# NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3263—3264 (1970)

## Some Thermal Properties of Deuterated Copper(II) Sulfate Pentahydrate

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(Received October 25, 1969)

Few papers can be found on the thermal behavior of the deuterated copper(II) sulfate pentahydrates except for that by Heinzinger and Rao,[1] who pointed out that the ratio of the quantity of the deuterium to that of hydrogen gradually increased as dehydration proceeded in partially deuterated copper(II) sulfate pentahydrates. The effect of deuteration in copper(II) salt hydrates upon thermochemical functions has been fully investigated so far.

The present work was undertaken to determine the thermochemical functions in the dehydration of copper(II) sulfate pentahydrates deuterated to different extents in order to find difference in thermal properties of hydrates.

### Experimental

**Preparation.** Copper(II) sulfate pentahydrates, $CuSO_4 \cdot 4H_2O \cdot D_2O$, $CuSO_4 \cdot 3H_2O \cdot 2D_2O$, $CuSO_4 \cdot 2H_2O \cdot 3D_2O$, $CuSO_4 \cdot H_2O \cdot 4D_2O$ and $CuSO_4 \cdot 5D_2O$ deuterated to different extents, were prepared according to the following schemes:

$$CuSO_4 \cdot 5H_2O \xrightarrow{50^\circ C} CuSO_4 \cdot 3H_2O \xrightarrow{D_2O} CuSO_4 \cdot 3H_2O \cdot 2D_2O$$

$$CuSO_4 \cdot 5H_2O \xrightarrow{150^\circ C} CuSO_4 \cdot H_2O \xrightarrow{D_2O} CuSO_4 \cdot H_2O \cdot 4D_2O$$

$$CuSO_4 \cdot 5H_2O \xrightarrow{260^\circ C} CuSO_4 \xrightarrow{D_2O} CuSO_4 \cdot 5D_2O$$

$$CuSO_4 \cdot 5D_2O \xrightarrow{53^\circ C} CuSO_4 \cdot 3D_2O \xrightarrow{H_2O} CuSO_4 \cdot 2H_2O \cdot 3D_2O$$

$$CuSO_4 \cdot 5D_2O \xrightarrow{150^\circ C} CuSO_4 \cdot D_2O \xrightarrow{H_2O} CuSO_4 \cdot 4H_2O \cdot D_2O$$

Each formula is reasonable for the preparation of respective hydrates.

Heavy water from Merck Co., Germany was used.

**Measurements.** Thermal analysis was carried out with a Metrimpex Derivatograph MOM Type-OD-102 made in Hungary, and the enthalpy changes and the activation energies on each step of dehydration were calculated by analyzing the DTA curves in the same manner as described previously.[2]

Infrared absorption spectra of these salts were measured in the Nujol mull state with a Nippon-Bunko DS-301 IR-Spectrophotometer. The X-ray powder patterns were obtained with a Rigaku-Denki Geiger-Flex X-ray Analyser.

### Results and Discussion

**Thermal Analyses.** Dehydration of copper(II) sulfate pentahydrate and those deuterated partially or completely was found by derivatography to proceed in the following three distinct steps: the first and the second steps indicate liberation of each two moles of water from the hydrates and the DTA peaks in both steps are, to some extent, overlapped. The third one corresponds to the liberation of the last one mole of water.

The values of the weight loss percent due to the liberation of all the five moles of water determined from the derivatograms for the hydrates and the corresponding values calculated on the basis of each formula are listed in the second column of Table 1, together with the thermochemical data. We see that the above values of the two groups are almost consistent with each other in the respective hydrates. This supports the validity of the formulas for the hydrates.

The temperatures at which dehydration begins to take place are given in the third column of Table 1, where the values under I, II, and III deal with the first, second and third steps of dehydration, respectively. The activation energies, $E^*$, and enthalpy changes, $\Delta H$, calculated by

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1) K. Heinzinger and T. S. Rao, *Z. Naturforschg.*, **22a**, 2111 (1967).

2) R. Tsuchiya, Y. Kaji, A. Uehara and E. Kyuno, This Bulletin, **42**, 1881 (1969).

Table 1. Thermal data for the deuterated copper(II) sulfate pentahydrates

| | Total weight loss | | The dehydration temperature (°C) | | | Activation energy $E^*$ (kcal/mol) | | | Enthalpy change $\Delta H$ (kcal/mol) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | obsd (%) | calcd (%) | I | II | III | I | II | III | I | II | III |
| $CuSO_4 \cdot 5H_2O$ | 36.0 | 36.1 | 45 | 82 | 201 | 19 | 45 | 30 | 14 | 14 | 17 |
| $CuSO_4 \cdot 4H_2O \cdot D_2O$ | 36.6 | 36.6 | 45 | 82 | 212 | 21 | 44 | 49 | 14 | 14 | 17 |
| $CuSO_4 \cdot 3H_2O \cdot 2D_2O$ | 37.0 | 37.1 | 49 | 82 | 213 | 24 | 44 | 47 | 14 | 14 | 17 |
| $CuSO_4 \cdot 2H_2O \cdot 3D_2O$ | 37.5 | 37.6 | 52 | 83 | 212 | 26 | 43 | 48 | 14 | 14 | 17 |
| $CuSO_4 \cdot H_2O \cdot 4D_2O$ | 38.0 | 38.0 | 53 | 82 | 214 | 29 | 43 | 53 | 14 | 14 | 17 |
| $CuSO_4 \cdot 5D_2O$ | 38.6 | 38.5 | 55 | 84 | 214 | 33 | 43 | 53 | 14 | 14 | 17 |

analyzing the DTA curves are also included in both the forth and fifth columns of Table 1.

From these values the following information can be obtained. The temperatures at which the first step of dehydration begins are gradually elevated as the ratio of amounts of heavy water to those of ordinary water contained increases in the series of the hydrates except for $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 4H_2O \cdot D_2O$ which have comparable data with each other, and the activation energies thereof also increase more and more in the same order. The results suggest that the liberation of ordinary water predominates in the first step of dehydration in both $CuSO_4 \cdot 5H_2O$ and $CuSO_4 \cdot 4H_2O \cdot D_2O$, whereas the ratio of heavy water against ordinary water liberated in the dehydration step becomes progressively greater in the order of $CuSO_4 \cdot 3H_2O \cdot 2D_2O$ through $CuSO_4 \cdot 5D_2O$.

On the other hand, the corresponding temperatures and the activation energies in the second step of dehydration are not so remarkably different from each other. The reason is not clear because of the ambiguity in the structure of each intermediate hydrates.

In the last step, the temperatures and activation energies of dehydration do not differ from each other as remarkably as in the first step, except for the especially smaller values for $CuSO_4 \cdot 5H_2O$. The results can be explained by assuming that the last one mole of water liberated is that of ordinary water in $CuSO_4 \cdot 5H_2O$, whereas in other hydrates, the last one mainly consists of heavy water, because the contribution of heavy water on dehydration becomes larger in the order of $CuSO_4 \cdot 4H_2O \cdot D_2O$ through $CuSO_4 \cdot 5D_2O$.

The enthalpy changes of dehydration do not differ sufficiently from each other in each step to give data for a discussion on dehydration.

**X-Ray Powder Pattern.** The X-ray powder patterns in several, stepwise deuterated copper sulfate pentahydrates were compared with each other in order to determine whether or not the structures of the salts differ depending upon the ratio of the amounts of heavy water to ordinary water. Their patterns are almost the same, however, and it seems that there is no appreciable structure deformation from the original according to the replacement of water by heavy water.

**Infrared Absorption Spectra.** Infrared absorption spectra of these copper(II) sulfate pentahydrates are shown Fig. 1. Despite the fact that the X-ray diffraction patterns of the sulfates are almost the same, the splitting of IR band assigned to $SO_4$ asymmetric vibration is complicated in the cases of $CuSO_4 \cdot 2H_2O \cdot 3D_2O$ and $CuSO_4 \cdot 3H_2O \cdot 2D_2O$. The reason is not clear. The ratio of the wave number of the absorption peak measured as the assignment to the stretching vibration of OH (3280 $cm^{-1}$) against that of OD (2410 $cm^{-1}$) was calculated to be 1.36, which is in good agreement with that generally accepted.

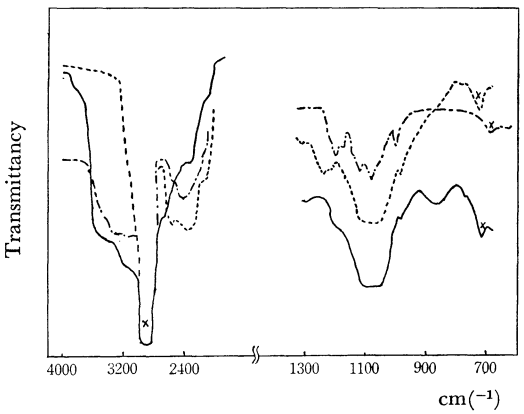


Fig. 1. IR-spectra of $CuSO_4$–$5H_2O$ (———), $CuSO_4 \cdot 2H_2O \cdot 3D_2O$ (— — —) and $CuSO_4 \cdot 5D_2O$ (– – – – –). × is absorption of nujol.