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The Kinetics of Oxygen-exchange Reaction between Chromate Ions and Water

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The oxygen-exchange reaction between chromate ions and water has been studied under the following conditions: 25 °C, pH=7—12, [Cr(VI)]=0.075 mol dm^{-3}, I=0.2 and 1 mol dm^{-3}. The rate law of the exchange reaction has been found to be:

$$R = k_1[\mathrm{CrO_4}^{2-}] + k_2[\mathrm{HCrO_4}^-] + k_3[\mathrm{H}^+][\mathrm{HCrO_4}^-] + k_4[\mathrm{HCrO_4}^-][\mathrm{CrO_4}^{2-}] + k_5[\mathrm{HCrO_4}^-]^2.$$

The exchange rate has been analyzed in terms of this rate law to obtain the values of k_1—k_5. The presence of the third-order rate term in [Cr(VI)] has been suggested. The activation energy of the overall exchange reaction (I=1 mol dm^{-3}) is (25.5±0.7) kJ/mol at pH 7.4 and (98.9±1.0) kJ/mol at pH 11.0. The salt effect is negative at pH<10.5 and absent at pH>10.5.

In a series of papers on the 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 interactions of these two oxoanions. As a preliminary to a study of the interaction of chromate ions with another oxoanion by the oxygen-exchange reaction,[3] we have examined the oxygen exchange of chromate ions with water.

This reaction has been studied by several authors.[4-6] Holyer and Baldwin[5] have interpreted the exchange reaction (pH 6.7—12, [Cr(VI)]=0.64—2.7 M,** 25 °C) in terms of these reactions:

$$\mathrm{HCrO_4}^- + \mathrm{CrO_4}^{2-} \rightleftharpoons \mathrm{Cr_2O_7}^{2-} + \mathrm{OH}^-,$$

$$\mathrm{HCrO_4}^- + \mathrm{HCrO_4}^- \rightleftharpoons \mathrm{Cr_2O_7}^{2-} + \mathrm{H_2O},$$

$$\text{and}\quad \mathrm{CrO_4}^{2-} + \mathrm{H_2}^{18}\mathrm{O} \rightleftharpoons \mathrm{CrO_3}^{18}\mathrm{O}^{2-} + \mathrm{H_2O}.$$

Mak[6] has extended the study up to pH 4.5 ([Cr(VI)]= 0.1 and 0.2 M, 25 °C), and proposed these exchange paths:

$$\mathrm{Cr_2O_7}^{2-} + \mathrm{HCrO_4}^- \rightleftharpoons \mathrm{Cr_3O_{10}}^{2-} + \mathrm{OH}^-,$$

$$\text{and}\quad \mathrm{HCr_2O_7}^- + \mathrm{HCrO_4}^- \rightleftharpoons \mathrm{Cr_3O_{10}}^{2-} + \mathrm{H_2O},$$

the former being important at pH 6.7—7.6, and the latter, at pH<6.0. The chloride-ion catalysis of the oxygen-exchange reaction of chromate ions has been noted by this author at pH>6.8. The absence of the salt effect on the exchange reaction has been claimed in these papers.

In the present paper, the uncatalyzed and acid-catalyzed oxygen exchanges of hydrogenchromate ions with water have been proposed as additional exchange paths, the presence of the third-order rate term in [Cr(VI)] has been suggested, and the salt effect on the exchange reaction has been established.

Experimental

Materials. The sodium chromate tetrahydrate (guaranteed reagent, Merck), sodium chloride (guaranteed reagent JIS), and other chemicals (guaranteed reagent JIS) were used without further purification. Sodium chromate enriched in oxygen-18 was prepared by the exchange reaction of sodium chromate with $\mathrm{H_2}^{18}\mathrm{O}$ at 100 °C for 2 h.

Procedure. The procedures were almost the same as those previously reported.[7] The exchange reaction was initiated by dissolving a weighed amount of the enriched sodium chromate in normal water. The normal water was boiled before use to expel the dissolved carbon dioxide. The pH of the solution was fixed by adding a small amount of a hydrochloric acid or sodium hydroxide solution. The pH of the solution was measured with a Hitachi-Horiba pH-meter (Model F-7) or with a Radiometer PHM-26 pH-meter equipped with a glass electrode (Type 202 C) and a reference electrode (Type K 401). The ionic strength was adjusted to 1 M by the addition of sodium chloride. The ionic strength of 0.2 was maintained by means of the chromate. 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 above series of operations were carried out under an atmosphere of nitrogen.

To avoid the precipitation-induced oxygen exchange of the chromate ion, which becomes appreciable at pH values smaller than 8, the pH of the solution was, when necessary, brought to ≈9 before the addition of the precipitant by adding an appropriate amount of a sodium hydroxide solution.

The precipitate was separated by means of a centrifuge, washed three times with absolute ethanol, dried in an oven at 110 °C, and converted into carbon dioxide by the guadinium-chloride method.[8] 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 this formula:

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

where O_0, O_t, and O_∞ are the oxygen-18 contents of the chromate at the times 0, t, and infinity respectively, and where [Cr(VI)] and [H$_2$O] are the molar concentrations of the chromate and water respectively.

Dissociation and Condensation Constants of Hydrogenchromate Ions. The values of the equilibrium constants, K_1 and K_d, defined by:

$$K_1 = [\mathrm{HCrO_4}^-]/a_{\mathrm{H}^+}[\mathrm{CrO_4}^{2-}],$$

$$\text{and}\quad K_d = [\mathrm{Cr_2O_7}^{2-}]/[\mathrm{HCrO_4}^-]^2,$$

were obtained as follows. The values at I=0.2 M and 25 °C were interpolated from the literature values[9] by means of the Debye-Hückel equation. The literature values at 20 °C were corrected to 25 °C and used in the interpolation. The results are log(K_1/M)=6.03 and log(K_d/M)=1.75.

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

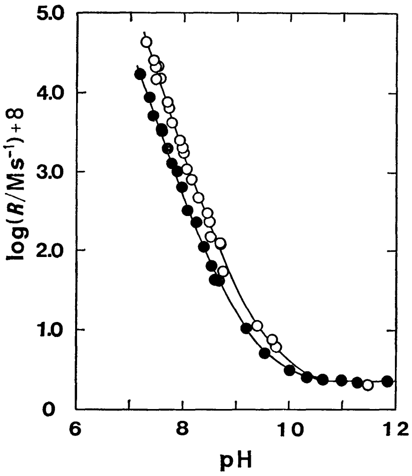

Fig. 1. The rate of oxygen exchange reaction of chromate ions with water *versus* pH.
([Cr(VI)]=0.075 M, 25 °C)
○: I=0.2 M, ●: I(NaCl)=1.0 M.

The values at I(NaCl)=1.0 M and 25 °C were determined by means of potentiometric titrations with a glass electrode. Solutions of sodium chromate of known concentrations and a unit ionic strength were titrated with standardized hydrochloric acid. Seven series of titrations were carried out with chromate solutions of varied concentrations, ranging from 1.157×10^{-3} M to 6.198×10^{-2} M. The titration curves were treated by the method of Sillén[10] and Sasaki[11] to obtain the values of K_1 and K_d. The value of the activity coefficient of the hydrogen ion in the medium of I(NaCl)=1.0 M necessary for the treatment was obtained by the potentiometric titration of a 1 M NaCl solution with standardized hydrochloric acid. The results are $\log(K_1/\mathrm{M})=5.73$ and $\log(K_d/\mathrm{M})=2.14$.

Results and Discussion

pH *Dependence of the Exchange Rate.* The dependence of the exchange rate on the pH was studied at I=1.0 and 0.2 M, the concentration of Cr(VI) being kept at ≈0.075 M. The rate-pH profiles are shown in Fig. 1. In the pH region smaller than 8.7, $\log(R/\mathrm{M\,s^{-1}})$ decreases linearly with the increase in pH. The slopes of the lines obtained by the method of the least-squares are -1.89 ± 0.04 (I=0.2 M) and -1.82 ± 0.03 (I=1.0 M). From pH=8.7 upwards, the rate decreases increasingly less rapidly, and above pH=10.5, where CrO_4^{2-} is the predominating ionic species, it becomes independent of the pH. The exchange rate in this region is so slow (half-life=*ca.* 25 d) that it was difficult to follow the reaction for more than a half-period without the interference of the atmospheric carbon dioxide. In these runs, the final values were borrowed from the runs under more acidic conditions.

[Cr(VI)] Dependence of the Exchange Rate. This was studied at four different pH's: 7.2, 7.4, 7.7, and 8.0 (25 °C, I=1.0 M). The concentration of Cr(VI) was varied from 0.036 to 0.14 M at pH=7.2, 7.7, and 8.0, and from 0.010 to 0.14 M at pH=7.4. Plots of $\log(R/\mathrm{M\,s^{-1}})$ against $\log([\mathrm{Cr(VI)}]/\mathrm{M})$ are shown in Fig. 2. The slopes of the four straight lines through each set of plotted points are 1.23 ± 0.02 (pH: 7.2), 1.05 ± 0.03 (pH: 7.4), 1.17 ± 0.02 (pH: 7.7), and 0.93 ± 0.01 (pH: 8.0). It may be inferred that the order of the exchange reaction with respect to [Cr(VI)] tends to the value of unity with the increase in the pH.

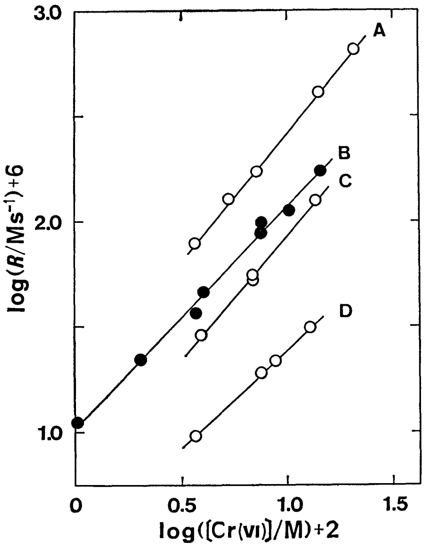

Fig. 2. Dependence of the exchange rate on [Cr(VI)].
(25 °C, I(NaCl)=1 M)
○ A: pH=7.2, C: pH=7.7, D: pH=8.0 ([Cr(VI)]=0.036—0.14 M).
● B: pH=7.4 ([Cr(VI)]=0.010—0.14 M).

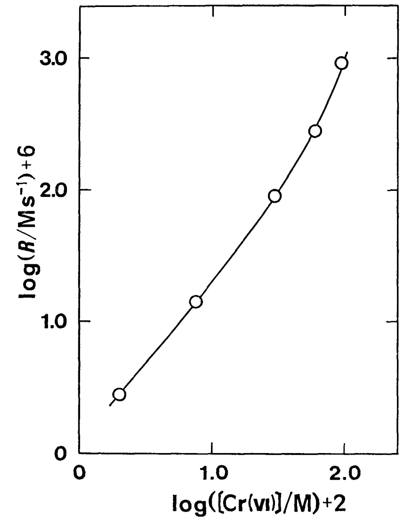

Fig. 3. Dependence of the exchange rate on [Cr(VI)].
[Cr(VI)]=0.02—0.96 M, I(NaCl)=4 M, pH=7.5, 25 °C.

Holyer and Baldwin[5] have reported a value of 1.98 ± 0.07 for the corresponding slope at pH=7.5 with Cr(VI) concentrations ranging from 0.15 to 2.7 M. In order to explain the apparent discrepancy between this and the present results, we have studied the [Cr(VI)] dependence over a wider range of Cr(VI) concentrations (0.02—0.96 M, I(NaCl)=4.0 M). The logarithmic plot of R against [Cr(VI)] gives a curve concave upwards (Fig. 3), the slope of the curve in-

Table 1. Effect of the supporting electrolytes on the rate of the oxygen exchange of chromate ions

$\frac{[\mathrm{Cr(VI)}]}{\mathrm{M}}$	pH[a]	Supporting electrolyte ($I=1.0$ M)	$R/10^{-5}$ M s^{-1}
0.0721	7.60	$NaClO_4$	0.828±0.006
0.0739	7.60	NaCl	0.792±0.006
0.0720	7.51	$NaClO_4$	1.83±0.06
0.0741	7.51	NaCl	1.75±0.05

a) In measuring the pH, the inner solution of the reference electrode was replaced by 4 M NaCl.

creasing from unity to 2.6 with the increase in the concentration of Cr(VI). It appears that the observed [Cr(VI)] dependence of the exchange reaction is dependent on the value of [Cr(VI)]. The kinetics of the oxygen exchange of chromate ions involves both the first-order and the higher-order rate terms in [Cr(VI)]. At lower concentrations of Cr(VI), the first-order term predominates, while at higher concentrations the second- and third-order terms come into play.

Effect of Chloride Ions on the Exchange Rate. Since hydrogenchromate ions react with chloride ions to form trioxochlorochromate(VI) ions in acidic aqueous solutions,[12,13] it may be suspected that the $HCrO_4^- + Cl^- + H^+ \rightleftharpoons CrO_3Cl^- + H_2O$ reaction might contribute to the oxygen exchange of chromate ions. Perlmutter-Hayman and Wolff[14] have noted the absence of chloride-ion catalysis of the hydrolysis of dichromate ions.

In order to examine the possibility of nucleophilic catalysis by chloride ions, the exchange rate was studied in the perchlorate media and compared with the rate in NaCl media (Table 1). The results indicate that the catalysis of the oxygen exchange of chromate ions by chloride ions is absent, at least under the present experimental conditions.

Mechanism of the Oxygen-exchange Reaction. The above results may be summarized as follows:

pH: 7.2—8.7 $R \propto [\mathrm{H^+}]^{1.8}[\mathrm{Cr(VI)}]^{1.2-1.0}$,
pH: 8.7—10.5 $R \propto [\mathrm{H^+}]^{1.8-0}[\mathrm{Cr(VI)}]$,
pH: >10.5 $R \propto [\mathrm{H^+}]^{0}[\mathrm{Cr(VI)}]$.

In the pH region greater than 10.5, the exchange reaction may be interpreted in terms of the process:

$$CrO_4^{2-} + H_2{}^{18}O \rightleftharpoons CrO_3{}^{18}O^{2-} + H_2O. \qquad (1)$$

Since the more acidic species of an oxoanion is usually more reactive in the oxygen-exchange reaction, it is natural to assume the exchange mechanism:

$$HCrO_4^- + H_2{}^{18}O \rightleftharpoons HCrO_3{}^{18}O^- + H_2O, \qquad (2)$$

along with Reaction 1.

The nearly first-order dependence on [Cr(VI)] (see Fig. 2, [Cr(VI)]<0.14 M) and the nearly second-order dependence on $[H^+]$ observed at pH<8.7 suggest that the acid-catalyzed oxygen exchange of hydrogenchromate ions with water:

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-,$$
$$HCrO_4^- + H_2{}^{18}O + H^+ \rightleftharpoons HCrO_3{}^{18}O^- + H_2O + H^+, \qquad (3)$$

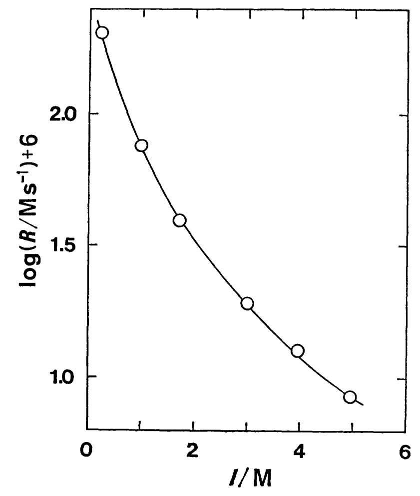

Fig. 4. The effect of ionic strength on the exchange rate.
$I=0.2$—5 M, [Cr(VI)]=0.075 M, pH=7.5, 25 °C.

plays a dominant role in this pH region.

The order of the exchange reaction with respect to [Cr(VI)] is definitely greater than unity at pH<7.7. This fact suggests that there is some contribution of the two dimerization mechanisms, 4 and 5, to the exchange reaction:

$$HCrO_4^- + CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + OH^-, \qquad (4)$$
$$HCrO_4^- + HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O. \qquad (5)$$

The rate law of the oxygen exchange of chromate ions with water may now be written as:

$$\begin{aligned} R &= R_1 + R_2 + R_3 + R_4 + R_5 \\ &= k_1[CrO_4^{2-}] + k_2[HCrO_4^-] + k_3[H^+][HCrO_4^-] \\ &\quad + k_4[HCrO_4^-][CrO_4^{2-}] + k_5[HCrO_4^-]^2. \end{aligned} \qquad (6)$$

Salt Effect. The effect of the ionic strength on the exchange rate can be seen from Fig. 1. The salt effect is negative at pH<10.5 and is absent above pH=10.5. The salt effect at pH=7.50 has been studied over a wider range of ionic strength (I(NaCl)= 0.2—5.0 M) (Fig. 4), [Cr(VI)] being kept at 0.075 M. The exchange rate decreases with the increase in the ionic strength.

At pH 7.50, the exchange reaction proceeds for the most part through the k_3 and k_5 paths (*ca.* 65% and 30% respectively). The kinetic salt effect on the k_3 path may be expected to be negative, and that on the k_5 path, to be positive. The equilibrium salt effect on K_1 and K_d reduces the concentration of $HCrO_4^-$, which is the more active species in the oxygen exchange of chromate ions. The observed salt effect is a result of these effects.

Temperature Dependence of the Exchange Rate. This has been studied at pH 7.38 (0 °C, 15 °C, and 25 °C) and at pH 11.0 (25 °C, 35 °C, and 45 °C). The concentration of chromium(VI) was kept at 0.075 M, the ionic strength being fixed at 1.0 M. The Arrhenius plots are shown in Fig. 5. The activation energies are (25.5±0.7) kJ/mol at pH 7.38 and (98.9±1.0) kJ/mol at pH 11.0.

Since the oxygen exchange proceeds exclusively through the k_1 path at pH=11.0, the value obtained

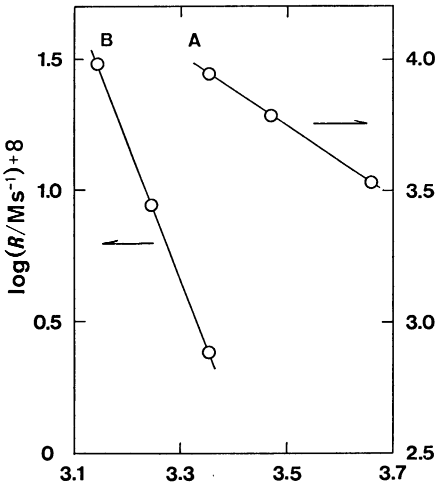

Fig. 5. Temperature dependence of the exchange rate at pH=7.4(A) and pH=11.0(B). ([Cr(VI)]=0.075 M, I(NaCl)=1 M).

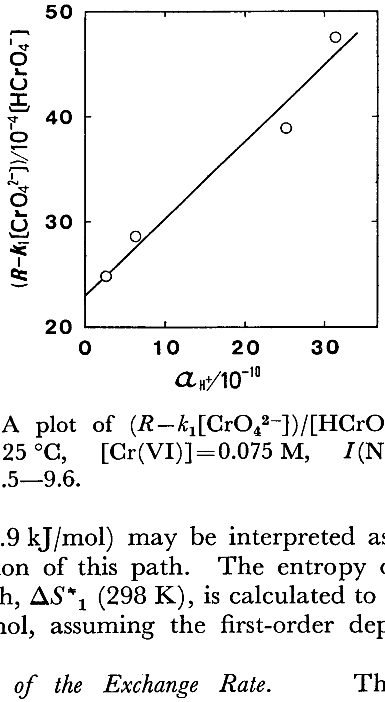

Fig. 6. A plot of $(R-k_1[CrO_4^{2-}])/[HCrO_4^-]$ against a_{H^+}. 25 °C, [Cr(VI)]=0.075 M, I(NaCl)=1 M, pH=8.5—9.6.

above (98.9 kJ/mol) may be interpreted as the energy of activation of this path. The entropy of activation of this path, ΔS^{*}_1 (298 K), is calculated to be (−45.1± 3.3) J/K mol, assuming the first-order dependence on $[H_2O]$.

Analysis of the Exchange Rate. The exchange rates plotted in Fig. 1 were analyzed as follows. The concentrations of the ionic species of Cr(VI) were calculated by the relations:

$$[Cr(VI)] = [HCrO_4^-] + [CrO_4^{2-}] + 2[Cr_2O_7^{2-}],$$

$$K_1 = [HCrO_4^-]/a_{H^+}\cdot[CrO_4^{2-}],$$

$$K_d = [Cr_2O_7^{2-}]/[HCrO_4^-]^2.$$

In the pH region greater than 10.5, the exchange reaction proceeds exclusively through the k_1 path. The appropriate rate law is:

$$R = k_1[CrO_4^{2-}].$$

The average of five values of k_1, calculated from the data in Fig. 1, pH>10.5, is:

$$k_1 = (3.2\pm0.2)\times10^{-7}\,s^{-1}.$$

Since the order of the exchange reaction with respect to [Cr(VI)] is 0.93 at pH=8.0, the contribution of the condensation mechanism (k_4 and k_5 paths) may be ignored in the pH region greater than 8.0. The rate law (6) then reduces to:

$$R = k_1[CrO_4^{2-}] + k_2[HCrO_4^-] + k_3[H^+][HCrO_4^-],$$

or $$(R-k_1[CrO_4^{2-}])/[HCrO_4^-] = k_2 + k_3[H^+].$$

In Fig. 6, the left-hand side of the equation is plotted against a_{H^+} for the runs at pH 8.5—9.57 and I= 1.0 M. The least-squares treatment of the plot yields the values:

$$k_2 = (2.30\pm0.19)\times10^{-3}\,s^{-1},$$

and $$k_3 = (0.37\pm0.09)\times10^{6}\,M^{-1}\,s^{-1}.$$

The rate law (6) may then be written as:

$$\frac{R-k_1[CrO_4^{2-}]-k_2[HCrO_4^-]-k_3[H^+][HCrO_4^-]}{[HCrO_4^-][CrO_4^{2-}]} = k_4 + k_5[HCrO_4^-]/[CrO_4^{2-}]. \quad (7)$$

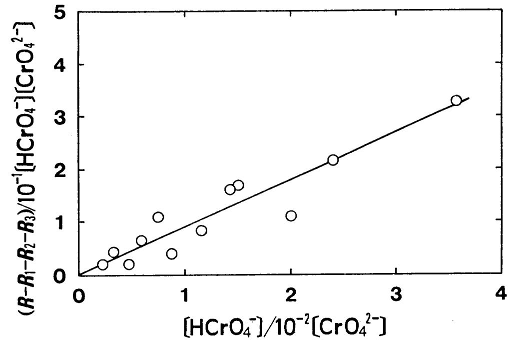

Fig. 7. $(R-R_1-R_2-R_3)/[HCrO_4^-][CrO_4^{2-}]$ as a function of $[HCrO_4^-]/[CrO_4^{2-}]$.
25 °C, [Cr(VI)]=0.075 M, I(NaCl)=1 M, pH=7.2—8.5.

The left-hand side of the equation was calculated by using the values of k_1, k_2, and k_3 obtained above; in Fig. 7 it is plotted against $[HCrO_4^-]/[CrO_4^{2-}]$ for the runs at pH 7.2—8.5 and I=1.0 M. From the intercept and the slope of the straight line, the values of k_4 and k_5 are found to be $(0.8\pm17)\times10^{-3}\,M^{-1}\,s^{-1}$ and $(9.0\pm1.1)\,M^{-1}\,s^{-1}$ respectively.

The runs at I=0.2 M were treated similarly. The values of the rate constants thus obtained are summarized in Table 2. The sign of the salt effect for each of these rate constants is as would be expected for the charge type of each reaction. In Fig. 1 the curves show the exchange rates calculated by using the rate constants obtained above. The agreement with the experimental values is satisfactory.

Our values of k_1 and k_4 agree satisfactorily with those of the earlier works.[5,15,16] Table 3 shows the value of k_5 obtained by various methods. The values of k_5 obtained in this study are larger by one order of magnitude than those determined by the methods other than oxygen-exchange. We have obtained a k_5 value of a similar magnitude (k_5=8.4 $M^{-1}\,s^{-1}$, at I=1.0 M and 25 °C) in the KCl medium. The discrepancy must be due to the occurrence of the third-order rate terms, $k_a[HCrO_4^-]^3$ and/or $k_b[HCrO_4^-]^2[CrO_4^{2-}]$, which increase in importance as the total concentration increases. It has been noted above that

Table 2. Rate constants of the oxygen-exchange reaction of chromate ions with water at 25 °C

I(NaCl) / M	k_1 / s^{-1}	k_2 / s^{-1}	k_3 / $M^{-1} s^{-1}$	k_4 / $M^{-1} s^{-1}$	k_5 / $M^{-1} s^{-1}$
0.2	$(3.2\pm0.2)\times10^{-7}$	$(2.4\pm0.9)\times10^{-3}$	$(1.9\pm0.2)\times10^{6}$	$\approx10^{-3}$	5.0 ± 1.1
1.0		$(2.3\pm0.2)\times10^{-3}$	$(0.73\pm0.09)\times10^{6}$	$\approx10^{-3}$	9.0 ± 1.1

Table 3. Rate constants of the dimerization of hydrogenchromate ions at 25 °C

$k_5/M^{-1}s^{-1}$ [a]	[Cr(VI)]/M	I/M	Reference
9.0	0.075	1.0(NaCl)	This work[b]
5.0	0.075	0.2	This work[b]
1.3	1—2.7	Not controlled 2.5—6.0	5[b]
5.5	0.1, 0.2	0.15, 0.45	6[b]
0.45[c]	0.02	0.1(KNO_3)	17
0.25	$(3—4)\times10^{-4}$	0.2($NaNO_3$)	18
0.38	0.002	0.1(KNO_3)	15

a) While the value of k_5 obtained by the oxygen-exchange method usually refers to the transfer of four oxygen atoms between chromate ions and water, the rate constant of the $2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-}+H_2O$ reaction corresponds to the transfer of one atom of oxygen. In this column, the rate constants obtained by other methods are divided by 4 for comparison. b) Oxygen-exchange method. c) 23 °C.

Table 4. Effect of protonation on the reactivity of oxoanions towards water

Reaction	Rate constants / s^{-1}	Temp / °C	I / M	Reference
$HCrO_4^- + H_2O \rightarrow$	2.4×10^{-3}	25	1.0, 0.2	This work
$CrO_4^{2-} + H_2O \rightarrow$	3.2×10^{-7}	25	1.0, 0.2	This work
$H_2AsO_4^- + H_2O \rightarrow$	1×10^{-4}	30	0.55	7
$HAsO_4^{2-} + H_2O \rightarrow$	1.2×10^{-5}	30	0.55	7
$AsO_4^{3-} + H_2O \rightarrow$	1.5×10^{-6}	30	0.55	7
$HSeO_3^- + H_2O \rightarrow$	2×10^{-4}	0	0.16	21
$SeO_3^{2-} + H_2O \rightarrow$	1.5×10^{-4}	0	0.16	21

the order of the exchange reaction in [Cr(VI)] increases above 2 with the increase in [Cr(VI)].

Perlmutter-Hayman *et al.*[14,19] have noted the general acid and base catalyses of the hydrolysis of dichromate ions. From the catalytic constants of other acids, Pladziewicz and Espenson[20] estimated the value of the rate constant of the hydrogenchromate-catalyzed hydrolysis of dichromate ions to be 0.1 $M^{-1} s^{-1}$. This value is, however, too small to account for the discrepancy noted above.

Mak[6] has determined the rate constant of the reaction:

$$HCrO_4^- + Cr_2O_7^{2-} \rightleftharpoons Cr_3O_{10}^{2-} + OH^-,$$

to be 13.6 $M^{-1} s^{-1}$ at 25 °C. This reaction might explain a part of the discrepancy.

The remaining possibility is the chromate-ion catalysis of the dimerization of hydrogenchromate ions:

$$2HCrO_4^- + CrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O + CrO_4^{2-}.$$

On the assumption that the discrepancy is due entirely to the general-base catalysis, Eq. 7 may be written as:

$$\frac{R-(R_1+R_2+R_3)}{[HCrO_4^-][CrO_4^{2-}]} = k_4 + (k_5+k_b[CrO_4^{2-}])\frac{[HCrO_4^-]}{[CrO_4^{2-}]}.$$

Under the present experimental conditions, the dominating ionic species of Cr(VI) is CrO_4^{2-} (>95%), and $[CrO_4^{2-}]$ may be regarded as nearly constant. The plot of $(R-(R_1+R_2+R_3))/[HCrO_4^-][CrO_4^{2-}]$ against $[HCrO_4^-]/[CrO_4^{2-}]$ (Fig. 7) remains linear. Using 0.36 (the average of the last three values in Table 3) as the value of k_5, the upper limit of the value of k_b may be calculated as 65 $M^{-2} s^{-1}$, or 2.6×10^2 $M^{-2} s^{-1}$ (referred to the transfer of 1 atom of oxygen) (I=0.2 M).

On the contrary, if it is assumed that the rate term, $k_a[HCrO_4^-]^3$, accounts for all of the discrepancy, Eq. 7 becomes:

$$\frac{R-(R_1+R_2+R_3)}{[HCrO_4^-][CrO_4^{2-}]} = k_4 + (k_5+k_a[HCrO_4^-])\frac{[HCrO_4^-]}{[CrO_4^{2-}]}.$$

As $[HCrO_4^-]$ changes 20-fold between pH=7.2 and 8.5, the plot of $(R-(R_1+R_2+R_3))/[HCrO_4^-][CrO_4^{2-}]$ against $[HCrO_4^-]/[CrO_4^{2-}]$ should be a concave curve upwards. Figure 7 does not show such a trend.

The rate-determining step of the nucleophilic catalysis of the dimerization of hydrogenchromate ions[15] is the attack of a nucleophile on the hydrogenchromate ion. In the case of chromate ions as the nucleophile this is nothing but the dimerization of chromate ions and does not result in the acceleration of the rate of oxygen exchange between chromate ions and water. The analysis of the third-order rate terms is beyond the scope of this work.

The hydrogen-ion-catalyzed oxygen exchange of hydrogenchromate ions with water which has been found in this work may be formulated as:

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

$$H_2CrO_4 + H_2{}^{18}O \rightleftharpoons H_2CrO_3{}^{18}O + H_2O.$$

The dissociative mechanism seems unlikely because of the small activation energy (25.5 kJ/mol) at pH=7.38.

$$H_2CrO_4 \rightleftharpoons H_2O + CrO_3.$$

Table 4 shows the effect of protonation on the reactivity of oxoanions towards water. The enhanced reactivity of hydrogenchromate ions as compared with that of chromate ions is noteworthy. Since the role of a proton in facilitating the oxygen exchange of oxoanions probably consists in the polarization of the bond between the oxygen and the central atom, this bond seems to be more polarizable in chromate ions than in arsenate and selenite ions.

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