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Kinetics of Oxygen Exchange between Arsenate Ions and Water. II. Catalysis by Arsenious Acid

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Oxygen exchange between arsenate ions and water is catalyzed by arsenious acid. The catalytic effect has been studied at 14.5 °C and 30.0 °C over the pH region of 7.5—10.2. The increase in the exchange rate due to the addition of arsenious acid, R_c, may be expressed as: $R_c \approx k[H^+][As(III)][As(V)]$. The results are interpreted in terms of the rapid reversible condensation of the As(III) with the As(V) species to form the arsenitoarsenate ions.

In a previous study of the oxygen exchange between arsenate ions and water,[1] it has been shown that the reversible condensation of the arsenate ions to form diarsenate ions occurs in aqueous solutions. Itse ems that it would be interesting to see whether or not the arsenate ion reacts with other oxyanions to form heteropolyanions, and to compare the reactivities of these oxyanions towards the arsenate ions. These reaction open an additional path for the oxygen exchange of arsenate ions, and, if the reactions are reversible and sufficiently rapid, the exchange reaction can be catalyze by these oxyanions. In the present paper, catalysis by arsenious acid will be reported.

Experimental

Materials. The arsenic trioxide (Guaranteed reagent, JIS) and perchloric acid(Guaranteed reagent, JIS) were used without further purification. All the other chemicals were the same as those used in the previous work.[1]

Procedure. The procedures were almost the same as those used in the previous work.[1] The exchange reaction was started by diluting an isotopically-equilibrated solution of Na_2HAsO_4 in oxygen-18 water with a relatively large amount of isotopically normal water, a proper amount of an arsenious acid solution being added. The pH of the solution was adjusted by the addition of a small amount of perchloric acid or of a sodium hydroxide solution. After appropriate intervals, the arsenate ions were precipitated by the addition of a barium chloride solution. The precipitate, after being washed three times with absolute ethanol and dried, was converted into carbon dioxide by the guanidine hydrochloride method. The isotopic analysis of the carbon dioxide was made on a Hitachi RMS-I-type mass spectrometer. The contribution of a small amount of the precipitate of barium arsenite to the ^{18}O-content of the carbon dioxide was neglected. Oxygen exchange between arsenious acid and water is very rapid at room temperature, and is completed within the time necessary for the separation. The rate of the oxygen exchange of arsenate ions was calculated by means of the formula:

$$R = -\frac{[As(V)][H_2O]}{4[As(V)]+[H_2O]}\cdot\frac{1}{t}\cdot\ln\left\{1-\frac{O_0-O_t}{O_0-O_\infty}\right\},$$

where O_0, O_t, and O_∞ are the ^{18}O-contents of the carbon dioxide at times 0, t, and infinity respectively, and where [As(V)] and [H_2O] are the concentrations of the arsenate and water respectively.

Determination of Dissociation Constants. The dissociation constants of arsenious and arsenic acid under the conditions of the kinetic experiments were determined by potentiometric titration with a glass electrode. The pK_2 of arsenic acid was determined by titrating a solution of Na_2HAsO_4 containing the amount of sodium chloride necessary to maintain the desired ionic strength with hydrochloric acid. For the determination of the pK_1 of arsenious acid, a solution of arsenious acid was titrated with a solution of sodium hydroxide, an appropriate amount of sodium chloride being added to adjust the ionic strength. The pH of the solution was measured with a Radiometer PHM-26 pH meter. The results obtained from two series of titrations at I=0.2 M, where I is the ionic strength, are shown in the following table. For the definition of the pK's, see Part I of this series.

Table 1. The dissociation constants of arsenic acid (pK_2) and arsenious acid (pK_1) at I=0.2 M.

	14.5°C	30.0°C
pK_2 of arsenic acid	$6.59_6 \pm 0.00_4$	$6.55_6 \pm 0.00_6$
pK_1 of arsenious acid	$9.34_1 \pm 0.00_3$	$9.10_8 \pm 0.01_7$

Results and Discussion

pH *Dependence.* Fig. 1 shows the pH-rate profile of the oxygen exchange of arsenate ions with and without the added arsenious acid at 14.5 °C and 30.0

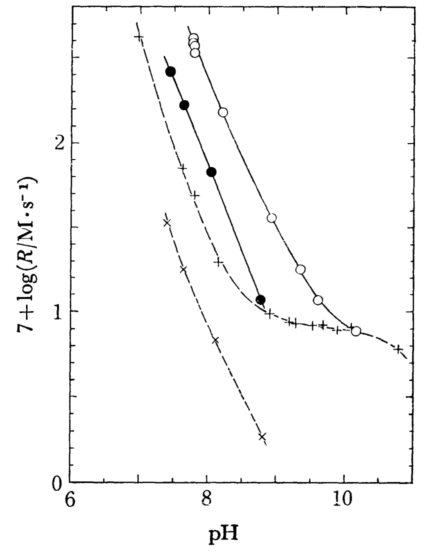

Fig. 1. pH-rate profiles of the oxygen exchange between arsenate ions and water ([As(V)]=0.07 M, I=0.2 M): + (30 °C), × (14.5 °C), without added arsenious acid. ○ (30 °C), ● (14.5 °C), with added arsenious acid ([As(III)] $\simeq 1.2\times10^{-4}$ M).

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[1] A. Okumura and N. Okazaki, This Bulletin, **46**, 2937 (1973).

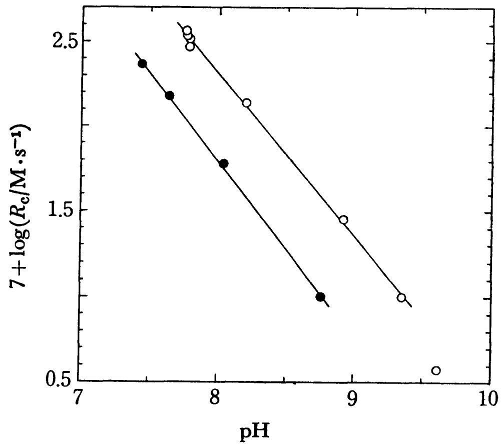

Fig. 2. pH dependence of the catalysed portion of the exchange rate R_c: ○ 30 °C, ● 14.5 °C.

°C([As(V) : [As(III)] ≈ 50 : 1).2) The addition of arsenious acid increases the exchange rate about 8-fold at pH 7.44. The catalytic effect decreases with the increase in pH, and it disappears above pH 10. From the pH-rate profile and the values of the dissociation constants of arsenic and arsenious acids, it may be inferred that $H_2AsO_4^-$ and H_3AsO_3 are the active species in the catalytic process.

Figure 2 shows a plot of the logarithm of $R_c(=R-R_0)$ against pH, where R and R_0 are the exchange rates observed with and without the addition of arsenious acid. The slopes of the lines passing through the plots are −0.96±0.01 at 30.0 °C and −1.01±0.02 at 14.5 °C. The catalyzed portion of the exchange rate, R_c, depends upon the first power of the hydrogen-ion concentration. The role of the hydrogen ion is to shift the pre-equilibrium:

$$H_2AsO_4^- \rightleftharpoons HAsO_4^{2-} + H^+,$$

in favor of $H_2AsO_4^-$, which is the active species in the exchange reaction.

Dependence of the Catalytic Rate R_c on [As(III)]. This has been studied at 30 °C, pH 7.83, [As(V)] = 0.07 M, and I=0.2 M. [As(III)] was varied between 3×10^{-4} and 13×10^{-4} M. The observed rates were corrected for the small differences in pH(<0.05) and in [As(V)](<0.0015 M). A plot of log R_c against log [As(III)] is shown in Fig. 3. A line drawn through the plots has a slope of $0.95\pm0.00_1$. The catalytic rate, R_c, depends on the first power of [As(III)].

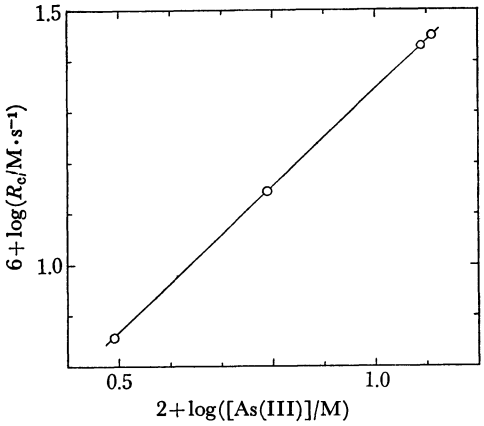

Fig. 3. Dependence of log R_c on log [As(III)] (30 °C, pH 7.83, [As(V)]=0.07 M, I=0.2 M).

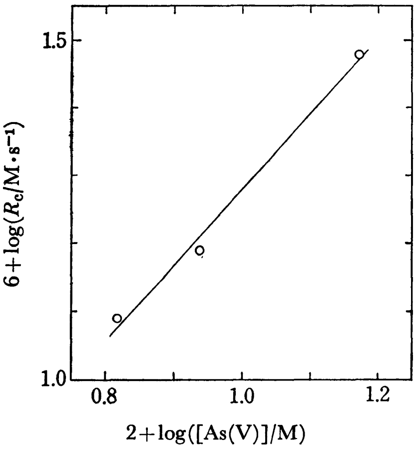

Fig. 4. Dependence of log R_c on log [As(V)] (30 °C, pH 7.78, [As(III)]=6.2×10^{-4} M, I=0.4 M).

Dependence of the Catalytic Rate on [As(V)]. The dependence of R_c on [As(V)](0.066—0.15 M) has been studied at 30 °C, pH 7.78; [As(III)] = 6.2×10^{-4} M, and I=0.43 M (Fig. 4). Corrections were applied to the observed rates for the small differences in pH (<0.1). The plots of log R_c against log [As(V)] fall on a straight line with a slope of 1.10±0.07. The catalytic process is approximately first-order with respect to [As(V)].

The rate law of the catalytic process may be written as:

$$R_c = k[H^+][As(III)][As(V)]. \tag{1}$$

Mechanism of the Catalytic Process. Wilson and Dickinson3) have shown that the exchange of radioactive arsenic does not occur between arsenite and arsenate ions in dilute acid(0.1 M HCl) and alkaline(*ca* 1 M NaOH) solutions. This indicates that the direct transfer of oxygen atoms does not occur between these ions. Thus, a mechanism of the catalysis of the oxygen exchange which involves a rapid interchange of oxygen between arsenious acid and water, followed by a transfer of oxygen from the arsenate to the arsenious acid, may be excluded.

Another possibility is the general acid catalysis of the exchange reaction between arsenate ions and water by arsenious acid. In this case, it is natural to interpret the bimolecular rate term of the arsenate-water exchange,1) $k_4[H_2AsO_4^-]^2$, also in terms of the general acid catalysis by $H_2AsO_4^-$. However, since $H_2AsO_4^-$ is a stronger acid than H_3AsO_3, the mechanism involving the general acid catalysis is inconsistent with the fact that the arsenate-water exchange is catalyzed by arsenious acid.

The catalytic process may be considered to be the reversible condensation of arsenate ions with arse-

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2) [As(III)] is the total concentration of the arsenious acid; [As(III)] = $[H_3AsO_3]+[H_2AsO_3^-]$.

3) J. N. Wilson and R. G. Dickinson, *J. Amer. Chem. Soc.*, **59**, 1358 (1937).

nious acid or arsenite ion to form arsenitoarsenate ions:

$$H_2AsO_4^- + H_3AsO_3 \rightleftharpoons H_3As_2O_6^- + H_2O, \text{ etc.}$$

The rate law of the catalytic process may now be written as:

$$R_c = k_1[H_2AsO_4^-][H_3AsO_3] + k_2[HAsO_4^{2-}][H_3AsO_3] + k_3[H_2AsO_4^-][H_2AsO_3^-] + k_4[HAsO_4^{2-}][H_2AsO_3^-]. \quad (2)$$

Since $R_c \approx 0$ at pH≈ 10, the contribution of the k_4-term may be ignored. The rate law (2) becomes:

$$\frac{R_c}{[H_2AsO_4^-][H_3AsO_3]} = k_1 + \frac{K_2}{[H^+]}\left\{k_2 + k_3\frac{K_1'}{K_2}\right\}, \quad (3)$$

where K_2 and K_1' are the dissociation constants of $H_2AsO_4^-$ and H_3AsO_3 respectively.

In Fig. 5, the data in Fig. 1 are replotted according to the above equation. From the intercepts of the lines drawn through the plots, the values of k_1 are determined to be k_1(30 °C) = 6.8 $M^{-1} s^{-1}$ and k_1(14.5 °C) = 2.2 $M^{-1} s^{-1}$. The activation parameters of the k_1-path are $E_a = 52.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -38$ J K^{-1} mol^{-1}.

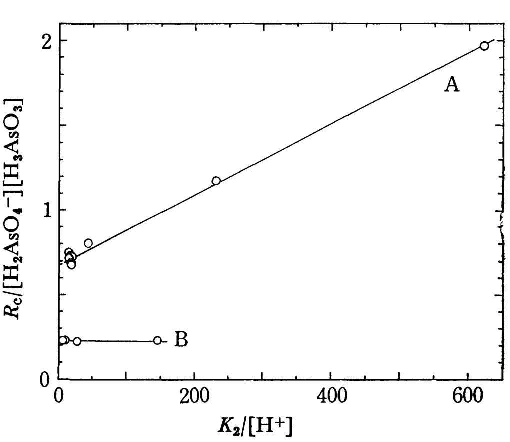

Fig. 5. $R_c/[H_2AsO_4^-][H_3AsO_3]$ as a function of $K_2/[H^+]$: A; 30 °C, B; 14.5 °C.

Table 2. Rates and activation parameters of several reactions of $H_2AsO_4^-$.

	Rate const. ($M^{-1} s^{-1}$), 30°C	Act. energy (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J $K^{-1} mol^{-1}$)
$H_2AsO_4^-$ + H_2O,[a]	1.1×10^{-4}	≈ 92	≈ -46
$H_2AsO_4^-$ + $H_2AsO_4^-$,[a]	7.4×10^{-2}	<54	<-71
$H_2AsO_4^-$ + H_3AsO_3,[b]	6.8	52	-38

a) $I = 0.55$ M, b) $I = 0.2$ M.

From the slope of the line A (Fig. 5), the value of $\{k_2 + k_3(K_1'/K_2)\}$ at 30 °C is evaluated as 0.02 $M^{-1} s^{-1}$. Since k_2 may reasonably be assumed to be larger than k_3 and since $K_1'/K_2 = 2.8 \times 10^{-3}$ at 30 °C, the value of k_2 may be put equal to 0.02 $M^{-1} s^{-1}$. This path plays a dominant role above pH 9. To estimate the value of k_2 at 14.5 °C is beyond the scope of the present work.

The reactivities of several nucleophiles towards $H_2AsO_4^-$ obtained in the present and the previous[1] works are listed in Table 2. The higher reactivity of arsenious acid as compared with $H_2AsO_4^-$ may be attributable to the entropy factor.

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