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Kinetic Studies of the Catalytic Oxygen Exchange of Chromate Ions with Water by Periodate Ions

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The oxygen exchange reaction between chromate ions and water is catalyzed by the addition of a small amount of periodate ions. The catalytic reaction has been studied by using ^{18}O tracer work (0 °C, pH=8—12, [Cr(VI)]=0.075 mol dm^{-3}, [I(VII)]=10^{-5} mol dm^{-3}) and an ^{17}O NMR line broadening technique(30 °C, pH=4—6, [Cr(VI)]=1 mol dm^{-3}, [I(VII)]=0.043 mol dm^{-3}). The catalytic process has been interpreted in terms of the reversible condensation of chromate ions with periodate ions to form chromatoperiodate ions. The rate law is given as: $R_c=k_1[HCrO_4^-][H_4IO_6^-]+k_2[HCrO_4^-][H_3IO_6^{2-}]+k_3[CrO_4^{2-}][H_4IO_6^-]+k_4[CrO_4^{2-}][H_3IO_6^{2-}]$, where R_c is defined as the increase in the rate of the oxygen exchange of chromate upon the addition of periodate ions. The catalytic rates were analyzed according to the rate law to obtain the values of the rate constants (k_1-k_4); k_1, k_2, and k_3 are on the order of magnitude of 10^3—10^4 mol^{-1} dm^3 s^{-1}, and k_4=5 mol^{-1} dm^3 s^{-1} at 0 °C. For the reaction between $H_3IO_6^{2-}$ and CrO_4^{2-}, the energy and entropy of activation were obtained to be 26 kJ mol^{-1} and −143 J K^{-1} mol^{-1}, respectively.

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; 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 a previous paper,[5] we reported on the kinetics of the oxygen exchange of chromate ions catalyzed by arsenious acid. In this paper we report on a study of the interaction of chromate ions with periodate ions by the oxygen exchange between chromate ions and water in the presence of a catalytic amount of the periodate. The catalytic exchange reaction in the pH region greater than 8 was studied by using the ordinary oxygen-18 tracer method. In the pH region below 6, the fast oxygen exchange rates were measured by the use of an ^{17}O NMR line-broadening technique. In the latter method, the NMR signals for chromate oxygens in different environments are observed separately, the more precise information concerning the interaction between chromate and periodate ions can be obtained.

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 (guaranteed reagent, Merck), sodium dichromate dihydrate (guaranteed reagent, Wako), and sodium periodate (guaranteed reagent, Merck) were used without further purification.

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

Procedure. I. ^{18}O Tracer Method: The procedures were almost the same as those used earlier.[5] 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 periodate. 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. The reactions were carried out in an ice bath (0 °C). At intervals aliquots of the reacting solution were drawn, 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 guanidinium 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:

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

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.

II. ^{17}O NMR Line-Broadening Technique. Solutions for ^{17}O NMR measurements were prepared as follows: 3 ml of ^{17}O-enriched water (10 atom%) was distilled under vacuum into a tube containing a known amount of dehydrated sodium dichromate. A small amount of the stock solution of periodate (5 mol dm^{-3}) was added, and the pH of the solution was adjusted by the addition of a small amount of concentrated sulfuric acid or of saturated aqueous sodium hydroxide solution. The concentration of chromate in the solution finally obtained was checked spectrophotometrically (λ_{max} ($CrO_4{}^{2-}$)=395 nm, ϵ_{395}=2582).

The ^{17}O NMR spectra were recorded at 36.6 MHz on a FT-NMR spectrometer (JEOL-GX270), and the line widths of signals due to chromate and water were measured. The relevant spectral parameters are as follows: spectral width, 60 kHz; digital resolution, 1.86 Hz; number of scans, 4096. Before making a Fourier transformation, the FID was multiplied by an exponential function in which the broadening parameter(LB) was 2 Hz.

The ^{17}O-chemical shifts (referred to H_2O signal) for the bridging and terminal oxygens of $Cr_2O_7{}^{2-}$ were observed to be δ=336 and 1116 (remains unchanged at the pH range from 1.9 to 8.1), and that for $CrO_4{}^{2-}$ to be δ=816 (pH=12). The chemical shift of $HCrO_4{}^-$ ($\delta(HCrO_4{}^-)$) was estimated to be δ=871 by using the observed chemical shifts of the monomeric chromate ion (δ_{obsd}) in the pH region between 5.6 and 8.1, according to the Eq. 1:

$$\delta_{obsd} = \{\delta(HCrO_4{}^{2-})[HCrO_4{}^-] + \delta(CrO_4{}^{2-})[CrO_4{}^{2-}]\} /([HCrO_4^-] + [CrO_4{}^{2-}]) \quad (1)$$

The oxygen exchange rates were evaluated from the measured line widths of the ^{17}O NMR signals as follows. In the slow exchange limit, where the mean lifetime of an oxygen nucleus at site A (τ_A) is small compared with the chemical shift, τ_A is given by the following equation:

$$\tau_A^{-1} = k_A = T_{2A}^{-1} - T^{\circ}{}_{2A}^{-1}, \quad (2)$$

where T_{2A} is the measured transverse relaxation time of an oxygen nucleus at site A and $T^{\circ}{}_{2A}$ is its magnitude in the absence of an oxygen exchange. By using the relation: $1/T_2=\pi\times\nu_{1/2}$, τ_A^{-1} is expressed as

$$\tau_A^{-1} = k_A = \pi(\nu_{1/2,A} - \nu^{\circ}_{1/2,A}), \quad (3)$$

where $\nu_{1/2,A}$ and $\nu^{\circ}{}_{1/2,A}$ are the line widths of the oxygen nucleus at site A in the presence and absence of an oxygen exchange, respectively. (A=$(Cr\underline{O}_3)_2O^{2-}$, $(CrO_3)_2\underline{O}^{2-}$, or ($CrO_4{}^{2-}$+$HCrO_4{}^-$)).

The mean lifetime of the oxygen nucleus of species A between exchanges (τ_A), is related to the conventional rate constant (k) of the oxygen exchange by the following relation:[8)]

$$\tau_A^{-1} = k_A = (1/[A])d[A]/dt = k[A]^{m-1}[B]^n, \quad (4)$$

where B is a reactant other than A (in this case, periodate), and m and n are the order of the reaction with respect to the concentrations of A and B, respectively.

Results

I. ^{18}O Tracer Work. pH Dependence of the Exchange Rate. The rates of the oxygen exchange reaction between chromate ions and water with the added periodate ions were measured in the pH region greater than 8 and at 0 °C. The concentrations of the chromate and periodate are 0.075 and 1×10^{-5} mol dm^{-3}, respectively. The rate without the added periodate (R_0) at 0 °C was measured only at pH 8.56 in this work (R_0=6.3×10^{-7} mol dm^{-3}). R_0 at pH=11.5 (0 °C) can be estimated to be 5.2×10^{-10} mol dm^{-3} by the use of the activation energy of 98.9 kJ mol^{-1} at the pH.[4)] In Fig. 1, log R (curve A, 0 °C) and log R_0 (curve B, 25 °C[4)]) are plotted against pH. Even in the low concentration ratio: [I(VII)]/[Cr(VI)]=1.3×10^{-4}, the catalytic effect (R/R_0) is so large as to increase the oxygen exchange rate 677 fold at pH 8.56 and 5.8×10^3 fold at pH 11.5. The R_0 value above pH 10.5 has been considered to be for the exchange reaction of $CrO_4{}^{2-}$ with water.[4)] It is surprising that the $CrO_4{}^{2-}$ ion is very reactive towards the periodate ion, while it is quite inactive towards water.

The catalytic oxygen exchange rate (R_c), which is defined as ($R-R_0$), can therefore be taken as equal to R. The slope of the plots of R_c (=R) obtained by the least-squares method is −0.69±0.03.

Dependence of the Catalytic Oxygen Exchange Rate R_c on [I(VII)]. The order of the reaction with respect to [I(VII)] was determined at pH 10.58 (0 °C, [Cr(VI)]=0.075 mol dm^{-3}). The concentration of periodate was varied from 5×10^{-6} to 1×10^{-4}

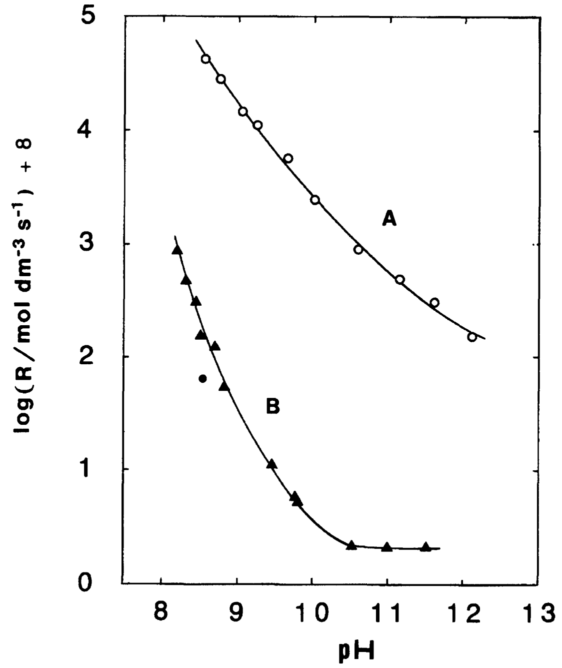


Fig. 1. pH Dependence of the oxygen exchange rate of chromate with water ([Cr(VI)]=0.075 mol dm^{-3}, I=0.22 mol dm^{-3}). A(○): with the added periodate ([I(VII)]=1.00×10^{-5} mol dm^{-3}, 0 °C). B: without the added periodate, ▲: 25 °C; ●: 0 °C.

mol dm^{-3}. In Fig. 2, plots of log R_c against log [I(VII)] are shown. The deviation of one plot(●) at [I(VII)] 5×10^{-6} mol dm^{-3} from a straight line is probably due to the decomposition of the periodate by a trace amount of reducing impurities present in the solution. The slope of the straight line is 1.05±0.04. In a more concentrated range of periodate ([I(VII)] = (2—6)×10^{-4} mol dm^{-3}), the order with respect to [I(VII)] was found to be less than 1 (0.86±0.05). Buist et al. have shown that in an aqueous alkaline solution greater than 8, the monomeric periodate dianion is in equilibrium with the dimeric ion $H_2I_2O_{10}^{4-}$.[9] It is reasonable to assume that the dimeric periodate ion with a large negative charge (−4) is unreactive towards the chromate ion, and that the R_c value changes depending on the monomeric periodate concentration ([I(VII)]$_{mono}$). Based on the assumption, the order with respect to [I(VII)]$_{mono}$ was estimated to obtain the value of 1.07±0.10 ([I(VII) = (2—6)×10^{-4}) and 1.09±0.03 ([I(VII)] = 1×10^{-5}—1×10^{-4} mol dm^{-3}), where [I(VII)]$_{mono}$ was calculated by the use of the dimerization constant of 780 mol dm^{-3} (1 °C, I=0.1[9]). The result shows that the monomeric periodate is involved dominantly in the catalytic rate.

Dependence of the Catalytic Rate on [Cr(VI)]. The dependence was studied under the following condition: [Cr(VI)] = 0.038—0.19 mol dm^{-3}, [I(VII)] = 3.7×10^{-5} mol dm^{-3}, I=1.0 mol dm^{-3} (NaNO$_3$), 0 °C, pH = 10.58. Preliminarily, it was ascertained spectrophotometrically that the sodium nitrate used for adjusting the ionic strength was inert to periodate. Plots of log R_c against log [Cr(VI)] are shown in Fig. 3a. The slope of the straight line was obtained to be 0.74±0.03.

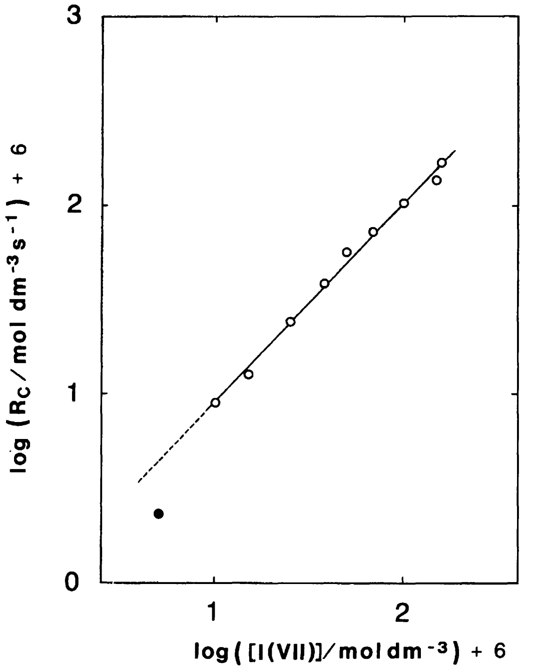


Fig. 2. Dependence of the catalytic oxygen exchange rate (R_c) on [I(VII)] (0 °C, pH=10.58, [Cr(VI)]= 0.075 mol dm^{-3}).

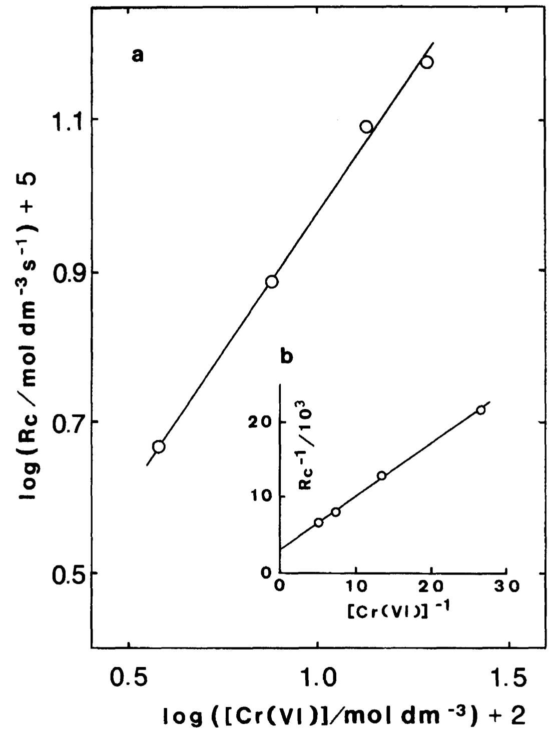


Fig. 3. a) Dependence of the catalytic oxygen exchange rate R_c on [Cr(VI)] (0 °C, pH = 10.58, [I(VII)]=3.7×10^{-5} mol dm^{-3}, I(NaNO$_3$)=1.0 mol dm^{-3}; b) Plots of $1/R_c$ against 1/[Cr(VI)].

By analogy with other catalytic oxygen exchanges,[1—3,5] it is natural to interpret the catalytic effect of periodate ions in terms of the reversible condensation of chromate ions with periodate 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 chromatoperiodate ions, Cr(VI)·I(VII),

$$\mathrm{Cr(VI)} + \mathrm{I(VII)} \underset{K}{\overset{k}{\rightleftharpoons}} \mathrm{Cr(VI)\cdot I(VII)}. \tag{5}$$

The formation of the Cr(VI)·I(VII) species reduces the effective concentration of periodate ions which take part in the condensation reaction with the chromate ions. Substitution of the effective concentration of periodate ions, [I(VII)]$_{eff}$, calculated based on the above assumption into the rate law with first order dependence, R_c= k[Cr(VI)][I(VII)]$_{eff}$, gives

$$R_c = \frac{k[\mathrm{Cr(VI)}][\mathrm{I(VII)}]}{1 + K[\mathrm{Cr(VI)}]}, \tag{6}$$

where k and K are the rate constant and the equilibrium constant of reaction 5, respectively. Equation 6 can be rearranged as

$$\frac{1}{R_c} = \frac{K}{k[\mathrm{I(VII)}]} + \frac{1}{k[\mathrm{I(VII)}][\mathrm{Cr(VI)}]}. \tag{7}$$

Plots of $1/R_c$ 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 and K were obtained to be 5.2×10^4 and 4.14, respectively. In order to obtain spectrophotometric evidence for the existence of a chromatoperiodate ion, the absorbances (from 220 to 300 nm) were measured at pH = 11 for the solutions: (a) sodium chromate (1.0×10^{-4} mol dm^{-3}), (b) sodium periodate (7.3×10^{-5} mol dm^{-3}), and (c) sodium chromate plus sodium periodate (the concentration of the respective compound is the same as in (a) or (b)). The absorbance of solution (c) was found to be in accordance with the added value of the absorbances for solutions (a) and (b). No spectrophotometric evidence for the formation of the chromatoperiodate ion could be obtained.

Effect of the Ionic Strength on the Catalytic Rate. The catalytic rates obtained at $I\,(\mathrm{NaNO_3})=1$ mol dm^{-3} and without the added inert salt are listed in Table 1. The catalytic rates show a positive salt effect, which is consistent with the assumed reaction between like-charged ions.

Temperature Dependence of the Catalytic Rate. The catalytic rate was measured at the temperature range between 0 and 15 °C. ([Cr(VI)] = 0.075 mol dm^{-3}, [I(VII)] = 2.0×10^{-4} mol dm^{-3}, and pH = 10.58). The values of R_c (10^{-4} mol dm^{-3} s^{-1}) obtained are: 1.23 (0 °C); 1.32 (5 °C); 1.84 (10 °C); 2.14 (15 °C). The values of the activation energy was estimated to be 25.9 ± 4.5 kJ mol^{-1} for the catalytic rate (R_c), which is significantly smaller than that of 98.9 ± 1.0 kJ mol^{-1} for R_0. The activation entropy of k calculated in terms of the equation $R_\mathrm{c}=k[\mathrm{Cr(VI)}][\mathrm{I(VII)}]$ was obtained to be -143 J mol^{-1} K^{-1}. Since at pH 10.58 the dominant ionic species of Cr(VI) and I(VII) are $\mathrm{CrO_4}^{2-}$ and $\mathrm{H_3IO_6}^{2-}$, the activation parameters obtained may be considered to be for the reaction between these two anions.

II ^{17}O NMR Study. A. Catalytic Oxygen Exchange Rate of Monomeric Chromate Ions. ^{17}O NMR spectra of chromate ions were measured on the solutions with (A) and without (B) the added periodate at 30 °C and in the pH range between 4 and 6 ([Cr(VI)] = 1.0 mol dm^{-3}, [I(VII)] = 0.043 mol dm^{-3}). The measurement could not be extended to a pH region greater than 6, because of the formation of the precipitate, which seemed to be $\mathrm{Na_4I_2O_9}$. The line widths of the ^{17}O signals of the monomeric chromate ion for solution A ($\nu_{1/2,\mathrm{mono}}$) and those for solution B ($\nu_{1/2,0,\mathrm{mono}}$) are plotted against the pH in Fig. 4. By using $\nu_{1/2,\mathrm{mono}}$ and $\nu_{1/2,0,\mathrm{mono}}$, k_mono (τ_mono^{-1}) and $k_{0,\mathrm{mono}}$ ($\tau_{0,\mathrm{mono}}^{-1}$) can be calculated from Eq. 3, where k_mono and $k_{0,\mathrm{mono}}$ are the oxygen exchange rate constants observed with and without the addition of periodate. As $\nu^\circ{}_{1/2,\mathrm{mono}}$ in Eq. 3, a value of 11.5 Hz (measured value at pH = 8—12) was used. In Fig. 5, the logarithms of k_mono, $k_{0,\mathrm{mono}}$, and $k_{\mathrm{c,mono}}(=k_\mathrm{mono}-k_{0,\mathrm{mono}})$ are plotted as a function of the pH. The slopes of the plots of $k_{\mathrm{c,mono}}$ and $k_{0,\mathrm{mono}}$ are $+0.14\pm0.01$ and -0.90 ± 0.03, respectively. It is noticeable that the catalyzed portion of the exchange rate ($k_{\mathrm{c,mono}}$) decreases with an increase in [H$^+$], while the chromate oxygen exchange ($k_{0,\mathrm{mono}}$) increases depending on the first power of [H$^+$].

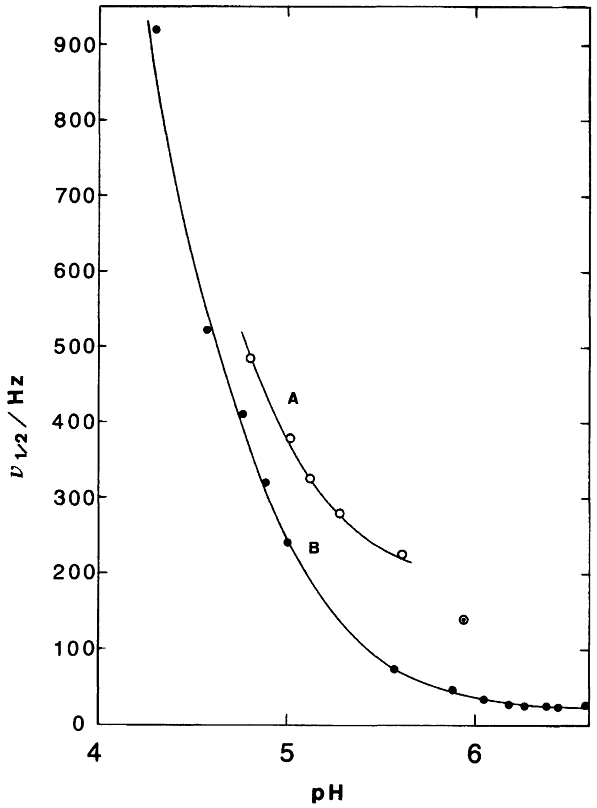


Fig. 4. Line widths of the ^{17}O NMR signal of monomeric chromate ion (pH = 4—7, 30 °C, [Cr(VI)] = 1.0 mol dm^{-3}). A(○): with the added periodate ([I(VII)] = 0.043 mol dm^{-3}). B(●): without the added periodate.

Dependence of the Catalytic Oxygen Exchange Rate on [I(VII)]. The dependence was studied at 30 °C, pH 5.22, and [Cr(VI)] = 1.0 mol dm^{-3}. [I(VII)] was varied between 3.8×10^{-3} and 5.3×10^{-2} mol dm^{-3}. A plot of $\log k_{\mathrm{c,mono}}$ against $\log[\mathrm{I(VII)}]$ is shown in Fig. 6. A line drawn through the plots has a slope of 0.95 ± 0.05. The catalytic rate depends on the first power of [(VII)].

Dependence of the Catalytic Rate on [Cr(VI)]. The dependence on [Cr(VI)] (0.2—1.0 mol dm^{-3}) was studied at 30 °C, pH = 5.22, [I(VII)] = 0.027 mol dm^{-3}, and $I(\mathrm{NaNO_3})=1.4$ mol dm^{-3}. In Table 2, the line widths $\nu_{1/2,\mathrm{mono}}$ ([I(VII)] = 0.027 mol dm^{-3}) and $\nu_{1/2,0,\mathrm{mono}}$ ([I(VII)] = 0) are shown, from which the rate constants; $k_{0,\mathrm{mono}}$, k_mono, and $k_{\mathrm{c,mono}}$ were evaluated (Table 2). According to Eq. 4, the order of the catalytic process with respect to [Cr(VI)] and $[\mathrm{Cr(VI)}]_\mathrm{mono}$ (the concentration of monomeric chromtate) was obtained to be 1.53 ± 0.001 and 1.44 ± 0.07. The Table 2 shows that the line widths ($\nu_{1/2,0,\mathrm{mono}}$ ([I(VII)] = 0])) are strongly affected by the addition of $\mathrm{NaNO_3}$. Thus,

Table 1. The Effect of the Ionic Strength on the Catalytic Rate (0 °C, pH=10.58, [I(VII)]=3.7×10^{-5} mol dm^{-3})

[Cr(VI)]/mol dm^{-3}	I(NaNO$_3$)/mol dm^{-3}	$R_c/10^{-5}$mol dm^{-3} s^{-1}
0.0377	1.0	4.64
0.0375	0.112	1.82
0.0751	1.0	7.70
0.0750	0.225	3.85
0.134	1.0	12.39
0.134	0.401	7.87
0.192	1.0	15.02
0.192	0.575	12.03

Table 2. The Dependence of the Catalytic Rate on [Cr(VI)] (30 °C, pH=5.22, [I(VII)]= 0.027 mol dm^{-3}, I(NaNO$_3$)=1.4 mol dm^{-3})

[Cr(VI)] / mol dm^{-3}	[Cr(VI)]$_{\text{mono}}$ / 10^{-2}mol dm^{-3}	$\nu_{1/2,\text{ mono}}$ / Hz	$\nu_{1/2,0,\text{mono}}$ / Hz	k_{mono} / s^{-1}	$k_{0,\text{mono}}$ / s^{-1}	$k_{c,\text{mono}}$ / s^{-1}
0.10	3.12	349	300	1060	905	155
0.20	4.52	290	229	876	684	192
0.50	7.34	255	183	764	537	227

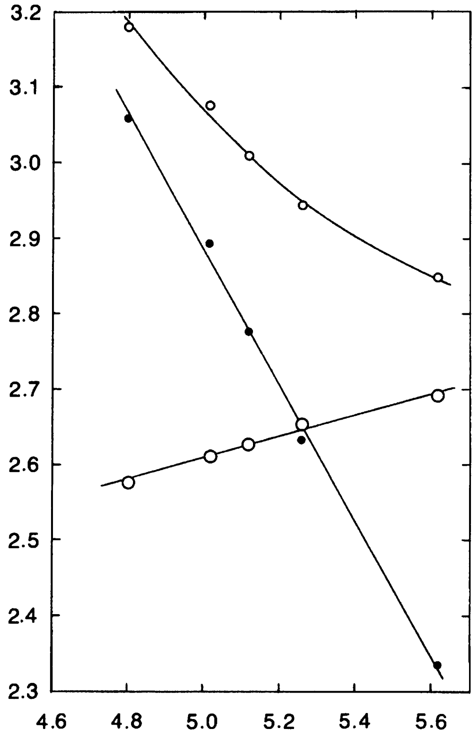


Fig. 5. Plots of the logarithms of k (mono) against pH. ○: k_{mono}; ●: $k_{0,\text{mono}}$; O: $k_{c,\text{mono}}$.

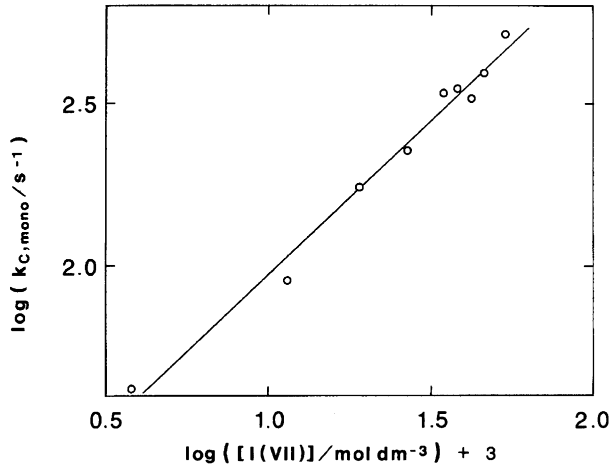


Fig. 6. Dependence of the catalytic oxygen exchange of monomeric chromate ion on the concentration of periodate. (30 °C, pH = 5.22, [Cr(VI)] = 1.0 mol dm^{-3}).

the line widths in the table involve a contribution of the added inert salt as well as the kinetic contribution. For this reason, the value of 1.4 seems to be unreliable. It is assumed that the order with respect to [Cr(VI)] is unity.

B. Catalytic Oxygen Exchange Rate of Dichromate Ion. ^{17}O NMR spectra of dichromate ion were measured on the solutions with and without the added periodate at 30 °C and in the pH range between 2 and 7 ([Cr(VI)]=1.0 mol dm^{-3}). [I(VII)] was in the range from 2.4×10^{-3} to 1.2×10^{-2} mol dm^{-3}. The line widths of the terminal and bridging oxygens of $Cr_2O_7{}^{2-}$ are shown in Fig. 7, where the open circles (terminal) and triangles (bridging) are for the signals measured in the presence of periodate, and the solid marks for the signals in the absence of periodate. For both terminal and bridging oxygens, the open and solid marks fall on a curve. This result indicates that the periodate ions do not catalyze the exchange of the terminal and bridging oxygens of the dichromate ion with the solvent water oxygen.

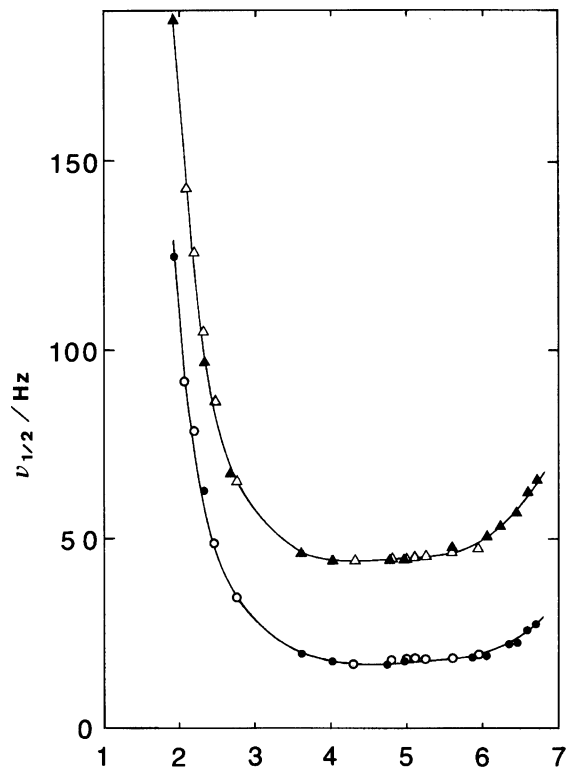


Fig. 7. Line widths of the ^{17}O NMR signals of dichromate ion (30 °C, pH=2—7, [Cr(VI)]=1.0 mol dm^{-3}). Bridging ^{17}O: △: [I(VII)]=2.4×10^{-3}—1.2×10^{-2} mol dm^{-3}; ▲: [I(VII)]=0, Terminal ^{17}O: ○: [I(VII)]=2.4×10^{-3}—1.2×10^{-2} mol dm^{-3}; ●: [I(VII)]=0.

Discussion

As already described, the catalytic process can be identified with the reversible condensation of chromate ions with periodate ions. In the pH range between 5 and 12, at which the catalytic exchange was studied, the dominating ionic species of chromate are $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}, and those of periodate are $H_4IO_6^-$, IO_4^-, $H_3IO_6^{2-}$, $H_2IO_6^{3-}$, and $H_2I_2O_{10}^{4-}$. The catalytic rate R_c, then, may be written by the following rate law:

$$\begin{aligned} R_c &= k_1[HCrO_4^-][H_4IO_6^-] + k_2[HCrO_4^-][H_3IO_6^{2-}] \\ &\quad + k_3[CrO_4^{2-}][H_4IO_6^-] + k_4[CrO_4^{2-}][H_3IO_6^{2-}] \\ &\quad + k_5[CrO_4^{2-}][H_2IO_6^{3-}] \\ &= R_1 + R_2 + R_3 + R_4 + R_5. \end{aligned} \tag{8}$$

In Eq. 8, $[H_4IO_6^-]$ designates the concentration of the periodate monoanion inclusive of IO_4^-. (The concentrations of $H_4IO_6^-$ and IO_4^- are mutually related by the relation $K_d = a_{IO_4^-} a^2_{H_2O}/a_{H_4IO_6^-} = 40$,10) and the rate terms involving $H_4IO_6^-$ are kinetically equivalent to those involving IO_4^-.) The catalytic rate constants (condensation rate constants) were evaluated according to the rate law (8) by the procedure describe below.

Estimation of the Concentrations of the Ionic Species of Periodate and Chromate. The concentrations of the ionic species of periodate were evaluated by means of the apparent first and second acid dissociation constants written in the forms:

$$K'_{1a}(I) = a_{H^+}(a_{IO_4^-} + a_{H_4IO_6^-})/a_{H_5IO_6}$$

and

$$K'_{2a}(I) = a_{H^+}a_{H_3IO_6^{2-}}/(a_{IO_4^-} + a_{H_4IO_6^-}),$$

and by using the relation

$$\begin{aligned} [I(VII)] &= [H_5IO_6] + [H_4IO_6^-] + [H_3IO_6^{2-}] \\ &\quad + [H_2IO_6^{3-}] + 2[H_2I_2O_{10}^{4-}]. \end{aligned}$$

The values of the acid dissociation constants and dimerization constants necessary to calculate the concentrations of the ionic species of the chromate and the periodate are listed in Table 3, where K_2 (Cr) and K_{22} (Cr) are the second dissociation constant and the dimerization constant of chromate, and K_3 (I) and K_{22} (I) are the third dissociation constant and the dimerization constant ($2\cdot I(VII)_{mono} \rightleftharpoons H_2I_2O_{10}^{4-}$). K_{2a}(Cr) (0 °C)11) and K'_{1a}(I)(0 °C) determined by Crouthamel et al.12) were converted to K_2(Cr) and K'_1(I) (0 °C, I= 0.22) using Güntelberg's equation, respectively. K'_2(I) and K_3(I) were evaluated similarly by using K'_{2a}(I) and K_3(I) (I=0.1) determined by Bruist et al.9) at various temperatures.

Evaluation of the Catalytic Rate Constants. I. Analyses of R_c by ^{18}O Tracer Study (pH=8—12). At pH >9.5, the k_1-term in Eq. 8 can be ignored since the the values of $[HCrO_4^-][H_4IO_6^-]$ are very small ($[HCrO_4^-][H_4IO_6^-]/[Cr(VI)][I(VII)]=5\times10^{-6}$ at pH 9.5). Furthermore, at pH>10.6, while $[H_2IO_6^{3-}]$ increases with an increase in pH and amounts to over 56% of total periodate concentration ($[CrO_4^{2-}]$ remains constant), the value of R_c continues to decrease. This fact suggests that the contribution of the k_5-term (R_5) may be ignored. The rate law (8) can be rewritten as follows:

$$\begin{aligned} &R_c/\{[CrO_4^{2-}][H_3IO_6^{2-}]\} = \\ &\quad k_4 + \{k_2K'_2(I)/K_2(Cr) + k_3\}[H^+]/K'_2(I). \end{aligned} \tag{9}$$

The values of left-hand side of Eq. 9, calculated by using the R_c data at pH=9.5—12 (Fig. 1, curve A), are plotted against $[H^+]/K'_2(I)$ (not shown). From the intercept of the straight line through the plots, the value of k_4 was determined to be 4.6±0.6 mol^{-1} dm^3 s^{-1}. From the slope of the line, the value of $\{k_2\cdot K'_2(I)/K_2(Cr)+k_3\}$ was obtained as 5071±46 mol^{-1} dm^3 s^{-1}. Then, the rate law (9) was again rearranged as

$$\begin{aligned} R_c - R_4 &= k_1[HCrO_4^-][H_4IO_6^-] \\ &\quad + k_2[HCrO_4^-][H_3IO_6^{2-}] + k_3[CrO_4^{2-}][H_4IO_6^-]. \end{aligned}$$

By using the k_4-value obtained above, the values of $\{R_c - R_4\}$ were calculated for all of the data

Table 3. Acid Dissociation Constants and Dimerization Constants of Chromic Acid and Periodic Acid under the Condition of the Kinetic Runs

Cr(VI)	0°C I=0.22	30 ° I=1.5	I(VII)	0°C I=0.22	30 ° C I=1.5
K_2	7.24×10^{-7}	1.74×10^{-6}	K_1'	5.75×10^{-3}	5.75×10^{-2}
K_{22}	67.6	138	K_2'	2.45×10^{-8}	2.57×10^{-8}
			K_3	1.55×10^{-12}	
			K_{22}	820	

given in Fig. 1. A least-squares treatment of a set of numerical equations, thus obtained, gave the values (mol^{-1} dm^3 s^{-1}) of $k_1=(3.1\pm15)\times10^4$, $k_2=(1.7\pm4.6)\times10^4$, and $k_3=(3.4\pm0.9)\times10^3$. The extraordinary large values of rate constants k_1, k_2, and k_3 are noticeable. In the pH range studied, [$HCrO_4^-$] involved in the R_1 and R_2 terms is a very small (mole fraction of the ion<0.005). The large error for the k_1 and k_2 values are mainly caused by the uncertainty in the estimated value of [$HCrO_4^-$].

II. Analyses of $R_{c,mono}$ ($=k_{mono}[Cr(VI)]_{mono}$) by ^{17}O NMR Method (pH=4.8—6). In the pH range from 4.8 to 6, the ionic species of monomeric chromate are $HCrO_4^-$ and CrO_4^{2-}, and that of periodate is mono-anion ($H_4IO_6^-$ and IO_4^-). $R_{c,mono}$ can be expressed simply as

$$R_{c,mono}=k_1[H_4IO_6^-][HCrO_4^-]+k_3[H_4IO_6^-][CrO_4^{2-}], \tag{10}$$

where [$H_4IO_6^-$] is again inclusive of [IO_4^-]. The Eq. 10 was rewritten as:

$$R_{c,mono}/\{[CrO_4^{2-}][H_4IO_6^-]\}=k_3+k_1\{[H^+]/K_2(Cr)\}. \tag{11}$$

The values of left-hand side are plotted against $[H^+]/K_2(Cr)$ in Fig. 8. From the slope and the intercept of the straight line, the value of k_1 was obtained to be $(7.56\pm0.29)\times10^3$ mol^{-1} dm^3 s^{-1} and that of k_3 to be $(1.85\pm0.17)\times10^4$ mol^{-1} dm^3 s^{-1}. In agreement with the observation that the catalytic rate increases with an increase in pH, it was shown that the reactivity of $H_4IO_6^-$ towards CrO_4^{2-} is 2.5-times larger than that towards $HCrO_4^-$.

The condensation rate constants between the chromate and periodate ions obtained in this work are listed in Table 4. The values of k_1 and k_3 could be obtained by two methods: ^{18}O tracer and ^{17}O NMR. However, the experimental conditions used were different between two methods. The k_3 values by both methods were obtained with comparable reliability. The result that the k_3 value by ^{17}O NMR (30 °C, I=1.5) is larger than that by the ^{18}O tracer (0 °C, I=0.22) is reasonable, since the k_3-path is expected to exhibit a positive salt effect. The agreement in the k_3 values between the two methods is considered to be satisfactory. As for k_1, the value obtained by ^{17}O NMR can be taken as being more reliable.

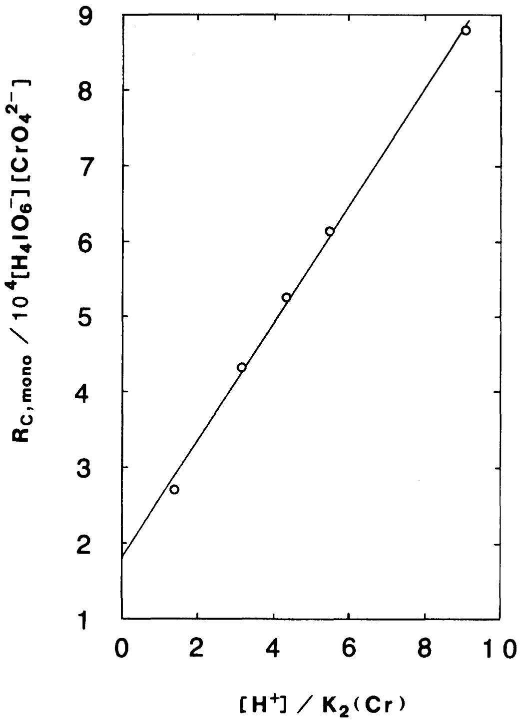


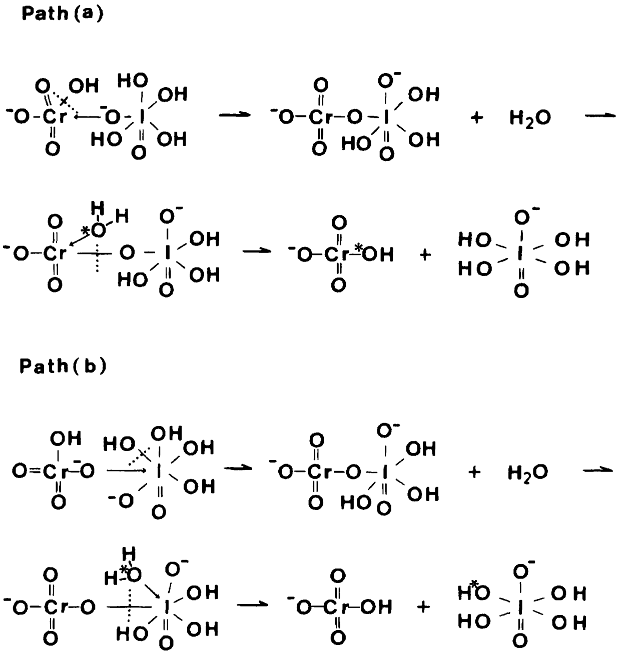
Fig. 8. $R_{c,mono}/\{[CrO_4^{2-}][H_4IO_6^-]\}$ vs. $[H^+]/K_2(Cr)$.

Mechanistic Consideration of the Condensation Reactions. For the reversible condensation process, two paths are possible. In path(a), the periodate ion acts as a nucleophile, and the chromate acts as the substrate; the oxygen atom of the periodate ion attacks the chromium atom of the chromate ion. In path (b), on the other hand, the chromate ion acts as a nucleophile. (Scheme 1) In both cases, an identical chromatoperiodate ion is formed. However, the result that the oxygen-exchange reaction of chromate with water is catalyzed by periodate requires the reaction to proceed via path(a). Path(b) does not lead to an oxygen exchange of chromate with water. If path(b) is an important pathway for the formation of the chromatoperiodate ion, and proceeds faster than the direct oxygen exchange of periodate with water, it is expected that the oxygen exchange of periodate would be affected by the added chromate ion. The possible catalytic effect of chromate on the periodate oxygen exchange was examined by using ^{17}O NMR method. The ^{17}O signal due to periodate oxygen could be detected at 250 ppm down field referred to H_2O. Its signal is, however, very broad (^{17}O line width ranges from 1500 to 1850 Hz depending on pH), and the shape of the signal is much

Table 4. The Rate Constants of the Condensation Reactions between Anions

Reactions	Temp/°C	I/mol^{-1} dm^3	k/mol^{-1} dm^3 s^{-1}	Method	Ref.
$HCrO_4^- + H_4IO_6^-$	0	0.22	k_1: $(3.1\pm15)\times10^4$	^{18}O	This work
	30	1.5	k_1: $(7.6\pm0.3)\times10^3$	^{17}O	″
$HCrO_4^- + H_3IO_6^{2-}$	0	0.22	k_2: $(1.7\pm4.6)\times10^4$	^{18}O	″
$CrO_4^{2-} + H_4IO_6^-$	0	0.22	k_3: $(3.4\pm0.9)\times10^3$	^{18}O	″
	30	1.5	k_3: $(1.9\pm0.2)\times10^4$	^{17}O	″
$CrO_4^{2-} + H_3IO_6^{2-}$	0	0.22	k_4: (4.6 ± 0.6)	^{18}O	″
$HCrO_4^- + H_3AsO_3$	25	0.22	$(1.9\pm0.3)\times10^2$	^{18}O	4
$Cr_2O_7^{2-} + H_3AsO_3$	25	0.22	$(2.0\pm0.2)\times10^3$	^{18}O	4
$CrO_4^{2-} + H_2AsO_3^-$	25	0.22	$(7.0\pm2.0)\times10^{-3}$	^{18}O	4
$HCrO_4^- + HCrO_4^-$	25	0.22	9.0 ± 1.1	^{18}O	5
$HCrO_4^- + CrO_4^{2-}$	25	0.22	$(0.8\pm17)\times10^{-3}$	^{18}O	5
$HCrO_4^- + H_2O$	25	0.22	$(2.4\pm0.9)\times10^{-3}$ a)	^{18}O	5
$CrO_4^{2-} + H_2O$	25	0.22	$(3.2\pm0.2)\times10^{-7}$ a)	^{18}O	5
$H_2AsO_4^- + H_4IO_6^-$	30	0.2	$(3.4\pm0.3)\times10^2$	^{18}O	2
$H_2AsO_4^- + H_3AsO_3$	30	0.2	6.8	^{18}O	1
$HAsO_4^{2-} + H_5TeO_6^-$	30	0.2	0.22	^{18}O	3
$H_2AsO_4^- + H_2AsO_4^-$	30	0.55	7.4×10^{-2}	^{18}O	15
$H_2AsO_4^- + H_2O$	30	0.55	1×10^{-4} a)	^{18}O	15

a) s^{-1}.



Scheme 1.

deviated from a Lorenzian form, especially at the first neutralization point of H_5IO_6. In spite of this observation, the line width for the solution of the periodate including the chromate ion ([Cr(VI)] = 1.0 mol dm^{-3}, [I(VII)] = 0.12 mol dm^{-3}, pH = 5.30) was compared with that for the solution of the periodate without the added chromate. The values of the line width for both solutions were found to be almost the same. It may be said that the condensation reaction via path(b) is not so important to affect the line shape of the ^{17}O-signal of periodate ion.

The oxidation of some organic substances by periodate has been studied extensively.[13] It is concluded that the oxidation of pinacol and propane-1,2-diol by periodate proceeds via a mechanism in which the formation of a periodate monoester is followed by ring closure to a cyclic ester, and then the decomposition of it to the reaction products. The first step, the formation of a monoester, is concerned with the condensation reaction in this work. Bunton et al.[13] have shown by the use of oxygen-18 as a tracer that in the periodate oxidation of pinacol and 2-methylpropane-1,2-diol, an intermediate ester is formed by an electrophilic attack of a periodate ion, whereas the oxidation of biacetyl in a basic solution proceeds via a mechanism involving a nucleophilic attack by a periodate ion upon the carbonyl-carbon atom. Thus, in the periodate oxidation of organic substances the periodate ion acts as an electrophile or nucleophile, depending on the nature of the substrate.

Comparison of the Condensation Reactions. It can be seen from Table 4 that the rate constant for the condensation reaction between dianions of chromate and periodate (k_4) has a rather small value compared to those for the reactions between the monoanion and dianion (k_2 and k_3) and between the monoanions (k_1). The reactivity of $H_3IO_6^{2-}$ towards CrO_4^{2-} is 10^3-times smaller than that of $H_4IO_6^-$ towards CrO_4^{2-}. The increase in the nucleophilicity of $H_3IO_4^{2-}$ expected upon increasing the negative charge is more compensated by other factors. For the reaction of $H_3IO_6^{2-}$ with CrO_4^{2-}, the activation energy (E_a) and the activation entropy ($\Delta S^{\neq}$) are obtained to be 25.9 kJ mol^{-1} and −143 J mol^{-1} K^{-1}, respectively. The small value of E_a

and the large negative value of $\triangle S^{\neq}$ are characteristic. Of the factors which affect the ionic reactions, the entropy factor often turns out to the dominant one.[14] The result that the value of k_4 is smaller than that of k_2 or k_3 by a factor of 10^3 seems to be ascribed to the difference in the contribution of the electrostatic effect ($\triangle S^{\neq}_{\text{el}}$) to the activation entropy for these reactions.[14] However, the same reasoning failed to interpret the rate result (30 °C, $I=1.5\ \text{mol dm}^{-3}$) that k_3 ($H_4IO_6^-+CrO_4^{2-}$) is 2.5-times larger than k_2 ($H_4IO_6^-+HCrO_4^-$), since the rate retarding-effect due to the contribution of $\triangle S^{\neq}_{\text{el}}$ is expected to be larger for k_3 than for k_2. The positive kinetic salt effect on the ionic reaction, which is larger for k_3 than for k_2, may compensate for the effect due to $\triangle S^{\neq}_{\text{el}}$.

The condensation rate constants so far obtained by studying the oxygen exchange reactions of the chromate and arsenate ions with water catalyzed by another oxoanion are summarized in Table 4. The following are worth noting: 1) Towards the chromate ion, the reactivity of the periodate is outstanding as compared to the arsenite ion; towards CrO_4^{2-}, $H_4IO_6^-$ is at least 10^6-times more reactive than $H_2AsO_3^-$. Towards the arsenate ion as the substrate, the periodate ion has been shown to be a more excellent reactant compared to arsenious acid or the tellurate and arsenate ions. That the reversible condensation reactions of the periodate ion with another oxoanion to form a heteropolyanion proceed very rapidly may be considered to be rather general. 2) In the oxygen exchange of the chromate ion catalyzed by arsenious acid, the reaction between $Cr_2O_7^{2-}$ and H_3AsO_3, whose rate constant has the order of magnitude of 10^3, has been found. On the other hand, we could not detect any kinetic contribution of the periodate ion on the line width of signals due to the bridging and terminal oxygens of $Cr_2O_7^{2-}$ ion. Unfortunately, it is impossible to study the detailed mechanism by which H_3AsO_3 interacts with $Cr_2O_7^{2-}$ by using ^{17}O NMR method, since the redox reaction between these ions proceeds very fast at the pH where H_3AsO_3 exists dominantly.[5]

Summary. The rate constants for the reversible condensation reactions between the chromate ions ($HCrO_4^-$ and CrO_4^{2-}) and the periodate ions ($H_4IO_6^-$ and $H_3IO_6^{2-}$) were obtained by studying the catalytic oxygen (^{17}O, ^{18}O) exchange reaction of the chromate ions with water by the periodate ions. The condensation rate constants are of the order of magnitude of 10^3—$10^4\ \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$. The extraordinary large values are due to the small value of the activation energy; the activation entropy has a large negative value.

The ^{17}O NMR study on the system shows that in the NMR time scale the oxygen of the monomeric chromate ion interacts with the solvent water oxygen, while both the terminal and bridging oxygens of the dichromate ions do not.

The condensation rate constants between various kinds of oxoanions so far obtained are summarized in Table 4. That the reversible condensation reactions of the periodate ion with another oxoanion to form heteropolyanion proceed very rapidly may be considered to be rather general.

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