The Fractionation of Tritiated Water in an Equilibrium between Organic Hydrates and Their Aqueous Solutions

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(Received August 6, 1973)

The fractionation of the tritiated water (HTO) was examined during the crystallization of hydrates, such as $(COOH)_2 \cdot 2H_2O$, $(COOK)_2 \cdot H_2O$, $Cu(HCOO)_2 \cdot 4H_2O$, and $Sr(HCOO)_2 \cdot 2H_2O$. The dilution of HTO in the organic salts was found to be comparable to that in inorganic salts observed previously. The fractionation of HTO was explained on the basis of an ionic process in an aqueous solution, and the crystal growth mechanism, in a way similar to that described in a previous paper. On the contrary, a considerable dilution was observed for oxalic acid dihydrate. The proton effect on the fractionation in both the ionic and dehydration processes was also discussed.

It has been reported by many workers that the fractionation of deuterated water occurs during the crystallization of various hydrated inorganic salts from aqueous solutions.[1] A similar fractionation of tritiated water (HTO) has been investigated for a number of metal sulfates[2,3] and chlorides[4] by the present authors. It has been found that a dilution of HTO of a few percent occurs in the water of crystallization of these inorganic salts. From these studies, some information has been derived concerning the kinetics of the deposition of the hydration water on the crystal from an aqueous solution.

In order to study the dilution in a more systematic way, it seems worthwhile to determine the separation factor, S, of metal organic salts and to compare it with those of inorganic salts. For this purpose, copper formate tetrahydrate and strontium formate dihydrate have been examined. It may also be quite interesting to examine the fractionation in an organic acid hydrate, *e.g.*, oxalic acid dihydrate, since the acid contains hydrogen atoms besides those of the hydration water. For the estimation of the proton effect in the carboxyl groups on the fractionation, the S value for the hydration water in the metal salt of the acid can properly be used. Potassium oxalate monohydrate has been chosen as the salt in the present study.

Experimental

Strontium formate was prepared by adding strontium carbonate to formic acid. The other samples were obtained from a commercial source and purified by recrystallization. The solvent consisted of twice-distilled water containing a trace of tritiated water (HTO). A large well-developed single crystal of the hydrate was grown from a very slightly supersaturated solution by lowering the temperature gradually within a narrow range. The temperature ranges were 32.5—29.0 °C, 33.0—32.1 °C, 36.3—34.3 °C, and 29.8—28.8 °C for $Sr(HCOO)_2 \cdot 2H_2O$, $Cu(HCOO)_2 \cdot 4H_2O$, $(COOK)_2 \cdot H_2O$, and $(COOH)_2 \cdot 2H_2O$ respectively.

Water from both the mother liquid and the hydration water of the single crystal was recovered by dehydrating them *in vacuo* at 45 °C. The β-activity of the dehydrated water was measured with a liquid scintillation counter, a Packard Model 2002 Tri-Carb Scintillation Spectrometer. Besides, the activity due to the tritium in the dihydrate was directly measured by dissolving it in a scintillant in the case of the oxalic acid dihydrate, $(COOH)_2 \cdot 2H_2O$. As a scintillant we used a solution composed of toluene, ethylene glycol monomethyl ether, 2,5-diphenyloxazole (PPO), and 1,4-bis-2′-(5′-phenyloxazolyl)benzene (POPOP).

Results and Discussion

The separation factor, S, of HTO for the crystallization of a hydrated salt from an aqueous solution can be given as $S = N_s/N_l$, where N_s and N_l are the mole fractions of HTO in the solid and liquid phases respectively. Table 1 shows the observed fractionation of HTO, together with the average net cpm for 0.1 g of water, which is proportional to the fraction of HTO. We see in copper formate tetrahydrate a very slight dilution of HTO and no practical fractionation, whereas appreciable dilutions are found in the other hydrates, particularly in the oxalic acid dihydrate.

TABLE 1. THE SEPARATION FACTOR, S, OF HTO FOR ORGANIC HYDRATES

Crystal	Net cpm of HTO[a)]		$S(N_s/N_l)$
	N_s	N_l	
$Sr(HCOO)_2 \cdot 2H_2O$	22248±168	23329±157	0.954±0.010
$Cu(HCOO)_2 \cdot 4H_2O$	21570±83	21640±91	0.997±0.006
$(COOK)_2 \cdot H_2O$	20326±125	20837±92	0.976±0.007
$(COOH)_2 \cdot 2H_2O$	25324±152	29278±177	0.865±0.007

a) Averaged for 6—8 measurements with a counter of 35% efficiency.

The HTO Fractionation in the Water of Crystallization. It has been reported that HTO is diluted in the water of crystallization during the crystal growth from a solution if a surface-diffusion mechanism in which the growth unit diffuses over a wide range of the crystal surface before integrating into the kink controls the crystal growth.[2)] The R_{HTO}/R_{H_2O} ratio has been approximately derived for the free water on the crystal growth of a hydrated salt *via* surface diffusion:

$$R_{HTO}/R_{H_2O} = (m_{H_2O}/m_{HTO})^{1/2} = 0.949, \qquad (1)$$

where R_{HTO}/R_{H_2O} is the ratio of integration of HTO into the crystal to that of H_2O and where m_{H_2O}/m_{HTO}

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is the molecular weight ratio of H_2O to HTO. It can be assumed that minimum S value becomes *ca.* 0.95 when the free water integrates into the crystal from the solution.

In the hydration water of cations in the solution, the fractionation of HTO from the bulk water, if any, has been disregarded in a previous work.[4] Although such a simplification can be justified in the cases of Na^+ and K^+, which exert weak hydration, it may not be justified in the cases of most of the other cations.[5] It seems that HTO should be slightly enriched in the hydration water if the hydration water is held more rigidly in the sphere than in the solvent water itself, as can be seen from the theory of the isotope effect in the exchange reaction.[5,6] Such an ion is frequently referred to as a structure-former. As for the anion, the hydration water can be assumed to exert no considerable effect on the fractionation in the present case. Accordingly, it can be suggested that the more free water molecules and the less hydration water molecules of a structure-former ion there are, in the solution, the more dilution of HTO in the crystal hydrates should result.

In the case of $Sr(HCOO)_2 \cdot 2H_2O$, the hydration water of a Sr^{2+} ion in the solution is taken to become free in order to be integrated into the crystal,[4] since the lifetime of the hydrated cation is extremely short.[7] It can thus be expected that a considerable dilution of HTO occurs for the salt, *i.e.*, the S value becomes close to 0.95.

As for $Cu(HCOO)_2 \cdot 4H_2O$, half of the hydration water of a Cu^{2+} ion in the solution can be assumed to become free to be integrated, because half of the water of crystallization is not coordinated to the Cu^{2+} ion in the crystal.[8] On the other hand, the remaining half, which is coordinated to the cation in the crystal, seems to come from the hydration water in the aqueous solution.

It follows that HTO is diluted in the former according to Eq. (1), whereas a slight enrichment of HTO results in the latter since the Cu^{2+} ion is known to be a structure-former. In these estimations, we assume that no exchange of the proton in the $HCOO^-$ ion with others occurs.[9]

For $(COOK)_2 \cdot H_2O$, the S value can be estimated to be nearly equal to that of $Sr(HCOO)_2 \cdot 2H_2O$, because the lifetime of the hydrated K^+ ion is also very short; *ca.* 10^{-9} s.[7] However, the observed S value was found to be a little larger than the estimated one. The cause of the disagreement is not clear at this stage. A small deviation of the estimated value from the observed value seems to be inevitable, as was the case with a few other salts.[4] It appears, at least qualitatively, that the present treatment is still applicable. The S value for $(COOK)_2 \cdot H_2O$ will help to estimate the value for $(COOH)_2 \cdot 2H_2O$.

It can be seen that, in general, the degree of dilution of HTO in the water of crystallization of the metal organic salts is a few percent or so, comparable to that in the metal inorganic salts. It can thus be suggested that the former dilution can also be explained on the basis of an ionic process in an aqueous solution and the crystal growth mechanism, as is the case with the latter.

The HTO Fractionation in the Oxalic Acid. It is worth noting that a considerable dilution is found to occur in the oxalic acid dihydrate. In order to estimate the fractionation in the carboxyl groups, $(COOH)_2$, we assume that the partial dilution due to the water of crystallization in $(COOH)_2 \cdot 2H_2O$ is nearly equal to be dilution for $(COOK)_2 \cdot H_2O$, 0.976.

The dilution resulting from the others is considered to come from the following three steps: (1) the proton-exchange reaction in an aqueous solution, (2) the proton integration into the crystal from an aqueous solution, and (3) the proton-exchange reaction between $(COOH)_2$ and the hydration water during the course of the vacuum dehydration.

It is well known that deuterium is slightly diluted in the hydronium ion in the exchange reaction:[10]

$$H_2O + H_2DO^+ \rightleftharpoons HDO + H_3O^+. \qquad (2)$$

The same process should proceed in the case of tritium, *i. e.*; $H_2O+H_2TO^+ \rightleftharpoons HTO+H_3O^+$.
The HT_2O^+ and T_3O^+ ions can be neglected as a source of tritium, since the mother liquid used contains only a trace of tritium.

For the other species containing hydrogen atoms, $(COOH)_2$ and $C_2O_4H^-$, we can infer that tritium should be diluted, because the bond energy of the hydrogen atoms of H_2O is larger than those of $(COOH)_2$ and $C_2O_4H^-$, as can be seen from the proton level given by Gurney.[11,12] In fact, the dilution of deuterium in $(COOH)_2$ was evidenced by the work of Okazaki and Takemura.[13]

Consequently, tritium should be diluted in all the species in the aqueous solution of oxalic acid. Moreover, these species are subjected to further dilution to a small extent during the integration into the crystal according to the surface-diffusion mechanism. The possible dilution estimated above for the $(COOH)_2$ groups of the crystal can be confirmed by measuring the tritium concentration in the oxalic acid dihydrate, $(COOH)_2 \cdot 2H_2O$.

It is well known that a labeled organic compound containing a weak β-emitter, *e. g.*, tritium, causes a quenching in the liquid scintillation counting. The quenching of the oxalic acid was, therefore, corrected according to the method of Peng.[14] The tritium concentration ratio in the $(COOH)_2 \cdot 2H_2O$ crystal to the mother liquid was thus found to be 0.876 ± 0.009. It can thus be concluded that tritium is diluted in the $(COOH)_2$ groups of the crystal by *ca.* 0.676, assuming the S value of 0.976 for the hydration water, as has been described above.

Tritium Fractionation during the Dehydration. It is generally accepted that hydrogen atoms directly bonded to oxygen atoms are labile and can be exchanged with other hydrogen atoms.[9] In the case of oxalic acid dihydrate, it is likely that there occurs a ready exchange of protons between $(COOH)_2$ and H_2O by mere shifts of protons through the hydrogen bonds in the crystal.[15] The ready exchange under a vacuum dehydration was confirmed using deuterium by Okazaki and Takemura.[13]

In the exchange reaction, the hydrogen isotope effect can also occur. Okazaki and Takemura reported that deuterium is slightly enriched in the water molecules, as is the case with the aqueous solution of oxalic acid.[13] According to the study, we can assume that tritium is slightly enriched in the water molecules relative to the carboxyl groups during the dehydration. It can be considered qualitatively that the small S value observed for the dehydrated water of $(COOH)_2 \cdot 2H_2O$, 0.865, should result from the fact that the dilution of tritium in the water due to the proton exchange between $(COOH)_2$ and H_2O surpasses the enrichment through the proton exchange during the dehydration.

Although the present discussion is somewhat qualitative, it seems worthwhile to examine the HTO fractionation in the hydrated crystal containing hydrogen atoms other than those of the hydration water, because a very large fractionation may be possible. Such an examination can also contribute to a better understanding of the proton exchange in the solution and/or in the dehydration.

The authors wish to express their thanks to Dr. Osamu Yamamoto for his help in analyzing the activity of tritium.

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