A Study of Dehydration and Hydration of Sodium Dihydrogen Phosphate and Racemic Acid by Means of the Deuterium Exchange Reaction

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In a study of dehydration and hydration of oxalic acid by means of the deuterium exchange reaction[1], the following facts have been observed; (1) the difference of exchange behavior of the anhydrate with the method of its preparation, and the amorphous character of the anhydrate prepared by dehydration in vacuo at low temperatures, (2) recrystallization of the amorphous anhydrate under the catalytic action of water vapor, and (3) deuterium

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[1] N. Okazaki and E. Takemura, This Bulletin, 34, 977 (1961).

exchange reaction in anhydrate-hydrate mixture. It is the purpose of the present work to examine with other salt hydrates whether or not the phenomena are of general occurrence.

The experimental procedures were almost the same as those used in the previous work[1].

Difference of Exchange Behavior of Anhydrate with the Method of Dehydration. — *Sodium Dihydrogen Phosphate.* — Commercial sodium dihydrogen phosphate dihydrate (special grade reagent) was used without further purification. Two sorts of samples of the anhydrate were used; one was prepared by dehydration of dihydrate to constant weight at 130°C in a drying oven, and the other by dehydration in vacuo at ordinary temperatures. The procedures for the deuterium exchange experiment were the same as those used previously.

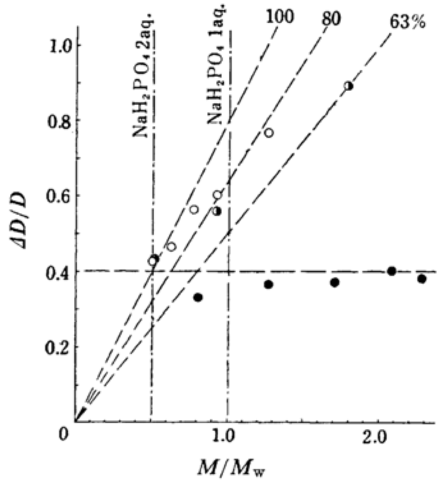

Fig. 1. Difference of the deuterium exchange reaction between anhydrous sodium dihydrogen phosphate prepared by dehydration in vacuo at ordinary temperatures (○; 20°C, ◑; 11°C) and that prepared at 130°C (●).

The results are shown in Fig. 1, in which the degree of exchange $\Delta D/D_f$ is plotted against the molar ratio of the reactants M/M_w (for notations and formulas, see the previous work). As in the case of oxalic acid[1], there is a qualitative difference of exchange behavior between the two sorts of anhydrous sodium dihydrogen phosphate.

The exchange reaction of the anhydrous phosphate prepared at 130°C was studied at 11°C. In these experiments, the values of $\Delta D/D_f$ are about 0.4 for the values of the molar ratio ranging from 1.0 to 2.5. This fact means that, in these cases, the amount of the anhydrous phosphate which takes part in the exchange reaction is always in a definite ratio to the amount of water used, irrespective of the presence of the excess anhydrous phosphate. This ratio M'/M_w may be calculated by the relation,

$$M'/M_w = (2/kn)(\Delta D/D_f)$$

where, k is the partition coefficient of deuterium between anhydrous phosphate and water, and n is the number of exchangeable hydrogen atoms in sodium dihydrogen phosphate.

The value of k has been determined from the exchange reaction in solution to be 0.806 ±0.008 (mean of four determinations), which is somewhat smaller than the value commonly accepted for the partition coefficient of hydroxyl hydrogen[2].

By using the above value of k and taking $n=2$, the values of M'/M_w are calculated to be 0.5 or 1 : 2, which corresponds to the composition $NaH_2PO_4 \cdot 2H_2O$. It may be concluded that the exchange reaction of the anhydrate prepared at 130°C proceeds through the formation of dihydrate.

The existence of monohydrate of sodium dihydrogen phosphate is known, but the formation of monohydrate was not observed under the condition of the experiments. In correspondence with this, the dehydration of dihydrate yielded anhydrate directly; dehydration curves were constructed at 11.0, 20.0 and 28.0°C, but no sign of the formation of monohydrate has been observed. The values of the dissociation pressure obtained from the dehydration curves are 3.84 mmHg at 11.0°C, 7.98 mmHg at 20.0°C, and 14.77 mmHg at 28.0°C. Each of these values is the mean of seven to ten measurements obtained at various stages of dehydration. These values gave a good linear plot of $\log p$ against $1/T$, from which the heat of dissociation of sodium dihydrogen phosphate dihydrate into anhydrate has been calculated to be 13.5 kcal. per mol. H_2O. In these experiments, the dissociation pressure was measured by a mercury U-tube manometer (1.8 cm. bore). The temperature was measured by a mercury thermometer graduated in 0.1°C (uncalibrated).

As exemplified by the above results, the exchange reaction in question may be used to determine the composition of the hydrate formed on hydrating an anhydrate or a lower hydrate. Another example may be found in the previous paper[3], where the hydration product of copper sulfate monohydrate was identified by this method with trihydrate or with a mixture of tri- and pentahydrate according to the condition of hydration.

The exchange reaction of the anhydrous phosphate prepared in vacuo was studied at

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2) See, for example, V. Gold and D. P. N. Satchell, *Quart. Rev.*, 9, 51 (1955).

3) N. Okazaki, A. Okumura, and K. Nakagawa, This Bulletin, 45, 983 (1961).

two temperatures, 11 and 20°C. The increased exchangeability of the phosphate prepared in vacuo as compared with the phosphate prepared at 130°C may be seen in Fig. 1. As in the cases of oxalic acid and copper sulfate, it should be attributed to the exchange reaction between adsorbed water and the phosphate occurring in the extended surface of the latter.

The values of the degree of exchange obtained at 11°C are considerably lower than those obtained at 20°C. It is probably due to the increased adsorption of water in the reaction zone during the preliminary dehydration and the consequent increase in the degree of recrystallization of the dehydration product at the lower temperature.

The values of the ratio of the amount of the anhydrous phosphate which takes part in the exchange reaction to the total amount used, as calculated by the relation,

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

are 0.77~1.06 for the specimens of anhydrous phosphate prepared in vacuo at 20°C and 0.63 ~1.03 for those prepared at 11°C. The values obtained for oxalic acid and copper sulfate[1,3] are 0.71~0.85 and 0.75~1.08, respectively.

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

$$\beta = [(1/k)(\Delta D/D_f) - 0.5] / [(M/M_w) - 0.5]$$

The values obtained are 0.59~0.71 for the specimens of anhydrous phosphate prepared in vacuo at 20°C, and 0.48 for two specimens prepared at 11°C.

Racemic Acid Monohydrate. — Racemic acid monohydrate was prepared from *d*-tartaric acid by the usual method, and purified by repeated crystallization from aqueous solution. The specimens of anhydrous racemic acid were prepared partly by dehydration of monohydrate in vacuo at 20°C, and partly by dehydration at 100°C under atmospheric pressure.

The results are shown in Table I.

TABLE I. EXCHANGE REACTION OF ANHYDROUS RACEMIC ACID AT 20°C

Specimen	M/M_w	$\Delta D/D_f$	M'/M	β
Anhydrous racemic acid prepared in vacuo at 20°C	1.383	2.34	0.94	0.71
	1.438	2.61	0.91	0.70
	1.851	3.20	0.86	0.69
Anhydrous racemic acid prepared at 100°C	1.120	2.22	—	—
	1.495	2.03		
	1.591	2.27		

As with the other hydrates previously studied, the degree of exchange is independent of the molar ratio in the case of the anhydrous acid prepared at 100°C, and increases with the value of the molar ratio in the case of the anhydrous acid prepared in vacuo at 20°C. The number of exchangeable hydrogen atoms is calculated to be 4, that is, two carboxyl hydrogen and two hydroxyl hydrogen atoms, from the results of the exchange reaction of anhydrous acid prepared at 100°C.

The values of the surface to bulk ratio β as defined by the deuterium exchange reaction are calculated by[1],

$$\beta = [(1/2k)(\Delta D/D_f) - 1] / [(M/M_w) - 1]$$

The values obtained are compared with those of the other hydrates in Table II.

TABLE II

Specimen	β	Temp. of Dehydration °C
Anhydrous oxalic acid	0.60~0.70	25
Copper sulfate monohydrate	0.44~1.10	35
Anhydrous sodium dihydrogen phosphate	0.59~0.71	20
	0.48	11
Anhydrous racemic acid	0.70	20

It will be seen that the values for four substances are comparable with each other. The copper sulfate monohydrate prepared by dehydration in vacuo at low temperature is known to be amorphous[4], and the dehydration product of oxalic acid dihydrate in the vacuum of electron microscope has also been shown to be amorphous[1]. Though the above ratio does not bear a definite physical significance, yet it would be useful for semi-quantitative discussion. Thus, the similarity of the values of the ratio suggests that the dehydration products of racemic acid, sodium dihydrogen phosphate as well as oxalic acid in vacuo at ordinary temperatures are amorphous, and adds new evidence to the postulate that dehydration of salt hydrates proceeds through the intermediate formation of an amorphous product.

Effect of Adsorbed Water on the Recrystallization of Amorphous Anhydrous Sodium Dihydrogen Phosphate.—The anhydrous phosphate prepared in vacuo at 20°C was exposed to water vapor of 2 mmHg in a vacuum system at 11°C for twenty minutes, liquid water maintained at −10°C being used as the source of the vapor. Then, the anhydrous phosphate was isolated from the vapor source, and kept in contact with the adsorbed water at 11°C for definite times. After a given time of contact, the anhydrous phosphate was hydrated with a known amount of water vapor of a definite pressure, and subsequently redehydrated. The water obtained on redehydration was analyzed for its deuterium content.

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[4] V. Kohlschütter and H. Nitschmann, *Z. physik. Chem.*, Bodensteinfestband, 494 (1931).

As in the case of the oxalic acid, the pressure of the water vapor above the anhydrous phosphate increases during the time of contact of the phosphate with adsorbed water vapor. It may be attributed to the recrystallization of the amorphous phosphate and the consequent desorption of the water vapor. The pressure begins to increase after the induction period of 30 to 40 min., and within a few hours it reaches a maximum value of about 4.8 mmHg which is well above the dissociation pressure of dihydrate (3.8 mmHg at 11°C). The pressure increase begins to decline at about 4 mmHg, which is probably due to the beginning of hydrate formation. After the maximum has been attained, the pressure decreases at first rather rapidly to about 4 mmHg, and then very slowly toward 3.8 mmHg. The amount of water liberated by the phosphate during the period of pressure increase is estimated to be 3×10^{-4} mol. per mol. of the phosphate.

The results of the exchange reaction are shown in Fig. 2. The exchangeability M'/M of the amorphous phosphate decreases with the time of contact of the phosphate with water vapor, while in the absence of water vapor the exchangeability decreases only slightly.

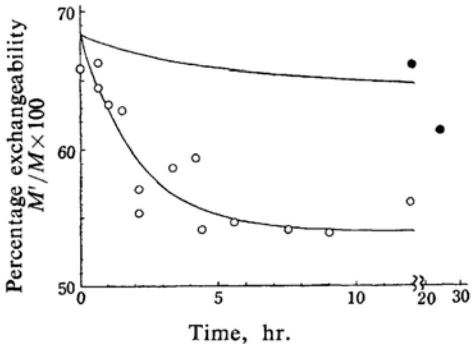

Fig. 2. Decrease in the exchangeability of amorphous anhydrous sodium dihydrogen phosphate due to recrystallization under the catalytic action of water vapor. $M/M_W=1.25$. Solid circle; in the absence of water vapor. Open circle; in the presence of water vapor.

It appears that catalysis of the recrystallization of highly dispersed dehydration intermediate by adsorbed water is of general occurrence.

The process of recrystallization may be visualized as dissolution of the energy-rich anhydrate into adsorbed water; that is, the formation of two-dimensional solution and recrystallization from it of crystalline anhydrate. Below a particular concentration of this two-dimensional solution, it comes to be in equilibrium with hydrate instead of anhydrate, that is, nucleation of hydrate begins. Thus, according to this view, the relation of recrystallization to nucleation of hydrate would be analogous to the relation of anhydrate to hydrate, each in equilibrium with its saturated solution.

Deuterium Exchange Reaction between Unhydrated and Hydrated Phosphate in Partially Hydrated Amorphous Sodium Dihydrogen Phosphate. — Anhydrous phosphate prepared by dehydration in vacuo at 20°C was hydrated with heavy water vapor of 9 mmHg pressure and left for a given time at 15°C. Then, it was dehydrated in vacuo at 20°C, and the water obtained was analyzed for its deuterium content.

The results are shown in Fig. 3. As in the case of oxalic acid, the degree of exchange M'/M of the phosphate increases with the time during which the phosphate has been kept in the partially hydrated state. The increase is probably due to the deuteration of the primary phosphate ions in the interior of the crystallites. A possible mechanism of this process has been suggested with reference to the exchange reaction of oxalic acid[1].

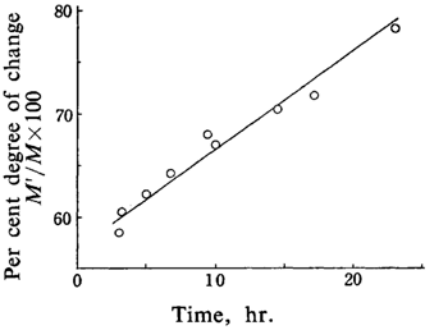

Fig. 3. Progress of deuteration of sodium dihydrogen phosphate in partially hydrated state.

Summary

In order to examine the generality of the results obtained with oxalic acid, the following questions were studied with sodium dihydrogen phosphate and in part with racemic acid: (1) the relation between the deuterium exchange reaction and the surface area of the anhydrate, and the amorphous character of the anhydrate prepared by dehydration in vacuo at low temperatures, (2) recrystallization of the amorphous anhydrate under the catalytic action of adsorbed water, and (3) deuterium exchange reaction in anhydrate-hydrate mixture.

The results obtained with sodium dihydrogen phosphate and racemic acid are similar to those obtained with oxalic acid. It appears that formation of amorphous anhydrate in the dehydration of crystal hydrate in vacuo at low

temperatures and its recrystallization under the catalytic action of adsorbed water are phenomena of general occurrence.

The deuterium exchange reaction of crystalline anhydrate may be used to determine the composition of the hydrate formed on hydrating an anhydrate under a given condition.

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