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THERMAL STUDIES OF BIS 2-AMINO-5-PHENYL-1,3,4-THIADIAZOLE COPPER(II) SULPHATE

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Thermal decomposition of bis 2-amino-5-phenyl-1,3,4-thiadiazole copper(II) sulphate has been studied by TG, DTA and DTG. The electrical conductivity of the compound in the solid state have also been measured at different temperatures. It is believed that decomposition is a nucleation controlled process and starts at the site of defects.

A large number of studies on the kinetics and mechanism of thermal decomposition of simple compounds have been made during the last few years. However, the data on metal complexes are limited. During the recent years, much attention has been given to the study of thermal decomposition of metal complexes in order to investigate the nature of intermediates and the mechanism of decomposition [1–4]. The present paper describes the mechanism of decomposition of the complex 'bis 2-amino-5-phenyl-1,3,4-thiadiazole copper(II) sulphate'.

Experimental

Materials: All the materials used for the preparation of the complex are BDH AnalaR grades.

Preparation and characterization of the complex: The complex was prepared and characterized in a manner as described earlier [5]. The complex hereafter referred to as $Cu(2a\text{-}5\text{-}ph.1,3,4\text{-}thd.)_2SO_4$ required $C = 37.39\%$, $H = 2.72\%$, $N = 16.35\%$, $Cu = 12.36\%$ and $S = 18.69\%$ and the values obtained are $C = 36.64\%$, $H = 2.74\%$, $N = 16.20\%$, $Cu = 12.10\%$ and $S = 18.50\%$. IR spectra of the complex was recorded with a Perkin Elmer 621 grating infrared spectrophotometer in Nujol Mull and this indicated that the coordination occurs through the S atom and the N atom of the NH_2 group [5].

Thermal decomposition: TG, DTA and DTG of the complex was studied with Paulik–Paulik–Erdey MOM derivatograph (Hungary) with a heating rate of 5°/min in static air. Kinetics of decomposition was studied in three different temperature ranges using thermobalance in an isothermal manner. In the first temperature range (433–493 K) the complex $Cu(2a\text{-}5\text{-}ph.\text{-}1,3,4\text{-}thd.)_2SO_4$ was taken and in the second temperature range (513–613 K) the decomposition product of the first temperature range was taken and in the third temperature range (653 – 713 K), the decomposition product of the second temperature range was taken.

Electrical conductivity measurements: The electrical conductivity of the complex in the form of pellet was measured between platinum electrodes using philips conductivity bridge in a temperature range 353 – 433 K.

X-ray diffraction studies: Powder X-ray diffraction of the complex and the decomposition products were taken with an X-ray machine using CuKα radiation.

Gas analysis: Qualitative analyses of the gases evolved during decomposition were also carried out.

Results and discussion

The results of thermal analyses are given in Table 1 and the graphs for TG, DTA and DTG are given in Fig. 1. The temperature quoted in Table 1 are those for the beginning and the end of a decomposition step under the conditions used. From Fig. 1 (TG), it is clear that a weight loss starts at around 90° corresponding to about 1% loss in weight. This loss in weight may be due to decomposition of adsorbed gases or moisture. The weight loss starts at a very low rate right from the start, and then increases rapidly from about 140°. Above 140°, there is a rapid loss in weight and the break at 220° corresponds to the loss of 0.75 molecule of ligand. There is another break in the TG curve at about 340° corresponding to the loss of one molecule of ligand. The third break comes at about 460° in the TG curve and this corresponds to the complete removal of ligand molecules leaving only copper sulphate. The copper sulphate further decomposes to Cu_2O and in the end, there is an increase of about 2% in the weight. This weight increase is due to oxidation of Cu_2O into CuO by atmospheric oxygen.

Table 1

Scheme of thermal decomposition of Cu(2a.5ph.1,3,4-thd)$_2$ SO$_4$

Stable phases of thermal decomposition	Temp. range, °C	Total % wt. loss	
		Found	Cal.
Cu(2a.5ph.1,3,4-thd.)$_2$SO$_4$			
↓	140 – 220	25.7	25.8
Cu(2a.5ph.1,3,4-thd.)$_{1.25}$SO$_4$			
↓	230 – 340	35.7	34.4
Cu(2a.5ph.1,3,4-thd.)SO$_4$			
↓	350 – 475	68.5	68.9
CuSO$_4$			
↓	475 – 620	86.0	86.1
1/2Cu$_2$O			

The above results have been supported by DTA and DTG results. The peaks in the DTA and DTG curves at 220, 340 and 460° correspond to the breaks in the TG curve. Further the increase in weight due to oxidation of Cu_2O is indicated by a peak in the DTG curve and a broad exothermic peak in DTA.

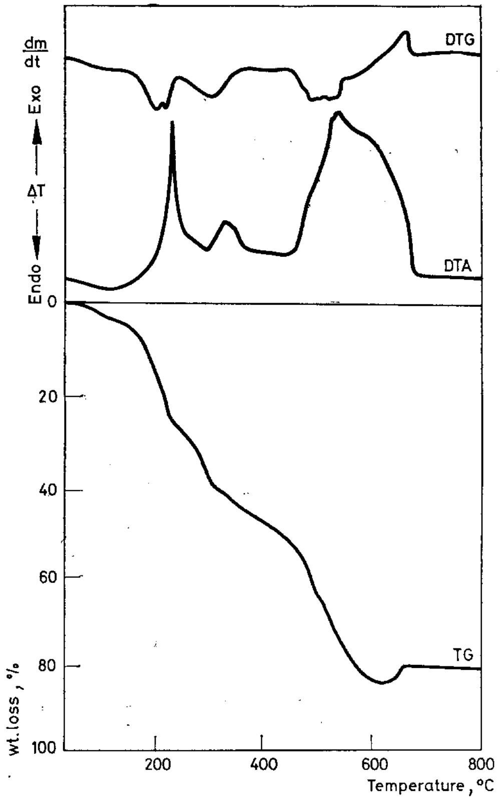

Fig. 1. Thermal decomposition of $Cu(2a.5ph.1,3,4thd.)_2SO_4$

The intermediates obtained during decomposition were confirmed by elemental analyses and X-ray diffraction techniques. There were no lines in the X-ray diffraction patterns of $Cu(2a.5ph.1,3,4\text{-}thd.)_2SO_4$, $Cu(2a.5ph.1,3,4\text{-}thd.)_{1\cdot 25}SO_4$ and $Cu(2a.5ph.1,3,4\text{-}thd.)SO_4$, indicating that these compounds are poorly crystalline

Compound	Found		Required	
	Cu%	S%	Cu%	S%
$Cu(2a.5ph.1,3,4thd.)_{1\cdot 25}SO_4$	16.88	18.62	16.67	18.91
$Cu(2a.5ph.1,3,4thd.)SO_4$	17.70	17.80	17.70	17.70

in nature. The X-ray diffraction patterns of the compounds $CuSO_4$, Cu_3O and CuO were identical as reported in the literature. The metal and sulphur estimations of the decomposition products are given below.

Some of the gases evolved during decomposition were tested qualitatively and were found to be CO_2 and H_2O.

The kinetics of decomposition were also followed and the kinetic data were found to obey the following equation.

$$1 - (1 - \alpha)^{1/3} = kt + C \quad \ldots \qquad (1)$$

where α is the fraction decomposed at any time t, k is the rate of decomposition and C is a constant. The validity of Eq. (1) was tested by plotting graphs between $1 - (1 - \alpha)^{1/3}$ *vs* t, where straight lines are obtained. From the slope of the lines, the rate of decomposition, k, were calculated at different temperatures (Table 2) and by Arrhenius plots (Fig. 2), the energies of activation were calculated. The energies of activation are low and increase with the increasing temperature range. This suggests that the removal of 0.75 molecule of the ligand is easier than the removal of one molecule of the ligand and the complete removal of the ligand is comparatively more difficult.

Table 2

Kinetic parameters of Eq.(1)

Temperature, K	k, minute^{-1}	C	E, cals/mole
433	0.0024	0.20	1384
453	0.0027	0.21	
473	0.0029	0.22	
493	0.0031	0.24	
513	0.0022	0.17	1769
553	0.0024	0.18	
593	0.0028	0.23	
613	0.0029	0.24	
653	0.0029	0.03	5570
673	0.0034	0.07	
693	0.0038	0.09	
713	0.0039	0.12	

The decomposing crystals of the complex when examined under a microscope, showed that the decomposition started only at certain points. It may be the regions, where the concentrations of dislocations or other crystal defects are more. It appears that first of all small nucleii are formed which then grows with time. Thus the decomposition rate can be correlated with the growth of nucleii. It is thus obvious that the decomposition is a nucleation controlled process.

In order to understand the nature of the compound, the electrical conductivity of the complex in solid state were measured in the form of a pellet in the temperature range 353–433 K. The following equation was found to hold good.

$$\sigma = \sigma_0{}^{-E/RT} \quad \ldots \qquad (2)$$

where σ is the specific conductivity, σ_0 is the constant, R is a gas constant, T is the temperature in absolute degrees and E is the energy of activation for conduction. A plot of log σ *vs.* $1/T$ gave straight line and from the slope, the energy of activation for the conduction was found to be 1357 cals/mole. The energy of activation for conduction is very low. This indicates that probably surface conduction predominates.

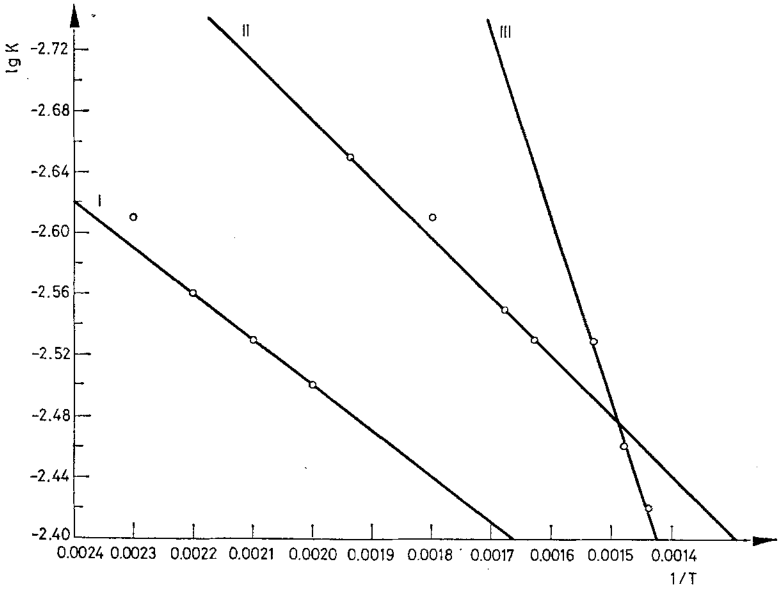

Fig. 2. Arrhenius plot for the decomposition of the complex I — 433–493 K, II — 513–613 K, III — 653–713 K

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Résumé — La décomposition thermique du "sulfate de cuivre(II) bis(amino-2 phényl-5 thiodiazole-1,3,4) a été étudiée par TG, ATD et TGD. La conductibilité électrique de ce composé a également été mesurée à l'état solide à diverses températures. La décomposition est sans doute un processus contrôlé par la nucléation et s'amorce sur des défauts de sites.

Zusammenfassung — Die thermische Zersetzung von 'Bis- 2-Amino-5-Phenyl-1,3,4-Thiadiazol-Kupfer(II)-Sulfat' wurde durch TG, DTA und DTG untersucht. Die elektrische Leitfähigkeit^{5}der Verbindung im festen Zustand wurde ebenfalls bei verschiedenen Temperaturen gemessen. Es wird angenommen, dass die Zersetzung ein durch Keimbildung gesteuerter Vorgang ist und an den Defektstellen anfängt.

Резюме — С помощью ТГ, ДТА и ДТГ было изучено термическое разложение бис-(2-амино)-5-фенил-1,3,4-тиадиазол сульфата меди(II). Электропроводность этого соединения в твердом состоянии была измерена при различных температурах. Считается, что контролирующим процессом разложения является образование центров кристаллизации, которое начинается со стороны дефектов.