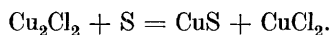


CLIV.—*The Action of Sulphur on Cuprous Chloride.*

By FREDERIC WILLIAM PINKARD and WILLIAM WARDLAW.

IN experiments on the oxidation of cuprous chloride by sulphur dioxide in the presence of dilute hydrochloric acid (this vol., p. 210) the present authors obtained a precipitate of cuprous sulphide, which they considered was formed by the interaction of cuprous chloride and the sulphur initially produced.

Vortman and Padberg (*Ber.*, 1899, **22**, 2642) state that when cuprous chloride is boiled with sulphur, cupric chloride is formed and cupric sulphide precipitated, the reaction being represented by the equation :



In our previous experiments the amount of sulphide produced in this way was so small that it was not possible to analyse it. Vortman and Padberg (*loc. cit.*) met with the same difficulty, and the present experiments were made with a view to determine the composition of the sulphide obtained and thereby test our hypothesis as to the mode of formation of the cuprous sulphide obtained in our oxidation experiments with cuprous chloride and sulphur dioxide (*loc. cit.*).

EXPERIMENTAL.

Cuprous chloride and finely powdered sulphur in the presence of dilute hydrochloric acid (180 c.c. of 33 per cent. acid and 320 c.c. of water) were heated under reflux for several days while carbon dioxide was continuously bubbled through the liquid, the temperature being kept constant by means of an oil-bath maintained at 120°. The cuprous chloride was prepared by the method described (*loc. cit.*), and the sulphur was purified by recrystallisation from chloroform. The black precipitate obtained was filtered by the aid of the pump in a current of carbon dioxide, the funnel being jacketed with water at 90—95°. It was washed thoroughly with a hot concentrated solution of sodium chloride to remove all traces of cuprous chloride, and then with hot water to remove sodium chloride. The funnel-jacket was cooled and the precipitate washed with ether three times, the temperature of the jacket being then raised to 90—95° in order to dry the precipitate. The filtrate contained cupric chloride.

In the earlier experiments, attempts to remove the free sulphur from the precipitate by extraction with chloroform or carbon disulphide in a Soxhlet apparatus were unsuccessful. After fourteen days' continuous extraction an examination of the precipitate

showed that free sulphur was still present. This appears to be due to the fact that the sulphide forms a coating on the sulphur and protects it from the action of the solvent used. This supposition, which also accounts for the small yield of sulphide obtained, seems to be verified by the following simple experiment.

Sulphur was moistened and rolled into balls and allowed to react with cuprous chloride in the usual way. After filtration and drying, several of the balls remained unbroken. The precipitate was placed in a small flask and gently warmed with concentrated hydrochloric acid in a current of carbon dioxide. The black precipitate slowly dissolved and the unbroken balls remained as balls of sulphur of approximately the original size and shape.

The inability to obtain the sulphide uncontaminated with sulphur led to efforts to obtain qualitative evidence of its nature. The dried precipitate was warmed with concentrated hydrochloric acid in a flask through which carbon dioxide was passing. The flask was fitted, in addition to the carbon dioxide entrance and exit tubes, with a short entrance tube terminating above, and an exit tube dipping below, the surface of the liquid. This entrance tube was connected, through a tap, with the carbon dioxide supply. By diverting the carbon dioxide through this branch and closing the usual exit passage, the liquid in the flask could be expelled through the special exit tube and collected in any desired vessel without coming into contact with air. It was found in this way that when a small amount of the solution was passed into water, a white precipitate, which had the reactions of cuprous chloride, was obtained. Moreover, when about 20 c.c. of the solution were thus transferred to a flask containing 10 c.c. of standard ferric alum solution, 10 c.c. of concentrated hydrochloric acid, and excess of potassium thiocyanate solution, and the whole was titrated with titanous chloride solution, the titration showed that no cupric salt was present.

The presence of sulphide in the precipitate was shown by the evolution of hydrogen sulphide on treatment with concentrated hydrochloric acid.

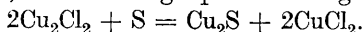
Finally, an indirect analysis of the black precipitate was made in the following way. The dried precipitate was dissolved in concentrated hydrochloric acid contained in a flask through which a slow current of carbon dioxide was passing. The evolved gases were passed through three flasks containing concentrated hydrochloric acid saturated with sulphur dioxide. Sulphur was deposited by the interaction of the sulphur dioxide and hydrogen sulphide in accordance with the equation $\text{SO}_2 + 2\text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}$ (Debus, T., 1888, 53, 278).

When all the black precipitate had dissolved, the absorption flasks were warmed to coagulate the sulphur, which was filtered off and weighed in a Gooch crucible. Two-thirds of this sulphur came from the original sulphide as hydrogen sulphide.

The solution obtained by the action of the hydrochloric acid on the black precipitate was diluted and filtered to remove the free sulphur, the latter being washed free from copper by hydrochloric acid. The filtrate was oxidised with sodium peroxide to convert any cuprous to cupric salt, and the copper present was estimated gravimetrically as cupric oxide. The weight of copper thus found must have been combined with the sulphur evolved as hydrogen sulphide. From this the ratio of the number of atoms of copper to the number of atoms of sulphur present in the original compound was calculated and found to be 2.1 : 1. This shows the sulphide in question to be cuprous sulphide.

Summary.

1. The indirect analysis made, in conjunction with the qualitative evidence obtained, justifies the conclusion that when sulphur acts on cuprous chloride in the presence of dilute hydrochloric acid (180 c.c. of 33 per cent. acid and 320 c.c. of water) cuprous sulphide is formed, the following equation being suggested :



2. The cuprous sulphide thus produced forms a coating on the unchanged sulphur, preventing further action. The yields are consequently very small and the unchanged sulphur very difficult to remove.

3. The view put forward by the authors as to the mode of formation of the cuprous sulphide obtained in their experiments on the oxidation of cuprous chloride with sulphur dioxide (*loc. cit.*) is supported by the results now obtained. It may be noted that in the experiments referred to, the conversion of the sulphur to sulphide was in some cases complete. The increased yield of sulphide can be easily understood when it is recalled that the sulphur in those experiments was originally produced in a very finely divided form and consequently the possibility of any considerable amount of the sulphur being protected by a coating of the sulphide was extremely small.

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