Reactivity of Normal Chain Diols in T-for-H Exchange Reaction

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In order to clarify the reactivity of normal chain diols, the hydrogen-isotope exchange reaction (T-for-H exchange reaction) between solid poly (vinyl alcohol) labeled with tritium and each normal chain diol dissolved in 1,4-dioxane has been observed in the range of 30 to 70 °C (or 90 °C). The observed data was analyzed with the A^-McKay plot method, and the following three matters are consequently found. (1) The greater the number of methylene groups in a diol is, the smaller is the reactivity of the diol. (2) A significant difference in the reactivity is found between diols having even number of methylene groups and those having odd number of ones, and the reactivity of the former is larger than that of the latter. (3) As to the ratio of the decrease of the reactivity of the diols having increasing number of methylene groups, the ratio of diols having even number of methylene groups is greater than the ratio of diols having odd number of ones.

Key Words: normal chain diol, T-for-H exchange reaction, liquid-solid reaction, A^-McKay plot method, rate constant

1. Introduction

In general, environmental pollution has become a serious problem. Radioactive materials are one of the major sources of environmental pollution. Especially, manmade isotopes are troublesome because of their inconstantness. Tritium (T or ^3H) is formed by high energy cosmic ray and is also formed during nuclear power generation. The concentration of the former is approximately constant, but the latter is not. T emits electron and its maximum energy is low (18.6 keV). So external exposure from T can be disregarded. However, when T is incorporated into a living body, it causes internal exposure to tissue, and hydrogen-isotope exchange reaction occurs between T and the compound in the body^{1,2}. Therefore, it is important to quantitatively clarify the reactivity of T.

Previously, a lot of hydrogen-isotope exchange reactions (T-for-H exchange reactions) were observed in gas-solid system and liquid-solid one^{3-6}. Using both the data observed and the A^-McKay plot method^{7,8}, the rate constants (k) for the materials in the reaction were obtained. Using each k, the reactivity of the materials used was quantitatively compared with each other. The following conclusions were consequently obtained: (1) T-incorporation into some kinds of functional groups (e.g., -OH, -COOH, -NH2, etc.) easily occurs; (2) T-incorporation into the materials largely depends on
both the kind of the functional groups and the molecular structure of the materials; (3) T-incorporation into polymers depends on the degree of polymerization of the polymers\(^9,10\).

Based on the above-mentioned, the purposes of this work is to clarify: (1) the effect of temperature on the reactivity of normal chain diols; (2) the effect of the number of methylene groups in each diol on the reactivity of the diol; (3) the effect of the even number (or odd number) of methylene groups in each diol on the reactivity of the diol. For these purposes, we observed the T-for-H exchange reaction between a T-labeled compound and one of the normal chain diols having several methylene groups in a liquid-solid system.

2. Experimental

2.1 HTO water

HTO water (the specific activity was \(1.9 \times 10^8\) Bq \(\cdot\) g\(^{-1}\)) was purchased from Japan Radioisotope Association and was diluted to \(6.0 \times 10^5\) Bq \(\cdot\) g\(^{-1}\) with deionized water. Its specific activity was measured with a liquid scintillation counter (Aloka LSC-703). Because the half-life of T is 12.3 y, the specific activity of HTO water thus prepared was corrected about every 3 months by calculation. The HTO water thus measured was used for synthesizing the T-labeled compound that was used as a solid sample.

2.2 Poly (vinyl alcohol)

Based on the previous report\(^11\), poly (vinyl alcohol) having a mean polymerization-degree of 2000 (abbreviated as PVA\(_{2000}\)) was used as a solid sample labeled with T. The method of synthesis of T-labeled PVA\(_{2000}\) (abbreviated as PVA\(_{2000}\)(T)) was roughly as follows: (1) PVA\(_{2000}\) was dried, and sieved to obtain narrow fractions (53 – 75 \(\mu\m\)); (2) PVA\(_{2000}\) thus obtained was in contact with HTO vapor, and a part of OH groups in PVA\(_{2000}\) was labeled with T (i.e., OT groups). The ratio of OH groups and OT ones in PVA\(_{2000}\)(T) can be shown as follows by calculation\(^8\): \((-\text{OH}) : (-\text{OT}) = 6 \times 10^8 : 1\).

2.3 1,4-Dioxane

1,4-dioxane was used as a solvent. To dry the solvent, about 20 g of dried CaSO\(_4\) was placed in 200 cm\(^3\) of 1,4-dioxane. After mixing, the 1,4-dioxane was allowed to stand for one day. After that, the 1,4-dioxane was filtered, and was used for a solution of each normal chain diol.

2.4 Normal chain diol

The following seven normal chain diols were purchased as Guaranteed Reagent (or Extra Pure), and each material was dissolved in above-mentioned 1,4-dioxane to get a liquid sample: ethylene glycol (HO\((\text{CH}_2)\_2\text{OH}\), 1,3-propanediol (HO\((\text{CH}_2)\_3\text{OH}\), 1,4-butanediol (HO\((\text{CH}_2)\_4\text{OH}\), 1,5-pentanediol (HO\((\text{CH}_2)\_5\text{OH}\), 1,6-hexanediol (HO\((\text{CH}_2)\_6\text{OH}\), 1,7-heptanediol (HO\((\text{CH}_2)\_7\text{OH}\), 1,8-octanediol (HO\((\text{CH}_2)\_8\text{OH}\).

Prior to the observation of the reaction, it was confirmed (by calculation or experiment) that the three conditions for the application of the \(A^\prime\)-McKay plot method were satisfied (i.e., the T-for-H exchange reaction can be treated as the pseudo-first-order reaction)\(^8,12\). After the confirmation, each diol was dissolved in 1,4-dioxane and set at 1.0 mol \(\cdot\) dm\(^{-3}\) (only 1,8-octanediol was 0.25 mol \(\cdot\) dm\(^{-3}\)).

2.5 T-for-H exchange reaction

The observation of the T-for-H exchange reaction between PVA\(_{2000}\)(T) as solid sample and the liquid sample (prepared as shown in the former section) was roughly as follows: (1)
17.6 mg of PVA₂₀₀₀(T) was placed in each vial (about 20 vials); (2) 5.00 cm³ of a liquid sample was also placed in the vial, and the vial was sealed; (3) the vial was dipped in the thermostatic water bath (with a shaker) at the prescribed temperature, and the T-for-H exchange reaction occurred; (4) after the prescribed time passed, the vial was taken out of the bath, and was rapidly dipped in ice water (<4 °C) to stop the reaction; (5) the liquid sample in the vial was filtered, and the activity of 2.00 cm³ of the liquid was measured with the liquid scintillation counter; (6) similar experiments were carried out at the other temperatures (or were carried out using one of other liquid samples).

3. Results and Discussion

3.1 Reactivity of ethylene glycol in T-for-H exchange reaction

Prior to the experiments, it was clarified using the same method reported previously¹³) that the 1,4-dioxane as solvent has not been concerned in the T-for-H exchange reaction under the condition in this work. The T-for-H exchange reaction between PVA₂₀₀₀(T) and 1.0 mol·dm⁻³ ethylene glycol in 1,4-dioxane was observed at 30(50, and 70) °C, and the result is shown in Fig. 1. In this figure, the plot for 50 °C was removed for simplification, but the tendency of the plot was similar to the other temperature plots in this figure. From the figure, it is found that (1) for each plot, the activity of ethylene glycol increased with increasing time at each temperature, (2) the higher the temperature is, the larger is the activity, (3) each plot has one inflection point, and the point is shifted toward the origin of the figure with increasing the temperature. As a result, it can be considered that the T-for-H exchange reaction at the surface of PVA₂₀₀₀(T) reaches equilibrium at the point⁷,⁸). In other words, it seems that the reaction time at the surface is short when temperature is high.

To obtain the reactivity of ethylene glycol, the A"-McKay plot method was applied to Fig. 1, and the A"-McKay plots are made (Fig. 2). In Fig. 2, two straight lines are shown, and there are good relationship in each straight
Based on the previous report\(^7,8\), it is found that the gradient of each straight line in Fig. 2 corresponds to \(k\) for ethylene glycol at each temperature.

### 3.2 Reactivity of normal chain diols in T-for-H exchange reaction

Using the same method mentioned in 3.1, \(k\) for each diol was obtained at each temperature, and shown in Table 1. From the table, it is found that the reactivity of each diol is large when temperature is high. Considering the relation between the number of methylene groups and the reactivity of the diols, the following two groups can be compared: (1) the number of methylene groups in a diol is even number (Even-Number); (2) that is odd number (Odd-Number). It is also found that the greater the number of methylene groups is, the lower is the reactivity of the diol. On the basis of Table 1, Fig. 3 is made. It is found from the figure that (1) the decreasing ratio of Even-Number group is larger than that of Odd-Number one, and (2) for both groups, the reactivity decreases at a constant ratio with the number of methylene groups per molecule.

As to the reactivity of diols, the following expression may be considered that (1) each methylene groups in a compound has electron-donative effect (i.e., M-effect)\(^14,15\), as a result, the reactivity of each OH group decreases, (2) the reactivity of the compound tends to decrease when the number of methylene groups is great.

According to the previous report\(^13\), above-mentioned tendency was seen in some kinds of aliphatic dicarboxylic acids. For Even-Number group and Odd-Number one in this work, a similar concept to the concept of aliphatic dicarboxylic acid may be accepted. As to Odd-
Number group, it is easy to form an intramolecular hydrogen-bond. The molecule is consequently to be stable against the T-for-H exchange reaction. On the other hand, Even-Number group is hard to form an intramolecular hydrogen-bond, and the molecule is to be unstable against the reaction. Accordingly, the reactivity of Even-Number ones is higher than that of Odd-Number ones. It also seems that the similar effect of the hydrogen-bond appears in the T-for-H exchange reaction at the range of 30 °C to 70 °C.

References


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