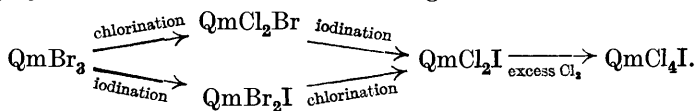# CCCXXXI.—*Quaternary Ammonium Perhalides.*

By Thomas Harold Reade.

WHEN quaternary ammonium halides are treated with chlorine, bromine, or iodine, addition compounds are formed containing three halogen atoms. These trihalides are coloured substances which are stable enough to be recrystallised from alcohol or acetic acid. To this class belong, not only tri-iodides and tribromides—one tri-chloride only is known—but also " mixed " trihalides (*e.g.*, dibromo-iodides) which have been investigated by McCombie and Reade (J., 1923, **123**, 143), Reade (J., 1924, **125**, 148), and by Reade and Sim (J., 1924, **125**, 157).

The trihalides are often referred to as " molecular compounds," but the term is misleading, for, although a dichloroiodide is obtained by chlorinating an iodide, the substance decomposes into the chloride and iodine monochloride, but not into the two components from which it was formed.

The facts that the absorption spectra of quaternary ammonium trihalides and of the corresponding metallic trihalides are almost identical, and that sulphates and nitrates do not form stable addition-products with the halogens whereas chlorides, bromides, and iodides do so, are most simply interpreted as signifying the existence of complex trihalogen ions in these compounds. The chemical properties of the three halogen atoms in a trihalide are not, how-ever, identical. Means of splitting off halogen atoms from tri-halides were described by McCombie and Reade (*loc. cit.*), and constitutional formulæ based on this process were tentatively put forward for trihalides. For example, a dichloroiodide was regarded as an addition compound of the chloride and iodine monochloride because the quaternary ammonium chloride exclusively was pre-cipitated when the trihalide was dissolved in warm acetone. Since, however, it is now known that the relative solubilities in acetone of the quaternary ammonium halides are far from equal, and since the least soluble will tend to accumulate if the trihalide can decom-pose in more than one way, the constitutional deductions previously put forward are open to question. The evidence afforded by the results of submitting these trihalides to the further action of the halogens, which is set forth in the table (p. 2530), shows that electrical charge also must be taken into account. The reasoning employed will be clear from the following scheme.

$$\mathrm{QmBr_3} \underset{\textit{iodination}}{\overset{\textit{chlorination}}{\rightrightarrows}} \begin{matrix} \mathrm{QmCl_2Br} \\ \mathrm{QmBr_2I} \end{matrix} \underset{\textit{chlorination}}{\overset{\textit{iodination}}{\rightrightarrows}} \mathrm{QmCl_2I} \xrightarrow[\text{excess Cl}_2]{} \mathrm{QmCl_4I}.$$

When a tribromide $Qm*Br_3$ is chlorinated it gives a dichloro-bromide, one bromine atom escaping replacement; when it is iodinated, however, only one bromine atom is replaced, a dibromo-iodide resulting. The atom which is replaced in the latter process must be the same as that which is unaffected during the chlorin-ation, because it can be displaced by iodine from the dichloro-bromide, giving the dichloroiodide. This argument can be sub-mitted to a further check by determining whether the two bromine atoms which are displaced by chlorine from the tribromide are the same two as those which escape displacement by iodine; if so, then the two bromine atoms in the dibromoiodide should be dis-placeable by chlorine, but the iodine should remain. This is con-firmed by experiment, for the product is the dichloroiodide $QmCl_2I$, a large excess of chlorine giving the tetrachloroiodide $QmCl_4I$.

The conclusion is irresistible that in a tribromide two bromine atoms behave alike and are replaceable only by the lighter halogen, whereas the third bromine atom is replaceable only by the heavier halogen, iodine. The former behaviour is characteristic of negatively charged bromine, as in the ordinary bromide ion, the latter of the halogen in a bromate. But since the tribromide ion carries a single negative charge and yet contains two negatively charged atoms, the remaining bromine atom must be electropositive. The tri-bromide would then be represented as $\overset{+}{Qm} \ldots \overset{-}{Br}\overset{+}{Br}\overset{-}{Br}$ so far as charge alone is concerned.

This tendency amongst trihalides for one atom to function electropositively whilst the remaining two atoms are negatively charged appears to be quite general, and can be traced throughout all the reactions shown in the table. Although it is more difficult to detect in the lower half of the table, where the formation of more than one trihalide frequently occurs, the principle is never actually violated. To be more precise, where a single trihalide is formed, there are 100% of agreements; where two trihalides are simultaneously produced, one always agrees whilst one disagrees, thus affording neither proof nor disproof. Neglecting the latter, the probability of a fortuitous agreement with this generalisation is so extremely small—about 1 in 10^{15}—as to be negligible.

One further question arises : If the formula of a trihalide is known, is it possible to predict which halogen atom will behave electropositively and which two negatively? Reference to the table shows that the electropositive atom is always the heaviest halogen which the trihalide complex contains.

It is of interest that crystals of metallic trihalides appear to

* Qm denotes the phenyltrimethylammonium radical.

have the heaviest halogen atom between the other two halogen atoms, the three atoms being in line along the diagonal of the cell the corners of which are occupied by the metal (Wyckoff, *J. Amer. Chem. Soc.*, 1920, **42**, 1100; Clark, *Proc. Nat. Acad. Sci.*, 1922, **8**, 90). The central atom spatially is that of highest atomic weight; it is also the atom the chemical properties of which indicate that it is positively charged. This is probably the reason why dichlorobromides are less stable than dichloroiodides, whilst trichlorides are so unstable that only one has so far been isolated, for the tendency for the halogens to function electropositively admittedly decreases in the order iodine, bromine, chlorine.

The view to which these considerations lead is that the chemical reactions of quaternary ammonium trihalides are more directly dependent upon the electrical charges carried by the three halogen atoms than upon the arrangement of these atoms in space. It now becomes clear why the common classification of quaternary ammonium trihalides as " molecular compounds " is so much out of harmony with many of their chemical reactions; for to regard a dichloroiodide as a molecular compound of chlorine and a quaternary ammonium iodide implies that the iodine atom still retains its negative charge, whereas actually it functions electropositively.

The following table contains a complete summary of experiments in which a trihalide has been chlorinated, brominated, or iodinated in glacial acetic acid, and is largely taken from previously published papers (see McCombie and Reade, *loc. cit.*; Reade, *loc. cit.*). In accordance with the ideas developed in this communication, the heaviest halogen in each trihalide is written centrally.

	Qm = Phenyltrimethyl-ammonium.			Qm = p-Bromophenyltri-methylammonium.		
	Product of halogenation by			Product of halogenation by		
Trihalide.	chlorine.	bromine.	iodine.	chlorine.	bromine.	iodine.
Qm–ClICl	–ClICl / –ClICl$_3$	–ClICl	–ClICl	–ClICl$_3$	–ClICl / –BrICl	–ClICl*
Qm–BrICl	–ClICl$_3$	–BrICl	–BrICl	–ClICl$_3$	–BrICl / –BrIBr	–BrICl / –BrII
Qm–BrIBr	–ClICl$_3$	–BrIBr	–BrIBr / –BrII	–ClICl$_3$	–BrIBr	–BrIBr / –BrII
Qm–ClBrCl	–ClBrCl	–ClBrCl	–ClICl	–ClBrCl	–ClBrCl	–ClICl / –BrICl
Qm–BrBrBr	–ClBrCl	–BrBrBr / –Br$_5$ } –BrIBr		–ClBrCl	–BrBrBr	–BrIBr
Qm–BrII	–ClICl$_3$	–BrIBr	–BrII	–ClICl$_3$	–BrIBr	–BrII / –I$_3$
Qm–III	–ClICl$_3$	–BrIBr	–I$_5$	–ClICl$_3$	–BrIBr	–III / –I$_5$

* Also products containing iodine.

EXPERIMENTAL.

The solubilities in acetone of p-bromophenyltrimethylammonium chloride, bromide, and iodide were determined by shaking an excess of each salt with warm acetone, and then leaving it with occasional shaking in a thermostat at 15° for 24 hours. 25 C.c. of the filtered saturated solution were boiled with aqueous silver nitrate and the silver halides were weighed : 25 c.c. gave 0·0356 g. AgCl, 0·0079 g. AgBr, and 0·0101 g. AgI, respectively; whence 100 c.c. of acetone dissolved 0·000992 g.-mol. $C_6H_4Br\cdot NMe_3Cl$, 0·000168 g.-mol. $C_6H_4Br\cdot NMe_3Br$, and 0·000172 g.-mol. $C_6H_4Br\cdot NMe_3I$.

Iodination of p-*Bromophenyltrimethylammonium Dichlorobromide.* —0·94 G. of iodine in 40 c.c. of acetic acid was shaken with 1·36 g. of p-bromophenyltrimethylammonium dichlorobromide in 60 c.c. of acetic acid and set aside for 24 hours in a cool place. The crystals which separated were fractionally crystallised from acetic acid. The more soluble portion was identified as p-bromophenyltrimethyl-ammonium chlorobromoiodide, m. p. 178°, by comparison with an authentic specimen. The less soluble portion, m. p. 176°, was identified as the dichloroiodide, by conversion by acetone into p-bromophenyltrimethylammonium chloride, the double salt of which with mercuric chloride was analysed (Found : Cl, 19·3. $C_9H_{13}NClBr,HgCl_2$ requires Cl, 20·4%). The original mother-liquor was proved to contain iodine monochloride and iodine mono-bromide by adding it to aqueous potassium iodide solution, removal of iodine and acetic acid by distillation, addition of sodium nitrite, extraction five times with chloroform, and precipitation of the halides with silver nitrate (Found : Br, 0·0363 g.; Cl, 0·0110 g.). The complete reaction is therefore $2I_2 + 2C_6H_4Br\cdot NMe_3Cl_2Br \longrightarrow$ $C_6H_4Br\cdot NMe_3ClBrI + C_6H_4Br\cdot NMe_3Cl_2I + ICl + IBr$.