XVIII.—*Note on Persulphocyanic Acid.*

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THE constitution of this body still remains a matter of uncertainty; for of the several possible formulæ, experiments hitherto undertaken do not pronounce in favour of the one rather than of the other. Two different formulæ have been proposed, either of which would explain the reactions of the acid so far as they are at present known, but one of which would seem to be a closer expression of certain properties to be described.

The following decompositions must be indicated by any proposed formulæ:—

1st. Hydric iodide in the nascent state yields carbonic disulphide, and hydriodide of sulphurea.

2nd. Nascent hydrogen (tin and hydric chloride) forms hydrochloride of sulphurea.

3rd. Persulphocyanic acid combines with one molecule of aniline, with separation of one atom of sulphur:—

There is thus a very close connection between persulphocyanic acid and sulphurea, and this connection is best explained in the formula proposed by L. Glutz (*Deut. Chem. Ges Ber.*, iii, 343), in which we

see that by the addition of two atoms of hydrogen, sulphurea and carbonic disulphide would be formed. The formula proposed by A. Henninger (*Wurtz's Dictionnaire de Chimie*), also explains this reaction, though not quite so easily.

In order to throw some further light upon the properties of this body, the following experiments were carried out, and, though they

are not complete, it may be of some interest to publish them as they are.

The substance employed was prepared in the usual way by passing a current of hydric chloride through a saturated solution of potassic sulphocyanate. A thick magma of yellow crystals was formed, which was thoroughly washed with cold water, after which it was dissolved in boiling water and crystallised. This is a somewhat tedious operation when a considerable quantity is required, because the amount dissolved by boiling water is so small that a large number of boilings and filtrations has to be made. The nature of the decomposition by which the persulphocyanic acid is prepared has not hitherto been explained, but the author hopes at a future time to return to this question. It is, however, to be noticed that the composition of the precipitate which has merely been washed with cold water differs from that of the product obtained by crystallisation from hot water. It follows, therefore, that the process given in most books for preparing the acid by merely washing with cold water is not sufficient to yield a pure product.

The acid crystallises from hot water in long and often curved, woolly tufts, presenting a remarkable appearance. After drying in the air and pressing between blotting-paper, these crystals do not lose more than a trace of moisture when heated to 120° in an air bath. When they are placed in contact with cold water and a piece of blue litmus paper, no change of colour is produced at ordinary temperatures; but when the liquid is warmed, the paper becomes faintly reddened, the colour increasing in intensity as the boiling is prolonged. If this liquid be now tested by the addition of barium chloride solution, it is easy to prove the presence of sulphuric acid. This decomposition, although slight, is sufficient to prevent any deductions being drawn as to the effect of persulphocyanic acid upon litmus paper.

Persulphocyanic acid dissolves to a slight extent in cold alcohol, the solution assuming a distinct yellow colour, and it dissolves in boiling alcohol to a much greater extent. One litre of alcohol containing 89 per cent. dissolves at 12.5° 1.58 gram of acid, and at the boiling point dissolves 12.774 grams.

When silver nitrate is added to a warm aqueous solution of the acid, a light yellow precipitate is first produced, which almost immediately becomes orange-yellow, and afterwards passes through various shades of orange to black. If a cold alcoholic solution of the acid be employed, the precipitate remains undecomposed for a much longer time, especially if the temperature be kept low, but even at ordinary temperatures (from 15° to 20° during the time these experiments have been conducted) after two or three hours, the decomposition is very pronounced. The author, however, noticed that on one or two days

when the temperature was as low as 10° or 12° , the decomposition was not nearly so rapid as under ordinary circumstances. Ammonia added to the yellow silver precipitate dissolves it, producing a dark-brown solution, which is reprecipitated by the addition of hydric nitrate.

Mercurous nitrate produces a light-yellow precipitate, which is insoluble in cold nitric acid, but on heating dissolves with effervescence, leaving a white precipitate, soluble in aqua regia, and not blackened by ammonia.

Solution of iodine, when heated with the acid, becomes decolorised, producing at the same time an orange-red precipitate. This is soluble to some extent in water, and yellow crystals are deposited, which are alluded to by A. Fleischer (*Deut. Chem. Ges. Ber.*, iv, 190), but the author has been unable to prove the presence of iodine in these crystals. They possess, indeed, the appearance of ordinary persulphocyanic acid, and perhaps are produced by the decomposition of the iodine precipitate.

The production of compounds with silver and with mercurous mercury leads to the question of the composition of these bodies. There appear to be possible only two compounds in each case, there being but two atoms of hydrogen in the acid. The composition of the silver salt has only been approximately determined, as it undergoes decomposition so quickly; but if there can be produced two silver compounds only, it would appear that the yellow precipitate has the formula $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$.

The following experiments were made to ascertain the weight of the silver compound relatively to the acid employed:—

(1.) 0.2857 grm. acid was dissolved in alcohol (sp. gr. = 0.8254 at 12.5°) with the aid of heat; the solution then allowed to cool, and an excess of an alcoholic solution of silver nitrate added. The precipitate was quickly collected upon a weighed filter-paper, washed with cold alcohol, dried in the air at first, and afterwards at 100° , until the weight was constant. The precipitate thus obtained weighed 0.6705 grm. If the composition of the silver compound were $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$, the weight of the precipitate should be 0.6933 grm.

(2.) 0.0235 grm. acid was dissolved in alcohol as in (1), and precipitated by an alcoholic solution of silver nitrate, containing a weight of metallic silver corresponding to four atoms, thus $\text{H}_2\text{C}_2\text{N}_2\text{S}_3 : \text{Ag}_4$; the compound was collected as above. It weighed 0.0580, the hypothetical weight for $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$ being 0.05703.

(3.) 0.0573 grm. acid treated as in (2), with four atoms of silver in alcoholic solution, yielded a precipitate which weighed 0.140 gram. Theory = 0.139 gram.

(4.) 0.0345 grm. acid treated as above with two atoms (the

weight theoretically necessary), yielded a precipitate which weighed 0.0745 grm. Theory = 0.0837.

From the last experiment it seems that in order to precipitate the whole of the acid, it is necessary to add more than the theoretically exact amount of silver. The following experiments show the amount of silver which enters into the composition of the precipitate.

(5.) The precipitate obtained in (2) was ignited, and the resulting metallic silver dissolved in nitric acid and estimated as chloride. It contained 0.032 grm. silver. Theory for $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3 = 0.0338$.

(6.) The precipitate obtained in (3) contained 0.0839 grm. silver. Theory = 0.0825.

(7.) 0.0965 grm. acid was dissolved in alcohol; three atoms of silver in alcoholic solution added, the precipitate quickly collected, washed, dried, and ignited. The residue was dissolved in nitric acid, and the silver estimated as chloride. The silver amounted to 0.1549 gram. Theory = 0.139 gram Ag.

(8.) 0.093 grm. acid treated as in (7) with three atoms of silver yielded a precipitate which contained 0.1356 gram Ag. Theory = 0.1381 gram Ag.

(9.) 0.1695 grm. acid treated with a little more than the equivalent quantity of silver nitrate yielded a precipitate containing 0.2446 gram Ag. Theory = 0.2441 gram Ag.

(10.) The precipitate obtained in (4) by the use of an equivalent quantity of silver nitrate contained 0.0391 grm. Ag. Theory = 0.0501. The weight of silver entering into the composition of the precipitate is thus less than it should have been if the whole of the acid had been thrown down, a result confirming Exp. (No. 4).

These results therefore lead to the conclusion that a weight of silver approaching two atoms enters into the reaction between the two substances. They distinguish between the formulæ $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$ and $\text{AgHC}_2\text{N}_2\text{S}_3$. Whether such a compound as the latter exists remains to be proved. It would be of peculiar interest as an acid silver salt. On one occasion, after boiling the silver salt with nitric acid, a yellow or orange-yellow substance was left undissolved, and long boiling failed to decompose it. The precipitate was collected, washed with hot water, and a portion of it ignited in a porcelain crucible, a residue of silver and carbon being left and sulphurous acid being evolved. The silver was determined in the usual way and amounted to 43.18 per cent. The acid silver salt, $\text{AgHC}_2\text{N}_2\text{S}_3$, would contain 42.02 per cent. Ag. Other attempts to procure this substance in a similar manner have failed, but the author still hopes for success in another direction.

When the yellow silver persulphocyanate is boiled with water, it quickly decomposes with effervescence and with production of a heavy black precipitate, which rapidly sinks to the bottom of the

liquid. Attempts were made to ascertain the nature of the decomposition by collecting this black precipitate and determining its composition, but the results obtained vary so widely from one another in different experiments, apparently depending upon the proportion of silver nitrate present and upon the temperature, that no single equation will represent the decomposition under all circumstances.

(11.) 0.04 gram. acid was dissolved in hot water and boiled with a considerable excess of aqueous silver nitrate till no further action was observable. The black precipitate was collected, dried at 100 C., and weighed. The weight was 1.739 gram. It was then dissolved in fuming nitric acid and the silver estimated as chloride. The silver amounted to 1.463 gram. Taking the molecular weight of persulphocyanic acid as 150 ($\text{H}_2\text{C}_2\text{N}_2\text{S}_3 = 150$), the weight of the black precipitate would correspond to 652.1 per molecule of acid, and the silver to 548.6 per molecule.

(12.) A second experiment carried out in the same way with a similar excess of silver nitrate gave the numbers 658 per molecule of acid for the black precipitate and 560 for the silver contained in the precipitate.

(13.) 0.1456 gram of acid boiled with water and a moderate excess of silver nitrate yielded a black precipitate which contained 0.490 gram Ag. This corresponds to 505 per molecule of acid.

(14.) 0.0795 gram of acid treated as in (13) with a moderate excess of silver nitrate yielded 0.316 gram of black precipitate containing 0.2712 gram Ag. These numbers correspond to 607.5 of black precipitate and 512 of silver per molecule of acid.

(15.) 0.0277 gram of acid, treated as above with a slight excess of silver nitrate, gave 0.106 gram of black precipitate and 0.087 gram. Ag. These numbers correspond respectively to 574 and 471 per molecule of acid.

A consideration of these results will show that the weight of black precipitate and of silver is greater where the nitrate of silver solution is used in excess. It will also be noticed that the percentage of silver in the black precipitate is greater when a considerable excess of nitrate of silver was used than when only a slight excess was employed. Thus the percentages of silver in the previous experiments are—

Experiment	11.	12.	14.	15.
Percentage of silver	84.1	85.3	84.2	82.1

(16.) Some quantity of the black precipitate was prepared by boiling the acid with a small excess of silver nitrate. After washing

and drying at 100° C. a weighed portion was heated with fuming nitric acid, when it was attacked with strong effervescence commencing even in the cold, and becoming violent on gently heating. When the substance was completely dissolved, the silver was estimated as chloride and the sulphur determined in the filtrate as baric sulphate—

	(1.)	(2.)
Silver	81.12	81.10
Sulphur	17.45	16.85
Diff. from 100	1.43	2.05
	<hr/> 100.00	<hr/> 100.00

The ratio of the atoms of silver to the atoms of sulphur is 3 : 2.

(17.) In experiments (11) and (12) the silver and sulphur were determined—

	(1.)	(2.)
Silver	84.1	85.3
Sulphur	14.7	14.3
Diff. from 100	1.2	.4
	<hr/> 100.0	<hr/> 100.0

The ratio of silver atoms to sulphur atoms is in (1) 17 : 10, and in (2) 17.5 : 10.

The only known compound of silver and sulphur is the sulphide Ag_2S in which the ratio of the atoms is 2 : 1; it is probable therefore that the black precipitate is a mixture of sulphide of silver and some substance containing a larger proportion of sulphur, perhaps silver sulphocyanate, while the ratios in which the two products are formed changes with differences in the amount of silver nitrate employed. With an excess of silver nitrate the proportion of silver sulphide in the black precipitate will be greater, as is seen from experiments (16) and (17). In the former, where only a slight excess of nitrate of silver was used, the ratios are 15 : 10, while in the latter, where a considerable excess was used, the ratios are 17 : 10 and 17.5 : 10.

The following equation is given, not as being an exact representation of any particular experiment, but as probably indicating the general nature of the reaction—

The author hopes to be able to communicate further experiments upon this subject on a future occasion.

The yellow precipitate produced by mercurous nitrate in a solution of persulphocyanic acid does not appear to be decomposed by boiling like the silver salt. Only a single experiment was made upon this body.

(18.) 0.147 gram of the acid gave 0.553 grm. of the precipitate dried at 100° C. If it has the formula $\text{Hg}'_2\text{C}_2\text{N}_2\text{S}_3$ the weight of the precipitate would be 0.537. The precipitate was dissolved in aqua regia and the mercury determined as sulphide. The weight of mercury obtained was 0.3925. The formula $\text{Hg}'_2\text{C}_2\text{N}_2\text{S}_3$ would require 0.392 gram. It seems therefore that the yellow precipitate is represented truly by the formula given.

If we adopt the formula given by L. Glutz (*loc. cit.*) for this acid, the existence of the salts above described can be accounted for as easily as the silver salt of parabanic acid. There is, indeed, some resemblance between the two bodies which would justify somewhat similar formulæ. Thus parabanic acid forms a silver salt containing two atoms of silver, and it decomposes into urea and hydric oxalate by treating with acids. The resemblance will be better seen by a comparison of the explicit formulæ.

The silver salts of each acid are formed by replacement of hydrogen in the same way, the metal becoming united with nitrogen, while the greater stability of the parabanate is explained by the smaller attraction of silver for oxygen than for sulphur.