

XII.—*On the Action of Chlorine upon Arsenious Acid.*

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BEING desirous of preparing a considerable quantity of terchloride of arsenic by a more direct method than those usually prescribed, for which arsenic itself must first be obtained, I distilled a mixture of arsenious acid with strongly ignited charcoal-powder in a current of washed and dried chlorine. This process furnished very much less than the calculated quantity of terchloride of arsenic, and the residue in the retort was found to contain a large quantity of arsenic acid, notwithstanding that a considerable excess of charcoal had been employed. This led me to examine the action of chlorine upon arsenious acid itself.

When powdered arsenious acid is very gently heated in a current of chlorine, the gas is absorbed, a colourless liquid distils over, and the powder melts to a perfectly transparent and colourless liquid, which solidifies to a transparent glass on cooling. On continuing the action of heat and chlorine upon the fused mass, it gradually volatilises entirely, with evolution of oxygen.

Liquid product of the action of chlorine upon Arsenious acid.—This liquid had all the characters of terchloride of arsenic.

8.28 grains of it, when decomposed by water and precipitated by nitrate of silver, gave
19.84 grns. of chloride of silver, corresponding to
4.9081 grns. of chlorine, or 59.27 per cent.

Pure terchloride of arsenic contains only 58.67 per cent.

On redistilling the liquid, almost all of it passed over between 267° and 268° F.*

9.69 grns. of the redistilled liquid, decomposed by water and precipitated by hydrosulphuric acid, gave 6.52 grns. of tersulphide of arsenic, representing 3.9756 grns. of arsenic, or 41.02 per cent.

9.79 grns. gave 23.29 grns. of chloride of silver, representing 5.7616 grns. of chlorine, or 58.85 per cent.

These numbers prove the liquid to be terchloride of arsenic, containing as might be expected, a trifling excess of chlorine:

* Gmelin states the boiling-point of terchloride of arsenic to be 132° C. (269.6° F.) apparently on the authority of Dumas.

	Eqt.	Calculated.	Found.
As	75·0	41·32	41·02
Cl ₃	106·5	58·68	58·85
	<hr/> 181·5	<hr/> 100·00	<hr/> 99·87

The action of chlorine upon arsenious acid may be recommended as a convenient laboratory process for the preparation of terchloride of arsenic.* Since the solidification of the residue always cracks the retort, it is better to employ a Florence flask in which a tubulated aperture has been made with the help of the blowpipe, to receive the tube delivering the chlorine. With a moderately long-necked flask no condenser is necessary, and the terchloride may pass at once into the receiver. 1,000 grns. of dry powdered arsenious acid will be found a convenient charge, and will require the chlorine from about 20 measured ounces of common yellow hydrochloric acid and 1,500 grns. of black oxide of manganese. As a slow current of chlorine is required, the mixture must be very gently warmed, the chlorine being passed first through water and then through oil of vitriol.

Arsenious acid yields rather less than one-third of its weight of terchloride of arsenic.

Solid product of the action of chlorine upon arsenious acid.—The vitreous residue cracked in all directions, with some violence, in the act of cooling, splitting glass tubes and bulbs containing it, and often projecting fragments of them to some distance. Brilliantly transparent when freshly prepared, it gradually became opaque throughout when kept for a few days, like vitreous arsenious acid. When moistened with water it became opaque, and on boiling gradually dissolved, yielding a strongly acid solution which deposited crystals of arsenious acid on cooling. The solution was found to contain arsenic acid, arsenious acid, and a small quantity of hydrochloric acid.

10 grns. of the vitreous mass yielded only 0·23 grn. of chloride of silver, representing 0·05 grn. chlorine, or 0·5 per cent.†

The amount of arsenious acid was determined by dissolving the

* It is mentioned by Dr. Miller, in his "Elements of Chemistry," 1864; Part II. p. 689, my experiments upon it being then in an incomplete state.

† Wallace (Phil. Mag. Nov. 1853) obtained a glassy substance by the action of hydrochloric acid upon arsenious acid, to which he assigned the composition 2AsO_3 , AsClO_2 , requiring 10·9 per cent. of chlorine.

glass in solution of potash, acidulating with hydrochloric acid, and adding a standard solution of permanganate of potash.

The result of this determination in several different specimens of the glass showed that the proportion of arsenious acid varied very considerably, as might be expected, from the difficulty of arresting the action of chlorine at a definite stage.

Some experiments were therefore made upon the direct synthesis of the glass with arsenious and arsenic acids.

At the closed end of a tube of hard glass some arsenious acid was placed, and in front of it a layer of arsenic acid in powder, the latter was heated to a temperature below its melting-point, and after some time the vapour of arsenious acid was driven over it by applying heat to the end of the tube, when the arsenic acid liquefied immediately, forming a glass similar to that obtained by the action of chlorine.

A mixture of one equivalent (99) of arsenious acid with one equivalent (115) of arsenic acid was found to undergo fusion at a far lower temperature than arsenic acid alone, but did not form a transparent glass. When two equivalents of arsenious acid were employed, the glass was quite transparent.

In the experiments recorded in the following table, the mixtures of arsenious and arsenic acids were heated in bulbs blown in the centre of tubes, open at both ends, until a perfectly clear liquid had been produced. The ends of the tubes, with any excess of arsenious acid which had sublimed, were then cut off, the bulb with its contents weighed, soaked in weak potash until the vitreous mass was dissolved off, and again weighed to ascertain the weight of the vitreous mass; the arsenious acid was then determined in the solution by acidifying with hydrochloric acid, and adding a standard solution of permanganate of potash:—

					AsO ₃ found in 100 parts.	
	AsO ₃ in eqts. employed.	AsO ₃ in eqts. employed			Of the mixture.	Of the glass.
I*	2	..	1	..	63·25	.. 55·30
II	3	..	1	..	72·00	.. 61·76
III	4	..	1	..	77·40	.. 66·34
IV	5	..	1	..	81·10	.. 63·02
V	5	..	1	..	81·10	.. 66·63

* A little arsenious acid sublimed during the fusion. even in this instance.

These results render it probable that when arsenious acid in excess is fused with arsenic acid, the compound $2\text{AsO}_3 \cdot \text{AsO}_5$ (containing 63·25 per cent. of AsO_3) is formed, though it is difficult to obtain it in a perfectly pure form, because the temperature at which it is decomposed is but little above that at which the last portion of the excess of arsenious acid volatilises.

After very careful fusion of arsenious acid in chlorine, arresting the action as soon as a perfectly clear liquid glass was produced, the latter was found to contain 62·38 per cent. of arsenious acid ($2\text{AsO}_3 \cdot \text{AsO}_5$ requires 63·25).

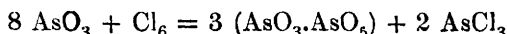
In several of the earlier experiments it had been observed that the period at which fumes of terchloride of arsenic ceased to be evolved at a moderate heat, and at which the liquid glass had just become transparent, was that at which the glass weighed 88 to 89 per cent. of the arsenious acid employed.

According to the equation—



100 grns. of arsenious acid should furnish 86·2 grns. of the vitreous residue, containing 63·25 per cent. of arsenious acid, whilst the terchloride of arsenic produced should amount to one-third of the weight of the arsenious acid, as was, in fact, the general result of the experiments.

For the equation—



100 grns. of arsenious acid should yield 81 grns. of the glass, containing 46·26 per cent. of arsenious acid, whilst the terchloride of arsenic produced would amount to nearly half the weight of the arsenious acid (45 per cent.)

The conclusion to which I have been led by the foregoing experiments is, that the action of chlorine upon arsenious acid at a moderate heat consists in the oxidation of one portion of arsenious acid at the expense of another, the arsenic of which is converted into terchloride, whilst the arsenic acid which has been formed combines with the remainder of the arsenious acid to form a transparent glass, having the composition $2\text{AsO}_3 \cdot \text{AsO}_5$, which may also be produced by heating arsenic acid with an excess of arsenious acid.