Kinetic Studies of the Catalytic Oxygen Exchange Reaction of Chromate Ions with Water by Arsenious Acid and the Redox Reaction between Chromate Ions and Arsenious Acid
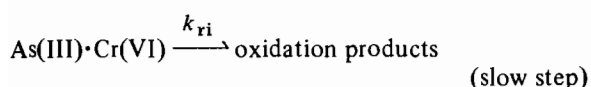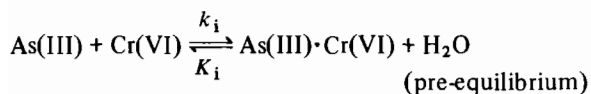
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Abstract

The oxygen exchange reaction between chromate ions and water is catalyzed by a small amount of arsenious acid. The catalytic oxygen exchange reaction was studied at 25 °C over the pH range of 7–12 ($[Cr(VI)]$ = 0.072 M, $[As(III)]$ = 1.4 × 10^{-4} M, I = 0.2 M). The catalytic action has been interpreted in terms of the reversible complex formation between various kinds of As(III) and Cr(VI) to form hetero-polyanions As(III)·Cr(VI). The redox reaction between arsenic(III) and chromium(VI) was studied over the pH range of 2.5 ~ 13 under the same conditions as was used in the oxygen exchange except that the concentration of As(III) was chosen to be 1.4 × 10^{-3} M. The rate of the redox reaction is considerably lower than that of oxygen exchange. The observed results are consistent with the mechanism:

$$As(III) + Cr(VI) \underset{K_i}{\overset{k_i}{\rightleftharpoons}} As(III)\cdot Cr(VI) + H_2O$$

(pre-equilibrium)

$$As(III)\cdot Cr(VI) \overset{k_{ri}}{\longrightarrow} \text{oxidation products}$$
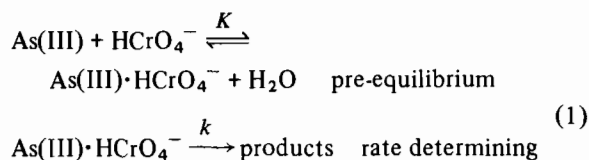
(slow step)

On the basis of this mechanism, the kinetic results were analyzed to obtain the values of the rate constants of the complex formation k_i and the apparent rate constants of the slow redox process $k'_i (\equiv (K_i \cdot k'_{ri}))$.

Introduction

In a series of papers on the oxoanion catalysis of the oxygen exchange reaction of arsenate ions with water [1–3], the catalytic effect of oxoanion was interpreted by the reversible condensation of arsenate ions with the oxoanion to form hetero-polyanions. It has been suggested that a study of the oxygen exchange of oxoanion in the presence of a catalytic amount of another oxoanion may provide a means

of elucidating the interaction of these two oxoanions. Preliminary experiments have shown that the same type of catalytic effect is also observed for the oxygen exchange reaction of chromate ions with water; a small amount of arsenious acid, periodate, tellurate, and tellurite was found to accelerate the reaction significantly. In this paper, we report the effect of arsenious acid on the chromate oxygen exchange reaction with water. As it is well known that arsenic(III) is oxidized by chromium(VI) in both acidic and alkaline solutions, the redox reaction between them was also studied under similar conditions as those used for the oxygen exchange reaction.

The kinetics of the chromate oxidation reaction of arsenic(III) by chromate ions has been studied extensively by several authors [4–7]. Mason and Kowalak [5] investigated the reaction over a wide range of As(III) and Cr(VI) concentrations in 0.2 M* acetate buffers and I = 1.5 M. They have found the rate law − d$[Cr(VI)]$/dt = $kK[As(III)][Cr(VI)]$/$(1 + K[As(III)])$ ($[As(III)] \gg [Cr(VI)]$), which is consistent with the following mechanism;

$$As(III) + HCrO_4^- \overset{K}{\rightleftharpoons}$$
$$As(III)\cdot HCrO_4^- + H_2O \quad \text{pre-equilibrium}$$

$$As(III)\cdot HCrO_4^- \overset{k}{\longrightarrow} \text{products} \quad \text{rate determining}$$

(1)

At higher concentrations of Cr(VI), a second path involving $Cr_2O_7^{2-}$ should be taken into account. Gupta and Chakladar [7] studied the reaction at pH 4.5 (acetate buffer) in the temperature range 30–45 °C. From the results that the activation parameters of the reaction are almost independent of the $[As(III)]/[Cr(VI)]$ ratio, they suggested that, in the cases where the ratio $[Cr(VI)]/[As(III)]$ is very large, the same type of mechanism as shown in eqn. (1) may also be operative. In agreement with the proposed mechanism, we have found that the catalytic oxygen exchange reaction proceeds faster than the redox reaction in the wide pH range studied.

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

If the redox reaction proceeds via the proposed mechanism (eqn. (1)), and if the Cr–O bond is broken in the complex formation step, the rate of the oxygen exchange reaction of chromate ions with water in the presence of arsenious acid gives the rate of complex formation between As(III) and Cr(VI) in the pre-equilibrium step, while the kinetics of the redox reaction provides the information about the slow step in eqn. (1). The kinetic results and the analysis of the results carried out on the assumed mechanism will be reported.

Experimental

I. Kinetics of the Oxygen Exchange Reaction of Chromate Ions with Water

The procedures were almost the same as those previously reported [8]. 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 the stock solution of arsenious acid. The pH of the solution was adjusted by the addition of a small amount of hydrochloric acid or sodium hydroxide solution and was measured with a Hitachi-Horiba pH Meter (Model F-7) or with Radiometer pHM 26 pH-Meter. The reactions were carried out at 25 °C. At appropriate intervals, aliquots were drawn and the chromate ion was precipitated as barium chromate by adding a solution of barium chloride. The precipitate was separated by means of centrifuge, washed three times with absolute ethanol. It was then dried in an oven at 110 °C and converted into carbon dioxide by the guanidinium chloride method [9]. 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:

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

where O_0, O_t, and O_∞ are the oxygen-18 contents of the chromate at the times 0, t, and infinity respectively, and where $[Cr(VI)]$ and $[H_2O]$ are the molar concentrations of the chromate and water, respectively.

II. The Kinetics of the Redox Reaction

The rate data of the reaction were obtained titrimetrically by following the arsenic(III) concentration as a function of time. The procedures were essentially the same as those of Mason and Kowalak [5]. A weighed amount of sodium chromate tetrahydrate was dissolved into a known volume of water, either

nitric acid or sodium hydroxide being added for pH adjustment and sodium nitrate for ionic strength adjustment. The reaction was started by adding the fixed volume of arsenious acid stock solution into the mixture. Aliquots were removed periodically, quenched with a large volume of ice-cold saturated borate solution, and titrated immediately with standard I_2 solution.

Pseudo-first-order conditions were maintained throughout the kinetic studies ($[Cr(VI)] = 7 \times 10^{-2}$ M, $[As(III)]_0 = 1.4 \times 10^{-3}$ M). Plots of $\log[As(III)]$ against time were linear for two half-lives, confirming that the reaction is first order in $[As(III)]$. The rate of the redox reaction is given in terms of the equation:

$$-d[As(III)]/dt = k'_{obs}[As(III)]$$
$$k'_{obs} = k'[Cr(VI)]^n$$

where k' is the rate constant of the overall redox reaction, and n is the order of the reaction with respect to $[Cr(VI)]$.

III. Acid Dissociation Constant of Arsenious Acid

The values of the dissociation constant of arsenious acid, $K_1(As)$, defined by the equation: $K_1(As) = a_{H^+}[H_2AsO_3^-]/[H_3AsO_3]$, were determined by potentiometric titration with a glass electrode. Solutions of arsenious acid containing an amount of sodium chloride necessary to maintain the desired ionic strength at the half neutralization point were titrated with a carbonate free sodium hydroxide solution. The values obtained at 25 °C are as follows. $9.29(3) \pm 0.00(9)$ ($I = 0.2$), $9.22(2) \pm 0.01(8)$ ($I = 0.5$), $9.13(5) \pm 0.01(0)$ ($I = 1.0$).

Results

I. The Oxygen Exchange Reaction

pH Dependence of the exchange rate

In Fig. 1, $\log R_0$ and $\log R$ are plotted against pH, where R_0 and R designate the rates of oxygen exchange reaction between chromate ions and solvent water without and with the addition of arsenious acid, respectively. The concentrations of the chromate and arsenious acid were 0.072 M and 1.4×10^{-4} M, respectively. The catalytic effect ($=R/R_0$) increases with the increase in the value of pH, and in the pH region between 9 and 10.5 it becomes so significant as to increase the oxygen exchange rate 100 fold. The observed large catalytic effect of arsenious acid on chromate oxygen exchange in alkaline region is in contrast with the effect of arsenious acid on the arsenate oxygen exchange which decreases with the increase in pH and disappears above pH 10 [1]. Figure 2 shows the dependence of R_c on pH. R_c is defined as $R - R_0$
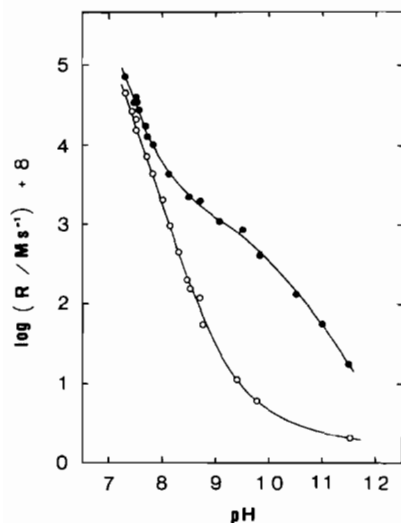
Fig. 1. The rate of oxygen exchange reaction of chromate ions with water against pH ($[Cr(VI)] = 7.2 \times 10^{-2}$ M, $I = 0.2$ M, 25 °C). ○, without added arsenious acid; ●, with added arsenious acid ($[As(III)] = 1.4 \times 10^{-4}$ M).
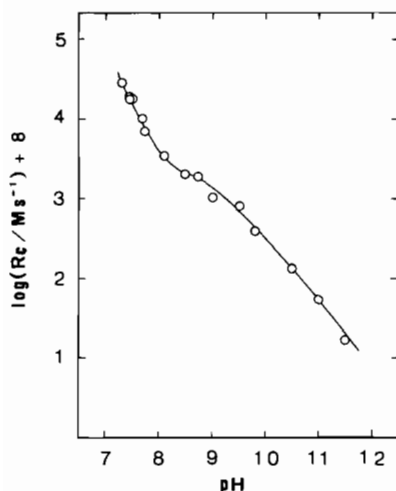

Fig. 2. The pH dependence of the catalytic oxygen exchange reaction, R_c ($[Cr(VI)] = 7.2 \times 10^{-2}$ M, $[As(III)] = 1.4 \times 10^{-4}$ M, $I = 0.2$ M, 25 °C).

and corresponds to the catalyzed portion of the exchange reaction. The slopes of a plot of log R_c *versus* pH were found to be -1.6 in the pH region smaller than 8, and -0.8 in the pH region greater than 8.

Dependence of the catalytic oxygen exchange rate R_c on [Cr(VI)]

The order of the reaction with respect to [Cr(VI)] was determined at pH 7.4 and 8.0 (25 °C, I(NaCl) = 1.0 M, $[As(III)] = 1.4 \times 10^{-4}$ M). The concentration of [Cr(VI)] was varied from 0.037 to 0.146 M at pH 7.4 and from 0.032 to 0.126 M at pH 8.0. Plots of log R_c against log[Cr(VI)] are shown in Fig. 3. The

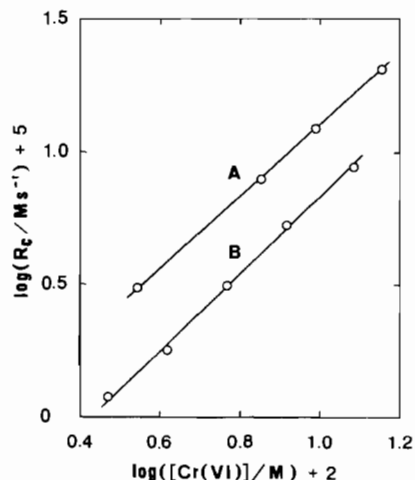Fig. 3. Dependence of log R_c on log[Cr(VI)] at 25 °C, I-(NaCl) = 1.0 M, and $[As(III)] = 1.4 \times 10^{-4}$ M. A: pH 7.4, $[Cr(VI)] = (3.7 \sim 14.6) \times 10^{-2}$ M; B: pH 8.0, $[Cr(VI)] = (3.2 \sim 12.6) \times 10^{-2}$ M.

TABLE I. Dependence of the Catalytic Rate R_c on [As(III)]. Experimental Conditions

	pH	[As(III)] (M)	[Cr(VI)] (M)
A	8	$6.7 \times 10^{-5} \sim 2.68 \times 10^{-4}$	0.072
B	11	$4.04 \times 10^{-4} \sim 1.33 \times 10^{-3}$	0.073

slopes of the straight lines obtained by the least-squares treatment are 1.37 ± 0.01 at pH 7.4 (A) and 1.46 ± 0.04 at pH 8.0 (B).

Dependence of the catalytic rate R_c on [As(III)]

This was studied under the conditions shown in Table I. The plots of log R_c against log[As(III)] are shown in Fig. 4. The slopes of the straight lines are 0.84 ± 0.03 for A and 0.90 ± 0.02 for B.

II. The Redox Reaction

pH Dependence of the redox reaction

The pH–rate profile was obtained under the following condition: $[Cr(VI)] = 7 \times 10^{-2}$ M, $[As-(III)]_0 = 1.4 \times 10^{-3}$ M, pH 2.8–13.5. The logarithm of R' was plotted against the pH in Fig. 5. R' is defined as the initial rate of the redox reaction and was calculated as $k_{obs}[As(III)]_0$ where $[As(III)]_0$ is the initial concentration of arsenic(III). The curve has a peculiar form with a broad minimum at the pH values between 4 and 5.5 and a maximum at pH 6.5. (These will be discussed later.)

Dependence of the redox reaction on [Cr(VI)]

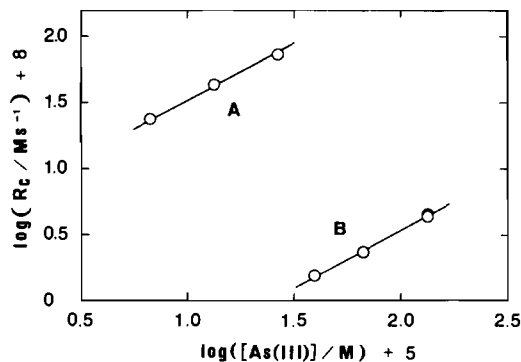The order of the reaction with respect to Cr(VI), n, is obtained from the slope of a log–log plot of

Fig. 4. Dependence of log R_c on log[As(III)] at 25 °C. A: pH 8.0, [Cr(VI)] = 7.2 × 10^{-2} M, [As(III)] = (0.67 ~ 2.7) × 10^{-4} M; B: pH 11, [Cr(VI)] = 7.3 × 10^{-2} M, [As(III)] = (0.4 ~ 1.3) × 10^{-3} M.
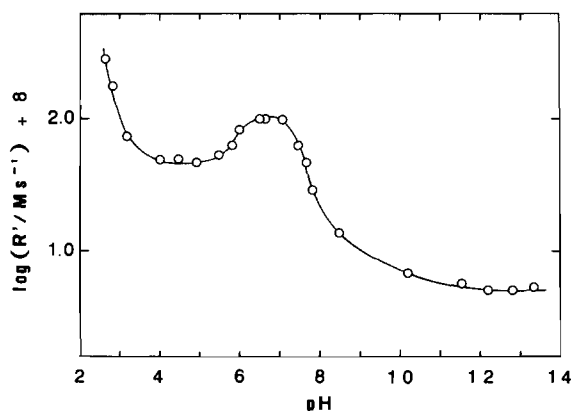

Fig. 5. The pH dependence of the redox rate, R' (25 °C, [As(III)]$_0$ = 1.4 × 10^{-3} M, [Cr(VI)] = 0.072 M).

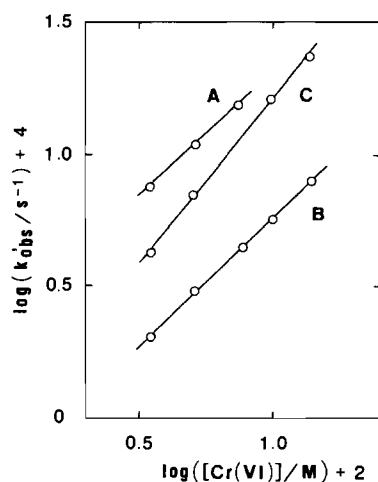Fig. 6. Dependence of log k_{obs} on log[Cr(VI)] at 25 °C and I(NaCl) = 0.5 M. A: pH 2.8, [Cr(VI)] = (3.5 ~ 10.0) × 10^{-2} M; B: pH 4.5, [Cr(VI)] = (3.5 ~ 14.0) × 10^{-2} M; C: pH 6.3, [Cr(VI)] = (3.5 ~ 14.0) × 10^{-2} M.

TABLE II. The Order of the Redox Reaction with Respect to [Cr(VI)]

pH	t (°C)	I (M)	[Cr(VI)] (10^{-2} M)	k'_{obs} (10^{-4} s^{-1})	n
2.8	25	0.5	3.48	7.62	0.92 ± 0.00
			5.10	10.9	
			7.50	15.5	
			9.95	18.6	
4.50	25	0.5	3.50	2.03	0.98 ± 0.02
			5.11	3.04	
			7.50	4.45	
			9.95	5.70	
			14.0	7.74	
4.50	25	1.0	3.51	2.23	0.98 ± 0.02
			7.50	4.86	
			14.0	8.70	
4.50	10	0.5	3.51	0.715	0.98 ± 0.02
			7.49	1.54	
			9.93	1.98	
4.50	0	0.5	3.51	0.325	1.00 ± 0.02
			7.50	0.716	
			14.0	1.28	
6.33	25	0.2	3.47	3.34	1.23 ± 0.02
			7.51	8.82	
			9.97	12.2	
6.33	25	0.5	3.47	4.23	1.23 ± 0.04
			5.11	7.10	
			9.96	16.4	
			14.0	23.5	
6.33	25	1.0	3.48	4.91	1.37 ± 0.05
			5.01	8.64	
			10.0	21.1	
12.8	25	0.2	3.68	0.219	0.86 ± 0.00
			5.03	0.285	
			6.75	0.367	

k'_{obs} *versus* [Cr(VI)] (k'_{obs} = k'[Cr(VI)]^n, [Cr(VI)] = [Cr(VI)]$_0$). Some typical plots are shown in Fig. 6, and the values of n are listed in Table II.

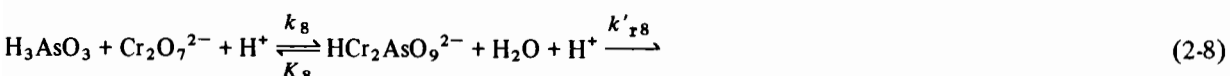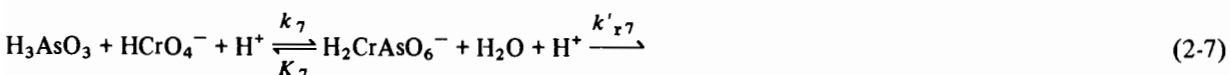### Interpretation of the Results of the Exchange and Redox Reactions

From the kinetic results of the catalytic oxygen exchange and redox reactions, it follows that:

(i) The rate laws of the two reactions are similar to each other,

$$R_c = k[As(III)]^{0.84}[Cr(VI)]^{1.46}$$

(pH 8.0 and 7.4, I = 1.0 M)

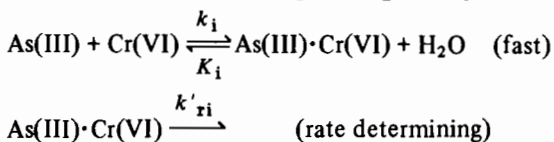$$R' = k'[As(III)]_0^{1.0}[Cr(VI)]^{1.37} \quad (pH\ 6.3,\ I = 1.0\ M)$$

(ii) The values of R' (the initial rate of the redox reaction) are 10^2–10^4 times larger than those of R_c (the catalytic oxygen exchange rate). For example, the values (in M s^{-1}) of R_c and R' are 2.84

$$H_3AsO_3 + CrO_4{}^{2-} \underset{K_1}{\overset{k_1}{\rightleftharpoons}} HCrAsO_6{}^{2-} + H_2O \xrightarrow{k'_{r1}} \tag{2-1}$$

$$H_3AsO_3 + HCrO_4{}^{-} \underset{K_2}{\overset{k_2}{\rightleftharpoons}} H_2CrAsO_6{}^{-} + H_2O \xrightarrow{k'_{r2}} \tag{2-2}$$

$$H_3AsO_3 + Cr_2O_7{}^{2-} \underset{K_3}{\overset{k_3}{\rightleftharpoons}} HCr_2AsO_9{}^{2-} + H_2O \xrightarrow{k'_{r3}} \tag{2-3}$$

$$H_2AsO_3{}^{-} + CrO_4{}^{2-} \underset{K_4}{\overset{k_4}{\rightleftharpoons}} CrAsO_6{}^{3-} + H_2O \xrightarrow{k'_{r4}} \tag{2-4}$$

$$H_2AsO_3{}^{-} + HCrO_4{}^{-} \underset{K_5}{\overset{k_5}{\rightleftharpoons}} HCrAsO_6{}^{2-} + H_2O \xrightarrow{k'_{r5}} \tag{2-5}$$

$$H_2AsO_3{}^{-} + Cr_2O_7{}^{2-} \underset{K_6}{\overset{k_6}{\rightleftharpoons}} Cr_2AsO_9{}^{3-} + H_2O \xrightarrow{k'_{r6}} \tag{2-6}$$

$$H_3AsO_3 + HCrO_4{}^{-} + H^+ \underset{K_7}{\overset{k_7}{\rightleftharpoons}} H_2CrAsO_6{}^{-} + H_2O + H^+ \xrightarrow{k'_{r7}} \tag{2-7}$$

$$H_3AsO_3 + Cr_2O_7{}^{2-} + H^+ \underset{K_8}{\overset{k_8}{\rightleftharpoons}} HCr_2AsO_9{}^{2-} + H_2O + H^+ \xrightarrow{k'_{r8}} \tag{2-8}$$

Scheme 1.

$\times 10^{-4}$ and 6.27×10^{-8} at pH 7.33, 1.20×10^{-5} and 1.39×10^{-8} at pH 8.48, and 1.8×10^{-6} and 5.9×10^{-9} at pH 11.5, respectively. ($[Cr(VI)] = 7.2 \times 10^{-2}$ M, $[As(III)]_0 = 1.34 \times 10^{-4}$ M, 25 °C, $I = 0.2$ M.)

These results may be interpreted by assuming the same type of the mechanism as proposed by Kowalak, which may be expressed generally as:

$$As(III) + Cr(VI) \underset{K_i}{\overset{k_i}{\rightleftharpoons}} As(III) \cdot Cr(VI) + H_2O \quad \text{(fast)}$$

$$As(III) \cdot Cr(VI) \xrightarrow{k'_{ri}} \quad \text{(rate determining)}$$

where K_i is the formation constant of the complex between As(III) and Cr(VI), and k_i and k'_{ri} are the rate constants of the complex formation and the slow step, respectively, and where As(III) and Cr(VI) designate the various kinds of ionic species of the arsenious acid and chromate in the solution. The fact that the order of the reaction with respect to Cr(VI) is greater than 1 in the exchange and the redox reactions, suggests that the dimeric forms of Cr(VI) take part in these reactions. The reversible condensation reactions of As(III) with Cr(VI) (monomeric and dimeric) give rise to the oxygen exchange of chromate ions with water, and the rate constants of the complex formation steps can be obtained from the catalytic exchange reaction rate R_c.

In the pH range between 2.8 and 12.5, the dominating ionic species of As(III) and Cr(VI) are H_3AsO_3 and $H_2AsO_3{}^{-}$, and $HCrO_4{}^{-}$, $CrO_4{}^{2-}$, and $Cr_2O_7{}^{2-}$ respectively, and the above mechanism may

be replaced by the sum of the following reactions between different ionic species of As(III) and Cr(VI) (Scheme 1). The specific acid catalyzed paths 7 and 8 are assumed in order to account for the steep increase in the rate of the redox reaction in the pH region smaller than 4. From the above mechanism, the observed catalytic oxygen exchange rate R_c over the pH range 7–12 is written as:

$$\begin{aligned} R_c &= k_1[H_3AsO_3][CrO_4{}^{2-}] + k_2[H_3AsO_3][HCrO_4{}^{-}] \\ &\quad + k_3[H_3AsO_3][Cr_2O_7{}^{2-}] + k_4[H_2AsO_3{}^{-}] \times \\ &\quad \times [CrO_4{}^{2-}] + k_5[H_2AsO_3{}^{-}][HCrO_4{}^{-}] \\ &\quad + k_6[H_2AsO_3{}^{-}][Cr_2O_7{}^{2-}] \end{aligned} \tag{3}$$

while the rate law for the redox reaction over the pH range 2–13 may be expressed as:

$$\begin{aligned} R' &= k'_{r1}K_1[H_3AsO_3][CrO_4{}^{2-}] + k'_{r2}K_2[H_3AsO_3] \times \\ &\quad \times [HCrO_4{}^{-}] + k'_{r3}K_3[H_3AsO_3][Cr_2O_7{}^{2-}] \\ &\quad + k'_{r4}K_4[H_2AsO_3{}^{-}][CrO_4{}^{2-}] \\ &\quad + k'_{r5}K_5[H_2AsO_3{}^{-}][HCrO_4{}^{-}] \\ &\quad + k'_{r6}K_6[H_2AsO_3{}^{-}][Cr_2O_7{}^{2-}] \\ &\quad + k'_{r7}K_7[H^+][H_3AsO_3][HCrO_4{}^{-}] \\ &\quad + k'_{r8}K_8[H^+][H_3AsO_3][Cr_2O_7{}^{2-}] \end{aligned} \tag{4}$$
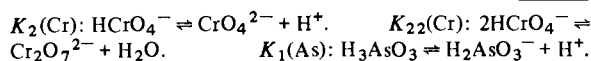
Since R' is the initial velocity, the concentrations of the ionic species in the above formula are their initial concentrations. As it is impossible to obtain the separate values of k'_{ri} and K_i from the present work, the product $(k'_{ri}K_i)$ is replaced by k'_i and eqn. (4) is rewritten in terms of k'_i as follows:

$$R' = R'_1 + R'_2 + R'_3 + R'_4 + R'_5 + R'_6 + R'_7 + R'_8$$
$$= k'_1[H_3AsO_3][CrO_4{}^{2-}] + k'_2[H_3AsO_3][HCrO_4{}^-]$$
$$+ k'_3[H_3AsO_3][Cr_2O_7{}^{2-}] + k'_4[H_2AsO_3{}^-] \times$$
$$\times [CrO_4{}^{2-}] + k'_5[H_2AsO_3{}^-][HCrO_4{}^-]$$
$$+ k'_6[H_2AsO_3{}^-][Cr_2O_7{}^{2-}] + k'_7[H^+] \times$$
$$\times [H_3AsO_3][HCrO_4{}^-] + k'_8[H^+][H_3AsO_3] \times$$
$$\times [Cr_2O_7{}^{2-}] \qquad (5)$$

The initial concentrations of individual ionic species of arsenic(III) and chromium(VI) were calculated by using the acid dissociation constants of H_3AsO_3 and $HCrO_4{}^-$ and the dimerization constant of $HCrO_4{}^-(K_{22})$ shown in Table III. The decrease in the concentration of H_3AsO_3 or $H_2AsO_3{}^-$ due to the complex formation was ignored.

TABLE III. The Values of Acid Dissociation Constants and Dimerization Constants

Temperature (°C)	I (M)	pK_2(Cr)	$\log K_{22}$(Cr)	pK_1(As)
25	0.2	6.02(7)	1.75(0)	9.29(3)
25	0.5	5.88(6)	1.84(5)	9.22(2)
25	1.0	5.73(0)	1.99(1)	9.13(5)
10	0.5		2.02(8)	
0	0.5		2.16(0)	

K_2(Cr): $HCrO_4{}^- \rightleftharpoons CrO_4{}^{2-} + H^+$. K_{22}(Cr): $2HCrO_4{}^- \rightleftharpoons Cr_2O_7{}^{2-} + H_2O$. K_1(As): $H_3AsO_3 \rightleftharpoons H_2AsO_3{}^- + H^+$.

The Evaluation of the Rate Constants

I. The analysis of the catalytic oxygen exchange reaction rate, R_c

The procedures of the analysis were as follows:

(i) In the pH region greater than 10.5, the dominating ionic species of chromium(VI) is $CrO_4{}^{2-}$ and the catalytic exchange reaction proceeds exclusively through the k_1, k_4, and k_5 paths. As the k_5 path is equivalent kinetically to the k_1 path, eqn. (3) may be simplified to eqn. (6)

$$R_c = k_1[H_3AsO_3][CrO_4{}^{2-}] + k_4[H_2AsO_3{}^-][CrO_4{}^{2-}]$$
$$+ k_5[H_2AsO_3{}^-][HCrO_4{}^-]$$
$$= \{k_1 + k_5(K_1(As)/K_2(Cr))\}[H_3AsO_3][CrO_4{}^{2-}]$$
$$+ k_4[H_2AsO_3{}^-][CrO_4{}^{2-}] \qquad (6)$$

where K_1(As) and K_2(Cr) are the acid dissociation constants of H_3AsO_3 and $HCrO_4{}^-$, respectively. Equation 6 is rewritten as:

$$R_c/[H_2AsO_3{}^-][CrO_4{}^{2-}] = k^*_1(a_{H^+}/K_1(As)) + k_4 \qquad (7)$$
$$k^*_1 = k_1 + k_5(K_1(As)/K_2(Cr))$$
$$R^*_1 = k^*_1[H_3AsO_3][CrO_4{}^{2-}]$$
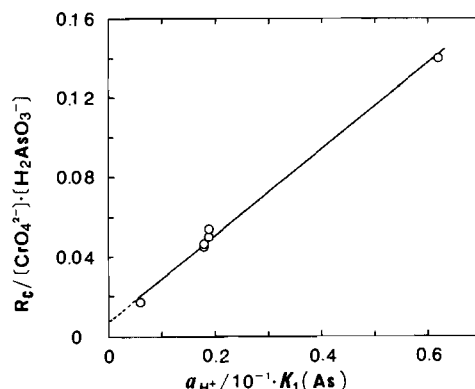
Fig. 7. $R_c/[CrO_4{}^{2-}]\cdot[H_2AsO_3{}^-]$ as a function of a_{H^+}/K_1 (As).

The data in Fig. 2 (pH–rate profile, pH > 10.5) and in Fig. 4B (dependence of R_c on As(III) at pH 11.0) were replotted in Fig. 7 according to eqn. (7) and treated by the method of the least-squares. From the slope and intercept of the straight line, the values of k^*_1 and k_4 were determined to be 2.18 ± 0.00 M^{-1} s^{-1} and $(6.98 \pm 1.96) \times 10^{-3}$ M^{-1} s^{-1}, respectively.

(ii) For the pH region smaller than 10.5 where all the rate terms contribute to R_c, the rate law is rewritten as:

$$R_c - k^*_1[H_3AsO_3][CrO_4{}^{2-}] - k_4[H_2AsO_3{}^-] \times$$
$$\times [CrO_4{}^{2-}]$$
$$= R_c - R^*_1 - R_4 = k_2[H_3AsO_3][HCrO_4{}^-]$$
$$+ k_3[H_3AsO_3][Cr_2O_7{}^{2-}]$$
$$+ k_6[H_2AsO_3{}^-][Cr_2O_7{}^{2-}] \qquad (8)$$

The values of the left hand side were calculated by using k^*_1 and k_4 obtained above, and were fitted to eqn. (8) by the method of least-squares. k_6 was obtained as a small negative value, and it was assumed that k_6 is relatively small. The k_6 term was then omitted from eqn. (8) and the equation was rewritten as

$$(R_c - R^*_1 - R_4)/[H_3AsO_3][HCrO_4{}^-]$$
$$= k_2 + k_3K_{22}[HCrO_4{}^-] \qquad (9)$$

In Fig. 8, the data in Fig. 2 (pH < 10.5) are replotted according to eqn. (9). From the slope and intercept of the line drawn through the plots, the values of k_2 and k_3 were evaluated as 191 ± 29 M^{-1} s^{-1} and 1960 ± 248 M^{-1} s^{-1}, respectively. The values of the rate constants obtained are listed in Table IV which reproduced satisfactorily the observed values of R_c.

II. The analysis of the redox reaction

The redox reaction was analyzed by using the data shown in Table II. The procedures were as follows:

TABLE IV. Rate Constants of the Complex Formation and Redox Reaction between Arsenic(III) and Chromium(VI).

$$As(III) + Cr(VI) \underset{K_i}{\overset{k_i}{\rightleftharpoons}} As(III) \cdot Cr(VI) + H_2O. \quad As(III) \cdot Cr(VI) \xrightarrow{k'_{ri}} Products^a$$

No. of reactions	k_i	$k'_i \, (\equiv K_i k'_{ri})$		
		$I = 0.2$	$I = 0.5$	$I = 1.0$
1 $H_3AsO_3 + CrO_4^{2-}$	$(2.18 \pm 0.00)*$			
2 $H_3AsO_3 + HCrO_4^-$	191 ± 29	6.7×10^{-3}	$(6.9 \pm 0.7) \times 10^{-3}$	$(7.3 \pm 1.5) \times 10^{-3}$
3 $H_3AsO_3 + Cr_2O_7^{2-}$	1960 ± 248	1.00×10^{-2}	$(1.08 \pm 0.05) \times 10^{-2}$	$(1.21 \pm 0.08) \times 10^{-2}$
4 $H_2AsO_3^- + CrO_4^{2-}$	$(7.0 \pm 2.0) \times 10^{-3}$	5.4×10^{-4}	8.0×10^{-4}	10.4×10^{-4}
5 $H_2AsO_3^- + HCrO_4^-$		$(10.3 \pm 1.6)*$	$(21.3 \pm 3.1)*$	$(17.5 \pm 5.5)*$
6 $H_2AsO_3^- + Cr_2O_7^{2-}$		29.7 ± 1.9	36.1 ± 3.1	54.3 ± 6.0
7 $H_3AsO_3 + HCrO_4^- + H^+$			15.3 ± 0.03	
8 $H_3AsO_3 + Cr_2O_7^{2-} + H^+$			14.3 ± 0.03	

^{a}The suffix i refers to the number of the reaction.
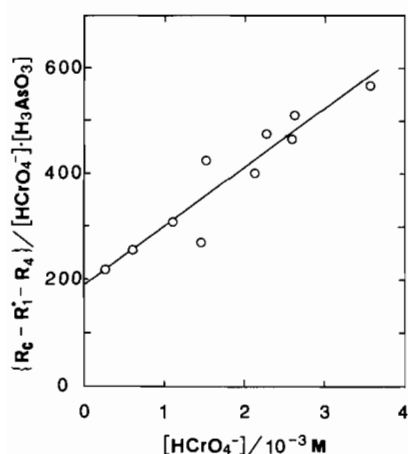
Fig. 8. $\{R_c - R^*_1 - R_4\}/[HCrO_4^-] \cdot [H_3AsO_3]$ vs. $[HCrO_4^-]$ ($I = 0.2$ M, 25 °C).

(i) At pH 12.8, the dominating ionic species of Cr(VI) and As(III) are CrO_4^{2-} and $H_2AsO_3^-$, and the initial redox rate, R' may be written as $R'_4 = k'_4[H_2AsO_3^-][CrO_4^{2-}]$. From the data at pH 12.8 in Table II, the value of k'_4 was evaluated as 5.4×10^{-4} M^{-1} s^{-1}.

Due to the comparatively large value of K_4, a part of the arsenite ion would exist in the form of the complex, and the initial concentration of arsenite, $[As(III)]_0$ may be written as:

$$[As(III)]_0 = [As(III)]_e + [As(III) \cdot Cr(VI)]$$

$$= [H_2AsO_3^-]_e + [AsCrO_6^{3-}]$$

where $[As(III)]_e$ is the equilibrium concentration of the arsenite ion and the following relation has to be introduced in terms of the reaction mechanism eqn. (2-4):

$$R'_4 = k'_{r4}[AsCrO_6^{3-}] = \frac{k'_{r4}K_4[As(III)]_0[CrO_4^{2-}]}{1 + K_4[CrO_4^{2-}]}$$

$$= \frac{k'_{r4}K_4[As(III)]_0[Cr(VI)]}{1 + K_4[Cr(VI)]} \quad (10)$$

In the derivation of eqn. (10), the decrease in the concentration of Cr(VI) due to the complex formation was ignored since [Cr(VI)] is in excess relative to $[As(III)]_0$. Equation 10 can be rearranged as:

$$\frac{[As(III)]_0}{R'_4} = \frac{1}{k'_{obs}} = \frac{1}{k'_{r4}} + \frac{1}{k'_{r4}K_4[Cr(VI)]}$$

The plots of $1/k'_{obs}$ against $1/[Cr(VI)]$ are shown in Fig. 9. The data used for the plot are the same as those used to obtain k'_4 (Table II, pH = 12.8) and the values of k'_{r4} and K_4 were obtained to be 1.96×10^{-4} s^{-1} and 3.41 M^{-1}, respectively.

(ii) At pH = 4.5, where the dominant ionic species of As(III) is H_3AsO_3 and those of Cr(VI) are $HCrO_4^-$ and $Cr_2O_7^-$, the rate law is expressed as:
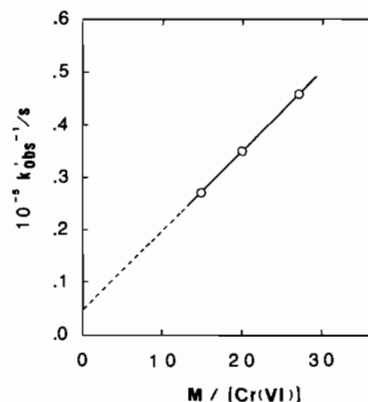

Fig. 9. $1/k'_{obs}$ as a function of $1/[Cr(VI)]$ (pH 12.8, 25 °C, $I = 0.2$ M).
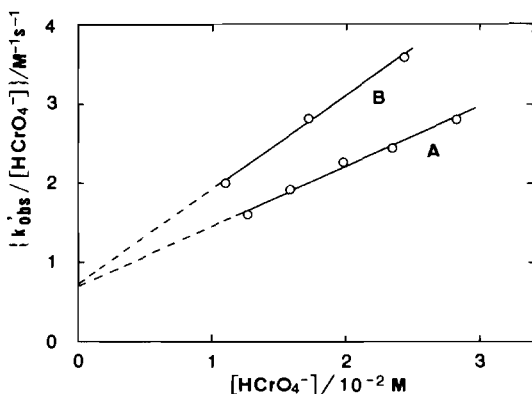
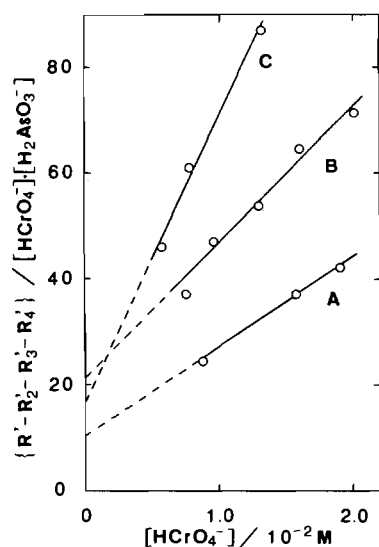Fig. 10. $k'_{obs}/[HCrO_4^-]$ as a function of $[HCrO_4^-]$ (pH 4.5, 25 °C). A: $I = 0.5$ M; B: $I = 1.0$ M.

Fig. 11. $(R' - R'_2 - R'_3 - R'_4)/[HCrO_4^-] \cdot [H_2AsO_3^-]$ as a function of $[HCrO_4^-]$ (pH 6.33, 25 °C). A: $I = 0.2$ M; B: $I = 0.5$ M; C: $I = 1.0$ M.

$R' = R'_2 = R'_3 = k'_2[H_3AsO_3][HCrO_4^-] + k'_3$ $[H_3AsO_3][Cr_2O_7^{2-}]$. The equation may be rewritten as:

$$R'/[H_3AsO_3][HCrO_4^-]$$
$$= k'_{obs}/[HCrO_4^-] = k'_2 + k'_3 K_{22}[HCrO_4^-] \quad (11)$$

According to eqn. (11), the redox rate data in Table II obtained at various concentration of Cr(VI) and at pH 4.5, were replotted in Fig. 10 (A: $I = 0.5$ M, B: $I = 1.0$ M). The least-squares treatment was applied to those plots, and the following values (in $M^{-1} s^{-1}$) of k'_2 and k'_3 were obtained: $k'_2 = 0.69 \times 10^{-2}$ ($I = 0.5$ M) and 0.73×10^{-2} ($I = 1.0$ M); $k'_3 = 1.08 \times 10^{-2}$ ($I = 0.5$ M) and 1.21×10^{-2} ($I = 1.0$ M).

(iii) At pH 6.3 where all the rate terms in eqn. (5) would contribute to the redox rate, eqn. (5) is re-written as:

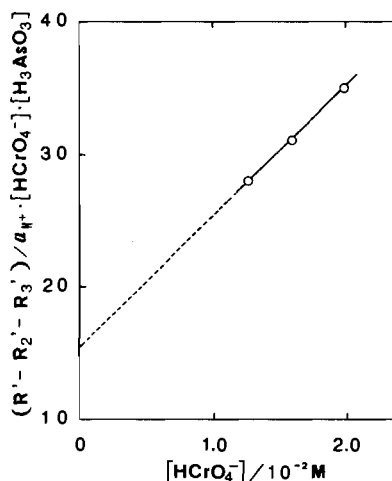Fig. 12. $(R' - R'_2 - R'_3)/a_{H^+}[HCrO_4^-] \cdot [H_3AsO_3]$ as a function of $[HCrO_4^-]$ (pH 2.8, 25 °C, $I = 0.5$ M).

$$\frac{(R' - R'_2 - R'_3 - R'_4)}{[H_2AsO_3^-][HCrO_4^-]}$$
$$= \{k'_5 + k'_1 K_2(Cr)/K_1(As)\} + k'_6 K_{22}[HCrO_4^-]$$
$$= k'_5{}^* + k'_6 K_{22}[HCrO_4^-] \quad (12)$$

According to the eqn. (12), the redox rate data in Table II obtained at pH 6.33 and at various concentrations of Cr(VI), were replotted in Fig. 11 (A: $I = 0.2$ M, B: $I = 0.5$ M, C: $I = 1.0$ M). The least-squares treatment of the plots gave the values of the rate constants as:
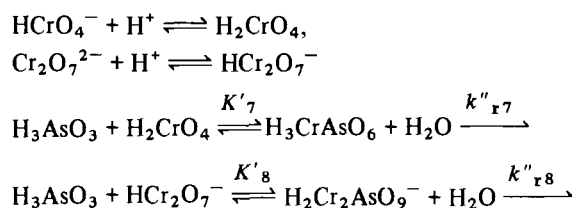
	I (M)		
	0.2	0.5	1.0
$k'_5{}^*$ ($M^{-1} s^{-1}$)	10.3 ± 1.6	21.3 ± 3.1	17.5 ± 5.5
k'_6 ($M^{-1} s^{-1}$)	29.7 ± 1.9	36.1 ± 3.1	54.3 ± 6.0

(iv) At pH 2.8, the rate law is expressed as $R' = R'_2 + R'_3 + R'_7 + R'_8$, which can be written as:

$$(R' - R'_2 - R'_3)/(a_{H^+}[H_3AsO_3][HCrO_4^-])$$
$$= k'_7 + k'_8 K_{22}[HCrO_4^-] \quad (13)$$

The redox rate data in Table II at pH 2.8 were replotted in Fig. 12 according to eqn. 13). A similar treatment of the plots gave the rate constant values of $k'_7 = 15.3 \pm 0.03$ and $k'_8 = 14.3 \pm 0.03$ $M^{-2} s^{-1}$ ($I = 0.5$ M).

An alternative mechanism to eqns. (7) and (8) of the acid catalysis would be represented as follows:

$$HCrO_4^- + H^+ \rightleftharpoons H_2CrO_4,$$

$$Cr_2O_7^{2-} + H^+ \rightleftharpoons HCr_2O_7^-$$

$$H_3AsO_3 + H_2CrO_4 \overset{K'_7}{\rightleftharpoons} H_3CrAsO_6 + H_2O \overset{k''_{r7}}{\longrightarrow}$$

$$H_3AsO_3 + HCr_2O_7^- \overset{K'_8}{\rightleftharpoons} H_2Cr_2AsO_9^- + H_2O \overset{k''_{r8}}{\longrightarrow}$$
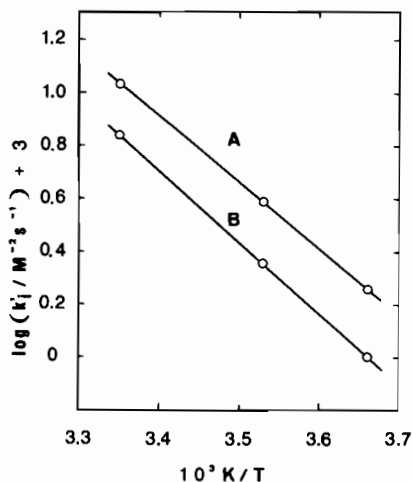
Fig. 13. Temperature dependence of k'_i. A: k'_3; B: k'_2.

The rate constants k''_7 $(= K'_7 k_{r7})$ and k''_8 $(= K'_8 k_{r8})$ in the equations would be equivalent to $k'_7 K_1$-(Cr) and $k'_8 K_{23}$(Cr), where K_1(Cr) and K_{23}(Cr) are the acid dissociation constants of H_2CrO_4 and $HCr_2O_7^-$, respectively. A rough estimate of k''_7 and k''_8 by using K_1(Cr) = 1.26 $(I = 1.0$ M) and K_{23}-(Cr) = 0.85 $(I = 1.0$ M) [10] leads to the values of 19.3 and 12.2 $M^{-1} s^{-1}$, respectively.

The values of the redox rate constants are listed in Table IV, which reproduced satisfactorily the observed values of R'.

Temperature dependence of the redox reaction was studied at pH 4.50 and $I = 0.5$ M (0, 10, and 25 °C) and the data obtained are shown in Table II. These data were analyzed to obtain the rate constants k'_2 and k'_3 by the same procedure as described above. In Fig. 13, plots of log k'_2 (A) and log k'_3 (B) against $1/T$ are shown. The values of the activation energy and the entropy of activation were obtained as follows:

$k'_2; E_a = 51.5 \pm 0.1$ kJ/mol, $\Delta S^{\ddagger} = -71.5$ J/K mol

$k'_3; E_a = 48.3 \pm 0.3$ kJ/mol, $\Delta S^{\ddagger} = -64.3$ J/K mol

Discussion

As to the rate constants of the complex formation reactions, the reactivity of H_3AsO_3 is 10^2 times larger towards $HCrO_4^-$ than towards CrO_4^{2-}, while the reactivity of H_3AsO_3 towards CrO_4^{2-} is 10^2 times larger than that of $H_2AsO_3^-$. These results are consistent with the general trend that most of the oxoanion reactions are acid-catalyzed. H_3AsO_3 is ten times more reactive towards $Cr_2O_7^{2-}$ than towards $HCrO_4^-$. The failure to find any contribution to R_c of the kinetic term including $H_2AsO_3^-$ and $Cr_2O_7^{2-}$ may be ascribed to the fast redox reaction rate between them. In this case, the As(III)–Cr(VI) complex, when formed, would be immediately involved in the redox reaction, and does not contribute to the oxygen exchange.

As mentioned in the introduction, the oxygen exchange of chromate ions ($[Cr(VI)] = 7 \times 10^{-2}$ M) with water is also catalyzed significantly by a small amount of periodate ($[I(VII)] = 1.0 \times 10^{-5}$ M) and tellurate ions ($[Te(VI)] = 1.4 \times 10^{-4}$ M). Preliminary results on the rate constants of the reactions between chromate and the oxoanions cited above are shown in Table V. The remarkable reactivity of $H_4IO_6^-$ and $H_3IO_6^{2-}$ towards $HCrO_4^-$ will be seen. The spectrophotometric studies of the complex formation reactions of chromate with other oxoanions have been reported by several authors, and some of these results are shown in Table V.

As seen from the Table, the rate constant of the complex formation of $HS_2O_3^-$ with $HCrO_4^-$ is comparable to that of periodate ions with $HCrO_4^-$, while the complex formation constant is 10^4 for $HS_2O_3^-$ ion and 4 for the periodate ion. As expected from the large stability of the complex between $HS_2O_3^-$ and $HCrO_4^-$ ions, no catalytic effect of the $HS_2O_3^-$ ion on the chromate oxygen exchange was observed. Some results on the chromate oxygen exchange in the presence of $HS_2O_3^-$ (a) and phosphite ions (b) are shown in Table VI.

For the catalytic effect of an oxoanion on the oxygen exchange of oxoanions to be observed, the

TABLE V. Rate Constants of the Complex Formation and Complex Formation Constants between Chromate Ion and Another Oxoanion

Reactions	t (°C)	I (M)	k ($M^{-1} s^{-1}$)	K (M)	Methods[a]	Reference
$HCrO_4^- + CrO_4^{2-}$	25	1.0	10^3		^{18}O	8
$HCrO_4^- + HCrO_4^-$	25	1.0	9	138	^{18}O	8
$HCrO_4^- + H_4IO_6^-$	0	0.2	3.1×10^4	4.1	^{18}O	11
$HCrO_4^- + H_3IO_6^{2-}$	0	0.2	2.8×10^4		^{18}O	11
$CrO_4^{2-} + H_4IO_6^-$	0	0.2	3.2×10^3		^{18}O	11
$CrO_4^{2-} + H_3IO_6^{2-}$	0	0.2	3.8		^{18}O	11
$HCrO_4^- + HS_2O_3^-$	25	0.1	2×10^4	1.1×10^4	sp	12
$HCrO_4^- + H_2PO_3^-$	25	3		8	sp	13

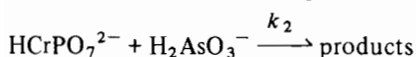[a] ^{18}O: catalytic oxygen exchange reaction; sp: spectrophotometric method.
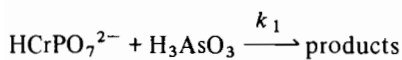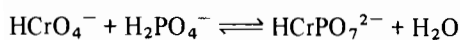
TABLE VI. The Rate of Chromate Oxygen Exchange Reaction with Water in the Presence of $HS_2O_3^-$ (a) and Phosphite (b) Ions

[Anion] (M)	[Cr(VI)] (M)	pH	R (M s^{-1})	R_0 (M s^{-1})
1.39×10^{-2} (a)	6.94×10^{-2}	7.99	2.11×10^{-5}	2.08×10^{-5}
1.40×10^{-2} (a)	6.80×10^{-2}	7.41	2.36×10^{-4}	2.62×10^{-4}
8.61×10^{-4} (b)	7.07×10^{-2}	7.80	4.95×10^{-5}	4.74×10^{-5}

R; with added oxoanion. R_0; without added oxoanion.

complex formation reactions should be rapid and reversible and the complex formed should be relatively unstable. The study of the catalytic oxygen exchange reaction may provide a means of obtaining information on relatively unstable complex formation reaction between oxoanions which is difficult to detect by conventional methods.

With respect to the redox reaction, the data in Table IV show that the value of k'_6 for the reaction between $Cr_2O_7^{2-}$ and $H_2AsO_3^-$ is particularly large and the reactivity of arsenite anion towards both $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions is larger than that of arsenious acid (the ratio of k'_5/k'_2 and k'_6/k'_3 being 1.5×10^3 and 3.0×10^3, respectively). The broad peak at pH 6.5 in the pH–redox rate profile would be due to the rate term $R'_6 = k'_6[H_2AsO_3^-] \cdot [Cr_2O_7^{2-}]$. The ionic product has a maximum at pH 6.5, and the value of k'_6 is very large relative to other rate constants. The contribution of the rate term R'_6 to the total rate R' calculated by using the value of k'_6 of 30 M^{-1} s^{-1} is larger than 50% in the pH range from 6 to 7.5 and attains a maximum value at pH 6.6 (70%). In a study on the chromium(VI)–arsenic(III) reaction in acetate buffer (0.2 M), Mason and Kowalak [5] suggested that the dichromate ion is more effective than $HCrO_4^-$ as an oxidant, and the complex formation constant for $As(III) \cdot Cr_2O_7^{2-}$ is significantly smaller than that for $As(III) \cdot HCrO_4^-$. The higher reactivity of $H_2AsO_3^-$ relative to H_3AsO_3 was also suggested by Mason *et al.* [6]. They have investigated the kinetics of the Cr(VI)–As(III) reaction in phosphate buffers and showed that the rate term corresponding to the direct reaction between As(III) and Cr(VI) is absent and that the results point to the reaction proceeding via two activated complexes $H_2PO_4^- \cdot HCrO_4^- \cdot As(III)$ and $HPO_4^{2-} \cdot HCrO_4^- \cdot As(III)$. From these facts, they proposed the following mechanism:

$$HCrO_4^- + H_2PO_4^- \rightleftharpoons HCrPO_7^{2-} + H_2O$$

$$HCrPO_7^{2-} + H_3AsO_3 \xrightarrow{k_1} products$$

$$HCrPO_7^{2-} + H_2AsO_3^- \xrightarrow{k_2} products$$

and gave a ratio of k_2/k_1 of approximately 5.1×10^3 and $k_1 = (2.4 \pm 0.14) \times 10^{-2}$ M^{-2} s^{-1}. It is interesting to note that the ratio of the reactivities of arsenite ion towards $HCrPO_7^{2-}$ and $Cr_2O_7^{2-}$ to those of arsenious acid towards the same ions have a similar value of 10^3 (for $HCrPO_7^{2-}$; 5.1×10^3 [6], $Cr_2O_7^{2-}$; 3.0×10^3).

A broad minimum in the pH range between 4 and 5.5 in the pH–rate curve in Fig. 5 would be explained as follows: over the above pH range, the existing ionic species are H_3AsO_3, $HCrO_4^-$, and $Cr_2O_7^{2-}$, and the rate terms, R'_2 $(= k'_2[H_3AsO_3][HCrO_4^-])$ and R'_3 $(= k'_3[H_3AsO_3][Cr_2O_7^{2-}])$ contribute dominantly to the redox rate. When the pH value exceeds 5.5, the dissociation of H_3AsO_3 beings and the contribution of the rate terms, R'_5 and R'_6 involving more reactive species $H_2AsO_3^-$ to the total redox rate becomes important ($k'_2 < k'_5$ and $k'_3 < k'_6$). The increase in the redox rate on the other side of the minimum (pH < 4), is due to the additional rate terms R'_7 and R'_8 for the acid catalyzed reactions of H_3AsO_3 with $HCrO_4^-$ and $Cr_2O_7^{2-}$.

The effect of the ionic strength on the rate constants, k'_4, k'_5, and k'_6 for the reaction between arsenite and chromate ions is positive and the salt effect on the process between H_3AsO_3 and chromate ions is very small as expected.

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