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The Kinetic Study of the Oxygen-Exchange Reaction of Some Alkylarsonates and Dialkylarsinates with Water

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The rates (R_S) of the oxygen exchange reaction of alkylarsonates (methyl-, butyl-, hexyl-, and benzyl-) and dialkylarsinates (dimethyl- and dibutyl-) with solvent water were measured in the pH range greater than 6, and at temperatures between 30 and 0 °C. For arsonates, the rate (R) is expressed by the following rate law: $R=k_1[A^{2-}]+k_2[HA^-]+k_3[H_2A]+k_4[HA^-]^2+k_5[HA^-][H_2A]+k_6[H_2A]^2$, where A^{2-}, HA^-, and H_2A designate $R'AsO_3{}^{2-}$, $R'AsO_3H^-$, and $R'AsO_3H_2$ (R′=alkyl), respectively. For arsinates, $R=k_1[R'_2AsO_2{}^-]+k_2[R'AsO_2H]$ (pH>9). The exchange rates of arsonates at 0 and 30 °C were analyzed in terms of the rate law to obtain the values of the rate constants (k_1—k_6). The activation parameters were obtained for the k_1 paths of both arsonates and arsinates, which are the reaction between $R'AsO_3{}^{2-}$ or $R'_2AsO_2{}^-$ and water. It is noticeable that the values of the activation entropies of the arsonates were found to be negative, while those of the arsinate were found to be positive. It was suggested that the oxygen exchange of arsonate ions proceeds via an S_N2 mechanism, while that of arsinates preceeds via S_N1.

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 was studied in order to determine the substituent effects of the alkyl groups on the rate of oxygen exchange. In a previous paper,[2] the first-order exchange rate constants of monovalent methyl- and butylarsonate anions were reported, and the relation between the electronic properties and reactivities of arsenate and alkylarsonate ions were examined through a molecular orbital calculation. It has been concluded that the steric effect does not affect the rates predominantly. In this paper, we present more extensive kinetic results concerning the alkylarsonates, $R'AsO_3Na_2$ (R′=CH_3, n-C_4H_9, n-C_6H_{13}, or $C_6H_5CH_2$), and the dialkylarsinates, R'_2AsO_2Na (R′=CH_3 or n-C_4H_9).

Experimental

Materials. Alkylarsonates were prepared according to the method of Quick.[3] Disodium methylarsonate was recrystallized five times or more from an aqueous ethanol solution (50 vol%), and then converted to methylarsonic acid by the addition of hydrochloric acid. Crude products of butyl-, hexyl-, and benzylarsonates were acidified to form the corresponding arsonic acids, which were purified by crystallization from water and ethanol. The results of the elemental analyses, melting points, and the ^{1}H NMR chemical shifts of alkylarsonic acids (R'-AsO_3H_2, R′=CH_3, n-C_4H_9, n-C_6H_{13}, and $C_6H_5CH_2$) are shown in Tables 1a and 1b.

Sodium dimethylarsinate (cacodylate) (guaranteed reagent, Wako) was used after being vacuum-dried. Dibutylarsinic acid was prepared according to the method of Quick[3] via butyldichloroarsine from butylarsonic acid. The preparation of butyldichloroarsine was as follows: A solution of 100 g of butylarsonic acid and a few crystals of potassium iodide (as a catalyst) in 200 ml of concentrated hydrochloric acid was saturated with sulfur dioxide for 3 h. An oily product of butyldichloroarsine was fractionated at reduced pressure (bp. 192—194 °C at 1 atm). To obtain sodium dibutylarsinate, 45 g of butyldichloroarsine, thus obtained, was mixed with 90 ml of a 10 mol dm^{-3} sodium hydroxide solution and 30 g of butylbromide, and reacted for 3 h at 80 °C. The crude product was carefully acidified to pH 7 in order to produce dibutylarsinic acid, which was purified by repeated

Table 1a. The Elemental Analyses and Melting Points of Alkylarsonic Acids ($R'AsO_3H_2$) and Dialkylarsinic Acids (R'_2AsO_2H)

Substrate	Elemental analyses/%				Melting point/°C	
	C		H			
	(Obsd)	(Calcd)	(Obsd)	(Calcd)	(Obsd)	(Refs.)
$R'AsO_3H_2$						
$CH_3AsO_3H_2$	8.66	8.58	3.62	3.60	161	159—160[a]
n-$C_4H_9AsO_3H_2$	26.53	26.40	6.12	6.10	161	159—160[a]
n-$C_6H_{13}AsO_3H_2$	33.63	34.50	7.18	7.20	162	—
$C_6H_5CH_2AsO_3H_2$	38.98	38.91	4.30	4.20	168—170	167—168[a]
$(R')_2AsO_2H$						
$(CH_3)_2AsO_2H$					194—196	—
$(n$-$C_4H_9)_2AsO_2H$	42.44	43.26	8.92	8.62	134	137—138[a]

a) Ref. 3.

Table 1b. ^{1}H NMR Chemical Shifts of Arsonic and Arsinic Acids (Referred to $C_6H_{15}NaO_3SSi$)

$$H_2O_3As\text{-}\overset{1}{C}H_2\text{-}\overset{2}{C}H_2\text{-}\overset{3}{C}H_2\text{-}\overset{4}{C}H_2\text{-}\overset{5}{C}H_2\text{-}\overset{6}{C}H_3$$

$$HO_2As(CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)_2$$

Substrates	Chemical shifts/ppm					
	1	2	3	4	5	6
$CH_3AsO_3H_2$	2.16					
n-$C_4H_9AsO_3H_2$	2.59	1.75	1.45	0.86		
n-$C_6H_{13}AsO_3H_2$	2.20	1.63	1.42	1.29	1.29	0.90
$C_6H_5CH_2AsO_3H_2$	3.54	7.38$^{b)}$				
$(CH_3)_2AsO_2H$	1.98					
$(n$-$C_4H_9)_2AsO_2H$	1.91	1.57	1.40	0.88		

a) Phenyl radical.

crystallization to reach a constant melting point. The melting point and elemental analyses of dibutylarsinic acid are shown in Table 1a, and ^{1}H-chemical shifts of dimethyl- and dibutylarsinic acids in Table 1b.

[^{18}O] water (2 atom%) was obtained from a fractionating column.

Rate Measurements. The oxygen-exchange rates of methyl- and benzylarsonates were measured by using the ^{18}O-tracer method. The reaction was started by diluting an isotopically equilibrated solution of $CH_3AsO_3Na_2$ or $C_6H_5CH_2AsO_3Na_2$ in [^{18}O] water with a large amount of isotopically normal water. A portion of the solution was drawn periodically, and the arsonates were recovered by a freeze-dry method for methylarsonate, and by the precipitation as barium salt for benzylarsonate. The oxygen in the precipitate was converted into carbon dioxide by the guanidinium chloride method.[4] An isotopic analysis of the carbon dioxide was carried out on a Hitachi-I-type mass spectrometer.

The oxygen-exchange rates of butyl- and hexylarsonates and dimethyl- and dibutylarsinates were followed by the ^{17}O NMR method. A known amount of compounds enriched in ^{17}O (obtained by the isotopic exchange with 10% [^{17}O] water) was dissolved into 3 ml of normal water containing an appropriate amount of sodium hydroxide, or hydrochloric acid, in an ice bath; the solution was transferred to a sample tube for running the NMR spectra. During the measurements, both the decrease in the intensity of the ^{17}O-signal of the arsonates, or the arsinates, and the increase in that of water were followed. The rates obtained from these two signals agreed satisfactorily. ^{17}O NMR spectra were recorded at 36.6 MHz on a FT-NMR spectrometer (JEOL-GX270). The ^{17}O-chemical shifts for various kinds of arsonic and arsinic acids, as well as for arsenic and arsenious acids, are shown in Table 2.

The rate of oxygen exchange (R) in mol per dm^3 in unit of time was calculated by means of the following two formulas:

$$R=\frac{[AsO][H_2O]}{n[AsO]+[H_2O]}\times k_{ex} \tag{1}$$

and

$$k_{ex}=-\frac{1}{t}\ln\frac{{}^*O_t-{}^*O_\infty}{{}^*O_0-{}^*O_\infty}.$$

Here $^*O_0$, $^*O_t$, and $^*O_\infty$ are ^{18}O (for methyl- and benzylarsonates) or ^{17}O (for butyl- and hexylarsonates, and dimethyl- and dibutylarsinates) contents at times 0, t, and infinity, respectively. [AsO] and [H_2O] are the molar concentrations (mol dm^{-3}) of the arsonates or arsinates, and water, respectively. The value of n is 3 for arsonates and 2 for arsinates. The oxygen-exchange reaction or arsonates was followed by two different methods, ^{18}O-tracer and ^{17}O NMR. The comparative results are as follows: 1) methylarsonate (30 °C, pH=10.7, [MA]=0.20 mol dm^{-3}); $k_{ex}(^{18}O)=(2.70\pm0.04)\times10^{-4}\ s^{-1}$ and $k_{ex}(^{17}O)=(2.67\pm0.01)\times10^{-4}\ s^{-1}$, and 2) benzylarsonate (30 °C, pH=10.22, [BzA]=0.56 mol dm^{-3}); $k_{ex}(^{18}O)=(5.36\pm0.30)\times10^{-5}\ s^{-1}$ and $k_{ex}(^{17}O)=(5.51\pm0.07)\times10^{-5}\ s^{-1}$. The values of k_{ex} obtained by the two methods agree satisfactorily.

The dissociation constants of arsonic acids and arsinic acids were determined by potentiometric titration at various temperatures and ionic strengths. The pH was measured using a radiometer PHM type-26 pH meter.

Results and Discussion

The Dissociation Constants of Arsonic Acids and Arsinic Acids. The dissociation constants (K_1 and K_2

Table 2. ^{17}O NMR Chemical Shifts of Alkylarsonic, Dialkylarsinic, Arsenic, and Arsenious Acids Reffered to H_2O Signal (0.3 mol dm^{-3}, 30 °C)

Substrates	Chemical shifts/ppm		
R′ (arsonic acids)	$R'AsO_3H_2$ (pH)	$R'AsO_3H^-$ (pH)	$R'AsO_3^{2-}$ (pH)
CH_3	95 (2)	111 (6)	130 (11)
n-C_4H_9	90 (2.5)	106 (6.5)	124 (11)
n-C_6H_{13}	—	—	120 (11)
$C_6H_5CH_2$	—	—	124 (11)
R′ (arsinic acids)	R'_2AsO_2H (pH)	$R'_2AsO_2^-$ (pH)	
CH_3	88 (4)	115 (8.5)	
n-C_4H_9	80 (4)	103 (10)	
Arsenic acid	H_3AsO_4 (pH) 88 (1.5)	$H_2AsO_4^-$ (pH) 97 (4)	$HAsO_4^{2-}$ (pH) 110 (9)
Arsenious acid	H_3AsO_3 (pH) 101 (7)	$H_2AsO_3^-$ (pH) 133 (11)	

for arsonates, and K'_1 for arsinates) are defined according to the following:

$$K_1=\frac{a_{\mathrm{H^+}}[\mathrm{R'AsO_3H^-}]}{[\mathrm{R'AsO_3H_2}]},\qquad K_2=\frac{a_{\mathrm{H^+}}[\mathrm{R'AsO_3^{2-}}]}{[\mathrm{R'AsO_3H^-}]},$$

and

$$K_1'=\frac{a_{\mathrm{H^+}}[\mathrm{R'_2AsO_2^-}]}{[\mathrm{R'_2AsO_2H}]}.$$

The observed values of $\mathrm{p}K_1$, $\mathrm{p}K_2$, and $\mathrm{p}K'_1$ are shown in Table 3a (0—40 °C, ionic strength I=0.55 mol dm^{-3}) and in Table 3b (I=0.01—1.0 mol dm^{-3}, 30 °C). Table 3a shows that $\mathrm{p}K_1$ and $\mathrm{p}K_2$ of methylarsonic acid are smaller than those of butylarsonic acid, while those of butyl- and hexylarsonic acids are comparable to each other, and that the $\mathrm{p}K'_1$ value of dimethylarsinic acid is smaller than that of dibutylarsinic acid. Lewis et al.6) have studied the effect of the alkylchain length on the thermodynamic parameters of ionization of arsonic and arsinic acids. The pK values (I=0, 30 °C) calculated from their ΔG° and ΔH° (thermally determined) values are as follows: For arsonic acids they are $\mathrm{p}K_1$=4.200 (CH_3), 4.376 (n-C_4H_9), 4.347 (n-C_6H_{13}); $\mathrm{p}K_2$=8.797 (CH_3), 9.334 (n-C_4H_9), 9.437 (n-C_6H_{13}). For dialkylarsinic acids, they are $\mathrm{p}K_1$=6.156 (CH_3), 6.546 (n-C_4H_9). The changes in pKs with increasing chain length for both arsonic and arsinic acids shown above are similar to those found in this work (Table 3a). They concluded that both the chain-lengthening effect and the substituent effect are inexplicable due to the complex nature of the solvent, as well as a poor understanding of the solvation processes. From the data given in Table 3, the values of ΔH of the 1st and 2nd ionization processes were obtained as -7.2 ± 3.0 kJ mol^{-1} and 21 ± 14 kJ mol^{-1} for benzylarsonic acid and as -7.0 ± 1.9 kJ mol^{-1} (-6.44 ± 0.16 kJ mol^{-1} 6)) and 7.3 ± 5.3 kJ mol^{-1} (7.9 ± 0.16 kJ mol^{-1} 6)) for hexylarsonic acid, respectively.

The concentrations of the various kinds of ionic species of the arsonates or arsinates for a given pH can be calculated by using the values of K_1 and K_2, or K'_1, and the following relations:

$$[\mathrm{arsonate}]=[\mathrm{R'AsO_3H_2}]+[\mathrm{R'AsO_3H^-}]+[\mathrm{R'AsO_3^{2-}}]$$

and

$$[\mathrm{arsinate}]=[\mathrm{R'_2AsO_2H}]+[\mathrm{R'_2AsO_2^-}].$$

Here, [arsonate] and [arsinate] are the total concentrations of arsonate and arsinate, respectively. The mole fractions of various ionic species of arsonates and arsinates at 30 °C and I=0.55 mol dm^{-3} are plotted

Table 3. The Acid Dissociation Constants of Alkylarsonic and Dialkylarsinic Acids
(a) The Dependence on the Temperature (I=0.55 mol dm^{-3})

Substrates	Temperature/°C			
	0	20	30	40
pK_1				
$CH_3AsO_3H_2$	$3.79\ \pm0.01$	—	$3.87_8\pm0.00_0$	—
n-$C_4H_9AsO_3H_2$	—	—	$4.13_1\pm0.00_3$	—
n-$C_6H_{13}AsO_3H_2$	—	$4.10_9\pm0.00_3$	$4.13_2\pm0.00_2$	$4.18_9\pm0.00_2$
$C_6H_5CH_2AsO_3H_2$	$3.67_1\pm0.03_4$	$3.72_1\pm0.02_0$	$3.81_9\pm0.01_1$	—
pK_1'				
$(CH_3)_2AsO_2H$	—	—	$6.06_7\pm0.00_2$	—
(n-$C_4H_9)_2AsO_2H$	—	—	$6.65_0\pm0.00_5$	—
PK_2				
$CH_3AsO_3H_2$	$8.64\ \pm0.03$	—	$8.49_8\pm0.00_0$	—
n-$C_4H_9AsO_3H_2$	—	—	$8.88_8\pm0.06_8$	—
n-$C_6H_{13}AsO_3H_2$	—	$8.85_4\pm0.00_3$	$8.86_3\pm0.00_4$	$8.77_0\pm0.00_4$
$C_6H_5CH_2AsO_3H_2$	$8.95_4\pm0.00_6$	$8.87_8\pm0.00_5$	$8.49_7\pm0.00_5$	—

(b) The Dependence on the Ionic Strength (30 °C)

	Ionic strength/mol dm^{-3}			
	0.010	0.025	0.55	1.0
pK_1				
n-$C_6H_{13}AsO_3H_2$	—	$4.39_6\pm0.00_3$	$4.13_2\pm0.00_2$	$4.07_1\pm0.00_4$
pK'				
$(CH_3)_2AsO_2H$	$6.23_7\pm0.00_3$	$6.11_0\pm0.00_2$	$6.06_7\pm0.00_2$	$6.03_9\pm0.00_3$
pK_2				
n-$C_6H_{13}AsO_3H_2$	—	$9.34_8\pm0.00_5$	$8.86_3\pm0.00_4$	$8.67_2\pm0.00_5$

Lit. values($CH_3AsO_3H_2$): $\mathrm{p}K_1=4.11_4\pm0.01$, $\mathrm{p}K_2=9.14\pm0.01$ (I=0, 25 °C);5) $\mathrm{p}K_1=4.11_2\pm0.02_9$, $\mathrm{p}K_2=8.61_9\pm0.03_7$, ($I$=0, 30 °C).6)

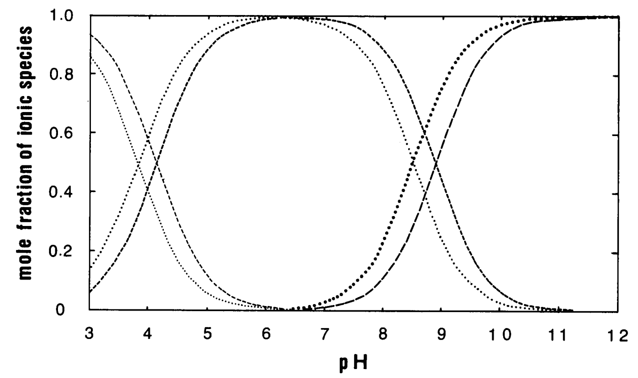

Fig. 1a. Mole fractions of various ionic species of alkylarsonates against pH. ($R'AsO_3H_2=H_2A$, $R'AsO_3H^-=HA^-$, $R'AsO_3^{2-}=A^{2-}$). Dotted lines; $R'=CH_3$ or $C_6H_5CH_2$: ······· H_2A, ······· HA^-, •••••• A^{2-}. Broken lines; $R'=n\text{-}C_4H_9$ or $n\text{-}C_6H_{13}$: —— H_2A, ----- HA^-, — — — A^{2-}.

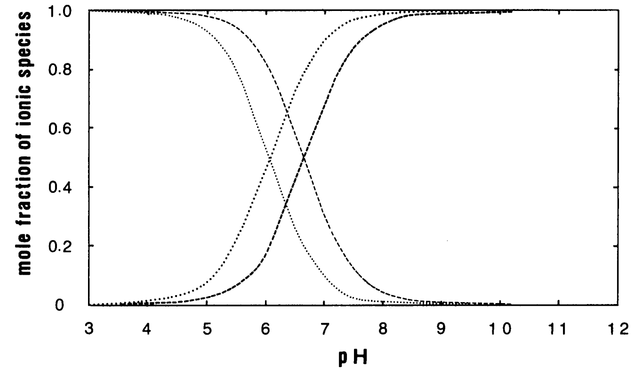

Fig. 1b. Mole fractions of various ionic species of dialkylarsinates against pH. ($R'_2AsO_2H=HA$, $R'_2AsO_2^-=A^-$). Dotted line; $R'=CH_3$: ······· HA, •••••• A^-. Broken line; $R'=n\text{-}C_4H_9$: —— HA, ------ A^-.

against pH in Figs. 1a and 1b, respectively.

pH Dependence of the Exchange Rate. Arsonates: The dependence of the exchange rate on the pH is shown in Fig. 2 for methylarsonate (MA) (0 and 30 °C, [MA]=0.1 mol dm^{-3}) and benzylarsonate (BzA) (30 °C, [BzA]=0.1 mol dm^{-3}), and in Fig. 3 for butylarsonate (BuA) and hexylarsonate (HxA) (30 °C, [BuA]=[HxA]=0.2 mol dm^{-3}). Throughout the experiments, the ionic strength was adjusted to 0.55 mol dm^{-3}. Because of the low solubility of the acidic species, $C_6H_{13}AsO_3H^-$ and $C_6H_{13}AsO_3H_2$, the experiments with hexylarsonate could not be extended to a pH region lower than 9. In Fig. 2, the pH-rate profile of the oxygen-exchange rate of arsenate ions with water at 30 °C[1] is also shown ([arsenate]=0.07 mol dm^{-3}) as a comparison.

From Fig. 2, it can be seen that the pH-rate curves for methyl- and benzylarsonates are similar to each other regarding their shape. In the pH region between 7.5 and 10, where the dominant ionic species are monovalent and divalent anions, the exchange rate slowly decreases with an increase in pH. At pH>10, the dissociation of monovalent anion is almost complete, and the rate

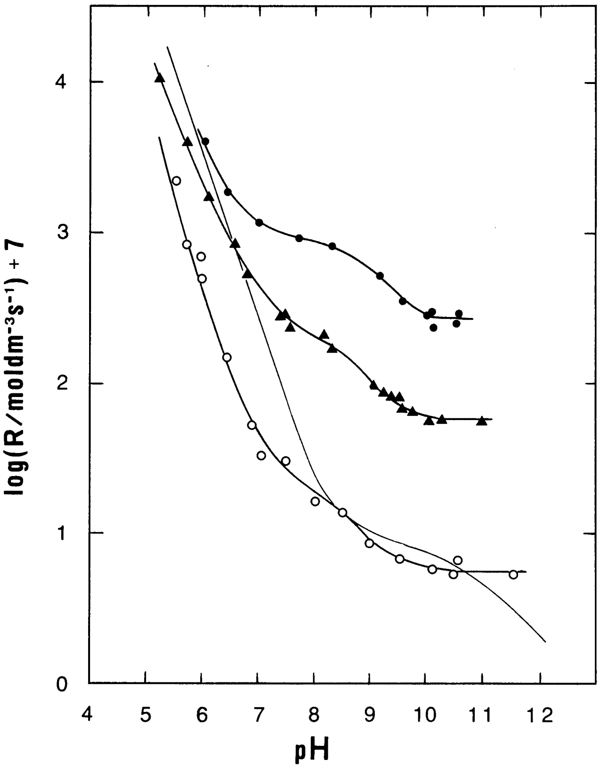

Fig. 2. pH-Rate profiles of the oxygen exchange between arsonate ions and water. I=0.55 mol dm^{-3}. Methylarsonate; ●: 30 °C, ○: 0 °C. Benzylarsonate; ▲: 0 °C, Arsenate; ——: 30 °C.

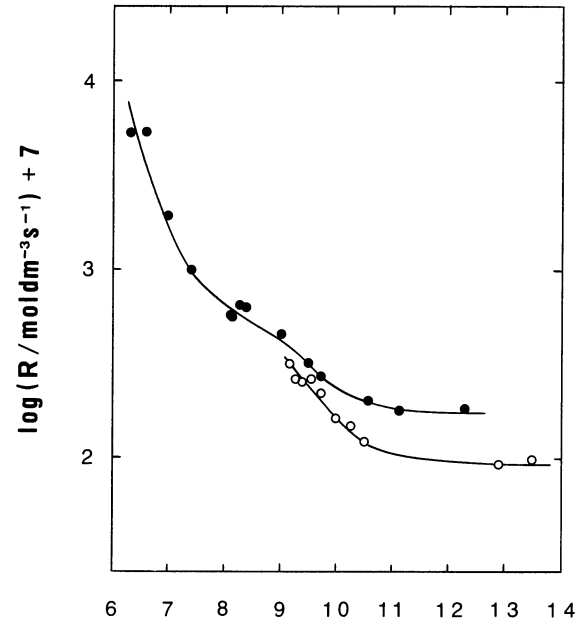

Fig. 3. pH-Rate profiles of the oxygen exchange between arsonate ions and water at 30 °C.
●: Butylarsonate, ○: Hexylarsonate.

becomes independent of the pH. On the other hand, in a more acidic region (pH<7.5), the increase in the rate with a decrease in the pH becomes more significant. As the undissociated acid begins to appear in the solution at pH<7.5, the steep increase in the rate is probably due to the participation of undissociated arsonic acid in the reaction. These facts suggest that the reactivity of the ionic species of arsonates is in the following order: Undissociated acid (neutral)≫monovalent anion>divalent anion.

The pH-dependence of the exchange rate for butyl- and hexylarsonates shown in Fig. 3 is similar to that for methyl- and benzylarsonates.

Although the oxygen exchange rate of methylarsonate is four-times larger than that of benzylarsonate at pH>7.5, the difference in the rate between both arsonates gradually becomes small with a decrease in pH (pH<7.5).

Comparison of the Oxygen-Exchange Rate of Arsenate with Those of Methyl- and Benzylarsonates: At pH>8, the oxygen exchange rate of arsenate is much smaller than those of the arsonates. At pH<8, the pH-dependence of the arsenate oxygen exchange rate becomes larger than that of the arsonates; at pH=6 the exchange rate of arsenate exceeds those of methyl- and benzylarsonates. In the case of arsenate oxygen exchange, the reactive species is $H_2AsO_4^-$ in the pH region between 6 and 12.

Arsinates: The oxygen exchange of arsinates proceeds very rapidly ($t_{1/2}$<10 min, at 2 °C for dimethylarsinate), and the rates could be measured under limited conditions. The results for dimethyl- and dibutylarsinates are shown in Table 4.

Dependence of the Rate of Oxygen Exchange on the Concentration of the Arsonates and Arsinate.

For arsonates, the concentration dependence was studied at two different values of the pH (pH=11 and another pH smaller than 8.5) for each arsonate studied. The order of the reaction with respect to the concentration of arsonate (n) was obtained from the slope of a log–log plot of R versus [arsonate]. Typical results for butylarsonate (BuA) are shown in Fig. 4 (30 °C, I=0.55 mol dm^{-3}, A; pH=11, [BuA]=0.15—0.40 mol dm^{-3}, B; pH=8.05, [BuA]=0.15—0.32 mol dm^{-3}). The plots yield straight lines with slopes of 1.12±0.06 for A, and 1.51±0.06 for B. The values of n obtained for other arsonates are listed in Table 5, along with the rate data. For all of the arsonates, it may be inferred that the order of the exchange reaction with respect to [arsonate] is about unity in the pH region greater than 9; it is greater than unity below pH 8.

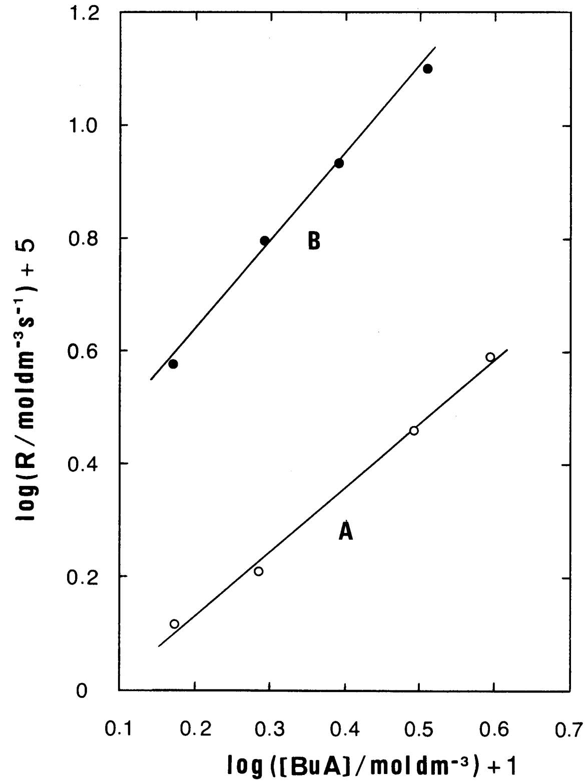

Fig. 4. Dependence of the exchange rate on the concentration of butylarsonate, [BuA] at 30 °C and I= 1.0 mol dm^{-3}. A(○): pH=11, B(●): pH=8.05.

The value (n) for the dibutylarsinate is unity according to the data shown in Table 4b.

The Mechanism of the Oxygen Exchange of Arsonates. The first-order dependence of the oxygen exchange rates on [arsonate] at pH>9, where are the dominating ionic species of arsonates are R′-AsO_3^{2-} and

Table 4. The Rate of Oxygen Exchange Reaction of Dialkylarsinates with Water
a: Dimethylarsinate (2 °C, [$(CH_3)_2AsO_2Na$]=0.50 mol dm^{-3}, I=0.50 mol dm^{-3})
b: Dibutylarsinate (pH=10)

a: $(CH_3)_2AsO_2Na$		b: $(n\text{-}C_4H_9)_2AsO_2Na$		
pH	R/10^{-4} mol dm^{-3} s^{-1}	Temp/°C	Concn/mol dm^{-3}	R/10^{-4} mol dm^{-3} s^{-1}
7.70	15.4	2	0.335	0.572
7.92	9.35	2	0.681	1.22
8.10	6.97	7	0.331	1.55
8.40	6.41	7	0.512	2.38
8.95	6.46	12	0.355	3.32
9.35	6.18	12	0.559	5.47
13.20	4.66			

Table 5. The Dependence of the Exchange Rates on the Concentration of Arsonates (30 °C,[a] 20 °C)

R′	pH	[Arsonate] mol dm^{-3}	10^5 *R* mol dm^{-3} s^{-1}	*n*	pH	[Arsonate] mol dm^{-3}	10^5 *R* mol dm^{-3} s^{-1}	*n*
CH_3	10.6	0.0994	2.89	$0.8_7 \pm 0.0_5$	8.6	0.152	4.80	$1.5_8 \pm 0.1_5$
		0.147	3.97			0.195	7.03	
		0.200	5.34			0.244	10.7	
						0.245	9.59	
n-C_4H_9	11.0	0.148	1.45	$1.1_2 \pm 0.0_6$	8.1	0.147	3.77	$1.5_1 \pm 0.0_6$
		0.194	1.67			0.195	6.33	
		0.312	2.79			0.246	8.65	
		0.397	3.94			0.324	12.8	
n-C_6H_{13}	9.6	0.141	1.85	$1.0_2 \pm 0.0_1$				
		0.201	2.66					
		0.229	3.03					
$C_6H_5CH_2$	10.2	0.098	0.558	0.9_2	5.3[a]	0.100	170	$1.6_0 \pm 0.3_8$
		0.557	2.90			0.154	136	
						0.201	57.1	

$R'\text{-}AsO_3H^-$, suggests that the oxygen exchange of arsonates proceeds through the following two parallel paths:

$$R'\text{-}AsO_3^{2-} + H_2{}^*O \overset{k_1}{\rightleftharpoons} R'\text{-}AsO_2{}^*O^{2-} + H_2O \qquad (1)$$

and

$$R'\text{-}AsO_3H^- + H_2{}^*O \overset{k_2}{\rightleftharpoons} R'\text{-}AsO_2{}^*OH^- + H_2O. \qquad (2)$$

Since the more acidic species of an oxoanion is usually more reactive in an oxygen exchange reaction,[7] it is natural to assume the following exchange mechanism:

$$R'\text{-}AsO_3H_2 + H_2{}^*O \overset{k_3}{\rightleftharpoons} R'\text{-}AsO_2{}^*OH_2 + H_2O. \qquad (3)$$

The order of the exchange reaction with respect to [arsonate] greater than 1 at pH<8 suggests that there is some contribution of the bimolecular paths (4, 5, and 6) to the following exchange reactions:

$$R'\text{-}AsO_3H^- + R'\text{-}AsO_3H^- \overset{k_4}{\rightleftharpoons} (R'\text{-}AsO_2)_2O^{2-} + H_2O, \qquad (4)$$

$$R'\text{-}AsO_3H^- + R'\text{-}AsO_3H_2 \overset{k_5}{\rightleftharpoons} (R'\text{-}AsO_2)_2OH^- + H_2O, \qquad (5)$$

and

$$R'\text{-}AsO_3H_2 + R'\text{-}AsO_3H_2 \overset{k_6}{\rightleftharpoons} (R'\text{-}AsO_2H)_2O + H_2O. \qquad (6)$$

The rate law for the oxygen exchange of arsonate ions with water may be written as follows:

$$\begin{aligned} R &= R_1 + R_2 + R_3 + R_4 + R_5 + R_6 \\ &= k_1[R'AsO_3^{2-}] + k_2[R'AsO_3H^-] + k_3[R'AsO_3H_2] \\ &\quad + k_4[R'AsO_3H^-]^2 + k_5[R'AsO_3H^-][R'AsO_3H_2] \\ &\quad + k_6[R'AsO_3H_2]^2. \end{aligned}$$

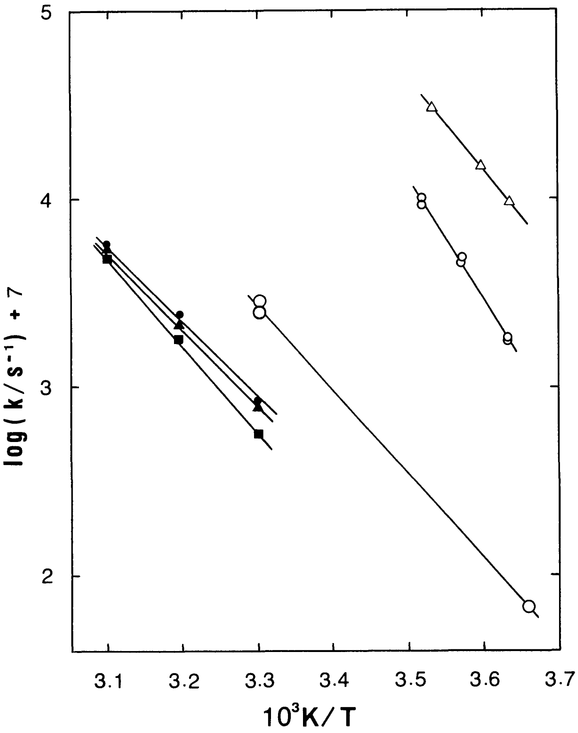

Fig. 5. Temperature dependence of the oxygen exchange rates of alkylarsonates ($R'AsO_3^{2-}$) and dialkylarsinates ($R'_2AsO_2^-$). Arsonates; ○: R′=CH_3, pH=10, ●: R′=*n*-C_4H_9, pH=11, ▲: R′=*n*-C_6H_{13}, pH=13, ■: R′=$C_6H_5CH_2$, pH=11. Arsinates; △: R′=CH_3, pH=13, ○: R′=*n*-C_4H_9, pH=10.

Temperature Dependence of the Exchange Rates. The dependence was studied over the pH region between 10 and 13 for all of the arsonates and arsinates studied, and at pH=6 for methyl- and benzylarsonates. From the observed rate (*R* (pH>10)) at various temperatures, the rate constants (*k*) were calculated using the following relation: *R*=*k*[arsonate] or *R*=*k*[arsinate]. Plots of log *k* against 1/*T* are given in Fig. 5. From the slopes and intercepts of the plots, the values of the activation energy and activation entropy were obtained; they are summarized in Table 6a. Since at pH>10 and 30 °C, the oxygen exchange occurs predominantly through path 1, the values of E_a and $\Delta S^{\neq}$ obtained at these pH give the approximate values of path 1. For methyl- and benzylarsonates, the oxygen exchange rates at pH 6 and at various temperature and activation energies from these data are shown in Table 6b. The value of E_a at pH=6 (51 kJ mol^{-1}) is rather small, compared to those at pH>10, which may be interpreted as being the contribution of bimolecular paths having smaller activation energies for an oxygen exchange.

Table 6a. The Activation Parameters for the Oxygen Exchange Reaction of Arsonates ($R'AsO_3Na_2$) and Arsinates (R'_2AsO_2Na) with Water in the pH Region Greater than 10 (I=0.55 mol dm^{-3},[a)] 30 °C)

	R′	pH	E_a	$\Delta S^{\neq}$[a)]
			kJ mol^{-1}	J K^{-1} mol^{-1}
Arsonates	CH_3	10	84.8±2.9	−42± 9
	n-C_4H_9	11	77.5±3.1	−76±10
	n-C_6H_{13}	13	76.6±1.9	−79± 6
	$C_6H_5CH_2$	11	90.5±1.7	−36± 5
Arsinates	CH_3	13	95.1±1.9	34± 7
	n-C_4H_9	10	110.8±4.7	78±17

Table 6b. The Temperature Dependence of the Exchange Rate of Methyl- and Benzylarsonates at pH 6 (I=0.55 mol dm^{-3})

R′	pH	Temp	R	E_a
		°C	10^{-5} mol dm^{-3} s^{-1}	kJ mol^{-1}
CH_3	6.0	0	4.46	51
		30	40.1	
$C_6H_5CH_2$	6.1	0	1.91	51.4±0.9
		20	8.67	
		30	18.0	

The Analyses of the Exchange Rate. The exchange rates plotted in Figs. 2 and 3 were analyzed using the rate law 1. The procedure used for analyzing the exchange rate of methylarsonate at 0 °C is given as an example. Over the range pH>9, the exchange reaction proceeds exclusively through paths 1 and 2, and the appropriate rate law is $R=k_1[CH_3AsO_3^{2-}]+k_2[CH_3AsO_3H^-]$. By using the relation and rate data at pH>9 (Fig. 2), the values of k_1 and k_2 were obtained to be (5.88±0.64)×10^{-6} s^{-1} and (1.47±0.17)×10^{-5} s^{-1}, respectively. In the pH range between 7 and 8.5, the contribution of the bimolecular rate terms (R_4 and R_5) to the total rate becomes important. Since, in this pH region, the concentration of $CH_3AsO_3H_2$ is very low (below 0.08% of the total concentration), the contribution of terms R_3 and R_6 may be ignored, and rate law 1 becomes $R-k_1[CH_3AsO_3^{2-}]-k_2[CH_3AsO_3H^-]=k_4[CH_3AsO_3^-]^2+k_5[CH_3AsO_3H^-][CH_3AsO_3H_2]$. For each run at pH 7—8.5, the left-hand side of the equation was calculated by using the values of k_1 and k_2 obtained above; the concentration products in the right-hand side of the equation were also calculated. A least-squares treatment of a set of numerical equations, thus obtained, gave values of k_4=(5.7±6.4)×10^{-5} mol^{-1} dm^3 s^{-1} and k_5=0.39±0.1 mol^{-1} dm^3 s^{-1}. In the pH region between 5.5 and 6.5, rate terms R_3 and R_6, including neutral species, methylarsonic acid, becomes important; rate analyses in this region were carried out in terms of a rearranged rate law 1, as follows:

$$\begin{aligned}&R-k_1[CH_3AsO_3^{2-}]-k_2[CH_3AsO_3H^-]-k_4[CH_3AsO_3H^-]^2\\&-k_5[CH_3AsO_3H^-][CH_3AsO_3H_2]=k_3[CH_3AsO_3H_2]\\&+k_6[CH_3AsO_3H_2]^2.\end{aligned}$$

Table 7. Rate Constants of the Oxygen Exchange of Arsonates and Arsinates with Water (30 and 0 °C, I=0.55 mol dm^{-3})

R′	Temp	CH_3	C_4H_9	C_6H_{13}	$C_6H_5CH_2$
(arsonates)					
$k_1/10^{-5}$ s^{-1}	30	23.5 ±0.9	9.3±0.3	7.2±0.2	5.8±0.3
	0	0.59±0.06			
$k_2/10^{-4}$ s^{-1}	30	15.8 ±7.4	4.4±0.2	3.7±0.4	2.3±0.2
	0	0.15±0.02			
$k_3/10^{-2}$ s^{-1}	30				13 ±4
	0	1.4 ±1.2			
$k_4/10^{-5}$ M^{-1} s^{-1}	30		2.8±19		3.2±2.2
	0	5.7 ±6.4			
k_5/M^{-1} s^{-1}	30		2.1±0.5		1.6±1.2
	0	0.39±0.10			
k_6/M^{-1} s^{-1}	30				
	0	28 ±10			
(arsinate)					
$k_1/10^{-2}$ s^{-1}	30	4.4[a)]	1.6[a)]		
	2	0.1 ±0.01	0.018		
$k_2/10^{-2}$ s^{-1}	2	4.8 ±0.8			

a) Extrapolated value.

The left-hand side of this equation was calculated using the values of k_1, k_2, k_4, and k_5 obtained above. By the least-squares treatment the values of k_3 and k_6 were obtained to be $(1.4\pm1.2)\times10^{-2}$ s^{-1} and 28 ± 10 mol^{-1} dm^3 s^{-1}, respectively. In order to obtain more reliable values of these rate constants, a preliminary experiment using an ^{17}O NMR line broadening technique was carried out for methylarsonic acid at pH 2, where the undissociated species, $CH_3AsO_3H_2$ prevailed. The experiment gave an estimate of $k_3=2.3\times10^{-2}$ s^{-1} and $k_6=13.3$ mol^{-1} dm^3 s^{-1} at 0 °C.[8] These values are in satisfactory agreement with those obtained by the ^{18}O exchange method.

The exchange rates for the other arsonates shown in Figs. 2 and 3 were treated similarly. The values of the rate constants obtained are summarized in Table 7. In Figs. 2 and 3, the curves show the exchange rates calculated by using the rate constants thus obtained (Table 7). The agreement with the experimental values is satisfactory.

The exchange-rate data of dimethylarsinate at 2 °C (Table 4a) were analyzed in terms of the following relation:

$$R=k_1[(CH_3)_2AsO_2^-]+k_2[(CH_3)_2AsO_2H].$$

The values of k_1 and k_2 at 2 °C were obtained to be $(1.00\pm0.14)\times10^{-3}$ s^{-1} and $(4.79\pm0.75)\times10^{-2}$ s^{-1}, respectively. For dibutylarsinate, experiments were carried out at a fixed pH=10, where the dominant ionic species is monovalent anion, the relevant rate law is $R=k_1[(C_4H_9)_2AsO_2^-]$. The average values of k_1, calculated from the data in Table 4b, are 0.175×10^{-3} s^{-1} (2 °C), 0.468×10^{-3} s^{-1} (7 °C), and 0.957×10^{-3} s^{-1} (12 °C). For dialkylarsinates, the k_1 values at 30 °C were calculated by using the Arrhenius equation; the values are also listed in Table 7.

Effect of Protonation on the Reactivity of Alkylarsonate Ions: As can be seen from the values of Table 7, protonation enhances the reactivity of arsonate ions, as is the case with other oxoanions. The reactivity of undissociated arsonic acid is especially large. The role of a proton in facilitating the oxygen exchange of oxoanion probably involves the polarization of the bond between the oxygen and the central atom; the protonation lowers the values of the activation energy: The E_a value for the reaction between $CH_3AsO_3H_2$ and water was obtained to be 69 kJ mol^{-1} by using ^{17}O NMR line-shape analyses;[8] that for the reaction between $CH_3AsO_3^{2-}$ and water is 85 kJ mol^{-1} (Table 6a).

Effect of the Alkylsubstitution on the Oxygen Exchange Rate: The kinetic behaviors of various anions of alkylarsonates are similar to each other. The values of k_1 and k_2 are in the following order; methyl>butyl>hexyl. However, the difference between them is not large, but of the same order (see Table 7). The oxygen exchange of benzylarsonate proceeds more slowly than that of methylarsonate. Substitution of a methyl-hydrogen by a phenyl group leads to a reduction in the rate by a factor of 3—5; substitution does not affect the acid dissociation constant, the values of pK_1 and pK_2 being almost the same for both arsonates (Table 3). These results show that a noticeable steric or hydrophobic effect of the butyl, hexyl, and benzyl substituents is absent. In a previous paper,[2] on the bases of an orbital extension of LUMO, it was concluded that the alkyl group is apart from the path of the entering group, and that the rate is therefore insensitive to the size of the alkyl-chain. Furthermore, it was shown that the rate constants for monovalent anions (k_2's) correlate well with the energy levels of the lowest unoccupied molecular orbital (E_{LUMO}'s) of these anions.

The values of the activation entropy of the overall exchange reaction at pH 11 ($\Delta S^{\ne}$), were obtained to be −42, −76, and −79 J mol^{-1} K^{-1} for methyl-, butyl-, and hexylarsonates, respectively (Table 6a). Theses values give the values of $\Delta S^{\ne}$ of path 1, and are consistent with a mechanism which involves a bimolecular substitution process between the arsonate ions and water molecule as the rate-limiting step (S$_N$2). The kinetic results agree with the conclusion from a MO calculation.[2]

Contribution of the Second-Order Paths to the Oxygen Exchange of Alkylarsonates: The second-order pathway involves a nucleophilic displacement of water on arsenic by an arsonate ion or arsonic acid, while the first-order path involves a displacement of water by water. At pH=6, the contribution of the second-order rate terms (R_4, R_5, and R_6) was estimated to be 80% of the total rate for methylarsonate (0 °C), those of R_4 and R_5 being 80 and 38% for butyl- and benzylarsonates, respectively (30 °C). At this pH, the activation energy was obtained to be 51 kJ mol^{-1} for both methyl- and benzylarsonates (Table 6b), which gives an upper limit for the activation energy of these bimolecular paths between various species of alkylarsonates. The smaller values of the activation energy for the bimolecular paths, compared with the values for the first-order path, are considered to be responsible for the larger values of rate constants k_5 and k_6. Furthermore, the second-order rate constants so far obtained for methyl-, butyl-, and benzylarsonates are in the order $k_6>k_5>k_4$; the rate constant of the reaction between two undissociated acids (k_6) is two orders of magnitude larger than that between undissociated acid and monovalent anion (k_5), which, in turn, is 4 to 5 orders of magnitude larger than that between two monovalent anions (k_4). The explanation for the fact that the reaction between undissociated acids proceeds very fast is that two neutral arsonic acids come together to form a neutral transition state without any significant Coulombic repulsion, and without any significant solvent reorganization.

Comparison of the Oxygen Exchange Rates between Alkylarsonates and Dialkylarsinates: In the most alkaline region, where both alkylarsonic and dialkylarsinic acids dissociate completely, the dimethylarsinate and dibutylarsinate exchange their oxygens 170-times faster than the respective alkylarsonates. It is worth noting that the values of the activation entropies for dialkylarsinates have positive values ($34\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (methyl) and $78\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (butyl)) compared with the negative values for alkylarsonates (Table 6a). This result suggests that the faster rates found in dialkylarsinates are due to the positive values of activation entropy, the values of activation energies obtained for dialkylarsinates being larger than those for alkylarsonates. This facts can be explained by the difference in the exchange mechanism: the reaction of dialkylarsinates proceeds via monomolecular nucleophilic displacement (S_N1), as required from the positive value of the activation entropy.

An amphoteric character of the dimethylarsinic acid has been proposed in earlier studies: by the electric conductivity measurement[9] and kinetic method,[10] the acid and base dissociation constants (K_a and K_b (for the reaction 8 or 9)) are estimated to be 6.4×10^{-7},[9] 7.5×10^{-7},[10] and 3.2×10^{-13},[9] 5.6×10^{-13},[10] respectively.

$$(CH_3)_2AsO_2^- + H^+ \overset{K_a^{-1}}{\rightleftharpoons} (CH_3)_2AsO_2H \tag{7}$$

$$(CH_3)_2AsO_2H \overset{K_b}{\rightleftharpoons} (CH_3)_2AsO^+ + OH^- \tag{8}$$

or

$$(CH_3)_2AsO_2H + H_2O \rightleftharpoons (CH_3)_2As(OH)_3$$
$$\overset{K_b}{\rightleftharpoons} (CH_3)_2As(OH)_2^+ + OH^- \tag{9}$$

The kinetic result that the oxygen exchange of dimethylarsinate ion proceeds via the S_N1 mechanism may be explained by assuming a reversible dissociation of (i) $(CH_3)_2AsO_2H$ into OH^- and $(CH_3)_2AsO^+$ (reaction 8) or (ii) $(CH_3)_2As(OH)_3$ into OH^- and $(CH_3)_2As(OH)_2^+$ (reaction 9).

In the alkaline hydrolysis of a series of phosphinate esters[11] it was observed that the reaction proceeds by a cleavage of the P–O bond, and that second-order kinetics is followed. They also presented evidence for a pentacoordinate intermediate, which breaks down in the rate-determining step. It is well known that the oxygen exchange of oxoanions and the hydrolysis of the esters of oxoanions proceeds via analogous mechanisms. It is interesting to note that exchange path 9 (via pentacoordinate arsinic acid) is consistent with the mechanism presented regarding the hydrolysis of phosphinate esters.

According to the Raman and infrared spectroscopic investigations,[12] the values of the As–O valence force constant and As–O bond order in $(CH_3)_2AsO_2^-$ are slightly larger than those in $CH_3AsO_3^{2-}$. This fact may be considered to explain, at least, partly the larger activation energy observed in the oxygen exchanges of dimethylarsinate.

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