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Kinetics of Oxygen Exchange between Arsenic Acid and Solvent Water

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The rates (R) of the oxygen exchange of arsenic acid with solvent water were measured over a wide range of hydrogen-ion concentrations. At pH>4, a ^{18}O tracer method was used ([As(V)]=0.07 mol dm^{-3}, 0—50 °C). At pH<5, ^{17}O NMR line broadening technique was used ([As(V)]=1 mol dm^{-3}, 50—90 °C). Over the whole pH range studied, the variation of R amounts to 10^{10}, and the comprehensive rate law is expressed as: $R=k_{11\text{h}}[\text{H}^+][\text{H}_3\text{AsO}_4]+k_{11}[\text{H}_3\text{AsO}_4]+k_{12}[\text{H}_2\text{AsO}_4{}^-]+k_{13}[\text{HAsO}_4{}^{2-}]+k_{14}[\text{AsO}_4{}^{3-}]+k_{21}[\text{H}_3\text{AsO}_4]^2+k_{22}[\text{H}_3\text{AsO}_4][\text{H}_2\text{AsO}_4{}^-]+k_{23}[\text{H}_2\text{AsO}_4{}^-]^2+k_{24}[\text{H}_2\text{AsO}_4{}^-][\text{HAsO}_4{}^{2-}]+k_{25}[\text{HAsO}_4{}^{2-}]^2$. The rate constant for each elementary process in the equation was obtained. The activation parameters of each elementary process were evaluated. The oxygen exchange rate of arsenic acid was compared with that of phosphoric acid. The contrast of an S$_\text{N}$2-type exchange of the former acid vs. an S$_\text{N}$1-type one of the latter is suggested.

Since the As and P atoms belong to the nonmetal 5B group, arsenic and phosphoric acids have similarities regarding their structures and physical properties in aqueous solution. On the other hand, the difference in the reactivities between them is enormous; the oxoarsenate ions are reactive, while the oxophosphate ions are stable and unreactive. It would be interesting to make a more precise comparison of the kinetic behavior between P(V) and As(V). The oxygen exchange of oxophosphate(V) and oxoarsenate(V) ions with water is a primitive reaction, and may be used as a probe for examining their reactivities. While the oxygen exchange of phosphoric acid has been well studied,[1,2] studies of arsenic acid have been rather few.[3,4]

In a previous paper[4] we reported extensive kinetic results concerning the oxygen-exchange reaction between arsenate ions and water. The exchange rates were measured at 14.5 and 30 °C over a pH range of 6.5—12.5 using an ^{18}O tracer method. The rate (R) may be expressed by the rate law:

$$\begin{aligned}R&=k_{12}[\text{H}_2\text{AsO}_4{}^-]+k_{13}[\text{HAsO}_4{}^{2-}]+k_{14}[\text{AsO}_4{}^{3-}]\\&\quad+k_{23}[\text{H}_2\text{AsO}_4{}^-]^2+k_{24}[\text{H}_2\text{AsO}_4{}^-][\text{HAsO}_4{}^{2-}]\\&\quad+k_{25}[\text{HAsO}_4{}^{2-}]^2\\&=R_{12}+R_{13}+R_{14}+R_{23}+R_{24}+R_{25}.\end{aligned} \tag{1}$$

It has been considered that the rate terms (R_{12}, R_{13}, and R_{14}) are for an oxygen exchange of the arsenate ions with water; (R_{23}, R_{24}, and R_{25}) are for the reversible condensation reactions between two arsenate ions involved in each rate term. The exchange rates at 30 °C were analyzed in terms of this rate law to obtain the values of the rate constants, $k_{12}-k_{14}$ and $k_{23}-k_{25}$.

In this paper we present the kinetic results concerning the fast oxygen exchange reaction of As(V) (mainly ionic species of H_3AsO_4 and $\text{H}_2\text{AsO}_4{}^-$) using recently available NMR instrumentation ([H$^+$]= 10^{-4}—3 mol dm^{-3}). Some additional results from an ^{18}O tracer study (pH>4) are also described.

As one part of a series of studies concerning the kinetic behavior of arsenic oxygens, we have studied the oxygen-exchange reaction of the alkyl derivatives of arsenic acid with water.[5—7] The substituent effect of the alkyl groups on the arsenic oxygen exchange has been determined. The arsenic oxygen exchange reported here is very important for precisely understanding these substituent effects.

As additional information, the solvent effect on the oxygen exchange reaction of arsenic acid with water is reported.

Experimental

Materials. Disodium hydrogenarsenate heptahydrate (guaranteed reagent, Merck) was used without further purification. Sodium dihydrogenarsenate dihydrate was prepared by acidifying a solution of disodium hydrogenarsenate to pH 4, and was purified by repeated crystallization. Arsenic acid (Special grade JIS) was received as a 60% aqueous solution. The concentration of the arsenic acid solution was determined by both potentiometric titration and chemical analysis methods.

Procedure. ^{18}O Tracer Work: The procedure was almost the same as that used in a previous study.[4] The exchange reaction was initiated by diluting an isotopically-equilibrated solution of disodium hydrogenarsenate in (^{18}O)water with a relatively large amount of isotopically normal water. The pH of the solution was adjusted by adding a small amount of hydrochloric acid, and was measured at each reaction temperature. The ionic strength (I) of the solution was adjusted by adding NaCl. At appropriate intervals, aliquots were drawn; the arsenate ion was precipitated as barium arsenate by adding a solution of barium chloride. The precipitation-induced oxygen exchange of the arsenate ion becomes appreciable at pH values smaller than 9. To avoid this exchange, the pH of the solution was brought to 10 before adding of the precipitant by adding an appropriate amount of sodium hydroxide solution.

The precipitate was separated by means of a centrifuge, washed three times with absolute ethanol, dried in an oven at 110 °C, and converted into carbon dioxide by the guanidiniumchloride method.[8] The isotopic analysis of the carbon dioxide was carried out on a Hitachi RMS-I-type mass spectrometer.

The rate (R) of the oxygen exchange was calculated by means of the following formula:

$$R=\frac{[\mathrm{As(V)}][\mathrm{H_2O}]}{4[\mathrm{As(V)}]+[\mathrm{H_2O}]}k_{\mathrm{ex}},$$
$$k_{\mathrm{ex}}=-\frac{1}{t}\ln\frac{O_t-O_\infty}{O_0-O_\infty}, \tag{2}$$

where O_0, O_t, and O_∞ are the oxygen-18 contents of the arsenate at times 0, t, and infinity, respectively. [As(V)] and [H_2O] are the molar concentrations of the arsenate and water, respectively.

NMR Measurements. Solutions for the ^{17}O NMR spectra were prepared as follows: A known amount of NaH_2AsO_4 was dissolved into 3 ml of 10% (^{17}O)water containing 25 vol % D_2O added for NMR lock ([As(V)]=0.95 mol dm^{-3}). The pH of the solution was adjusted by adding a small amount of either concentrated sulfuric acid or perchloric acid. The pH of the solution was measured both before and after the NMR measurement at 30 °C using a Radiometer PHM type-26 pH meter.

The ^{17}O NMR spectra were recorded at 36.6 MHz on an 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.

The Dissociation Constants of Arsenic Acid. The first-dissociation constant (K_1) was determined by using potentiometric titration under the NMR experimental conditions ([As(V)]=0.32, 0.60, and 0.95 mol dm^{-3}, 30 °C). Solutions of sodium dihydrogenarsenate containing 25 vol % D_2O were titrated by concentrated hydrochloric acid. The pH was measured using a Radiometer PHM type-26 pH meter. The K_1 values were obtained from two series of titration, each with more than ten titrations. During the course of titration, the ionic strengths (I's) of the solution remain constant, since any decrease in I due to a change of the species from $H_2AsO_4^-$ to H_3AsO_4 is compensated by the formation of an equal amount of NaCl to that of H_3AsO_4 (I=[As(V)]). The values of pK_1 were estimated by using the relation $\mathrm{p}K_1=\mathrm{pH}+\log\{([\mathrm{H_3AsO_4}]_f-[\mathrm{H^+}])/([\mathrm{H_2AsO_4^-}]_f+[\mathrm{H^+}]\}=\log\{[\mathrm{H_3AsO_4}]/[\mathrm{H_2AsO_4^-}]\}$, where the subscript f designates the stoichiometric concentration, and [H^+] was approximated to $a_{\mathrm{H^+}}$. The pK_1 values were obtained to be 1.992±0.001 ([As(V)]=0.32 mol dm^{-3}), 2.018±0.001 ([As(V)]=0.60 mol dm^{-3}), and 1.897±0.010 ([As(V)]=0.95 mol dm^{-3}). It may be said that the pK_1 values are almost independent of the ionic strength of the solution.

Results and Discussion

I. ^{18}O Tracer Study. pH Dependence of the Oxygen Exchange Rate: The pH dependence of R was studied at 0 °C (4<pH<10) and 50 °C (7.5<pH<12) ([As(V)]=0.07 mol dm^{-3}, I=0.55 mol dm^{-3}). Plots of log R against pH are shown in Fig. 1 (A: 0 °C, D: 50 °C). At pH<6, log R varies linearly with the pH, and the slope of the line is −0.87 (0 °C). The pH-rate profiles previously obtained at 14.5 °C (B) and 30 °C (C)[4] are also included in Fig. 1.

Dependence of the Rate on [As(V)]: The dependence of R on [As(V)] was studied at pH 5.4 and 0 °C (I=0.55 mol dm^{-3}). The values of R at [As(V)]= 0.0413, 0.0617, and 0.100 mol dm^{-3} were obtained to be 8.03×10^{-4}, 1.41×10^{-3}, and 1.81×10^{-3} mol dm^{-3} s^{-1}, respectively. The order of the reaction with respect to [As(V)] was evaluated to be 1.91±0.25, showing that the contribution of a bimolecular reaction to the exchange is important at this pH.

Mechanism of the Oxygen Exchange and Rate Analyses: For a mechanistic consideration of the exchange rate, the concentrations of the ionic species under the conditions of kinetic runs are needed. The concentrations were calculated by the following relations:

$$[\mathrm{As(V)}]=[\mathrm{H_3AsO_4}]+[\mathrm{H_2AsO_4^-}]+[\mathrm{HAsO_4^{2-}}]+[\mathrm{AsO_4^{3-}}],$$
$$K_1=a_{\mathrm{H^+}}[\mathrm{H_2AsO_4^-}]/[\mathrm{H_3AsO_4}],$$
$$K_2=a_{\mathrm{H^+}}[\mathrm{HAsO_4^{2-}}]/[\mathrm{H_2AsO_4^-}],$$
$$K_3=a_{\mathrm{H^+}}[\mathrm{AsO_4^{3-}}]/[\mathrm{HAsO_4^{2-}}],$$
and
$$[\mathrm{H_2AsO_4^-}]=[\mathrm{As(V)}]/(1+a_{\mathrm{H^+}}/K_1+K_2/a_{\mathrm{H^+}}+K_2K_3/a_{\mathrm{H^+}}^2). \tag{3}$$

As the dissociation constants (I=0.55 mol dm^{-3}) in Eq. 3, the following values were used: pK_1=2.24 (0 °C);[9] pK_2=6.531 (14.5 °C), 6.596 (30 °C),[4] 6.494 (50 °C); pK_3=11.015 (14.5 °C), 11.190 (30 °C),[4] 10.81 (50 °C). The values at 50 °C were obtained by extrapolation ($\Delta H°$=3.44 (K_2) and 19.07 (K_3) kJ mol^{-1} [4]). The concentration of various ionic species at a definite pH ($a_{\mathrm{H^+}}$) can be estimated from these pK values in terms of Eq. 3. It is seen that each species (H_3AsO_4, $H_2AsO_4^-$, or $HAsO_4^{2-}$) exists predominantly at pH of 0, 4.8, or 9, respectively.

As already described, the oxygen-exchange rate (R) in the pH range above 6.5 may be expressed by the rate law (Eq. 1). By using a method similar to that described earlier,[4] the rates (R) at 14.5 and 50 °C were analyzed in order to evaluate the rate constants ($k_{12}-k_{25}$ in Eq. 1). They are listed in Table 1. The

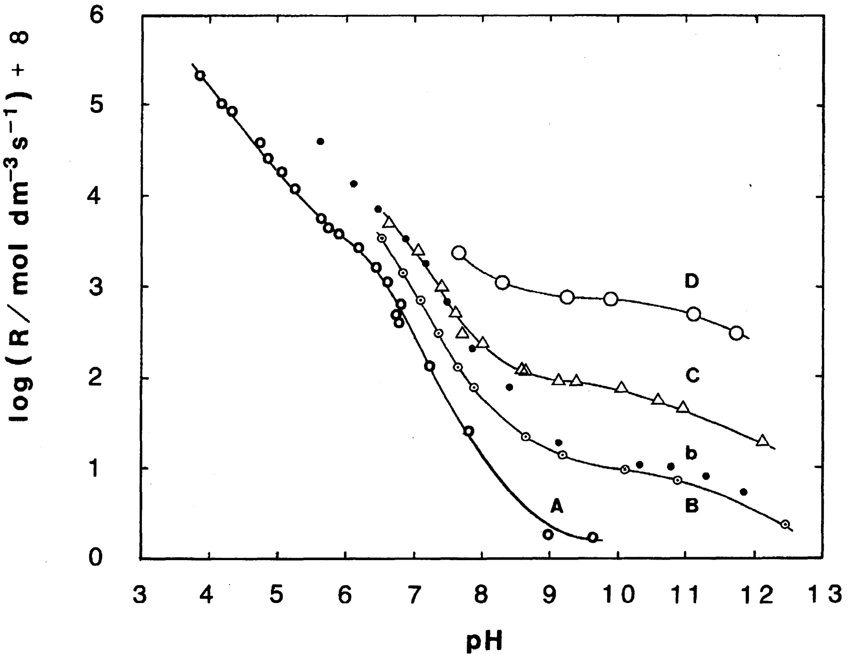


Fig. 1. pH dependence of the oxygen exchange rate (R) ([As(V)]=0.07 mol dm^{-3}, I=0.55 mol dm^{-3}). A(○): 0 °C, B(⊙): 14.5 °C (aqueous solution); b(●): 14.5 °C (aqueous methanol solution), C(△): 30 °C, D(○): 50 °C.

Table 1. Rate Constants and Activation Parameters of the Oxygen Exchange of Arsenic Acid by ^{18}O Tracer Work $R=k_{12}[H_2AsO_4^-]+k_{13}[HAsO_4^{2-}]+k_{14}[AsO_4^{3-}]+k_{23}[H_2AsO_4^-]^2+k_{24}[H_2AsO_4^-][HAsO_4^{2-}]+k_{25}[HAsO_4^{2-}]^2$

Temp	k_{12}	k_{13}	k_{14}	k_{23}	k_{24}	k_{25}
° C	$10^{-4}s^{-1}$	$10^{-6}s^{-1}$	$10^{-6}s^{-1}$	$10^{-2}M^{-1}s^{-1}$	$10^{-3}M^{-1}s^{-1}$	$10^{-5}M^{-1}s^{-1}$
0	—	0.1	(0.03)[b]	(0.7)[b]	(0.2)[b]	(0.3)[b]
14.5	0.6±0.2	0.8±0.8	0.33±0.02	2.3±0.1	1.2±0.3	1.5±1.3
30[a]	1	12	1.5	7.4	6.4	4.2
50	—	93 ±12	33 ±2	—	52 ±2	36 ±4
E_a/kJ mol^{-1}		103±12	103±7	55	82±2	70±11
$\Delta S^{\neq}$/J mol^{-1} K^{-1}		−10±3	−22±2	−93	−24±0.5	−104±3

a) Ref. 4. b) Extrapolated values.

numbers appearing after plus–minus represent the standard deviations obtained in the rate analysis. The activation energy and activation entropy (30 °C) for the elementary processes were calculated, and are also given in Table 1.

In the pH region from 6.5 to 3.8 and at 0 °C, the rate of oxygen exchange may be expressed as $R=k\cdot a_{H^+}{}^{0.9}[As(V)]^{1.9}$. In this pH range the dominant ionic species of oxoarsenate (V) is the $H_2AsO_4^-$ ion; the fraction of $[H_2AsO_4^-]/[As(V)]$ is more than 0.98 at a pH between 4 and 4.8; a further decrease in the pH decreases the fraction. On the other hand, H_3AsO_4 comes to exist in an appreciable concentration at pH 5; its concentration continues to increase with decreasing pH ($f=[H_3AsO_4]/[As(V)]=5.7\times10^{-5}$ (pH 6), 1.5×10^{-3} (pH 5), 8.3×10^{-3} (pH 4.3), 2.4×10^{-2} (pH 3.8)). The fact that the oxygen-exchange rates continue to increase with decreasing pH over the entire pH range from 6.5 to 3.8 may be interpreted by assuming that the participation of the more reactive H_3AsO_4 species into the rate process becomes important. The role of the hydrogen ion is to shift the pre-equilibrium,

$$H_2AsO_4^- + H^+ \rightleftharpoons H_3AsO_4,$$

from left to right in favor of the more reactive H_3AsO_4 species.

The possible mechanism is as follows:

$$H_3As^{17}OO_3 + H_2O \overset{k11}{\rightleftharpoons} H_3AsO_4 + H_2{}^{17}O, \tag{4}$$

$$H_3AsO_4 + H_2AsO_4^- \overset{k22}{\rightleftharpoons} H_3As_2O_7^- + H_2O. \tag{5}$$

The contribution of the bimolecular path between two molecules of undissociated arsenic acid (Eq. 12), which corresponds to the rate-term ($k_{21}[H_3AsO_4]^2$), was neglected because the hydrogen-ion dependence is smaller than 1 and there is a small concentration product $[H_3AsO_4]^2$ in the k_{21}-term.

The rate law ($4<\mathrm{pH}<6.5$) is then expressed as:

$$\begin{aligned} R &= R' + k_{11}[\mathrm{H_3AsO_4}] + k_{22}[\mathrm{H_3AsO_4}][\mathrm{H_2AsO_4}^-] \\ &= R' + R_{11} + R_{22}, \end{aligned} \qquad (6)$$

where $R'=(R_{12}+R_{13}+R_{14}+R_{23}+R_{24}+R_{25})$ in Eq. 1. Eq. 6 can be rewritten as:

$$R - R' = k_{11}[\mathrm{H_3AsO_4}] + k_{22}[\mathrm{H_3AsO_4}][\mathrm{H_2AsO_4}^-] \qquad (7)$$

The exchange rates at 0 °C (pH=4—7) were analyzed in terms of Eq. 7. For each run, the left side of Eq. 7 ($R-R'$) was calculated by using the rate constants extrapolated to 0 °C from higher temperatures (Table 1); the concentration products were also calculated. The contribution of R' to the total rate (R) is 58% (pH=6.8), 35% (pH=5.9), 7% (pH=4.8), and 1% (pH=3.8). By a least-squares treatment of a set of numerical equations, thus obtained, the values of k_{11} and k_{22} were obtained to be nearly 1 (1.1±3.9) $\mathrm{s^{-1}}$ and 2 (1.7±6.2) $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively. The large-error attendant on k_{11} and k_{22} may originate from an uncertainty involved in the small value of $[\mathrm{H_3AsO_4}]$. More precise values of these rate constants will be obtained from the ^{17}O NMR rate results in the pH range between 3.5 and 1.5 where the contributions of the k_{11}- and k_{22}-terms are most significant.

II. ^{17}O NMR Study. The fast oxygen exchange rates of arsenic acid with water were evaluated by measuring the line widths of ^{17}O NMR signals due to arsenic acid and water. The fast exchange of ^{17}O nucleus between the arsenic site and water caused (**a**) line broadening (pH=1.5—3.1) and (**b**) line narrowing ($[\mathrm{H^+}]>0.2$ $\mathrm{mol\,dm^{-3}}$), depending on the exchange rate. Details concerning the procedure to calculate the kinetic data are described in Eqs. 8, 9, 10, and 11 of the Appendix. The kinetic results are shown separately for the acidic regions, (**a**) and (**b**), as follows:

(a) pH=1.5—3.1: In this region, both the oxygen signals due to arsenic acid (site A) and solvent water were observed separately. The ^{17}O chemical shifts of arsenic oxygen (referred to the $\mathrm{H_2O}$ signal) are 110 (pH=9), 97 (pH=4.8), and 88 (pH=1.4) ppm. The line widths were measured for both signals at temperatures ranging from 0 to 90 °C in the pH region between 1.5 and 5. The typical values of the line widths of the ^{17}O signals at site A are plotted against the temperatures in Fig. 2. The values of k_A (the exchange rate constant of the oxygen nucleus at site A) can be calculated by means of Eq. 9 (Appendix).

The pH Dependence of R. The pH dependence of R was studied at temperatures ranging from 50 to 90 °C ($[\mathrm{As(V)}]=I=0.95$ $\mathrm{mol\,dm^{-3}}$). The logarithms of k_A are plotted as a function of the pH at 30 °C in Fig. 3 (60 and 90 °C). The slopes of the plots were obtained to be −1.03±0.02 (60 °C) and −0.88±0.01 (90 °C); the rate has an approximately first-order dependence in the hydrogen-ion activity. The difference in the slopes at two

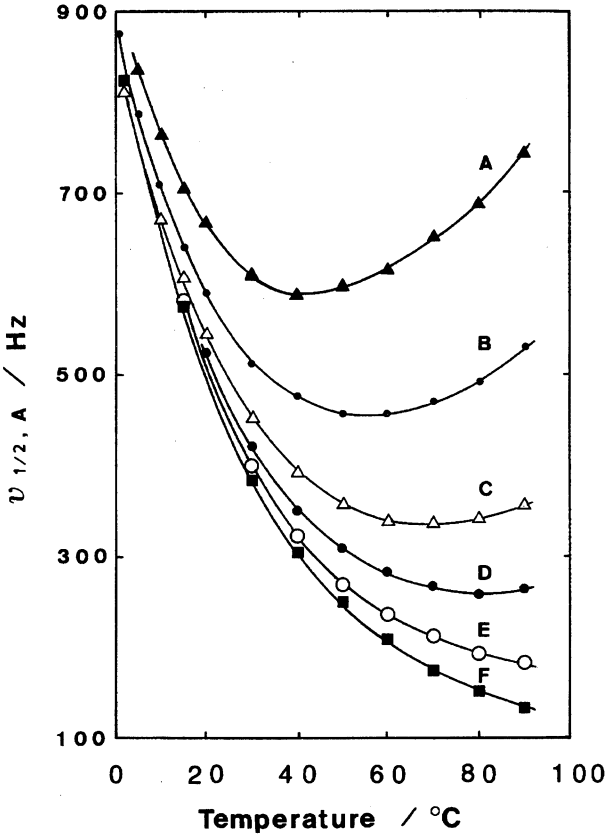


Fig. 2. Measured ^{17}O NMR line widths of arsenate oxygens as a function of the temperature ($[\mathrm{As(V)}]=0.95$ $\mathrm{mol\,dm^{-3}}$). pH; A(▲): 1.41, B(•): 1.70, C(△): 2.01, D(●): 2.27, E(○): 2.68, F (■): 4.52.

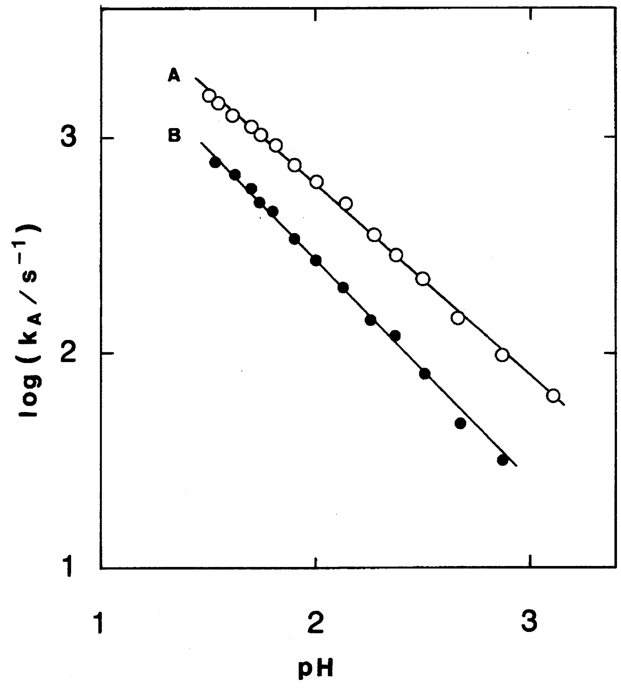


Fig. 3. pH dependence of the oxygen-exchange rate of arsenic acid ($[\mathrm{As(V)}]=0.95$ $\mathrm{mol\,dm^{-3}}$). A: 90 °C, B: 60 °C. k_A is defined in Eq. 9 of Appendix.

temperatures reveals that the activation energy (E_a) of the k_A values depends on the pH. The k_A values obtained at various pH give the E_a values (kJ mol^{-1}) as: 39±2 (pH=3.1), 36±1 (pH=2.5), 30±1 (pH=2), 24±1 (pH=1.6)(60, 70, 80, and 90 °C). The pH dependence of E_a shows that the mechanism of a low activation energy prevails in a lower pH region.

The Dependence of *R* on [As(V)]. The concentration dependence of R was studied at pH 2.37 ([As(V)]=0.32−0.96 mol dm^{-3}, 60—90 °C). In a series of the experiments, the ionic strength was not adjusted, since it was found that the added inert salt affects the line widths of the arsenic oxygens. The kinetic salt effect may be considered to be small, if any, since the elementary processes which contribute mainly to the total rate at pH 2.4 are the reactions of a neutral H_3AsO_4 molecule with H_2O, H_3AsO_4, and $H_2AsO_4{}^-$, as discussed later. Plots of $\log R$ ($=k_A$[As(V)]) against log [As(V)] yield straight lines (not shown) with slopes of 1.27±0.14 (90 °C), 1.20±0.13 (80 °C), 1.15±0.14 (70 °C), 1.06±0.09 (60 °C).

(b) $[H^+]>0.2$ mol dm^{-3}: At $[H^+]$=0.1 mol dm^{-3}, two peaks began to coalesce. Then, at $[H^+]$=0.2—3 mol dm^{-3} only one peak was given, where line narrowing of the peak was observed. The line width of the single peak was measured (90 °C, [As(V)]=0.3 mol dm^{-3}) (Table 2). By using Eq. 10 (Appendix), the values of $(\tau_A{}^{-1}+\tau_B{}^{-1})=(k_A+k_B)$ were calculated, and are shown in Table 2.

The order of the exchange rate (k_A+k_B) with respect to $[H^+]$ was obtained to be 0.7 on the basis of the data given in Table 2.

The dependence of R on [As(V)] was studied at $[H^+]$= 1.6 mol dm^{-3} ([As(V)]=0.3−2.5 mol dm^{-3}, 30 °C). The values of (k_A+k_B) (Table 3) are nearly constant over the concentration range. On the basis of Eq. 11 (Appendix), it is inferred that the oxygen exchange of arsenic acid at $[H^+]>0.3$ shows a first-order dependence on [As(V)].

Table 3. Dependence of the Oxygen Exchange Rate of Arsenic Acid on [As(V)] ($[H^+]$=1.63 mol dm^{-3}, 30 °C)

[As(V)] / mol dm^{-3}	$\nu_{1/2}$ / Hz	(k_A+k_B) / 10^4s^{-1}
0.287	115	5.6
0.518	182	4.7
0.707	219	5.0
0.898	262	5.0
1.62	412	5.2
2.46	563	5.6

Mechanism of the Oxygen Exchange and Rate Analyses. **(a)** In the pH range from 1.5 to 3.1, there exist undissociated arsenic acid (H_3AsO_4) and dihydrogenarsenate ion ($H_2AsO_4{}^-$). At pH 4.8, where $H_2AsO_4{}^-$ exists predominantly, line broadening due to oxygen exchange does not occur. Therefore, the observed oxygen exchange in this pH region can be ascribed to the participation of undissociated acid into the rate process. The fact that the order (m) (Eq. 11) is 1.3—1.2 suggests that oxygen exchange proceeds through both unimolecular (Eq. 4) and bimolecular (Eqs. 12 and 5) paths:

$$H_3AsO_4+H_3AsO_4 \xrightleftharpoons{k21} H_4As_2O_7+H_2O. \qquad (12)$$

Furthermore, the rate law in the more acidic region (**b**) ($[H^+]>0.2$ mol dm^{-3}) is given as $R=k[H^+]^{0.7}$ [As(V)]. Since in region (**b**) undissociated arsenic acid is the only species of As(V), the fact that the oxygen exchange rate continues to increase along with an increase in $[H^+]$ suggests that the catalytic effect of H^+ on the oxygen exchange of H_3AsO_4 is important. The first-order dependence of R on [As(V)] ($[H^+]$=1.6 mol dm^{-3}) is consistent with the H^+-catalyzed oxygen exchange of H_3AsO_4 with water (Eq. 13). The contribution of a H^+-catalyzed bimolecular reaction between two molecules of H_3AsO_4 to the total rate may be neglected.

$$H_3As^{17}OO_3+H_2O+H^+ \xrightleftharpoons{k11h} H_3AsO_4+H_2{}^{17}O+H^+. \qquad (13)$$

The path (Eq. 13) which prevails in region (**b**) may also be an important reaction in pH range (**a**). Then, the rate law for the oxygen exchange of arsenic acid with water may be expressed as follows:

$$R=k_{11}[H_3AsO_4]+k_{21}[H_3AsO_4]^2+k_{22}[H_3AsO_4][H_2AsO_4{}^-]$$
$$+k_{11h}[H^+][H_3AsO_4]. \qquad (14)$$

The exchange results were analyzed using the rate law

Table 2. Hydrogen-Ion Concentration Dependence of Line Widths and Rate Constants ($(\tau_A{}^{-1}+\tau_B{}^{-1})=(k_A+k_B)$): Exchange Narrowing of a Coalesced Oxygen Signal (90 °C, [As(V)]=0.3 mol dm^{-3})

$[H^+]$/mol dm^{-3} (H_2SO_4)	$\nu_{1/2}$ / Hz	(k_A+k_B) / 10^4 s^{-1}	$[H^+]$/mol dm^{-3} ($HClO_4$)	$\nu_{1/2}$ / Hz	(k_A+k_B) / 10^4 s^{-1}
0.39	83.8	5.35	0.51	69.0	7.02
0.72	66.4	7.43	1.00	51.6	11.1
1.00	57.2	9.34	1.50	43.8	15.0
1.40	50.4	11.5	1.99	40.2	17.8
1.80	45.8	13.7	2.47	38.4	19.7
2.20	42.8	15.7	3.01	37.5	20.9

(Eq. 14). The concentrations of H_3AsO_4 and $H_2AsO_4^-$ in Eq. 14 were estimated by using the pK_1 value (30 °C) and the pH values of the solutions for the ^{17}O NMR spectra measured at 30 °C. Both values at temperatures other than 30 °C were not measured. It was therefore assumed that the value of $f=[H_2AsO_4^-]/[H_3AsO_4]$ estimated at 30 °C remains constant at elevated temperatures. This assumption may be rationalized by expressing f as: $f=([H_2AsO_4^-]_f+a_{H^+})/([H_3AsO_4]_f-a_{H^+})=K_1/a_{H^+}$ (cf. Experimental section). For a given solution having a definite $[H_2AsO_4^-]_f$ and $[H_3AsO_4]_f$, any change in the pH (a_{H^+}) with increasing temperature is too small to affect $[H_2AsO_4^-]$ and $[H_3AsO_4]$ estimated at 30 °C ($[\mathrm{As(V)}]=0.95$ mol dm^{-3}, $\Delta H°$ for $pK_1=-5$ kJ mol^{-1} [9]).

In the pH region above 2.3, the contribution of the k_{11h}-term to the total rate may be neglected. Rate law (Eq. 14) can be rewritten as

$$\frac{R}{[H_3AsO_4]}=k_{11}+\{k_{21}+\frac{K_1}{a_{H^+}}k_{22}\}[H_3AsO_4]. \qquad (15)$$

By using the same data as shown in Fig. 3, the values on the left-hand side of Eq. 15 are plotted against $[H_3AsO_4]$ in Fig. 4. From the intercept of the straight line the k_{11} values were obtained, and are listed in Table 4. The rate law is again rewritten as

$$R-k_{11}[H_3AsO_4]=k_{21}[H_3AsO_4]^2+k_{22}[H_3AsO_4][H_2AsO_4^-]. \qquad (16)$$

For each run at pH>2.3, the left-hand side of Eq. 16 was calculated using the above value of k_{11}. The concentration products on the right-hand side were also calculated. By a least-squares treatment of a set of numerical equations, thus obtained, the values of k_{21} and k_{22} at 90 °C are $(1.9\pm0.2)\times10^3$ and $(8.1\pm0.6)\times10^2$, respectively. The k_{21} and k_{22} values at other temperatures and the activation parameters are listed in Table 4. k_{22} has a value of 1.3 mol^{-1} dm^3 s^{-1} at 0 °C (extrapolated by using $E_a=60$ kJ mol^{-1}). This value, obtained by the ^{17}O NMR method, is in agreement with the 2 mol^{-1} dm^3 s^{-1} obtained above by the ^{18}O tracer method.

At pH<2, the contribution of the k_{11h}-term becomes important, and the rate law is given in terms of Eq. 14.

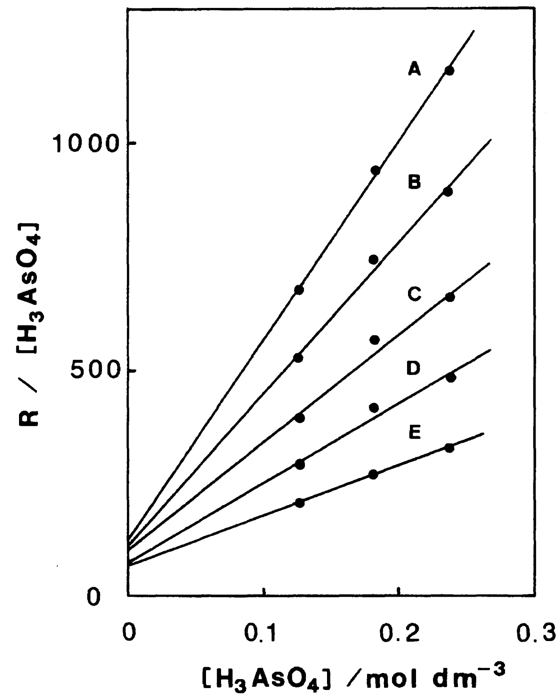


Fig. 4. Plots of $R/[H_3AsO_4]$ against $[H_3AsO_4]$ (pH=2.37). A: 90 °C, B: 80 °C, C: 70 °C, D: 60 °C, E: 50 °C.

The equation can be rewritten as

$$\{R-R_{11}-R_{21}-R_{22}\}/[H_3AsO_4]=k_{11h}[H^+]. \qquad (17)$$

The values on left side of Eq. 17 were calculated using the observed R at pH<2 and the rate constants (k_{11}, k_{21}, and k_{22}). These values were plotted against $[H^+]$ (not shown). The value of k_{11h} obtained from the slope of the straight line is $(2.77\pm0.04)\times10^4$ mol^{-1} dm^3 s^{-1} at 90 °C (Table 4).

(b) In the range $[H^+]=0.5$—2.2 mol dm^{-3} the observed rate law is given as $R=k[H^+]^{0.7}[\mathrm{As(V)}]$. Since the dominating species of As(V) in this $[H^+]$ range is H_3AsO_4, the oxygen exchange was expected to proceed via Eq. 13 and Eqs. 4 and 12. The latter two are important reactions in pH range (**a**). The k_A values were estimated in terms of the rate law, $k_A=k_{11h}[H^+]+k_{11}+k_{21}[H_3AsO_4]$, using the rate constants shown in Table 4.

Table 4. Rate Constants and Activation Parameters of the Oxygen Exchange of Arsenic Acid by ^{17}O NMR Work $R=k_{11h}[H^+][H_3AsO_4]+k_{11}[H_3AsO_4]+k_{21}[H_3AsO_4]^2+k_{22}[H_3AsO_4][H_2AsO_4^-]$

Temp	k_{11h}	k_{11}	k_{21}	k_{22}
° C	10^4M^{-1} s^{-1}	10^2s^{-1}	10^3M^{-1} s^{-1}	10^2M^{-1} s^{-1}
60	$2.1_3\pm0.0_5$	$0.7_3\pm0.2_2$	$1.2_2\pm0.2_5$	$1.4_4\pm0.6_6$
70	$2.2_1\pm0.0_3$	$1.0_4\pm0.3_5$	$1.4_8\pm0.1_4$	$2.7_1\pm0.3_7$
80	$2.3_4\pm0.0_3$	$1.1_2\pm0.2_8$	$1.7_5\pm0.1_4$	$5.1_1\pm0.3_6$
90	$2.7_7\pm0.0_4$	$1.2_7\pm0.1_7$	$1.8_8\pm0.2_3$	$8.0_8\pm0.6_0$
E_a/kJ mol^{-1}	$8._6\pm2._4$	$15._6\pm3._2$	$15._3\pm1._7$	$59._7\pm1._8$
$\Delta S^{\neq}$/J mol^{-1} K^{-1}	-146 ± 1	-170 ± 1	-149 ± 1	-32 ± 1

The obtained values of k_A are 1.1×10^4 s^{-1} ($[H^+]=0.39$ mol dm^{-3}) and 6×10^4 s^{-1} ($[H^+]=2.2$ mol dm^{-3}). These k_A values were corrected to (k_A+k_B) using the relation $k_A/k_B=P_B/P_A=55/1.2$. P_A and P_B are the populations at sites A and B. Contrary to the expectation, the observed (k_A+k_B) values (Table 2) were found to be much larger than the calculated (k_A+k_B) values. Regarding this observation the referee gave us the following plausible suggestion. There are two things that may be relevant. In the higher $[H^+]$ range, the coordination number of arsenic(V) may change according to

$$AsO(OH)_3+H_3O^+\rightleftharpoons As(OH_2)(OH)_4{}^+.$$

This would alter the value of P_A (but not P_B), so that the ratio of P_B/P_A would decrease. The five-coordination arsenic might exchange more rapidly than a four-coordination arsenic.

Another possible source of deviations in a strong acid is the non-linear ability of these solutions to protonate substrates, as indicated by Hammett and Deyrup H_0. At 3 mol dm^{-3} $HClO_4$, a positive deviation in the rate by a factor of three is likely.

By using both ^{18}O tracer and ^{17}O NMR methods, the oxygen exchange rates (R) of As(V) over a wide pH range (0—12) could be obtained. The values of R (mol dm^{-3} s^{-1}) normalized to [As(V)]=0.07 mol dm^{-3} and 30 °C are as follows: 2.8×10^3 (0); 6.6 (2.0); 0.36 (3.1); 4.2×10^{-3} (5.0); 2.7×10^{-5} (7.1); 9.3×10^{-7} (9.1); 2.1×10^{-7} (12.1) (pH values are shown in parentheses.). Over the whole pH range studied, the variation of R amounts to 10^{10} and the comprehensive rate law is expressed as

$$\begin{aligned}R={}&k_{11h}[H^+][H_3AsO_4]+k_{11}[H_3AsO_4]+k_{12}[H_2AsO_4{}^-]\\&+k_{13}[HAsO_4{}^{2-}]+k_{14}[AsO_4{}^{3-}]+k_{21}[H_3AsO_4]^2\\&+k_{22}[H_3AsO_4][H_2AsO_4{}^-]+k_{23}[H_2AsO_4{}^-]^2\\&+k_{24}[H_2AsO_4{}^-][HAsO_4{}^{2-}]+k_{25}[HAsO_4{}^{2-}]^2.\end{aligned}\tag{18}$$

The rate constants for the elementary processes in the Eq. 18 are summarized in Table 5 (30 °C). The kinetic results for methyl arsonic acid (MAA)[6,7] are also given in the same table. We shall discuss the data in Tables 4 and 5.

Comparison of the Oxygen Exchange of As(V) with That of P(V). Bunton et al[1] have studied the oxygen exchange of phosphoric acid with water at 100 °C. They expressed the exchange rate at pH 0—9 ([P(V)]=0.4—0.8 mol dm^{-3}) in terms of the following equation:

$$R=k_A[H^+][H_3PO_4]\exp(\beta I)+k_N[H_3PO_4]+k_M[H_2PO_4{}^-].\tag{19}$$

The rate constants in Eq. 19 are $k_A=5.45\times10^{-7}$ mol^{-1} dm^3 s^{-1}, $k_N=1.28\times10^{-6}$s^{-1}, and $k_M=4.03\times10^{-6}$s^{-1}.[1] In order to obtain the activation parameters, we investigated the oxygen exchange of phosphoric acid under the following conditions: [P(V)]=0.1 mol dm^{-3}, 90 and 100 °C, pH=4.5. Here, P(V) exists predominantly as $H_2PO_4{}^-$. The McKay plots (Eq. 2) are given in Fig. 5. The k_M values at 90 and 100 °C were calculated to be $(2.62\pm0.04)\times10^{-7}$ s^{-1}, and $(1.05\pm0.01)\times10^{-6}$ s^{-1}, respectively. From these two k_M values, the energy and entropy of activation for the oxygen exchange of the $H_2PO_4{}^-$ ion were estimated to be 156 kJ mol^{-1} and +48 J mol^{-1} K^{-1}, respectively.

The kinetics of the oxygen-exchange reaction of arsenic acid (As(V)) is quite different from that of phosphoric acid (P(V)) in the following respects:

1) The rate constants for the oxygen exchange between monoanion and water at 30 °C are $k_{12}=1\times10^{-4}$ s^{-1} for $H_2AsO_4{}^-$ and $k_M=4\times10^{-11}$ s^{-1} (extrapolated

Table 5. Rate Constants and Activation Parameters for the Oxygen Exchange Reactions of Arsenic Acid (a) and Methylarsonic Acid (b) (30 °C) (a): $R=k_{11h}[H^+][H_3AsO_4]+k_{11}[H_3AsO_4]+k_{12}[H_2AsO_4{}^-]+k_{13}[HAsO_4{}^{-2}]+k_{14}[AsO_4{}^{3-}]+k_{21}[H_3AsO_4]^2+k_{22}[H_3AsO_4][H_2AsO_4{}^-]+k_{23}[H_2AsO_4{}^-]^2+k_{24}[H_2AsO_4{}^-][HAsO_4{}^{2-}]+k_{25}[HAsO_4{}^{2-}]^2$ (b): $R=k_{11h}[H^+][R'AsO_3H_2]+k_{11}[R'AsO_3H_2]+k_{12}[R'AsO_3H^-]+k_{13}[R'AsO_3{}^{2-}]+k_{21h}[H^+][R'AsO_3H_2]^2+k_{21}[R'AsO_3H_2]^2+k_{22}[R'AsO_3H_2][R'AsO_3H^-]+k_{23}[R'AsO_3H^-]^2$ (R'=CH_3–)

Rate const[c]	(a) k_i	E_a	$\Delta S^{\neq}$	(b) k_i[b]	E_a	$\Delta S^{\neq}$
		kJ mol^{-1}	J mol^{-1} K^{-1}		kJ mol^{-1}	J mol^{-1} K^{-1}
k_{11h}/M^{-1} s^{-1}	1.6×10^4	9	−146	6.0×10^2	33	−92
k_{11}/s^{-1}	5.6×10	16	−170	2.8	45	−97
k_{12}/s^{-1}	$1\ \times10^{-4}$ [a]			6.6×10^{-4}		
k_{13}/s^{-1}	1.2×10^{-5} [a]	103	−10	2.7×10^{-4}	85	−42
k_{14}/s^{-1}	1.5×10^{-6} [a]	107	−8			
k_{21h}/M^{-2} s^{-1}				6.8×10^2	18	−125
k_{21}/M^{-1} s^{-1}	7.5×10^2	15	−149	1.8×10	31	−120
k_{22}/M^{-1} s^{-1}	2.1×10	60	−32	2.5×10	33	−124
k_{23}/M^{-1} s^{-1}	7.4×10^{-2} [a]	55	−93	5.7×10^{-5}		
k_{24}/M^{-1} s^{-1}	6.4×10^{-3} [a]	79	−35			
k_{25}/M^{-1} s^{-1}	8.5×10^{-6} [a]					

a) Ref. 4. b) Refs. 6 and 7. c) M=mol dm^{-3}.

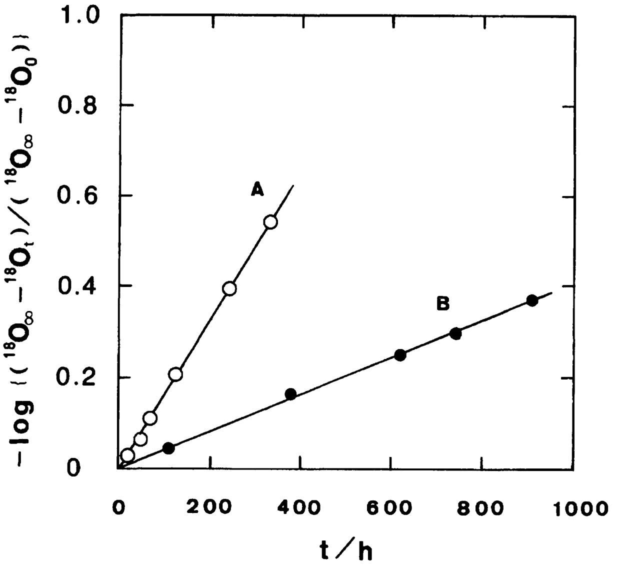


Fig. 5. Plots of $-\log((^{18}O_\infty - ^{18}O_t)/(^{18}O_\infty - ^{18}O_0))$ against time (h) (McKay plots). ([P(V)] = 0.1 mol dm^{-3}, pH=4.5). A(○): 100 °C, B(●): 90 °C.

from 100 °C) for $H_2PO_4^-$. k_{12} is larger by a factor of 10^6 than k_M.

2) The small value of E_a (28 kJ mol^{-1}) for k_{12} is in contrast to that for a k_M of 156 kJ mol^{-1}. This contrast may be responsible for the large difference between k_{12} and k_M, although the E_a values for both constants are not sufficiently accurate to allow a more precise discussion.

It is worth noting that the value of $\Delta S^{\neq}$ for k_M has a positive value (+48 J K^{-1} mol^{-1}). For the oxygen exchange of the dihydrogenphosphate ion ($H_2PO_4^-$), Bunton et al.[1] presented a first-order path via a reversible formation of the metaphosphate ion, (PO_3^-) as:

$$H_2PO_4^- \rightleftharpoons PO_3^- + H_2O \qquad (20)$$

Furthermore, they suggested a hydrogen-bonded cyclic intermediate between a dihydrogenphosphate ion and a water molecule for this reaction (Eq. 20). The positive value of $\Delta S^{\neq}$ for the oxygen exchange of $H_2PO_4^-$ (k_M) obtained here is consistent with their dissociative S_N1 mechanism.

3) The order of the reactivity of undissociated acid and monoanion towards water (100 °C) is as follows:

$$\text{As(V)};\ H_3AsO_4\ (k_{11} = 1.5 \times 10^2\ \text{s}^{-1}) \gg H_2AsO_4^-\ (k_{12} = 8 \times 10^{-4}\ \text{s}^{-1}),$$
$$\text{P(V)};\ H_3PO_4\ (k_N = 1.3 \times 10^{-6}\ \text{s}^{-1}) \lesssim H_2PO_4^-\ (k_M = 4.0 \times 10^{-6}\ \text{s}^{-1}).$$

For As(V), H_3AsO_4 is much more reactive than $H_2AsO_4^-$. On the other hand, for P(V) the reactivity of undissociated acid and monoanion is almost equal, and $H_2PO_4^-$ is rather more reactive than H_3PO_4.

4) In the concentration range below 1 mol dm^{-3} and at pH<4, for both P(V) and As(V), undissociated acid and monoanion exist predominantly. There, bimolecular reactions between the species of As(V) make an important contribution to the exchange of the arsenic oxygens. On the other hand, the exchange of phosphoric oxygens proceeds exclusively via monomolecular paths. Keisch et al.[2] have shown that in the [P(V)] range above 10 mol dm^{-3}, the exchange path of phosphoric acid via the reversible formation of $H_4P_2O_7$ becomes important.

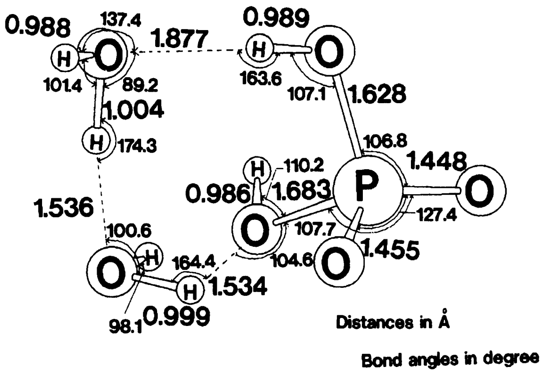
Comparison of the Oxygen Exchange Rates between Arsenic Acid (As(V)) and Methylarsonic Acid (MAA). Surprisingly, the reactivity of As(V) is different from that of MAA,[5—7] depending on the ionic species of these two compounds. As to an undissociated acid, H_3AsO_4 exchanges its oxygens with water 20-times faster than does $CH_3AsO_3H_2$. The proton-assisted exchange of H_3AsO_4 is also 26-times faster than that of $CH_3AsO_3H_2$. On the other hand, the order of reactivity between As(V) and MAA for a negatively charged ion has a trend opposite to that for undissociated acid; $CH_3AsO_3H^-$ and $CH_3AsO_3^{2-}$ react 6- and 20-times faster than do $H_2AsO_4^-$ and $HAsO_4^{2-}$, respectively. For monoanion, the substituent effects have been investigated with the aid of an ab initio molecular-orbital calculation. The rate constants (k_{12}'s) correlate well with energy levels of the lowest unoccupied molecular orbitales (LUMO's) of univalent anions of arsenic and alkylarsonic acids.[5] The higher reactivity of H_3AsO_4 towards H_2O compared to $CH_3AsO_3H_2$ may be interpreted in terms of the activation energy; E_a for $k_{11}(H_3AsO_4)$ of 16 kJ mol^{-1} is significantly smaller than that for $k_{11}(CH_3AsO_3H_2)$ of 45 kJ mol^{-1}. The activation entropy for a $k_{11}(H_3AsO_4)$ of −170 J K^{-1} mol^{-1} is found to be more negative than that for a $k_{11}(CH_3AsO_3H_2)$ of −97 J K^{-1} mol^{-1}.

It is noticeable that large negative values of $\Delta S^{\neq}$ for the k_{11} of both compounds have been found. These values fall into the range from −90 to −140 J K^{-1} mol^{-1} found for a nucleophilic displacement reaction, which is known to be termolecular.[10] This fact suggests that the transition state may have a cyclic structure involving an additional water molecule, in which a proton transfer may be facilitated.[11] The smaller E_a value and the larger negative $\Delta S^{\neq}$ value of the oxygen exchange of H_3AsO_4, compared to those of $CH_3AsO_3H_2$, indicate that one more OH bond involved in H_3AsO_4 would make a special contribution to the stabilization of a cyclic transition state by hydrogen-bonding.

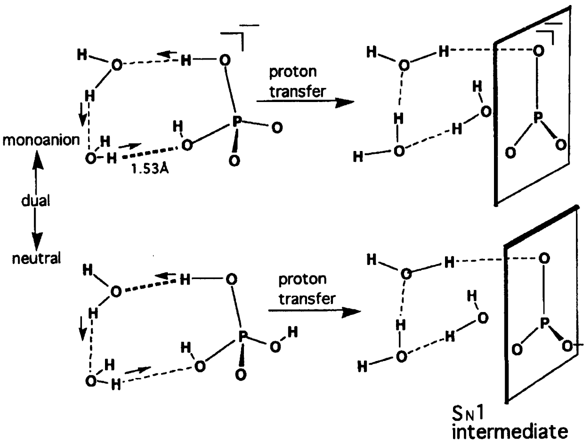
The reversible condensation reactions between two molecules of As(V) or MAA are discussed (cf. Eqs. 5 and 12). $k_{21}(H_3AsO_4)$ is 42-times larger than $k_{21}(CH_3AsO_3H_2)$, and $k_{23}(H_2AsO_4^-)$ is also 10^3-times larger than $k_{23}(CH_3AsO_3H^-)$. The higher reactivity of $H_2AsO_4^-$ than that of $CH_3AsO_3H^-$ in a bimolecular reaction is in contrast with the observation that towards water $H_2AsO_4^-$ is less reactive than $CH_3AsO_3H^-$. For a reaction between two ions, the steric inhibition of a methyl group substituted on As is considered to become important. It is noted that the proton-catalyzed condensation reaction between two undissociated methylarsonic acids has been observed, while the corresponding reaction between two H_3AsO_4 molecules could not be found. The latter may be swamped by a fast oxygen exchange between H_3AsO_4 and water catalyzed by a proton.

A characteristic common to both acids (As(V) and MAA) is that the reactivity of an undissociated acid towards water is significantly larger than that of a monoanion. $k_{11}(H_3AsO_4)$ and $k_{11}(CH_3AsO_3H_2)$ are 5.6×10^5- and 4.2×10^3-times larger than $k_{12}(H_2AsO_4{}^-)$ and $k_{12}(CH_3AsO_3H^-)$, respectively. The small value of the activation energy may be responsible for the reactivity of undissociated acids. The reactivity ratio of monoanion to dianions, on the other hand, is less than ten.

Solvent Effect on the Oxygen Exchange of Arsenate Ions. 1) The pH dependence of the oxygen-exchange rate of arsenate ions in an aqueous methanol solution (25 weight %) was examined in the pH region between 6 and 12 ($[As(V)]=0.07$ mol dm^{-3}, $I=0.55$ mol dm^{-3}, 14.5 °C). The pH-rate profile is shown in Fig. 1 (curve b). Its shape is quite similar to that for a run in an aqueous solution (curve B). The rate was analyzed according to the rate law (Eq. 1) to obtain the rate constants involved in Eq. 1. These values were obtained as: $k_{12}=0.29(0.6)\times10^{-4}$ s^{-1}; $k_{13}=1(0.81)\times10^{-6}$ s^{-1}; $k_{14}=0.1(0.33)\times10^{-6}$ s^{-1}; $k_{23}=2.5(2.3)\times10^{-2}$ mol^{-1} dm^3 s^{-1}; $k_{24}=0.9(1.2)\times10^{-3}$mol^{-1} dm^3 s^{-1}; $k_{25}=0.7(1.5)\times10^{-5}$ mol^{-1} dm^3 s^{-1}. The values in parentheses are those in an aqueous solution. The rate constants in an aqueous methanol solution ($\epsilon_r=69$) are quite similar to, or two- or three-times smaller than, those in an aqueous solution ($\epsilon_r=82$). For a reaction between like-charged ions, the rate constants are expected to decrease along with a decrease in the dielectric constant of the solution.[12] The trend observed for k_{24} and k_{25} agrees with this expectation.



Scheme 1.



Scheme 2.

2) The solvent effect on the oxygen-exchange rate of arsenate ions was studied in some aqueous organic solvents (Table 6). The reaction was carried out under the following condition: 15 °C, $I=0.19$ mol dm^{-3}, pH=7.32 (in H_2O). The apparent pK_2 values in Table 6 were obtained with the ordinary method used for an aqueous

Table 6. Solvent Effect on the Oxygen Exchange Rate of Arsenate Ions with Water ($[As(V)]=0.07$ mol dm^{-3}, Mole Fraction of Solvent=0.144, 15 °C) a): Comparison between Miscellaneous Solvents. $I=0.19$ mol dm^{-3} b): Effect of Ionic Strength. $I=0.19$, 0.55 mol dm^{-3}

a)

	H_2O	CH_3OH	C_2H_5OH	$(CH_3)_2CO$	$t-C_4H_9OH$	Dioxane
pK_2	6.68	7.12	7.35	7.54	7.19	7.72
pH	7.32	7.76	7.99	8.18	7.83	8.36
$k_{ex}/10^{-5}$s^{-1}	8.6±0.1	7.7±0.1	6.8±0.1	11.3±0.3	14.7±0.2	14.9±0.2
ϵ_r	82	69	64	61	53	41

b)

	H_2O	C_2H_5OH	H_2O	C_2H_5OH
	$I=0.19$ mol dm^{-3}		$I=0.55$ mol dm^{-3}	
pK_2	6.68	7.35	6.47	6.86
pH	6.64	7.29	6.56	6.85
$k_{ex}/10^{-5}$s^{-1}	48.3±0.5	32.5±0.3	45.2±0.4	60±1

solution without paying any special attention to the pH measurement in aqueous organic solvents. These pK_2 values are quite different from each other. Therefore, the pH values for the kinetic measurement in solvents other than H_2O were chosen so that the value of $(pH-pK_2)=\log([H_2AsO_4^-]/[HAsO_4^{2-}])$ become equal. At pH=7.32 the contribution of bimolecular paths (k_{23}, k_{24}, k_{25}) to the total rate can be estimated to be 50% for an aqueous solution. For aqueous methanol and ethanol solutions, the rate constant of the ^{18}O exchange reaction k_{ex} (Eq. 2) decreases in the order of the decrease in a macroscopic dielectric constants, while for aqueous solutions of acetone, *t*-butyl alcohol, and dioxane, the k_{ex} value increases in that order.

Concluding Remarks

In this work, the following results were obtained:

1. The oxygen-exchange rates of arsenic acid with water could be successfully measured over a wide pH range (0—12) using both ^{18}O tracer and ^{17}O NMR methods. The rate law is expressed in terms of Eq. 18. The rate constant for each elementary process in the equation was obtained. The activation parameters of each elementary process were evaluated.

2. The kinetics of the oxygen-exchange reaction of arsenic acid (As(V)) is quite different from that of phosphoric acid (P(V)) in the following respects:

1) For an oxygen exchange between monoanion and water, the kinetic parameters at 30 °C are as follows:

$$k_{12}(H_2AsO_4^-);\quad 1\times10^{-4}\ s^{-1},\ E_a;\ 28\ kJ\,mol^{-1}$$
$$k_{12}(H_2PO_4^-)=k_M;\quad 4\times10^{-11}\ s^{-1},\ E_a;\ 156\ kJ\,mol^{-1}.$$

$k_{12}(H_2AsO_4^-)$ is 10^6-times larger than k_M. The small E_a value for $k_{12}(H_2AsO_4^-)$ is in contrast to the large E_a value for k_M. The value of $\Delta S^{\neq}$ for k_M was estimated to be +48 $J\,K^{-1}\,mol^{-1}$. The positive value of $\Delta S^{\neq}$ is consistent with the dissociative S_N1 mechanism proposed by Bunton et al.[1)]

2) The order of the reactivity of undissociated acid and monoanion towards water (100 °C) is as follows:

$$As(V);\ H_3AsO_4\ (k_{11}=1.5\times10^2\ s^{-1})\gg H_2AsO_4^-\ (k_{12}=8\times10^{-4}\ s^{-1}),$$

$$P(V);\ H_3PO_4\ (k_N=1.3\times10^{-6}\ s^{-1})\lesssim H_2PO_4^-\ (k_M=4.0\times10^{-6}\ s^{-1}).$$

For As(V) H_3AsO_4 is much more reactive than $H_2AsO_4^-$. On the other hand, for P(V) the reactivity of undissociated acid and monoanion is almost equal and $H_2PO_4^-$ is rather more reactive than H_3PO_4.

As for As(V), the result of $k_{11}\gg k_{12}$ is considered to reflect the S_N2 reaction. A neutral substrate with a more positive nucleophilic center is naturally much more reactive than its conjugated anion. That is, a neutral substrate has a much lower orbital energy of LUMO than the anion. In fact, the good correlation between the LUMO energies and the rate constants for the oxygen exchange of monoanions with water[5)] has proven the S_N2 nature. Also, the large negative $\Delta S^{\neq}$ value of $-170\ J\,mol^{-1}\,K^{-1}$ for k_{11} (Table 4) has indicated a compact form of the S_N2 transition state with a cyclic hydrogen-bond network. On the other hand, for P(V) the S_N1 reaction has been confirmed on the basis of the small positive $\Delta S^{\neq}$ value ($+48\ J\,mol^{-1}\,K^{-1}$). Bunton et al. suggested a PO_3^- intermediate for the S_N1 path via the following self cleavage:[1)]

$$H_2PO_4^- \rightleftharpoons PO_3^- + H_2O.$$

In their scheme, one water (or methanol[13)]) molecule is involved to facilitate proton transfer for yielding PO_3^-. However, our preliminary computational result has shown that two water molecules are needed to cause the transfer (Scheme 1).[14)]

For the monoanion substrate ($H_2PO_4^-$), the water dimer works primarily as a proton donor (vide supra). For the neutral substrate (H_3PO_4), the dimer would do as a proton acceptor. Since this dehydration is a rate-determining step in the S_N1 reaction, this dual role of the water dimer may be related to the almost equal rate constants, $k_N\lesssim k_M$ (Scheme 2).

The remarkable contrast between the S_N2 of As(V) and the S_N1 of P(V) is a significant mechanistic finding; theoretical work concerning this contrast is in progress.[14)]

3. The oxygen exchange rate constant for each elementary process is compared between the arsenic and

Table 7. ^{17}O NMR Line Widths of Arsenic Oxygen in the Absence of the Oxygen Exchange with Water

pH	[As(V)] / mol dm^{-3}	$\nu^0_{1/2,A}$ / Hz										
		Temp/°C										
		3	10	15	20	30	40	50	60	70	80	90
9	0.3					310	250	202	168	140	121	105
4.8	0.3					290	232	176	159	133	115	101
	1.0					373	294	239	198	167	145	127
4.5	1.0	824		576		387	305	250	209	177	152	134
4.0	1.0	817		582		383	305	249	208	176	151	135
2.5	1.0	808	664	581	519							

methylarsonic acid (MAA). As for an undissociated acid, the reactivity of H_3AsO_4 towards water is larger than that of $CH_3AsO_3H_2$. On the other hand, for a negatively charged species, an opposite trend in the reactivity was observed between As(V) and MAA.

Appendix

Evaluation of the Oxygen-Exchange Rate. (a) Line Broadening (Slow Exchange Limit): In the slow exchange limit, where the mean lifetime of an oxygen nucleus at site A (τ_A) is small compared to the chemical shift of ^{17}O at site A (referred to H_2O), two signals were observed separately, and τ_A is given by

$$\tau_A{}^{-1} = k_A = T_{2A}{}^{-1} - T_{2A,0}{}^{-1}. \tag{8}$$

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

$$\tau_A{}^{-1} = k_A = \pi(\nu_{1/2,A} - \nu^0_{1/2,A}), \tag{9}$$

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

To evaluate the oxygen-exchange rates from the observed line widths, it is required to estimate an appropriate value of $\nu^0_{1/2,A}$ under the condition in which $\nu_{1/2,A}$ is measured. A detailed method for estimating these $\nu^0_{1/2,A}$ values has already been described.[7] Table 7 gives some measured values of the line widths of oxygens at site A in the absence of an oxygen exchange.

(b) Line Narrowing (Fast Exchange Limit): As the exchange rate is increased, two signals are broadened and tend to merge. At the coalescence point, the curve loses its two maxima to give only one peak. Over the point, the spectrum then becomes narrowed and, in the fast exchange limit, an averaged signal is observed at a frequency which is the weighted mean over the frequencies of the individual resonance. In the condition under which line narrowing is observed, the oxygen-exchange rate is given by

$$\pi \cdot \nu_{1/2} = \frac{P_A}{T_{2A,0}} + \frac{P_B}{T_{2B,0}} + \frac{P_A P_B (\delta\omega)^2}{(1/\tau_A + 1/\tau_B)}, \tag{10}$$

where P_A and P_B are the populations at sites A and B. $T_{2A,0}$ and $T_{2B,0}$ are the transverse relaxation times of an oxygen nucleus at sites A and B in the absence of an exchange (sites A and B are arsenic acid and solvent water, respectively). $\delta\omega$ is the difference in the chemical shifts (without any exchange) between sites A and B (rad s^{-1}).

The mean lifetime of the oxygen nucleus of species A between exchanges (τ_A) is related to the conventional rate constant (k) of the arsenic oxygen exchange with water by

$$\tau_A{}^{-1} = k_A = (1/[A])d[A]/dt = k[A]^{m-1}, \tag{11}$$

where m is the order of the reaction with respect to the concentration of A (=[As(V)]).

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