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Kinetic Studies of the Oxygen Exchange of Chromate and Arsenate Ions with Water.
Catalysis by Tellurate and Tellurite Ions

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The oxygen exchange reaction of the chromate ions with water is catalyzed by the tellurate and tellurite ions. The catalytic reaction rate (R_C), which is defined as the increase in the rate of the chromate-oxygen exchange upon the addition of Te(VI) or Te(IV), was studied by an ^{18}O tracer method. The catalytic process has been interpreted in terms of the rapid reversible condensation of the Cr(VI) with Te(VI) or Te(IV) species to form hetero-poly anions. As exemplified for the Cr(VI)–Te(VI) reaction system, the rate law is given as the sum of kinetic terms: $R_C = \sum k_{ij}[\mathrm{Cr(VI)}]_i \times [\mathrm{Te(VI)}]_j$ where $[\mathrm{Cr(VI)}]_i$ and $[\mathrm{Te(VI)}]_j$ denote the concentration of the various ionic species of the chromate and tellurate ions, respectively, and k_{ij} is the rate constant of the elementary reaction between $(\mathrm{Cr(VI)})_i$ and $(\mathrm{Te(VI)})_j$. The catalytic rates were analyzed according to the rate law in order to obtain the rate constants k_{ij}. The catalytic reaction system As(V)–Te(IV) was also studied. The values of k_{ij} obtained for various catalytic systems were compared with each other.

It has been found that the oxygen exchange reaction of arsenate ions with water is strongly accelerated by the addition of a small amount of another oxoanion. Kinetic studies concerning the catalytic oxygen exchange of arsenate by arsenious acid,[1] periodate ions,[2] and tellurate ions[3] have been reported. In a series of papers, the catalytic effect of an oxoanion was interpreted in terms of a reversible condensation of arsenate ions with the oxoanions to form hetero-polyanions. It has been suggested that a study of the oxoanion in the presence of a catalytic amount of another oxoanion may provide a means of elucidating the interaction of these two oxoanions.

The same type of the catalytic effect has also been observed for the oxygen exchange reaction between chromate ions and water; in a preliminary study, a small amount of arsenious acid, tellurate, tellurite, and periodate ions were found to accelerate the reaction significantly. As a preliminary effort to a study of the interaction of chromate ions with another oxoanion, we have studied the oxygen exchange of chromate ions with water in the pH range between 7 and 12 by using the ^{18}O-tracer method.[4] In previous papers,[5,6] we reported on the kinetics of the oxygen exchange of chromate ions catalyzed by arsenious acid and periodate ions. In this paper we report on a study of the interaction of chromate ions with tellurate and tellurite ions by the oxygen exchange between chromate ions and water in the presence of a catalytic amount of the tellurate and tellurite, using ^{18}O tracer method. Additionally, a kinetic result concerning the oxygen exchange of arsenate ions with water catalyzed by tellurite ions will also 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. The sodium chromate tetrahydrate, disodium hydrogenarsenate heptahydrate, and sodium salts of tellurate and tellurite (guaranteed reagent, Merck) were used without further purification.

Procedure. ^{18}O tracer method was used for studying the oxygen exchange reactions of both chromate and arsenate ions with solvent water. Here, the procedure used for the chromate exchange will be described. The exchange reaction was started by dissolving a weighed amount of the enriched sodium chromate in water of normal isotopic composition and by adding a small amount of a stock solution of sodium tellurate or sodium tellurite. Sodium chromate enriched in oxygen-18 was prepared by the exchange reaction of sodium chromate with $H_2{}^{18}O$ at 100 °C for 2 h. The pH of the solution was fixed by the addition of a measured quantity of either a solution of hydrochloric acid or sodium hydroxide, and measured with a Hitachi–Horiba pH Meter (Model F-7) or with Radiometer PHM 26 pH-Meter. Ionic strength of the solution was adjusted to 1 mol dm^{-3} by adding NaCl. At intervals aliquots of the reacting solution were drawn out, and the reaction was quenched by precipitating the chromate ions as $BaCrO_4$ with a barium chloride solution. The precipitate, after being washed three times with absolute ethanol and dried, was converted into carbon dioxide by a guanidium chloride method.[7] An isotopic analysis of the carbon dioxide was carried out on a Hitachi RMS-I type mass-spectrometer.

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

$$R = \frac{1}{t}\frac{[\mathrm{Cr(VI)}][\mathrm{H_2O}]}{4[\mathrm{Cr(VI)}]+[\mathrm{H_2O}]}\ln(1-F), \quad F = \frac{O_0 - O_t}{O_0 - O_\infty}, \tag{1}$$

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 [Cr(VI)] and [H_2O] are the molar concentrations of the chromate and water, respectively.

The procedures for the arsenate-oxygen exchange were essentially the same as those for the chromate, and have been described precisely in earlier papers.[8,9]

The catalytic oxygen exchange rate (R_C) is defined as ($R-R_0$), where R and R_0 are the oxygen exchange rates with and without the addition of another oxoanion (tellurate or tellurite ion), respectively.

Estimation of the Concentration of Ionic Species. For the rate analysis of the kinetic results, it is necessary to know the ionic equilibria under the kinetic runs. The total concentrations of chromate and tellurate under these condition are given in Eqs. 2 and 3, respectively.

$$\begin{aligned}[\mathrm{Te(VI)}] = {} & [\mathrm{H_6TeO_6}] + [\mathrm{H_5TeO_6}^-] + [\mathrm{H_4TeO_6}^{2-}] \\ & +2\left([\mathrm{H_9Te_2O_{11}}^-] + [\mathrm{H_8Te_2O_{11}}^{2-}]\right. \\ & \left. +[\mathrm{H_7Te_2O_{11}}^{3-}]\right) \end{aligned} \tag{2}$$

$$[\mathrm{Cr(VI)}] = [\mathrm{HCrO_4}^-] + [\mathrm{CrO_4}^{2-}] + 2[\mathrm{Cr_2O_7}^{2-}] \tag{3}$$

The values of the acid dissociation constants and the dimerization constants necessary to calculate the concentrations of the ionic species of the chromate and the tellurate are listed in Table 1. The dimerization constants between various species of tellurate were calculated in terms of the stability constants[10] and the acid dissociation constants of telluric acid.[10,11] The concentrations of the ionic species of chromate were evaluated as described earlier.[4]

Results

I. Catalytic Oxygen Exchange of Chromate Ions by Tellurate Ions. pH Dependence of the Exchange Rate. The rates of the oxygen exchange reaction between chromate ions and water with the added tellurate ions (R) were measured in the pH region between 7 and 12 (25 °C, I(NaCl)=1.0 mol dm^{-3}). The concentrations of the chromate and tellurate are 0.075 and 7.5×10^{-4} mol dm^{-3}, respectively ([Te(VI)]/[Cr(VI)]=10^{-2}). The oxygen exchange rates without the added tellurate (R_0) at 25 °C were measured in earlier work.[4] In Fig. 1, $\log R$ and $\log R_0$ are plotted against pH (R: A(⊙); R_0: B(●)). The symbol R^* in an ordinate in the figure represents collectively the oxygen exchange rates; R, R_0, and R_C: R^* designates R for A and R_0 for B. In the pH region greater than 9, the catalytic effect (R/R_0) is so large as to increase the oxygen exchange rate 204 fold (pH 8.56), 2.4×10^3 fold (pH 10.2) and 1.1×10^3 fold (pH 11.2). At a pH value above 9, R_C (=$R-R_0$) can therefore be taken as equal to R. The values of $\log R_C$ are plotted against pH in Fig. 1 (plots C (○), R^*=R_C). It is seen that the R_C value does not change appreciably with pH in the pH range from 7.2 to 10.5, while at a pH above 10.5, it decreases with increasing pH.

Dependence of the Catalytic Oxygen Exchange Rate R_C on [Te(VI)]. The order of the reaction with respect to [Te(VI)] was determined at pH 7.70 (A) and 10.57 (B) (25 °C, [Cr(VI)]=0.069 mol dm^{-3}, I(NaCl)=1.0 mol dm^{-3}). The concentrations of the added tellurate ([Te(VI)]/10^{-4} mol dm^{-3}) were 1.47, 4.75, and 9.31 for A and 1.58, 3.16, and 5.17 for B. The R_0 values were obtained under the same conditions as used for R but [Te(VI)]=0. In Fig. 2, plots of $\log R_C$ (=$R-R_0$) against log [Te(VI)] are shown. The slope of the straight line is 0.84±0.05 for A and 0.89±0.03 for B.

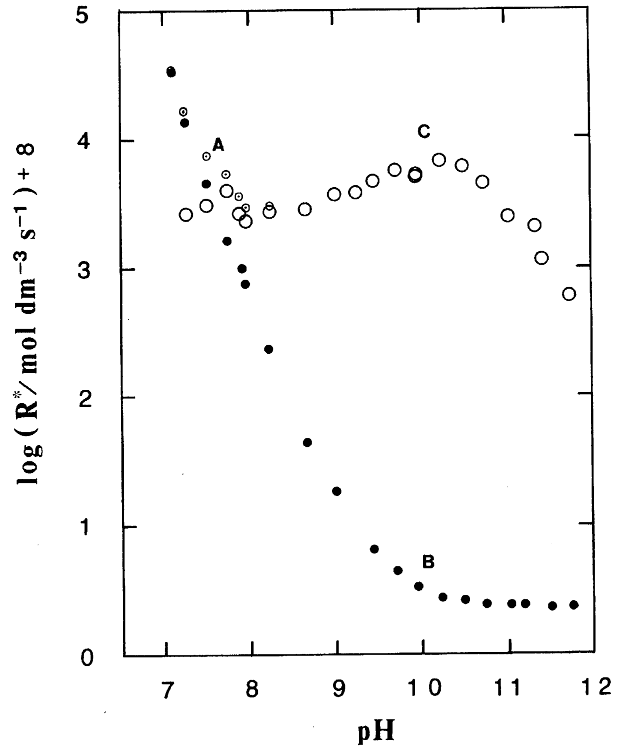

Fig. 1. pH dependence of the oxygen exchange rate of chromate with water. Catalysis by tellurate ion. (25 °C, [Cr(VI)]=0.075 mol dm^{-3}, I(NaCl)=1.0 mol dm^{-3}). A(⊙): Exchange rate (R) with the added tellurate ([Te(VI)]=7.5×10^{-4} mol dm^{-3}); B(●): Exchange rate (R_0) without the added tellurate; C(○): Catalytic exchange rate (R_C=$R-R_0$). The symbol R^* in an ordinate in the figure represents collectively the oxygen exchange rates; R, R_0, and R_C. The values of R_0 are taken from Ref. 4.

Dependence of the Catalytic Rate on [Cr(VI)]. The dependence was studied under the following conditions. A: pH 7.7, [Cr(VI)]=0.040—0.139 mol dm^{-3}, [Te(VI)]=4.75×10^{-4} mol dm^{-3} for R and [Te(VI)]=0 for R_0; B: pH=10.57, [Cr(VI)]=0.035−0.147 mol dm^{-3}, [Te(VI)]=1.57×10^{-4} mol dm^{-3} for R and [Te(VI)]=0 for R_0 (I(NaCl)=1.0 mol dm^{-3}, 25 °C). Each value of R_C at fixed [Cr(VI)] was obtained after subtracting R_0 from R. Plots of $\log R_C$ against log [Cr(VI)] are shown in Fig. 3a. The slopes of the straight lines were obtained to be 0.77±0.07 for A and 0.95±0.03 for B. By analogy with other catalytic oxygen exchanges,[1—3,5] it is natural to interpret the catalytic effect of tellurate ions in terms of the reversible condensation of chromate ions with tellurate ions. The fact that the order of the reaction with respect to chromate was found to be less than 1 may be interpreted by assuming the formation of an appreciable concentration of chromatotellurate ions, Cr(VI)·Te(VI),

Table 1. The Acid Dissociation Constants and Dimerization Constants of Chromate and Tellurate under the Condition of the Kinetic Runs (25 °C, I(NaCl)=1.0 mol dm^{-3} (=M))

Reactions	K	log$K$	Refs.
$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$	K_2(Cr)	−5.73	4
$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$	K_{22}(Cr)	2.14	4
$H_6TeO_6 \rightleftharpoons H_5TeO_6^- + H^+$	K_1(Te(VI))	−7.28	10
$H_5TeO_6^- \rightleftharpoons H_4TeO_6^{2-} + H^+$	K_2(Te(VI))	−10.45	11
$H_6TeO_6 + H_5TeO_6^- \rightleftharpoons H_9Te_2O_{11}^- + H_2O$	K_{21}(Te(VI))	1.04	
$H_5TeO_6^- + H_5TeO_6^- \rightleftharpoons H_8Te_2O_{11}^{2-} + H_2O$	K_{22}(Te(VI))	1.28	
$H_5TeO_6^- + H_4TeO_6^{2-} \rightleftharpoons H_7Te_2O_{11}^{3-} + H_2O$	K_{23}(Te(VI))	2.31	

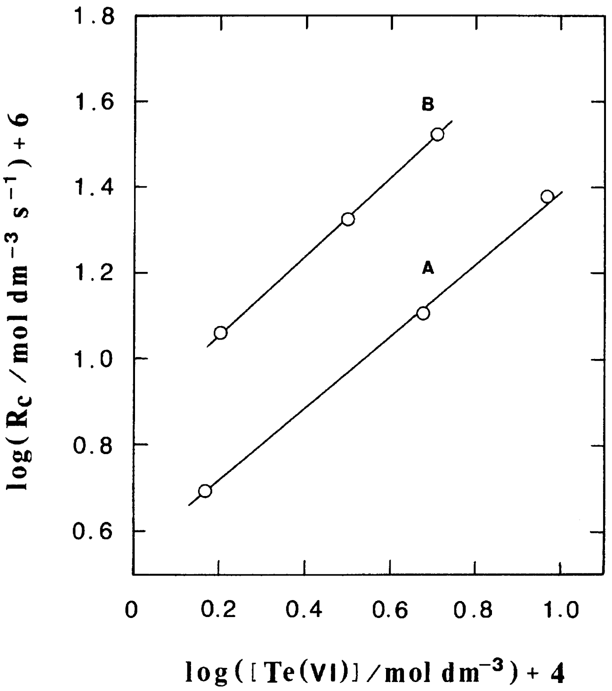

Fig. 2. Dependence of the catalytic oxygen exchange rate R_C on [Te(VI)]. (25 °C, [Cr(VI)]=0.069 mol dm^{-3}, I(NaCl)= 1.0 mol dm^{-3}). A: pH=7.70; B: pH=10.57.

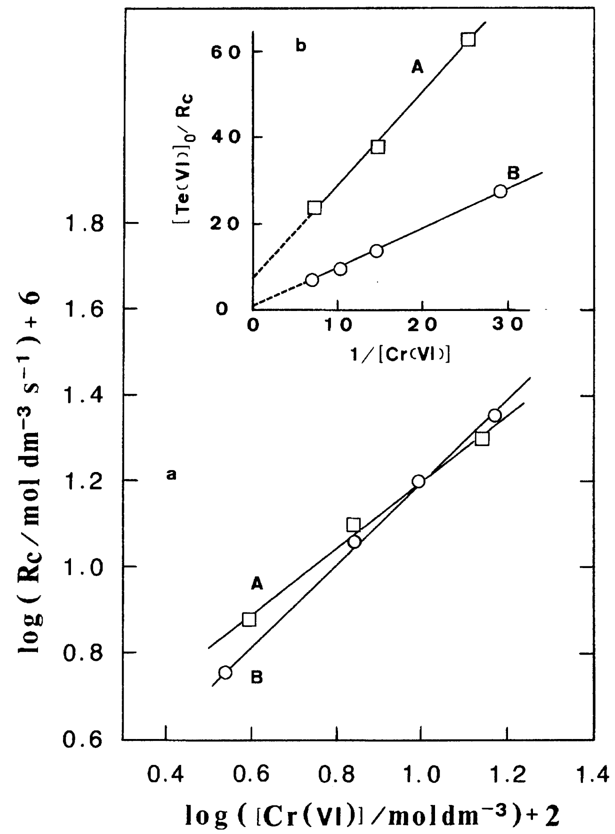

Fig. 3. a) Dependence of the catalytic oxygen exchange rate (R_C) on [Cr(VI)]. Catalysis by tellurate. (25 °C, I(NaCl) = 1.0 mol dm^{-3}). A(□): pH = 7.70, [Te(VI)]=4.75×10^{-4} mol dm^{-3}, B(○): pH=10.57, [Te(VI)]= 1.57×10^{-4} mol dm^{-3}. b) Plots of [Te(VI)]$_0$/R_C vs. 1/[Cr(VI)] according to Eq. 6. The data in Fig. 3a were used.

$$\mathrm{Cr(VI)} + \mathrm{Te(VI)} \underset{K}{\overset{k}{\rightleftharpoons}} \mathrm{Cr(VI){\cdot}Te(VI)} + \mathrm{H_2O}. \tag{4}$$

The formation of the Cr(VI)•Te(VI) species reduces the effective concentration of tellurate ions which take part in the condensation reaction with the chromate ions. The effective concentration of tellurate ions, [Te(VI)]$_{\rm eff}$, can be calculated based on the above assumption, using the relation : [Te(VI)]$_0$ = [Te(VI)]$_{\rm eff}$ + K[Cr(VI)][Te(VI)]$_{\rm eff}$ ([Te(VI)]$_0$ = total concentration of tellurate). Substitution of this relation into the rate law with first order dependence, R_C=k[Cr(VI)][Te(VI)]$_{\rm eff}$, gives

$$R_C = \frac{k[\mathrm{Cr(VI)}]\,[\mathrm{Te(VI)}]_0}{1 + K[\mathrm{Cr(VI)}]}, \tag{5}$$

where k and K are the rate constant and the equilibrium constant of reaction 4, respectively. Equation 5 can be rearranged as

$$\frac{[\mathrm{Te(VI)}]_0}{R_C} = \frac{K}{k} + \frac{1}{k[\mathrm{Cr(VI)}]}. \tag{6}$$

Plots of [Te(VI)]$_0$/R_C against 1/[Cr(VI)] are shown in Fig. 3b. For plotting, the same data as shown in Fig. 3a were used. The values of k (mol^{-1} dm^3 s^{-1}) and K (mol^{-1} dm^3) were obtained to be 0.46 and 3.30 for A (pH 7.70) and 1.07 and 0.48 for B (pH 10.6), respectively.

Temperature Dependence of the Catalytic Rate. The catalytic rate was measured at the temperature range between 0 and 35 °C. ([Cr(VI)] = 0.075 mol dm^{-3}, [Te(VI)] = 7.4×10^{-4} mol dm^{-3}, and pH = 9.45). The values of k (=R_C/[Cr(VI)][Te(VI)]) (mol^{-1} dm^3 s^{-1}) obtained are : 0.0746 (0 °C); 0.834 (25 °C); 2.207 (35 °C). The value of the activation energy was estimated to be 68.5±4.5 kJ mol^{-1} for the catalytic rate constant, which is significantly smaller than that of 98.9±1.0 kJ mol^{-1} for R_0. The activation entropy of k was obtained to be −24.9 J mol^{-1} K^{-1}.

II. Catalytic Oxygen Exchange by Tellurite Ions (Te(IV)). a. Catalytic Oxygen Exchange of Chromate by Tellurite.

pH Dependence of the Exchange Rate. The rates of the oxygen exchange reaction between chromate ions and water with the added tellurite ions (R) were measured in the pH region between 7.8 and 11.5 and at 25 °C. The concentrations of the chromate and tellurite are 0.070 and 1.4×10^{-4} mol dm^{-3}, respectively (I=0.2 mol dm^{-3}). The experimental conditions for R_0 were the same as those used for R but [Te(IV)]=0. In Fig. 4, $\log R$ (⊙) and $\log R_0$ (•) are plotted against pH (25 °C). The catalytic effect (R/R_0) is 5.5 (pH=7.9), 19 (pH=8.7), 59 (pH=9.2), and 8.4 (pH=10.2). The plot of $\log R_C$ (=$R-R_0$) against pH (Fig. 4, ○) gives a straight line with a slope of −1.14±0.02.

Dependence of the Catalytic Oxygen Exchange Rate R_C on [Te(IV)]. The dependence of R_C on [Te(IV)] was determined at pH 8.2 (25 °C, [Cr(VI)]=0.070 mol dm^{-3}). The values of (R_C/10^{-5} mol dm^{-3}) at the tellurite concentrations ([Te(IV)]/10^{-4} mol dm^{-3}) of 0.711, 1.42, and 2.82 were obtained to be 3.77, 7.59, and 14.6, respectively. The order of the reaction with respect to [Te(IV)] was found as 0.98±0.01.

Dependence of the Catalytic Rate on [Cr(VI)]. The dependence was studied under the condition: [Cr(VI)]= 0.069—0.200 mol dm^{-3}. [Te(IV)]=1.4×10^{-4} mol dm^{-3} for R and=0 for R_0, and at pH=8.2 (I(NaCl)=1.0 mol dm^{-3}, 25 °C). Plots of $\log R_C$(=$R-R_0$) against log [Cr(VI)] are shown in Fig. 5a. The slopes of the straight lines were obtained to be 0.89±0.05. The order of the catalytic rate R_C with respect to [Cr(VI)] was again found to be less than unity. The data in Fig. 5a were treated by the same procedure as used for Te(VI) (Eq. 6). Plots of [Te(IV)]$_0$/R_C against 1/[Cr(VI)] are shown in Fig. 5b. The values of k and K were obtained to be 5.9 mol^{-1} dm^3 s^{-1} and 1.23 mol^{-1} dm^3, respectively.

b. Catalytic Oxygen Exchange of Arsenate by Tellurite.

pH Dependence of the Exchange Rate. The rates of the oxygen exchange reaction between arsenate ions and water with the added tellurite ions were measured in the pH region from 7.2 to 10.0 and at 30 °C. The arsenate concentration, [As(V)] is 0.071 mol dm^{-3} (I=0.2 mol dm^{-3}) and the tellu-

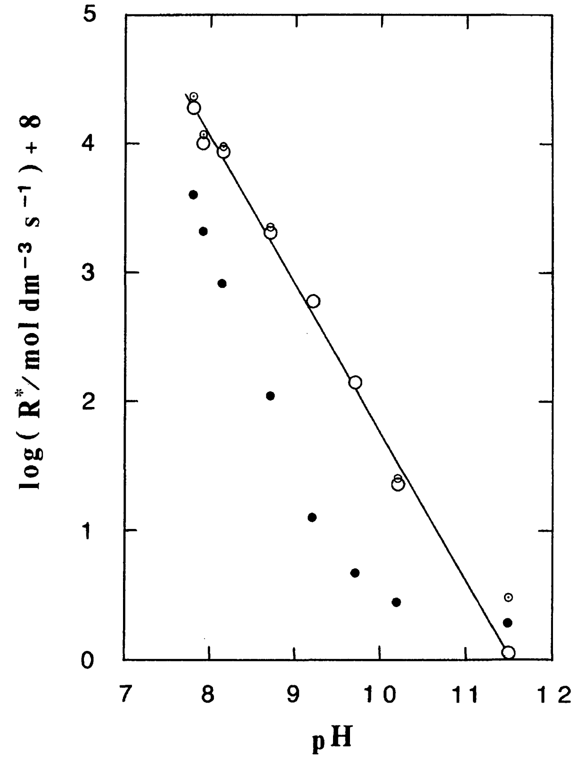

Fig. 4. pH dependence of the oxygen exchange rate of chromate with water. Catalysis by tellurite ion. (25 °C, [Cr(VI)]=0.070 mol dm^{-3}, [Te(IV)]=1.4×10^{-4} mol dm^{-3}, I= 0.2 mol dm^{-3}). ⊙: Exchange rate (R) with the added tellurite, •: Exchange rate (R_0) without the added tellurite, ○: Catalytic exchange rate (R_C=$R-R_0$). The symbol R^* in an ordinate in the figure represents collectively the oxygen exchange rates; R, R_0, and R_C. The values of R_0 are taken from Ref. 4.

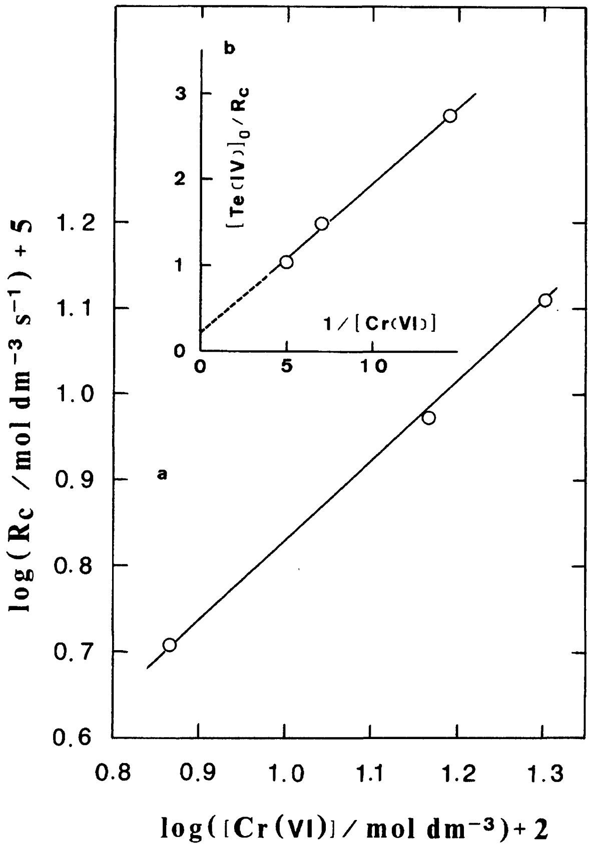

Fig. 5. a) Dependence of the catalytic oxygen exchange rate (R_C) on [Cr(VI)]. Tellurite ion catalysis. (25 °C, pH 8.2, [Te(IV)]=1.4×10^{-4} mol dm^{-3}, I(NaCl)=1.0 mol dm^{-3}). b) Plots of [Te(IV)]$_0$/R_C vs. 1/[Cr(VI)] according to the same type of Eq. 6. The data in Fig. 5a were used.

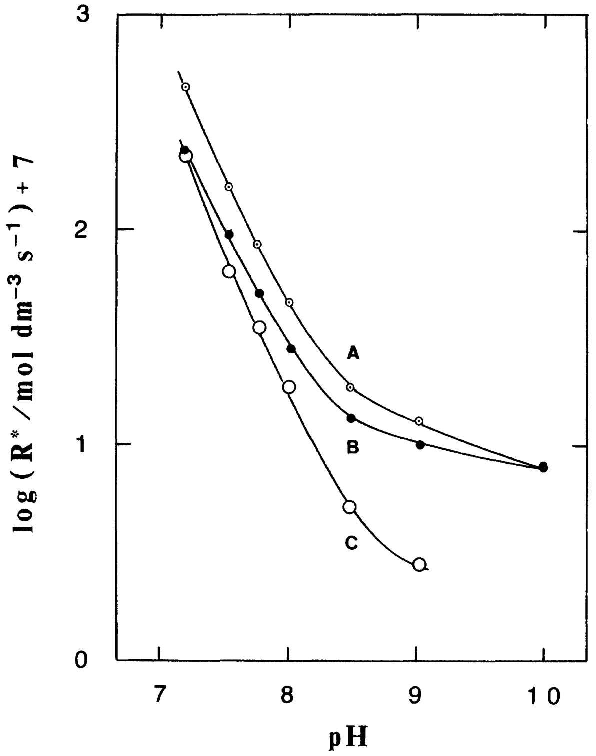

Fig. 6. pH dependence of the oxygen exchange rate of arsenate with water. Catalysis by tellurite ion. (30 °C, [As(V)]=0.071 mol dm^{-3}, [Te(IV)]=7.0×10^{-4} mol dm^{-3}, I=0.2 mol dm^{-3}). A (⊙): Exchange rate (R) with the added tellurite, B (●): Exchange rate (R_0) without the added tellurite, C (○): Catalytic exchange rate ($R_C = R - R_0$). The symbol R^* in an ordinate in the figure represents collectively the oxygen exchange rates; R, R_0, and R_C. The values of R_0 are take from Ref. 1.

rite concentrations, [Te(IV)]=7.0×10^{-4} mol dm^{-3} for R and =0 for R_0. In Fig. 6, log R (curve A) and log R_0 (curve B) are plotted against pH (30 °C). The catalytic effect (R/R_0) of Te(IV) on the arsenate–oxygen exchange is rather small. It decreases with an increase in pH and finally the effect disappears at pH 10 (R/R_0=2 (pH=7.2), 1.7(pH=7.5—8), and 1.3 (pH=9.0)). The plots of R_C against pH (Fig. 6, curve C) gives a straight line of a slope of −1.15 (pH 7.2—8.5).

Dependence of R_C on [Te(IV)]. The dependence was determined at pH 7.74 (30 °C, [As(V)]=0.070 mol dm^{-3}, I=0.2 mol dm^{-3}). The tellurite concentration was varied between 3.03×10^{-4} and 1.4×10^{-3} mol dm^{-3}. The values of R, R_0, and R_C are shown in Table 2. The order of the reaction with respect to [Te(IV)] was found as 1.1±0.1.

Dependence of R_C on [As(V)]. The dependence was determined at pH 7.74 (30 °C, I(NaCl)=0.57 mol dm^{-3}). [Te(IV)]=7.25×10^{-4} mol dm^{-3} for R and =0 for R_0. The arsenate concentration was varied between 0.0421 and 0.104 mol dm^{-3}. The values of R, R_0, and R_C are also shown in Table 2. The order of the reaction with respect to [As(V)] was found as 1.0±0.2.

The rate law of the catalytic process may be written as $R_C = k[\mathrm{As(V)}][\mathrm{Te(IV)}]$.

Rate Analysis

I. Tellurate Ion Catalysis. As already described, the catalytic process can be identified with the reversible condensation of chromate ions with tellurate ions. The catalytic reaction rate, R_C may be expressed generally as the sum of kinetic terms as follows:

$$R_C = \sum k_{ij}\,[\mathrm{Cr(VI)}]_i \cdot [\mathrm{Te(VI)}]_j\ ,$$

Table 2. The Concentration Dependence for the Oxygen Exchange Rates of As(V) Catalyzed by Te(IV)

a : Dependence on [Te(IV)]
(30 °C, pH = 7.74, [As(V)] = 0.0700 mol dm^{-3}, I = 0.2 mol dm^{-3})

[Te(IV)] / 10^{-4} mol dm^{-3}	R / 10^{-6} mol dm^{-3} s^{-1}	R_C / 10^{-6} mol dm^{-3} s^{-1}
0	5.178	—
3.031	7.089	1.911
4.966	8.077	2.899
6.946	8.614	3.436
10.10	11.959	6.781
14.13	14.992	9.814

b : Dependence on [As(V)]
[Te(IV)] = 7.25×10^{-4} mol dm^{-3} for R and [Te(IV)] = 0 for R_0 .(30 °C, pH = 7.74, I = 0.57 mol dm^{-3})

[As(V)] / 10^{-2} mol dm^{-3}	R / 10^{-6} mol dm^{-3} s^{-1}	R_0 / 10^{-6} mol dm^{-3} s^{-1}	R_C / 10^{-6} mol dm^{-3} s^{-1}
4.212	4.003	1.553	2.450
7.082	9.678	4.662	5.016
10.35	16.624	10.453	6.171

where $[\mathrm{Cr(VI)}]_i$ denotes the concentration of the various ionic species of the chromate ions, and $[\mathrm{Te(VI)}]_j$ that of the tellurate ions, and k_{ij} is the rate constant of the elementary reaction between $(\mathrm{Cr(VI)})_i$ and $(\mathrm{Te(VI)})_j$. In the pH range from 7 to 12 where the exchange was studied, the dominating ionic species of chromate are $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-} and those of tellurate are H_6TeO_6, $H_5TeO_6^-$, $H_4TeO_6^{2-}$, and the dimerized species formed between these tellurate species. The contribution of the dimerized species of Cr(VI) and Te(VI) to R_C, however, may be ignored, since R_C showed nearly first order dependence on both [Cr(VI)] and [Te(VI)]. The catalytic rate R_C, then, may be written by the following rate law:

$$\begin{aligned}R_C &= k_1[HCrO_4^-][H_5TeO_6^-] + k_2[HCrO_4^-][H_4TeO_6^{2-}] \\ &\quad + k_3[CrO_4^{2-}][H_6TeO_6] + k_4[CrO_4^{2-}][H_5TeO_6^-] \\ &\quad + k_5[CrO_4^{2-}][H_4TeO_6^{2-}] \\ &= R_1 + R_2 + R_3 + R_4 + R_5 . \end{aligned} \tag{7}$$

The catalytic rate constants (condensation rate constants) were evaluated according to the rate law Eq. 7 by the procedure described below.

Evaluation of the Catalytic Rate Constants. The concentrations of all the ionic species in Eq. 7 can be evaluated as described in the Experimental section. Based on the suggestion that the condensation reaction between the chromate and tellurate ions may form rather stable Cr(VI)·Te(VI) species, Eq. 2 for the total tellurate concentration should be replaced by the relation involving these species as follows:

$$\begin{aligned}[\mathrm{Te(VI)}] &= [H_6TeO_6] + [H_5TeO_6^-] + [H_4TeO_6^{2-}] \\ &\quad + 2\left([H_9Te_2O_{11}^-] + [H_8Te_2O_{11}^{2-}] + [H_7Te_2O_{11}^{3-}]\right) \\ &\quad + [H_4CrTeO_9^{2-}] + [H_3CrTeO_9^{3-}] .\end{aligned}$$

However, it is impossible to estimate the additional last two terms from the data so far obtained. In the calculation of $[\mathrm{Te(VI)}]_j$, therefore, the formation of any Cr(VI)·Te(VI) species was ignored. The values of $[\mathrm{Cr(VI)}]_i[\mathrm{Te(VI)}]_j$ in Eq. 7, then, were calculated ($[\mathrm{Cr(VI)}]=0.07$ mol dm^{-3}, $[\mathrm{Te(VI)}]=7.5\times10^{-4}$ mol dm^{-3}). The values of $[\mathrm{Cr(VI)}]_i\cdot[\mathrm{Te(VI)}]_j$ are shown as a function of pH in Fig. 7, where the number of a curve corresponds to that of a rate term in Eq. 7. The pH-rate profile (○) is also included in Fig. 7. It is seen that none of the ionic-product curves has any similarly with the pH-rate profile. Therefore, it may be said that all the rate terms in Eq. 7 make some contribution to the total catalytic rate R_C.

Since the rate terms R_1 and R_3, and R_2 and R_4 are kinetically indistinguishable from each other, the rate law Eq. 7 may be rewritten as

$$\begin{aligned}R_C &= \{k_1\cdot K_1(\mathrm{Te(VI)})/K_2(\mathrm{Cr}) + k_3\}[CrO_4^{2-}][H_6TeO_6] \\ &\quad + \{k_2\cdot K_2(\mathrm{Te(VI)})/K_2(\mathrm{Cr}) + k_4\}[CrO_4^{2-}][H_5TeO_6^-] \\ &\quad + k_5[CrO_4^{2-}][H_4TeO_6^{2-}] .\end{aligned} \tag{8}$$

The rate constants in Eq. 8 were evaluated by applying the least squares treatment to the values of R_C (Fig. 1) in the pH range between 7.2 and 10.5. The values of $\{k_1\cdot K_1(\mathrm{Te(VI)})/K_2(\mathrm{Cr}) + k_3\}$, $\{k_2\cdot K_2(\mathrm{Te(VI)})/K_2(\mathrm{Cr}) + k_4\}$, and k_5 were obtained to be 0.4±0.2, 0.58 ± 0.07, and 2.6 ± 0.3 mol^{-1} dm^3 s^{-1}, respectively. The value of $K_1(\mathrm{Te(VI)})/K_2(\mathrm{Cr})$ was estimated to be 2.8×10^{-2}. If $\{k_1\cdot K_1(\mathrm{Te(VI)})/K_2(\mathrm{Cr})\} > k_3$, the value of 14 mol^{-1} dm^3 s^{-1} would give an upper limit for k_1, and if $k_1 < k_3$, the value of 0.4 mol^{-1} dm^3 s^{-1} would give an upper limit for k_3. Since the value of $\{K_2(\mathrm{Te(VI)})/K_2(\mathrm{Cr})\}$ is equal to 1.9×10^{-5} and it seems unreasonable that k_2 is 10^4 times larger than k_4, k_4 may be put equal to 0.58 mol^{-1} dm^3 s^{-1}. The rate constants thus obtained are listed in Table 4. By using these rate constants, the observed values of R_C at the pH below 10.5 can be reproduced satisfactorily (within 10%). However, in the region of pH greater than 10.8, the calculated R_C deviates positively from the observed one (R_C(calcd)/R_C(obsd)=2 (pH=10.75) and 4 (pH=11.50)). Such a type of deviation has been observed in a previous work for the oxygen exchange of the arsenate catalyzed by the tellurate.[3] In that work, the observed deviation has been attributed to the formation of the dehydrated species TeO_4^{2-} ($H_4TeO_6^{2-} \rightleftharpoons TeO_4^{2-} + 2H_2O$), which may be inactive for the condensation reaction with arsenate. Its formation leads to a decrease in the effective concentration of $H_5TeO_6^-$ and $H_4TeO_6^{2-}$. On the basis of the kinetic result, it has been shown that the dehydration constant should have the value of 10. The same reasoning was applied to the present results. The rate analysis in terms of Eq. 8 was repeated by substituting $[H_5TeO_6^-]_{\mathrm{eff}}$ and $[H_4TeO_6^-]_{\mathrm{eff}}$

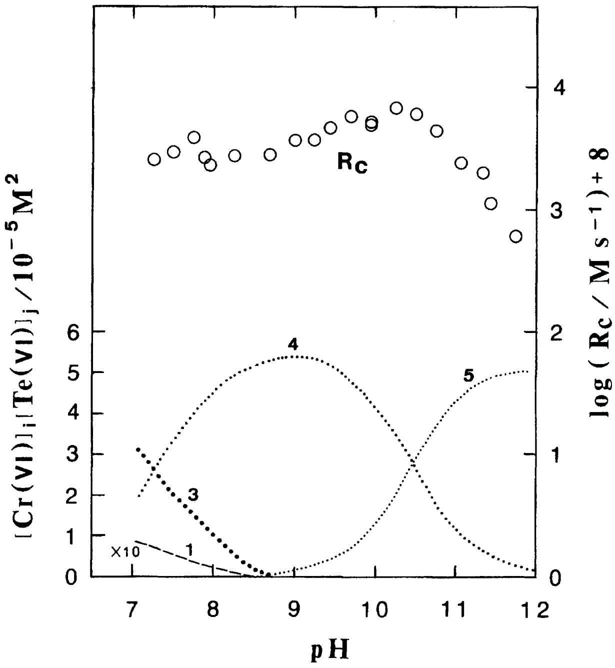

Fig. 7. Concentration product of the various kinds of ionic species of chromate and tellurate ions, $[\mathrm{Cr(VI)}]_i[\mathrm{Te(VI)}]_j$ as a function of pH (25 °C, I=1.0 mol dm^{-3}, [Cr(VI)]=0.07 mol dm^{-3}, [Te(VI)]=7.5×10^{-4} mol dm^{-3}). A number of curve corresponds to that of the rate term in Eq. 7. The value of curve 1 is magnified 10 times, and a curve for k_2-term is omitted because of its smallness. The same plots (○) of R_C vs. pH as shown in Fig. 1 are also included.

for the respective concentration in the equation. The rate constants, $\{k_1 \cdot K_1(\mathrm{Te(VI)})/K_2(\mathrm{Cr})+k_3\}$, k_4, and k_5 revised to 0.7±0.2, 0.43±0.07, and 13±8 $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively. These rate constants can reproduce more satisfactorily the observed rates R_C, except for the most alkaline region. The rate constants based on an assumption are not shown in the Table.

II. Tellurite Ions Catalysis. a. Catalytic Oxygen Exchange of Chromate by Tellurite. The catalyzed oxygen exchange rates of the chromate by the tellurite ions were analyzed by a similar method used for the tellurate ion catalyzed exchange reaction. In the pH region from 7.8 to 11.5 where the kinetic runs were carried out, the dominating ionic species of Te(IV) are $\mathrm{HTeO_3^-}$ and $\mathrm{TeO_3^{2-}}$. The catalytic rate R_C may be expressed by the following rate law:

$$R_C = k_1[\mathrm{HCrO_4^-}][\mathrm{HTeO_3^-}] + k_2[\mathrm{HCrO_4^-}][\mathrm{TeO_3^{2-}}] \\ + k_3[\mathrm{CrO_4^{2-}}][\mathrm{HTeO_3^-}] + k_4[\mathrm{CrO_4^{2-}}][\mathrm{TeO_3^{2-}}]. \quad (9)$$

Since the k_2- and k_3- terms are kinetically indistinguishable, Eq. 9 can be rewritten as

$$R_C = k_1[\mathrm{HCrO_4^-}][\mathrm{HTeO_3^-}] \\ + \{k_2 \cdot K_2(\mathrm{Te(IV)})/K_2(\mathrm{Cr}) + k_3\}[\mathrm{CrO_4^{2-}}][\mathrm{HTeO_3^-}] \\ + k_4[\mathrm{CrO_4^{2-}}][\mathrm{TeO_3^{2-}}]. \quad (10)$$

The concentrations of the ionic species in Eq. 10 were calculated by using $\mathrm{p}K_2(\mathrm{Cr})=6.03$ and $\log K_{22}(\mathrm{Cr})=1.75$ for the chromate,[4] and $\mathrm{p}K_2(\mathrm{Te(IV)})=7.74$ for tellurite[12] (25 °C, I=0.2 $\mathrm{mol\,dm^{-3}}$). While the values of $[\mathrm{CrO_4^{2-}}][\mathrm{TeO_3^{2-}}]$ in Eq. 10 increase with a increase in pH, the tellurite catalysis (R_C) show a trend to decrease with increasing pH (Fig. 4). Therefore, the contribution of the R_4-term to the total rate R_C may be ignored.

The values of k_1 and $\{k_2 \cdot K_2(\mathrm{Te(IV)})/K_2(\mathrm{Cr}) + k_3\}$ were evaluated by applying the least squares treatment to all the R_C data shown in Fig. 4. These values were obtained to be $(1.3\pm0.4)\times10^3$ and $(1.5\pm0.6)\times10$ $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively. Since $K_2(\mathrm{Te(IV)})/K_2(\mathrm{Cr})=2\times10^{-2}$, the latter value may be equated to k_3 on the assumption that k_2 is comparable with k_3.

b. Catalytic Oxygen Exchange of Arsenate by Tellurite. The rate law of R_C was obtained as $R_C=k[\mathrm{As(V)}][\mathrm{Te(IV)}]$. In the pH region between 7 and 10, the dominating ionic species of arsenate are $\mathrm{H_2AsO_4^-}$ and $\mathrm{HAsO_4^{2-}}$ and those of tellurite are $\mathrm{HTeO_3^-}$ and $\mathrm{TeO_3^{2-}}$. The rate law of the catalytic process may be expressed as :

$$R_C = k_1[\mathrm{H_2AsO_4^-}][\mathrm{HTeO_3^-}] + k_2[\mathrm{H_2AsO_4^-}][\mathrm{TeO_3^{2-}}] \\ + k_3[\mathrm{HAsO_4^{2-}}][\mathrm{HTeO_3^-}] \\ + k_4[\mathrm{HAsO_4^{2-}}][\mathrm{TeO_3^{2-}}]. \quad (11)$$

Since R_C=0 at pH=10 while the ionic product $[\mathrm{HAsO_4^{2-}}]$-$[\mathrm{TeO_3^{2-}}]$ increases with an increase in pH, the contribution of the k_4-term may be ignored. The k_2- and k_3-terms are kinetically indistinguishable from each other. The rate law Eq. 11, then, becomes:

$$R_C = k_1[\mathrm{H_2AsO_4^-}][\mathrm{HTeO_3^-}] \\ + \{k_2 \cdot K_2(\mathrm{Te(IV)})/K_2(\mathrm{As}) + k_3\}[\mathrm{HAsO_4^{2-}}][\mathrm{TeO_3^{2-}}], \quad (12)$$

where $K_2(\mathrm{As})$ is the dissociation constant of $\mathrm{H_2AsO_4^-}$ and $\mathrm{p}K_2(\mathrm{As})=6.556$ [1] was used.

The R_C values shown in Fig. 6 were analyzed in terms of Eq. 12. By using a least squares treatment, the values of k_1 and $\{k_2 \cdot K_2(\mathrm{Te(IV)})/K_2(\mathrm{As}) + k_3\}$ were evaluated to be 1.6±0.7 and 5.5×10^{-2} $\mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively.

General Discussion

The rate and equilibrium constants for the overall condensation reactions of Cr(VI) and As(V) with Te(VI) or Te(IV) to form hetero-polyanions are listed in Table 3, along with those obtained before. In Tables 4 and 5, all the rate constants

Table 3. The Rate and Equilibrium Constants of the Condensation Reaction of Chromate and Arsenate Ions with Other Oxoanions

$$\mathrm{S} + \mathrm{C} \underset{K}{\overset{k}{\rightleftharpoons}} \mathrm{S{\cdot}C} + \mathrm{H_2O} \qquad R_C = \frac{k[\mathrm{S}][\mathrm{C}]}{1+K[\mathrm{S}]}$$

S	C	pH	Temp/°C	$k/\mathrm{mol^{-1}dm^3s^{-1}}$	$K/\mathrm{mol dm^{-3}}$
Cr(VI)+Te(VI)		7.70	25	0.46	3.30
		10.6	25	1.07	0.48
Cr(VI)+Te(IV)		8.2	25	5.9	1.23
Cr(VI)+I(VII)[6]		10.6	0	5.2×10^4	4.18
As(V)+Te(VI)[3]		7.51	30	0.22	2.0
		8.47	30	0.35	1.6
		10.00	30	0.011	1.0
		7.07	14.5	0.047	3.5
		8.72	14.5	0.078	2.1

Table 4. The Rate Constants of the Condensation Reactions of Chromate with Other Oxoanions

Reaction		Temp °C	I mol dm^{-3}	Rate constants mol^{-1} dm^3 s^{-1}	Refs.
$HCrO_4^-$ + $H_5TeO_6^-$	k_1	25	1.0	<14	This work
CrO_4^{2-} + H_6TeO_6	k_3	25	1.0	<(4±2)×10^{-1}	This work
CrO_4^{2-} + $H_5TeO_6^-$	k_4	25	1.0	(5.8±0.7)×10^{-1}	This work
CrO_4^{2-} + $H_4TeO_6^{2-}$	k_5	25	1.0	(2.6±0.3)	This work
$HCrO_4^-$ + $HTeO_3^-$		25	0.2	(1.3±0.4)×10^3	This work
CrO_4^{2-} + $HTeO_3^-$		25	0.2	(1.5±0.6)×10	This work
$HCrO_4^-$ + $H_4IO_6^-$		0	0.22	(3±15)×10^4	6
		30	1.5	(7.6±0.3)×10^3	6
$HCrO_4^-$ + $H_3IO_6^{2-}$		0	0.22	(2±5)×10^4	6
CrO_4^{2-} + $H_4IO_6^-$		0	0.22	(3.4±0.9)×10^3	6
		30	1.5	(1.9±0.2)×10^4	6
CrO_4^{2-} + $H_3IO_6^{2-}$		0	0.22	(4.6±0.6)	6
$HCrO_4^-$ + H_3AsO_3		25	0.22	(1.9±0.3)×10^2	5
$Cr_2O_7^{2-}$ + H_3AsO_3		25	0.22	(2.0±0.2)×10^3	5
CrO_4^{2-} + H_3AsO_3		25	0.22	<2.2	5
CrO_4^{2-} + $H_2AsO_3^-$		25	0.22	(7±2)×10^{-3}	5
$HCrO_4^-$ + $HCrO_4^-$		25	0.22	5±1	4
$HCrO_4^-$ + $HCrO_4^-$		25	1.0	9±1	4
$HCrO_4^-$ + CrO_4^{2-}		25	0.22	10^{-3}	4
$HCrO_4^-$ + H_2O		25	0.22,1.0	(2.3±0.2)×10^{-3}	4
CrO_4^{2-} + H_2O		25	0.22,1.0	(3.2±0.2)×10^{-7}	4

Table 5. The Rate Constants of the Condensation Reactions of the Arsenate with Other Oxoanions (30 °C)

Reactions	I mol dm^{-3}	Rate constants mol^{-1} dm^3 s^{-1}	Refs.
$H_2AsO_4^-$ + H_6TeO_6	0.55	1.2×10^{-1} (14.5 °C)	3
$HAsO_4^{2-}$ + H_6TeO_6	0.55	<6.6×10^{-2}	3
$HAsO_4^{2-}$ + $H_5TeO_6^-$	0.55	2.2×10^{-1}	3
$H_2AsO_4^-$ + $HTeO_3^-$	0.2	(1.6±0.7)	This work
$HAsO_4^{2-}$ + $HTeO_3^-$	0.2	<(5.5±0.6)×10^{-2}	This work
$H_2AsO_4^-$ + $H_4IO_6^-$	0.22	3.4×10^2	2
$HAsO_4^{2-}$ + $H_4IO_6^-$	0.22	<3.6×10	2
$H_2AsO_4^-$ + H_3AsO_3	0.22	6.8	1
$HAsO_4^{2-}$ + H_3AsO_3	0.22	2×10^{-2}	1
$H_2AsO_4^-$ + $H_2AsO_4^-$	0.55	7.4×10^{-2}	8
$H_2AsO_4^-$ + $HAsO_4^{2-}$	0.55	6.4×10^{-3}	8
$H_2AsO_4^-$ + H_2O	0.55	1×10^{-4}	8
$HAsO_4^{2-}$ + H_2O	0.55	1.2×10^{-5}	8

are compiled for the elementary condensation processes involving the two oxo-anions (a chromate or arsenate ion and another oxoanion), so far obtained by the same method as used in this work.

These rate constants which were estimated by the analyses of the R_C data are, in turn, useful to interpret the observed kinetic behavior such as the pH dependence of R_C. As evidenced in Figs. 1 and 4, the catalytic behavior by Te(VI) and that by Te(IV) for the oxygen exchange of chromate are significantly different. For Te(VI), the catalytic effect is remarkable in alkaline region (pH > 8) and becomes difficult to be detected at pH 7, while for Te(IV), the effect is large at pH=7 and decreases linearly with increasing pH. For the oxygen exchange of the chromate itself,[4] it is known that, at pH 7, the reversible condensation process 2 $HCrO_4^- \rightleftharpoons H_2O + Cr_2O_7^{2-}$ plays a dominant role in the overall exchange rate. In the chromate–oxygen exchange in the presence of another oxoanion at the pH, therefore, another ion is required to compete with the $HCrO_4^-$ ion for $HCrO_4^-$ ion. Table 4 shows that as to the reactivity towards $HCrO_4^-$, $H_5TeO_6^-$ is comparable to $HCrO_4^-$ while $HTeO_3^-$ is 2.6×10^2 times larger than $HCrO_4^-$. This fact may be responsible for the difference in the catalytic behavior at pH 7 between Te(VI) and Te(IV). On the other hand, at pH>9, the only pathway for the chromate–oxygen exchange is the exchange reaction of CrO_4^{2-} with water. All the ions of Te(VI), $H_5TeO_6^-$ and $H_4TeO_6^{2-}$ have reactivity towards CrO_4^{2-}, while for Te(IV), only the $HTeO_3^-$ is reactive towards CrO_4^{2-}. Disappearance of [Te(IV)] catalysis at pH 9.5 can be ascribed to $[HTeO_3^-]\cong 0$ at the pH. It is surprising that the tellurate and tellurite ions are very reactive towards CrO_4^{2-}, while H_2O is quite inactive towards it.

The condensation rate constants in Tables 4 and 5 reveal some obvious trends regarding the reactivity of the oxoanion towards Cr(VI) and As(V).

The reactive oxoanions towards As(V) are also reactive towards Cr(VI). Furthermore, the order of the reactivity of the oxoanions found for Cr(VI) is the same as that for As(V) : I(VII) > Te(IV) > As(III) > Te(VI). It is noticeable that the periodate ions have an extraordinarily large catalytic activity both for the chromate- and arsenate–oxygen exchanges.

Additionally, there are several interesting facts to be noted: 1) The oxoanions which are highly reactive towards As(V) and Cr(VI) also rapidly exchange their oxygens with water. 2) The order of the oxygen-exchange rates: I(VII)[13]> As(III)[14]> Te(VI)[15] is consistent with the order found for the catalytic activities. (no available data for the oxygen exchange of Te(IV).) 3) For I(VII) and Te(VI) of the larger central atom, it is proposed that the rate of the oxygen exchange with water is controlled by the elimination of water molecules from the oxoanions and the exchange proceeds via a monomolecular mechanism.[13,15] It is surprising that, in spite of such kinetic behavior of I(VII) and Te(VI), the oxygen atom of the periodate ion or the tellurate ion can attack effectively the nucleophilic center of the arsenate ion or the chromate ion to form a hetero-polyanion.

For the reversible condensation process, two paths are possible. Path a): The oxoanion added as catalyst acts as the nucleophile, and the arsenate or chromate ion as the substrate, i.e. an oxygen atom of the catalyst attacks the electrophilic center atom (As or Cr) of substrate, followed by the As–O or Cr–O bond fission. Path b) : The arsenate or chromate ion acts as the nucleophile, and the catalyst as the substrate (I–O or Te–O bond fission). In both cases, an identical hetero-polyanion is formed. By the principle of microscopic reversibility, the bond fission must occur at the same position as in the forward reaction.

The result that the oxygen exchange of the arsenate or chromate is catalyzed by the catalyst ion requires the reaction to proceed via a). Path b) does not lead to the oxygen exchange of the arsenate or chromate with water.

If it is assumed that Path a) and Path b) occur simultaneously in a solution containing As(V) or Cr(VI) and a catalyst ion, a mechanism in which the condensation proceeds through Path b) and the hydrolysis through Path a) would be an alternative mechanism for the catalytic reaction.

Another possibility is a mechanism which involves the rapid exchange of catalyst ions with water and subsequent condensation through Path a) and hydrolysis through Path b). This mechanism is consistent with the fact that the catalysts of a high exchangeability with water also have a high reactivity towards the arsenate or chromate ion.

The Effect of Protonation on the Condensation Reaction. The following order is found for the condensation rate constants between ions (Tables 4 and 5, k_{ij} is expressed in $mol^{-1}\,dm^3\,s^{-1}$):

$$\begin{array}{lccccccc}
HCrO_4^- : & H_4IO_6^- & \approx & H_3IO_6^{2-} & > & HTeO_3^- & > & \\
k_{ij} & 10^4 & & 10^4 & & 10^3 & & \\
 & H_3AsO_3 & > & H_5TeO_6^- & \approx & HCrO_4^- & > & CrO_4^{2-} \\
 & 10^2 & & <14 & & 9 & & 10^{-3}
\end{array}$$

$$\begin{array}{lccccccc}
CrO_4^{2-} : & H_4IO_6^- & \gg & HTeO_3^- & > & H_3IO_6^{2-} & > & \\
k_{ij} & 10^4 & & 15 & & 5 & & \\
 & H_4TeO_6^{2-} & > & H_3AsO_3 & > & H_5TeO_6^- & > & H_2AsO_3^- \\
 & 3 & & <2 & & 0.6 & & 7\times10^{-3}
\end{array}$$

$$\begin{array}{lccccccc}
H_2AsO_4^- : & H_4IO_6^- & \gg & H_3AsO_3 & > & HTeO_3^- & > & \\
k_{ij} & 10^2 & & 6 & & 2 & & \\
 & H_6TeO_6 & > & H_2AsO_4^- & > & HAsO_4^{2-} & & \\
 & 10^{-1} & & 7\times10^{-2} & & 6\times10^{-3} & &
\end{array}$$

$$\begin{array}{lccccccc}
HAsO_4^{2-} : & H_4IO_6^- & > & H_5TeO_6^- & > & H_3AsO_3 & \approx & \\
k_{ij} & <36 & & 0.2 & & 2\times10^{-2} & & \\
 & H_6TeO_6 & \approx & HTeO_3^- & > & H_2AsO_4^- & & \\
 & <7\times10^{-2} & & <6\times10^{-2} & & 6\times10^{-3} & &
\end{array}$$

It may be said that interaction between two highly protonated species is generally large. No catalytic activity of TeO_3^{2-} could be observed. As to Te(VI), however, $H_5TeO_6^-$ is 3 times more reactive than H_6TeO_6 towards $HAsO_4^{2-}$. It is interesting that this trend has been also found in the oxygen exchange reaction of tellurate ions with water.[15]

Activation Parameters. The E_a and $\Delta S^{\neq}$ values were obtained to be 68.5 ± 4.5 kJ mol^{-1} and -24.9 J K^{-1} mol^{-1} for the catalytic reaction (R_C) of Cr(VI) by Te(VI) at pH 9.45, where the reactions of CrO_4^{2-} with $H_5TeO_6^-$ and $H_4TeO_6^{2-}$ prevail. The activation energy (E_a/kJ mol^{-1}) and activation entropy ($\Delta S^{\neq}$/J K^{-1} mol^{-1}) so far obtained for the elementary reaction are : ($CrO_4^{2-}+H_3IO_6^{2-}$): $E_a=25.9$, $\Delta S^{\neq}=-143$; ($H_2AsO_4^-+H_3AsO_3$): $E_a=52$, $\Delta S^{\neq}=-38$; ($H_2AsO_4^-+H_2AsO_4^-$): $E_a=55$, $\Delta S^{\neq}=-93$. On the other hand, these parameters for the oxygen exchange of an anion with water are: ($CrO_4^{2-}+H_2O$): $E_a=99$; ($H_2AsO_4^-+H_2O$): $E_a=92$, $\Delta S^{\neq}=-46$. It should be noticed that the activation energies for the condensation reactions are significantly smaller than those for the oxoanion–water reactions. The fact may be responsible for the fast oxygen exchange of the chromate and arsenate ions via the reversible condensation mechanism.

References

1) A. Okumura, N. Yamamoto, and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 3633 (1973).

2) A. Okumura, S. Watanabe, M. Sakaue, and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **52**, 2783 (1979).

3) A. Okumura, M. Somiya, S. Asai, and N. Okazaki, *Inorg. Chim. Acta*, **87**, 53 (1984).

4) A. Okumura, M. Kitani, Y. Toyomi, and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **53**, 3143 (1980).

5) A. Okumura and Y. Daido, *Inorg. Chim. Acta*, **144**, 63 (1988).

6) A. Okumura, M. Kitani, and M. Murata, *Bull. Chem. Soc. Jpn.*, **67**, 1522 (1994).

7) P. D. Boyer, D. J. Graves, C. H. Suelter, and M. E. Dempsey, *Anal. Chem.*, **33**, 1906 (1961).

8) A. Okumura and N. Okazaki, *Bull. Chem. Soc. Jpn.*, **46**, 2937 (1973).

9) A. Okumura, Y. Matsumiya, K. Yamamoto, R. Ueno, and M. Suzuki, *Bull. Chem. Soc. Jpn.*, **68**, 1839 (1995).

10) H. Kaehler, S. Mateo, and F. Brito, *Anal. Quim.*, **68**, 1215 (1972).

11) H. Kaehler, S. Mateo, and F. Brito, *Anal. Quim.*, **69**, 1273 (1973).

12) L. G. Sillen and A. E. Martell, "Stability Constants," Chem. Soc., Spec. Publ., No. 17, London (1964).

13) I. Pecht and Z. Luz, *J. Am. Chem. Soc.*, **87**, 4068 (1965).

14) W. C. Copenhafer and P. H. Rieger, *J. Am. Chem. Soc.*, **100**, 3776 (1978).

15) Z. Luz and I. Pecht, *J. Am. Chem. Soc.*, **88**, 1152 (1966).