# *A Study of Dehydration and Hydration of Oxalic Acid by Means of the Deuterium Exchange Reaction*

By Nobukazu OKAZAKI and Eiko TAKEMURA

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The dehydration of hydrated salts has been studied by various method, but the use of isotopic tracer in the study of the dehydration process has seldom been reported[1,2]. The process is generally considered to involve the following three steps[3]: (1) the decomposition of the hydrate to give an amorphous intermediate, which then crystallizes, (2) diffusion of the liberated water molecules through the product, and (3) evaporation of the water molecules from the surface of the product. The hydration process would follow the above steps in reverse. In the course of these events, there may occur interchange of protons between water and anhydrous substance. The study of such proton exchange reaction by the use of deuterium tracer may give some information as to the behavior of protons and water molecules in the process of dehydration, and possibly also as to the nature of the dehydration product.

In this work, the following facts have been noted; (1) relation of the deuterium exchange reaction to the surface area of the dehydrated product, and the amorphous character of the product formed on dehydration in vacuo at low temperatures, (2) recrystallization of the amorphous anhydrous acid in the presence of the adsorbed water vapor, (3) deuterium exchange reaction in partially hydrated oxalic acid, and (4) the effect of water vapor upon the rehydration rate of the amorphous anhydrous oxalic acid.

## Experimental

**Procedures.** — A known amount of anhydrous oxalic acid was hydrated in a vacuum system with a known amount of heavy water vapor. The pressure of the vapor was chosen to be lower than the vapor pressure of the saturated solution of oxalic acid, and higher than the dissociation pressure of oxalic acid dihydrate, at the temperature of the experiment. After the completion of the hydration, which was checked manometrically, the oxalic acid dihydrate formed was dehydrated in vacuo by condensing the water vapor from the dihydrate into a receiver cooled by solid carbon dioxide. The water was then distilled into a glass tube, purified thoroughly, and its deuterium content was determined by the floatation method. The deuterium content of heavy water used was ca. 1%.

**Materials.**—Anhydrous oxalic acid was prepared from commercial oxalic acid dihydrate (special grade), by the following two methods.

Sample I. Oxalic acid dihydrate was dehydrated at 100°C in a drying oven, until its loss in weight exceeded the theoretical value[4]. It was weighed in a glass vessel, attached to the vacuum system, pumped for a while to remove a small quantity of water which might have been absorbed during the manipulations, and then hydrated with heavy water vapor.

Sample II. A known amount of dihydrate was placed in the vacuum system, and dehydrated in vacuo at ordinary temperatures (usually at 25°C), as mentioned above. The anhydrous acid so prepared was used directly for exchange reaction without taking it out of the vacuum system.

It has been observed that, especially at lower temperatures (ca. 10°C or below), a small amount of water remaining at the final stage of dehydration is difficult to remove, and, as will be shown later, it plays an important role in the recrystallization of metastable anhydrous acid formed on dehydration in vacuo (Sample II). But the amount of this water is estimated to be so small that it can not affect the deuterium content to any serious extent.

**The Relation between the Degree of Deuterium Exchange and the Molar Ratio of the Reactants.** —The exchange reaction in question may be expressed by the following equation:

$$\begin{aligned}&(\mathrm{COOH})_2 + \mathrm{HDO(vapor)}\\ &\xrightarrow{\text{hydration}} \text{Oxalic acid dihydrate}\\ &\qquad\qquad + \text{Anhydrous oxalic acid}\\ &\xrightarrow{\text{dehydration}} \mathrm{COOH{\cdot}COOD} + \mathrm{H_2O}\ \text{(vapor)}\end{aligned}$$

It should be mentioned that the anhydrous acid was always used in excess, and a part of it was left unhydrated even after the completion of the hydration process.

With regard to the balance of deuterium atoms, the reaction may be written simply as,

$$(\mathrm{COOH})_2 + \mathrm{HDO} \rightleftarrows \mathrm{COOH{\cdot}COOD} + \mathrm{H_2O}$$

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[1] A. W. C. Menzies and F. T. Miles, *J. Am. Chem. Soc.*, 56, 3502 (1934).

[2] J. S. Anderson, R. H. Purcell, J. G. Pearson, A. King, F. W. Jones, H. J. Emeleus and H. V. A. Briscoe, *J. Chem. Soc.*, 1937, 1492.

[3] W. E. Garner, "The Chemistry of the Solid State", Butterworths, London, (1955), Chap. 8, p. 213.

[4] This sort of anhydrous acid may be of the $\beta$-form (Dr. H. Chihara, private communication).

The equilibrium condition for this reaction is

$$k=M_w(D_i-D_f)/(M_oD_f)=M_w\cdot\Delta D/(M_oD_f) \qquad (1)$$

where, $M_o$ and $M_w$ are the numbers of moles of anhydrous oxalic acid and heavy water vapor, $D_i$ and $D_f$ are the initial and final deuterium contents of heavy water, respectively, and $k$ is the deuterium partition coefficient between oxalic acid and water, or the ratio of the equilibrium atomic fraction of deuterium in oxalic acid to that in water. From a study of the deuterium exchange reaction between oxalic acid and water in solution, $k$ was determined to be $0.94\pm0.01$.

Since the anhydrous oxalic acid is always used in excess, the total amount used does not take part in the exchange reaction. If, of the $M_o$ moles of anhydrous acid used, $M_o'$ moles take part in the exchange reaction, Eq. 1 must be rewritten as,

$$k=M_w\cdot\Delta D/(M_o'D_f) \qquad (2)$$

A probable assumption is involved in this equation; namely that those parts of anhydrous oxalic acid which take part in the reaction, or more precisely, which are brought into contact with adsorbed water, are brought into exchange equilibrium with water rapidly relative to the time required for hydration or dehydration.

Eq. 2 may be written as,

$$\Delta D/D_f=(kM_o'/M_o)(M_o/M_w) \qquad (3)$$

where $M_o'/M_o$ is the molar ratio of oxalic acid which takes part in the exchange reaction to the total amount of oxalic acid used. According to this equation, if we plot the result of the exchange reaction, taking $\Delta D/D_f$ as ordinate, and $M_o/M_w$ as abscissa, the slope of the line passing through the plotted point and the origin gives the value of $kM_o'/M_o$, and hence of $M_o'/M_o$.

In a particular case, where heavy water exchanges its deuterium atoms with anhydrous acid in equivalent proportion, the value of $M_w/M_o'$ in Eq. 2 is 2, as can be readily seen from the formula $(COOH)_2\cdot 2H_2O$. In this case, according to Eq. 2, the value of $\Delta D/D_f$ should be 0.5 ($k\doteqdot1$) irrespective of the value of $M_o/M_w$.

## Results and Discussion

**Deuterium Exchange Reaction in Relation to the Nature of the Dehydration Product.**—The dependence of the degree of deuterium exchange ($\Delta D/D_f$) on the molar ratio of the reactants ($M_o/M_w$) is shown in Fig. 1. These results were obtained at 25°C and with the use of heavy water vapor of 4.6 mmHg for the hydration process. Other data were obtained under various conditions of temperature (0～28°C) and relative pressure (0.17～0.85) of heavy water vapor. But the temperature and the relative pressure were found to have little effect upon the exchange reaction.

It will be seen from the figure that there exists between Sample I and Sample II a remarkable difference in the dependence of deuterium exchange reaction on $M_o/M_w$. The difference appears to be qualitative rather than quantitative, and it seems to suggest the existence of a qualitative difference between the natures of the two sorts of anhydrous oxalic acid.

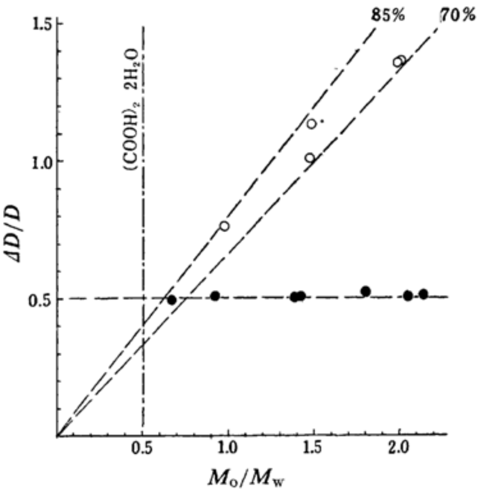

Fig. 1. Difference of the degree of deuterium exchange with the method of preparation of anhydrous oxalic acid. Solid circles: Sample I, prepared at 100°C. Open circles: Sample II, prepared in vacuo at room temperature.

In the case of Sample I, which is prepared from the dihydrate at 100°C (probably $\beta$-form), the value of $\Delta D/D_f$ is always about 0.5, irrespective of the value of $M_o/M_w$. From the reasoning mentioned in the experimental part, it may be concluded that, in this case, heavy water exchanges its deuterium atoms with anhydrous acid always in equivalent proportion.

On the other hand, the $\Delta D/D_f$ value of Sample II, which is prepared by dehydration in vacuo at room temperature, increases with increasing $M_o/M_w$. That is, the amount of anhydrous oxalic acid which takes part in the exchange reaction increases with the increasing excess of the anhydrous oxalic acid.

To visualize the ratio of oxalic acid which takes part in the exchange reaction to the total amount of oxalic acid used, the lines having the slopes ($kM_o'/M_o$) of 0.8 and 0.67 respectively, are drawn in Fig. 1. Taking $k=0.94$, these values correspond to the values of $M_o'/M_o$ of 0.85 and 0.71, respectively. It will be seen that 70 to 85% of the anhydrous acid takes part in the exchange reaction, the percentage decreasing from 85 to 70 with increasing $M_o/M_w$.

The results obtained with Sample II show considerable scatter. This is probably due to the persistence in the dehydrated product of a small uncontrollable quantity of water, which accelerates the recrystallization and consequently reduces the exchange reaction of the anhydrous acid (see later).

From the mechanism of the processes of the dehydration and the hydration of crystal hydrate, mentioned in the introduction of this paper, it may be inferred that, in the exchange reaction in question, the places where the reaction occurs, or the sites of the reaction, are, (1) the surfaces of the dehydration product, and (2) the reaction zone and the crystal lattice of the hydrate.

If the exchange reaction occurs exclusively in (2), where heavy water and anhydrous acid react always in equivalent proportion, $\Delta D/D_f$ should be 0.5, irrespective of the value of $M_o/M_w$. This is the case with the exchange reaction of Sample I (oxalic acid prepared at 100°C).

On the other hand, if the exchange reaction takes place in the surfaces of anhydrous acid, the increasing amount of anhydrous acid implies an increase in the number or the area of the site of the exchange reaction, and $\Delta D/D_f$ should increase with increasing $M_o/M_w$. This type of exchange reaction is observed with Sample II (anhydrous oxalic acid prepared in vacuo at low temperatures).

Consequently, it may be concluded that, in the case of Sample I, the exchange reaction occurs mainly in the crystal lattice of the dihydrate, and/or in the reaction zone on the occasion of the formation and the decomposition of the hydrate lattice. In the crystal lattice of the oxalic acid dihydrate[5], the water molecules are linked to the oxygen atoms of the carboxyl groups by hydrogen bonds. In such a structure, there may occur ready exchange of protons between carboxyl groups and water molecules by mere shifts of protons. It is well-known that, in aqueous solution, the hydrogen atoms linked to electronegative atoms are easily replaced by the deuterium atoms of heavy water. The exchange reaction in aqueous solution of oxalic acid would be quite analogous to that in the solid oxalic acid and would proceed through such a hydrogen-bonded intermediate.

As to the exchange reaction in the surfaces of anhydrous acid, a possible mechanism would be the one which involves capillary condensation of water vapor and the subsequent dissolution of oxalic acid in the condensed phase. But, as it has been observed that 70 to 85% of anhydrous acid used takes part in the exchange reaction, the above mechanism requires the dissolution of most of the anhydrous acid used. This seems to be incompatible with the observations during the experiments. Moreover, if capillary condensation and solution played an important role in the reaction, the degree of exchange would probably depend upon the relative pressure and the temperature. But, as mentioned above, such dependence has not been observed.

Therefore, in the case of Sample II, it is necessary to consider that the increase in the degree of exchange relative to that of Sample I is due to direct exchange of deuterium between adsorbed water molecules and solid anhydrous acid. The oxalic acid molecules involved in such a direct exchange mechanism would be restricted within a few outermost molecular layers of the solid anhydrous acid, and except in the case of a highly dispersed solid, the surface exchange mechanism could not contribute any appreciable portion to the total exchange reaction.

From the results of deuterium exchange reaction, the molar ratio of oxalic acid in the surface to that of the bulk may be estimated as follows: The amount of oxalic acid which takes part in the exchange reaction is given by Eq. 2.

$$M_o' = M_w \cdot \Delta D/(k \cdot D)$$

Of this amount, a part which is equivalent to the amount of water vapor used for the hydration takes part in the reaction through hydrate formation. The remainder $M_o' - (M_w/2)$ is the number of moles of oxalic acid which contributes to the surface exchange. The total number of moles of anhydrous oxalic acid which is left unhydrated at the completion of the hydration process is given by $M_o - (M_w/2)$. Thus the desired ratio $\beta$ is,

$$\begin{aligned}\beta &= [M_o' - (M_w/2)]/[M_0 - (M_w/2)] \\ &= [(1/k)(\Delta D/D) - 0.5]/[(M_o/M_w) - 0.5]\end{aligned} \tag{4}$$

The values of $\beta$ are calculated to be 0.59～0.71 for five specimens of anhydrous oxalic acid dehydrated in vacuo at 25°C. That is, 60 to 70% of the molecules of the anhydrous acid are in the surface.

If it is assumed that only the outermost molecular layer is involved in the exchange reaction during the hydration and the redehydration, the exchange of inner layers being associated with a slow diffusion process, then, on the average, 60 to 70% of the molecules in a crystallite of the anhydrous oxalic acid are in the outermost molecular layer. A substance composed of such crystallites may be termed amorphous.

It is well known that amorphous intermediates result from the dehydration of some

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5) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, **1936**, 1817; J. D. Dunitz and J. M. Robertson, ibid., **1947**, 142.

hydrated salts in vacuo at low temperatures³⁾. In the present case, the X-ray diffraction method has failed to detect the amorphous character of the anhydrous oxalic acid. But it has been observed that the electron micro-diffraction patterns of oxalic acid dihydrate change from spots or sharp rings to diffuse halos characteristic of an amorphous substance in the course of dehydration in the vacuum of electron microscope. Yet the electron microscopic image remains unaltered. This fact ensures that it is the dehydration process and not the decomposition by electron beams which is responsible for the change in diffraction patterns. The failure of the X-ray diffraction method is probably due to the recrystallization by the catalytic action of a small amount of residual water.

**Recrystallization of Amorphous Anhydrous Oxalic Acid in the Presence of Adsorbed Water Vapor.** — Anhydrous oxalic acid prepared by dehydration in vacuo at 25°C (Sample I) was exposed to heavy water vapor of 2 mmHg pressure for 15 min. Then the anhydrous acid was isolated from the source of water vapor, and kept in contact with adsorbed water at 25°C for definite times. During this period of contact, the pressure of water vapor above the anhydrous acid increased from 2 to 2.7 mmHg (dissociation pressure of the dihydrate at 25°C). This is probably due to the contraction of the surface area of the anhydrous acid and the consequent desorption of water vapor. This fact may be regarded as an evidence of the recrystallization process. In the experiments with longer times of contact, the recrystallized crystals having the form of a six-sided plate became visible even to the naked eye. It was identified with $\alpha$-form by X-ray diffraction method.

After a given time of contact, the anhydrous acid was hydrated with heavy water vapor and subsequently redehydrated in vacuo at 25°C, and the water obtained on dehydration was analysed for deuterium content.

In Fig. 2, per cent $\alpha(=M_o'/M_o\times 100)$ of oxalic acid which takes part in the exchange reaction is plotted against the time of contact of anhydrous acid with adsorbed water. As controls, deuterium exchange of the anhydrous acid kept for definite times in the absence of water vapor was also studied. The results are given by the upper curve in Fig. 2.

Fig. 2 shows that, whereas in the control experiments percentage exchangeability $\alpha$ of anhydrous oxalic acid decreases only slightly with time, that of anhydrous acid treated preliminarily with water vapor decreases definitely with time.

As discussed above, the increase in the exchangeability of highly dispersed anhydrous acid relative to that of crystalline anhydrous acid is due to the exchange reaction in the surface, and this surplus exchangeability may be considered to be a measure of the surface area of the anhydrous acid. Consequently, the decrease in the value of $\alpha$ means the progress of recrystallization, and the completion of it is characterized by the value of $\alpha$ which is characteristic of the crystalline anhydrous acid (in the present case, $\alpha=0.354$).

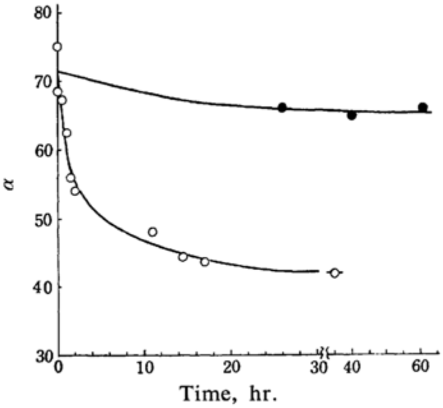

Fig. 2. Decrease in the degree of deuterium exchange due to the recrystallization of highly dispersed oxalic acid at 25°C. $M_o/M_w=1.5$. Upper curve: in the absence of water vapor. Lower curve: in the presence of water vapor.

The comparison of two curves in Fig. 2 shows that adsorbed water exerts considerable effect on the recrystallization of amorphous oxalic acid. Recrystallization in the presence of water vapor (2 mmHg initially) at 25°C proceeds rather rapidly for the first few hours and goes almost to completion within about 10 hr.

The catalytic effect of water on the recrystallization of amorphous intermediates in the dehydration of salt hydrates has been studied by several authors. Volmer and Seydel⁶⁾ have found by the X-ray diffraction method that, whereas the anhydrous manganous oxalate formed on dehydration in vacuo is amorphous, the dehydration in the presence of water vapor yields crystalline manganous oxalate, and attributed its formation to the recrystallization of amorphous product by the catalytic action of water vapor. Frost, Moon and Tompkins⁷⁾ have deduced from thermal measurements the fractional amounts of amorphous intermediate in the dehydration products of copper sulfate pentahydrate prepared under

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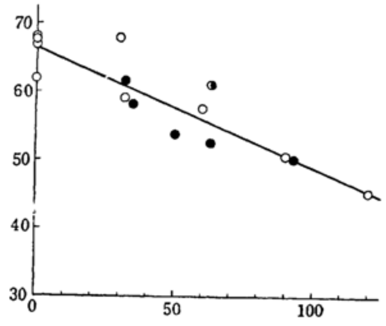
6) M. Volmer and G. Seydel, *Z. physik. Chem.* (*Leipzig*), **A179**, 153 (1937).

7) G. B. Frost, K. A. Moon and E. H. Tompkins, *Can. J. Chem.*, **29**, 604 (1951).

various pressures of water vapor, and found that the fractional amount decreases with increasing water vapor pressure.

Oxalic acid offers a new example of the formation of amorphous intermediate and of the catalytic effect of water on its recrystallization. In this example, the two processes were studied separately and the course of the latter was followed by deuterium exchange reaction.



Time, min.

Fig. 3. The effect of temperature on the recrystallization rate of highly dispersed oxalic acid. $M_0/M_W=2.0$.
●: 35.1°C, ◑: 30.0°C, ○: 25.0°C

In order to gain further information as to the nature of the recrystallization process, the effect of temperature has been studied at 25 and 35°C.

Fig. 3 shows that the recrystallization rates are scarcely affected by the change of temperature. It appears that oxalic acid molecules are almost free to move on the surface of the highly dispersed oxalic acid.

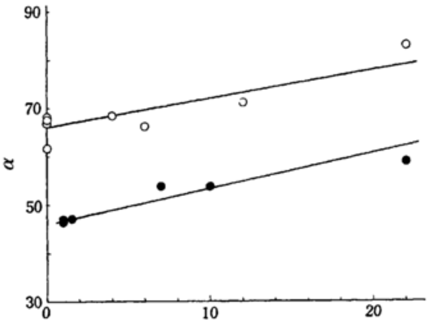
**Deuterium Exchange Reaction in Partially Hydrated Oxalic Acid.** — When amorphous oxalic acid is partially hydrated with heavy water vapor and left for a time, the oxalic acid molecules which are left undeuterated in the process of hydration, become progressively deuterated,

Oxalic acid + Oxalic acid dihydrate-*d*

$\rightleftarrows$ Oxalic acid-*d* + Oxalic acid dihydrate

As a consequence, the deuterium content of water obtained upon dehydration of oxalic acid partially hydrated with heavy water vapor decreases with the time during which oxalic acid is kept in the partially hydrated state.

The results are shown in Fig. 4, in which per cent of oxalic acid which takes part in the exchange reaction is plotted against time. Within experimental errors, the percentage increases almost linearly with time, and the curves for the two temperatures are almost parallel to each other. This seems to suggest that the rate of this exchange is almost independent of temperature.



Time, hr.

Fig. 4. Deuterium exchange reaction within partially hydrated oxalic acid.
○: 25°C, ●: 15°C

It is probable that this increase in the degree of exchange is caused by the propagation of deuterium exchange into the inner layers of anhydrous oxalic acid, since the surface layer would be completely deuterated during the hydration process.

A possible mechanism of this process consistent with the fact that the process is associated with small or zero activation energy would be the following: During the recrystallization by the action of adsorbed water, oxalic acid molecules leave the original lattices and migrate to the new crystals. Thus the adsorbed water molecules are brought into contact successively with the fresh layer of anhydrous acid, and exchange deuterium atoms with these fresh surface molecules. The deuterium atoms of the adsorbed water are supplied by the surface migration of protons or water molecules, or from the vapor phase by adsorption and desorption.

**The Effect of Water Vapor on the Rehydration Rate of Amorphous Oxalic Acid.**—In the course of this investigation, it has been observed that treatment of amorphous anhydrous oxalic acid with a small amount of water vapor gives rise to a characteristic change in the rehydration rate according to the amount of water vapor.

A known amount of water vapor was introduced from a gas burette into a vessel containing amorphous oxalic acid prepared in vacuo at 25°C. The pressure of water vapor in the vessel, as measured by an oil manometer and a traveling microscope, changed with time as a result of the progress of adsorption and recrystallization. It was lower than 0.01 mmHg in most of the runs. After the treatment with water vapor for 1.5 hr. at 25°C, the anhydrous acid was hydrated with water vapor of 4.6 mmHg pressure, liquid water maintained at 0°C being used as the source of the vapor.

The results are given in Fig. 5, in which rehydration rates are plotted against the amounts of water vapor initially introduced into the reaction vessel. As a measure of the rehydration rate, the reciprocal of time required for a definite amount of oxalic acid (0.11 mol.) to absorb 1 g. of water vapor was taken. This measure, though giving only an integrated rate would serve for qualitative discussions.

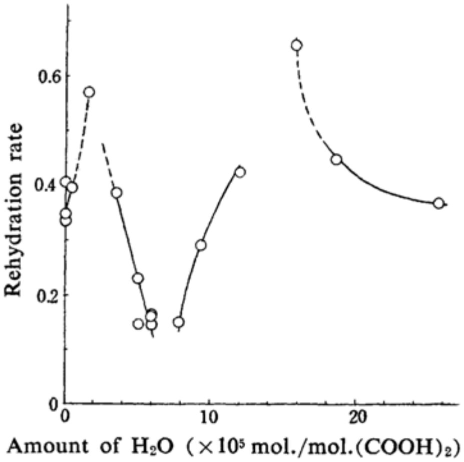


Fig. 5. Effect of preliminary water vapor treatment on the rehydration rate of amorphous anhydrous oxalic acid.

It will be seen that there is a minimum of rehydration rate in the region of $6\sim8\times10^{-5}$ mol. $H_2O$ per mol. of oxalic acid, with a maximum on each side of the minimum. This effect bears an apparent resemblance to the effect of water vapor on the nucleation rate of chrome alum observed by Garner and Jennings[8]. They have found that water vapor causes nucleation of the dehydration product in a slightly dehydrated surface of chrome alum, and that it has an optimum effect for a particular value of its pressure. The results have been interpreted by them as due to the conversion of collapsed lattice into product lattice under the loosening action of water.

In the present case, it seems probable that a high rate of nucleation or a high rate of recrystallization would retard the rehydration rate by decreasing the surface area of anhydrous acid. Or, it seems also possible that formation of anhydrous acid nuclei at a high rate would consume those parts of the collapsed lattice which are responsible for the formation of dihydrate nuclei. At present, it is not possible to give any reasonable interpretation to this phenomenon. It will be studied further.

## Summary

The deuterium exchange reaction in the course of the hydration of anhydrous oxalic acid with heavy water vapor and subsequent dehydration of the product has been studied.

Two exchange mechanism have been suggested to be operative; the hydrate formation mechanism and the surface exchange mechanism. A distinction may be made between the two by the dependence of exchange reaction on the molar ratio of the reactants.

Anhydrous oxalic acid prepared by dehydration at 100°C takes part in the exchange reaction through hydrate formation; while, with the anhydrous acid prepared by dehydration in vacuo at ordinary temperatures, the surface exchange mechanism comes into play.

For the specimens of anhydrous acid prepared in vacuo, the molar ratio of oxalic acid in the surface to that of the bulk is estimated to be 0.6~0.7 from the results of the deuterium exchange reaction. Dehydration of oxalic acid dihydrate in the vacuum of electron microscope yields amorphous anhydrous acid.

The recrystallization of amorphous anhydrous oxalic acid was studied by the use of deuterium exchange reaction as a measure of surface area. It has been shown that adsorbed water exerts catalytic effect on the recrystallization. The process is associated with small or zero activation energy. Anhydrous oxalic acid recrystallized in the presence of water has been identified with $\alpha$-form.

Deuterium exchange reaction between unhydrated oxalic acid and hydrate water occurs in anhydrous oxalic acid partially hydrated with heavy water vapor. The rate of this exchange is practically independent of temperature. The reaction probably consists in the deuteration of the molecules in the interior of the anhydrate lattice.

Treatment of amorphous anhydrous acid with a small amount of water vapor causes a peculiar change in the rate of subsequent rehydration. There is a considerable retarding effect on the rehydration rate for a particular range of the amount of water vapor.

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*Department of Chemistry*
*Nara Women's University*
*Nara*

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[8] W. E. Garner and T. J. Jennings, *Proc. Roy. Soc.*, **224A**, 460 (1954).