The Kinetics of Oxygen Exchange between Arsenate Ions and Water. III. Catalysis by Periodate Ions

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Oxygen exchange between arsenate ions and water is remarkably catalyzed by the addition of a small amount of periodate ions.† The reaction has been studied at 30.0 °C over the pH range of 6.7—11.4. The rate law of the catalytic reaction has been found to be $R_C = k\cdot[H^+][As(V)][I(VII)]$, where R_C is defined as the increase in the rate of oxygen exchange of arsenate ions by the addition of periodate ions. The catalytic process has been interpreted in terms of the reversible condensation of arsenate ions with periodate ions to form the arsenatoperiodate ions, and the rate constant of the condensation reaction between $H_2AsO_4^-$ and $H_4IO_6^-$ has been estimated to be 340 $M^{-1}\,s^{-1}$ at 30.0 °C.

In a previous paper,[1] it has been shown that the oxygen exchange reaction of arsenate ions with water is strongly accelerated by the addition of a small amount of arsenious acid. The catalytic process has been identified with the reversible condensation of arsenate ions with arsenite species to form the arsenatoarsenite ions, and the rate constants of this condensation reaction have been estimated.

The study of an oxygen exchange reaction of an oxoanion in the presence of a catalytic amount of another oxoanion may provide a means of studying the kinetics and equilibriums of the condensation reactions involving the two oxoanions. In this paper a study of the interaction of arsenate ions with periodate ions in solution by means of the oxygen exchange reaction will be reported.

Experimental

Materials. Water enriched in oxygen-18 (2 atom %) was obtained from a fractionating column in this laboratory. It was refluxed with alkaline permanganate, and distilled twice. Normal water was treated in the same way. Disodium hydrogenarsenate heptahydrate(Guaranteed reagent, Merck), sodium periodate (Guaranteed reagent, Merck), and all the other chemicals (Guaranteed reagent, JIS) were used without further purification.

The concentration of the stock solution of sodium periodate (1.63×10^{-2} M) was checked spectrophotometrically each time before use with iron(II)-2,4,6-tri-2-pyridyl-1,3,5-triazine.[2]

Procedure. The procedures were almost the same as those used earlier.[1,3] The exchange reaction was started by mixing an isotopically equilibrated solution of disodium hydrogenarsenate in $H_2{}^{18}O$ with water of normal isotopic composition. A small amount of the stock solution of periodate was added, and the pH of the solution was fixed by the addition of a measured quantity of either a solution of sodium hydroxide or hydrochloric acid. The pH of the solution was measured with a Radiometer PHM type-26 pH meter. All experiments were performed at 30.0 °C. At intervals aliquots of the reacting solution were drawn, and the reaction was quenched by precipitating the arsenate ions as $BaHAsO_4\cdot H_2O$ with barium chloride solution. The precipitate, after being washed three times with absolute ethanol and dried, was converted into carbon dioxide by the guanidinium chloride method.[4] The isotopic analysis of the carbon dioxide was made on a Hitachi RMS-I type mass-spectrometer.

The rate of the oxygen exchange of arsenate ions was calculated by means of the formula:

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

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 molar concentrations of the arsenate and water, respectively.

Results and Discussion

pH *Dependence.* In Fig. 1, log R_0 and log R are plotted against pH, where R_0 and R designate the rates of the oxygen exchange reaction between arsenate ions and solvent water without and with the addition of periodate ions, respectively. The concentration of arsenate was 0.07 M, and no inert salt was added. The concentrations of the periodate were 10^{-5} M for series

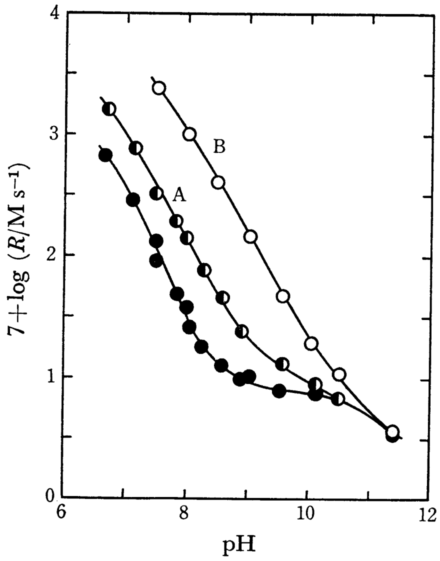

Fig. 1. The rate of oxygen exchange reaction of arsenate ions with water *versus* pH.
([As(V)]=0.07 M, I=0.2 M, 30.0 °C)
●: In the absense of periodate ions.
◐ (A): in the presence of periodate ions, [I(VII)]= 8.4×10^{-6} M.
○ (B): in the presence of periodate ions, [I(VII)]= 8.2×10^{-5} M.

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† In this paper the word "periodate" is used to signify both periodate and orthoperiodate.

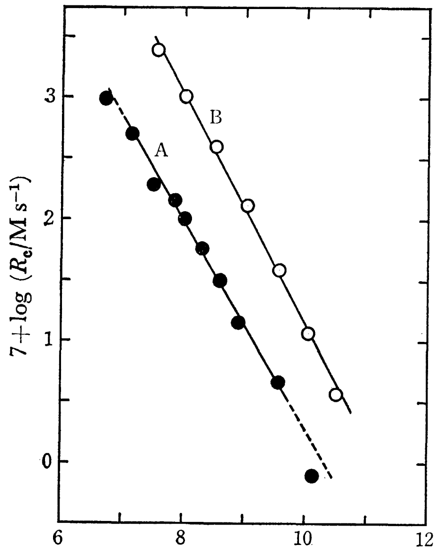

Fig. 2. pH dependence of the catalyzed portion of the exchange rate R_c.
● (A): [I(VII)]=8.4×10^{-6} M.
○ (B): [I(VII)]=8.2×10^{-5} M.

A and 10^{-4} M for series B. The catalytic effect decreases with the increasing pH value and disappears at pH 10.5 for series A and at 11.4 for series B. Even in the low concentration ratio: [I(VII)]/[As(V)]=10^{-4}, the catalytic action of periodate ions is so large as to increase the oxygen exchange rate 3.5 fold at pH 8.5.

Figure 2 shows the dependence of R_c on pH. R_c is defined as $R-R_0$ and corresponds to the catalyzed portion of the exchange reaction. The slopes of the lines passing through the plots are -0.86 ± 0.02 for series A and -0.95 ± 0.03 for series B within the pH regions 7.17—9.57 and 7.52—10.51, respectively. R_c depends upon the first power of the hydrogen ion concentration in both series. It may be inferred from these results that the acidic species of arsenate and periodate ions are more reactive. The role of hydrogen ion in the rate equation is to shift the acid dissociation equilibrium of the oxoanions in favor of the more reactive ionic species.

Dependence of the Catalytic Rate R_c on [I(VII)]. This has been studied at two pH's, 8.0 and 9.2. The concentration of periodate was varied between 3.0×10^{-5} M and 11.6×10^{-5} M (pH 8.0) and between 8.9×10^{-5} M and 44.0×10^{-5} M (pH 9.2). The plots of log R_c against log [I(VII)] are shown in Fig. 3. The slopes of the straight lines obtained by least square fits of the data are 1.03 ± 0.01 and 0.93 ± 0.07 for the pH values of 8.0 and 9.2, respectively. The log R_c: log [I(VII)] plot deviates downwards from the straight line at [I(VII)] $<3.0\times10^{-6}$ M (pH 8.0) (not shown in the figure). This is probably due to the decomposition of the periodate by a trace amount of reducing impurities which are present in the solution.

Dependence of the Catalytic Rate R_c on [As(V)]. This has been studied under the following conditions. A: pH=8.00, [I(VII)]=8.10×10^{-5} M, I(NaCl)=0.55 M, [As(V)]=0.034—0.138 M; B: pH=9.08, [I(VII)]=8.84×10^{-5} M, I(NaCl)=1.00 M, [As(V)]=0.035—0.275 M. The plots of log R_c against log [As(V)] are shown in Fig. 4. The slopes of the straight lines obtained are 0.97 ± 0.07 for A and 1.04 ± 0.11 for B.

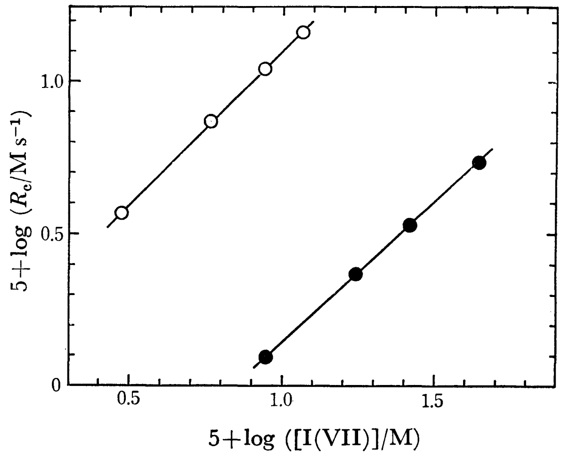

Fig. 3. Dependence of the catalytic rate R_c on [I(VII)] ([As(V)]=0.07 M, I=0.2 M)
○: pH=8.0, [I(VII)]=(3.0−11.6)×10^{-5} M.
●: pH=9.2, [I(VII)]=(8.9—44.0)×10^{-5} M.

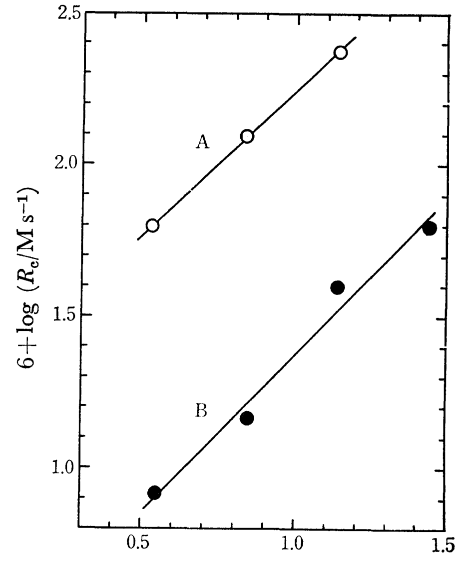

Fig. 4. Dependence of the catalytic rate R_c on [As(V)].
○ (A): pH=8.0, [I(VII)]=8.10×10^{-5} M, I(NaCl) =0.55 M, [As(V)]=0.034−0.138 M.
● (B): pH=9.08, [I(VII)]=8.84×10^{-5} M, I(NaCl) =1.0 M, [As(V)]=0.035—0.275 M

Evaluation of the Rate Constants. The catalytic reaction rate R_c may be expressed generally as the sum of the kinetic terms as follows:

$$R_c = \sum k_{ij}[\mathrm{As(V)}]_i[\mathrm{I(VII)}]_j$$

where $[\mathrm{As(V)}]_i$ denotes the various ionic species of the arsenate ions, and $[\mathrm{I(VII)}]_j$ those of the periodate ions, and k_{ij} is the rate constant of the reaction between $[\mathrm{As(V)}]_i$ and $[\mathrm{I(VII)}]_j$. In the pH range 6—11, the dominating ionic species of the arsenate are $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}, and those of the periodate are $H_4IO_6^-$, IO_4^-, and $H_3IO_6^{2-}$. The concentrations of

$H_4IO_6^-$ and IO_4^- are mutually related by the relation $K_d = a_{IO_4^-} \cdot a_{H_2O}^2 / a_{H_4IO_6^-} = 40$ [5] and are kinetically equivalent.

The rate law of the catalytic process may now be given as

$$\begin{aligned} R_c &= k_1[H_4IO_6^-][H_2AsO_4^-] + k_2[H_3IO_6^{2-}][H_2AsO_4^-] \\ &+ k_3[H_4IO_6^-][HAsO_4^{2-}] + k_4[H_3IO_6^{2-}][HAsO_4^{2-}] \\ &+ k_5[H_4IO_6^-][AsO_4^{3-}] + k_6[H_3IO_6^{2-}][AsO_4^{3-}], \end{aligned}$$

where $[H_4IO_6^-]$ is the concentration of the periodate monoanions inclusive of IO_4^-. The value of R_c becomes negligible at the pH values greater than 10.5, where the dominating ionic species are $H_3IO_6^{2-}$, $HAsO_4^{2-}$, and AsO_4^{3-}, the concentration of AsO_4^{3-} increasing with the increase in pH. If the rate constants k_4, k_5, and k_6 had significant values, the k_4-, k_5-, and k_6-terms should contribute appreciably to the catalytic rate R_c. The contributions of the k_4-, k_5-, and k_6-terms may be ignored.

The rate law can be rewritten as:

$$\frac{R_c}{[H_2AsO_4^-][H_4IO_6^-]} = k_1 + \left(k_3 + \frac{K_2'(I)}{K_2(As)} \cdot k_2\right) \frac{K_2(As)}{[H^+]} \tag{1}$$

where K_2(As) and K_2'(I) are the second ionization constant of arsenic acid and the apparent second ionization constant of periodic acid, respectively, under the conditions of the kinetic runs. The concentrations of the ionic species of the periodate were evaluated by means of the apparent ionization constants written in the forms:

$$a_{H^+}(a_{IO_4^-} + a_{H_4IO_6^-})/a_{H_5IO_6} = K_1'(I)$$

$$a_{H^+} \cdot a_{H_3IO_6^{2-}}/(a_{H_4IO_6^-} + a_{IO_4^-}) = K_2'(I)$$

The values of the ionization constants necessary to calculate the concentrations of the ionic species of the arsenate and the periodate are indicated in Table 1.

Table 1. Acid dissociation constants of arsenic acid and periodic acid under the condition of the kinetic runs: I=0.2 M, 30 °C.

As(V)	pK_2 [3]	6.56	I(VII)	pK_1'	1.34
	pK_3 [3]	11.33		pK_2'	7.87
				pK_3	11.35

$K_1'(I)(I=0)$ at 30.0 °C was obtained by interpolation of the data determined by Crouthamel *et al.*[5] to 30.0 °C, and this value was converted to $K_1'(I)(I=0.2\ M)$ using Guntelberg's equation. $K_2'(I)$ and $K_3(I)$ were evaluated similarly by using $K_2'(I)(I=0)$ and $K_3(I)(I=0.1\ M)$ determined by Buist and coworkers[6] at various temperatures.

In Fig. 5, the data corresponding to pH 6.7—9.8 in Fig. 1 are replotted according to equation 1. From the intercept of the straight line through the plots, the value of k_1 is determined to be $338 \pm 27\ M^{-1}\,s^{-1}$. From the slope of the line, the value of $[k_3 + k_2 \cdot K_2'(I)/K_2(As)]$, is obtained as $35.9 \pm 0.1\ M^{-1}\,s^{-1}$. It is impossible to evaluate the values of k_2 and k_3 separately. Taking 4.8×10^{-2} as the value of $K_2'(I)/K_2(As)$, $k_3 = 36\ M^{-1}\,s^{-1}$ and $k_2 = 750\ M^{-1}\,s^{-1}$ may be obtained as the upper limits of these constants.

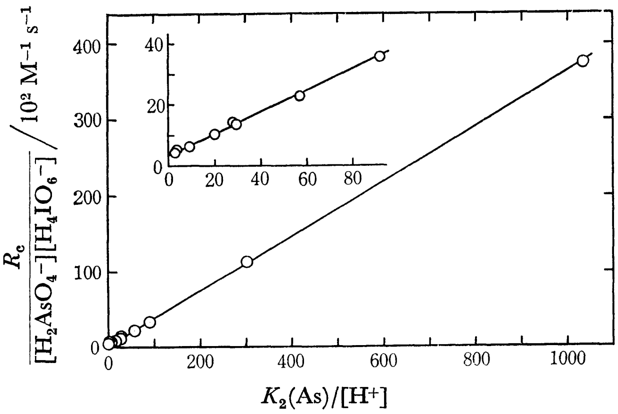

Fig. 5. $R_c/[H_2AsO_4^-][H_4IO_6^-]$ as a function of $K_2(As)/[H^+]$.

By analogy with the case of arsenious acid catalysis of the arsenate oxygen exchange,[1] it is natural to interpret the rate term $k_{ij}[As(V)]_i[I(VII)]_j$ in terms of the reversible condensation of arsenate ions with periodate ions. The possibility of general acid catalysis of the arsenate oxygen exchange by oxoanions has been ruled out in the previous paper.[1] In the present case, general acid catalysis by periodate ions is also ruled out by the fact that the value of k_1 in the rate term $k_1[H_2AsO_4^-][H_4IO_6^-]$ is larger than that of k in the rate term $k[H_2AsO_4^-][H_2AsO_4^-]$, since $H_4IO_6^-$ is weaker acid than $H_2AsO_4^-$. The hydrogen-bond association of arsenate ions with periodate ions would not affect the rate of the oxygen exchange of arsenate ions significantly.

The rate constants of the condensation reactions between anions obtained in this work are listed in Table 2, along with those obtained before.[1,3]

Table 2. The rate constants of the condensation reactions between anions

Reactions	Rate const/$M^{-1}\,s^{-1}$	Ref.
$H_2AsO_4^- + H_2AsO_4^-$	0.074	3
$H_2AsO_4^- + HAsO_4^{2-}$	0.0064	3
$H_2AsO_4^- + H_3AsO_3$	6.8	1
$H_2AsO_4^- + H_2AsO_3^-$	<7	1
$HAsO_4^{2-} + H_3AsO_3$	<0.02	1
$H_2AsO_4^- + H_4IO_6^-$	338	This work
$H_2AsO_4^- + H_3IO_6^{2-}$	<750	This work
$HAsO_4^{2-} + H_4IO_6^-$	<36	This work

For the reversible condensation process, two paths are possible. Path a): Periodate acts as the nucleophile, and arsenate as the substrate (an oxygen atom of periodate ion attacking the arsenic atom of the arsenate). Path b): Arsenate acts as the nucleophile, and periodate as the substrate (an oxygen atom of the arsenate ion attacking the iodine atom of the periodate). In both cases an identical dianion, arsenatoperiodate, is formed.

In the periodate oxidation of the organic substances, the periodate ion acts as an electrophile or a nucleophile depending on the nature of the substrate.[7,8]

By the principle of microscopic reversibility, the bond fission in the reverse reaction must occur at the same position as in the forward reaction. The result that the oxygen exchange reaction of arsenate is catalyzed by periodate ions requires the reaction to proceed *via* Path a). Path b) does not lead to the oxygen exchange of arsenate with water.

If it is assumed that Path a) and Path b) occur simultaneously in a solution containing arsenate and periodate ions, a path in which the condensation proceeds through Path b) and the hydrolysis through Path a) would be an alternative mechanism for the periodate catalysis.

Another possibility is a mechanism which involves the rapid exchange of periodate ions with solvent water[9] and subsequent condensation through Path a) and hydrolysis through Path b).

In order to see whether or not the catalytic action of the periodate ion is observed in the oxygen exchange of other oxoanions, we have studied the oxygen exchange reactions of selenic acid, phosphate ions, and chromate ions with water in the presence of periodate ions. It was found that the periodate ion has a remarkable effect on the oxygen exchange between chromate and water, the effect being greater than that on the arsenate exchange. From the results obtained so far, the rate constant for the reaction: $HCrO_4^- + H_4IO_6^- \rightleftharpoons H_3CrIO_9^{2-} + H_2O$, may be estimated to be 10^4 M^{-1} s^{-1} at 0 °C. The effect could not be found with selenic acid and phosphate ions. It is known that the reversible condensation process: $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$, plays a dominant role in the oxygen exchange of chromate ion with water,[10] while the oxygen exchange of selenic acid[11] and phosphate ions[12] does not involve the condensation mechanism. It is probable that the condensation process is responsible for the periodate catalysis.

The catalysis of the hydration of carbon dioxide by various anions has been studied by Dennard and Williams.[13] They have found that $H_4IO_6^-$ is a weak catalyst, and $H_2AsO_3^-$ is a far better catalyst than H_3AsO_3, the catalytic constant of $H_2AsO_3^-$ being 1.9×10^3 M^{-1} s^{-1} at 0 °C. These results are in contrast with those obtained for the arsenate exchange, for which H_3AsO_3 and $H_4IO_6^-$ are excellent catalysts and H_3AsO_3 is a better catalyst than $H_2AsO_3^-$. The mechanism of the oxoanion catalysis of the hydration of carbon dioxide would be different from that of the oxygen exchange of arsenate ions.

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