# The Kinetics of Oxygen Exchange between Arsenate Ions and Water. IV. Catalysis by Tellurate Ions

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*The oxygen exchange reaction between arsenate ions and water is catalyzed by the addition of a small amount of tellurate ions. The reaction has been studied at 30.0 and 14.5 °C over the pH range of 6.5– 11.4. The rate law of catalytic reaction has been found to be $R_c = k[As(V)]^n[Te(VI)]$, where $R_c$ is defined as the increase in the rate of oxygen exchange of arsenate ions by the addition of tellurate ions, and n has a value of 0.8–1.0 depending on the value of pH. The catalytic process has been interpreted in terms of the reversible condensation of arsenate ions with tellurate ions to form the arsenatotellurate ions, and the rate constant of the condensation reaction between $HAsO_4^{2-}$ and $H_5TeO_6^-$ has been estimated to be 0.22 mol dm$^{-3}$ at 30 °C.*

## Introduction

In a series of papers on oxoanion catalysis of the oxygen exchange reaction of arsenate ions [1, 2], it has been suggested that a study of the oxygen exchange reaction of an oxoanion in the presence of a catalytic amount of another oxoanion may provide a means of elucidating the interaction of these two oxoanions. In this paper, catalysis by tellurate ions will be reported as an additional example of the oxoanion catalysis.

## Experimental

### Materials

Water enriched in oxygen-18 (2 atom%) was obtained from a fractionating column. Disodium hydrogenarsenate heptahydrate (guaranteed reagent, Merck), telluric acid (guaranteed reagent, Nakarai), and all other chemicals (guaranteed reagent, JIS) were used without further purification.

### 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 telluric acid 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. At appropriate intervals, aliquots were drawn and the arsenate ion was precipitated as $BaHAsO_4 \cdot H_2O$ with barium chloride solution. The oxygen in the precipitate was converted into carbon dioxide by the guanidinium chloride method [3, 4]. The isotopic analysis of the carbon dioxide was done on a Hitachi RMS-I-type mass spectrometer.

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

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

where $O_0$, $O_t$, and $O_\infty$ 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.

### Determination of Acid Dissociation Constants of Telluric Acid

These have been determined by potentiometric titration with a glass electrode. The solution of telluric acid containing an amount of sodium chloride necessary to maintain the ionic strength of 0.2 *M\** was titrated with sodium hydroxide free from carbonate. The values obtained will be given later (Table IV).

## Results and Discussion

### pH Dependence

In Fig. 1, the logarithm of the rate of the oxygen exchange reactions between arsenate ions and water at 30 and 14.5 °C was plotted against pH. The curves

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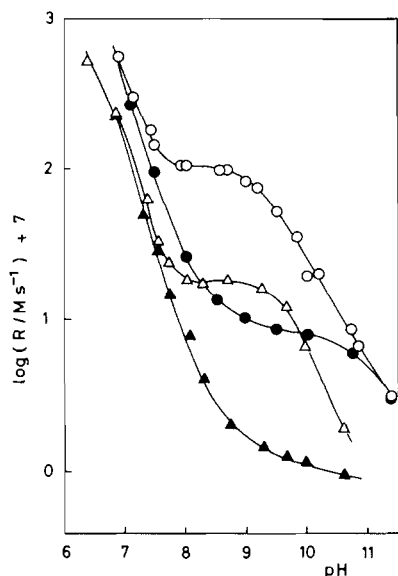*Author to whom all correspondence should be addressed.

*1 *M* = 1 mol dm$^{-3}$.

Fig. 1. The rate of the oxygen exchange reaction of arsenate ions with water against pH. ([As(V) = 0.07 $M$, I = 0.2 $M$). ●; 30.0 °C, ▲; 14.5 °C without added tellurate ions. ○; 30.0 °C, △; 14.5 °C with added tellurate ions ([Te(VI)] = 6.2 × $10^{-4} M$).
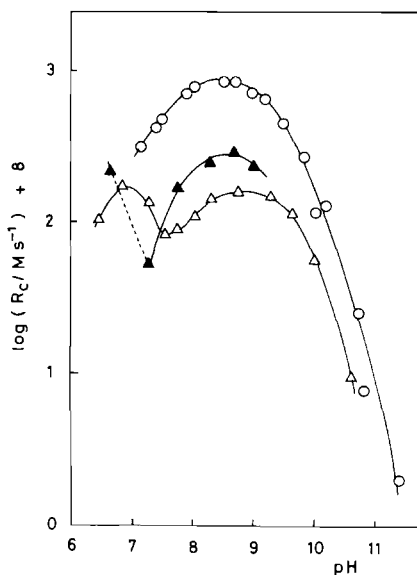


Fig. 2. pH Dependence of the catalytic rate $R_c$. ([Te(VI)] = 6.2 × $10^{-4} M$). ○; 30.0 °C, I = 0.2 $M$, △; 14.5 °C, I = 0.2 $M$, ▲; 14.5 °C, I = 0.55 $M$.

with open marks show the exchange rate with the addition of tellurate ions, R, and curves with solid marks correspond to that in the absence of tellurate ions, $R_0$. The concentration ratio of tellurate to arsenate ions was less than 0.01 ([As(V)] = 7.0 × $10^{-2} M$, [Te(VI)] = 6.2 × $10^{-4} M$), and no inert salt was added. Figure 1 shows that catalytic effect of

tellurate ions is very large in the pH region between 8 and 10.

Figure 2 shows the pH dependence of $R_c$ which is defined as R – $R_0$ and corresponds to the catalyzed portion of the oxygen exchange of arsenate. Results obtained at I = 0.55 $M$ and 14.5 °C were also shown in Fig. 2 by solid triangles. The bell-shaped pH-rate profiles are characteristic of this reaction. A curve for the rate at 30 °C has a maximum at pH 8.5, while in the curves for the rate at 14.5 °C maxima are seen at pH 6.8 and 9. This behavior makes a contrast to those shown by the arsenate oxygen exchange catalyzed by arsenious acid and periodate ions, where $R_c$ depends on the first power of the hydrogen ion concentration. Positive salt effect is observed, which is consistent with the reaction between similarly charged ions.

*Dependence of the Catalytic Rate on [Te(VI)]*

This has been studied at pH 8.02 and 10.03 ([As(V)] = 0.07 $M$, I = 0.2 $M$, 30 °C). The concentration of tellurate was varied from 1.9 × $10^{-4}$ $M$ to 6.1 × $10^{-4}$ $M$ at pH 8.02 and to 8.1 × $10^{-4}$ $M$ at pH 10.03. Plots of log $R_c$ against log [Te(VI)] (Fig. 3) yield straight lines with slopes of 1.09 ± 0.05 and 0.97 ± 0.05 for the pH values of 8.02 and 10.03, respectively. The catalytic rate is first order with respect to [Te(VI)].
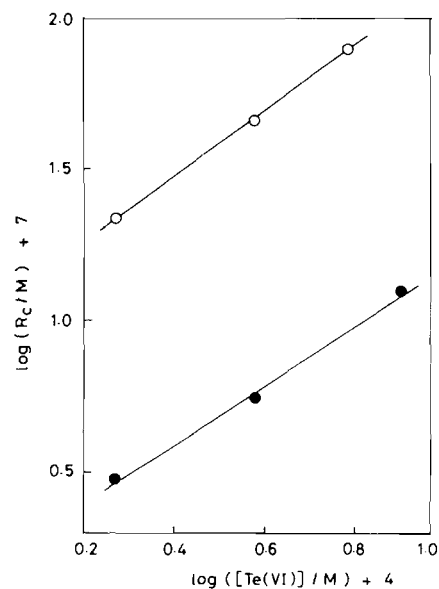


Fig. 3. Dependence of the catalytic rate $R_c$ on [Te(VI)]. ([As(V)] = 0.07 $M$, I = 0.2 $M$, 30.0 °C). ○; pH 8.02, [Te(VI)] = (1.9–6.1) × $10^{-4}$ $M$, ●; pH 10.03, [Te(VI)] = (1.9–8.1) × $10^{-4} M$.

*Dependence of the Catalytic Rate, $R_c$ on [As(V)]*

This has been studied at two pH's for both 30 and 14.5 °C. The plots of log $R_c$ against log [As(V)] shown in Fig. 4 gave straight lines, A, B, C, and D.
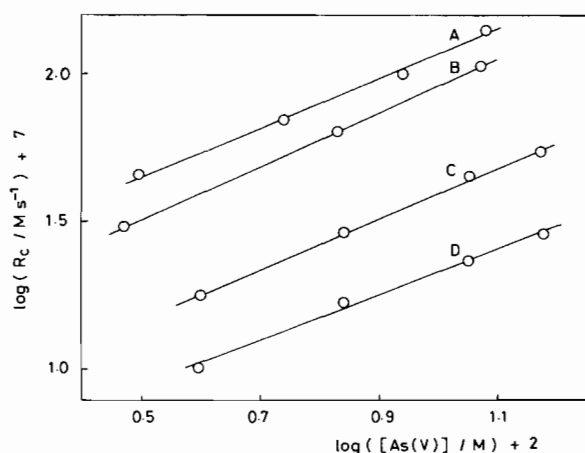
Fig. 4. Dependence of the catalytic rate $R_c$ on [As(V)]. (I = 0.55 $M$, [As(V)] = (3–15) × $10^{-2}$ $M$). A; 30.0 °C, pH 7.51, [Te(VI)] = 6.3 × $10^{-4}$ $M$, B; 30.0 °C, pH 8.47, [Te(VI)] = 3.0 × $10^{-4}$ $M$, C; 14.5 °C, pH 8.72, [Te(VI)] = 6.3 × $10^{-4}$ $M$, D; 14.5 °C, pH 7.77, [Te(VI)] = 6.3 × $10^{-4}$ $M$.

The slope of each line was obtained as follows: A; 0.84 ± 0.03 (30 °C, pH 7.51), B; 0.92 ± 0.01 (30 °C, pH 8.47), C; 0.85 ± 0.03 (14.5 °C, pH 8.72), and D; 0.77 ± 0.05 (14.5 °C, pH 7.77). In these experiments, ionic strength was adjusted to 0.55 $M$ by sodium chloride, and [Te(VI)] was 6.3 × $10^{-4}$ $M$ except for B (3.0 × $10^{-4}$ $M$), while [As(V)] was varied between 0.04 and 0.11 $M$ for A and B, and 0.04 and 0.15 $M$ for C and D. An additional experiment at 30 °C was done in the condition; pH 10.03, I = 2.0 $M$, [Te(VI)] = 6.0 × $10^{-4}$ $M$, [As(V)] = 0.04–0.27 $M$, and the slope of similar plots was obtained as 0.97 ± 0.03.

The order of the catalytic rate with respect to [As(V)] is significantly smaller than 1. The rate law of the catalytic process may be written as: $R_c$ = $k[As(V)]^n \cdot [Te(VI)]^m$, where n and m are the orders with respect to arsenate and tellurate, respectively. The values of n and m are summarized in Table I.

TABLE I. The Dependence of the Rate of Oxygen Exchange of Arsenate Ions on [As(V)] and [Te(VI)] ($R_c$ = $k[As(V)]^n$-$[Te(VI)]^m$).[a]

| $t/°C$ | pH | n | pH | m |
|---|---|---|---|---|
| 30.0 | 7.51 | 0.84 ± 0.03 | 8.02[b] | 1.09 ± 0.05 |
| 30.0 | 8.47 | 0.92 ± 0.01 | 10.04[b] | 0.97 ± 0.05 |
| 30.0 | 10.00[c] | 0.97 ± 0.03 | | |
| 14.5 | 7.77 | 0.77 ± 0.05 | | |
| 14.5 | 8.72 | 0.85 ± 0.03 | | |

[a] I = 0.55 $M$.    [b] I = 0.2 $M$.    [c] I = 2.0 $M$.

## Interpretation of the Observed Rate Law

By analogy with arsenious acid and periodate ion catalyses of the arsenate oxygen exchange [1, 2], it is natural to interpret the catalytic effect of tellurate ions in terms of the reversible condensation of arsenate ions with tellurate ions. However, as Table I shows, the order with respect to arsenate is found to be less than 1, while in the cases of arsenious acid and periodate ion catalyses, the corresponding order has been found to be almost 1. This result may be interpreted by assuming the formation of an appreciable concentration of arsenatotellurate ions, As(V)·Te(VI) (eqn. 1).

$$As(V) + Te(VI) \underset{K}{\overset{k}{\rightleftharpoons}} As(V) \cdot Te(VI) \qquad (1)$$
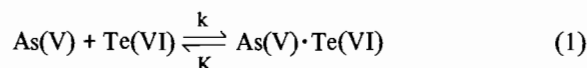
The formation of As(V)·Te(VI) species reduces the effective concentration of tellurate ions which take part in the condensation reaction with arsenate ions. The substitution of the effective concentration of tellurate ions, $[Te(VI)]_{eff}$, calculated on the above assumption into the rate law with first order dependence, $R_c$ = $k[As(V)][Te(VI)]_{eff}$, yields relation (eqn. 2);

$$R_c = \frac{k[As(V)][Te(VI)]}{1 + K[As(V)]} \qquad (2)$$

where k and K are the rate constant and the equilibrium constant of the reaction 1 respectively. Equation 2 can be rearranged as:

$$\frac{[Te(VI)]}{R_c} = \frac{K}{k} + \frac{1}{k[As(V)]} \qquad (3)$$

The plots of $[Te(VI)]/R_c$ against $1/[As(V)]$ are shown in Figs. 5 and 6. The data used for plotting are the same as those used in Fig. 4. The data of A and B
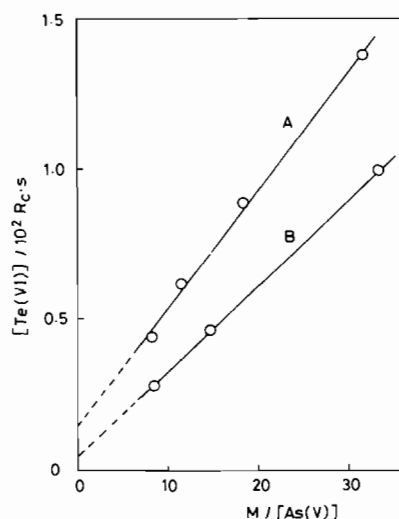


Fig. 5. $[Te(VI)]/R_c$ as a function of $1/[As(V)]$. (30.0 °C, I = 0.55 $M$). A; pH 7.51, [Te(VI)] = 6.3 × $10^{-4}$ $M$, B; pH 8.47, [Te(VI)] = 3.0 × $10^{-4}$ $M$.
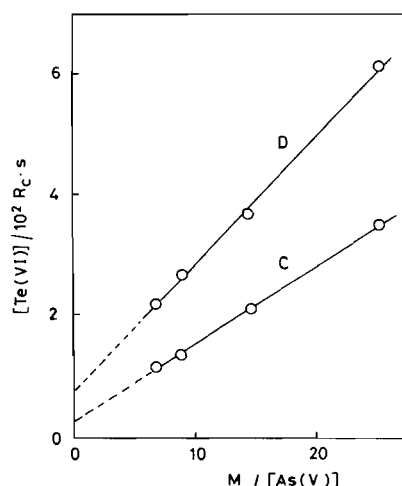
Fig. 6. $[Te(VI)]/R_c$ as a function of $1/[As(V)]$. $(14.5 \,°C, I = 0.55 \, M$, $[Te(VI)] = 6.3 \times 10^{-4} \, M)$. C; pH 8.72, D; pH 7.77.

in Fig. 5 and C and D in Fig. 6 correspond to those of A, B, C, and D in Fig. 4. The values of k and K are evaluated from the slope and intercept obtained by least squares treatment of the plots, and are shown in Table II.

TABLE II. The Rate and Equilibrium Constants of the Condensation Reaction of Arsenate Ions with Tellurate Ions $(I = 0.55 \, M)$.

$$As(V) + Te(VI) \overset{k}{\underset{K}{\rightleftharpoons}} As(V) \cdot Te(VI) + H_2O$$
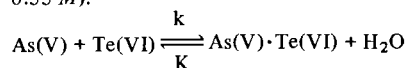
| $t/°C$ | pH | $k/M^{-1} \, s^{-1}$ | $K/M^{-1}$ |
|---|---|---|---|
| 30.0 | 7.51 | 0.22 | 2.0 |
| 30.0 | 8.47 | 0.35 | 1.6 |
| 30.0 | 10.00 | 0.011 | 1.0 |
| 14.5 | 7.77 | 0.047 | 3.5 |
| 14.5 | 8.72 | 0.078 | 2.1 |

It is seen from Table II that the values of the equilibrium constant of eqn. 1 increase with acidity. This trend is generally observed for the formation of polyanions in solution. A trial was done to obtain spectrophotometric evidence for the existence of arsenatotellurate ions in aqueous solution without any success.

Richmond *et al.* [5] have estimated a value of 0.1 for the dimerization equilibrium constant for the process:

$$H_2AsO_4^- + HAsO_4^{2-} \rightleftharpoons HAs_2O_7^{3-} + H_2O$$
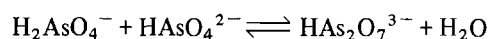
by combining their rate constant for the hydrolysis of $HAs_2O_7^{3-}$ with the dimerization of arsenate ions obtained from the result of the arsenate oxygen exchange with water [3]. The formation constants of As(V)·

Te(VI) are ten times larger than that for the pyroarsenate ion.

The temperature dependence of the rate and equilibrium of oxoanion catalysis of oxoanion exchange reaction involves the contribution from the change of the concentrations of various species of the oxoanions, due to the change of the acid dissociation of oxoanions with temperature. In this experiment, the pH of the solution was deliberately changed to keep the concentrations of the various species of the catalyst oxoanion (tellurate) constant, for example, pH 7.51 at 30 °C and pH 7.77 at 14.5 °C. This procedure also served to cancel to some extent the change of the concentrations of the ionic species of the substrate oxoanion (arsenate). The values of k and K involve the contributions from the various processes in which different kinds of ionic species of tellurate and arsenate take part. Since in the pH range between 8.47 and 8.72 most of the arsenate ions exist as $HAsO_4^{2-}$ $(pK_2 \, (30 \,°C) = 6.56, \, pK_2 \, (14.5 \,°C) = 6.60)$ and more than 90% of tellurate ions as $H_5TeO_6^-$ $(pK_1 \, (30 \,°C) = 7.29, \, pK_1 \, (14.5 \,°C) = 7.64)$, the values of k and K and the activation parameters obtained in this condition may be considered to be the approximate values for the process;

$$HAsO_4^{2-} + H_5TeO_6^- \rightleftharpoons H_4AsTeO_9^{3-} + H_2O$$
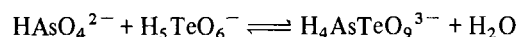
The thermodynamic and activation parameters are listed in Table III.

TABLE III. Temperature Dependence of the Rate Constant and the Equilibrium Constant of the Condensation Reaction. $(I = 0.55 \, M)$. $As(V) + Te(VI) \rightleftharpoons As(V) \cdot Te(VI) + H_2O$

| $t/°C$ | 30.0 | 14.5 | 30.0 | 14.5 |
| pH | 8.47 | 8.72 | 7.51 | 7.77 |
|---|---|---|---|---|
| $E_a/kJ \, mol^{-1}$ | 70.3 | | 73.2 | |
| $\Delta S^{\ddagger}/J \, mol^{-1} \, K^{-1}$ | -29 | | -25 | |
| $\Delta H/kJ \, mol^{-1}$ | -13 | | -26 | |
| $\Delta S/J \, mol^{-1} \, K^{-1}$ | -38 | | -79 | |

*The Evaluation of the Rate Constants*

The catalytic reaction rate, $R_c$ may be expressed generally as the sum of kinetic terms as follows:

$$R_c = \Sigma k_{ij} [As(V)]_i \cdot [Te(VI)]_j$$

where $[As(V)]_i$ denotes the concentration of the various ionic species of the arsenate ions, and $[Te(VI)]_j$ that of the tellurate ions, and $k_{ij}$ is the rate constant of the reaction between $(As(V))_i$ and $(Te(VI))_j$. In the pH range 6.5–11, the dominating ionic species are $H_2AsO_4^-$, $HAsO_4^{2-}$, and $AsO_4^{3-}$, and those of the tellurate are $H_6TeO_6$, $H_5TeO_6^-$, and $H_4TeO_6^{2-}$. The catalytic rate, $R_c$ may be expressed by the rate law:

$$R_c = k_1 [H_2AsO_4^-][H_6TeO_6] + k_2[H_2AsO_4^-][H_5TeO_6^-] + k_3[H_2AsO_4^-][H_4TeO_6^{2-}] +$$
$$+ k_4[HAsO_4^{2-}][H_6TeO_6] + k_5[HAsO_4^{2-}][H_5TeO_6^-] + k_6[HAsO_4^{2-}][H_4TeO_6^{2-}] +$$
$$+ k_7[AsO_4^{3-}][H_6TeO_6] + k_8[AsO_4^{3-}][H_5TeO_6^-] + k_9[AsO_4^{3-}][H_4TeO_6^{2-}] \qquad (4)$$

TABLE IV. The Values of Acid Dissociation Constants of Arsenic Acid and Telluric Acid at I = 0.2 $M$.

|  | 30 °C | 14.5 °C | Ref. |
|---|---|---|---|
| $pK_2(As)$ | 6.56 | 6.60 | 1 |
| $pK_3(As)$ | 11.22 | 11.31 | 3 |
| $pK_1(Te)$ | 7.29 | 7.64 | This work |
| $pK_2(Te)$ | 10.59 | 11.11 | This work |

For the analysis of the catalytic rate in terms of eqn. 4, the values of $[As(V)]_i[Te(VI)]_j$ were calculated. The values of acid dissociation constants of arsenic and telluric acids used for the calculation of individual ionic species are shown in Table IV. In this calculation, the formation of heteropolyanions between arsenate and tellurate ions and the polymerization of tellurate ions were not taken into consideration. For the polymerization of tellurate ions, the equilibrium constants are given in Table V.

TABLE V. The Dimerization Constants of Tellurate Ions.

| Reaction | log (K/$M^{-1}$) |
|---|---|
| $H_6TeO_6 + H_5TeO_6^- \rightleftharpoons H_9Te_2O_{11}^- + H_2O$ | 0.97 |
| $H_5TeO_6^- + H_5TeO_6^- \rightleftharpoons H_8Te_2O_{11}^{2-} + H_2O$ | 1.13 |
| $H_5TeO_6^- + H_4TeO_6^{2-} \rightleftharpoons H_7Te_2O_{11}^{3-} + H_2O$ | 2.15 |

These constants were calculated in terms of the stability constants at I(KCl) = 1 $M$ and 25 °C by Kaehler *et al.* [6] and acid dissociation constants of telluric acid. These constants show that the polymerization of tellurate ions becomes more extensive in alkaline region, but the amount of polymerized species was estimated to be only 2% of total tellurate ions even at pH 10. The calculated values of $[As(V)]_i[Te(VI)]_j$ for 30 °C are shown in Fig. 7 ($[As(V)] = 7 \times 10^{-2}$, $[Te(VI)] = 6 \times 10^{-4}$), where a number of curve corresponds to that of rate term in eqn. 4. The values for the curves 2 and 8 are magnified 10 times, and those for $k_3$ and $k_7$ are omitted because of their smallness ($[H_2AsO_4^-]\cdot[H_4TeO_6^{2-}] = [AsO_4^{3-}][H_6TeO_6] < 5 \times 10^{-9}$).

The similarity of curve 5 to the pH-rate profile in Fig. 2 suggests that $k_5$-term should contribute dominantly to the catalytic rate, $R_c$. If $k_6$, $k_8$, and $k_9$ in eqn. 4 had significant values, the contributions of these terms to $R_c$ should be appreciable in the pH region greater than 9 and become important with increasing pH. Figure 2 shows that is not the case.
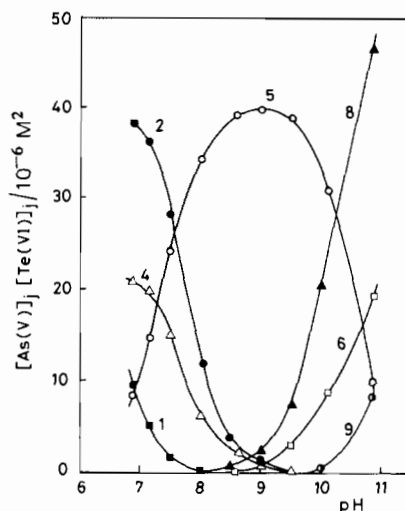


Fig. 7. The concentration product of the various kinds of ionic species of arsenate and tellurate ions, $[As(V)]_i \cdot [Te(VI)]_j$ against pH. (30.0 °C, I = 0.2 $M$, $[As(V)] = 0.07 M$, $[Te(VI)] = 6 \times 10^{-4} M$).

Therefore, $k_6$-, $k_8$-, and $k_9$- terms may be ignored. As $k_2$- and $k_4$- terms and $k_3$-, $k_5$- and $k_7$- terms are kinetically equivalent, eqn. 4 may be rewritten as:

$$R_c = k_1[H_2AsO_4^-][H_6TeO_6] + \left(k_4 + k_2 \frac{K_1(Te)}{K_2(As)}\right) \times$$

$$[HAsO_4^{2-}][H_6TeO_6] + \left(k_5 + k_3 \frac{K_2(Te)}{K_2(As)} + \right.$$

$$\left. + k_7 \frac{K_3(As)}{K_1(Te)}\right)[HAsO_4^{2-}][H_5TeO_6^-] \qquad (5)$$

where $K_1(Te)$ and $K_2(Te)$ are the first and the second dissociation constants of the telluric acid, and $K_2(As)$ and $K_3(As)$ are the second and the third dissociation constant of the arsenic acid. As $K_2(Te)/K_2(As)$ and $K_3(As)/K_1(Te)$ have order of magnitude of $10^{-4}$--$10^{-5}$, the constant in the parentheses of the last term in eqn. 5 may be equated to $k_5$.

The rate constants of the equation thus simplified were evaluated by applying the least squares treatment to the values of $R_c$ for 30 °C and 14.5 °C and the values obtained were shown in Table VI. The values of $k_5$ at both temperatures agree satisfactorily with values of k at pH 8.47 (30 °C) and 8.72 (14.5 °C) shown in Table II. The $k_1$ value at 30 °C was obtained as a very small negative value. In an acidic region, the condensation mechanism between two $H_2AsO_4^-$ ions becomes very important for arsenate oxygen ex-
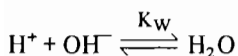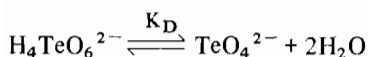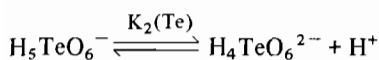
TABLE VI. Rate Constants of the Condensation Reactions between Arsenate and Tellurate Ions.

| $t/°C$ | pH | $k_1/M^{-1} s^{-1}$ | $\left(k_4 + k_2 \dfrac{K_1(Te)}{K_2(Te)}\right)/M^{-1} s^{-1}$ | $k_5/M^{-1} s^{-1}$ |
|---|---|---|---|---|
| 30 | 7.1–8.5 | | $0.065_6$ | $0.21_9$ |
| 14.5 | 6.8–9.3 | 0.12 | $0.0022_4$ | $0.038_2$ |

change. In order to detect any catalytic process between arsenate and tellurate ions in such pH region, the rate constant for the process must be significantly larger than that for the condensation between $H_2AsO_4^-$ ions (0.074 $M^{-1} s^{-1}$ at 30 °C [3]), because [As(V)] is about a hundred times larger than [Te(VI)] in our experimental conditions.

By using these rate constants, the observed values of $R_c$ at pH values smaller than 8.5 (30 °C) or 9.3 (14.5 °C) can be reproduced satisfactorily, except for a value at pH 6.4 and 14.5 °C. The calculated value for this point is larger than the observed one, and could not reproduce the first maximum found in the rate curve at 14.5 °C (Fig. 2). In the acidic region both the arsenate oxygen exchange rates with and without tellurate ions become very large, and the catalytic rate, $R_c$, obtained as a small difference between them, may involve some experimental error, which makes it difficult to analyse in detail. Furthermore, the same calculation led to a very large positive deviation of the calculated $R_c$ from the observed one in the region of pH greater than the value cited above. For instance, $R_c$ calculated is 2 and 6 times larger than $R_c$ observed at 9.5 and 10 respectively (30 °C).

As a possible explanation of the present result, it is assumed that the dehydrated species, $TeO_4^{2-}$, may be produced from $H_5TeO_6^-$ with the aid of $OH^-$ by the following equation;

$$H_5TeO_6^- \overset{K_2(Te)}{\rightleftharpoons} H_4TeO_6^{2-} + H^+$$

$$H_4TeO_6^{2-} \overset{K_D}{\rightleftharpoons} TeO_4^{2-} + 2H_2O$$

$$H^+ + OH^- \overset{K_W}{\rightleftharpoons} H_2O$$

and that $TeO_4^{2-}$ is inactive for the condensation reaction with arsenate ions. $H_4TeO_4^{2-}$ is also inactive for the reaction as described above. Thus, the effective concentration may be calculated as:

$$[H_5TeO_6^-]_{eff} = \dfrac{[H_5TeO_6^-]}{1 + \dfrac{K_D \cdot K_2(Te) \cdot [OH^-]}{K_W}} \quad (6)$$

If the observed deviation of $R_c$ was to be attributed entirely to the decrease in the effective concentration

of $H_5TeO_6^-$, the dehydration constant of $H_4TeO_6^{2-}$, $K_D$, should have the value of 10 from the kinetic results at pH 9.5 and 10 (30 °C) in terms of the relation 6.

Ellison *et al.* [7] have studied the glycol–tellurate complex formation reaction and to explain their rate law: rate = $k[H_5TeO_6^-][OH^-][glycol]$, they have assumed the formation of $TeO_4^{2-}$ prior to the rate determining step. In their complex formation reaction, $TeO_4^{2-}$ ion may react as a reactive intermediate. Although there is no evidence for the existence of $TeO_4^{2-}$ [8], they considered it possible that this species is present in such small concentrations that it cannot be detected by the usual methods.

The analogous equilibrium constant for the dehydration reaction,

$$H_4IO_6^- \rightleftharpoons IO_4^- + 2H_2O$$
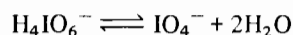
has been found to be 40 at 25 °C by Crouthamel *et al.* [9]. The value of 10 for the dehydration of $H_4TeO_6^{2-}$ seems reasonable.

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

TABLE VII. The Rate Constants of the Condensation Reactions between Anions at 30 °C.

| Reaction | Rate Const/$M^{-1} s^{-1}$ | Ref. |
|---|---|---|
| $H_2AsO_4^- + H_2AsO_4^- \longrightarrow$ | 0.074 | 3 |
| $H_2AsO_4^- + HAsO_4^{2-} \longrightarrow$ | 0.0064 | 3 |
| $H_2AsO_4^- + H_3AsO_3 \longrightarrow$ | 6.8 | 1 |
| $HAsO_4^{2-} + H_3AsO_3 \longrightarrow$ | <0.02 | 1 |
| $H_2AsO_4^- + H_4IO_6^- \longrightarrow$ | 338 | 2 |
| $HAsO_4^{2-} + H_4IO_6^- \longrightarrow$ | <36 | 2 |
| $H_2AsO_4^- + H_6TeO_6 \longrightarrow$ | 0.12(14.5 °C) | This work |
| $HAsO_4^{2-} + H_6TeO_6 \longrightarrow$ | <0.066 | This work |
| $HAsO_4^{2-} + H_5TeO_6^- \longrightarrow$ | 0.22 | This work |

As compared to other oxoanions, the catalytic effect is not large. However, it is worth noting that $H_5TeO_6^-$ is at least 3 times more reactive than $H_6TeO_6$ towards the $HAsO_4^{2-}$ ion. This trend has been also found in the rapid oxygen exchange reac-

tion of tellurate ions with water by Luz and Pecht [10]. They have expressed the rate law as: $R = k_T[H_6TeO_6] + k_T^-[H_5TeO_6^-]$, and proposed the following dehydration mechanism for the oxygen exchange of the tellurate ions;

$$H_6TeO_6 \overset{k_T}{\rightleftharpoons} H_4TeO_5 + H_2O$$

$$H_5TeO_6^- \overset{k_T^-}{\rightleftharpoons} H_3TeO_5^- + H_2O$$
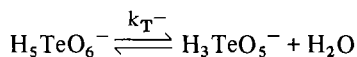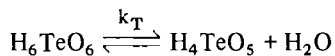
with the rate constant, $k_T = 2.3 \times 10^{-3} \text{ s}^{-1}$ and $k_T^- = 58 \text{ s}^{-1}$. Thus, the reactivity of $H_5TeO_6^-$ is larger than that of $H_6TeO_6$ by three orders of magnitude. As pointed out by Ellison [7], the fact that the reactions including tellurate ions are base-catalyzed is somewhat surprising, because most oxoanion reactions are acid-catalyzed.

In the mechanistic explanation of catalytic effect of tellurate ions on the arsenate oxygen exchange in terms of the rapid reversible formation of arsenato-tellurate ion, it is probable that because of the rapid rate of Te—O bond fission [10], the substitution occurs at both arsenic and tellurium centers as assumed in the discussion of the catalytic effect by periodate ions on the same reaction [2].

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