MEASUREMENT METHOD OF "ACIDITY BASED ON KINETIC LOGIC" BY APPLYING HYDROGEN-ISOTOPE EXCHANGE REACTION IN A HETEROGENEOUS SYSTEM

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Abstract Hydrogen-isotope exchange reaction between HTO vapor and one of solid materials (or between Poly(vinyl alcohol) labeled with tritium and one of liquid materials) was observed. The reaction was analyzed with both the data obtained and the A"-McKay plot method, and "the acidity based on kinetic logic" of each material was obtained. It has been found that the A"-McKay plot method is useful to obtain "the acidity" of a slightly soluble material.

Key words Hydrogen-isotope exchange reaction, A"-McKay plot method, gas-solid reaction, liquid-solid reaction

The pK of a material is generally used when the reactivity (or acidity) of the material is discussed. However, it is difficult to express (by using pK) the acidities of the materials which are dissociative slightly (and/or soluble slightly). In order to express acidity for such materials easily, new measurement method (the A"-McKay plot method[1]) for the acidity based on the following idea was proposed[2]: such a material will separate the hydrogen atom(s) easily if the acidity is large. The idea has been developed as follows: as to a compound including hydrogen (^1H) atom(s), an increase in the exchange rate observed in the replacement between ^1H atom(s) and hydrogen-isotope (e.g., ^3H (or T)) atom(s) results in an increase in the ability to offer ^1H atom(s); the increase in this ability results in an increase in the acidity. Accordingly, the observation of the hydrogen-isotope exchange reaction will enable one to determine the acidity (of a material) based on this idea. The acidity obtained based on this idea has been named "acidity based on kinetic logic"[1]. Considering the above history, the following three aims were chosen in this work: (1) to ascertain whether "acidity based on kinetic logic" is useful to clarify the reactivity of a material; (2) to ascertain whether the A"-McKay plot method is useful to analyze a reaction in a heterogeneous system; (3) to clarify the relation between "the acidity" and pK.

EXPERIMENTAL

Gas-solid reaction The vacuum[2] line was used to observe the hydrogen-isotope exchange reaction between each of solid sample materials (unlabeled) and HTO vapor (gas-solid reaction). The amount of solid sample used was about 20 mg per run, and that of HTO water used was 7.22 mg. The specific activity of HTO water used was $6 \times 10^5 \text{ Bq g}^{-1}$. The experimental method used was the same as that described previously[1,2].

Liquid-solid reaction In order to observe a liquid-solid reaction, poly(vinyl alcohol) labeled with tritium (abbreviated below as PVA(T)) was synthesized as the solid sample material by using the method mentioned above. A constant-temperature water bath was used in order to observe the hydrogen-isotope exchange reaction between each of liquid sample materials (unlabeled) and PVA(T). The amount of liquid sample used was 2.0 ml (or 5.0 ml) per run, and that of PVA(T) used was 17.6 mg. The method used for observation of the reaction was the same as that described previously [3,4].

Measurement of activity The activity of each sample used was measured with a liquid scintillation counter (Aloka LSC-703).

Sample material For gas-solid reaction, solid sample materials used were PVA, succinic acid, and monohydrogenphosphates, etc. For liquid-solid reaction, several liquid materials (methanol, acetic acid, benzaldehyde,

aniline, phenol, etc.) were used.

RESULTS AND DISCUSSION

Comparison of "the acidities" The hydrogen-isotope exchange reaction between HTO vapor and one of solid materials (gas-solid reaction) was observed. The reaction was analyzed with both the data obtained and the A"-McKay plot method, and the rate constant (i.e., "the acidity based on kinetic logic") for the solid material used was obtained. As to liquid-solid reaction, the rate constant obtained for the liquid material used was named "the acidity based on kinetic logic mediated with PVA(T)"[5]. A part of "the acidities" obtained are shown in Tables 1 and 2.

Table 1. "Acidities" obtained in gas-solid reaction at 70°C

Material	"Acidity"
PVA ₅₀₀ *	1.3
PVA ₂₀₀₀ *	1.0
Succinic acid	2.0×10^{-1}
CaHPO ₄	6.2×10^{-2}
SrHPO ₄	5.4×10^{-2}
H ₂ NCH ₂ CO ₂ Na	5.2×10^{-2}

Table 2. "Acidities" obtained in liquid-solid reaction at 70°C

Material	"Acidity"
Methanol	3.8×10^1
Acetic acid	1.1×10^1
Phenol	5.2
Benzoic acid	4.6
Aniline	2.8
Benzaldehyde	4.5×10^{-1}

* 500 (or 2000) means the degree of polymerization.

From the tables the following matters have been found: (1) "the acidity based on kinetic logic" is useful to estimate the reactivity of the material; (2) the materials can be compared in "the acidity" with each other; (3) "the acidity" of a slightly dissociative (and/or slightly soluble) material can be obtained with A"-McKay plot method by applying hydrogen-isotope exchange reaction in a heterogeneous system.

Application of the Hammett rule The data obtained from the exchange reaction using monosubstituted benzoic acids[6], monosubstituted benzaldehydes[4], monosubstituted anilines[7] or monosubstituted phenols[8] were analyzed with the A"-McKay plot method. The rate constants for respective monosubstituted ones were derived therefrom. Based on both the rate constants derived and the substituent constants[6] of respective materials, a Hammett plot[9] was made. The correlation coefficient for the straight line in the plot can satisfy the condition of significance at the 1 % level. The gradient of the straight line (i.e., the reaction constant) in the plot was also obtained.

Hammett plots for the other three monosubstituted materials were also made. The reaction constants for these monosubstituted ones have been obtained. These four reaction constants obtained are as follows at 70°C: 0.37 for monosubstituted benzoic acids (gas-solid reaction); 1.3 for monosubstituted benzaldehydes (liquid-solid reaction); 1.1 for monosubstituted anilines (liquid-solid reaction); 2.1 for monosubstituted phenols (liquid-solid reaction).

On the basis of the above-mentioned, the following conclusions are obtained: (1) it is fairly certain that the reactivity of the monosubstituted materials used in this work follows the Hammett rule (in other words, there is a quantitative relation between pK and "acidity based on kinetic logic"); (2) the reactivity of these monosubstituted materials increases with the increase of electron-attractive effect of the corresponding substituent since the reaction constants obtained are greater than zero.

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