*Journal of Thermal Analysis, Vol. 34 (1988) 1257–1262*

# STUDIES ON MECHANISM AND KINETICS OF REACTION OF $CuSO_4$ WITH $Cu_2SO_2$

*J. Walczak, H. Dębiński, B. Muraszko* and *P. Wiśniewski*

INSTITUTE OF FUNDAMENTAL CHEMISTRY, TECHNICAL UNIVERSITY
OF SZCZECIN, AL. PIASTÓW 42, 71-065 SZCZECIN, POLAND

(Received September 21, 1987)

The reaction of $CuSO_4$ with $Cu_2SO_2$ to give $Cu_2SO_4$ was studied. The influence of the degree of reaction, the initial mixture composition and the temperature upon the reaction rate and the product composition was discussed. It was found that the reaction starts above 710 K and pure $Cu_2SO_4$ can be obtained under strictly defined conditions.

Studies of the reaction between copper(II) sulphate and copper(I) sulphide [1–4] have revealed that in $SO_2$ at 710–780 K it takes place via several intermediate steps, of which the most important are [3]:

$$2\,CuSO_{4(s)} + 2\,Cu_2S_{(s)} = 3\,Cu_2SO_{2(l)} + SO_{2(g)} \tag{1}$$

$$Cu_2SO_{2(l)} + 2\,CuSO_{4(s)} = 2\,Cu_2SO_{4(l)} + SO_{2(g)} \tag{2}$$

The overall equation of the process is:

$$2\,CuSO_4 + Cu_2S = 2\,Cu_2O + 3\,SO_2 \tag{3}$$

since the liquid intermediates are decomposed in further steps [1–3]:

$$3\,Cu_2SO_{2(l)} = 2\,Cu_2O_{(s)} + Cu_2S_{(s)} + 2\,SO_{2(g)} \tag{4}$$

$$3\,Cu_2SO_{4(l)} = 2\,Cu_2O_{(s)} + 2\,CuSO_{4(s)} + SO_{2(g)} \tag{5}$$

The aim of the present work was to investigate the isolated reaction 2, using $CuSO_{2(s)}$ obtained separately by a method described earlier [4, 5]. The thermal properties and X-ray diffraction pattern of $Cu_2SO_2$ were given previously [5].

Study of the hitherto not investigated reaction permitted establishment of the conditions for the synthesis of $Cu_2SO_4$ by a method not so far reported in the literature.

*John Wiley & Sons, Limited, Chichester*
*Akadémiai Kiadó, Budapest*

## Experimental

$Cu_2SO_2$ with a purity of 95 mol% (obtained by a method described earlier [5]) and anhydrous $CuSO_4$ (p.a., POCh, Gliwice) were used. Mixtures with $Cu_2SO_2$ to $CuSO_4$ mole ratios of $s=9$, 4.5, 3, 2.25, 1.8, 1.5 and 0.5 were made. The investigations were carried out gravimetrically under isothermal conditions in the temperature range from 753 to 803 K in $SO_2$ under about 101 kPa. The thermogravimetric and DTA measurements were performed under nonisothermal conditions from 298 to 890 K at a heating rate of 4 deg/min and at the same pressure of $SO_2$. The compositions of the reaction products were examined by means of X-ray powder diffraction analysis with a DRON 3 instrument ($CuK_\alpha$ radiation).

## Results and discussion

The results of the thermogravimetric measurements demonstrated that the maximum mass loss in the reaction of $CuSO_4$ with $Cu_2SO_2$ corresponds to the maximum mass loss calculated from the following equation (3):

$$\begin{aligned} &CuSO_4 + s\,Cu_2SO_2 = \\ &= (0.667s+1)\,Cu_2O + (0.333s-0.5)\,Cu_2S + (0.667s+1.5)\,SO_2 \end{aligned} \tag{6}$$

If $s \leq 1.5$, then $(0.33s-0.5)=0$.

This permitted the uniform determination of the fractional conversion ($\alpha$) and the reaction rate ($d\alpha/d\tau$). The fractional conversion $\alpha$ was defined as the ratio of the mass loss at a given instance to the maximum mass loss resulting from Eq. (6). The reaction rate was assigned by the graphical method from the mass loss *vs.* time records.

The results of nonisothermal examinations of pure $Cu_2SO_2$ (Fig. 1a) and of $Cu_2SO_2$ admixed with $CuSO_4$ showed that $Cu_2SO_2$ first melts congruently as about 620 K, and the liquid $Cu_2SO_2$ then reacts with $CuSO_4$ above 710 K. It follows from Fig. 1b–e that the process occurs through two separate steps if $s \geqslant 1.5$. In the first step, beginning above 710 K and completed below 790 K, the mass loss is much lower than that in the next step. This was confirmed by isothermal measurements and it was shown that the reaction rate in the first step increases with the progress of the reaction, achieving a characteristic maximum (Fig. 2). The value of this maximum is much higher than that of the reaction rate in the next step.

Table 1 shows $\alpha\frac{T}{1}$ values relating to the completion of the first step. These values

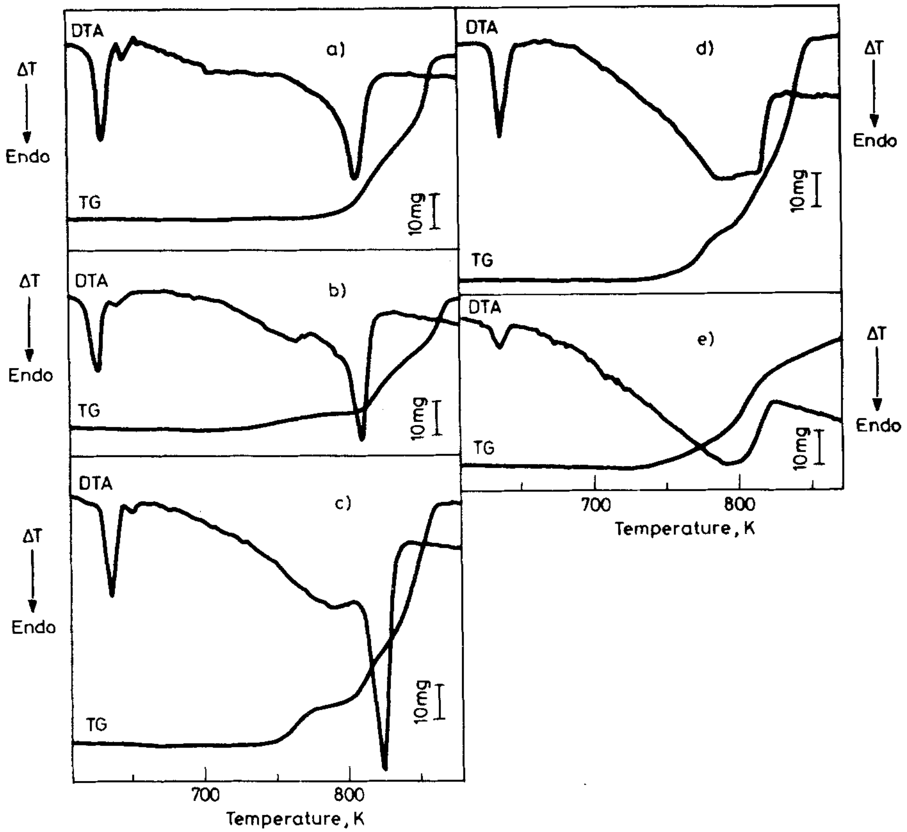

**Fig. 1** The DTA and TG (presenting mass loss) curves for heating rate 4 K/min and different compositions of initial mixtures: (a) $Cu_2SO_2$ alone; (b) $s=9$; (c) $s=2.25$; (d) $s=1.5$; (e) $s=0.5$

**Table 1** Position of first maximum in rate vs. $\alpha$ curve, $\alpha_{\max_1}$, and end of first step determined from TG curves, $\alpha_1^T$, in relation to completion of reaction 2, $\alpha_{cal}$

| | Initial composition, $s$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.5 | 1.5 | 1.8 | 2.25 | 3 | 4.5 | 9 |
| $\alpha_1^T$ | — | 0.20 | 0.18 | 0.17 | 0.17 | 0.16 | 0.10 |
| $\alpha_{\max_1}$ | 0.05 | 0.09 | 0.07 | 0.07 | 0.05 | 0.04 | 0.02 |
| $\alpha_{cal}$ | 0.60 | 0.20 | 0.19 | 0.17 | 0.14 | 0.11 | 0.07 |

were determined from TG curves (Fig. 1b–e). The $\alpha_{\max_1}$ values are also shown in Table 1. They correspond to the position of the first maximum in the rate vs. $\alpha$ curves obtained from isothermal examinations at 783 K. Finally, Table 1 presents $\alpha_{cal}$ values calculated by assuming that the process occurs in accordance with

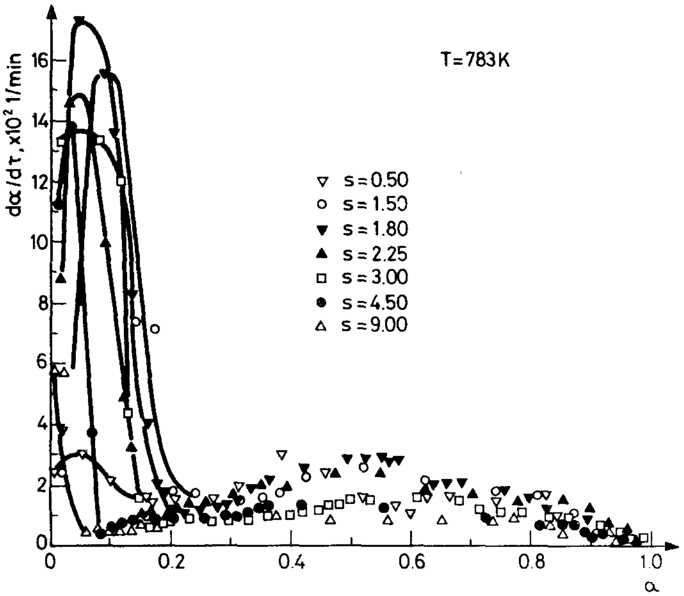

**Fig. 2** The results of isothermal examinations presented as rate-α curves.

reaction 2 and is related to the completion of the first step. Comparison of the values indicated that reaction 2 is the only reaction occurring in the first step whenever $s \geqslant 1.5$. This was confirmed by X-ray powder examinations of the reaction products, which proved that $Cu_2SO_4$ is the only reaction product if $s \geqslant 1.5$ and $\alpha < \alpha_{cal}$. The occurrence of the maximum rate at $0 < \alpha_{max} < \alpha_{cal}$ indicates that the rate of reaction 2 increases with the progress of the reaction, i.e. with increase in the liquid content of the reaction mixture.

Table 2 shows values of the maximum rate of $SO_2$ evolution in the first step, $V_{SO_2}$, which were calculated with respect to the surface area of reacting $CuSO_4$ from the equation

$$V_{SO_2} = \frac{dn_{SO_2}}{d\tau} \times \frac{1}{n^{\circ}_{CuSO_4}(1-\alpha^*)^{2/3}} \tag{7}$$

where:

$dn_{SO_2}/d\tau$ = $SO_2$ evolution rate calculated from $d\alpha/d\tau$ values at $\alpha_{max_1}$ and from Eqs 2 and 6:

$n^{\circ}_{CuSO_4}$ = initial number of $CuSO_4$ moles;

$(1-\alpha^*)$ = fraction of unreacted $CuSO_4$ at $\alpha_{max_1}$ calculated from Eq. 2;

$(1-\alpha^*)^{2/3}$ = surface area of reacting $CuSO_4$, assuming that the $CuSO_4$ grains are spherical.

The presented $V_{SO_2}$ values correspond to the liquid content of the reaction mixture, $r_1$, and to the composition of the liquid, $x_{Cu_2SO_2}$. These values of $r_1$ and $x_{Cu_2SO_2}$ were calculated from the equations

$$r_1 = \frac{n_{Cu_2SO_2} + n_{Cu_2SO_4}}{n_{(Cu_2SO_4}} \tag{8}$$

$$x_{Cu_2SO_2} = \frac{n_{Cu_2SO_2}}{n_{Cu_2SO_2} + n_{Cu_2SO_4}} \tag{9}$$

where $n$ = actual number of moles.

The $V_{SO_2}$ values are given in arbitrary units, the surface area of $CuSO_4$ at $\alpha=0$ for $s=0.5$ being taken as 1 unit.

The presented values of $V_{SO_2}$, $r_1$ and $x_{Cu_2SO_2}$ seem to confirm that the rate of reaction 2 increases with increase in the liquid content. On the other hand, if the liquid content were the only determinant of the rate of reaction 2, the rate maxima for $s=1.5$ and 0.5 would be observed at values of $x_{Cu_2SO_2}$ much lower than 0.74. Since such maxima do not appear, it may be supposed that the rate of the reaction under study is proportional to the concentration of $Cu_2SO_{2(l)}$ in the liquid (Table 2).

**Table 2** Rate of evolution of $SO_2$, $V_{SO_2}$, at first maximum in rate vs. $\alpha$ curves in relation to liquid content, $r_1$, and $Cu_2SO_2$ fraction in liquid, $x_{Cu_2SO_2}$

| | Initial composition, $s$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.5 | 1.5 | 1.8 | 2.25 | 3 | 4.5 | 9 |
| $V_{SO_2}$ | 2.8 | 60 | 64 | 69 | 79 | 85 | 60 |
| $r_1$ | 0.59 | 3.1 | 3.2 | 4.2 | 4.9 | 7.3 | 15.2 |
| $x_{Cu_2SO_2}$ | 0.85 | 0.74 | 0.81 | 0.83 | 0.89 | 0.92 | 0.97 |

The nonisothermal measurements show that, with the fall in the $s$ values, the two steps of the process overlap. Finally, the two steps proceed simultaneously in practice (Fig. 1). Under isothermal conditions, this is evident as a decrease in the difference between the maximum rates of the steps as the $s$ value decreases. This difference is the least outstanding for $s=0.5$. It is confirmed by the X-ray powder diffraction results, which proved that for $s<1.5$ only $Cu_2SO_4$ was formed in the first step, whereas for $s>1.5$ quite small amounts of $Cu_2O$ were formed at the end of the first step. Finally, for $s=0.5$, $Cu_2O$ was formed at the very beginning of this step.

It was found from X-ray examinations that, for $s=0.5$, the quantitative ratio of $Cu_2SO_4$ to $Cu_2O$ in the reaction mixture increases with increase of the temperature of reaction. The presented results indicate that the overlapping of the first step by the second one results from a decrease in the rate of reaction 2 compared with that of reaction 5, which arises from either a decrease in the $Cu_2SO_2$ concentration in the liquid (Table 2) or a decrease in temperature. Thus, pure $Cu_2SO_4$ could be prepared from $Cu_2SO_2$ and $CuSO_4$ at high temperature. It has been found that a product containing at least 95 mol% $Cu_2SO_4$ can be obtained by quenching a mixture of $CuSO_4$ with $Cu_2SO_2$ ($s=0.5$) on attainment of the mass loss relating to the value calculated from Eq. (3) when the mixture is heated at 803 K.

## References

1 H. Dębiński and J. Walczak, J. Thermal Anal., 29 (1984) 971.

2 H. Dębiński and J. Walczak, ibid., 29 (1984) 977.

3 H. Dębiński and J. Walczak, ibid., 31 (1986) 779.

4 H. Dębiński and J. Walczak, Chem. Stos., 29 (1985) 237.

5 H. Dębiński and J. Walczak, J. Thermal Anal., 32 (1987) 35.

**Zusammenfassung** — Es wurde die Reaktion von $CuSO_4$ mit $Cu_2SO_2$ zu $Cu_2SO_4$ untersucht. Dabei wurde der Einfluss des Reaktionsgrades, der Zusammensetzung der Ausgangsprodukte und der Temperatur auf die Geschwindigkeitskonstante und die Produktezusammensetzung beschrieben. Es wurde festgestellt, dass die Reaktion oberhalb 710 K anläuft und dass unter ganz bestimmten Bedingungen reines $Cu_2SO_4$ erhalten werden kann.

**Резюме** — Изучена реакция сульфате двухвалентной меди с сульфатом одновалентной меди. Обсуждено влияние степени реакции, состава исходной смеси и температуры на скорость реакции и состав продуктов реакции. Установлено, ччто реакция начинается при температуре выше 710 К и чистый сульфат одновалентной меди может быть получен при строго определенных условиях.