Intracrystalline Site Preference of Hydrogen Isotopes in the Water of Crystallization of Copper Sulfate Pentahydrate

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Difference in the isotopic partition at different sites of the water of crystallization of $CuSO_4 \cdot 5H_2O$ (the site preference) was estimated for the hydrogen isotopes. Fractional dehydration of $CuSO_4 \cdot 5H_2O$ under vacuum at 0 and 25 °C was used to determine the isotopic ratio, the amount of dehydrated water, and the rate process of dehydration. The following results were obtained. (1) Two maxima occur in the isotopic ratio in the dehydration range, $F < 0.8$. (2) The dehydration occurs by the three sequential zeroth-order rate processes which have different rate constants for dehydration. The three different rate constants may be explained by the combination of the rate constants of dehydration of the water molecules dehydrated. The estimation of the difference in hydrogen isotope distribution for different sites, i.e., four of the five water molecules in the coordination sphere of copper ion (site A) and one bonded to the sulfate ion through hydrogen bonding (site B) was made. The site preference of hydrogen isotopes (δD, ‰) was concluded to be -32.0 ± 5.2 for site A and $+22.6 \pm 20.9$ for site B, where the δD value was referred to the isotopic ratio of the mother liquor from which the crystal was formed.

Introduction

Intracrystalline site preference of cations was first elucidated by Matsui and Banno[1] in the study of Mg and Fe(II) exchange equilibrium between two silicate solid solutions (cummingtonite and actinolite), where one phase (cummingtonite) has two energetically nonequivalent sites which can accommodate Mg and Fe(II). They found that the bulk Mg–Fe exchange equilibrium constant is a function of the Mg/Fe ratio of the single-site phase (actinolite) and the Mg/Fe ratios of the two sites in cummingtonite are different. They proved that the apparent nonideality occurs even when ideal exchange equilibria are established between actinolite and each of the two sites in cummingtonite.

In some aqueous electrolyte solutions, $^{18}O/^{16}O$ and D/H ratios also differ between "free water" and water in the coordination sphere of cations and anions.[2-7] This effect can be called the intrasolution site preference of isotopes.

Barrer and Denny[8] first measured the dependence of the partition ratio, $\alpha_D = (D/H)_{hydrate}/(D/H)_{mother\ liquor}$, on the D/H ratio of the mother liquor at room temperature for several hydrate–water systems. Although a slight dependence of α_D on the D/H ratio of the mother liquor was observed for some systems, their measurements were too inaccurate to draw any definite conclusion about the isotopic site preference in the water of crystallization. Matsuo et al.[9] could not detect this type of effect on deuterium partitioning for the borax–water system for a narrow range of change in D/H ratio of the mother liquor.

Despite its great importance, intracrystalline site preference of isotopes has been rather poorly explored. Hamza

and Epstein[10] estimated oxygen isotopic fractionation between the OH group and other oxygen sites in hydroxyl-bearing silicate minerals. Heinzinger and Maiwald[11] tried to determine the site preference of hydrogen and oxygen isotopes in the water of crystallization of $CuSO_4 \cdot 5H_2O$ using a single crystal. They applied the fractional dehydration technique and postulated that water molecules in the coordination sphere of the copper ion are first dehydrated and the dehydration of a water molecule bonded to sulfate ion through hydrogen bonding follows. They concluded that D/H of the latter water was higher than D/H of waters coordinated to the copper ion on the basis of the change in D/H ratio of fractionally collected water without considering the mechanism of dehydration.

Copper sulfate pentahydrate is a hydrate whose structure including the positions of hydrogen atoms has been well established.[12,13] It is easy to synthesize, and hydrogen isotopic exchange equilibrium between the hydrate and the mother liquor is also easily attained.[9] Four of the waters of crystallization of copper sulfate pentahydrate are in the coordination sphere of the copper ion (site A), while the remaining one is bonded to sulfate ion through hydrogen bonding (site B),[12,13] and there are two energetically distinguishable sites for hydrogen isotopes.[14] In general, the water of crystallization should be energetically different in different sites of nonequivalent structure. The change in bonding and/or structural situation of the water of crystallization should result in the isotopic site preference.

In this paper, we discuss the site preference of hydrogen isotopes using the fractional dehydration technique. The major differences from the study by Heinzinger[15] are as follows: (1) powdered crystals were used, (2) dehydration was done at comparatively low temperature (0 and 25 °C)

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(13) G. E. Bacon and N. A. Curry, *Proc. R. Soc. London, Ser A*, **266**, 95 (1962).
(14) G. Soda and T. Chiba, *J. Chem. Phys.*, **50**, 439 (1969).
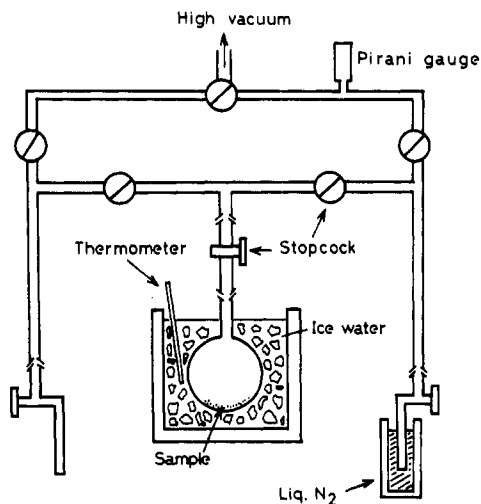(15) K. Heinzinger, *Z. Naturforsch. A*, **24**, 1502 (1969).

Figure 1. System for fractional dehydration used in this study.

Figure 2. Relationship between the fraction of water dehydrated (F) and duration time (t) of dehydration at 0 °C.

with the intention of preventing the possible exchange of water between site A and site B during dehydration, and (3) isotopic data were interpreted by the model for the rate process of dehydration.

Experimental Section

Synthesis of Copper Sulfate Pentahydrate at 25 °C. Reagent $CuSO_4 \cdot 5H_2O$ was pulverized and dissolved in distilled water to prepare a supersaturated solution (15% excess) in a stoppered flask. The flask containing the solution was placed in a water bath at 25 ± 0.1 °C for 3–10 days. The solution was then filtered, and the precipitate was dried by pressing between filter papers. The crystals were stored in an air-tight container.

Measurement of the D/H Ratio for the Bulk Water of Crystallization. The synthesized crystal was powdered just before dehydration. About 20 mg of the powder was put in a dehydration vessel and loaded into the vacuum line. The line was evacuated while the sample was cooled externally by liquid nitrogen. The sample was then warmed gradually and heated to a final temperature of 280 °C. Dehydrated water was converted to hydrogen gas through the reaction with uranium metal at 750 °C. The volume of evolved hydrogen was measured manometrically after complete collection of the gas with a Toepler pump. The D/H ratio of the gas was analyzed on a mass spectrometer with a dual inlet and collector system (Hitachi RMD).

The isotopic ratio was presented in the following form:

$$\delta D(\text{‰}) = \frac{(D/H)_{\text{sample}} - (D/H)_{\text{standard}}}{(D/H)_{\text{standard}}} \times 10^3$$

The D/H ratio of the mother liquor in equilibrium with a crystal of $CuSO_4 \cdot 5H_2O$ was taken as the standard in this paper. The standard deviation of δD measurement was ±1.0‰. δD of the bulk water of crystallization was –21.1‰, i.e., the D/H ratio of the bulk water of crystallization is lower than that of the mother liquor by 21.1‰. The fractionation factor, α, between the bulk water of crystallization and the mother liquor is 0.979 ± 0.001 at 25 °C. This value agrees well with that of Heinzinger.[15]

Fractional Dehydration. The system for fractional dehydration used in this study is shown in Figure 1. $CuSO_4 \cdot 5H_2O$ (synthesized at 25 °C) was pulverized to pass through a 200 mesh sieve, but not to pass through a 270 mesh sieve. A small amount of sample (400–450 mg) was used, and the sample powder was placed thinly on the bottom of a spherical flask to prevent temperature gradients during the dehydration process. The amount of
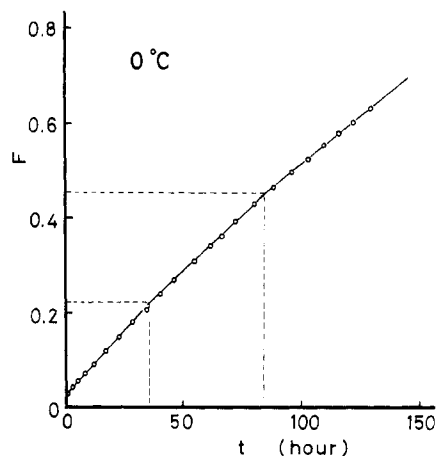
water obtained in a fraction was sometimes as small as 2 mg.

The spherical flask containing the sample powder was cooled by liquid nitrogen and then evacuated completely for 30–60 min to 10^{-3} torr. The flask was then immersed into a water bath at either 0 or 25 °C. It has been reported that, at or below room temperature, dehydration of CuSO$_4 \cdot 5H_2O$ does not give significant self-cooling;[16] thus, we set the starting time for fractional dehydration when the flask was immersed into the water bath. The water collected from each fraction was introduced into the conversion line for reduction to H_2 gas, and the quantity of water in each fraction was measured by the volume of H_2 gas to which the water was completely converted. Then the H_2 gas was introduced to the mass spectrometer to measure the D/H ratio of the water in each fraction. When the fraction of the dehydrated water, F, exceeded 0.8, it was necessary to warm the flask to 280 °C to completely dehydrate the water of crystallization in a reasonable period of time. The total quantity of the dehydrated water averaged to 100.05% of the theoretical value.

Results and Discussion

Results of Fractional Dehydration at 0 °C. The relationship between the fraction of water dehydrated and the duration of dehydration is shown in Figure 2, where F denotes the fraction, i.e., the amount of water dehydrated divided by the initial amount of water of crystallization. Three straight lines are drawn for the ranges, $0.06 < F < 0.23$,[17] $0.23 < F < 0.46$, and $0.46 < F$. This result indicates that dehydration of water from the crystal can be regarded as three zeroth-order rate processes with different rate constants.

The relationship between δD of the water of each fraction and F is reproducible, and a representative result is shown in Figure 3. At $F = 0.06$ and 0.35, maxima of δD occur. Gradual increases and decreases in δD alternate in the ranges, $0 < F < 0.23$ and $0.23 < F < 0.46$. Beyond $F = 0.46$, δD increases without maximum.

If dehydration takes place layer by layer from the surface, δD for the water dehydrated should remain constant because δD should be uniform in the crystal since the δD of the mother liquor was practically constant during crystal growth. The change in powder size (150 and 270 mesh

(16) M. L. Smith and B. Topley, *Proc. R. Soc. London, Ser. A,* **134,** 224 (1932).

(17) A sharp rise of the curve in the initial dehydration stage, $0 < F < 0.06$, has been observed although the actual curve cannot be given in Figure 2.
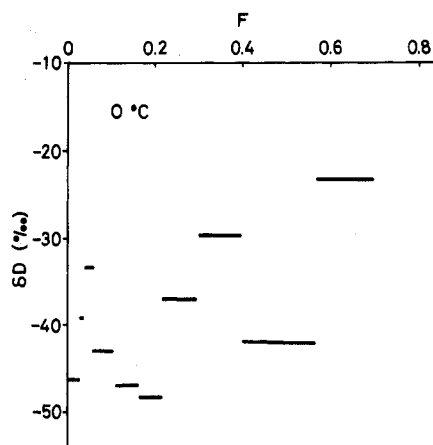
Figure 3. Relationship between δD of the fraction of water dehydrated and the fraction (F) at 0 °C.
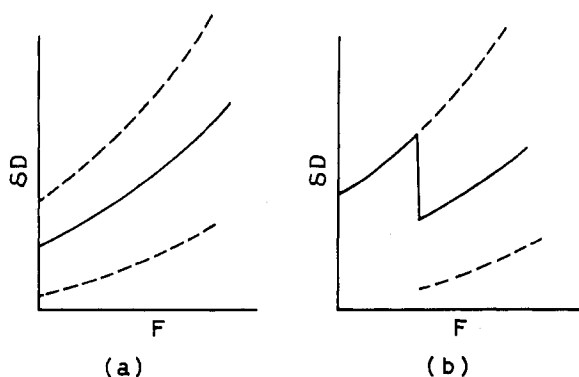

Figure 4. Schematic presentation of the relationship between δD of the water dehydrated and the fraction (F): (a) two species dehydrate simultaneously both by Rayleigh process; (b) retarded dehydration of one of the two species takes place to give a maximum of δD in a certain range.

under) also does not explain the pattern shown in Figure 2. That the rate of dehydration does not depend on the surface area strongly suggests that the dehydration takes place not only from the surface but also from the interior of the crystal randomly. If dehydration takes place randomly by unique mechanism, it can be treated as a "Rayleigh process".

When the water of crystallization is dehydrated, δD of each fraction increases $(\alpha < 1)$[18] or decreases $(\alpha > 1)$ monotonously, if a Rayleigh process prevails. When dehydration from different sites takes place simultaneously with the same starting time, the synthetic relationship should be monotonous as schematically exemplified in Figure 4a. On the other hand, when dehydration occurs from the different sites with different starting times, the synthetic relationship should not be monotonous. One special example is shown in Figure 4b, where the maxmum of δD appears, even though dehydration from the two sites is governed by Rayleigh processes.

Mechanism of Dehydration. The crystal structures of pentahydrate V and trihydrate III are precisely known from the X-ray diffraction studies by Beevers and Lipson[12] and by Zahrobsky and Baur,[19] respectively. It is assumed that the structure of tetrahydrate IV is the same as that of site A of pentahydrate V. The structure of the surroundings of the Cu^{2+} ion in the trihydrate III contains three molecules of the water originally in the tetrahydrate
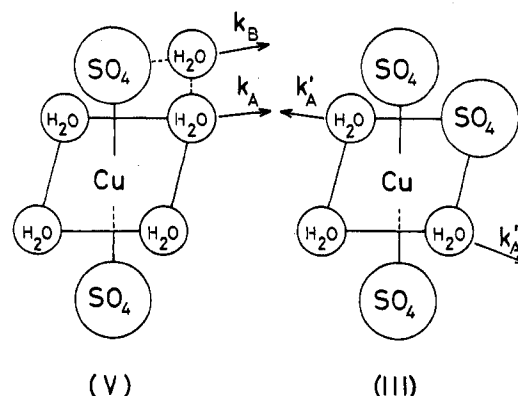
(18) $\alpha = (D/H)_{dehydrated\ water}/(D/H)_{remaining\ water}$.
(19) R. F. Zahrobsky and W. H. Baur, *Acta Crystallogr.*, Sect. B, **24**, 508 (1968).

Figure 5. Structure of the species assumed to exist in the process of dehydration.

and a sulfate ion rearranged as shown in Figure 5.

The dehydration process is postulated to occur as follows in order to explain the dehydration patterns shown in Figures 2 and 3.

(1) One water molecule in site B of V is dehydrated first, since dehydration rate changes at about $F = 0.2$ which corresponds to the amount of one of five water molecules. The rate constant for dehydration of V[20] is presented by k_B (Figure 5).

(2) That the change in dehydration rate takes place not at $F = 0.20$ but at $F = 0.23$, and a maximum of δD occurs in the range $0 < F < 0.23$ imply that IV[20] also dehydrates before dehydration of site B water is completed. In other words, delayed dehydration of one water molecule from site A of V occurs simultaneously with the dehydration of one water molecule from site B. The rate constant for dehydration of IV is presented by k_A (Figure 5).

(3) Since the dehydration rate changes at $F = 0.46$ and only one maximum of δD is observed in the range $0.23 < F < 0.46$, dehydration of III which was accumulated by the dehydration of IV up to $F = 0.23$ must also be occurring in this range in addition to that of IV. After dehydration of V is completed at $F = 0.23$, III starts to dehydrate independently of IV.

III dehydrates directly to the monohydrate I since if the intermediate phase, dihydrate, were to be formed during dehydration, not two but three changes of dehydration rate and maxima of δD should be observed through the range $0 < F < 0.8$. Therefore, we assume that either two molecules of water dehydrate simultaneously during the change from III to I or the residence time of dihydrate is quite short under these conditions. The rate constant for dehydration from III is presented by k_A' (Figure 5).

The structure of III is derived after one of four water molecules in IV is dehydrated and the oxygen of the sulfate ion in the neighboring position is rearranged to move into the vacant position. It is probable that, in III, the two water molecules adjacent to the SO_4^{2-} ion are subject to steric hindrance or a pushing effect which causes them to be dehydrated simultaneously. For this reason, k_A' is expected to be slightly larger than k_A.

When the III which is dehydrated independently of the dehydration of IV has been completely dehydrated, the remaining species which have not been dehydrated are IV and I. In the range, $0.46 < F < 0.8$, dehydration of III depends on the dehydration of IV, since III cannot be dehydrated if III is not generated by the dehydration of IV. Accordingly, the dehydration rate, k_A, of IV may be

(20) In our model, dehydration from V and IV means that one water molecule dehydrates from site B of V (dehydration of V), and one water molecule dehydrates from site A of V (dehydration of IV).
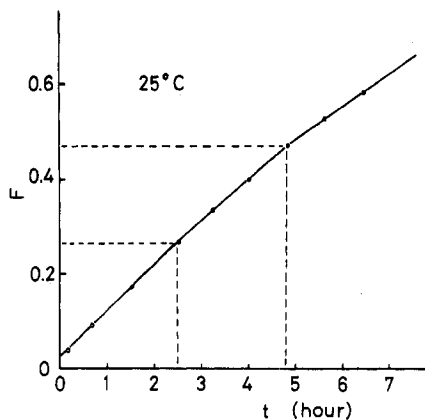
Figure 6. Relationship between the fraction of water dehydrated and duration time of dehydration at 25 °C.

Figure 7. Relationship between δD of the fraction of water dehydrated and the fraction (F) at 25 °C.

rate determining, and III dehydrates immediately after dehydration of IV. Apparently, IV may change to I with the rate constant, $3k_A$ directly.

(4) From the facts that dehydration beyond $F = 0.8$ does not take place and that δD increases without maximum beyond $F = 0.46$, I may not be dehydrated at 0 °C, viz., I is virtually inert to dehydration under the dehydration conditions applied in this study.

(5) Dehydration from all chemical species existing in the process of dehydration may take place by the zeroth-order reaction because, as shown in Figure 2, linear relationships exist between F and the time (t). Simultaneous zeroth-order reactions give an apparent zeroth-order reaction.

On the basis of the above postulates, the dehydraton rates (dF/dt) at 0 °C in the ranges mentioned already may be presented as follows:

$$dF/dt = k_B + k_A \qquad (0.06 < F < 0.23) \qquad (1)$$

$$dF/dT = k_A + 2k_A' \qquad (0.23 < F < 0.46) \qquad (2)^{[21]}$$

$$dF/dt = 3k_A \qquad (0.46 < F < 0.80) \qquad (3)$$

$$dF/dt = 0 \qquad (0.80 < F) \qquad (4)$$

If slopes of the straight lines in the ranges $0.06 < F < 0.23$, $0.23 < F < 0.46$, and $0.46 < F$ are measured, it is possible to calculate k_B, k_A, and k_A' by combining eq 1–3. The results of the calculation of rate constants of dehydration at 0 °C are $k_B = 3.96 \times 10^{-3}$ h^{-1}, $k_A = 1.40 \times 10^{-3}$ h^{-1}, $k_A' = 1.75 \times 10^{-3}$ h^{-1}, $k_B/(k_B + k_A) = 0.739$, and $k_A/(k_A + 2k_A') = 0.286$. It should be emphasized that both of the rate constants for dehydration and the ratios of those between different species are constant even when the grain size was changed. Though, generally, zeroth-order reaction may be regarded as the reaction at which rate is determined by the surface area of crystal, this fact suggests another mechanism for dehydration of $CuSO_4 \cdot 5H_2O$ under vacuum at low temperature, which will be mentioned later.

The same experiment was done at 25 °C. The relationship between the fraction dehydrated and the time after dehydration starts is shown in Figure 6. The same pattern was obtained also at 25 °C. Combining the corresponding rate constants of dehydration at 0 and 25 °C, we estimated the activation energies of dehydration for
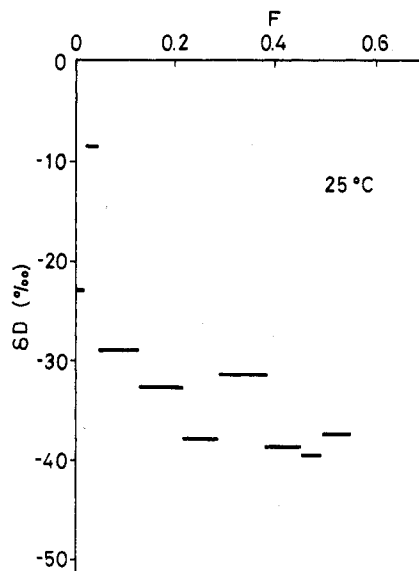
each chemical species by using Arrhenius' equation. Calculated activation energies for each chemical species are shown to be low[22] as follows: $E_{k_B} = 19.1$ kcal/mol, $E_{k_A} = 18.1$ kcal/mol, and $E_{k_A'} = 19.0$ kcal/mol.

It has been known that lattice defects, viz., dislocations, are multiplied by cooling and pulverizing. The number of dislocations increases upon pulverization. It has been reported that if decomposition (in our case, dehydration) takes place along dislocations, the rate is governed by zeroth-order kinetics and the activation energy of the reaction is small.[23,24] If dehydration takes place mainly along dislocations, the dehydration can be regarded as taking place inside the crystal grains quite randomly.

Calculation of the Site Preference in the Water of Crystallization. Under the assumption that dehydration takes place randomly throughout crystal grains, a Rayleigh process can be used to analyze the fluctuations in the isotopic ratio of water collected fractionally. For this process, the relationship between fluctuation of the isotopic ratio and the fraction of water remaining is

$$\delta D = \delta D^0 + 10^3 r(1 - \alpha) \ln F_R \qquad r = F_R/1 - F_R \qquad (5)$$

where δD is the integral mean value of δD up to the i-th fraction, i.e., $\delta D = \sum F_i \delta D_i / \sum F_i$, δD^0 denotes the δD of the water of crystallization before dehydration, α is the kinetic fractionation factor of hydrogen isotopes for dehydration (being equal to $(D/H)_{\text{dehydrated water}}/(D/H)_{\text{remaining water in crystal}})$, and F_R represents the remaining fraction of water in the crystal.

This model can be readily applied to the observations in the range $0 < F < 0.23$, if it is assumed that exchange of water molecules between site A and site B during dehydration does not take place at temperature below 25 °C, that one water molecule of site B of V and one of the four water molecules in site A of V are being dehydrated, and that site B water dehydrates earlier than site A water. Thus, the maximum of δD at $F = 0.06$ at 0 °C, and at $F = 0.04$ at 25 °C (Figure 7), is interpreted to indicate that dehydration of site A water[25] starts at or around $F = 0.06$

(21) According to Kohlschütter and Nitschmann, and Götz et al., trihydrate III is not formed in the region around $F \geq 0.4$ during the dehydration of pentahydrate V at room temperature (and below). In our model, however, III is not the major component around $F = 0.4$, because III as a transient product is calculated to be less than a few percent around $F \geq 0.4$. V. Kohlschütter and H. Nitschmann, *J. Phys. Chem.*, **35**, 494 (1931); D. Götz, K. Heinzinger, and A. Klemm, *Z. Naturforsch. A*, **30**, 1667 (1975).

(22) Activation energies obtained by DTA (gas flow system) are 45.0 kcal/mol for V → III and 47.7 kcal/mol for III → I. T. Ishii, T. Furumai, and G. Takeya, *Kogyo Kagaku Zasshi (Jpn).*, **70**, 1652 (1967) (in Japanese).

(23) J. Jach, *Nature (London)*, **196**, 827 (1962).

(24) J. M. Thomas and G. D. Renshaw, *J. Chem. Soc. A*, 2058 (1967).

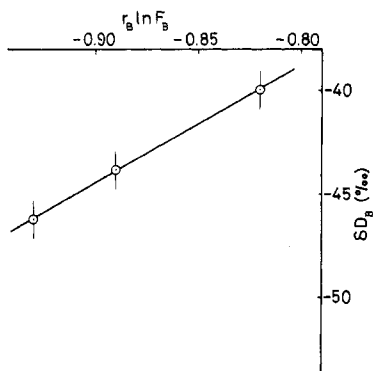(25) Dehydration of site A water means that from IV.

Figure 8. Linear relationship between δD_B and $r_B \ln F_B$ at 0 °C.

at 0 °C to add water with lower δD to the water from site B with higher δD, which is schematically shown in Figure 4b. The shift of the maximum with temperature is attributed to the change in the starting time of dehydration of IV.

Under these assumptions, dehydration in the range $0 < F < 0.06$ (0 °C) takes place exclusively from site B, and the equation for the water dehydrated from site B of V is

$$\delta D = \delta D_B^0 + 10^3 r_B (1 - \alpha_B) \ln F_B$$
$$r_B = F_B / 1 - F_B \tag{6}$$

where δD_B is the integral mean value of the water dehydrated from site B, δD_B° denotes the initial value of δD of site B water existing in the crystal before dehydration, α_B is the kinetic fractionation factor of hydrogen isotopes for dehydration of site B water and F_B represents the fraction of site B water remaining in the crystal. Plots of δD_B vs. $r_B \ln F_B$ in this interval yield a straight line as shown in Figure 8. Accordingly, δD_B° and α_B were calculated from the intersection with the δD_B axis and the slope of the line to be +8.2‰ and 0.940, respectively.

δD of site A water before dehydration, δD_A°, can be calculated from the following relation among δD_A°, δD_B°, and δD (−21.1‰) of the bulk water of crystallization:

$$0.2\delta D_B^\circ + 0.8\delta D_A^\circ = -21.1 \tag{7}$$

From eq 7, δD_A° was calculated to be −28.4‰.

In the range $0.06 < F < 0.23$, both of V and IV are dehydrated simultaneously. Therefore, the fluctuation of δD with respect to F should be represented by adding Rayleigh equations for site B and site A. The Rayleigh equation for site A is expressed in the same way as the equation for site B as follows:

$$\delta D_A = \delta D_A^0 + 10^3 r_A (1 - \alpha_A) \ln F_A$$
$$r_A = F_A / 1 - F_A \tag{8}$$

where subscript A indicates site A. In eq 8, the unknowns are δD_A, α_A, and F_A. The relation between δD and amount of dehydration water derives from the material balance equation for deuterium

$$M_B(1 + 10^{-3}\delta D_B) + M_A(1 + 10^{-3}\delta D_A) = M(1 + 10^{-3}\delta D) \tag{9}$$

where M denotes the integral amount of dehydrated water, δD is the integral mean δD value of dehydrated water, and M_A and M_B are the amounts of water dehydrated from site A and site B, respectively.

The amount of dehydrated water up to $F = 0.06$ comes exclusively from site B, while the amount of dehydrated water in the range $0.06 < F < 0.23$ comes 73.9% from site B and 26.1% from site A because $k_B/(k_B + k_A)$ (0.739 at 0 °C) is independent of the grain size as mentioned already.

Since δD_B°, δD_A°, and α_B have been calculated already, α_A is only unknown. Therefore, by combining eq 6–9, α_A can be calculated to be 0.870.

If the exchange of water between site A and site B does not occur during dehydration, δD_A° and δD_B° calculated from the experimental results of dehydration at 0 and 25 °C should agree with each other. The relationship between δD and the fraction (F) at 25 °C is shown in Figure 6. Because experimental difficulties limit the number of points obtained up to the δD maximum (at $F = 0.04$), these results yield only an imprecise estimate of δD_B°, in the range from +8 to +40‰. Thus, although a simple comparison is not possible, the result at 25 °C does not contradict that at 0 °C.

By repeating the same series of experiments, we obtained the following results (dehydration at 0 °C) for the crystal formed at 25 °C: $\delta D_B^\circ = +22.6 \pm 20.9‰$, $\delta D_A^\circ = -32.0 \pm 5.2‰$, $\alpha_B = 0.925 \pm 0.018$, $\alpha_A = 0.858 \pm 0.012$.

Concluding Remarks

Beevers and Lipson[12] determined the crystal structure of copper sulfate pentahydrate (V) precisely, using the X-ray diffraction method. According to them, the unit cell contains two molecules of $CuSO_4 \cdot 5H_2O$, the two copper ions in the unit cell are at inequivalent positions and both copper octahedra are distorted to different extents. One water molecule of the five is bound to a sulfate ion through a hydrogen bond, and the four are coordinated to both copper ions in the unit cell.

Beevers and Lipson,[12] and Taylor and Klug,[26] suggested that, during dehydration of $CuSO_4 \cdot 5H_2O$, the four waters coordinated to the copper ion in one of the two octahedra may be dehydrated first because that ion has the more distorted structure, that the four waters from the other octahedron may be dehydrated next, and that the two waters bound to SO_4^{2-} ions through hydrogen bonds remain to form the monohydrate.

Heinzinger[15] conducted the same fractional dehydration experiment as ours at room temperature, 50 °C, and 100 °C. He found that the D/H ratios of fractions dehydrated up to $F = 0.8$ were almost constant, but D/H ratios of fractions dehydrated beyond $F = 0.8$ is high. On the basis of this result only, he concluded that the dehydration mechanism is that deduced by Beevers and others and that D/H ratio of the water bound to the SO_4^{2-} ion is higher than D/H ratio of the four waters coordinated to the Cu^{2+} ion, which is qualitatively the same as our conclusion. However, the number of fractions collected in the experiment carried out by Heinzinger is so small that it is impossible to determine the fine structure of the δD fluctuation. Apparently, he did not take the mechanism of dehydration into consideration.

On the contrary, the result of this study indicates that the difference between two molecules ($CuSO_4 \cdot 5H_2O$) in the unit cell is not recognizable in the process of dehydration. It is reasonable to postulate that the site B water is dehydrated first, and the dehydration of the water in the coordination sphere follows.

The result of this study indicates that waters coordinated to the Cu^{2+} ion are bound more strongly than the water bound to the SO_4^{2-} ion. This may also be supported

(26) Taylor and Klug have demonstrated the existence of a tetrahydrate on the basis of differential thermal analysis. Their model for the tetrahydrate is entirely different from ours. Their model indicates that two molecules of water are lost from one of the two octahedrons involved in a unit cell of pentahydrate leaving one complete octahedron and one destructed octahedron. On the other hand, our model does not discriminate two octahedrons in a unit cell, and a tetrahydrate is the same as site A of the pentahydrate after losing site B water. T. I. Taylor and H. P. Klug, *J. Chem. Phys.*, **4**, 601 (1936).

by comparing the fractionation factors α_A and α_B; the kinetic isotope effect is much more remarkable for site A water.

Sofer and Gat,[3] and Stewart and Friedman,[4] reported that the D/H ratio of water coordinated to the metal ion in aqueous solution is relatively lower than that of the mother liquor. On the contrary, it is known that the D/H ratio of the water of crystallization bound by weak hydrogen bonding found in the case of ice, $Na_2SO_4 \cdot 10H_2O$,[27] and $Na_2CO_3 \cdot 10H_2O$ (unpublished) is relatively higher than that of the water of solution in equilibrium. If waters coordinated to metal ions in the solution are retained intact in the crystal, the result obtained in this study is quite consistent with these observations.

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Appendix

The Matsui-Banno[1] equilibrium constant is expressed in terms of D/H[28] as follows:

$$K = \frac{(K_A K_B - mK_A - nK_B)(D/H)_{ml} + mK_A + nK_B}{(nK_A + mK_B - 1)(D/H)_{ml} + 1} \quad (10)$$

where K represents $(D/H)_{\text{bulk water of crystallization}}/(D/H)_{ml}$, $(D/H)_{ml}$ denotes the D/H ratio of the mother liquor, and K_A and K_B represent $(D/H)_{\text{site A}}/(D/H)_{ml}$ and $(D/H)_{\text{site B}}/(D/H)_{ml}$, respectively ($m + n = 1$). In $CuSO_4 \cdot 5H_2O$, m and n are 0.8 and 0.2, respectively. The measured value of K at 25 °C is 0.979, and K_A and K_B are concluded to be 0.968 and 1.023, respectively, according to the present study.

K is obviously dependent on $(D/H)_{ml}$ in eq 10. We see, however, that K is practically constant even at very high $(D/H)_{ml}$ values of up to 0.9,[29] when the difference between K_A and K_B is smaller than 0.15. In other words, for the water of crystallization of the $CuSO_4 \cdot 5H_2O$–mother liquor system, the site preference is such that the equilibrium partition of hydrogen isotopes can be regarded as ideal for almost all concentration ranges of D/H for the mother liquor.

(27) M. K. Stewart, *Geochim. Cosmochim. Acta,* **38,** 167 (1974).

(28) When the deuterium content is high, D/H should be replaced by D/(D + H).
(29) In this case, 0.9 = D/(D + H).

Photochemical and Photocatalytic Properties of Adsorbed Organometallic Compounds. 2. Structure and Photoreactivity of Tris(2,2′-bipyridine)ruthenium(II) and -chromium(III) at the Solid–Gas Interface on Hectorite

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The structure of $Ru(bpy)_3{}^{2+}$ and $Cr(bpy)_3{}^{3+}$ (bpy = 2,2′-bipyridine) adsorbed in the interlamellar space of hectorite—an expanding layer lattice silicate—has been studied by IR and XPS spectroscopy. The adsorbed complexes appear to be slightly distorted, with weaker Ru–N bonds and stronger Ru–H$_2$O interactions than in pure $Ru(bpy)_3Cl_2 \cdot 6H_2O$ and $Cr(bpy)_3(ClO_4)_3 \cdot {}^1/_2H_2O$. The positive charge on the Ru nucleus in the adsorbed Ru complex is significantly higher than in its solid-state chloride salt. The pseudo C$_3$ axis of $Ru(bpy)_3{}^{2+}$ is perpendicular to the silicate sheets, whereas the pseudo C$_3$ axis of $Cr(bpy)_3{}^{3+}$ is nearly parallel to them. The photoreactivity of adsorbed $Cr(bpy)_3{}^{3+}$ has been studied at room temperature. The basic reaction is photoaquation, but the nature of the photoproducts, the kinetics of photoaquation, and also the reversibility of the reaction are dependent on the hydration state of the clay surface. $Ru(bpy)_3{}^{2+}$–hectorite samples are photoinert at room temperature, but irradiation at higher temperature leads to the formation of Ru(III) oxo-bridged dimers. The reaction mechanism appears to be photoaquation, followed by a purely thermal, and partially reversible, oxidation–dimerization reaction. The nature of the reactive excited state is discussed in the light of the spectroscopic data.

I. Introduction

With respect to the increasingly large amount of information which is being collected on the thermal reactivity and the catalytic properties of coordination compounds adsorbed on heterogeneous catalysts or anchored to a support, very little is known about the photoreactivity and the photocatalytic properties of this type of material, especially at the gas–solid interface. Although the uncertainties of heterogeneous catalysis are combined with those of photochemistry, this information could prove to be very fruitful as well for potential applications to a better fundamental understanding of the relationship between

electronically and thermally excited states.

Along this line, we recently started a study of tris-(2,2′-bipyridine)ruthenium(II) and -chromium(III) adsorbed on layer lattice silicates.[1] $Ru(bpy)_3{}^{2+}$ and related species on the one hand and $Cr(bpy)_3{}^{3+}$ on the other are among the best photophysically and photochemically characterized coordination compounds and are therefore well suited for this type of study. Layer lattice silicates—smectites particularly—have long been of great

(1) D. Krenske, S. Abdo, H. Van Damme, M. Cruz, and J. J. Fripiat, *J. Phys. Chem.,* in press.