XIV.—*Action of Sulphurous Acid on Flowers of Sulphur.*

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FLÜCKIGER found that by the action of sulphurous acid on flowers of sulphur, traces of thiosulphuric acid were formed. The reaction proceeded more easily if the temperature was maintained between 80° and 90° (*Jahresbericht*, 1863, 149).

Debus (Trans., 1888, **53**, 347) says: "The two tubes" (one containing 36 c.c. of a concentrated solution of sulphurous acid and 10 grams of sulphur, and the second the same volume of sulphurous acid without any sulphur) "remained for five days at common temperatures, and were then heated for several hours on a water-bath to 60—80°. This treatment did not appear to have effected any change in either of the tubes. Both were now opened, their contents transferred to evaporating dishes, and warmed on water-baths until all the sulphurous acid had volatilised. Both liquids were finally concentrated to one-fifth of their original volume."

Proceeding in this way, Debus found that the only product of the action of sulphur and sulphurous acid was an infinitesimal quantity of pentathionic acid, and that its presence was revealed only by one test, and this he regarded as insufficient to allow of the conclusion that pentathionic acid had been formed by the interaction of sulphurous acid and flowers of sulphur.

Quantities of from 3 to 5 grams of flowers of sulphur, which had been washed first with warm, then with cold water, until the washings were no longer acid and possessed no iodine titration, were introduced into glass tubes, sealed at one end. After partly drawing out the other ends of the tubes, and displacing the air by carbon dioxide, 30 c.c. of a solution of sulphur dioxide in boiled water were added to each tube. Equal volumes of the same solution of sulphurous acid were introduced into other tubes containing no sulphur, and served as standards of the strength of the sulphurous acid solution.

First Series of Experiments.—Four tubes were so charged with sulphurous acid and flowers of sulphur; two with sulphurous acid alone. The six tubes, sealed before the blowpipe, were placed in an air-bath and heated at 85° for six days. Their contents were then rinsed into flasks, and their iodine titrations determined.

The tubes containing sulphurous acid alone required—

I. 61·70 c.c. of the iodine solution.
II. 62·50 ,, ,, ,,

The tubes containing sulphur and sulphurous acid required—

I. 32·25 c.c. of the iodine solution.
II. 32·85 ,, ,, ,,
III. 35·40 ,, ,, ,,
IV. 31·70 ,, ,, ,,

No. III contained only a very small quantity of sulphur, about 0·5 gram.

Hence the sulphurous acid has acted upon the sulphur, and has undergone a corresponding diminution in its iodine titration.

Second Series of Experiments.—In this second series of experiments, the attempt was made to ascertain the nature of the product or products of the action of sulphurous acid on sulphur. The development of acidity after titration with iodine was used to determine what part of the titration value in terms of iodine was due to sulphurous acid still present.

10 c.c. of a solution of sulphurous acid, carefully prepared so as to be free from sulphuric acid, by dissolving in boiled water, sulphur dioxide displaced from its aqueous solution by a stream of hydrogen gas, required—

5·5 c.c. of an ammonia solution to neutralise it.

The neutralised solution required—

20·95 c.c. of an iodine solution.

The developed acidity required—

15·60 c.c. of an ammonia solution to neutralise it.

Hence, (1) The developed acidity titration $\times \frac{20·95}{15·60} = 1·34$

gives the iodine titration of the sulphurous acid.

(2) The developed acidity titration $\times \frac{5·50}{15·60} = 0·35$

gives the acidity titration of the sulphurous acid in terms of the iodine and ammonia solutions used.

Methyl-orange was used as an acidity indicator, and starch with the iodine titrations. The blue colour of the starch iodide was discharged by a drop of sodium thiosulphate before the determination of the developed acidity.

A number of tubes, prepared exactly as in the first series of experiments, were treated in different ways, and their contents titrated with the ammonia and iodine solutions. In ascertaining the end of the acidity titrations, it was found advisable to withdraw portions of the almost neutralised liquid into a clean flask. In the absence of sulphur, the end of these acidity reactions was so much more easily recognisable.

No. I contained 2 grams of sulphur, and, after standing at the ordinary temperature of the air for two months, was heated for a week to a temperature of from 80—90°.

Initial acidity titration ... = 15·8
Iodine titration.......... = 21·55
Developed acidity titration = 14·80.

14·80 × 0·35 = 5·2.
14·80 × 1·34 = 21·85.

1·75 c.c. iodine due to thiosulphuric acid.

No. II contained 3 grams of sulphur, and was treated exactly as No. I.

Initial acidity titration ... = 15·70
Iodine titration.......... = 24·85
Developed acidity titration = 16·30.

16·30 × 0·35 = 5·70.
16·30 × 1·34 = 21·85.

3·00 c.c. iodine due to thiosulphuric acid.

No. III contained 5 grams of sulphur, and, after standing at the temperature of the air for two months, was heated for a week at 80—90°, and then allowed to stand another month at the air temperature.

Initial acidity titration ... = 15·5
Iodine titration.......... = 23·1
Developed acidity titration = 14·7.

14·7 × 0·35 = 5·15.
14·7 × 1·34 = 19·7.

3·4 c.c. iodine due to thiosulphuric acid.

No. IV contained 3 grams of sulphur, and, after standing for two months at the temperature of the air, was titrated. It was not heated.

Initial acidity titration ... = 14·5
Iodine titration.......... = 38·2
Developed acidity titration = 27·7.

27·7 × 0·35 = 9·7.
27·7 × 1·34 = 37·1.

1·1 c.c. iodine due to thiosulphuric acid.

Two tubes containing sulphur and distilled water, one of which, after standing for the two months at the air temperature, was heated to 80—90°, and the other merely kept at the temperature of the air for the two months, were examined. In neither case was there anything acidic or possessing an iodine titration formed.

The mean of three titrations of the sulphurous acid solution, made at the time of sealing the tubes, gave:—

30 c.c. (the volume introduced into each of the tubes) required 48·3 c.c. of the iodine solution.

This gives for the initial acidity titration a value 12·6 c.c. of the ammonia solution.

This gives for the developed acidity titration a value 36·05 of the ammonia solution.

In considering the interpretations which the above results bear, it must be noticed—

I. That sulphurous acid titrated with ammonia, using methyl-orange as an indicator, shows neutrality when the point corresponding to the formation of $NH_4 \cdot HSO_3$ has been but slightly overstepped.

II. That where sulphurous acid oxidises to sulphuric acid, there is almost a doubling in the initial acidity value, and a complete loss of iodine titration, and of developed acidity.

III. That where sulphurous acid unites with sulphur there will be, if thiosulphuric acid is formed, almost a doubling of the initial acidity value, a halving of the iodine titration value, for

$$H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4,$$

but

$$2H_2S_2O_3 + I_2 = 2HI + H_2S_4O_6.$$

IV. That supposing the two equations

$$H_2SO_3 + S = H_2S_2O_3,$$
$$2H_2S_2O_3 + 3H_2SO_3 = 2H_2S_3O_6 + 3H_2O + S$$

to represent the change taking place when sulphur and sulphurous acid interact, the initial acidity will be approximately $\frac{4}{5}$ of its original value, if all the sulphurous acid becomes converted into trithionic acid. Further, as sulphurous acid becomes converted into trithionic acid, its iodine titration and developed acidity titration are completely lost.

V. That anything possessing an iodine titration, which is not sulphurous acid, may be thiosulphuric acid.

VI. That the initial acidity titration of sulphurous acid is about $\frac{1}{4}$ of its iodine titration in terms of the ammonia and iodine solutions used.

From the results of the titrations given above, the following conclusions may be drawn :—

1. That sulphur and sulphurous acid do react even at the ordinary temperature of the air. The action in this case is slow, but a temperature of from 80—90° greatly accelerates it.

2. There is in the solution a small quantity of something possessing an iodine titration, which is over and above the iodine titration of the still unaltered sulphurous acid. This may be thiosulphuric acid.

3. The initial acidity titration shows that there is present a quantity of something possessing an acidity, but no iodine titration. Some small part of this is, undoubtedly, oxidised sulphurous acid; but the greater part cannot be sulphuric acid, because, in that case, the initial acidity titration would be greater than 12·6 (the initial acidity value of the standard) by one-fourth of the diminution in the iodine titration. The increase in initial acidity titration due to thiosulphuric acid is approximately half the diminution in iodine titration consequent on its formation. There is present in the system something acidic, and without iodine titration. This may be a polythionic acid, trithionic, tetrathionic, or pentathionic acid.

The following qualitative tests were made with the contents of the tubes which had been, in the case of the first, allowed to stand the two months, then heated at 80—90°; in the case of the second, allowed to stand at the temperature of the air for two months; in the case of the third, kept in the dark at the temperature of the air for three months.

First Case. The tube had been heated at 80—90°.—Mercurous nitrate gave an instantaneous black precipitate (sulphurous acid will also give this). Silver nitrate produced a yellow precipitate, which very rapidly blackened on gently warming. Ammoniacal silver nitrate, in presence of excess of ammonia, did not give a precipitate. Cupric sulphate gave, on boiling, black copper sulphide.

Second Case. The tube had not been heated.—Silver nitrate gave a yellow precipitate, changing to black, even with a portion of the liquid from which sulphurous acid had been boiled off. Copper sulphate gave, on boiling, black copper sulphide. Ammoniacal silver nitrate produced no precipitate.

Third Case. The tube had been kept in the dark, wrapped in black paper, for three months.—Silver nitrate gave a white, changing to yellow and red, precipitate, which, on gently warming, became black. Ammoniacal silver nitrate produced no precipitate. Copper sulphate, on boiling, gave copper sulphide.

These qualitative tests point to the presence of thiosulphuric acid, trithionic acid, tetrathionic acid, or a mixture of any two or all three of these acids. Pentathionic is not present because of the absence of a precipitate with ammoniacal silver nitrate. Further, the precipitates were less bulky in the last two cases than in the first case.

Conclusions.

1. Sulphurous acid does react with flowers of sulphur, even in the dark, at the ordinary temperature of the air. With a higher temperature, the reaction proceeds still further, and there is formed, in addition to thiosulphuric acid, trithionic or tetrathionic acid, or both.

2. Pentathionic acid could not be detected by the ammoniacal silver nitrate test.

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