FORMATION OF DISULPHUR MONOXIDE BY THE REACTION BETWEEN SULPHUR AND COPPER SULPHATE

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ABSTRACT

Sulphur reacts with anhydrous copper sulphate at 300–400° C in vacuum to give disulphur monoxide, sulphur dioxide and cupric sulphide. The yield of disulphur monoxide is dependent upon the particle size of copper sulphate employed and the temperature of the reaction. Experiments with labelled copper sulphate show that the sulphur in copper sulphate is always converted to sulphur dioxide. A mechanism is proposed for the reaction which will account for the experimental results.

During a study of the reaction between cupric sulphide and anhydrous cupric sulphate in vacuum at 300–400° C Kutty and Murthy observed the formation of disulphur monoxide [1]. Cupric sulphide undergoes decomposition also at this temperature giving sulphur vapour and $Cu_{1.8}S$ [2], [3]. Cupric sulphate was found to react with other sulphides like those of nickel, cobalt, manganese, copper (I) and zinc also at $\sim 500°$ C. [4] In all these cases, where the sulphides are stable at the temperature of the reaction, only sulphur dioxide and not disulphur monoxide was formed. Therefore, it is possible that in the cupric sulphide–cupric sulphate system disulphur monoxide was formed by the reaction between sulphur and cupric sulphate. Some preliminary investigations showed that this indeed was the case [5]. Reaction between sulphur and copper sulphate was investigated in greater detail making use of labelled copper sulphate also and the results are reported in this paper.

MATERIALS AND METHODS

(a) Apparatus

The apparatus employed for this purpose was the same as that used previously for the study of sulphur-cupric oxide system [6]. The heating vessel was a pyrex glass tube (30 cm × 2 cm) fitted with appropriate ground glass joints and stopcocks and connected to a vacuum assembly through

traps cooled in liquid nitrogen. A plug of glass wool was inserted at the mouth of the reaction tube to prevent the solid particles flying off when connected to the vacuum line. The reaction vessel was heated in a tubular furnace and maintained at any required temperature between 300 and 400° C with the help of an energy regulator. The gaseous products of the reaction were sucked under vacuum into traps cooled by liquid nitrogen.

(b) Reagents

1. *Sulphur.*—A sample of reagent grade resublimed sulphur was recrystallised from carbon disulphide. The crystals were dried under vacuum at 50° C, pulverised and preserved over phosphorus pentoxide in a desiccator.

2. Anhydrous copper sulphate was prepared by heating about g5 of copper sulphate pentahydrate (A.R. Sample) at 300° C in vacuum for over four hours and cooled under dry nitrogen. The white powdered sample was analysed for its copper and sulphate content by standard gravimetric methods as cuprous thiocyanate and barium sulphate respectively [7]. The analytical results indicated that the purity of the sample was at least 99·5%.

LABELLED COPPER SULPHATE

The radioactive tracer employed in the present investigation was $^{35}_{36}S$. Stock solution containing 1 millicurie of S–35 in the form of sulphuric acid supplied by Bhabha Atomic Research Centre was used in the present investigation. The solution was diluted with distilled water. The acid was treated with excess of copper carbonate and the unreacted copper carbonate removed by filtration. The filtrate containing active copper sulphate was diluted with inactive copper sulphate solution. The concentration was adjusted in such a way that when samples were analysed finally in the form of barium sulphatr they would give about 3.000 counts per minute per 100 mg. The coppee sulphate solution was evaporated on a water-bath. The crystals were then dehydrated by heating in vacuum at 300° C. The powdered sample was preserved over phosphorus pentoxide in a desiccator.

(c) The Measurement of radioactivity

The radioactivity of the sulphate samples was measured by means of the PCS–14 Proportional Counting System obtained from B.A.R.C. The voltage employed was 3900 V.

(d) Procedure

An intimate mixture of about 0·5 g of anhydrous copper sulphate powder with about 10 g of sulphur was heated in the reaction tube under vacuum at 300–400° C for 60 minutes. The tube was continuously evacuated by means of a rotary vacuum pump and the pressure inside the system was maintained at around 10^{-2} mm of mercury. The gaseous products of the reaction were condensed in traps cooled in liquid nitrogen. A red band in the condensate indicated the presence of disulphur monoxide in the gaseous products. When there was no further evolution of the gaseous products (after about 1 hr) the heating was stopped. The reaction tube was cooled to room temperature and the vacuum was released under nitrogen. Sulphur dioxide and disulphur monoxide formed were analysed by the method described earlier [8]. The trap was gradually warmed upto 60° C when disulphur monoxide decomposed to elemental sulphur and sulphur dioxide according to the equation

$$2S_2O \rightarrow 3S + SO_2.$$
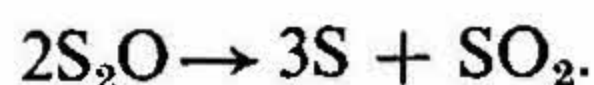
The sulphur dioxide in the trap was swept by a stream of nitrogen and absorbed in alkali. The sulphite formed was estimated iodimetrically. The elemental sulphur left behind in the trap was oxidised to sulphuric acid by a warm mixture of conc. nitric acid and bromine and estimated as barium sulphate.

RESULTS AND DISCUSSION

The analytical results of three typical experiments in which powdered copper sulphate was heated with sulphur at $\sim 360°$ C are given in Table I. It can be observed that sulphur dioxide and disulphur monoxide are formed in nearly equimolar proportions. However, the ratio of $SO_2 : S_2O$ was found to be variable with experimental conditions. It was found that this ratio was dependent on the particle size of copper sulphate employed. The finer the particles the larger was the amount of disulphur monoxide formed. The temperature at which the reaction was carried out also affected the relative amount of disulphur monoxide. The yield of disulphur monoxide was found to be higher at 360° C than at 300° C.

These observations can be explained on the basis that the reaction is a complicated one involving at least two simultaneous processes. First sulphur reacts with the surface layers of copper sulphate particles to form a layer of copper sulphide. Thereafter, copper sulphide and copper sulphate

TABLE I

Reaction between sulphur and copper sulphate at 360° C in vacuum

CuSO$_4$ taken moles × 10^3	SO$_2$ formed moles × 10^3	S formed g atom × 10^3	S$_2$O formed moles × 10^3	SO$_2$ formed from S$_2$O moles × 10^3	SO$_2$ formed directly moles × 10^3	SO$_2$: S$_2$O
4·508	5·229	4·721	3·148	1·574	3·655	1·161 : 1
3·909	5·255	4·909	3·272	1·636	3·619	1·106 : 1
3·271	5·379	4·772	3·182	1·591	3·788	1·191 : 1

exist in contact with each other and there is a possibility of sulphide-sulphate interaction. Sulphur also diffuses through the copper sulphide layer and reacts with the copper sulphate. The disulphur monoxide is probably formed during the sulphur-sulphate reaction since, as already said, it is not formed in the sulphide-sulphate systems where the metal sulphide is stable under the experimental conditions. It is possible that these two processes take place to different extents depending on experimental conditions.

## EXPERIMENTS WITH PELLETS OF COPPER SULPHATE

About 0·2 g of copper sulphate was pelletised in a mechanical pelletiser usually used in bomb calorimetric experiments. The pellet (~ 1 cm diameter and 1–2 mm thick) was placed in between layers of sulphur powder in the reaction tube. The tube was heated at 360° C for 2 hrs. The molten sulphur reacted easily with the pellet. The gaseous products were collected and analysed as described previously. The results of a few typical experiments are given in Table II. It can be seen that nearly 100% of the oxygen present in copper sulphate could be accounted for in terms of both the oxides of sulphur. The pellet after reaction was analysed for copper and sulphur by standard methods. The analysis gave Cu = 66·33% and S = 33·44% which showed it to be CuS (theoretical value for CuS is Cu = 66·46% and S = 33·54%). X-ray powder pattern of the sample also showed it to be cupric sulphide.

TABLE II. *Reaction between sulphur and copper sulphate pellet at 360° C*

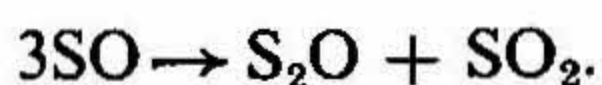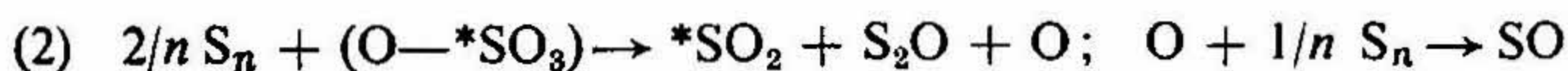| $CuSO_4$ taken in gm	O present in $CuSO_4$ in gm	SO_2 formed gm	SO_2 formed moles $\times 10^3$	O present in SO_2 in gm	% of O converted to SO_2 and S_2O	S formed gm atom $\times 10^3$	S_2O formed moles $\times 10^3$	SO_2 formed from S_2O mole $\times 10^3$	SO_2 formed directly moles $\times 10^3$	$SO_2 : S_2O$
0·1980	0·07939	0·1561	2·439	0·07805	98·3	0·4641	0·3094	0·1547	2·284	7·381 : 1
0·2095	0·08401	0·1633	2·552	0·08165	97·18	0·4617	0·3078	0·1539	2·398	7·798 : 1
0·2102	0·08424	0·1649	2·577	0·08245	97·88	0·04539	0·3026	0·1513	2·426	8·019 : 1

EXPERIMENTS WITH LABELLED COPPER SULPHATE

Experiments were conducted with labelled copper sulphate to throw some light on the possible mechanism of the reaction. All the samples for measurement of radioactivity were obtained in the form of barium sulphate. About 100 mg of powdered barium sulphate was made into a slurry with ethyl alcohol in an aluminium planchet ($\sim$2 cm^2 area). The alcohol was evaporated by means of an infrared lamp and the sample thus obtained was used for measurements. The results of two experiments in which the particle size of copper sulphate and temperature of reaction were altered to get different amounts of the two oxides of sulphur are given in Table III. It can be seen in both cases that the major part of the activity remained in sulphur dioxide. The activities of the copper sulphide and sulphur formed by the decomposition of disulphur monoxide are very small. These results can be explained as follows. If it is assumed that this small activity is due to contamination it can be seen that sulphur in copper sulphate is always converted to sulphur dioxide. This fact necessitates the assumption that the sulphate entity in copper sulphate resolves itself into two sets during the reaction, one involving the sulphur and a minimum of two oxygens and the other the rest of the oxygens. Since copper sulphate is known to give rise to sulphur trioxide during its decomposition it is safer to assume that these sets are — SO_3 and O. During the reaction with sulphur these sets can form equal amounts of sulphur dioxide and disulphur monoxide in one of the following ways:

(1) $1/n\ S_n + (O - {}^*SO_3) \rightarrow {}^*SO_2 + SO + O;\quad O + 2/n\ S_n \rightarrow S_2O$
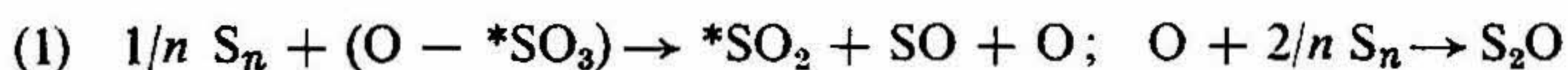
(where n is an integer. Sulphur is known to polymerise in liquid form at high temperatures [9]).

Sulphur monoxide (SO) is known [8] to decompose according to the equation

$$3SO \rightarrow S_2O + SO_2$$

(2) $2/n\ S_n + (O - {}^*SO_3) \rightarrow {}^*SO_2 + S_2O + O;\quad O + 1/n\ S_n \rightarrow SO$

$$3SO \rightarrow S_2O + SO_2.$$

The other possible interaction between the sulphide and sulphate in the system, as already said, will result only in sulphur dioxide and not disulphur monoxide. This interaction can be assumed to be similar to that in the nickle sulphide-copper sulphate system in which case also the radiochemical

Table III

Reaction between elemental sulphur and labelled copper sulphate

Average particle size of $CuSO_4$	Temperature of reaction	$SO_2 : S_2O$	Activity per gm (in CPM) of barium sulphate from			
			$CuSO_4$	CuS	S_2O	SO_2
16– 22 mesh	330° C	3·813:1	$1·123 \times 10^6$	$4·374 \times 10^2$	$3·239 \times 10^2$	$2·085 \times 10^5$
<150 mesh	380 C	1·247:1	$2·590 \times 10^5$	$2·703 \times 10^3$	$2·460 \times 10^3$	$7·252 \times 10^4$

experiments have shown that the sulphur in the copper sulphate is converted to sulphur dioxide [10]. The mechanism proposed above provides a satisfactory explanation for the experimental observations.

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