XXVI.—*The Oxidising Properties of Sulphur Dioxide.* *Part III. Copper Chlorides.*

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THE present communication is an account of experiments made with the object of extending our knowledge of the oxidising properties of sulphur dioxide. The earlier work on the subject is detailed in *Proc. Durham Phil. Soc.*, 1914, **5**, 187; T., 1920, **117**, 1093, 1241. By analogy with the reactions of ferrous chloride (T., 1920, **117**, 1093), it was thought that under appropriate conditions cuprous chloride could be oxidised by sulphur dioxide in the presence of hydrochloric acid.

EXPERIMENTAL.

The known instability of cuprous chloride in the presence of air made it essential that special precautions should be taken to ensure that the initial solution of cuprous chloride in the hydrochloric acid should be free from any cupric salt. The following method gave excellent cuprous chloride.

Preparation of Cuprous Chloride.

Into a strong aqueous solution of cupric chloride maintained at about 90° in a water-bath a continuous stream of sulphur dioxide was passed. Cuprous chloride separated in small crystals and after several hours a good yield of the salt was obtained. The flask was then sealed and kept over-night. It was found that, unless this was done, the fine condition of the salt first produced led, on filtration, to the formation of a pasty mass difficult to free from cupric chloride. On keeping, however, it became much more granular, and was easily filtered and washed. The filtration was carried out with a large Gooch funnel as the containing vessel. Cuprous chloride, especially in the moist condition, is very susceptible to the action of light (Vogel). The funnel therefore was enveloped in black paper to prevent this decomposition. After a thorough washing with sulphurous acid, the white product was finally washed in a current of carbon dioxide with glacial acetic acid, alcohol, and ether respectively. It was dried as completely as possible in the current of carbon dioxide and finally in a hot air-oven, the mass being turned over at intervals. Lastly, the salt was

placed in a dry bottle covered with black paper, sealed, and kept in a dark place.

Apparatus.

Fig. 1 represents the apparatus used in the first experiments.

In carrying out an experiment, the whole apparatus was first filled with carbon dioxide.* To ensure the burette being properly filled with the gas, G_2 was closed with G_1 open. When this was accomplished, G_2 was opened and G_1 closed. The apparatus

FIG. 1.

having been freed from air, the current of carbon dioxide was continued and a certain quantity of the prepared cuprous chloride was introduced from a weighing bottle into the flask *A*. A certain volume of acid was then poured into the thistle-funnel of the flask *A* and the current of carbon dioxide diverted by means of the T-piece *J* while the acid was running on to the cuprous chloride. On gently shaking, the bulk of the cuprous chloride dissolved. The carbon

* The carbon dioxide was drawn from a cylinder. The dissolved air escapes with the first portions of the liquid volatilising; the gas subsequently emitted contains only a minimal quantity of oxygen (compare Farmer, T., 1920, 117, 1446).

dioxide was then allowed to pass into the flask *A*, where it exerted a pressure and forced the solution direct into the reaction flask *B*. The same procedure was adopted until the whole of the cuprous chloride was dissolved in a definite volume of acid. Experiments showed that the oxidation of the cuprous salt was not measurable.

With the carbon dioxide now running through the solution, sulphur dioxide was admitted. The current of carbon dioxide was now discontinued, and the sulphur dioxide and cuprous salt were allowed to react for a definite period. In all experiments the temperature was kept constant by immersing the reaction flask in an oil-bath at 95°. At the end of the reaction the sulphur dioxide was driven out by the passage of carbon dioxide through the warm solution, and the solution cooled in a current of the gas.

Method of Analysis.

By closing clip G_3 and opening clip G_4 , the carbon dioxide was diverted from the solution. On closing clip G_2 and opening G_1 , the solution was driven from the reaction flask into the burette *H*. By closing G_1 and reopening G_2 , the solution was protected from atmospheric oxidation.

To determine the degree of oxidation of the mixture, use was made of the method detailed by Rhead (T., 1906, 89, 1491) and explained by Knecht and Hibbert ("New Reduction Methods in Volumetric Analysis," p. 55).

Ten c.c. of the cooled solution were run out of the burette *H* into a flask containing 10 c.c. of standard ferric alum solution, which had been acidified with concentrated hydrochloric acid and contained excess of potassium thiocyanate, and through which a current of carbon dioxide was passing. After the addition of the copper solution the contents of the flask were titrated with titanous chloride solution until the red colour of the ferric thiocyanate was just discharged. Knowing the titre of the 10 c.c. of ferric alum solution used, one could readily calculate the amount of cupric copper present in the mixture.

To determine the total copper in the solution, 5 c.c. were run directly from the burette *H* into a flask, water and sodium peroxide were added, and the solution was heated to boiling until chlorine was no longer evolved. The volume was then made up to 500 c.c., and 25 c.c. were used for the titration, as previously explained.

In connexion with the reaction between titanous chloride and ferric salts, Thornton and Chapman (*J. Amer. Chem. Soc.*, 1921, 43, 91) have specified definite conditions. The present authors'

experience substantially confirmed the main conclusions drawn by these investigators.

Description of the Phenomenon.

The solution obtained by dissolving the cuprous chloride in pure concentrated hydrochloric acid was colourless. On passing sulphur dioxide into this solution, the colour darkened immediately and became reddish-brown. On further passage of the gas, the colour continued to darken and a distinct opalescence was visible in the flask after about ten minutes. The opalescence became more pronounced as the reaction proceeded.

Quantitative Aspect of the Reaction.

When sulphur dioxide oxidises cuprous chloride in the presence of concentrated hydrochloric acid, two possible reactions may be involved. They correspond (*a*) with direct reduction of the sulphur dioxide to sulphur, (*b*) with initial reduction of the sulphur dioxide to hydrogen sulphide, which, with excess of sulphur dioxide, reacts to form sulphur. Both reactions are represented finally by the equation :

so that it is impossible to differentiate quantitatively between them.

To determine whether the reaction proceeded in accord with the above equation, known weights of cuprous chloride were dissolved in 250 c.c. of concentrated (33 per cent.) hydrochloric acid, and sulphur dioxide was passed into the solution for about four hours, whereby sulphur was liberated. The percentage of cupric salt was determined as described, and the sulphur estimated after the solution had been filtered through a Gooch crucible.

TABLE I.

Experi- ment.	Grams of copper in 250 c.c. of the cuprous chloride solution.	Cupric copper Total copper $\times 100$.	Sulphur.	
			Found. Gram.	Calc. Gram.
1	5.02	3.6	0.0248	0.0252
2	7.92	5.0	0.0508	0.0498
3	8.00	5.6	0.0532	0.0563

From these results it can be concluded that the equation formulated above represents the reaction.

Influence of Concentration of Cuprous Chloride.

Varying quantities of cuprous chloride were dissolved in 250 c.c. of concentrated hydrochloric acid. Sulphur dioxide was passed through the solution for four hours, and the amount of cupric chloride subsequently estimated.

TABLE II.

Experiment.....	4	5	6	7	8	9
Grams of cuprous copper in 250 c.c. of acid	3.44	5.02	6.94	8.00	8.25	13.35
$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100$	2.7	3.6	4.08	5.6	6.1	7.5

These results clearly indicate that the degree of oxidation is dependent on the initial concentration of cuprous salt.

Influence of Concentration of Acid.

Cuprous chloride (11 grams), dissolved in 250 c.c. of acid (1 part of 33 per cent. hydrochloric acid : 1 part of water) and treated with sulphur dioxide for four hours, was oxidised to the extent of 1.8 per cent. It was noticed that in addition to sulphur, a certain amount of a black precipitate was also produced. At a lower concentration of acid (1 part of acid : 2 parts of water) the cuprous chloride no longer reacted with the sulphur dioxide so as to give a deposition of sulphur, but instead, at the end of four hours, a heavy black precipitate was formed. A qualitative examination of the precipitate indicated cuprous sulphide.

The formation of this precipitate made it a matter of great difficulty to withdraw the solution directly from the burette for analysis, and the following filtration device was therefore added (Fig. 2).

The flask, *T*, containing 10 c.c. of ferric alum, an excess of concentrated hydrochloric acid, and potassium thiocyanate, having been filled with carbon dioxide, the current of gas was discontinued and the pump slowly started. Five or ten c.c. of the solution were allowed to flow from the burette, *H*, and filtered by means of the Gooch crucible, *R*. When all the solution had filtered through, the suction drew from the tube, *V*, dilute hydrochloric acid, which thoroughly washed the precipitate free from adhering copper salt. A rapid current of carbon dioxide was now passed and simultaneously the funnel in the bottle, *U*, cautiously opened. In this way

the cuprous salt was guarded from oxidation while the pressure was being readjusted. The solution in the flask, *T*, was then titrated with the standard titanous chloride.

FIG. 2.

The results obtained are given in the following table.

TABLE III.

Duration of experiment Four hours.
Solution Eleven grams of cuprous chloride in the acid specified in columns 2 and 3.

Experi- ment.	Concentrated acid. C.c.	Water. C.c.	Remarks.
10	250	0	Sulphur only.
11	175	75	" "
12	150	100	Much sulphur + small black precipitate.
13	125	125	Sulphur + black precipitate.
14	82	168	Black precipitate only.
15	62	188	Black precipitate.
16	50	200	Small black precipitate.
17	40	210	Slight brown precipitate.
18	38	212	Slight oxidation.
19	35	215	No oxidation.
20	30	220	" "

Apparently cuprous chloride in the presence of acid of smaller concentration than that used in experiment 18 is not acted on by sulphur dioxide. It also appears that there is some definite concentration of hydrochloric acid, above which cuprous chloride and sulphur dioxide react with the separation of sulphur only, an intermediate concentration of acid in which both sulphur and the black sulphide are precipitated, and a final stage in which the sulphur dioxide reacts to give the sulphide only.

In experiments 14 and 15, analysis showed that when the precipitate was washed with dilute hydrochloric acid and then with air-free water and dried, it still contained large and variable quantities of chloride. When, however, a concentrated solution of sodium chloride was used instead of the hydrochloric acid, the amount of chloride in the precipitate was negligible, and analysis gave percentages of copper and sulphur in close accord with those required by the formula Cu_2S (Found Cu = 78.7; S = 21.3. Calc., Cu = 79.8; S = 20.1 per cent.).

Degree of Oxidation in a Special Case.

With the apparatus shown in Fig. 2, the following results were obtained.

TABLE IV.

Duration of experiment	Four hours.		
Solution	Eleven grams of cuprous chloride in 250 c.c. of acid (82 c.c. of concentrated hydrochloric acid and 168 c.c. of water).		
Experiment	21	22	23
$\frac{\text{Cupric copper}}{\text{Total copper}} \times 100$	1.5	1.24	1.30

The above are results of experiments in which the black cuprous sulphide was deposited. It might be expected that in view of the withdrawal of one of the products of the reaction the degree of oxidation would have been greater. This, however, is not supported by the experimental evidence.

Limit of Reduction of Cupric Chloride by Sulphur Dioxide in Concentrated Hydrochloric Acid Solution.

It has been shown by Wardlaw and Clews (T., 1920, **117**, 1099) that ferric chloride dissolved in excess of hydrochloric acid is incompletely reduced by sulphur dioxide. It was thought that cupric chloride might behave similarly. Solutions were prepared

with a constant copper content but having as constituents varying percentages of cupric and cuprous chlorides.

TABLE V.

Concentration 0.33 Gram of copper in 250 c.c. of concentrated (33 per cent.) hydrochloric acid.
Duration of experiments Four hours.

Experi- ment.	Cupric copper Total copper $\times 100$.		Remarks.
	Initial value.	Final value.	
24	100	22.2	Sulphate formed.
25	22	16.5	" "
26	15	7.5	" "
27	9.8	8.8	" "
28	6.79	7.14	No sulphate.

TABLE VI.

Duration of experiments ... Four hours.

Experi- ment.	Grams of total copper in 250 c.c. of acid.	Cupric copper Total copper $\times 100$.		Remarks.
		Initial value.	Final value.	
29	3.516	100	56.69	Sulphate formed.
30	3.903	57	38.0	" "
31	5.477	28.7	26.39	" "
32	4.541	28.06	20.35	" "

Results (31) and (32) show that whilst at the concentration of copper employed in experiment 31, equilibrium is nearly attained, in experiment 32 such is not the case. From the above tables it can be readily seen that in concentrated hydrochloric acid sulphur dioxide does not effect a complete reduction. Instead, there is established, depending on the concentration of total copper, an equilibrium between the cuprous and cupric salts present.

Reaction of Sulphur with Cuprous Chloride.

In a paper by Vortman and Padberg (*Ber.*, 1889, **22**, 2642), in which are references to earlier work on the subject, it is shown that if an acid solution of cuprous chloride is boiled with flowers of sulphur, the reaction may be interpreted by the equation :

The present authors find that when finely divided sulphur is heated with cuprous chloride in dilute hydrochloric acid (112 c.c. of 33 per cent. acid and 138 c.c. of water) at 95° in a current of carbon dioxide, a black precipitate is slowly formed. From qualitative evidence, this precipitate undoubtedly contains a large proportion of cuprous

sulphide. However, attempts to obtain a sufficient quantity for analysis have so far proved futile, as the sulphide forms a coating on the free sulphur and brings the reaction to a standstill. The yield after seventy-two hours was very minute. In the paper by Vortman and Padberg no mention is made of the use of an inert atmosphere, the temperature of their experiments was much higher than ours, and, lastly, the sulphide was not specially isolated and analysed.

Some results by Rammelsberg and Huntington (*Eng. and Min. J.*, 1882, **34**, 150) in connexion with the Patio process seem germane to this subject. They showed that if silver sulphide and cupric chloride are made to act on each other in the presence of air and sodium chloride solution, either cuprous chloride, silver chloride, and sulphur are produced, or the cuprous chloride formed becomes converted into a sulphide :

The liberation of sulphur, however, is a secondary reaction taking place only to a very limited extent :

The amount of cuprous chloride formed and of sulphur set free is dependent on the strength of the solvent, the temperature, and the presence of air.

The last equation is distinctly interesting, as it represents the reverse of the reaction investigated by Vortman and Padberg (*loc. cit.*). Incidentally, the presence of air plays an important part.

Reaction of Sulphur with Cupric Chloride.

Fihlol and Senderens (*Compt. rend.*, 1881, **93**, 152) state that when the sulphate, nitrate, and chloride of copper respectively are heated with sulphur, no sensible decomposition occurs. This statement substantially confirms the results of experiments carried out by the authors in which cupric chloride in the presence of water and of dilute hydrochloric acid (112 c.c. of 33 per cent. acid : 138 c.c. of water) respectively was heated with sulphur for four hours in a current of carbon dioxide. It was found that no reaction had taken place. In the presence of concentrated hydrochloric acid, however, under the above conditions, a reduction of about 5 per cent. was effected and sulphuric acid was detected in the solution. The following equation therefore represents the reaction :

Discussion of Results.

The oxidation of cuprous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid has been shown to be represented by the equation :

Moreover, experiments have also shown that cupric chloride in the presence of concentrated hydrochloric acid is reduced by sulphur with the production of sulphuric acid. This may be represented by the equation :

From these facts it seems justifiable to assume that the first equation is reversible. This reversibility is normally obscured by the reaction represented in equation (2).

No sulphuric acid was ever detected when sulphur dioxide oxidised cuprous chloride in the presence of hydrochloric acid. We may therefore say that in reactions in which sulphur alone is precipitated, the reversible equation (1) represents the course of the reaction. This idea of a reversible reaction receives support from the fact that complete reduction of cupric solutions does not occur when sulphur dioxide reacts in the presence of concentrated hydrochloric acid. Instead, there seems to be established equilibrium solutions of cupric chloride-cuprous chloride in which sulphur dioxide does not produce any effect.

With reference to those reactions in which the black sulphide was precipitated, two possible explanations suggest themselves. This deposition may be due to a secondary reaction between the cuprous chloride and hydrogen sulphide produced by the reduction of the sulphur dioxide or between the cuprous chloride and sulphur initially formed. The authors are of opinion that there seem to be no special grounds for supposing that the sulphur dioxide undergoes direct reduction to hydrogen sulphide in these reactions, and consider that the precipitation is due to a secondary reaction between the cuprous chloride and the sulphur initially produced, as shown by the authors' experiments :

Owing to the continual disturbance of the equilibrium by the reaction represented in equation (3) one might expect a comparatively high degree of oxidation from this reaction. Reference to Table IV, however, shows that this is not so. This result can, however, be accounted for by a consideration of the oxidation

potentials of cuprous-cupric mixtures and of sulphurous acid. Each of these cuprous-cupric chloride mixtures has a definite oxidation potential, and it is the establishment of an oxidation potential equal to that of the sulphurous acid in the special acid concentrations that brings about the equilibrium value. It follows, therefore, that the ratio of cupric to cuprous chloride in a solution is the sole factor determining the amount of oxidation. As regards equation (1), therefore, once this definite ratio of cupric to cuprous salt is obtained, no further oxidation will take place, and as no further liberation of sulphur will occur, reaction (3) will cease to be operative.

To explain the increase in percentage oxidation with increase in the concentration of cuprous chloride recorded in Table II, a reference to some work by Poma (*Atti R. Accad. Lincei*, 1909, [v], 18, i, 192) seems to furnish the necessary data. He found that for a definite concentration of hydrochloric acid, as the concentration of cupric chloride increased, the amount of cuprous chloride which could be dissolved increased enormously, whilst the number of free cuprous ions showed only a very small increase, indicating that the cuprous copper was present in the form of a complex ion. From these results it may be stated that if we are to establish a mixed cuprous-cupric solution the potential of which will be equal to that of the sulphur dioxide in a given concentration of acid, a greater amount of cupric salt must be produced in the more concentrated than in the more dilute cuprous chloride solutions before the necessary free cupric ions will be present to give the requisite oxidation potential.

Summary.

1. The oxidation of cuprous chloride by sulphur dioxide in the presence of concentrated hydrochloric acid can be represented, as regards its quantitative aspect, by the equation :

2. The degree of oxidation is dependent on the initial concentration of cuprous chloride.

3. Oxidation by sulphur dioxide does not occur in solutions of cuprous chloride containing less than 38 c.c. of free hydrochloric acid (33 per cent.) in 250 c.c. of solution, and immersed in an oil-bath at 95°.

4. Oxidation by sulphur dioxide in solutions of cuprous chloride containing more than 150 c.c. of hydrochloric acid (33 per cent.) in 250 c.c. of solution results in precipitation of sulphur. In solutions containing between 150 c.c. and 112 c.c. of concentrated acid in

250 c.c. of solution the precipitate consists of sulphur and cuprous sulphide, whilst in solutions containing between 112 c.c. and 38 c.c. of concentrated acid in 250 c.c. of solution the precipitate is cuprous sulphide alone.

5. With decreased concentration of acid the degree of oxidation is lowered, and even in experiments where the black cuprous sulphide is precipitated the degree of oxidation is still very small.

6. In the presence of concentrated hydrochloric acid sulphur reduces cupric chloride with the production of cuprous chloride and sulphuric acid. In dilute acid and aqueous solutions, this reduction does not occur.

7. There is distinct evidence that when cuprous chloride reacts with sulphur in the presence of dilute hydrochloric acid at approximately 95° in a current of carbon dioxide, cuprous sulphide is produced.

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