Deuterium and Oxygen-18 Tracer Study of the Dehydration and the Hydration of Copper Sulfate

By Nobukazu OKAZAKI, Akiko OKUMURA and Keiko NAKAGAWA

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In a tracer study of dehydration and hydration of oxalic acid[1], it has been shown that amorphous anhydrous acid results from the dehydration of dihydrate in vacuo at low temperatures. The highly dispersed character of the dehydration product reveals itself in its increased degrees of deuterium exchange with heavy water vapor as compared with the crystalline anhydrous acid. It seems desirable to check this relation between the degree of deuterium exchange and surface area of the dehydration product with the hydrate whose dehydration product in vacuo at low temperatures is definitely known to be amorphous. As a hydrate of this kind, copper sulfate[2] was chosen as the subject of the present study.

There are a few reports of deuterium tracer study on the hydrate water of copper sulfate. Menzies and Miles[3] have found complete exchange of deuterium between water vapour and monohydrate in the course of its hydration and the subsequent dehydration of the product. In a work by Briscoe et al.[4], anhydrous copper sulfate was hydrated with heavy water to give monohydrate, and then with ordinary water to pentahydrate. On dehydrating the pentahydrate, they have found an interchange of deuterium between the fifth and the remaining four molecules of the hydrate water.

Since, as is well-known, the fifth water molecule is firmly held by copper sulfate, it seems interesting to see whether there is ready interchange of water molecules between monohydrate and water vapor. But, as it has been shown[1] that the interchange of proton occurs between anhydrous oxalic acid and water vapor, it seems possible that, in the above experiments with copper sulfate, the interchange of proton might occur independently of the interchange of water molecules as a whole between monohydrate and water. Therefore, the oxygen exchange between copper sulfate monohydrate and water vapor enriched in heavy oxygen has been studied at the same time.

Experimental

Experimental procedures were almost the same as those described in the previous paper[1]. The water enriched in heavy oxygen used in the earlier part of this study was kindly supplied by Professor N. Morita of Nagoya University. Later, it was obtained from a fractionating column of this laboratory, and had excess density due to heavy oxygen of about 600 γ. The deuterium content of the heavy water was normalized by repeated exchange with ammonium chloride. Copper sulfate monohydrate was prepared by dehydration of pentahydrate (special grade). Two kinds of samples of monohydrate were used; (1) amorphous monohydrate which was prepared by dehydration in vacuo at 35°C, and (2) crystalline monohydrate prepared by dehydration at 105 ± 5°C under atmospheric pressure to constant weight[2]. The monohydrate was hydrated with about 1 g. of heavy water vapor, whose pressure was kept higher than the dissociation pressure of pentahydrate at the temperatures of the experiments. Various conditions of the temperature of the monohydrate and the pressure of water vapor were tried. The time required for the completion of hydration varied from a few hours to several days according to the condition chosen, but it did not affect the result of the exchange reaction. After the completion of the hydration, the hydrated product was redehydrated in vacuo at 35°C, and the water obtained was analyzed for its isotopic content by the floatation method. The time required for redehydration ranged from a few to several days. In general, the hydrate from the amorphous monohydrate decomposed more slowly than that from the crystalline monohydrate.

Results and Discussion

The results are shown in Fig. 1, in which the degree of exchange $\Delta D/D$ is plotted against the molar ratio of the reactants M/M_w (ΔD is the decrease of deuterium content of water in the course of hydration of monohydrate and subsequent redehydration of the product, D is the deuterium content of heavy water obtained on redehydration, and M and M_w are the numbers of moles of copper sulfate and heavy water used for the reaction).

In the region for which the values of the

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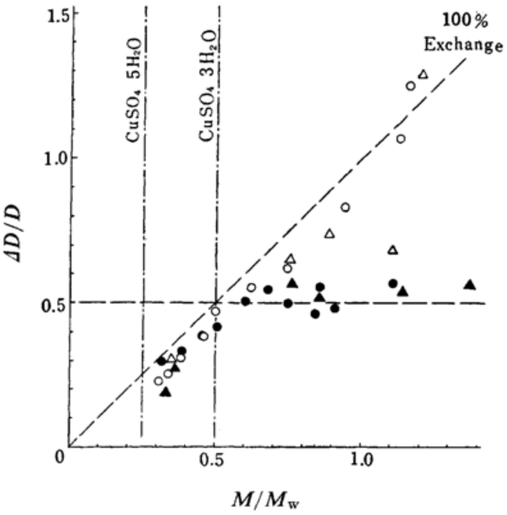

Fig. 1. Deuterium and oxygen-18 exchange reaction between amorphous and crystalline copper sulfate monohydrate and water. Deuterium exchange: ●; crystalline, ○; amorphous. Oxygen exchange: ▲; crystalline, △; amorphous

molar ratio M/M_w are greater than 0.5, increased exchangeability of amorphous monohydrate over that of crystalline monohydrate may be seen from the figure. The effect is similar to that observed with oxalic acid, and supports the suggestion of the previous report concerning the formation of highly dispersed anhydrous acid in the dehydration of oxalic acid dihydrate in vacuo and the relation of the deuterium exchange reaction to the surface area of the dehydration product.

In this molar ratio region, the values of $\Delta D/D$ for the crystalline monohydrate are almost constant ($\fallingdotseq 0.5$) independently of the value of the molar ratio. This implies that the monohydrate and heavy water vapor react in a constant proportion irrespective of the presence of the excess of the former, and it leads to the conclusion that the exchange reaction is associated with hydrate formation[1]. The value of the molar ratio M'/M_w is given by the relation,

$$M'/M_w = (1/k)(\Delta D/D)$$

as 0.5, which corresponds to the composition $CuSO_4 \cdot 3H_2O$ ($CuSO_4 \cdot H_2O : 2H_2O$). That is, exchange reaction of crystalline monohydrate under the given condition proceeds through the formation of trihydrate.

In the molar ratio region corresponding to the compositions between pentahydrate and trihydrate, the two sorts of samples of monohydrate behave similarly toward the deuterium exchange reaction. The values of $\Delta D/D$ in this region correspond to the almost complete equilibration of the monohydrate with heavy water vapor.

In this region, pentahydrate and trihydrate may be expected as the hydration product of the crystalline monohydrate, the deuterium content of the trihydrate being lower than that of the pentahydrate. As an extreme case, if the hydrate water of pentahydrate and that of trihydrate equilibrate with each other in the course of the experiment, the result is the complete equilibration of deuterium between the monohydrate and water vapor. In the case of the other extreme where pentahydrate and trihydrate are dehydrated independently without exchanging their deuterium atoms with each other, it may be easily shown by calculation that, though the value of $\Delta D/D$ is slightly lower than that of the complete equilibration, the difference is well within the range of experimental errors. Thus, if pentahydrate and trihydrate are formed as the product of hydration, the results are always the nearly complete equilibration of monohydrate with the water vapor, which may also be expected for amorphous monohydrate.

If, on the other hand, the pentahydrate alone was formed in this molar ratio region, the values of $\Delta D/D$ should be 0.25, irrespective of the values of the molar ratio, which is contrary to the results. Thus, the exchange reaction may be used to determine the composition of the hydrate formed on hydrating an anhydrate or a lower hydrate, provided that the anhydrate has an exchangeable hydrogen atom.

The increased exchangeability of amorphous monohydrate as compared with crystalline monohydrate is due to the exchange reaction between surface molecules and adsorbed water, as in the case of oxalic acid. The fractions of the amorphous monohydrate which takes part in the exchange reaction to the total amount used are calculated by the relation[1],

$$M'/M = (1/k)(\Delta D/D)/(M/M_w)$$

to be 0.75~1.08. The corresponding values obtained with oxalic acid are 0.71~0.85.

The molar ratio of the monohydrate in the surface as defined by the deuterium exchange reaction to the monohydrate of the bulk may be calculated by the relation[1],

$$\beta = [(1/k)(\Delta D/D) - x]/[(M/M_w) - x]$$

where x is a constant, which has the value of 0.5 if trihydrate is formed on hydrating the amorphous monohydrate, and of 0.25 if pentahydrate is formed.

Above the value of the molar ratio corresponding to the composition of trihydrate, the dissociation pressure of the partially hydrated amorphous monohydrate is of the order of that of monohydrate in the case of fast hydration, owing probably to the strong adsorptive power of the amorphous monohydrate, and is in the neighborhood of that of trihydrate in the case of slow hydration. It is probable that, in this region, amorphous monohydrate at first absorbs water vapor and subsequently combines with it rather slowly to form trihydrate as hydration product.

The surface to bulk ratios as given by the above relation are now calculated for the five specimens of the amorphous monohydrate whose exchange results are plotted in Fig. 1. The results are 0.44, 0.48, 0.75, 0.91 and 1.10. The values of the ratio obtained with amorphous oxalic acid are 0.60∼0.70(1). These values may compare nearly with each other. This result, together with the similarity of the results of the exchange reaction between oxalic acid and copper sulfate, confirms the view mentioned in the previous report(1) concerning the nature of the dehydration product and the relation between the degree of deuterium exchange and surface area of the product.

The results of oxygen exchange reaction are the same in essentials as those of deuterium exchange reaction. It may be concluded that interchange of water molecules as well as of protons occurs in the course of the hydration of monohydrate with heavy water vapor and subsequent dehydration of the product. Accordingly, in the dehydration of copper sulfate pentahydrate, the fifth water molecule is interchangeable with the remaining four. The discussions of the previous(1) and the present papers, concerning the nature of the dehydration products, the relation of the exchange reaction to the surface area of the dehydration products, and the mechanisms of the exchange reaction, are applicable with necessary change to the oxygen exchange reaction.

Summary

The deuterium and oxygen-18 exchange reaction of amorphous and crystalline copper sulfate monohydrate with water in the course of the hydration of the monohydrate with heavy water vapor and the subsequent dehydration of the product has been studied.

The exchange reaction of crystalline monohydrate is associated with the formation of hydrate. Amorphous monohydrate shows an increased degree of exchange over crystalline monohydrate. This increased exchangeability of amorphous monohydrate is due to the exchange reaction between surface molecules and adsorbed water. The similarity of the results of deuterium exchange reaction between oxalic acid and copper sulfate confirms the suggestion of the previous report that anhydrous oxalic acid prepared by dehydration in vacuo at low temperatures is amorphous and the degree of deuterium exchange reaction is related to the surface area of the dehydration product.

The results of the oxygen-18 exchange reaction of copper sulfate monohydrate with water vapor are almost identical in essentials with those of the deuterium exchange reaction. The fifth water molecule of copper sulfate is interchangeable with the other four in the process of dehydration of pentahydrate and the hydration of monohydrate.

Department of Chemistry
Nara Women's University
Nara