

## Reaction Between Copper Sulphide & Sulphur Trioxide

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Copper(II) sulphide reduces liquid sulphur trioxide at 45° vigorously and rapidly yielding copper sulphate and sulphur dioxide. Traces of moisture influence the reaction. The reaction takes place even at 20° forming an intense blue compound generally considered to be sulphur sesquioxide, S<sub>2</sub>O<sub>3</sub>, which decomposes slowly. Based on the analytical results of copper sulphate and sulphur dioxide a mechanism has been proposed for the possible course of the reaction. At 360°C, *in vacuo*, the reaction takes an entirely different course. Elemental sulphur, disulphur monoxide, sulphur dioxide and copper sulphate are found to be the products.

SULPHUR trioxide is known to behave as an oxidizing agent towards elemental sulphur as well as towards its compounds of lower oxidation state. In the presence of traces of moisture elemental sulphur and sulphur trioxide react to give an intense blue-coloured compound which gives off sulphur dioxide and fades in colour gradually<sup>1</sup>. This is attributed to the formation of sulphur sesquioxide and its subsequent decomposition. In the present investigation it was found that cupric sulphide reacts with sulphur trioxide under different experimental conditions giving rise to cupric sulphate and sulphur dioxide. In the presence of traces of moisture, here again 'blue compound' is formed which undergoes decomposition. The results of a detailed study of this reaction are presented in this paper.

### Materials and Methods

Sulphur trioxide was prepared by warming fuming sulphuric acid in the presence of phosphorus pentoxide as suggested by Vogel and Partington<sup>2</sup> (40 ml of acid and 50 g P<sub>2</sub>O<sub>5</sub> in a 500 ml distillation flask and heated to 150°). SO<sub>3</sub> formed was condensed in a distillation flask at 20°. (It is necessary to point out that this should not be collected at a lower temperature as SO<sub>3</sub> polymerizes easily below 18° in the presence of traces of moisture that may be present in the flask and it is difficult to melt this product.) The condensed SO<sub>3</sub> was further purified by redistillation into another flask maintained at 20°. About 5 ml of freshly distilled sulphur trioxide was collected for each experiment.

Copper sulphide was prepared by passing hydrogen sulphide into an aqueous solution of copper(II) salt. The final product obtained under such conditions does not conform to stoichiometric composition of CuS. This is attributed to partial oxidation of wet CuS to CuSO<sub>4</sub> in air during its preparation. This difficulty could be overcome if method of heating of stoichiometric amounts of copper and sulphur in evacuated sealed ampules is adopted. However, in the present case, precipitation of copper sulphide was carried out as follows: Anhydrous cupric

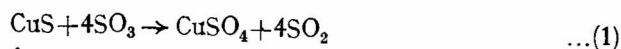
chloride (25 g), prepared by heating CuCl<sub>2</sub>·2H<sub>2</sub>O in a stream of hydrogen chloride at 150° for 2 hr and cooling in a desiccator was dissolved in 250 ml methanol. Dry hydrogen sulphide was passed through the solution to precipitate copper sulphide. The precipitate was filtered under dry nitrogen atmosphere, washed well with methanol and dried *in vacuo* at 100°. It was cooled and preserved over P<sub>2</sub>O<sub>5</sub>. Analysis of this product indicated that the sample was at least 99.5% CuS. This method was found to be simpler and reliable. X-ray diffraction pattern of the powder confirmed that it was CuS.

### Results and Discussion

*Reaction of copper sulphide and sulphur trioxide at low temperatures*—A known amount of copper sulphide (~0.3 g) was added to excess of sulphur trioxide in a flask immersed in a water-bath and attached to two traps. The sulphur dioxide formed during the reaction was swept by a current of dry nitrogen and bubbled through conc. sulphuric acid to absorb any sulphur trioxide present in the gas stream. The issuing gas was passed through a dilute solution (2M) of sodium hydroxide. (A few drops of glycerine had been added to this solution to prevent atmospheric oxidation of the sulphite formed.) The sulphite formed was estimated iodimetrically.

The reaction was very sluggish at 20°, became vigorous and rapid when it was warmed to 45°, the b.p. of sulphur trioxide and it was over in 5 min. During this process the black copper sulphide had changed to white anhydrous copper sulphate which was estimated. The results of two typical experiments are given in Table 1.

If the reaction were a simple oxidation of copper sulphide and had taken place in terms of Eq. (1), then



for every mole of copper sulphate formed 4 moles of sulphur-dioxide should be produced. The results show that this was around 3.5. It is likely that some side reactions are responsible for the lower value.

TABLE 1 — REACTION OF COPPER(II) SULPHIDE WITH SULPHUR TRIOXIDE

CuS taken moles $\times 10^3$	CuSO <sub>4</sub> formed moles $\times 10^3$	SO <sub>2</sub> formed moles $\times 10^3$	CuSO <sub>4</sub> : SO <sub>2</sub>
DRY CuS AT 45°			
2.955	2.870	10.12	1: 3.526
2.524	2.433	8.431	1: 3.465
CuS WITH MOISTURE AT 20°			
2.394	1.882	3.508	1: 1.863
2.636	1.758	3.021	1: 1.718
CuS WITH MOISTURE AT 45°			
2.104	2.073	5.855	1: 2.826
2.092	2.018	6.340	1: 3.142

*Reaction between moist copper sulphide and sulphur trioxide* — It was found that when copper sulphide contained small amounts of moisture the reaction took a different course.

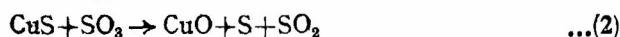
About 1 g of CuS was kept in a vacuum desiccator and exposed to water vapours for 3 hr. The copper sulphide gained in weight by about 5 mg. When such a sample was added to sulphur trioxide at 20° an intense blue colouration was observed which remained stable for several hours. Sulphur dioxide also was observed to be formed. Nitrogen was passed to sweep off all the sulphur dioxide. The blue colour faded gradually and vanished completely in about 24 hr. The sulphur dioxide was estimated as in the earlier case.

The residue was found to contain elemental sulphur in addition to copper sulphate. Copper sulphate was removed by dissolving in water and filtering. Sulphur on the filter paper was estimated as barium sulphate after oxidizing it to sulphuric acid by bromine/nitric acid mixture. It was found that for every mole of copper sulphate approximately 0.5 g atom of sulphur was formed.

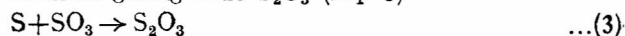
It can be seen from the results in Table 1 that the amount of sulphur dioxide produced during the reaction in these sets of experiments is very much less than the earlier case which was nearly 3.5 times the amount of copper sulphate.

It is of interest to point out that if the blue compound is warmed to 45° the colour fades and vanishes rapidly and the amount of sulphur dioxide formed is larger as given in Table 1. It is nearly 3 times the number of moles of copper sulphate. Also there is a decrease in the amount of sulphur formed which is only one-fifth of the number of moles of copper sulphate formed.

The results of these experiments could be explained by assuming that the blue compound is sulphur sesquioxide, S<sub>2</sub>O<sub>3</sub>. Its formation could be accounted for as follows. It is known that sulphur trioxide oxidizes H<sub>2</sub>S in the presence of traces of moisture giving rise to water, elemental sulphur and sulphur dioxide. A similar reaction could be expected between copper sulphide and sulphur trioxide (Eq. 2) whereby sulphur, sulphur dioxide and copper oxide can be formed.



The sulphur formed thus can react with sulphur trioxide giving blue S<sub>2</sub>O<sub>3</sub> (Eq. 3)



S<sub>2</sub>O<sub>3</sub> is an unstable species and it is known to decompose in two ways (Eqs. 4 and 5):



In the case where sulphur trioxide is continuously removed by passing nitrogen, both reactions can take place. If all the S<sub>2</sub>O<sub>3</sub> decomposed by reaction (4), calculations show that there should be one mole of sulphur dioxide produced for every mole of copper sulphate formed. If the decomposition of S<sub>2</sub>O<sub>3</sub> took place only by reaction (5), 2.5 moles of sulphur dioxide should be formed per mole of copper sulphate. The observed amount of sulphur dioxide is around 1.5 moles per CuSO<sub>4</sub>, indicating that S<sub>2</sub>O<sub>3</sub> decomposes in both ways. In the case where the blue compound is warmed probably reaction (5) dominates causing an increase in the amount of sulphur dioxide and decrease in the amount of sulphur formed. On this basis, about 2.5 moles of sulphur dioxide are expected per mole of copper sulphate. The observed value is around 3. This increase in the amount of sulphur dioxide probably shows that reaction (1) also takes place in this case. It has to be pointed out that it is rather difficult to evaluate quantitatively all these reactions which take place simultaneously.

*Reactions between copper sulphide and sulphur trioxide at 360° in vacuo* — Gaseous sulphur trioxide was passed over copper sulphide at 360° in vacuo and the products formed were collected in traps cooled in liquid nitrogen. A cherry red mass was deposited in the cold trap and it gradually turned blue. It was also noticed that elemental sulphur was deposited on the colder parts of the reaction tube.

The formation of cherry red mass in the cold trap indicated the presence of disulphur monoxide among the products of the reaction. It has been well established that when elemental sulphur is allowed to combine with a limited supply of oxygen, disulphur monoxide also is formed along with sulphur dioxide and appears as a cherry red mass in a trap cooled in liquid nitrogen<sup>3</sup>. The blue colour in the trap is probably due to the formation of sulphur sesquioxide by the reaction between sulphur trioxide and disulphur monoxide. Recently, Gillespie and Ummat<sup>4</sup>, based on their observation that a solution of this blue compound in 65% oleum contained S<sub>8</sub><sup>2+</sup> cations, put forward the hypothesis that it may have the composition S<sub>8</sub>(HS<sub>3</sub>O<sub>12</sub>)<sub>2</sub>.

It is rather difficult to make a quantitative study of this reaction because of the complexity arising from a number of reactions taking place simultaneously.

## References

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