XVI.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF TÔKIÔ, JAPAN.

II. *On Perthiocyanate of Silver.*

By R. W. ATKINSON, B.Sc. (Lond.), Professor of Analytical and Applied Chemistry in the University.

IN a communication presented to the Chemical Society (this Journal, 1877, 2, 254) I showed that the silver salt of perthiocyanic acid has the formula $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$, although, on account of the readiness with which it decomposes, the numbers obtained by analysis varied a little from the theoretical numbers. I also showed that the black precipitate obtained by boiling the yellow silver perthiocyanate with water varied in composition according to the treatment to which it had been subjected, the percentage of silver being greater when an excess of silver nitrate solution was used. The ratio of the numbers of atoms of silver and sulphur was found to vary, being in one case as 3 : 2, and in another as 17 : 10. I then conjectured that the variation was due to admixture of the silver sulphide, which forms the main product of the decomposition, with some substance containing a larger proportion of sulphur, and I was of opinion that this substance might be silver thiocyanate. Other matters have prevented me continuing the investigation until recently, but now I think I have obtained evidence in favour of a much simpler explanation, viz., that the substance containing a greater proportion of sulphur is undecomposed perthiocyanate, and that the extent of the decomposition is dependent upon the proportion of silver nitrate present, upon the temperature at which the decomposition is effected, and upon the time during which it is allowed to go on.

When the silver perthiocyanate was precipitated from an alcoholic solution of the acid and filtered off without boiling, the weight of the precipitate corresponded very nearly with that required by the formula $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$. The experimental numbers gave per molecule of acid ($\text{H}_2\text{C}_2\text{N}_2\text{S}_3 = 150$) 352, 370, 366·5, instead of 364 ($\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3 = 364$), and an amount of silver represented by the numbers 205, 220, 240, 219, 218, instead of 216 ($\text{Ag}_2 = 216$). When, however, the alcoholic solution was boiled, the weight of the precipitate formed when an excess of silver was used amounted in one case to 471, and in another to 521 per molecule of acid. The silver contained in the two precipitates weighed 434 and 432, almost exactly 4 mols. per molecule of acid.

When the silver perthiocyanate thrown down from an alcoholic solution of the acid was quickly filtered and washed, to remove the excess of silver nitrate, first with alcohol, then with water, and the precipitate afterwards boiled with water until no further change was apparent, the weight of the black precipitate was in three experiments 339, 342, and 300 per molecule of acid, and the weight of silver 261, 259, 232.

The supernatant liquid was coloured yellow, and the composition of the precipitate was probably that of a mixture of silver sulphide and perthiocyanate in nearly equal proportions, $\text{Ag}_2\text{S} + \text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$, which would require 306 of black precipitate, 216 of silver, and 62 of sulphur. The black precipitate contained in the three experiments above given 77.0, 75.8, and 77.7 per cent. of silver, the above formula requiring 70.6 per cent.

Having ascertained that in the decomposition of silver perthiocyanate 4 atoms of silver are necessary, and that, in order to gain the requisite amount, the silver salt itself splits up, a series of experiments under varying conditions was next instituted, first, to determine the weight and percentage of silver in the black precipitate when the proportion of silver nitrate added varied from 1 to 10 mols. per molecule of acid; secondly, to determine the influence which the duration of heating had upon the result, and, thirdly, to observe the effect of different temperatures upon the decomposition, it having been noticed on a previous occasion that the decomposition was much retarded at a temperature of 10–12°.

TABLE I.—*Experiments with varying proportions of Silver.*

	Number of atoms of silver added.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Percentage of silver in the black pre- cipitate.
<i>a</i>	1	127.5	108	84.7
<i>b</i>	2	261.2	216	82.7
<i>c</i>	3	386.0	324	83.9
<i>d</i>	4	513.9	432	84.1
<i>e</i>	5	622.2	540	86.8
<i>f</i>	6	659.0	574	87.1
<i>g</i>	10 ($\frac{3}{4}$ hour)	650.0	538	82.8
<i>h</i>	10 (1 hour)	644.0	526	81.6
<i>k</i>	10 ($1\frac{1}{2}$ hour)	612.0	490	80.2

The liquids of the first six experiments were boiled for about 20 minutes, and are quite comparable amongst themselves; but the solutions to which 10 atoms of silver had been added were boiled for the length of time mentioned in each case, and it will be noticed that

the weight of the black precipitate, the weight and the percentage of silver, all show a tendency to decrease on long boiling.

Considering the first six experiments, however, it will be observed that, up to the addition of 5 atoms of silver, the weight of silver contained in the precipitate increases proportionately, none whatever going into solution. With 6 atoms of silver added the whole of the silver was not thrown down, but sufficient to give a precipitate containing 87.1 per cent., and thus pure silver sulphide. With the exception of the first experiment the percentage of silver increases with the increased proportion of silver added, and this shows that the black precipitate contains more and more silver sulphide in proportion as the amount of silver added is greater. Assuming that the precipitate consists of a mixture of silver sulphide and perthiocyanate, we may calculate the proportion of each substance present in the above experiments:—

TABLE II.

	Percentage of Ag_2S .	Percentage of $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$.
<i>b</i>	84.9	15.1
<i>c</i>	88.5	11.5
<i>d</i>	89.2	10.8
<i>e</i>	98.9	1.1
<i>f</i>	100.0	0.0

This table shows very clearly the progress of the decomposition of the silver perthiocyanate under the influence of increasing quantities of silver nitrate. To test the action of nitric acid, two experiments were made—1st, one in which an amount of the acid equivalent to 2 mols. of HNO_3 was added, so that, on boiling, the liquid would contain 6 mols. of HNO_3 per molecule of perthiocyanic acid, and, 2nd, an experiment in which an amount of pure precipitated calcium carbonate was added in quantity just sufficient to neutralise the nitric acid that would be liberated in the course of the reaction. The liquids were then boiled for one hour, 4 atoms of silver being added.

TABLE III.

No.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Per- centage of silver.	Remarks.
1.....	457	365	80.0	Excess of nitric acid.
2.....	540	401	74.3	Calcium carbonate added.
3.....	518	428	82.6	No addition.

The effect of the increased quantity of nitric acid is thus to reduce the weight of the black precipitate, the weight of silver, and the percentage below those obtained without the addition of nitric acid. The addition of calcium carbonate, by neutralising the acid liberated, permits the formation of the two silver compounds in nearly equal proportions, the percentage 74·3 corresponding to 54 per cent. of silver sulphide, the weight of the black precipitate also being greater than when no calcium carbonate was present. It appears that the nitric acid acts first upon the silver perthiocyanate, and only when this is completely decomposed does it begin to touch the silver sulphide.

At temperatures below 100° C. the change on protracted boiling is not very marked, as will be seen from the following numbers. The temperature in each experiment was 50°, and the times one, two, and four hours respectively, the number of atoms of silver added being four.

TABLE IV.—*Four Atoms of Silver. Temperature 50°.*

No. of hours.	Weight of the black precipitate per molecule of acid.	Weight of silver in the precipitate per molecule of acid.	Percentage of silver.	Percentage of Ag_2S in the black precipitate (calculated).
1	498·0	392	78·8	70·0
2	541·5	408	75·3	57·5
4	542·5	411	75·8	59·3

It will be observed that the results are practically the same whether the precipitate be heated to 50° for two hours or for four hours. The effect of temperature upon the reaction is shown in the following table, which gives the results of experiments at the temperatures mentioned, the amount of silver added being 4 atoms per molecule of perthiocyanic acid, and the time of heating one hour. The numbers at 50° are the same as those for one hour given in the preceding table:—

TABLE V.—*Four Atoms of Silver. Time, one Hour.*

Temperature.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Percentage of silver.	Weight of free acid liberated per molecule of $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$.
20° C. ..	361	222	61·5	140
50 " ..	498	392	78·8	253
100 " ..	518	428	82·6	230

From these experiments it is evident that at 20° the silver perthiocyanate was very slightly decomposed, the amount of silver sulphide, however, being sufficient to blacken it completely. This is confirmed by the amount of nitric acid contained in the filtrate, that corresponding to a decomposition—

being 126 per molecule of $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$ against 140 found.

A little more than 2 mols. of silver nitrate was decomposed, resulting in the formation of some silver sulphide. At 50° in the same time the decomposition was much greater, the amount of nitric acid liberated corresponding almost exactly with 4 mols. At 100° the decomposition is still more pronounced, although boiling for one hour was not enough to make it complete. The percentage of silver sulphide at the three temperatures is given below.

TABLE VI.

Temperature.	Percentage of Ag_2S .	Percentage of $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$.
20° C.	7·9	92·1
50 „	70·0	30·0
100 „	83·8	16·2

The changes at the three temperatures can be shown by a comparison of the amounts of silver and sulphur contained in the precipitate. The ratio of the number of atoms is as follows:—

TABLE VII.

Temperature.	Ratio of the atoms of	
	Silver.	Sulphur.
20° C.	0·815	1·000
50 „	1·180	1·000
100 „	2·150	1·000

Thus at 20° the ratio approaches that in the silver perthiocyanate, *i.e.*, as 67 : 1, whilst the ratio increases at higher temperatures, until at 100° it is approximately 2 : 1, the ratio in which they exist in silver sulphide.

As further confirmation a specimen of the black precipitate which

had accumulated during these experiments was analysed, and found to contain—

Ag.....	82.15 per cent.
S	14.71 „
C	1.31 „
H	0.13 „
N (diff.)	1.70 „
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	100.00

The percentage of silver, assuming the precipitate to contain only silver sulphide and perthiocyanate would be—

Ag ₂ S	82.2 per cent.
Ag ₂ C ₂ N ₂ S ₃	17.8 „
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	100.0

a mixture which would require the following percentages:—

Ag	82.16 per cent.
S	15.30 „
C	1.17 „
N	1.37 „
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	100.00

The agreement of the calculated percentage with that actually found is sufficiently close to prove that the precipitate does consist of the two substances mentioned above. As a final test of this being the true explanation of the reaction, 0.1304 gram of silver nitrate in alcoholic solution was added to an excess of perthiocyanic acid, also dissolved in alcohol, and kept during the experiment at as low a temperature as possible. The bright yellow silver perthiocyanate, under these circumstances, preserves its colour and appears to undergo no decomposition. The precipitate was then thrown on a filter, well washed with alcohol, and, when no more was dissolved, the alcohol was replaced by water, and the silver precipitate afterwards washed into a beaker, and boiled with water for about half an hour. The whole was then filtered, and the precipitate, after drying, weighed 0.0974 gram, and, as it contained the whole of the silver added, there was thus 85.04 per cent. of silver. This corresponds with 92.6 per cent. of silver sulphide and 7.4 per cent. of silver perthiocyanate. If the silver sulphide, amounting to $\frac{92.6}{100} \times 0.0974 = 0.0902$ gram, had been formed according to the equation—

the corresponding amount of silver perthiocyanate decomposed would

be $\frac{364}{248} \times 0.0902 = 0.1324$ gram, and this, added to the amount of the undecomposed silver persulphocyanate, $= \frac{7.4}{100} \times 0.0974 = 0.0072$ would be $0.1324 + 0.0072 = 0.1396$, a sufficiently near approximation to the number 0.140, the amount of silver perthiocyanate actually used calculated from the weight of silver nitrate.

The nature of the decomposition of the silver perthiocyanate is, therefore, sufficiently clear, and may be formulated thus:—

and the actual proportions of the two insoluble silver salts will depend upon the conditions of the experiment as to time, temperature, and proportion of free acid present. The only point not yet cleared up is the existence of the compound $\text{C}_2\text{N}_2\text{S}_2$, cyanogen disulphide:—

The corresponding cyanogen monosulphide, $(\text{CN})_2\text{S}$, formed from thiocyanic acid, is known, but I have hitherto been unable to isolate the higher sulpho-compound. It is possible that during the heating with nitric acid, it may be decomposed thus:—

which is rendered probable by the fact that during the experiment some gas is evolved. I am at present examining the orange-red sublimate which forms when the dry silver perthiocyanate is heated, in the hope that it may contain the missing body.

In conclusion, I wish to thank my assistant, Mr. Nakazawa, for his assistance in carrying out some of these experiments.