPhMe}_3\text{Br}\cdot\text{Cl}_2$.—This substance could be obtained by the direct action of chlorine on the quaternary ammonium bromide, but was prepared best by chlorinating phenyltrimethylammonium bromide dibromide, $\text{NPhMe}_3\text{Br}\cdot\text{Br}_2$, in glacial acetic acid at 80° . The *dichloride* was precipitated by the addition of ether and when recrystallised from glacial acetic acid, in which it is somewhat easily soluble, it formed very pale yellow leaflets which melted at 111° (Found : C = 37.7; H = 5.0; Cl = 24.1; Br = 27.8. $\text{C}_9\text{H}_{14}\text{NCl}_2\text{Br}$ requires C = 37.7; H = 4.9; Cl = 24.7; Br = 27.85 per cent.). The constitution of this substance was established by its losing chlorine when kept in a vacuum desiccator over potassium hydroxide and also by its decomposition in the cold by acetone, when the quaternary bromide was produced (Found : Br = 36.7. Calc., Br = 37.0 per cent.).

Chlorine was without further action on the dichloride, and bromine at 60° in glacial acetic acid had no action. Iodine in acetic acid at the boiling point gave $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}$.

Phenyltrimethylammonium Bromide Iodochloride, $\text{NPhMe}_3\text{Br}\cdot\text{ICl}$.—This was prepared by heating together in glacial acetic acid for five minutes equivalent quantities of iodine monochloride and phenyltrimethylammonium bromide. When the solution was cooled, sandy-yellow crystals separated, which, after two crystallisations from glacial acetic acid, melted at 104° . The yield was 80 per cent. of the theoretical (0.2902 gave 0.4300 of mixed silver haloids, which yielded after chlorination the ratio silver haloids/ AgCl = 1.33. $\text{C}_9\text{H}_{14}\text{NClBrI}$ requires 0.434 mixed haloids and the ratio 1.316). The constitution of this substance was established by treatment with acetone, which yielded the quaternary ammonium bromide free from chloride or iodide.

This iodochloride, when treated with chlorine at 90° , gave $\text{NPhMe}_3\text{Cl}\cdot\text{ICl}_3$; bromine was without action on it; whilst iodine gave traces of $\text{NPhMe}_3\text{Br}\cdot\text{I}_2$.

Phenyltrimethylammonium Bromide Iodobromide, $\text{NPhMe}_3\text{Br}\cdot\text{IBr}$.—This substance was formed by the action of bromine on $\text{NPhMe}_3\text{Br}\cdot\text{I}_2$ or $\text{NPhMe}_3\text{I}\cdot\text{I}_2$, by the action of iodine on $\text{NPhMe}_3\text{Br}\cdot\text{Br}_2$, or by the action of iodine bromide on NPhMe_3Br . The best method of preparation consisted in the addition of a slight excess of bromine to an acetic acid solution of phenyltrimethyl-

ammonium iodide at 60° . The yield was nearly theoretical and the product, when recrystallised from glacial acetic acid, consisted of glistening orange plates which melted at 120° (Found : Br = 38.1; I = 29.1; N = 3.21. $C_9H_{14}NBr_2I$ requires Br = 37.8; I = 29.9; N = 3.3 per cent.). The constitution of this substance was established by treatment with acetone, when the quaternary ammonium bromide resulted. Chlorine acted on this iodobromide to produce a 96 per cent. yield of $NPhMe_3Cl, ICl_3$, whilst bromine was without action on it, and iodine gave only traces of $NPhMe_3Br, I_2$.

Phenyltrimethylammonium Bromide Di-iodide, $NPhMe_3Br, I_2$.—This compound was prepared by the addition of the calculated weight of iodine to a concentrated solution of the quaternary ammonium bromide in acetic acid. The mixture was kept at 100° for a few minutes, and, on cooling, the di-iodide separated. It was recrystallised from glacial acetic acid, when it formed deep orange-brown plates melting at 114° . The yield was about 83 per cent. of the theoretical (Found : Br = 16.1; I = 55.2. $C_9H_{14}NBrI_2$ requires Br = 17.4; I = 55.2 per cent.).

The constitution was inferred from its method of preparation and from the fact that it resembled the periodides in not being degraded by treatment with acetone.

When chlorine was passed into a solution of the di-iodide in glacial acetic acid, bromine was evolved and $NPhMe_3Cl, ICl_3$ separated. Bromine acted on the di-iodide and produced $NPhMe_3Br, IBr$, whilst iodine was without further action.

Phenyltrimethylammonium Chloride Iodomono-chloride,
 $NPhMe_3Cl, ICl$.

—This compound was originally prepared by Samtleben (*Ber.*, 1898, **31**, 1146), who obtained it by the action of chlorine on phenyltrimethylammonium iodide in hydrochloric acid solution. It can be obtained also by the action of ethyl malonate at 40° on $NPhMe_3Cl, ICl_3$, or by the action of iodine on $NPhMe_3Br, Cl_2$.

Samtleben's suggestion that this substance was the iodochloride of the quaternary ammonium chloride has been confirmed by means of degradation with acetone and the conversion of the very soluble chloride produced into the double salt with mercuric chloride, $NPhMe_3Cl, HgCl_2$, which melts at 184° . It was found possible also to synthesise the compound from the quaternary chloride and iodine mono-chloride in acetic acid solution.

The action of chlorine on the iodomono-chloride converted it partly into the iodotrichloride, $NPhMe_3Cl, ICl_3$, which usually crystallised along with the unchanged mono-chloride. Bromine and iodine were without action on the substance.

Phenyltrimethylammonium Chloride Iodotrichloride, $\text{NPhMe}_3\text{Cl}, \text{ICl}_3$.

—The best method for the preparation of this substance consisted in the action of chlorine on a glacial acetic acid solution of $\text{NPhMe}_3\text{Br}, \text{IBr}$ at $60\text{--}70^\circ$. When the solution was cooled, the product crystallised in long, yellow needles which melted at 144° . It can also be prepared by chlorination of the periodide ($0\cdot3225$ gave $0\cdot6461$ of mixed silver haloids, which after chlorination gave mixed haloids/ $\text{AgCl} = 1\cdot129$. $\text{C}_9\text{H}_{14}\text{NCl}_4\text{I}$ requires $0\cdot6450$ of mixed haloids and the ratio $1\cdot123$).

This product was also formed together with the iodonochloride by the chlorination of phenyltrimethylammonium iodide in glacial acetic acid at any temperature between 20° and 100° . The two products were separated by dissolving 3 grams in 60 c.c. of glacial acetic acid at $104\text{--}106^\circ$ and allowing the solution to cool slowly, when both products crystallised and could be separated by hand-picking with the aid of a lens; the addition of a few drops of bromine facilitated this separation by tinting the crystals to a different degree. For a long time the product of chlorination, which melts at 141° , was thought to be homogeneous and to have the formula $(\text{NPhMe}_3\text{Cl}, \text{ICl}_3)_2$, $\text{NPhMe}_3\text{Cl}, \text{ICl}$ (Found: $\text{C} = 28\cdot3$; $\text{H} = 3\cdot8$; $\text{N} = 3\cdot6$; $\text{Cl} = 30\cdot9$; $\text{I} = 33\cdot7$. Calc., $\text{C} = 28\cdot3$; $\text{H} = 3\cdot7$; $\text{N} = 3\cdot7$; $\text{Cl} = 31\cdot0$; $\text{I} = 33\cdot3$ per cent.). It is best regarded as a double salt.

The constitution of the iodotrichloride is established by (a) treatment with ethyl malonate, when the iodonochloride results, and (b) treatment with acetone and the addition of mercuric chloride, when the characteristic double salt derived from the quaternary ammonium chloride is precipitated. Further, it was possible to synthesise this substance by the action of iodine trichloride on the quaternary ammonium chloride and separation of the two constituents of the double salt.

Chlorine and bromine were found to be without action on the iodotrichloride. On grinding the substance with water, a red colour was formed immediately, and on standing a small quantity of $\text{NPhMe}_3\text{I}, \text{I}_4$ was precipitated. When the substance was treated with a concentrated aqueous solution of potassium hydroxide and the solution acidified with acetic acid, a small quantity of the same periodide was produced.

Solubilities of the Perhaloids in Acetic Acid at 38° .

Perhaloid.	Solubility in grams per litre.	Relative solubility in mols.	Perhaloid.	Solubility in grams per litre.	Relative solubility in mols.
$\text{NPhMe}_3\text{Br}, \text{Cl}_2$	50	35.1	$\text{NPhMe}_3\text{Br}, \text{IBr}$	6.6	3.1
$\text{NPhMe}_3\text{Br}, \text{Br}_2$	8	4.6	$\text{NPhMe}_3\text{Cl}, \text{ICl}$	13.3	8.0
$\text{NPhMe}_3\text{Br}, \text{I}_2$	6.5	2.8	$\text{NPhMe}_3\text{I}, \text{I}_2$	4.0	1.6

Vapour Pressures of the Perhaloids at Different Temperatures.

The apparatus used consisted of two small similar distilling flasks, to the side tubes of which were fused the two upper ends of a long narrow U-tube, fitted with small bulbs at the upper end of each limb. The U-tube, partly filled with mercury, acted as a manometer. The dried, finely powdered substances to be compared were introduced into the distilling flasks, the neck of one flask was sealed whilst the other distilling flask was connected with a pump, completely evacuated, and sealed. The bulbs of the flasks were immersed in a thermostat, and readings were taken at each temperature. A simpler form of the apparatus was made by fusing together a single distilling flask and a U-tube with a very long sealed limb. With this apparatus the absolute dissociation pressures of the substances were obtained directly.

Substance.	M. p.	Vapour pressures in mm. of mercury at						
		38°.	60°.	80°.	89°.	94—96°.	100°.	155°.
QmBr	214°	6	21	—	54	62		
QmBr, Br ₂	112	—	5.5	5.5	6	>322		
QmBr, Cl ₂	111	11	13	16.5	9(?)	—		
QmBr, I ₂	114	2.5	3	4	—	6	6.5	15
QmI	224	2	5	8	8.5	11		
QmI, I ₂	116	—	2	1	—	2	1.5	>170
QmI, I ₄	86	1.5	3	4	—	5		
QmCl, ICl ₃	144	1	1	—	—	10		

Summary.

The preparation and properties of the following new perhaloids are described: NPhMe₃Cl, ICl₃; NPhMe₃Br, Cl₂; NPhMe₃Br, IBr; NPhMe₃Br, I₂; NPhMe₃Br, ICl.

The results of chlorination, bromination, and iodination of each of the following are also described: (NPhMe₃)₂SO₄; NPhMe₃NO₃; NPhMe₃Cl; NPhMe₃Cl, ICl; NPhMe₃Cl, ICl₃; NPhMe₃Br; NPhMe₃Br, Cl₂; NPhMe₃Br, Br₂; NPhMe₃Br, I₂; NPhMe₃Br, I₂; NPhMe₃Br, ICl; NPhMe₃Br, ICl; NPhMe₃Br, IBr; NPhMe₃I; NPhMe₃I, I₂; NPhMe₃I, I₄.

The following deductions have been drawn from these results.

1. Since the sulphate and nitrate do not give stable perhaloids, perhaloid formation is due to the halogen of the quaternary ammonium salt and not to the nitrogen atom.

2. The bromide gives the widest range of stable perhaloids by direct addition.

3. Chlorine always replaces the *N*-halogen if iodine is also present.

4. In the absence of iodine, chlorine replaces the added halogen, not the *N*-halogen.

5. Bromine replaces *N*-iodine, but not *N*-chlorine or added chlorine to any appreciable extent.

6. Up to 95°, the perhaloids have smaller vapour pressures than the parent quaternary ammonium salts.

7. Low solubility is insufficient to explain these reactions.

8. The assumption that these perhaloids are molecular compounds fails in a similar manner.

9. True chemical affinity where the halogens are multivalent is the only explanation of these experiments.

10. Two methods of determining the constitution of the perhaloids by the successive removal of the most easily detached halogens by means of (*a*) ethyl malonate under reduced pressure and (*b*) acetone are given.

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[Received, September 20th, 1922.]
