2814 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 2814—2826(1993) [Vol. 66, No. 10

# Oxygen-17 Magnetic Resonance Study of the Oxygen Exchange of Methyl- and Butylarsonic Acids and Dimethylarsinic Acid with Solvent Water

Akiko Okumura,* Midori Fushimi, and Masako Yamamoto
Department of Chemistry, Faculty of Science, Nara Women's University, Kita-uoya-nishimachi, Nara 630

(Received April 6, 1993)

The rates of the oxygen-exchange reactions of methyl- and butylarsonic acids and dimethylarsinic acid with solvent water were measured in the pH range below 6, and at temperatures between 50 and 90 °C, by using the $^{17}$O NMR line-broadening technique. For methylarsonic acid, the rate $R_{\mathrm{MAA}}$ is expressed by the following rate law: $R_{\mathrm{MAA}}=k_{\mathrm{h1}}[\mathrm{H}^+][\mathrm{H_2A}]+k_1[\mathrm{H_2A}]+k_{\mathrm{h2}}[\mathrm{H}^+][\mathrm{H_2A}]^2+k_2[\mathrm{H_2A}]^2+k_3[\mathrm{H_2A}][\mathrm{HA}^-]$, where $H_2A$ and $HA^-$ designate $CH_3AsO_3H_2$ and $CH_3AsO_3H^-$, respectively. For butylarsonic acid, the rate law is expressed as: $R_{\mathrm{BAA}}=k_{\mathrm{h1}}[\mathrm{H}^+][n\text{-}\mathrm{C_4H_9AsO_3H_2}]$. For dimethylarsinic acid, its conjugated acid is involved in the rate law as: $R_{\mathrm{CAA}}=k'_{\mathrm{h1}}[(\mathrm{CH_3})_2\mathrm{AsO_2H_2^+}]+k'_{\mathrm{hh1}}[\mathrm{H}^+][(\mathrm{CH_3})_2\mathrm{AsO_2H_2^+}]$. The exchange rates of methyl- and butylarsonic acids and dimethylarsinic acid (50—90 °C) were analyzed in terms of the respective rate law to obtain the values of the rate constants involved in the rate laws. The activation parameters of these rate constants were obtained; for both the first- and second-order rate constants, the activation energies are characteristic of their small values (from 45 to 20 kJ mol$^{-1}$), while the activation entropies have large negative values, which are found in the range between $-92$ and $-145$ J K$^{-1}$ mol$^{-1}$.

As one part of a series of studies concerning the kinetic behavior of arsenic oxygens,[1] the oxygen-exchange reaction of the alkylderivatives of arsenic acid with water has been studied in order to determine the substituent effects of the alkyl groups on the rate of oxygen exchange.[2,3] In a former paper,[2] the relation between the electronic properties and the reactivities of arsonates was examined through a molecular-orbital calculation of the first-order exchange rate constants of monovalent methyl- and butylarsonate anions; it was concluded that the steric effect does not predominantly affect the rates. In a previous paper[3] we presented extensive kinetic results concerning the alkylarsonates, $R'AsO_3Na_2$ ($R'=CH_3$, $n\text{-}C_4H_9$, $n\text{-}C_6H_{13}$, or $C_6H_5CH_2$), and dialkylarsinates, $R'_2AsO_2Na$ ($R'=CH_3$ or $n\text{-}C_4H_9$). This work was carried out in the pH region greater than 6 and at temperatures between 0 and 30 °C; the rate constants and activation parameters have been found for elementary processes involving ionic species present in the pH region. The values of the activation entropies of the arsonates were found to be negative, while those of the arsinates to be positive. On the basis of these facts it was suggested that the oxygen exchange of arsonate ions proceeds via the $S_N2$ mechanism, while that of arsinate ions proceeds via $S_N1$. In this paper we present the kinetic results on the fast oxygen-exchange reactions of methyl- and butylarsonic acids and dimethylarsinic acid with water. This work was carried out in the pH region between 0 and 5 by using the $^{17}$O NMR line-broadening technique.

## Experimental

**Materials.** Disodium methyl- and butylarsonates were prepared according to a method of Quick.[4] The method for purification of methyl- and butylarsonic acids was described earlier.[3] Sodium dimethylarsinate (guaranteed reagent, Wako) was carefully acidified to pH 3 in order to produce dimethylarsinic acid, which was purified by repeated crystallization. The melting points, elemental analyses, and $^1$H-chemical shifts of methyl- and butylarsonic acids and dimethylarsinic acid have been shown elsewhere[3] (Table 1a and 1b in Ref. 3).

**NMR Measurements.** Solutions for the $^{17}$O NMR spectra were prepared as follows: A known amount of alkylarsonic acid or dimethylarsinic acid was dissolved into 3 ml of $^{17}$O-enriched water (ca. 10% enrichment). The pH of the solution was adjusted by the addition of a small amount of concentrated sulfuric or hydrochloric acid or a saturated aqueous sodium hydroxide solution. The pH of the solution was measured both before and after the NMR measurement using a Radiometer PHM type-26 pH meter.

The $^{17}$O NMR spectra were recorded at 36.6 MHz on a FT-NMR spectrometer (JEOL-GX270). The relevant spectral parameters were as follows: spectral width 20 kHz; digital resolution 1.2 Hz; number of scans 4096 to 8192. Before making a Fourier transformation, the FID was multiplied by an exponential function in which the broadening parameter (LB) was 2 Hz. In all of the experimental conditions used, both the oxygen signals due to arsonic or arsinic acid and solvent water were observed separately. The $^{17}$O chemical shifts (referred to the $H_2O$ signal) for methyl- and butylarsonic acids and dimethylarsinic acid are 95 (pH=2), 90 (pH=2), and 88 ppm (pH=4), respectively. The line widths were recorded for both signals. Since the line broadening in water signal due to an oxygen exchange with arsenic oxygens is very small, especially in the pH region greater than 2, the oxygen-exchange rate was obtained by using the line width of signals of arsenic oxygens (site A) (A: $CH_3AsO_3H_2$ (MAA), $n\text{-}C_4H_9AsO_3H_2$ (BAA), or $(CH_3)_2AsO_2H$ (CAA)).

The longitudinal magnetization recovery curve of methylarsonate oxygen was measured by the inversion recovery method, using a pulse sequence of 180°—$t$—90° pulses. For an experiment, fifteen to twenty values of $t$ were used, some $t$ values being chosen sufficiently long compared to $3T_1$ ($T_1$: longitudinal relaxation time).

The indicated temperature of the sample solution in the NMR probe was calibrated by a direct measurement using a thermocouple inserted in the solution: 3 (2.1), 10 (9.0), 15 (13.8), 20 (18.6), 30 (28.5), 40 (38.6), 50 (47.7), 60 (57.3), 70 (66.8), 80 (76.7), 90 (86.1) °C (The calibrated temperature values are shown in parentheses.)

**The Dissociation Constants of Methylarsonic Acid.** The dissociation constants ($K_1$ and $K_2$) are defined as follows:

$$K_1 = \frac{a_{\mathrm{H}^+}[\mathrm{CH_3AsO_3H^-}]}{[\mathrm{CH_3AsO_3H_2}]}$$

and

$$K_2 = \frac{a_{\mathrm{H}^+}[\mathrm{CH_3AsO_3^{2-}}]}{[\mathrm{CH_3AsO_3H^-}]}.$$

The determination of the values of $K_1$ and $K_2$ in the NMR experimental conditions is based on the measurement of $^{17}$O-chemical shifts at the MAA site (30 °C, [MAA]=1.1 mol dm$^{-3}$). The chemical shift ($\sigma_{\mathrm{MAA}}$) for a solution is given as a weighed average of the chemical shifts for various ionic species present in the solution (Eqs. 1 and 2):

$$\sigma_{\mathrm{MAA}} = \{\sigma(\mathrm{CH_3AsO_3H_2})[\mathrm{CH_3AsO_3H_2}] + \sigma(\mathrm{CH_3AsO_3H^-})[\mathrm{CH_3AsO_3H^-}] + \sigma(\mathrm{CH_3AsO_3^{2-}})[\mathrm{CH_3AsO_3^{2-}}]\}/[\mathrm{MAA}] \quad (1)$$

and

$$\sigma_{\mathrm{MAA}} = \frac{\sigma(\mathrm{CH_3AsO_3H_2})a^2_{\mathrm{H}^+} + \sigma(\mathrm{CH_3AsO_3H^-})K_1a_{\mathrm{H}^+}}{(a^2_{\mathrm{H}^+} + K_1a_{\mathrm{H}^+} + K_1K_2)} + \frac{\sigma(\mathrm{CH_3AsO_3^{2-}})K_1K_2}{(a^2_{\mathrm{H}^+} + K_1a_{\mathrm{H}^+} + K_1K_2)} \quad (2)$$

$\sigma(\mathrm{CH_3AsO_3H_2})$, $\sigma(\mathrm{CH_3AsO_3H^-})$, and $\sigma(\mathrm{CH_3AsO_3^{2-}})$ are the chemical shifts for each ionic species given in parentheses, and were obtained to be 95 (pH=1), 112 (pH=6), and 130 (pH=11) ppm, respectively. The values of $\sigma_{\mathrm{MAA}}$ for a series of solutions of varying pH were then fitted to Eq. 2 by a nonlinear least-squares procedure. The values of p$K_1$ and p$K_2$ were obtained to be 3.90 and 8.50, respectively, which are in satisfactory agreement with the values of $3.87_8\pm0.00_0$ and $8.49_8\pm0.00_0$ (30 °C, $I$=0.55 mol dm$^{-3}$)[3] by the method of a potentiometric titration.

**Acid Dissociation Constants of the Conjugate Acid of Methylarsonic Acid.** The acid dissociation constant $K_{1\mathrm{h}}$ (MAA) defined by Eq. 3 was determined spectrophotometrically by an indicator method,

$$K_{1\mathrm{h}}(\mathrm{MAA}) = \frac{[\mathrm{H^+}][\mathrm{CH_3AsO_3H_2}]}{[\mathrm{CH_3AsO_3H_3^+}]}. \quad (3)$$

This method is based on the determination of the hydrogen ion concentration [H$^+$] in a strong acid solution of $\mathrm{CH_3AsO_3H_2}$ by using *p*-nitroaniline (B) as an indicator base. The [H$^+$] in the solution is estimated according to the equation,

$$\log[\mathrm{H^+}] = \log([\mathrm{BH^+}]/[\mathrm{B}]) - \mathrm{p}K_{\mathrm{BH^+}}, \quad (4)$$

where $K_{\mathrm{BH^+}}$ is the acid dissociation constant of the conjugate acid (BH$^+$). Its value has been obtained to be 0.99 ($I$=0).[5] The concentration ratio [BH$^+$]/[B] in Eq. 4 can be estimated by measuring the extinction coefficient of the solution ($\epsilon_{\mathrm{obs}}$) according to the relation $[\mathrm{BH^+}]/[\mathrm{B}]=(\epsilon_{\mathrm{B}}-\epsilon_{\mathrm{obs}})/(\epsilon_{\mathrm{obs}}-\epsilon_{\mathrm{BH^+}})$. The values of $\epsilon_{\mathrm{B}}$ and $\epsilon_{\mathrm{BH^+}}$ (extinction coefficients of B and BH$^+$) were obtained separately from Beer–Lambert plots of the solutions in which B and BH$^+$ exist dominantly. At $\lambda$=380 nm, $\epsilon_{\mathrm{B}}$ and $\epsilon_{\mathrm{BH^+}}$ were obtained to be 13134±23 and 39, respectively. [$\mathrm{CH_3AsO_3H_3^+}$] in Eq. 3 may be equated to ([$\mathrm{H_0^+}$]−[H$^+$]), where [$\mathrm{H_0^+}$] is the hydrogen-ion concentration without added methylarsonic acid; that is, the reduction in the hydrogen-ion concentration caused by the addition of methylarsonic acid to a strong acid solution is due to the formation of the conjugate acid of methyl arsonic acid.

On the basis of the consideration shown above, $K_{1\mathrm{h}}$(MAA) is finally evaluated by using

$$K_{1\mathrm{h}}(\mathrm{MAA}) = [\mathrm{H^+}]\{[\mathrm{MAA}] - ([\mathrm{H^+}]_0 - [\mathrm{H^+}])\}/([\mathrm{H^+}]_0 - [\mathrm{H^+}]), \quad (5)$$

where [MAA] is the total concentration of methylarsonic acid. The absorbance was measured with a Hitachi 200-10 type spectrophotometer at $\lambda$=380 nm for the hydrochloric acid solutions of methylarsonic acid including *p*-nitroaniline (1.096×10$^{-4}$ mol dm$^{-3}$). The concentration varied over the range as [HCl]=0.2—0.4 mol dm$^{-3}$ and [MAA]=0.45—1.27 mol dm$^{-3}$. The value of $K_{1\mathrm{h}}$ (MMA) was obtained to be 1.3±0.2 (p$K_{1\mathrm{h}}$(MAA)=−0.11±0.07).

## Results

**Evaluation of the Oxygen Exchange Rate.** In the slow exchange limit, where the mean lifetime of an oxygen nucleus at site A ($\tau_{\mathrm{A}}$) is small compared to the chemical shift, $\tau_{\mathrm{A}}$ is given by

$$\tau_{\mathrm{A}}^{-1} = k_{\mathrm{A}} = T_{2\mathrm{A}}^{-1} - T_{2\mathrm{A},0}^{-1}, \quad (6)$$

where $T_{2\mathrm{A}}$ is the measured transverse relaxation time of an oxygen nucleus at site A and $T_{2\mathrm{A},0}$ is its magnitude in the absence of an oxygen exchange. By using the relation $1/T_2=\pi\times\nu_{1/2}$, $\tau_{\mathrm{A}}^{-1}$ is expressed as

$$\tau_{\mathrm{A}}^{-1} = k_{\mathrm{A}} = \pi \times (\nu_{1/2,A} - \nu^0_{1/2,A}), \quad (7)$$

where $\nu_{1/2,\mathrm{A}}$ and $\nu^0_{1/2,\mathrm{A}}$ are the line widths of oxygens at site A in the presence and absence of an oxygen exchange, respectively.

The mean lifetime of the oxygen nucleus of species A between exchanges ($\tau_{\mathrm{A}}$) is related to the conventional rate constant ($k$) of the arsenic oxygen exchange with water by Eq. 8,[6]

$$\tau_{\mathrm{A}}^{-1} = k_{\mathrm{A}} = (1/[\mathrm{A}])\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k[\mathrm{A}]^{m-1}, \quad (8)$$

where m is the order of the reaction with respect to the concentration of A. When the reaction is of the first order, $\tau_{\mathrm{A}}^{-1}$ ($k_{\mathrm{A}}$) is equal to the rate constant of the oxygen-exchange reaction.

**Estimation of $\nu^0_{1/2,\mathrm{A}}$.** To calculate the values of $k_{\mathrm{A}}$ by means of Eq. 7, it is required to estimate an appropriate value of $\nu^0_{1/2,\mathrm{A}}$ under the condition in which $\nu_{1/2,\mathrm{A}}$ is measured. To estimate $\nu^0_{1/2,\mathrm{MMA}}$, the following preliminary examinations were carried out for the solution of methylarsonic acid:

**1)** In order to detect whether the oxygen exchange affects the $^{17}$O line width at MAA, the possibility of using the longitudinal magnetization recovery was tested.

The slow chemical exchange of the oxygen nucleus at the MAA site with $H_2O$ would give a nonsingle exponential decay of the magnetization at site MAA.[7] Thus, without any chemical exchange, plots of $\ln(2M_0/(M_0-M_t))$ against the recovery time ($t$) are expected to give a straight line. $M_0$ and $M_t$ are the magnetization at recovery times of zero and $t$, respectively. Figure 1a shows plots obtained under the extreme conditions: A is for when no exchange occurs (pH=7.0, 90 °C); B is for when significant exchange broadening occurs (pH=2, 90 °C). Under condition A, the plots gave a linear curve (A) over 5 half times of the magnetization recovery, whereas under condition B, the plots gave a significantly curved line (B). In Fig. 1b, as a critical case, the magnetization recovery at pH 4.42 is shown as a function of the temperature. At temperatures higher than 70 °C, non-single exponential decay curves were observed. These results are considered to indicate that the contribution of oxygen exchange to the $^{17}$O NMR line shape is well reflected in the magnetization recovery curves.

**2) The pH Dependence of $\nu^0_{1/2,A}$:** On the basis of the criterion given above, it was confirmed that an oxygen exchange does not contribute to the line broadening of the $^{17}$O signal at the MAA site at temperatures between 0 and 20 °C. The values of $\nu^0_{1/2,\mathrm{MAA}}$ (Table 1) vary significantly, depending on the pH of the solution. It has been shown that the proton exchange of water contributes to the line width of $^{17}$O in water.[8] The observed changes in $\nu^0_{1/2,\mathrm{MAA}}$ with the pH can be partly ascribed to the fact that the fast exchange rate of the proton attached to arsenic oxygen (MAA) with that of water varies depending on the pH and partly to the change in the electric-field gradient at the site of the oxygen nucleus with the pH.

Table 1. Temperature Dependence of $^{17}$O NMR Line Widths of Arsonate Oxygen in the Absence of the Oxygen Exchange with Water ([MAA]=1.1 mol dm$^{-3}$)

| Temp/°C | $\nu^0_{1/2,\mathrm{MAA}}$/Hz | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| pH= | 1.96 | 2.68 | 3.01 | 3.42 | 3.71 | 3.97 | 6.50 | 7.01 |
| 3 | 554 | 607 | 619 | 660 | 693 | 745 | 846 | 1008 |
| 10 | 454 | 491 | 500 | 537 | 566 | 603 | 673 | 821 |
| 15 | 394 | 428 | 435 | 469 | 492 | 519 | 582 | 704 |
| 20 | 349 | 375 | 385 | 410 | 432 | 456 | 497 | 603 |
| $E_a$/kJ mol$^{-1}$ | 18.6 | 19.5 | 19.3 | 19.2 | 19.1 | 20.0 | 21.4 | 21.2 |

**3) Temperature Dependence of $\nu^0_{1/2,A}$:** The line width gives the transverse relaxation rate at site A ($R^0_{2A}$) by the relation $\pi\nu^0_{1/2,A}=1/T^0_{2A}=R_{2A}$. By using an Arrhenius-type equation for $R_2$: $\ln(R^0_{2A})=A\exp(E_a/RT)$, the activation energies ($E_a$) for the rate can be obtained. The $E_a$ values were calculated for $\nu^0_{1/2,\mathrm{MAA}}$ (3—20 °C) (Table 1). Furthermore, the temperature dependence of $R^0_{2,\mathrm{MAA}}$ was examined over a wider temperature range, between 0 and 90 °C, at pH 6.5 and 7.0, where any contribution of the oxygen exchange to the line width is absent. The Arrhenius plots gave lines which are curved in the range from 35 to 40 °C (Fig. 2). The values of the activation energy ($E_a$) are 20.8±0.3 (0—40 °C) and 16.2±0.4 kJ mol$^{-1}$ (40—90 °C) for pH 6.5 and 21.2±0.3 (0—40 °C) and 16.9±0.2 kJ mol$^{-1}$ (40—90 °C) for pH 7, respectively.

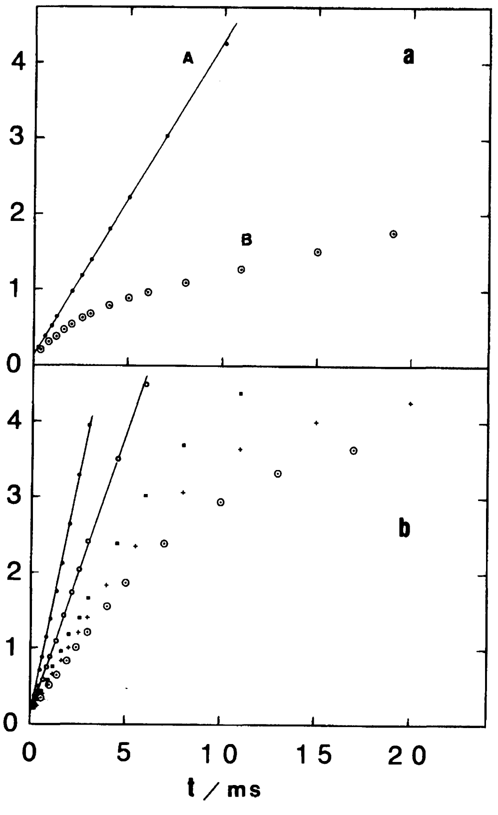

Fig. 1. a) Longitudinal magnetization recovery curves. A(-•-): pH=7.0, 90 °C; B(⊙): pH=2.0, 90 °C. b) Longitudinal magnetization recovery curves at pH 4.42. -•-: 40 °C; ○: 50 °C; ■: 70 °C; +: 80 °C; ⊙: 90 °C.

On the basis of the observation described above, the $\nu^0_{1/2,\mathrm{MAA}}$ values were estimated as follows. For all the kinetic runs (pH>2), the line widths were measured at temperatures ranging from 0 to 90 °C. The values at temperatures between 0 and 20 °C ($\nu^0_{1/2,\mathrm{MAA}}$) were then extrapolated to higher temperatures by using the $E_a$ values (Table 1). The thus-obtained $\nu^0_{1/2,\mathrm{MAA}}$ values were slightly corrected by taking account of the difference in the activation energies between the higher and lower temperature ranges.

For the calculation of $k_{\mathrm{MAA}}$ at pH<2, $\nu^0_{1/2,\mathrm{MAA}}$ at pH=2 was used, since in this region exchange line broadening occurs at temperatures even below 20 °C. Due to the broadness of the measured line width, itself, the uncertainty in $\nu^0_{1/2,\mathrm{MAA}}$ (if any) becomes less important in estimating of the $k_{\mathrm{MAA}}$ values at pH<2.

**I. Methylarsonic Acid (MAA). pH Dependence of the Oxygen Exchange Rate.** $^{17}$O NMR spectra were measured at temperatures ranging from 0 to 90 °C in the pH region between 0 and 7. The typical values of the line widths of the $^{17}O$ signals at the MAA site are plotted against the temperatures in Fig. 3 ([MAA]=1.1 mol dm$^{-3}$). By using of these line widths, $k_{MAA}$s were calculated according to Eq. 7. The values of $k_{MAA}$ at 90 °C are plotted against the pH in Fig. 4 ([MAA]=1.1 mol dm$^{-3}$). In the pH region grater than 2, the $k_{MAA}$ values slowly decrease with an increase in pH ($k_{MAA} \propto a_{H^+}^{0.3}$), whereas in the pH region smaller than 2, the increase in $k_{MAA}$ with a decrease in pH becomes more significant ($k_{MAA} \propto a_{H^+}^{0.6}$). All of the $k_{MAA}$ data observed at temperatures other than 90 °C ([MAA]=1.1 mol dm$^{-3}$) are given in Fig. 5 (Arrhenius plot). As is evidenced by the nearly parallel plots for the various pH, the activation energies ($E_a$) fall within a limited range between 29 and 33 kJ mol$^{-1}$.

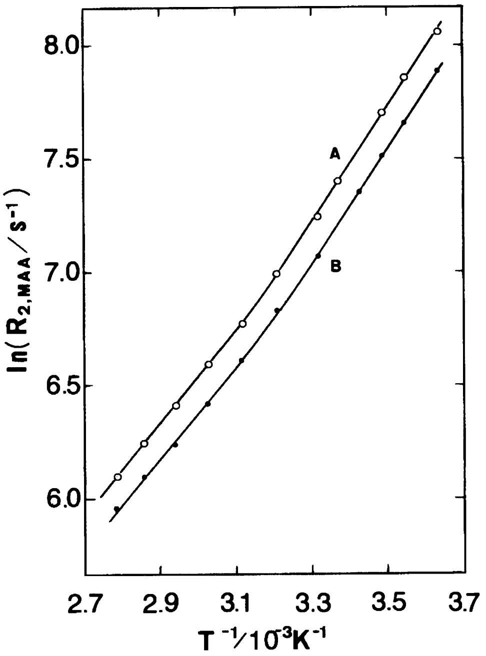

Fig. 2. Temperature dependence of the transverse relaxation rate of methylarsonic acid. ($R_{2,MAA} = 1/T_{2,MAA}$). A(○): pH=7.01; B(●): pH=6.50.

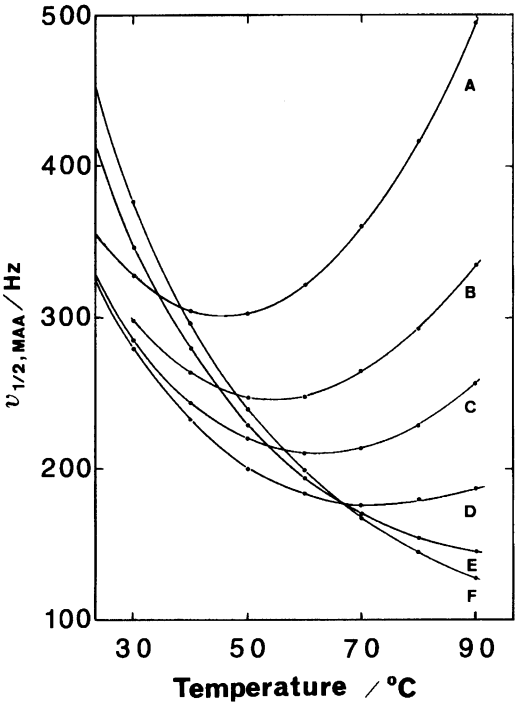

Fig. 3. Measured $^{17}O$ NMR line widths as a function of the temperature. ([MAA]=1.1 mol dm$^{-3}$). pH A: 0.84; B: 1.13; C: 1.42; D: 1.96; E: 3.97; F: 5.45.

In the region pH<2 the pH dependence was studied at three concentrations of MAA ([MAA]=0.3, 0.8, and 1.1 mol dm$^{-3}$) (Fig. 8).

**Dependence of the Rate of Oxygen Exchange on the Concentration of Methylarsonic Acid [MAA].** The concentration dependence was studied at pHs of 0.84 and 1.96 (50—90 °C). [MAA] was varied between 0.3 and 1.1 mol dm$^{-3}$. On the basis of Eq. 8, the order of the reaction with respect to [MAA], m was obtained from the slope of a log–log plot of $k_{MAA}$ versus [MAA]. These plots are shown in Figs. 6a (pH=0.84) and 6b (pH=1.96). The values of m are listed in Table 2.

**Oxygen Exchange Mechanism.** The concentrations of the various kinds of ionic species of methylarsonic acid for a given pH can be calculated by using the following relations:

$$[MAA] = [CH_3AsO_3H_3^+] + [CH_3AsO_3H_2] + [CH_3AsO_3H^-] + [CH_3AsO_3^{2-}]$$

and

$$[CH_3AsO_3H_2] = \frac{[MAA]}{(a_{H^+}/K_{1h}(MAA) + 1 + K_1/a_{H^+} + K_1K_2/a_{H^+}^2)}. \tag{9}$$

The mole fractions of various ionic species of methylarsonic acid at 30 °C are plotted against pH in Fig. 7.

In the pH region between 2 and 5, the rate law of the oxygen exchange is given as $R_{MAA} \propto a_{H^+}^{0.3}[MAA]^{1.7—1.9}$. In this region, the dominant ionic species are undissociated methylarsonic acid ($CH_3AsO_3H_2$) and its monoanion ($CH_3AsO_3H^-$). Since at pH 6.5, where monoanion exists predominantly, oxygen exchange does not occur, the observed oxygen exchange in this region can be ascribed to the participation of undissociated acid into the rate process. The role of the proton in the rate law is to shift the equilibrium, $CH_3AsO_3H^- + H^+ \rightleftharpoons CH_3AsO_3H_2$, from left to right in favor of the reactive species. The fact that the order ($m$) is 1.7—1.9 suggests that oxygen exchange proceeds through both the monomolecular (Eq. 10) and bimolecular (Eqs. 11 and 12) paths as follows:

$$CH_3As^{17}OO_2H_2 + H_2O \overset{k_1}{\rightleftharpoons} CH_3AsO_3H_2 + H_2^{17}O, \tag{10}$$

Table 2. The Dependence of the Exchange Rate on the Concentration of Methylarsonic Acid ([MAA]=0.3—1.1 mol dm$^{-3}$)

| Temp/°C | 50 | 60 | 70 | 80 | 90 |
|---|---|---|---|---|---|
| $m$ (pH=2) | $1.9_3 \pm 0.1_5$ | $1.9_1 \pm 0.0_6$ | $1.8_8 \pm 0.0_2$ | $1.8_1 \pm 0.0_4$ | $1.7_2 \pm 0.1_1$ |
| $m$ (pH=1) | $1.3_8 \pm 0.0_5$ | $1.3_5 \pm 0.0_3$ | $1.3_4 \pm 0.0_3$ | $1.3_2 \pm 0.0_3$ | $1.3_0 \pm 0.0_3$ |

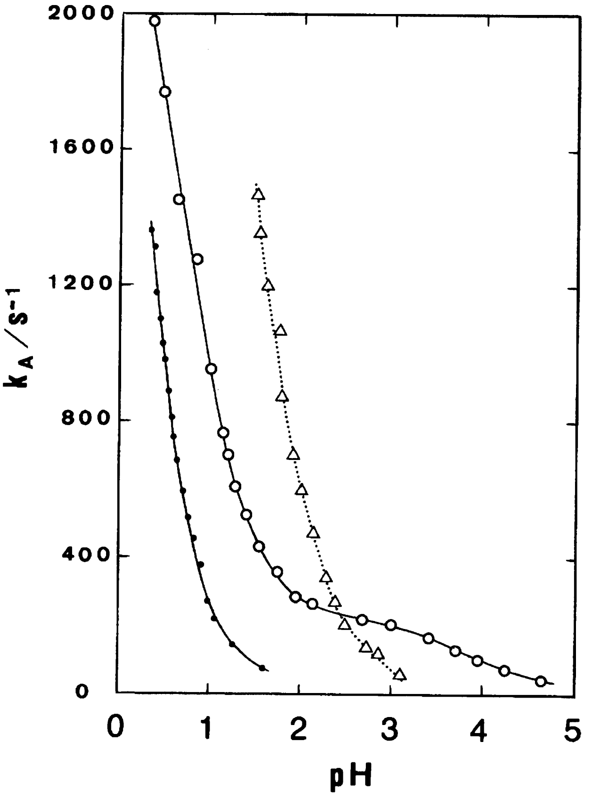

Fig. 4. pH dependence of $k_{\mathrm{A}}$s of alkylarsonic acids. -O-: methylarsonic acid (MAA); -●-: butylarsonic acid (BAA); ···△···: arsenic acid.

$$\mathrm{CH_3AsO_3H_2 + CH_3AsO_3H_2 \overset{k_2}{\rightleftharpoons} (CH_3AsO_2H)_2O + H_2O,} \qquad (11)$$

and

$$\mathrm{CH_3AsO_3H_2 + CH_3AsO_3H^- \overset{k_3}{\rightleftharpoons} (CH_3AsO_2)_2OH^- + H_2O.} \qquad (12)$$

In the region pH < 2, the rate law is given as $R_{\mathrm{MAA}} \propto a_{\mathrm{H}^+}^{0.6}[\mathrm{MAA}]^{1.3}$. Since at pH < 2 undissociated acid exists dominantly, the steep increase in the exchange rate with a decrease in pH is considered to be a catalytic effect of a proton on the exchange reactions of an undissociated methylarsonic acid with a water molecule (Eq. 13) and with another arsonic acid (Eq. 14):

$$\mathrm{CH_3As^{17}OO_2H_2 + H_2O + H^+ \overset{k_{h1}}{\rightleftharpoons} CH_3AsO_3H_2 + H_2^{17}O + H^+} \qquad (13)$$

and

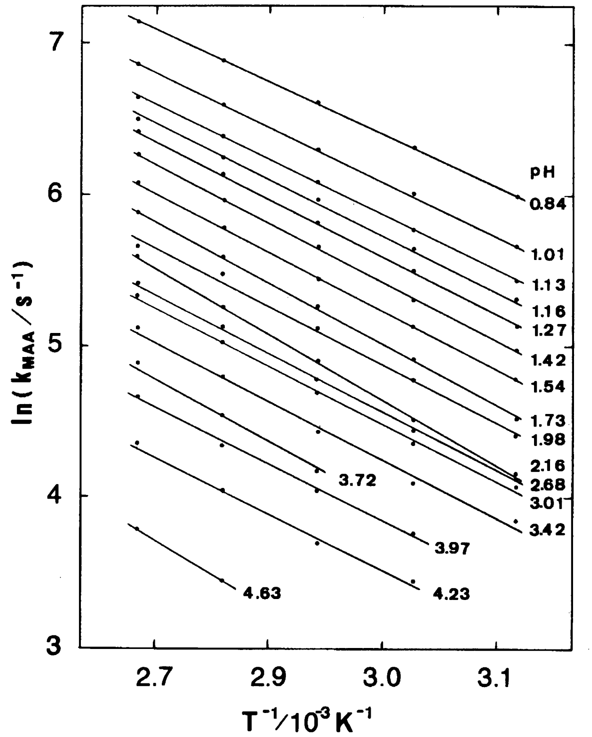

Fig. 5. Temperature dependence of the oxygen exchange rate of methylarsonic acid at various pH values.

$$\mathrm{CH_3AsO_3H_2 + CH_3AsO_3H_2 + H^+ \overset{k_{h2}}{\rightleftharpoons} (CH_3AsO_2H)_2O + H_2O + H^+.} \qquad (14)$$

Since, in this pH region the conjugate acid can exist (at pH=1.5, 2% of total concentration of MAA), the acid-catalyzed exchange of methylarsonic acid (Eqs. 13 and 14) may be considered as the following reactions (Eqs. 13a and 14a) in which the conjugate acid takes part:

$$\mathrm{CH_3As^{17}OO_2H_3^+ + H_2O \overset{k'_{h1}}{\rightleftharpoons} CH_3AsO_3H_3^+ + H_2^{17}O} \qquad (13a)$$

and

$$\mathrm{CH_3AsO_3H_3^+ + CH_3AsO_3H_2 \overset{k'_{h2}}{\rightleftharpoons} (CH_3AsO_2H)_2OH^+ + H_2O.} \qquad (14a)$$

However, reactions 13a and 14a are kinetically equivalent to reactions 13 and 14, respectively, and it is impossible to separate from each other ($k'_{\mathrm{h1}}=k_{\mathrm{h1}}K_{\mathrm{1h}}$ (MAA), $k'_{\mathrm{h2}}=k_{\mathrm{h2}}K_{\mathrm{1h}}$ (MAA)). Therefore, a rate analysis was carried out based on reactions 13 and 14. It must be noted that since the value of $K_{\mathrm{1h}}$ (MAA) is obtained to be

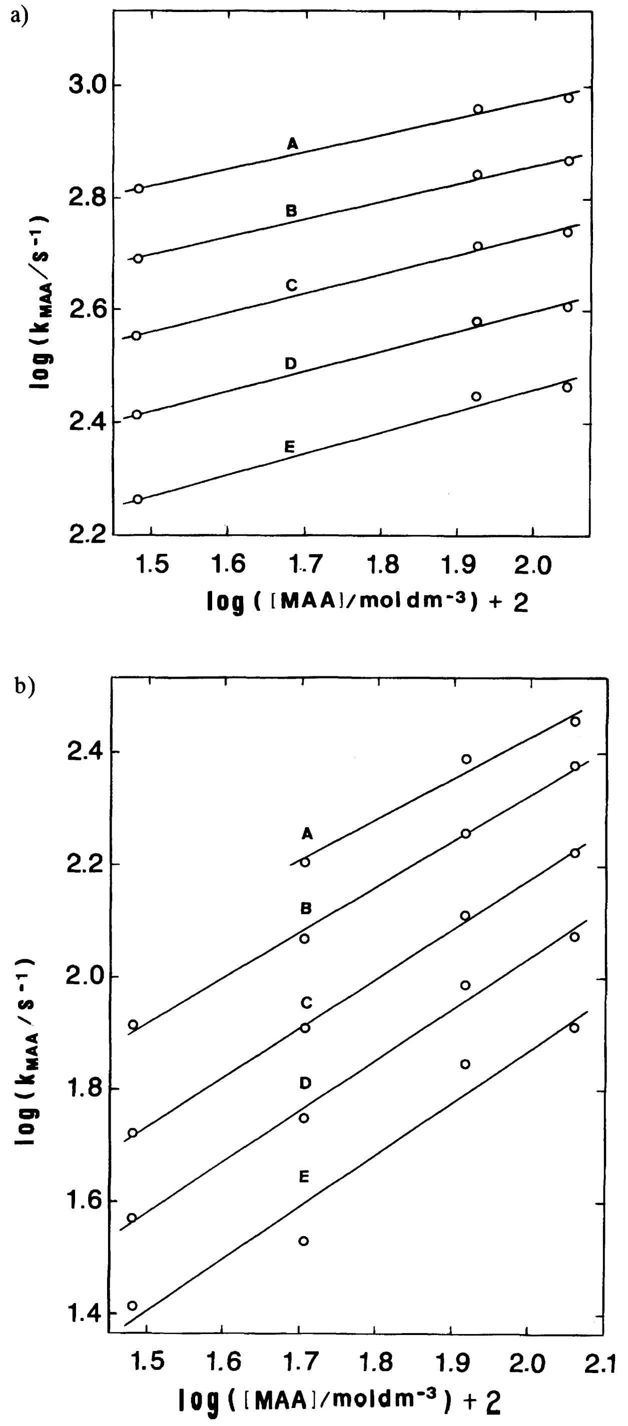

Fig. 6. a) Dependence of the oxygen exchange rate on the concentration of methylarsonic acid ([MAA]) at pH 0.84. (50—90 °C). A: 90 °C; B: 80 °C; C: 70 °C; D: 60 °C; E: 50 °C. b) Dependence of the oxygen exchange rate on the concentration of methylarsonic acid ([MAA]) at pH 1.96. (50—90 °C). A: 90 °C; B: 80 °C; C: 70 °C; D: 60 °C; E: 50 °C.

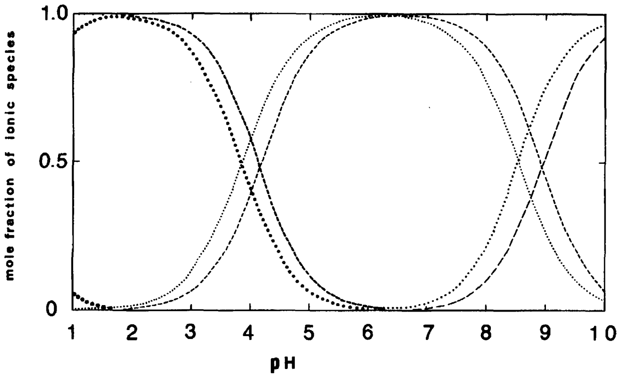

Fig. 7. Mole fractions of various ionic species of alkylarsonates against pH. Dotted lines: ••••$CH_3AsO_3H_3^+$; ····$CH_3AsO_3H_2$; ····$CH_3AsO_3H^-$; ····$CH_3AsO_3^{2-}$. Broken lines: ----$BuAsO_3H_2$; ----$BuAsO_3H^-$; ---$BuAsO_3^{2-}$.

1.3, the values of $k'_{h1}$ and $k'_{h2}$ are almost the same as those of $k_{h1}$ and $k_{h2}$. The rate law for the oxygen exchange of methylarsonic acid with water may therefore be expressed as follows:

$$R_{MAA} = k_{h1}[H^+][CH_3AsO_3H_2] + k_{h2}[H^+][CH_3AsO_3H_2]^2 + k_1[CH_3AsO_3H_2] + k_2[CH_3AsO_3H_2]^2 + k_3[CH_3AsO_3H_2][CH_3AsO_3H^-]. \quad (15)$$

**Analyses of the Exchange Rate.** The exchange results were analyzed using the rate law (15). Over the range pH<2 ([MAA]=[$CH_3AsO_3H_2$]), the contribution of the $k_3$-term to the total rate may be neglected. Rate law (15) is, then, rewritten as

$$k_{MAA} = (k_1 + k_2[CH_3AsO_3H_2]) + (k_{h1} + k_{h2}[CH_3AsO_3H_2])[H^+]. \quad (16)$$

According to Eq. 16, the $k_{MAA}$ values (pH<2, [MAA]=[$CH_3AsO_3H_2$]=0.3—11 mol dm$^{-3}$, 50—90 °C) were analyzed. In the rate analyses, $a_{H^+}$ was used instead of [$H^+$] in the rate laws. In Fig. 8a, the $k_{MAA}$ data at 90 °C (0.3, 0.8, and 1.1 mol dm$^{-3}$) are plotted against $a_{H^+}$. The figure shows that both the slopes and intercepts are dependent on [$CH_3AsO_3H_2$], as expected from Eq. 16. By a least-squares treatment of the plots (Fig. 8a), the values of the slope ($k_{h1}+k_{h2}[CH_3AsO_3H_2]$) and intercept ($k_1+k_2[CH_3AsO_3H_2]$) were obtained. A similar treatment was repeated for $k_{MAA}$s at other temperatures (Fig. 8b 1.1 mol dm$^{-3}$, 50—90 °C). The values of the slope, thus obtained, are plotted against [$CH_3AsO_3H_2$] in Fig. 9 (50—90 °C), which gave linear plots. By a least-squares treatment of the plots in Fig. 9, the values of $k_{h1}$ and $k_{h2}$ were obtained to be $(4.9\pm0.2)\times10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $(2.1\pm0.3)\times10^3$ (mol dm$^{-3}$)$^{-2}$ s$^{-1}$, respectively. By a similar treatment for the values of the intercept of the plots in

Table 3. Rate Constants and Activation Parameters of the Oxygen Exchange of Methylarsonic Acid (MAA)

M=mol dm$^{-3}$

| Temp<br>°C | $k_{h1}$<br>$10^3$ M$^{-1}$ s$^{-1}$ | $k_{h2}$<br>$10^3$ M$^{-2}$ s$^{-1}$ | $k_1$<br>10 s$^{-1}$ | $k_2$<br>$10^2$M$^{-1}$ s$^{-1}$ | $k_3$<br>$10^2$M$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 60 | 1.87±0.10 | 1.32±0.18 | 1.5 | 0.57±0.03 | 0.77±0.13 |
| 70 | 2.63±0.09 | 1.63±0.16 | 2.1 | 0.82±0.03 | 0.96±0.10 |
| 80 | 3.61±0.14 | 1.89±0.25 | 3.4 | 1.17±0.04 | 1.26±0.16 |
| 90 | 4.87±0.19 | 2.11±0.35 | 4.6 | 1.49±0.04 | 1.93±0.13 |
| $E_a$<br>kJ mol$^{-1}$ | 32.$_6$ ±0.$_2$ | 18.$_4$ ±1.$_5$ | 45±3 | 32.$_2$ ±1.$_4$ | 31.$_1$ ±3.$_5$ |
| $\Delta S^{\neq}$ a)<br>J mol$^{-1}$ K$^{-1}$ | −97 ±1 | −139 ±0 | −93±0 | −122 ±2 | −125 ±4 |

a) Values at 60 °C.

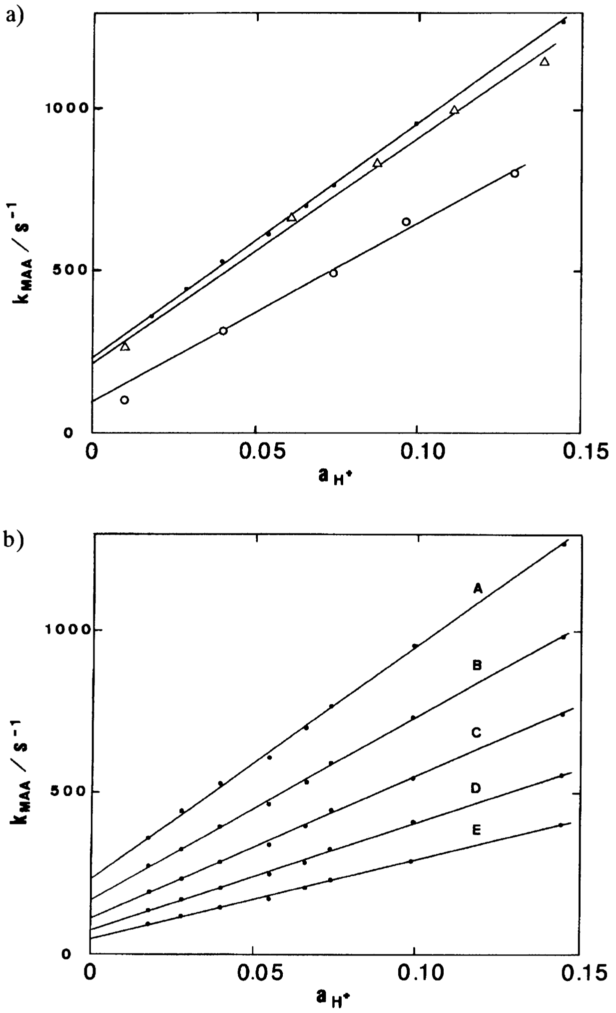

Fig. 8. a) Plots of $k_{MAA}$ vs. $a_{H^+}$ (90 °C). [MAA] ○: 0.3; △: 0.8; ●: 1.1 mol dm$^{-3}$. b) Plots of $k_{MAA}$ vs. $a_{H^+}$ ([MAA]=1.1 mol dm$^{-3}$). A: 90 °C; B: 80 °C; C: 70 °C; D: 60 °C; E: 50 °C.

Figs. 8a and 8b, the values of $k_1$ and $k_2$ were obtained to be 46 s$^{-1}$ and 177 mol$^{-1}$ dm$^3$ s$^{-1}$, respectively. More precise values of $k_2$ were obtained from the rate results at pH>2, where the contribution of the $k_2$ term to the total rate is more significant. The rate constants ($k_{h1}$, $k_{h2}$, $k_1$) obtained from the rate data at pH<2 are listed in Table 3.

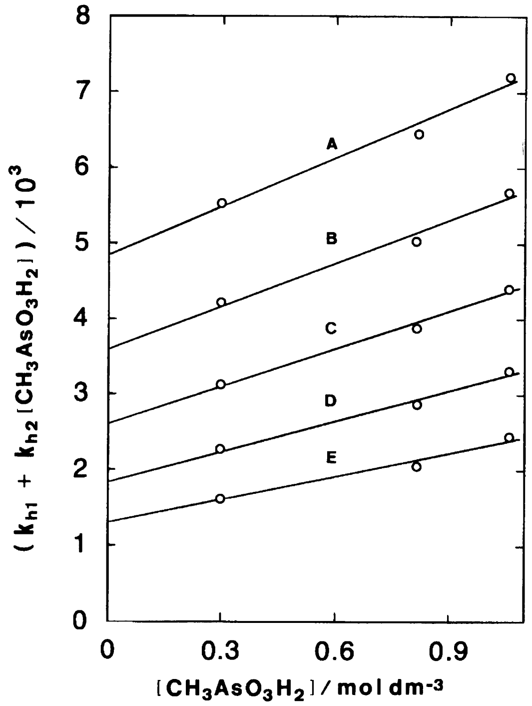

Fig. 9. Plots of the value, $k_{h1}+k_{h2}[CH_3AsO_3H_2]$ against $[CH_3AsO_3H_2]$. (pH<2) A: 90 °C; B: 80 °C; C: 70 °C; D: 60 °C; E: 50 °C.

At pH>2, the rate term including $CH_3AsO_3H^-$ becomes important; rate analyses in this region were carried out in terms of a rearranged rate law (Eq. 15) as follows:

$$\begin{aligned} &R_{MAA} - k_{h1}[H^+][CH_3AsO_3H_2] \\ &\quad -k_{h2}[H^+][CH_3AsO_3H_2]^2 - k_1[CH_3AsO_3H_2] \\ &= k_2[CH_3AsO_3H_2]^2 + k_3[CH_3AsO_3H_2][CH_3AsO_3H^-]. \end{aligned} \tag{17}$$

Table 4. The Dependence of the Line Widths at BAA Site in the Absence and Presence of Oxygen Exchange and of $k_{BAA}$ on [BAA] (90 °C)

| $[BAA]/mol\ dm^{-3}$ | $\nu^{0}_{1/2,BAA}$ (pH=2.3) | $\nu_{1/2,BAA}$ (pH=0.6) | $k_{BAA}/s^{-1}$ |
|---|---|---|---|
| 0.5 | 157 | 341 | 577 |
| 0.6 | 164 | 348 | 578 |
| 0.7 | 170 | 358 | 591 |
| 0.8 | 177 | 368 | 600 |
| 0.9 | 188 | 378 | 597 |

For each run at pH>2 (Figs. 4 and 5), the left-hand side of this equation was calculated using the values of $k_{h1}$, $k_{h2}$, and $k_1$ obtained above, the concentration products in the right hand side being also calculated. By a least-squares treatment of a set of numerical equations, thus obtained, the values of $k_2$ and $k_3$ were obtained to be $(1.49\pm0.04)\times10^{2}$ $mol^{-1}\,dm^{3}\,s^{-1}$ and $(1.93\pm0.13)\times10^{2}$ $mol^{-1}\,dm^{3}$, respectively (90 °C). The $k_2$ and $k_3$ values are listed in Table 3 (60—90 °C). The values of $k_2$ ($mol^{-1}\,dm^{3}\,s^{-1}$) were evaluated from the data at pH<2 to be 56 (60 °C), 84 (70 °C), 123 (80 °C), and 177 (90 °C) and from those at pH>2 to be 57 (60 °C), 82 (70 °C), 117 (80 °C), and 149 (90 °C). The agreement between the $k_2$ values obtained at different pH regions is satisfactory.

The activation energies and activation entropies (60 °C) for the elemental processes (Eqs. 10, 11, 12, 13, and 14) were calculated and are shown in Table 3.

**II. Butylarsonic Acid (BAA).** The $^{17}O$ NMR spectra were measured in the pH region between 2.5 and 0.34 ([BAA]=0.6—0.9 mol dm$^{-3}$). Since the solubility of undissociated butylarsonic acid ($n\text{-}C_4H_9AsO_3H_2$) is low and highly dependent on the temperature, most NMR measurements were carried out at 90 °C. At pH=2.32 where the undissociated acid of BAA exists predominantly, oxygen exchange does not occur. The values of $k_{BAA}$ were calculated by the use of the measured line widths ($\nu_{1/2,BAA}$) and $\nu^{0}_{1/2,BAA}$ (pH=2.32) according to Eq. 7.

**pH Dependence of $k_{BAA}$.** The dependence was studied in the pH region between 0.34 and 1.6 ([BAA]=0.6 mol dm$^{-3}$). In Fig. 4, the $k_{BAA}$ values (90 °C) are plotted as a function of the pH. The plots of $\log k_{BAA}$ against the pH yield a straight line with a slope of $-1.04\pm0.01$ (not shown): $k_{BAA}$ shows a first-order dependence on $a_{H^+}$. The plots of $k_{BAA}$ against $a_{H^+}$ yield a straight line through the origin (Fig. 10).

**Dependence of the Exchange Rate on [BAA].** The dependence was studied at pH=0.6 and at 90 °C. The measured line widths of oxygen signals at the BAA site in the absence and presence of oxygen exchange, and the values of $k_{BAA}$ are shown in Table 4 ([BAA]=0.5—0.9 mol dm$^{-3}$). The values of $k_{BAA}$ are nearly constant over the concentration range studied. On the basis of Eq. 8, it is inferred that the oxygen exchange of BAA at pH<2.32 shows a first-order dependence on [BAA].

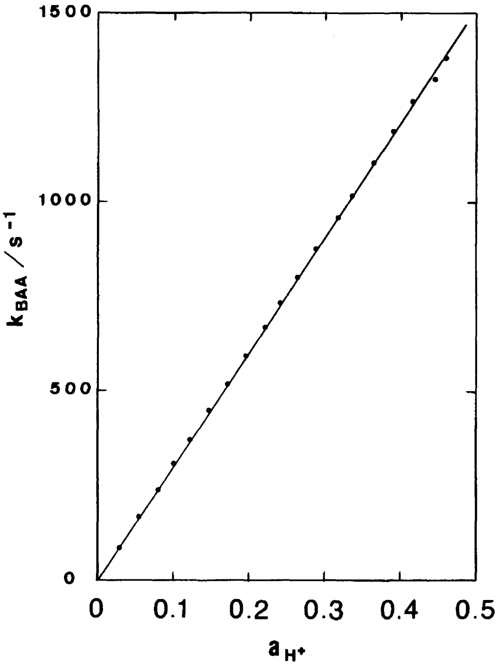

Fig. 10. Plots of $k_{BAA}$ against $a_{H^+}$. (90 °C, [BAA]= 0.6 mol dm$^{-3}$).

**Mechanism of the Oxygen Exchange of BAA.** The above results are summarized as: The oxygen exchange is observable only at pH<2.3, and the rate law is expressed as $R_{BAA}\propto a_{H^+}[BAA]$. Since, in the pH region studied the dominant ionic species of BAA is undissociated acid, the oxygen exchange mechanism consistent with the results may be considered to be the following acid-catalyzed reaction of an undissociated butylarsonic acid with water:

$$n\text{-}C_4H_9As^{17}OO_2H_2 + H_2O + H^{+} \overset{k_{h1}}{\rightleftharpoons} n\text{-}C_4H_9AsO_3H_2 + H_2{}^{17}O + H^{+}. \tag{18}$$

Then, the rate law is expressed by the relation

$$R_{BAA} = k_{BAA}[BAA] = k_{h1}(BAA)[H^{+}][n - C_4H_9AsO_3H_2]. \tag{19}$$

From the slope of the plots of $k_{BAA}$ against $a_{H^+}$ (Fig. 10), the value of $k_{h1}$ (BAA) is $(3.04\pm0.10)\times10^{3}$ $mol^{-1}\,dm^{3}\,s^{-1}$ (90 °C).

**Temperature Dependence of the Exchange Rate of BAA.** The dependence was studied at pH=0.45 and at [BAA]=0.5 mol dm$^{-3}$ (30—90 °C). Arrhenius plots of $k_{BAA}$ are shown in Fig. 11. From the slope of the plots, the value of the activation energy was obtained to be $24.4\pm0.2$ kJ mol$^{-1}$. The entropy of activation for $k_{h1}$(BAA) (Eq. 19) was obtained to be $-128.6\pm0.6$ J mol$^{-1}$ K$^{-1}$ from the intercept of the plots in Fig. 11.

**III. Dimethylarsinic Acid (Cacodylic Acid: CAA).** $^{17}O$ NMR spectra were measured in the pH

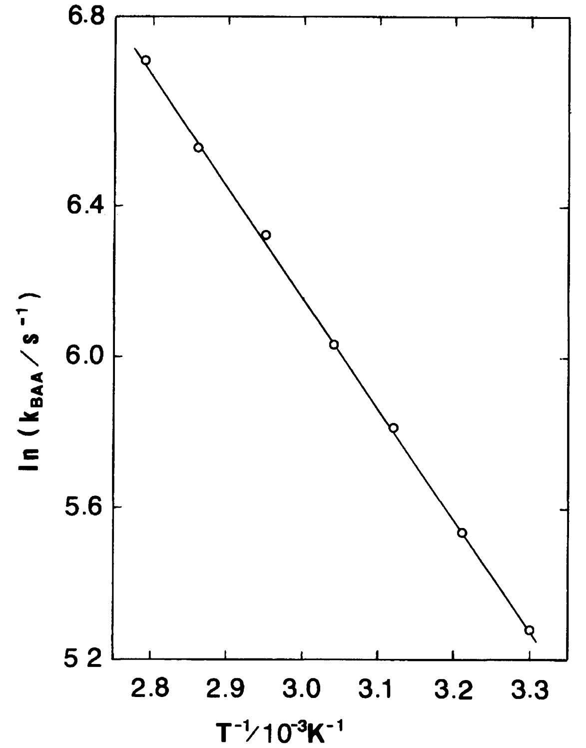

Fig. 11. Temperature dependence of the oxygen exchange rate of butylarsonic acid. (pH=0.45, [BAA]= 0.5 mol dm$^{-3}$)

Table 5. The Dependence of the Line Widths at CAA Site in the Absence and Presence of Oxygen Exchange and of $k_{\mathrm{CAA}}$ on [CAA]

| temp/°C | [CAA]/mol dm$^{-3}$ | $\nu^{\circ}_{1/2,\mathrm{CAA}}$ (pH=3.8) | $\nu_{1/2,\mathrm{CAA}}$ (pH=1.9) | $k_{\mathrm{CAA}}$/s$^{-1}$ |
|---|---|---|---|---|
| 50 | 0.467 | 160 | 239 | 248 |
| | 0.553 | 166 | 235 | 217 |
| | 0.643 | 168 | 239 | 223 |
| 70 | 0.467 | 120 | 239 | 374 |
| | 0.553 | 122 | 234 | 352 |
| | 0.643 | 124 | 234 | 346 |
| 90 | 0.467 | 99 | 271 | 540 |
| | 0.553 | 99 | 269 | 534 |
| | 0.643 | 104 | 271 | 524 |

region between 3.8 and 0.8 (30—90 °C, [CAA]=0.5 mol dm$^{-3}$). The values of $k_{\mathrm{CAA}}$ were calculated from the measured line widths by the use of Eq. 7. The line widths at pH=3.78 were used as the values of $\nu^{0}_{1/2,\mathrm{CAA}}$.

**pH Dependence of $k_{\mathrm{CAA}}$.** The dependence was studied in the pH region between 0.82 and 2.56. The plots of log $k_{\mathrm{CAA}}$ against pH are shown in Fig. 12. The slopes of the plots changed from −0.8 to −0.5, going towards the more acidic region.

**Dependence of the Exchange Rate on [CAA].** The dependence was studied at pH=1.9 (50, 70, and 90 °C). The measured line widths of oxygen signals at CAA site in the absence and presence of oxygen exchange, and the values of $k_{\mathrm{CAA}}$ are shown in Table 5. The values of $k_{\mathrm{CAA}}$ at [CAA]=0.47, 0.55, and 0.64 mol dm$^{-3}$ are nearly constant, which suggests that the order of the oxygen exchange with respect to [CAA] is unity.

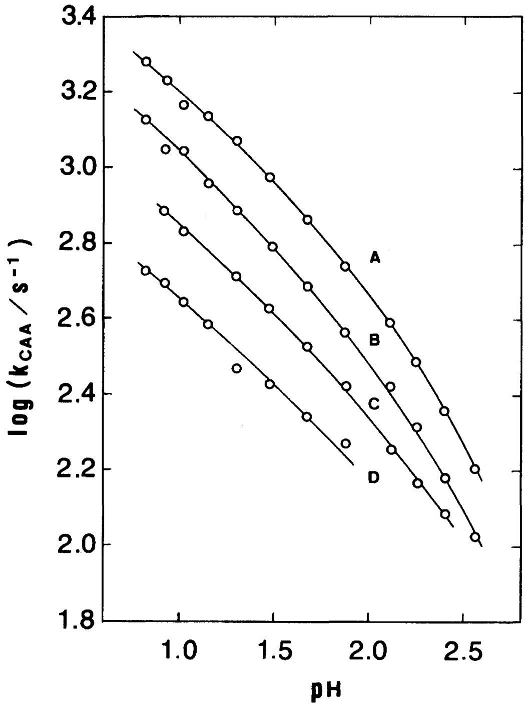

Fig. 12. Plots of log $k_{\mathrm{CAA}}$ against pH. ([CAA]=0.5 mol dm$^{-3}$). A; 90 °C; B: 70 °C; C: 50 °C; D; 30 °C.

**Mechanism of the Oxygen Exchange of CAA.** In the pH region studied, there exist the following acid dissociation equilibria:

$$\mathrm{(CH_3)_2AsO_2H} \overset{K_1\mathrm{(CAA)}}{\rightleftharpoons} \mathrm{(CH_3)_2AsO_2^-} + \mathrm{H^+} \tag{20}$$

and

$$\mathrm{(CH_3)_2AsO_2H_2^+} \overset{K_{1\mathrm{h}}\mathrm{(CAA)}}{\rightleftharpoons} \mathrm{(CH_3)_2AsO_2H} + \mathrm{H^+}. \tag{21}$$

The values of p$K_1$ (CAA) and p$K_{1\mathrm{h}}$ (CAA) were found to be 6.067 (30 °C, $I$=0.55 mol dm$^{-3}$)$^{3)}$ and 1.797 (30 °C),$^{9)}$ respectively. The concentrations of conjugate and undissociated acids and the monoanion of CAA were calculated by using the values of $K_1$ (CAA) and $K_{1\mathrm{h}}$ (CAA) and the following relation:

$$\begin{aligned}[\mathrm{CAA}] &= [\mathrm{(CH_3)_2AsO_2H_2^+}] \\ &\quad +[\mathrm{(CH_3)_2AsO_2H}] + [\mathrm{(CH_3)_2AsO_2^-}].\end{aligned}$$

The mole fraction of various ionic species of CAA is plotted against the pH in Fig. 13.

Since at pH 3.8 where an undissociated cacodylic acid exist predominantly, an oxygen exchange reaction does not occur, the observed exchange of cacodylic acid with water may be considered to be due to the contribution of the conjugate acid to the reaction. On the basis of the first-order dependence on [CAA], it was suggested that

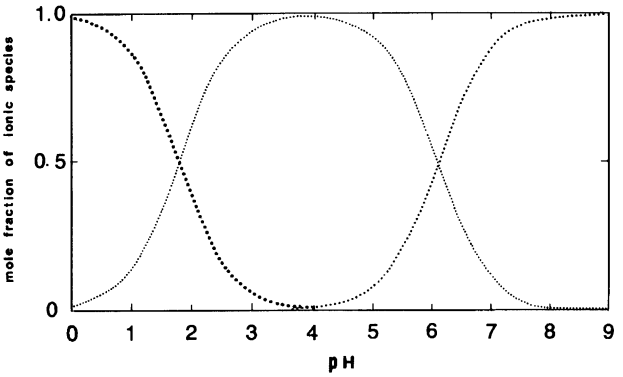

Fig. 13. Mole fractions of various ionic species of dimethylarsinic acid against pH. (30 °C) ····$(CH_3)_2AsO_2H_3^+$; ····$(CH_3)_2AsO_2H_2$; ····$(CH_3)_2AsO_2H^-$.

the cacodylic acid exchange proceeds via the following path:

$$(CH_3)_2As^{17}OOH_2^+ + H_2O \overset{k'_{h1}}{\rightleftharpoons} (CH_3)_2AsO_2H_2^+ + H_2{}^{17}O. \qquad (22)$$

If reaction (22) is the only pathway for the oxygen exchange of CAA, the rate law is given as

$$\begin{aligned} R_{CAA}/[CAA] &= k'_{h1}(CAA)[(CH_3)_2AsO_2H_2^+]/[CAA] \\ &= k'_{h1}(CAA)f_{CAAH^+} \end{aligned}$$

and the plots of $k_{CAA}$ against mole fraction $f_{CAAH^+}$ ($=[(CH_3)_2AsO_2H_2^+]/[CAA]$) are expected to give a straight line through an origin. However, the plots gave a curve which concaves upwards (Fig. 14). This fact requires an additional path, which contributes to the exchange, especially in the more acidic region. The mechanism may be a proton-assisted reaction of the conjugate acid of cacodylic acid as

$$(CH_3)_2As^{17}OOH_2^+ + H_2O + H^+ \overset{k'_{hh1}}{\rightleftharpoons} (CH_3)_2AsO_2H_2^+ + H_2{}^{17}O + H^+. \qquad (23)$$

Then, the rate law of the oxygen exchange of cacodylic acid id expressed as

$$\begin{aligned} R_{CAA} &= k'_{h1}(CAA)[(CH_3)_2AsO_2H_2^+] \\ &\quad + k'_{hh1}(CAA)[H^+][(CH_3)_2AsO_2H_2^+], \end{aligned}$$

and

$$k_{CAA}/f_{CAAH^+} = k'_{h1}(CAA) + k'_{hh1}(CAA)[H^+]. \qquad (24)$$

According to Eq. 24, the values of $k_{CAA}/f_{CAAH^+}$ are plotted against $a_{H^+}$ in Fig. 15. A least-squares treatment of the plots gives the values of $k'_{h1}$ and $k'_{hh1}$, which are listed in Table 6. By using these values, the energies and entropies of activation for $k'_{h1}$ and $k'_{hh1}$ were calculated; they are also included in Table 6.

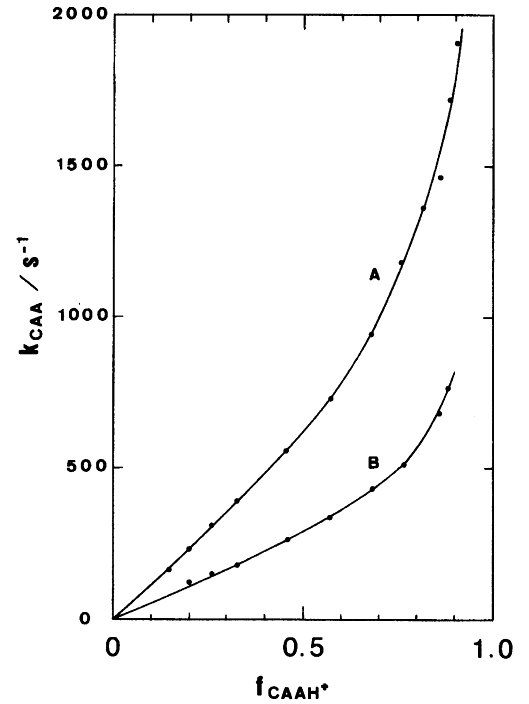

Fig. 14. Plots of $k_{CAA}$ against the mole fraction of conjugate acid of dimethylarsinic acid, $f_{CAAH^+}$. A: 90 °C, B; 50 °C.

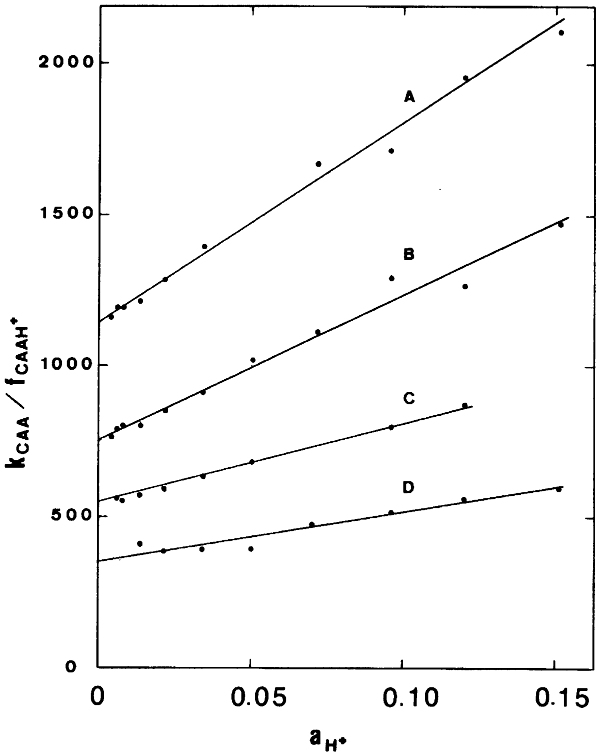

Fig. 15. Plots of $k_{CAA}/f_{CAAH^+}$ against $a_{H^+}$. A: 90 °C; B: 70 °C; C: 50 °C; D: 30 °C.

Table 7. Rate Constants and Activation Parameters for the Oxygen

a) Exchange Reactions of Methyl- and Butylarsonates with Water (30 °C)

| Reaction ($i$) | Unit ($k_i$) | R′=CH₃ $k_\mathrm{i}$ | R′=CH₃ $E_\mathrm{a}$ kJ mol$^{-1}$ | R′=CH₃ $\Delta S^{\neq}$ J mol$^{-1}$ K$^{-1}$ | R′=$n$-C₄H₉ $k_\mathrm{i}$ | R′=$n$-C₄H₉ $E_\mathrm{a}$ kJ mol$^{-1}$ | R′=$n$-C₄H₉ $\Delta S^{\neq}$ J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $R'AsO_3^{2-}+H_2O$ | s$^{-1}$ | $2.7\times10^{-4}$ a) | 85a) | −42a) | $9.3\times10^{-5}$ a) | 78a) | −78a) |
| $R'AsO_3H^-+H_2O$ | s$^{-1}$ | $6.6\times10^{-4}$ a) | | | $4.4\times10^{-4}$ a) | | |
| $R'AsO_3H_2+H_2O$ | s$^{-1}$ | 2.8 | 45 | −97 | | | |
| $R'AsO_3H_2+H_2O+H^+$ | M$^{-1}$ s$^{-1}$ | $6.0\times10^2$ | 33 | −92 | $7.6\times10^2$ | 24 | −117 |
| $R'AsO_3H^-+R'AsO_3H^-$ | M$^{-1}$ s$^{-1}$ | $5.7\times10^{-5}$ a) | | | $2.8\times10^{-5}$ a) | | |
| $R'AsO_3H^-+R'AsO_3H_2$ | M$^{-1}$ s$^{-1}$ | $2.5\times10$ | 33 | −124 | 2.1a) | | |
| $R'AsO_3H_2+R'AsO_3H_2$ | M$^{-1}$ s$^{-1}$ | $1.8\times10$ | 31 | −120 | | | |
| $R'AsO_3H_2+R'AsO_3H_2+H^+$ | M$^{-2}$ s$^{-1}$ | $6.8\times10^2$ | 18 | −125 | | | |

a) Ref. 3.

b) Exchange Reactions of Dimethylarsinate with Water (30 °C).

| Reaction ($i$) | Unit ($k_i$) | $k_i$ | $E_\mathrm{a}$/kJ mol$^{-1}$ | $\Delta S^{\neq}$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| $(CH_3)_2AsO_2^-+H_2O$ | s$^{-1}$ | $4.4\times10^{-2}$ a) | 95a) | 34a) |
| $(CH_3)_2AsO_2H+H_2O$ | s$^{-1}$ | $4.8\times10^{-2}$ (2°C)a) | | |
| $(CH_3)_2AsO_2H_2^++H_2O$ | s$^{-1}$ | $3.5\times10^2$ | 18 | −145 |
| $(CH_3)_2AsO_2H_2^++H_2O+H^+$ | M$^{-1}$ s$^{-1}$ | $1.6\times10^3$ | 23 | −115 |

Table 6. Rate Constants of the Oxygen Exchange of Dimethylarsinic (Cacodylic) Acid with Water

| Rate const. | Temp/°C 30 | 50 | 70 | 90 | $E_\mathrm{a}$ kJ mol$^{-1}$ | $\Delta S^{\neq}$ J mol$^{-1}$K$^{-1}$ |
|---|---|---|---|---|---|---|
| $k'_\mathrm{h1}$ / s$^{-1}$ | 351 | 551 | 750 | 1145 | $18.{}_1\pm0.{}_9$ | $-144\pm0.{}_4$ |
| $k'_\mathrm{hh1}$ / mol$^{-1}$ dm$^3$ s$^{-1}$ | 1627 | 2589 | 4829 | 6817 | $23.{}_1\pm1.{}_5$ | $-115\pm0.{}_6$ |

## Discussion

The rate constants of the elementary processes obtained in this work are summarized in Table 7; the values for methyl- and butylarsonic acids are in Table 7a and those for dimethylarsinic acid in Table 7b. These rate constants, obtained in a previous study,[3] are also shown in Table 7. All of the values are extrapolated to those at 30 °C.

**Comparison of the Oxygen Exchange Rate of Methylarsonic Aicd with that of Butylarsonic Acid.** In Fig. 4, the oxygen-exchange rate of arsenic acid is shown compared with the rates for methyl- and butylarsonic acids. It can be seen that the alkyl substitution on arsenic causes a retardation of the exchange of arsenic oxygens. A more precise kinetic result concerning the oxygen exchange of arsenic acid will be given elsewhere.

It is evident from Fig. 4 that the oxygen-exchange reaction of methylarsonic acid is observable over a rather wide pH region (pH < 5), while that of butylarsonic acid is observable only at pH < 1.5; the values of $k_\mathrm{MAA}$ are 2- or 3-times larger than those of $k_\mathrm{BAA}$ obtained in the same pH region. In order to clarify the difference in the kinetic behavior between two arsonic acids, the rate laws for both arsonic acids are shown together (pH < 1.5):

$$k_\mathrm{MAA} = R_\mathrm{MAA}/[\mathrm{MAA}] = k_\mathrm{h1}(\mathrm{MAA})[\mathrm{H}^+]$$
$$+k_1 + k_\mathrm{h2}[\mathrm{H}^+][\mathrm{MeAsO_3H_2}] + k_2[\mathrm{MeAsO_3H_2}]$$

and

$$k_\mathrm{BAA} = R_\mathrm{BAA}/[\mathrm{BAA}] = k_\mathrm{h1}(\mathrm{BAA})[\mathrm{H}^+]. \tag{25}$$

The oxygen exchange of butylarsonic acid proceeds exclusively via the $k_\mathrm{h1}$-path (the proton-catalyzed reaction of an undissociated acid with water). The values of $k_\mathrm{h1}$ (MAA) and $k_\mathrm{h1}$ (BAA) are almost the same: $k_\mathrm{h1}(\mathrm{MAA}) = 4.9\times10^3$ mol dm$^{-3}$ s$^{-1}$ and $k_\mathrm{h1}(\mathrm{BAA}) = 3.0\times10^3$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 90 °C. Therefore, the excess rate of methylarsonic acid over the rate of butylarsonic acid is attributable to the contributions of the $k_1$, $k_\mathrm{h2}$, and $k_2$ terms to $R_\mathrm{MAA}$ (pH < 1.5). For methylarsonic acid, the contribution of each rate terms to the over-all rate (0 < pH < 6) was calculated by using the corresponding rate constants (Table 3, 90 °C). The results are: $k_\mathrm{h1}$-term; 55% (pH=0.84), 25% (pH=1.7), $k_1$-term; 4% (pH=0.85), 13% (pH=1.7), 19% (pH=4); $k_\mathrm{h2}$-term; 27% (pH=0.85), 12% (pH=1.7), $k_2$-term; 13% (pH=0.85), 47% (pH=1.7), 57% (pH=2), 41% (pH=4), and $k_3$-term; 1% (pH=2), 39.2% (pH=4). The total contribution of the second-order rate terms amounts to 40% (pH=0.8), 60% (pH=2), and 80% (pH=4), and tends to decrease with the decrease in pH. For the exchange of butylarsonic acid, the second-order paths have also been found in an $^{18}$O tracer study carried out at pH > 6,[3] but could not be detected in this $^{17}$O NMR work. The second-order pathway involves a nucleophilic displacement of water on arsenic by an arsonic acid, while the first-order path involves a displacement of water by water. The longer butyl-chain, compared to methyl, would hinder the nucleophilic attack by another butylarsonic-acid molecule to form a condensed acid and would retard the rate via the mechanism.

The activation energy for the second-order path is smaller compared with the values for the first-order path. On the other hand, the activation entropy for the second-order path has larger negative values than that for the first-order path; the second-order path is unfavorable in terms of entropy.

**Effect of Protonation on the Reactivity of Alkylarsonate Ions.** The kinetic information concerning the reactivity of the various ionic species in a solution are most extensively obtained for the oxygen exchange of methylarsonic acid, because the reaction could be examined over wide pH range between 0.5 to 12 using the $^{17}$O NMR method ($pH<6$) and the $^{18}$O tracer method ($pH>6$). Table 7a shows that protonation enhances the reactivity of the arsonate ions towards water. The values of the first-order rate constants for MAA are in the following order:

$$\begin{aligned} &k(\mathrm{CH_3AsO_3^{2-}}) < k(\mathrm{CH_3AsO_3H^-}) \\ &<< k(\mathrm{CH_3AsO_3H_2})(= k_1) \\ &<< k(\mathrm{CH_3AsO_3H_3^+})(= k'_{\mathrm{h1}}). \end{aligned}$$

The reactivity of the monoanion towards the water molecule is only 2.5-times larger than that of dianion, whereas the reactivity of the conjugate acid is two orders of magnitude larger than that of undissociated acid, which in turn is three orders of magnitude larger than that of the monoanion. Since the role of a proton in facilitating the oxygen exchange of oxoanion probably involves a polarization of the bond between the oxygen and the arsenic atom, the protonation would lower the values of the activation energy. In fact, the $E_a$ values for $k(\mathrm{CH_3AsO_3^{2-}})$, $k_1$, and $k_{\mathrm{h1}}$ are found to be 85, 45, and 33 kJ mol$^{-1}$, respectively. On the other hand, the activation entropy has larger negative values for the reactions of undissociated acid ($-97$ and $-92$ J K$^{-1}$ mol$^{-1}$ for $k_1$ and $k_{\mathrm{h1}}$, respectively) than for that of the dianion ($-42$ J K$^{-1}$ mol$^{-1}$). Therefore, the enhancement of the reactivity of the arsonate ion with protonation can be considered to be due to a decrease in the activation energy caused by protonation.

The negative values of the activation entropy for the first-order oxygen exchange are consistent with a nucleophilic displacement by water on arsenic. However, the value of $-97$ J mol$^{-1}$ K$^{-1}$ observed for the reaction of undissociated acid with water is more negative than the values expected for the typical bimolecular nucleophilic displacement reaction, which are on the order of $-50$ to $-70$ J K$^{-1}$ mol$^{-1}$.[10] The observed value falls over the range from $-90$ to $-140$ J K$^{-1}$ mol$^{-1}$ found for a nucleophilic displacement reaction which is known to be termolecular.[11]

As suggested in a study concerning the arsenite oxygen exchange reaction,[12] it is reasonable to assume that the reaction proceeds through a cyclic transition state involving an additional water molecule, in which a proton transfer may be facilitated. The less negative value of activation entropy for the exchange of dianion may be due to enhanced hydration to the ion in a ground state.

Protonation has an effect on the second-order reaction between two arsonate species as well as on the first-order reaction. The reaction between the monoanion and undissociated acid proceeds 5 orders of magnitude faster than that between two monoanions. On the other hand, two reactions (between undissociated acid and the monoanion, and between two undissociated acids) are similar to each other regarding the rate constant and activation parameters (Table 7a). For the latter two reactions, an activation energy having a small value (30 kJ mol$^{-1}$) and an activation entropy having a large negative value ($-120$ J K$^{-1}$ mol$^{-1}$) are characteristic.

**Comparison of the Oxygen Exchange Rate of Dimethylarsinic Acid with That of Methylarsonic Acid.** Dimethylarsinate ($\mathrm{(CH_3)_2AsO_2^-}$) exchanges its oxygens 67- and 167-times faster than do monoanion ($\mathrm{CH_3AsO_3H^-}$) and dianion ($\mathrm{CH_3AsO_3^{2-}}$) of methylarsonate, respectively. It has been suggested that the faster rates found in dimethylarsinates are due to the positive value of the activation entropy, the values of activation energy obtained for dimethylarsinate being larger than that for methylarsonate.[3] On the other hand, the oxygen exchange rates for both conjugate acids of dimethylarsinic and methylarsonic acids have almost same values: $k(\mathrm{(CH_3)_2AsO_2H_2^+})=3.5\times10^2$ s$^{-1}$ and $k(\mathrm{CH_3AsO_3H_3^+})=7.8\times10^2$ s$^{-1}$ (30 °C). It may be said that both conjugate acids exchange their oxygens at a similar rate, irrespective of the number of substituents on the arsenic atom.

In previous work, the following mechanism was presented for the exchange reaction of the dimethylarsinate ion with water based on the amphoteric character of dimethylarsinic acid:

$$\mathrm{(CH_3)_2AsO_2^-} + \mathrm{H^+} \rightleftharpoons \mathrm{(CH_3)_2AsO_2H},$$

and

$$\mathrm{(CH_3)_2AsO_2H} \rightleftharpoons \mathrm{(CH_3)_2AsO^+} + \mathrm{OH^-}.$$

The kinetic result that the reaction proceeds via $\mathrm{S_N1}$ (consistent with positive activation entropy) was explained by assuming a reversible dissociation of $\mathrm{(CH_3)_2AsO_3H}$ into $\mathrm{OH^-}$ and $\mathrm{(CH_3)_2AsO^+}$. It is plausible to consider that an oxygen-exchange reaction between undissociated dimethylarsinic acid with water, if any, would proceed via the same mechanism; unfortunately, the reaction was impossible to observe in this NMR work. A large negative value of the activation entropy for the oxygen exchange of a conjugate acid of dimethylarsinic acid was obtained ($-145$ J $K^{-1}$ $mol^{-1}$), which is consistent with the $S_N2$ mechanism. The mechanistic change does occur between two reactions: The oxygen exchange of $(CH_3)_2AsO^-$ with water proceeds via $S_N1$, while that of $(CH_3)_2AsO_2H_2^+$ proceeds via $S_N2$. It is to be noted that an additional path was found in which the oxygen exchange of the conjugate acid of dimethylarsinic acid is further accelerated by a proton.

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