

## XI.—*Ammonium Perhaloids.*

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SEVERAL ammonium trihaloids have been prepared in order to compare them with the diazonium trihaloids, which, erroneously, have been regarded as similarly constituted.

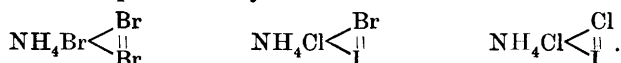
Ammonium tribromide (*Ber.*, 1881, **14**, 2398), ammonium dibromiodide (*Amer. Chem. J.*, 1900, **24**, 30), and ammonium tri-iodide (*T.*, 1878, **33**, 397) have been described, but apparently no attempts have been made hitherto to obtain the trihaloids containing chlorine.

Two of the latter compounds, namely, *ammonium dichloriodide*,  $\text{NH}_4\text{Cl}_2\text{I}$ , and *ammonium chlorobromiodide*,  $\text{NH}_4\text{ClBrI}$ , are described in this paper. They are well crystallised and remarkably stable substances which can be kept without change for years, and can even be heated for many hours at  $180\text{--}200^\circ$  in sealed tubes without permanent alteration, partial dissociation into ammonium chloride and iodine chloride or bromide only taking place.

When heated in the air or exposed over lime in a vacuum, they lose halogen, ammonium chloride in each case being left. Both are extremely readily soluble in water, and deliquesce in presence of moisture.

A comparison of the properties of the ammonium trihaloids and of the diazonium trihaloids shows that they cannot be regarded as analogously constituted. For example, ammonium perbromide is extraordinarily readily soluble in water, and loses two-thirds of its bromine if exposed for a few minutes in the air, whilst benzene-diazonium perbromide is insoluble in water, and can be kept in a vacuum over lime for a long period without any loss of halogen. Similar differences are observed between the other ammonium and diazonium perhaloids. There is, in fact, no resemblance whatever between the two classes of compounds except the unessential one that each contains three atoms of halogen.

The diazonium perhaloids are not perhaloids at all, but *N*-trihalogen derivatives of the hydrazines; for example, benzene-diazonium perbromide has the constitution  $\text{C}_6\text{H}_5\cdot\text{NBr}\cdot\text{NBr}_2$ , whilst the ammonium trihaloids may provisionally be regarded as having a constitution represented by the formulæ



Several trihaloids of aliphatic primary amines have also been prepared; they closely resemble the similarly constituted ammonium trihaloids, but are even more readily soluble in water.

*Ammonium Perbromide, NH<sub>4</sub>Br<sub>3</sub>.*

Ammonium perbromide was first obtained by Roozeboom (*Ber.*, 1881, **14**, 2398) by dissolving bromine in a saturated aqueous solution of ammonium bromide, and concentrating over sulphuric acid. He describes it as crystallising in columnar crystals, somewhat resembling potassium dichromate in colour.

Ammonium bromide combines with bromine, not only in aqueous solution, but also in the solid state. If powdered ammonium bromide is placed in a stoppered bottle with the calculated amount of bromine, or exposed, together with liquid bromine, in a closed space, combination slowly takes place, and the white bromide becomes ultimately completely converted into the orange-coloured, crystalline perbromide.

It can also be prepared, although the action is somewhat violent, by adding a concentrated solution of ammonia to excess of liquid bromine cooled in a freezing mixture.

Ammonium perbromide can be preserved unchanged only in the presence of free bromine. Its dissociation pressure at 15° is approximately 0.45 cm., and at 45° approximately 2.5 cm., of mercury.

To ascertain its stability, a quantity which had been kept in a sealed tube for four years was analysed by heating a known amount at 100° and weighing the ammonium bromide left, by titrating the iodine liberated when a weighed amount was added to an excess of a solution of potassium iodide acidified with acetic acid, and by ascertaining the amount of silver bromide precipitated by silver nitrate after reducing a known amount of the salt by sodium sulphite:

1.2138 gave 0.4580 NH<sub>4</sub>Br. Br=62.26.

0.7036 liberated I=54.5 c.c. N/10-iodine. Br=61.90.

0.4976 gave 1.0859 AgBr. Br=92.87.

NH<sub>4</sub>Br<sub>3</sub> requires  $\frac{3}{2}$ Br=62.0. Total Br=93.02 per cent.

A quantity was heated in a sealed tube for eight hours to 180°; it was then set aside for four years, and again heated to 180—200° for eight hours. On opening the tube, it was found that no nitrogen or hydrogen bromide had been produced, and, except for the formation of a slight superficial layer of ammonium bromide due to dissociation, some little bromine vapour escaping on opening the tube, the compound had apparently undergone no change.

*Ammonium Dichloroiodide, NH<sub>4</sub>Cl<sub>2</sub>I.*

This compound was prepared by suspending ammonium chloride in its own weight of water, adding slightly more than an equivalent

amount of powdered iodine, and passing in a rapid stream of chlorine until the free iodine had just disappeared, a point easily recognised by the change of colour. The liquid became distinctly warm during the passage of the chlorine, and on allowing it to remain overnight in a desiccator over sulphuric acid, ammonium dichloriodide crystallised out in stout, transparent scarlet prisms. These were rapidly collected, pressed between filter paper, and dried over phosphoric oxide, a few crystals of iodine monochloride having been previously placed in the desiccator.

It is equally easily prepared by passing chlorine through a warm, saturated aqueous solution of ammonium iodide. The iodine is first set free, and then disappears, leaving a bright red solution, which deposits ammonium dichloriodide on cooling.

It was analysed in the manner already described:

0.7122 gave 0.1756  $\text{NH}_4\text{Cl}$ .  $\text{ICl} = 75.34$ .

0.7050 liberated  $\text{I} = 65.4$  c.c.  $\text{N}/10$ -iodine.  $\text{ICl} = 75.31$ .

0.4446 gave 1.0698  $\text{AgCl} + \text{AgI}$ .

$\text{NH}_4\text{Cl}_2\text{I}$  requires  $\text{ICl} = 75.21$  per cent. and 1.0739  $\text{AgCl} + \text{AgI}$ .

*Ammonium dichloriodide* is the most stable of the trihaloids. It can be kept for an indefinite period without change if sealed up in a tube, but loses iodine monochloride slowly when exposed to dry air at the ordinary temperature, fairly quickly when exposed in a vacuum over lime, and very quickly when heated in the air to  $100^\circ$ , leaving ammonium chloride.

A specimen kept for four years in a sealed tube was found on analysis not to have altered in composition, and a quantity heated in a sealed tube for eight hours to  $180^\circ$ , kept for four years, and again heated for eight hours to  $180$ – $200^\circ$ , was found to have undergone no change, no nitrogen chloride, nitrogen, or halogen acid being produced.

It is very readily soluble in water, giving a deep red solution.

If through a saturated aqueous solution a stream of chlorine is passed as long as the gas is absorbed, some heat is evolved, and a bright yellow liquid is obtained, which on cooling deposits ammonium tetrachloriodide,  $\text{NH}_4\text{Cl}_4\text{I}$ , in long, golden-yellow prisms. This compound, which was the first of the ammonium perhaloids to be described, having been obtained by Filhol (*J. Pharm.*, 1839, **25**, 431) early in last century, can also be kept without change for an indefinite period if sealed up in a tube.

A specimen kept for four years thus sealed up showed an unaltered composition on analysis. What is more surprising is that it can be heated in a sealed tube for sixteen hours at  $180$ – $200^\circ$  without any production of nitrogen chloride, nitrogen, or halogen

acid. Partial dissociation into chlorine and dichloroiodide no doubt takes place, but these re-combine on cooling.

On exposure to air or in a vacuum over lime, ammonium tetrachloroiodide first loses chlorine, forming the dichloroiodide, which then on further exposure loses iodine monochloride, leaving ammonium chloride.

*Ammonium Chlorobromoiodide*,  $\text{NH}_4\text{ClBrI}$ .

Ammonium chlorobromoiodide was prepared by dissolving ammonium chloride in its own weight of warm water, and adding an equivalent amount of bromine and of iodine. A deep, brownish-red liquid was thus produced, which on cooling in a desiccator over sulphuric acid deposited the perhaloid in large, deep garnet-red prisms. It was separated, dried, and analysed as described above:

0.5347 gave 0.1092  $\text{NH}_4\text{Cl}$ .  $\text{IBr} = 79.57$ .

0.5420 liberated  $\text{I} = 41.5$  c.c.  $N/10$ -iodine.  $\text{IBr} = 79.18$ .

0.5676 gave 1.2316  $\text{AgBr} + \text{AgI}$ .

$\text{NH}_4\text{ClBrI}$  requires  $\text{IBr} = 79.45$  per cent. and 1.2388  $\text{AgBr} + \text{AgI}$ .

*Ammonium chlorobromoiodide* is a very stable compound, and can be kept in a sealed tube or heated to  $200^\circ$  without decomposition other than temporary partial dissociation into ammonium chloride and iodine bromide.

When heated in air or exposed over lime in a vacuum it loses iodine bromide and leaves ammonium chloride. It is very readily soluble in water, giving a deep red solution.

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