Vol.16 No.6 NUCLEAR SCIENCE AND TECHNIQUES December 2005

Simulataneous analysis of reactivity of anilines in the hydrogen-isotope exchange reaction

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Abstract In order to reveal the reactivity of a functional group in an aromatic compound having two substituents in the aromatic ring, the hydrogen-isotope exchange reaction (T-H exchange reaction) between tritiated water vapor (HTO vapor) and 4-amino-2-methylbenzenesulfonic acid (and 5-amino-2-methylphenol) were dynamically observed at 50℃ (and 70℃) in a gas-solid system. Consequently, the fact that the specific activity of the acid increased with time was obtained, and the T-for-H exchange reaction occurred. By applying the *A″*-McKay plot method to the data observed, the rate constant of each functional group for the reaction was obtained. After the additive property of the Hammett's rule was applied to this work, the new substituent constants were obtained. From the above-mentioned, the following four items have been confirmed: (1) the reactivity of the functional groups can be dynamically analyzed, and the *A″*-McKay plot method is useful to analyze the reactivity; (2) the additive property of the Hammett's rule is applicable to quantitative comparison of the reactivity of the functional groups; (3) the reactivity of the functional groups can be simultaneously analyzed by using the *A″*-McKay plot method in the T-H exchange reaction; and (4) the method used in this work is also useful for analyzing the reactivity of a certain material having some kinds of functional groups.

Key words Trisubstituted aromatic compound, Gas-solid system, T-H exchange reaction, Hammett's rule, *A″*-McKay plot method, Rate constant

CLC numbers O625.63^{+}1, O643.14, TL92^{+}3, X24

1 Introduction

Recently, environmental pollution by radioactive materials becomes a serious problem around the world. Tritium (^{3}H or T) contamination is one type of the pollution. T is a radioisotope of hydrogen. Since the maximum energy of the radiation (i.e. β-ray) from T is very low (18.6 keV), the external exposure from T is not so important. However, if T is incorporated into human body, the following problem must be considered since the half-life of T is relatively long (12.3a) compared with the human mean life. With development of society, now it seems that the more the number of nuclear power plants (the reprocessing plants for spent nuclear fuel, and advanced study of nuclear fusion) is, the more the amount of T is. The total radiation doses of tritium are relatively great among the radionuclides in atmospheric nuclear test.[1] So the study of tritium-impact on environment (and human being) turns more and more important. The exchange reaction between tritiated-water vapor and an aromatic compound in gas-solid system has been studied for last twenty years. To determine the rate constants (*k*) for the compound, the *A″*-McKay plot method was applied to the data obtained. Some Hammett plots were made using both *k* values and the substituent

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Supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars of State Education Ministry and the Scientific Research Foundation for the Returned Overseas Chinese Scholars of Heilongjiang Educational Committee (Grant No.1055HZ002).

Received date: 2005-07-12

constants, and the effect of the substituents on the reactivity was revealed. With regard to monosubstituted,[2-5] disubstituted (except ortho-position),[6-8] and 1,3,5-trisubstituted aromatic compounds,[9] the rate constants and the substituent constants were well fitted on the Hammett plot. As for trisubstituted aromatic compound having substituent(s) in ortho-position, the question of the applicability to the Hammett's rule is still open. Recently, two compounds for benzenesulfonic acid series have been studied.[10] However, as to the compound for aniline series, the applicability to the Hammett's rule has not been so far clarified. So the compounds of 4-amino-2-methylbenzenesulfonic acid (and 5-amino-2-methylphenol) were selected to employ the T-H exchange reaction with HTO water in a gas-solid system.

In this work, the following aims were chosen: (1) to quantitatively clarify the reactivity of NH_2 and SO_3H (or OH) groups in a compound, (2) to clarify the effect of the temperature (and the substituents) on the reactivity of the functional group, (3) to have a better ascertaining whether the A''-McKay plot method is applicable to clarify the reactivity of the groups, and (4) to ascertain further whether the Hammett's rule[11,12] is useful to analyze the reactivity of aromatic compounds which have three kinds of functional groups (i.e., two substituents and one functional group).

2 Experimental

2.1 Sample materials

HTO water whose specific activity is 185 MBq/g was purchased from Japan Radioisotope Association, and was diluted to 0.6 MBq/g with distilled water. The HTO water thus prepared was used in this work, whose specific activity was determined accurately with a liquid scintillation counter. The specific activity was corrected by calculation every three months because the specific activity gradually decreased due to radioactive decay.

The samples of 4-amino-2- methylbenzenesulfonic acid and 5-amino-2-methylphenol were purchased from Wako Pure Chemical Industries, Ltd. At first, the samples were sufficiently powdered in an agate mortar, and then sieved to obtain a grain size between 53 and 75 μm in diameter. Then the sieved samples were dried in a vacuum oven at 70℃ till constant weight. After that, the sample was preserved in a desiccator containing silica gel. Each sample thus prepared was used for the gas-solid exchange reaction.

2.2 The method of observation

The vacuum line [13] used in the experiments was shown in Fig.1. The hydrogen-isotope exchange reaction (i.e., T-H exchange reaction) was observed in a gas-solid system at 50℃ (and 70℃). The method of observation can be roughly described as follows: (1) the mass of each solid sample used was 12.0 mg per run, and the mass of HTO water used was 9.02 mg per run; (2) after the reaction, distilled water and ethanol were used to dissolve 4-amino-2-methylbenzenesulfonic acid and 5-amino-2-methylphenol, respectively, in the T-H exchange reaction; (3) the activity of the resulting solution was measured with a liquid scintillation counter; (4) the data observed were analyzed with the A''-McKay plot method, and k for each solid sample material used was obtained; (5) the Hammett plot was made of the common logarithm for the ratio of k value to k_0 value versus the substituent constant obtained in th

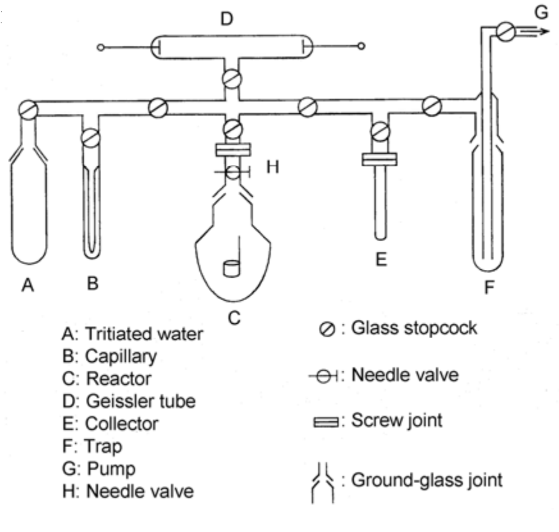

Fig.1 The vacuum line for this work.

Previously,[2] it was found that H atoms directly bonded to benzene ring could not exchange with T atoms in HTO vapor in the T-H exchange reaction. Accordingly, it was considered that only H atoms in the NH_2 and SO_3H (or OH) groups of the solid sample material used in this work could exchange with T in HTO vapor. Prior to the observation, it was confirmed (by calculation and experiment) that three conditions[3,8] for applying the *A*″-McKay plot method were satisfied.

3 Results and discussion

3.1 Reactivity of amino and sulfonic acid (or hydroxyl) groups

In order to clarify the reactivity of NH_2 and SO_3H (or OH) groups in a trisubstituted aromatic compound, the T-H exchange reaction between 4-amino-2-methylbenzenesulfonic acid (or 5-amino-2-methylphenol) and HTO vapor was observed at 50℃ (and 70℃). The time-dependence of the exchange reaction at each temperature and each sample material were similar to each other. For the simplicity, only the relation between the reaction time and specific activity of T in 4-amino-2-methylbenzenesulfonic acid at 50℃ was given in Fig.2, which showed that the reaction did occur because the activity of T in 4-amino-2-methylbenzenesulfonic acid increased with time.

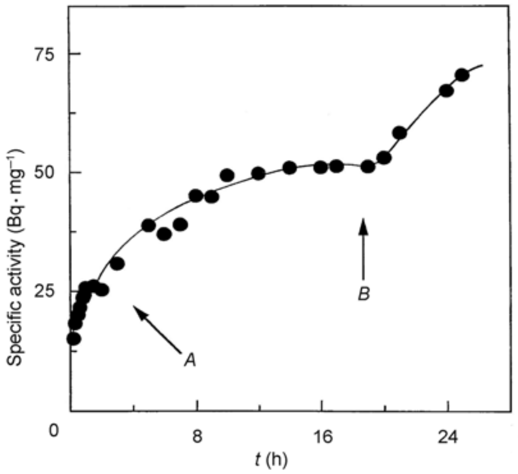

Fig.2 Specific activity *vs.* time for the reaction between 4-amino-2-methylbenzenesulfonic acid and HTO vapor at 50℃.

Fig.2 consists of the following three parts: (a) the first part is the area from the origin to point *A*; (b) the second one is the area from point *A* to point *B*; (c) the third is the area from point *B* to the right end of the line. Previously,[14] it was found that the reactivity of the SO_3H (or OH) group was much larger than that of the NH_2 group when the two groups existed in the same molecule. Accordingly, the three parts mentioned above correspond to the following three reactions, respectively: (a) two reactions (between HTO vapor and the SO_3H group (and the NH_2 one) at the surface of the solid sample) proceeded at the same time, and the former reaction between HTO vapor and the SO_3H group attained equilibrium at point *A*; (b) the latter reaction continued, and it also attained equilibrium at point *B*; (c) the T-diffusion reaction into the inner phase of the sample occurred. Consequently, the first part in Fig.2 corresponds to Reactions (1) and (2) shown as follows, the second one corresponds to Reaction (3), and the third one corresponds to the diffusion reaction.

$$HO_3S(CH_3)C_6H_3\text{-}NH_2+HTO \rightleftharpoons TO_3S(CH_3)C_6H_3\text{-}NH_2+H_2O \quad (1)$$

$$HO_3S(CH_3)C_6H_3\text{-}NH_2+HTO \rightleftharpoons HO_3S(CH_3)C_6H_3\text{-}NHT+H_2O \quad (2)$$

$$TO_3S(CH_3)C_6H_3\text{-}NH_2+HTO \rightleftharpoons TO_3S(CH_3)C_6H_3\text{-}NHT+H_2O \quad (3)$$

In order to apply the *A*″-McKay plot method to the data shown in Fig.2, $\chi_{\infty(F2)}$ is initially calculated, where $\chi_{\infty(F2)}$ means the specific activity of T in the NH_2 group at the surface of the sample when the exchange reaction between HTO vapor and the NH_2 group attained equilibrium because the reactivity of the SO_3H group was much larger than that of the NH_2 one. Using the values from point *A* to point *B* in Fig.2, the *A*″-McKay plot for the NH_2 group has been made (Fig.3). To obtain the straight line, the correlation coefficient has been calculated by applying the method of the least squares. In Fig.3, the dashed line shows the extrapolation from point *A* to the origin. The gradient of the straight line in Fig.3 can satisfy the condition of significance at the 1% level, and it is equal to *k* for the NH_2 group in the sample material. Then each value between point *A* and the origin in Fig.2 was subtracted from the value corresponding to the dashed line in Fig.3. Using the each data subtracted, the *A*″-McKay plot of the SO_3H group has been made (Fig.4). In Fig.4, $\chi_{\infty(F1)}$ means the specific activity of T in the sample when the reaction between HTO vapor and the SO_3H group attained equilibrium. In other words, $\chi_{\infty(F1)}$ is the specific activity of T in the SO_3H group at the surface of the sample in Reaction (1). The gradient of the straight line in Fig.4 can also satisfy the condition of significance at the 1% level, and it equals *k* for the SO_3H group in the reaction. In the same manner, the figures for the rest reactions were analyzed, and k values were obtained. The results are tabulated in Table 1.

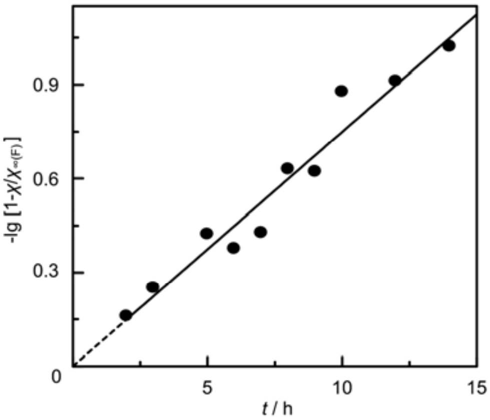

Fig.3 A''-McKay plot of NH_2 group for 4-amino-2-methylbenzenesulfonic acid at 50℃.

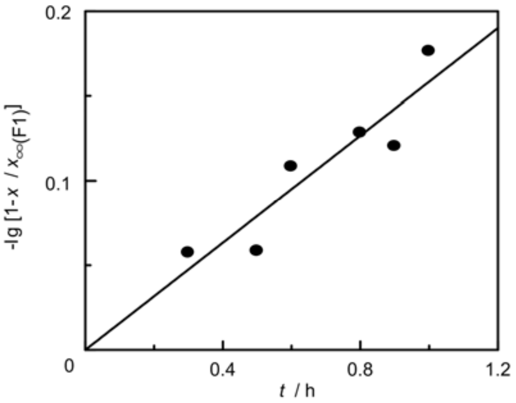

Fig.4 A''-McKay plot of SO_3H group for 4-amino-2-methylbenzenesulfonic acid at 50℃.

Table 1 Rate constants for the NH_2, OH and SO_3H groups, and substituent constants calculated in this work

Materials	Functional group	$k/10^{-2}h^{-1}$ (50 ℃)	$k/10^{-2}h^{-1}$ (70 ℃)	Substituent constant
4-amino-2-methylbenzenesulfonic acid	NH_2	7.4	8.6	0.571(σ_1)
	SO_3H	16	28	—
5-amino-2-methylphenol	NH_2	6.4	7.4	-0.049(σ_2)
	OH	14	27	—
p-aminobenzenesulfonic acid[14]	NH_2	7.7	8.7	
	SO_3H	28	39	
m-aminophenol[14]	NH_2	6.5	7.7	
	OH	28	40	

Note: $\sigma_1=\sigma$(p-SO_3H)+σ(m-CH_3), $\sigma_2=\sigma$(m-OH)+σ(p-CH_3)

From Table 1, the ratio of k value for the SO_3H group to k value for the NH_2 one in 4-amino-2-methylbenzenesulfonic acid molecule is shown as follows:

50℃ (-SO_3H) : (-NH_2)=2.2 : 1 (4)

70℃ (-SO_3H) : (-NH_2)=3.3 : 1 (5)

The ratios of k values for the same kind of group at different temperature are the next:

SO_3H group (70℃) : (50℃)=1.8 : 1 (6)

NH_2 group (70℃) : (50℃)=1.2 : 1 (7)

From the above comparison, the following characteristics can be obtained: a) the reactivity of the SO_3H group is 2-4 times greater than that of the NH_2 one; b) the reactivities of both the SO_3H group and the NH_2 one increase with temperature.

From Table 1, k values for the OH and NH_2 groups in 5-amino-2-methylphenol can be compared with each other at 50℃ (and 70℃):

50℃ (-OH) : (-NH_2)=2.2 : 1 (8)

70℃ (-OH) : (-NH_2)=3.6 : 1 (9)

The ratios of k values for the same kind of group at different temperatures are given as follows:

OH group (70℃) : (50℃)=1.9 : 1 (10)

NH_2 group (70℃) : (50℃)=1.2 : 1 (11)

From the comparison, it is found that the results are similar to those obtained in 4-amino-2-methylbenzenesulfonic acid.

3.2 The effect of methyl group in ortho-position on the rate constants of sulfonic acid group (or hydroxy one) in a trisubstituted aromatic compound

The substituents of 4-amino-2-methylbenzenesulfonic acid and *p*-aminobenzenesulfonic acid differ from a methyl group. Comparing the data of the above-mentioned compounds in Table 1, the following item was obtained regarding the effect of the methyl group on k for the SO_3H one: k value for the former compound at each temperature was lower than the value for the latter one.

As to 5-amino-2-methylphenol and *m*-aminophenol, methyl group is bonded with benzene ring in para-position in the former. Comparing the data of the above two compounds in Table 1, the following item can be obtained about the effect of the methyl group on *k* for the OH one: *k* value for the former compound at each temperature is lower than *k* value for the latter one.

It is generally known that the electronic effects (I-effect and R-effect) can be seen in substituted benzoic acids, and that these effects can be classified into the following four types according to the species of substituent[2]: (A) I-effect goes to an electron-attractive effect (abbreviated below as (+)); R-effect goes to an electron-donative one (abbreviated below as (-)). (B) I-effect goes to (+); R-effect goes to (+). (C) I-effect goes to (-); R-effect goes to (-). (D) I-effect goes to (-); R-effect goes to (+). As for methyl group as a substituent, since methyl group is an electron-donative group, it corresponds to Case (C).

Ortho-substituted benzenesulfonic acid usually has a peculiarity (ortho-effect). Since methyl group is a huge group, the result of the steric hindrance effect resists the T-H exchange reaction, and decreases *k* value for the SO_3H (or OH) group.

3.3 Applicability of the Hammett's rule

In general, the effect of the substituent of each aromatic compound on the reactivity of the compound can be quantitatively expressed with the Hammett's rule.[15] The rule is shown in the following equations:

$$\lg(k/k_0)=\rho\sigma \tag{12}$$

$$\lg(K/K_0)=\rho\sigma \tag{13}$$

where k is a rate constant for a meta (or para)- substituted aromatic compound, k_0 is the rate constant for the unsubstituted aromatic compound, K is the equilibrium constant for a meta (or para)-substituted aromatic compound, K_0 is the equilibrium constant for the unsubstituted aromatic compound, ρ is the reaction constant, σ is the substituent constant.

As far as this work is concerned, k is a rate constant for a substituted aminobenzene; k_0 is the rate constant for *m*-aminobenzenesulfonic acid, K is the equilibrium constant for the former material; and K_0 is the equilibrium constant for the latter one, ρ is the reaction constant, σ is the substituent constant. Accordingly, it seems that a quantitative relation exists between k and σ when the Hammett's rule can be applied to the reaction.

As for multi-substituted aromatic compound, if there is no substituent in ortho-position for functional group (in this work, the functional group is NH_2 group), the additive property of the Hammett rule can be adopted to obtain the total substituent constant (i.e., new σ) in the multi-substituted aromatic compound:[4]

$$\lg(k/k_0)=\rho\Sigma\sigma \tag{14}$$

In Eq.(14), the new substituent constant (σ_1) of the total substituents (i.e. CH_3 and SO_3H groups) in 4-amino-2-methylbenzenesulfonic acid and the new substituent constant (σ_2) of that (i.e. CH_3 and OH groups) in 5-amino-2-methylphenol can be calculated:

$$\sigma_1=\sigma(\text{m-CH}_3)+\sigma(\text{p-SO}_3\text{H})=-0.069+0.64=0.571 \tag{15}$$

$$\sigma_2=\sigma(\text{p-CH}_3)+\sigma(\text{m-OH})=-0.170+0.121=-0.049 \tag{16}$$

The calculated results are tabulated in Table 1. In order to clarify the reactivity of the two compounds used in this work the values of $\lg(k/k_0)$ and the new obtained substituent constants were added to the plots obtained previously, and new plots were obtained (Fig.5). In Fig.5, k is the rate constant for the functional group (i.e. NH_2 group) in each substituted aminobenzene, and k_0 is the rate constant for the NH_2 group in *m*-aminobenzenesulfonic acid. From Fig.5, at 50℃ both the gradient of the straight line and the

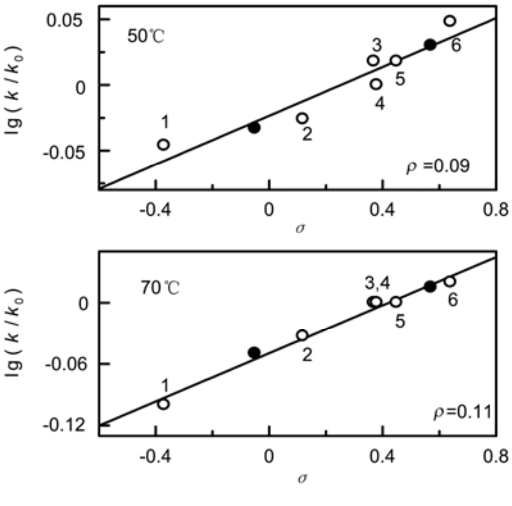

Fig.5 Each plot of the logarithm of the relative rate constant for substituted benzenesulfonic acid vs. substituent constant (σ). Symbol k is a rate constant for each substituted benzenesulfonic acid, and k_0 is the rate constant for *m*-aminobenzenesulfonic acid.

1: *p*-OH, 2: *m*-OH, 3: *m*-COOH, 4: *m*-SO_3H, 5: *p*-COOH, 6: *p*-SO_3H.

●: obtained in this work; ○: data from Ref.[14].

correlation coefficient of the line are 0.09 and 0.955 respectively, and are almost equal to those obtained previously (0.09 and 0.941 respectively); at 70℃ both the gradient of the straight line and the correlation coefficient of the line are 0.11 and 0.992 respectively, and are almost equal to those obtained previously (0.12 and 0.991 respectively). By parity of reasoning, it is confirmed that the reactivity of the compounds used in this work follows the Hammett's rule.

From the above-mentioned, it was found that (1) the Hammett's rule could be applied to clarify the reactivity of aromatic compounds in the T-H exchange reaction, (2) the reactivity of trisubstituted aromatic compound could be analyzed by applying the additive property of the Hammett's rule even if the compound had an ortho-substituent.

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