

## THE RELATIONSHIP BETWEEN THE STRUCTURES OF Cu(II) COMPLEXES AND THEIR CHEMICAL TRANSFORMATIONS

### (II) THE QUESTION OF THE RELATIONSHIP BETWEEN THE STRUCTURES OF COPPER(II) SULPHATE HYDRATES AND THE KINETICS OF THEIR THERMAL DECOMPOSITIONS

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The paper reports an attempt to correlate the structures of hydrates of copper(II) sulphate with some characteristic features of the kinetics of their thermal decompositions. Non-isothermal thermogravimetric measurements were employed to obtain values of experimental activation energy and entropy for the dehydration of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  and  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . The values of  $E^*$  and  $\Delta S^*$  for the dehydration of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  were found to be only little affected by the mode of preparation of this compound. On the other hand, the values of  $E^*$  and  $\Delta S^*$  for the dehydration of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  are strongly dependent on whether this compound was prepared by thermal decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  or  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ , or by crystallization from solution. As regards the crystalline hydrates of copper(II) sulphate, the greatest energetic hindrance for dehydration was observed for  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ . The experimental results are also discussed with respect to the present opinions concerning the possibilities of using thermal analyses to obtain information on the relationship between the structures and reactivities of solids.

At present, ever greater attention is being paid to the study of the relationship between the structures of coordination compounds and the courses of their thermal decompositions. It is becoming increasingly clear that thermal analysis methods can contribute considerably to the knowledge of the overall energetics of reactions induced by heat [1]. The courses of thermal decomposition reactions have also been found to be markedly affected by the crystal and molecular structures of the complexes undergoing decomposition [2, 3] up to the present, however, the opinions in the literature regarding the physical meanings of some currently-used terms, such as thermal stability, decomposition temperature, etc., have been somewhat different [4, 5]. Frequently, though not quite rightly, the kinetics and stoichiometries of thermal decomposition reactions are brought into relationship with the strengths of the bonds between the central atoms and the ligands. The facts that the bonds in coordination compounds are not isolated entities, and that the breaking of some bonds most often involves a total rearrangement of the crystal and molecular structures are then neglected.

The aim of this study was to investigate the influence of the structures of the starting compounds and of the thermal decomposition products on the activation energy and the decomposition reaction entropy values. The hydrates of copper(II) sulphate were chosen for study. The thermal decomposition intermediates of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , viz. the trihydrate and the monohydrate of copper(II) sulphate, after being cooled to room temperature, were found to exhibit the same molecular and crystal structures [6] as compounds of the same compositions, but prepared by other processes. It therefore appeared interesting to investigate whether the activation energy and entropy values of the dehydration reactions of these compounds are also the same.

### Experimental

#### Chemicals

$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , twice recrystallized; concentrated  $\text{H}_2\text{SO}_4$ , p.a.; methanol, p.a., all products of Czechoslovakian companies.

#### Synthesis and analytical methods

The compounds under investigation were prepared and analyzed as given in paper [6].

#### Apparatus and measurements

Thermogravimetric curves were obtained with an OD 102 derivatograph (MOM, Budapest). Platinum crucibles supplied with the apparatus, with an upper diameter of 14 mm, were used. Temperature was measured with Pt/Pt-Rh thermocouples.

Table 1

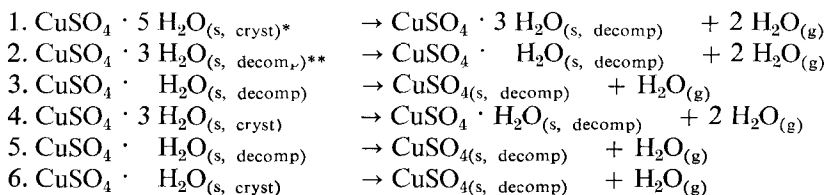
Values of the correlation coefficients of the dependence of  $y = f(1/T)$  [7] for different values of the apparent reaction order

Reaction No	Apparent reaction order	Correlation coefficient	Reaction No	Apparent reaction order	Correlation coefficient
1	1/3	0.992	4	1/3	0.965
	1/2	0.994		1/2	0.971
	2/3	0.997		2/3	0.975
2	1	0.999	5	1	0.986
	1/3	0.923		1/3	0.963
	2/3	0.940		1/2	0.971
	1/2	0.932		2/3	0.978
3	1	0.954	6	1	0.988
	1/3	0.957		1/3	0.982
	1/2	0.965		1/2	0.987
	2/3	0.972		2/3	0.992
	1	0.985		1	0.997

Before measurements, the samples were finely ground in an agate dish. They had a weight of 100 mg. The temperature was increased at a rate of  $3^\circ \cdot \text{min}^{-1}$  in an air atmosphere. The thermogravimetric curves were evaluated by the Coats – Redfern method [7]. The reaction order was chosen so that the dependence  $y = f(1/T)$  should be as close as possible to linearity. The values of  $y$  computed from experimental data were correlated with  $1/T$  using the least squares method. Computation of  $E^*$  was carried out *via* the slope of the straight line the correlation coefficient  $r$  of which was nearest to value 1. The value of the correlation coefficient  $r$  for all investigated reactions is nearest to one if the reaction order is one (Table 1). The method applied also allows computation of the preexponential factor in the Arrhenius equation, and hence the activation entropy [8].

### Results and discussion

Experimental data on the kinetics of thermal decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  were previously obtained mainly under isothermal conditions, and emphasis was laid on the study of the influence of the experimental conditions [9, 10]. The values of  $E^*$  determined for the decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  to  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  were in the range  $40 - 80 \text{ kJ} \cdot \text{mole}^{-1}$  [9]. The activation energy of the decomposition of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  according to [11] is  $67 \text{ kJ} \cdot \text{mole}^{-1}$ . The values of experimental activation energies for the different steps of thermal decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  under dynamic conditions [3] are far higher than those obtained for isothermal processes. Since the values of  $E^*$  are generally influenced considerably by the experimental conditions, it appeared necessary to determine these values for the following reactions:



The experimental values listed in Table 2 for the activation energies and entropies of the investigated reactions are the averages of at least five measurements. (The numbers of the reaction in Tables 1 and 2 are identical with the above reaction numbers.) The experimental values of activation energies determined in this study are higher than the  $E^*$  values determined under isothermal conditions and in vacuum [9, 10]; however, they are lower than those obtained in paper [3].

\* (s, cryst) = substance prepared by crystallization from solution.

\*\* (s, decomp) = substance prepared by thermal decomposition of copper(II) sulphate with a higher water content.

Table 2

Experimental values of activation energies and entropies for the studied dehydration reactions

Reaction No	$E^*$ kJ·mol <sup>-1</sup>	$S^*$ J·mol <sup>-1</sup> ·K <sup>-1</sup>
1	124.9 ± 5.8	7.4 ± 1.5
2	235.4 ± 9.4	40.2 ± 1.5
3	216.9 ± 10.1	16.5 ± 2.8
4	198.8 ± 5.3	40.9 ± 2.9
5	244.7 ± 16.9	34.9 ± 4.1
6	126.8 ± 5.5	6.7 ± 1.3

In the dehydration of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  under the experimental conditions applied here, the first definite intermediate formed was  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ . On cooling to laboratory temperature, this compound exhibits the same crystal and molecular structures as  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  obtained by crystallization from solution [6]. It has been suggested that in the thermal decomposition process this compound is formed first in the amorphous form, and then undergoes recrystallization [10]. However, it was found that in the dynamic atmosphere of air the crystalline product is formed directly. On comparing the values of  $E^*$  and  $\Delta S^*$  determined for the dehydration of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  (reactions 2 and 4), it is clearly seen that these values are very close to each other, i.e. they are practically independent of the mode of preparation. These results are in good agreement with those presented in [12], since it is known that the activation energy values also depend on whether the substance undergoing thermal decomposition is crystalline or amorphous [9]. On the other hand, the values of  $E^*$  and  $\Delta S^*$  for the dehydration of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  are considerably higher than those for the decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ . This fact is suggested to be connected with the structure of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  and with the changes occurring in the structure of the compound during its dehydration. In the coordination polyhedron of Cu(II) in  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ , the distance the copper from the oxygen of two coordinated water molecules is longer than that from the oxygen of the third coordinated water molecule, this one forming two hydrogen-bonds to oxygen atoms from the sulphate groups [13]. Thus, it may be expected that in the discussed reaction those water molecules are released which are linked to the central atom by longer bonds. However, these bonds are probably shorter than the Cu–H<sub>2</sub>O bond which breaks (together with loss of the uncoordinated water molecule) in the decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  [14]. The high value of the activation entropy for the decomposition of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  also points to the fact that the reaction is connected with marked structural changes of the coordination polyhedron and of the entire crystal structure of the compound in the formation of the activated complex.

For the activation energy and entropy of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  dehydration, three values were obtained (Table 2, reactions 3, 5 and 6). The values of  $E^*$  for reactions 3 and 5 are practically equal, within the values of the standard deviations, but those of the

activation entropies differ considerably. As compared with the values of  $E^*$  and  $\Delta S^*$  for reactions 3 and 5, the experimental activation energy and entropy for reaction 6 (decomposition of crystalline  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ ) are far lower. Therefore, it is concluded that  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  formed in the thermal decomposition process is more or less amorphous, and undergoes recrystallization before its further dehydration. These results show agreement with those in paper [10]. The higher value of  $E^*$  for reactions 3 and 5 may then be explained by the suggestion that it also involves the activation energy of recrystallization of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . The different values of the activation entropy for reactions 3, 5 and 6, obtained from the values of the pre-exponential factor in the Arrhenius equation, indicate that preparation of the monohydrate of copper(II) sulphate in different ways leads to differing presuppositions for the course of the dehydration reaction.

Comparison of the  $E^*$  values for decomposition of copper(II) sulphate hydrates prepared by crystallization from solution shows the highest  $E^*$  value to be found for the decomposition of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ . The formation of this compound as an intermediate of thermal decomposition of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  was doubted for a long time. The suggestion was that, in those cases when its formation was observed, this was due to rehydration of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Qualitative experiments showed, however, that this compound, differently from  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$ , was no longer hygroscopic. The fact that under certain experimental conditions (high heating rate, low tension of water vapour) the formation of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  was not observed, is probably connected with the circumstance that the temperature region for existence of  $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O}$  may overlap that in which dehydration of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  takes place. The low experimental values of activation energy and entropy for crystalline  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  are to a certain extent unexpected (reaction 6), for a considerable thermal stability has been assigned to this compound [15, 16]. In connection with this term, it is often discussed whether the decomposition temperature, mostly used as a measure of the "thermal stability" of a compound, reflects its kinetic inertness or its thermodynamic stability [4, 5]. The decomposition temperature is interpreted as the temperature at which a given experimental apparatus allows the decomposition rate to be registered [5]; however, the decomposition temperature is often brought into connection too with the strengths of the bonds between the central atom and the ligands [17]. In our opinion, the decomposition temperature may be interpreted as that temperature at which a given apparatus and given experimental conditions reveal some loss in weight caused by breaking of the bonds between the central atom and the volatile ligand, or by decomposition of the ligand itself. Thus, the decomposition temperature depends both on the kinetic inertness and on the thermodynamic stability of the compound undergoing decomposition under the given experimental conditions.

Quite often the value of the activation energy is taken as a measure of the strength of the bond between the central atom and the ligand [18], when the energetic hindrance of a reaction is assumed to depend mainly on the energies of breaking and formation of bonds. Using as example the experimental activation energies of the decomposition of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , it can be shown that this is not always right.

It was found that the bonding type of the water molecule in this compound does not depend on its mode of preparation [6]. Nevertheless, different  $E^*$  values were found for the decomposition of  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ , depending on its preparation mode. In this case the experimental values of the activation energies are affected by the overall state of the system, and do not reflect the central atom–ligand bond strength. Evaluation of the thermal stabilities of the hydrates of copper(II) sulphate by means of their decomposition temperatures (under the same conditions) shows  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  to have the greatest thermal stability, without respect to its preparation mode. From this standpoint the decomposition temperature appears to be a more reliable measure of the thermal stability of a compound than its activation energy, though the absolute value of the decomposition temperature also depends on the experimental conditions.

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RÉSUMÉ — L'article décrit l'étude effectuée dans le but de corrélérer la structure des hydrates du sulfate de cuivre (II) aux particularités de la cinétique de leur décomposition thermique. A partir de mesures thermogravimétriques non-isothermes, on a obtenu des données expérimentales sur l'énergie d'activation et l'entropie de la déshydratation de  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  et  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . On a trouvé que les valeurs d' $E^*$  et  $S^*$  de la déshydratation de  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  n'étaient que peu influencées par le mode de préparation de ce composé. Par contre, les valeurs d' $E^*$  et  $S^*$  de la déshydratation de  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  dépendent essentiellement du fait que l'échantillon qui subit la décomposition a été préparé par décomposition thermique de  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  ou  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , ou bien par cristallisation à partir d'une solution. On discute les résultats expérimentaux en considérant aussi les opinions actuelles sur les possibilités de l'analyse thermique pour obtenir des renseignements sur les relations entre la structure et la réactivité des corps solides.

ZUSAMMENFASSUNG — Der Beitrag berichtet über den Versuch die Struktur der Hydrate von Kupfer(II)sulfat mit einigen charakteristischen Beschaffenheiten der Kinetik ihrer thermischen Zersetzung in Zusammenhang zu bringen. Unter Einsatz nicht-isothermer thermogravimetrischer Messungen wurden die experimentellen Aktivierungsenergie- und Entropiewerte für die Dehydratisierung von  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  und  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  erhalten. Es wurde gefunden, daß die Werte der Dehydratisierung von  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  ( $E^*$  und  $S^*$ ) von der Art der Herstellung dieser Verbindung nur wenig beeinflußt werden. Andererseits sind diese Werte ausdrücklich davon abhängig, ob diese sich zersetzende Verbindung durch thermische Zersetzung von  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  oder  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ , oder durch Kristall aus einer Lösung hergestellt worden war. Von den kristallinen Hydraten des Kupfer(II)sulfat wurde das größte energetische Hindernis der Dehydratisierung bei  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  beobachtet. Die Versuchsergebnisse werden auch hinsichtlich der gegenwärtigen Meinungen betreffs Möglichkeiten der thermischen Analysen zum Erhalt von Informationen über die Zusammenhänge zwischen Struktur und Reaktivität von Festkörpern erörtert.

Резюме — В статье приведены попытки корреляции структуры гидратов сульфата меди(II) с некоторыми характерными особенностями кинетики их термического разложения. Используя для этой цели неизотермические термогравиметрические измерения, были получены экспериментальные энергия активации и энтропия дегидратации  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  и  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ . Найдено, что значения  $E^*$  и  $\Delta S^*$  дегидратации  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  в очень малой степени зависят от способа получения этого соединения. Однако, значения  $E^*$  и  $\Delta S^*$  процесса дегидратации  $\text{CuSO}_4 \cdot \text{H}_2\text{O}$  явно зависят от того что это соединение получено термическим разложением  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  или  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  или же кристаллизацией из раствора. Среди исследованных кристаллогидратов сульфата меди(II) наиболее энергетическое препятствие дегидратации отмечено для  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ . Экспериментальные результаты обсуждены в отношении существующих мнений, касающихся возможностей термического анализа в получении информации о взаимосвязи между структурой и реакционной способностью твердых веществ.