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The Kinetics of the Hydrolysis Reaction of Pentaamminechromatocobalt(III) Chloride

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Abstract

The hydrolysis reaction of pentaamminechromatocobalt(III) complex and the anation of the aqua complex by chromate ions:

$$\text{Chromato complex} + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{Aqua complex} + \text{Chromate}$$

were studied at 25 °C, and in the pH ranges 6.0–8.5 and 3.5–7.5, respectively. The equilibrium constant of the hydrolysis reaction has a minimum value at pH ~ 6. The important paths for the reaction (1) are: $RCrO_4H^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^-$ and $RCrO_4H^{2+} + H_2O + H^+ \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^- + H^+$, and the rate constants were obtained as: $k_1 = 2.2 \times 10^{-3}$ s^{-1}, $k_{-1} = 2.3$ M^{-1} s^{-1}, $k_0 = 151$ M^{-1} s^{-1}, and $k_{-0} = 1.7 \times 10^5$ M^{-2} s^{-1}*.

Introduction

In a previous paper [1], we reported a study of the oxygen exchange reaction of pentaamminechromatocobalt(III) ions and water in the presence of the concurrent hydrolysis of the complex ions under the following conditions: [Chromato complex] = 4.5×10^{-3} M, 0 and 25 °C, and pH 6.0–8.5

In order to elucidate the mechanism of the oxygen exchange reaction of chromato complex, the kinetics of the hydrolysis of the complex were studied in the same conditions as those used for the oxygen exchange reactions. A detailed study of the anation reaction was also done with the excess concentration of the aqua complex ([Aqua complex] = 3×10^{-3} M, [Cr(VI)] = 3×10^{-4} M) and pH 3.5–7.5.

The anation reaction of chromato complex was studied in a more acidic region of $[H^+] = (1 \sim 50) \times 10^{-4}$ M by Woods and Sullivan [2]. A mechanistic interpretation of their results was given by Haight [3].

In this paper we present the kinetic and equilibrium results obtained from the study of the hydrolysis and anation reactions.

Experimental

Materials

Pentaamminechromatocobalt(III) was prepared by the method of Briggs [4]. The crude product was purified by dissolving in water and salting out with sodium chloride at 0 °C. Analysis of the compound agreed well with the calculated value for $[CoCrO_4(NH_3)_5] \cdot Cl \cdot H_2O$. The method of analysis was described in an earlier paper [1].

Pentaammineaquacobalt(III) chloride was prepared by the usual method [5]. The molar extinction coefficient of the aqua complex at 492 nm agreed well with the published data [6].

$Na_2CrO_4 \cdot 4H_2O$ and other reagents [Guaranteed reagent, JIS] were used without further purification.

The Acid Dissociation Constant of Pentaammineaquacobalt(III) Chloride

This was determined by potentiometric titration of a solution of pentaammineaquacobalt(III) chloride with sodium hydroxide. The pH of the solution was measured with a Radiometer PHM-26 pH meter. The value of pK_1 (aqua complex) was obtained to be 6.076 at 25 °C and $I = 0.052$ M (Literature value: 5.75 and 5.70 at 22 °C and $I = 0$ [7]).

The Determination of the Equilibrium Constant

The equilibrium constant, K, for the reaction:

$$\text{Pentaamminechromatocobalt(III)} + H_2O \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{Pentaammineaquacobalt(III)} + \text{Chromate} \qquad (1)$$

was determined spectrophotometrically from the studies of the: (a) forward (hydrolysis) and (b)

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

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reverse (anation) reactions. The values of the equilibrium constants obtained from the forward and the reverse reactions agreed well with each other.

In the case of the hydrolysis reaction (a), the procedures were as follows. A weighed amount of the solid chromato complex was dissolved in a fixed amount of water containing an appropriate amount of sodium hydroxide or hydrochloric acid. The absorbance of the equilibrated solution was measured at 540 nm. For the anation reaction (b), the reactant solution was prepared by adding a fixed volume of each of the stock solutions of pentaammineaquacobalt(III) chloride and sodium chromate to a fixed amount of water containing sodium hydroxide or hydrochloric acid. The absorbance was read at 395, 400 and 405 nm. The equilibrium constant was obtained as a mean of the values from these three measurements. The pH value of the solution was measured after the attainment of the equilibrium.

The Evaluation of the Equilibrium Constant

The stoichiometry of the reaction (1) may be represented as:

$$A \rightleftharpoons B + C \tag{2}$$

where A stands for pentaamminechromatocobalt(III) complex, and B and C for pentaammineaquacobalt(III) complex and chromate, respectively. The equilibrium constant of the hydrolysis reaction (1) is defined as:

$$K = \frac{[B]_e[C]_e}{[A]_e} \tag{3}$$

In the hydrolysis reaction, $[B] = [C] = [A]_0 - [A]_e$, and the concentration of chromato complex at equilibrium, $[A]_e$, may be evaluated in terms of the relation:

$$[A]_e = \frac{(\mathrm{Abs})_e - (\epsilon_B + \epsilon_C) \times [A]_0}{\epsilon_A - \epsilon_B - \epsilon_C} \tag{4.1}$$

where $(\mathrm{Abs})_e$ denotes the absorbance of the equilibrated solution, and where ϵ_A, ϵ_B and ϵ_C are the apparent molar extinction coefficients of the chromato complex, the aqua complex, and the chromate, respectively.

For the anation reaction:

$$[A]_e = \frac{(\mathrm{Abs})_e - \epsilon_B[B]_0 - \epsilon_C[C]_0}{\epsilon_A - \epsilon_B - \epsilon_C} \tag{4.2}$$

the values of the apparent molar extinction coefficients at various pH values were evaluated as shown below.

Evaluation of the Apparent Molar Extinction Coefficients, ϵ_A, ϵ_B, and ϵ_C

The apparent molar extinction coefficients at various pH may be calculated by using the relations:

$$\epsilon_A = \frac{\epsilon(RCrO_4H^{2+})[RCrO_4H^{2+}] + \epsilon(RCrO_4^+)[RCrO_4^+]}{[RCrO_4H^{2+}] + [RCrO_4^+]} \tag{5.1}$$

$$\epsilon_B = \frac{\epsilon(ROH_2^{3+})[ROH_2^{3+}] + \epsilon(ROH^{2+})[ROH^{2+}]}{[ROH_2^{3+}] + [ROH^{2+}]} \tag{5.2}$$

$$\begin{aligned}\epsilon_C = {} & \{\epsilon(HCrO_4^-)[HCrO_4^-] + \epsilon(CrO_4^{2-})[CrO_4^{2-}] \\ & + \epsilon(Cr_2O_7^{2-})[Cr_2O_7^{2-}]\}/\{[HCrO_4^-] \\ & + [CrO_4^{2-}] + 2[Cr_2O_7^{2-}]\}\end{aligned} \tag{5.3}$$

where R stands for $Co(NH_3)_5\cdot$. The concentration of ionic species in the above formulae was calculated with the aid of the following pK values:

$[RCrO_4H^{2+} \rightleftharpoons RCrO_4^+ + H^+$
pK_1(chromato) = 4.44 [1]

$ROH_2^{3+} \rightleftharpoons ROH^{2+} + H^+$
pK_1(aqua) = 6.08 This work

$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+$
pK_2(chromate) = 6.50 [8]

$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$
$pK_d(HCrO_4^-) = -1.53$ [8]

The values of the extinction coefficients of each ionic species were taken from the literature values, when available, and the others were determined in this work (see next section). These values were listed in Table I.

ϵ_A and ϵ_B were evaluated in terms of eqn. (5.1) and eqn. (5.2), respectively. In order to check the results of the calculation, the values of ϵ_B were

TABLE I. The Extinction Coefficients of Chromato Complex, Chromate, and Aqua Complex at Different Wavelengths.

λ/nm	395	400	405	540	Refs.
$\epsilon(RCrO_4^+)^a$			3120	167.9	This work
$\epsilon(RCrO_4^+)^b$	3750	3510	3155	167.8	This work
$\epsilon(RCrO_4H^{2+})^b$	3462				This work
$\epsilon(HCrO_4^-)$		326			[9]
	444	356	311		[10]
			258		[11]
$\epsilon(Cr_2O_7^{2-})$		1162			[9]
	1644	1284	941		[10]
			1777		[11]
$\epsilon(CrO_4^{2-})$	2582	1922	1400		[12]
$\epsilon(ROH_2^{3+})$	8.88	8.21	8.43	27.8	This work
		8.2			[13]
$\epsilon(ROH^{2+})$	44.9	38.4	31.8	46.8	This work
		38.4			[13]

^{a}Method 1. ^{b}Method 2 (see text).

determined at 540 nm from the values of the absorbance measured at intervals of 0.2 pH in the pH range from 3 to 10 (Absorbance = ϵ_B[Aqua complex]), and compared with those calculated with the use of eqn. (5.2). The agreement between the observed and calculated values was excellent.

As seen from Table I, the values of $\epsilon(HCrO_4^-)$ and $\epsilon(Cr_2O_7^{2-})$ obtained by several authors do not agree satisfactorily with each other. Therefore, the values of ϵ_C were determined directly by measuring the absorbance of the chromate solution at various pH and at the chromate concentration of 3×10^{-4} M, equal to the initial concentration of chromate used for the determination of the equilibrium constant, K. The acidic solution of chromate does not obey Beer's law because the ratio $[Cr_2O_7^{2-}]/[HCrO_4^-]$ depends on the total concentration of the chromate. This behavior was observed even at 3×10^{-4} M, but the errors due to this fact do not affect the determination of the equilibrium constants. The variation of ϵ_C with pH is shown in Fig. 1.

The Determination of the Molar Extinction Coefficients of Each Ionic Species of Chromato Complex and Aqua Complex

The values of $\epsilon(RCrO_4^+)$ and $\epsilon(RCrO_4H^{2+})$ were evaluated from the observed values of absorbance of chromato complex at the specified conditions in terms of the relation:

$$\text{Absorbance (chromato complex)} = \epsilon(RCrO_4^+)[RCrO_4^+] + \epsilon(RCrO_4H^{2+})[RCrO_4H^{2+}] \quad (5.1')$$

The values of absorbance of chromato complex were obtained by the following methods. Method 1: due to the hydrolysis of the chromato complex, the observed values of the absorbance change with time, and these were corrected for the hydrolysis by extrapolating the observed values to time zero. The Beer-Lambert plots gave a satisfactory straight line. Method 2: enough chromate (at 540 nm) or aqua complex (at 395, 400 and 405 nm) to suppress the hydrolysis of the chromato complex was added to the solution of chromato complex, and the value of absorbance associated with chromato complex was obtained by subtracting the contribution from the chromate or the aqua complex.

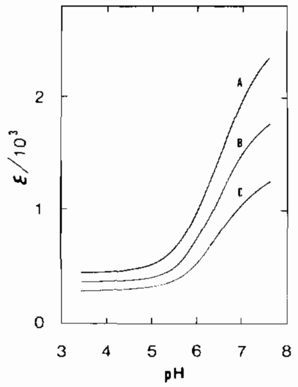


Fig. 1. The apparent molar extinction coefficient of chromate at various pH (25 °C, [Cr(VI)] = 3×10^{-4} M). A: 395 nm, B: 400 nm, C: 405 nm.

To obtain the value of $\epsilon(RCrO_4^+)$, the values of absorbance were measured in the pH range of 6–6.5 where the extent of the hydrolysis is expected to be small by preliminary observations and where the dominating ionic species of chromato complex is $RCrO_4^+$, and $[RCrO_4H^{2+}]$ is negligible in eqn. (5.1′) (pK = 4.44 [1]).

For the value of $\epsilon(RCrO_4H^{2+})$, method 2 was applied to the acidic solution of chromato complex. The absorbance values were measured at pH 5.44 and 5.00. At pH 5, 22 per cent of the chromato complex exists as $RCrO_4H^{2+}$. The values of $\epsilon(RCrO_4H^{2+})$ were found to be 3461 (pH 5.44) and 3463 (pH 5.00) by using eqn. (5.1′).

The molar extinction coefficients of ROH_2^{3+}($\epsilon(ROH_2^{3+})$) and ROH^{2+}($\epsilon(ROH^{2+})$) were determined from the slope of Beer-Lambert plots obtained at pH 1.1 and pH 10, respectively (pK_1(aqua) = 6.08).

Kinetic Measurements

Reactions were carried out in a thermostated cell under a nitrogen atmosphere. The change of the pH accompanying the reaction was compensated by the addition of a small amount of sodium hydroxide or hydrochloric acid solution with a pH stat device (Radiometer PHM 26 pH meter coupled with an automatic titrator TTTII and automatic buret ABU 12). At appropriate intervals aliquots of the solution were removed and the absorbance values were measured at specific wave lengths (540 nm for the hydrolysis reaction, and 395 or 405 nm for the anation reaction). The change of absorbance curves with time, at 25 °C and pH 6.0, is shown in Fig. 2.

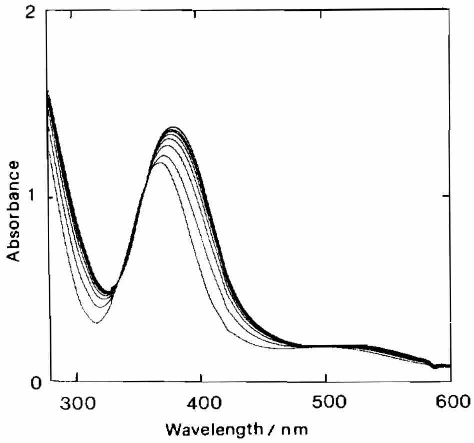


Fig. 2. The change of absorbance curves with time at 25 °C and pH 6.0.

Results and Discussion

Equilibrium Results

The reciprocal of the equilibrium constants are plotted against pH in Fig. 3, where solid circles and open circles designate the results obtained from the studies of the hydrolysis of chromato complex (the forward reaction of eqn. (1)) (a) and of the anation reaction of aqua complex with chromate (the reverse reaction of eqn. (1)) (b), respectively. The initial concentration of chromato complex in (a) was 5×10^{-3} M, while those of aqua complex and chromate in (b) were 3.3×10^{-4} and 2.4×10^{-4} M, respectively. Figure 3 shows that both closed and open circles fall on a curve, and the curve has a maximum in the pH range 5.75–6.25.

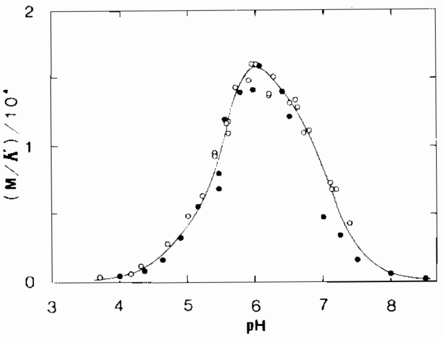


Fig. 3. The plots of $1/K$ against pH. ●: Equilibria of the hydrolysis of chromato complex at 25 °C ([Chromato complex]$_0$ = 4.5×10^{-3} M). ○: Equilibria of the anation reaction of aqua complex with chromate at 25 °C ([Aqua complex]$_0$ = 3.3×10^{-4} M, [Cr(VI)]$_0$ = 2.4×10^{-4} M).

The effect of ionic strength on the equilibrium constant, K was studied at 25 °C and Ph 6.1. Ionic strength was varied between 8×10^{-4} and 0.2 M by the addition of sodium chloride. The plots of $-\log K$ against $I^{1/2}/(1 + I^{1/2})$ (Fig. 4) gave a straight line, whose slope was obtained to be −3.1. By applying the Güntelberg equation to eqn. (1), the relation may be derived:

$$\log(1/K) = \log(1/K_a) - A(z^2_{Cr(VI)} + z^2_{aqua} - z^2_{chromato})(I^{1/2}/(1 + I^{1/2})),$$

where K_a is the thermodynamic equilibrium constant.

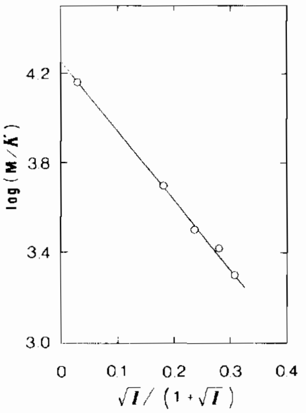


Fig. 4. The effect of ionic strength on $1/K$. (25 °C, pH 6.1, $I = 8.4 \times 10^{-4} \sim 0.2$ M).

Over the pH range from 3.5 to 8.5, the following four reactions are possible components of the generalized equilibrium (1).

$$RCrO_4H^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^- \qquad (1.1)$$

$$RCrO_4^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ROH_2^{3+} + CrO_4^{2-} \qquad (1.2)$$

$$RCrO_4^+ + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} ROH^{2+} + HCrO_4^- \qquad (1.3)$$

$$RCrO_4^+ + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} ROH^{2+} + CrO_4^{2-} \qquad (1.4)$$

The values of $A(z^2{}_{Cr(VI)} + z^2{}_{aqua} - z^2{}_{chromato})$ are estimated to be 3, 6, 2 and 3 for the processes (1.1) ~ (1.4) respectively. The salt effect on the dissociation and dimerization equilibria was not taken into account. The observed salt effect seems to be explained at least qualitatively.

The temperature dependence of the equilibrium constant was studied at pH 6.20 and 6.90. The results are shown in Table II. The temperature dependence of K gives $\Delta H^\circ = 14.4 \pm 1.9$ kJ mol^{-1} and $\Delta S^\circ = -31.3 \pm 6.3$ J mol^{-1} K^{-1} at pH 6.2, and $\Delta H^\circ = 14.4 \pm 0.3$ kJ mol^{-1} and $\Delta S^\circ = -26.3 \pm 6.4$ J mol^{-1} K^{-1} at pH 6.9.

TABLE II. The Temperature Dependence of the Equilibrium Constant for the Reaction (1).

T(°C)	pH = 6.10		pH = 6.90	
	K (10^{-5} M)	$1/K$ (10^4 M^{-1})	K (10^{-3} M)	$1/K$ (10^3 M^{-1})
25	6.93	1.44	0.124	8.07
30	7.47	1.33	0.136	7.33
35	8.36	1.20	0.150	6.68

The Evaluation of the Rate Constants

The hydrolysis reaction is a reversible first and second order reaction of the type, $A \rightleftharpoons B + C$, and its rate equation can be given by eqn. (6):

$$\ln\left\{\frac{[A]_0{}^2 - [A]_e[A]_t}{([A]_t - [A]_e)[A]_0}\right\} = k_f\left(\frac{[A]_0 + [A]_e}{[A]_0 - [A]_e}\right) t \qquad (6)$$

where the subscripts 0 and e indicate time zero and infinity, respectively, and k_f and k_r are the rate constants of the forward and reverse reactions.

By using the relations: $D_0 = \epsilon_A[A]_0$, $D_t = \epsilon_A[A]_t + [(\epsilon_B + \epsilon_C)([A]_0 - [A]_t)]$, and $D_e = \epsilon_A[A]_e + [(\epsilon_B + \epsilon_C)([A]_0 - [A]_e)]$, [A]'s in eqn. (6) can be expressed in terms of the measured absorbance, D, and eqn. (6) reduces to eqn. (7):

$$\ln\left(\frac{(2D_0 - D_e - D_t)}{D_t - D_e} - \frac{\epsilon_A(D_t - D_0) \times (D_e - D_0)}{(D_t - D_e) \times D_0 \times (\epsilon_A - \epsilon_B - \epsilon_C)}\right) = k_f\left(\frac{\epsilon_A(D_0 + D_e) - 2(\epsilon_B + \epsilon_C) \times D_0}{\epsilon_A(D_0 - D_e)}\right) t \qquad (7)$$

$$k_r = k_f/K.$$

The left hand side of the equation was plotted against time, and from the slope of the straight line thus obtained, the value of k_f was calculated.

As the anation reaction, $B + C \longrightarrow A$, was carried out in the presence of excess aqua complex, the reaction may be treated as a reversible first-first order reaction, and the rate constants are obtained by the relations:

$$\ln\{(D_e - D_0)/(D_e - D_t)\} = k_{obs}t$$

$$k_{obs} = k_r[B]_0 + k_f = k_r([B]_0 + K) \qquad (8)$$

The hydrolysis reaction was studied in the pH range of 6.2 ~ 8.5 ($[A]_0 = 4.5 \times 10^{-3}$ M), and the anation reaction in the pH range between 3.5 and 7.5 ($[B]_0 = 3 \times 10^{-3}$ and $[C]_0 = 3 \times 10^{-4}$ M).

In Figs. 5 and 6 log k_f and log k_r are plotted against pH, where curves A and B represent the values obtained by the study of the hydrolysis and the anation reactions, respectively. The pH–log k_f profile remains almost linear over the entire pH region studied and the slopes of the straight lines were calculated to be 0.89 ± 0.02 (pH 6.4–7.5)

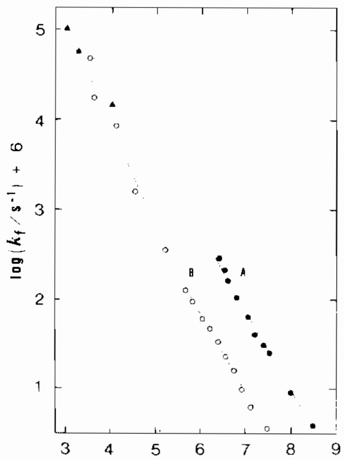


Fig. 5. pH Dependence of k_f at 25 °C. ● (A): for the hydrolysis of chromato complex ([Chromato complex] = 4.5×10^{-3} M). ○ (B): for the anation reaction ([Aqua complex] = 3×10^{-3} M, [Cr(VI)] = 3×10^{-4} M). ▲: Woods and Sullivan.

for A, and to be 0.91 ±0.02 (pH 5.3–7.2) for B. Figure 6 shows that the pH dependence of log k_r changes with pH. In the pH region greater than 6 the logarithm of k_r varies linearly with pH, and the slopes of the curves were obtained to be 1.80 ±0.05 (pH 6.4–8.0) for A and 1.30 ±0.06 (pH 6.05–7.5) for B (the discrepancy of the slopes between curves A and B is inexplicable.). In the region more acidic than pH 6, the variation of the value of k_r slows down increasingly with the decrease of pH, k_r being nearly independent of pH at pH ~ 4.

The maximum value of $1/K$ (k_r/k_f) observed at pH 6 may be explained by the difference in the pH dependencies of k_f and k_r. The pH dependence of k_r is larger compared to that of k_f in the region of pH > 6, while it becomes smaller than that of k_f in the region of pH < 6.

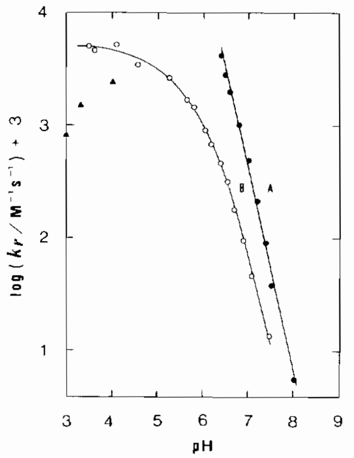


Fig. 6. pH Dependence of k_r at 25 °C. ● (A): for the hydrolysis of chromato complex ([Chromato complex] = 4.5 × 10^{-3} M). ○ (B): for the anation reaction ([Aqua complex] = 3 × 10^{-3} M, [Cr(VI)] = 3 × 10^{-4} M). ▲: Woods and Sullivan.

In Table III k_f and k_r obtained from the studies of the anation reaction are shown as a function of the ionic strength and the concentration of aqua complex and chromate. The positive salt effect on k_f is observed, which may be explained by the equilibrium salt effect on the acid dissociation reaction; $[RCrO_4H]^{2+} \rightleftharpoons [RCrO_4]^+ + H^+$. The increase of the ionic strength shifts the dissociation equilibrium to the left in favour of the more reactive species, $RCrO_4H^{2+}$. On the other hand, k_r is independent of the change in the ionic strength. In the reverse reaction, the equilibrium salt effect of the type described above leads to the increase in the concentration of the more reactive species of aqua complex, ROH_2^{3+} and the decrease in the concentration of the more reactive species of chromate ion, $HCrO_4^-$. The kinetic salt effect on the reverse reaction is expected to be negative. These effects counteract each other and k_r observed becomes nearly independent of the change in the ionic strength. The rate constants are slightly dependent on the concentration of aqua complex at pH 6.10 (k_f and $k_r \propto$ [Aqua complex]$^{0.2}$). The aqua complex has a small catalytic activity to the forward and the reverse reactions.

Figures 5 and 6 show that values of the rate constants (k_f and k_r) obtained from the hydrolysis reaction are always larger than those obtained from the anation reaction. Though these reactions were carried out in different ionic media ($I = 10^{-3}$ M for the hydrolysis and $I = 14 \times 10^{-3}$ M for the anation), the discrepancy is not explicable by the observed kinetic salt effect shown in Table III.

The temperature dependence of k_f and k_r was studied at pH 6.20 and 6.90 for the anation reaction. The results are shown in Table IV.

TABLE III. The Rate and Equilibrium Results of the Anation Reaction as a Function of Ionic Strength and the Concentrations of Aqua Complex and Chromate. pH = 6.10.

I (M)	$[Aqua]_0$ (10^{-3} M)	$[Cr(VI)]_0$ (10^{-4} M)	k_f (10^{-5} s^{-1})	k_r (M^{-1} s^{-1})	K (10^{-4} M)
0.2	3.35	2.81	34.6	0.691	5.01
0.2	6.99	2.81	40.0	0.798	5.01
0.2	9.97	2.81	42.7	0.853	5.01
0.15	3.35	2.81	26.2	0.688	3.82
0.10	3.35	2.81	22.2	0.706	3.15
0.05	3.35	2.81	15.4	0.771	2.00
0.033	7.44	2.03	8.42	1.21	0.693
0.034	7.47	3.07	7.68	1.11	0.693
0.033	7.38	4.04	8.27	1.19	0.693
0.033	7.35	4.85	8.48	1.22	0.693

TABLE IV. The Temperature Dependence of k_f and k_r.

T (°C)	pH = 6.20		pH = 6.90	
	k_f (s^{-1})	k_r (10^{-5} M^{-1} s^{-1})	k_r (s^{-1})	k_r (10^{-5} M^{-1} s^{-1})
25	0.672	4.65	0.095	1.17
30	0.847	6.32	0.116	1.59
35	0.867	7.25	0.108	1.61
$\frac{E_a}{kJ\ mol^{-1}}$	20 ± 9	34 ± 7	10 ± 12	24 ± 12

The Effect of Buffer on k_{obs}

Hydrolysis of the chromato complex is accelerated by the presence of the 0.1 M acetate buffer at pH 5.53 ($t_{1/2} < 1$ min, while $t_{1/2} = 12.5$ min without buffer). The catalytic effect of phosphate buffer on the anation reaction was studied at pH 6.84. The concentration of buffer was varied from 0.005 to 0.02 M, the buffer ratio and the ionic strength (0.1 M with NaCl) being kept constant. In Fig. 7, k_{obs} was plotted against the buffer concentration, and the apparent catalytic constant of phosphate buffer was estimated to be $(7.83 \pm 0.36) \times 10^{-2}$ M^{-2} s^{-1} from the slope of the line. The same type of catalysis was also observed for the aqua complex.

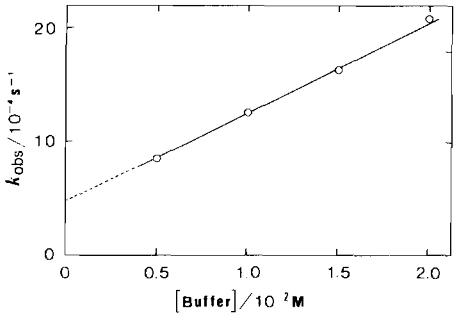


Fig. 7. The effect of buffer on k_{obs}. (25 °C, pH 6.84, [Buffer] = 0.005–0.02 M, I(NaCl) = 0.1 M).

The Analysis of k_f and k_r

The rate constant k_f for the generalized reaction 1 may be expressed in terms of the rate constants for assumed elementary processes (eqns. (1.1) ~ (1.4)). Reactions (1.2) and (1.3) are kinetically equivalent.

$$k_f = \frac{k_1[RCrO_4H^{2+}] + k_2[RCrO_4^{+}] + k_4[RCrO_4^{+}][OH^{-}]}{[\text{Chromato complex}]} \tag{9}$$

As shown above, the rate constants in eqn. (9) should include the catalytic part by aqua complex. The rate term, $k_1[RCrO_4H^{2+}]$ in eqn. (9), for example, should be equated to $(k_1'[RCrO_4H^{2+}] + k_1''[RCrO_4H^{2+}] \times [\text{Aqua complex}])$. As the contribution of the catalytic terms may be assumed to be relatively small compared to the uncatalyzed one, the analysis was done in terms of eqn. (9). In the pH region greater than 6.5 the dominant species of the chromato complex is $RCrO_4^{+}$, and its concentration is independent of pH. Therefore, if the k_2-term made a large contribution to the overall hydrolysis reaction, k_f should be independent of the change in the value of pH, and if k_4-term played an important role in the reaction, it should increase with the pH in this pH region. The slope of the plot of log k_f against pH was −0.9, which indicates that the k_1-term is dominant in eqn. (9).

The assumption that only the k_1-term is important in the hydrolysis reaction simplifies eqn. (9) to: $k_f = k_1[RCrO_4H^{2+}]/[\text{Chromato complex}] = k_1[H^+]/([H^+] + K_1(\text{chromato}))$, and the plots of k_f against $[H^+]/([H^+] + K_1(\text{chromato}))$ should give a straight line. The plots, however, deviate significantly upwards from the straight line with increasing $[H^+]$. By introducing a hydrogen ion catalyzed path, (1.0), as an additional one:

$$RCrO_4H^{2+} + H^+ + H_2O \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^{-} + H^+ \tag{1.0}$$

k_f can be written as:

$$k_f = (k_1[RCrO_4H^{2+}] + k_0[RCrO_4H^{2+}][H^+])/[\text{Chromato complex}]$$

or:

$$k_f/\{[H^+]/([H^+] + K_1(\text{chromato}))\} = k_1 + k_0[H^+]$$

By the least squares treatment, k_1 and k_0 were obtained to be $(2.18 \pm 0.41) \times 10^{-3}$ s^{-1} and 151 ± 5 M^{-1} s^{-1}. By using the k_f value at pH 7.5 where the contribution of k_1-term may be considered to be very small ($[RCrO_4H^{2+}]/[RCrO_4^{+}] = 1/1000$), the upper limit of k_2 is estimated to be 3.6×10^{-7} s^{-1}. The calculated values of k_f by using these rate contants agree well with those obtained by experiment.

The rate law for the anation reaction may be expressed as:

$$\begin{aligned} & k_r[\text{Aqua complex}][\text{Cr(VI)}] \\ & \quad = k_{-0}[ROH_2^{3+}][HCrO_4^{-}][H^+] \\ & \qquad + k_{-1}[ROH_2^{3+}][HCrO_4^{-}] + \left\{k_{-3} + k_{-2}\left(\frac{K_2(\text{Cr(VI)})}{K_1(\text{aqua})}\right)\right\}[ROH^{2+}][HCrO_4^{-}] \\ & \qquad + k_{-4}[ROH^{2+}][CrO_4^{2-}] \end{aligned} \tag{10}$$

where the constants in the braces are represented as k_{-2}'. In the region of pH > 6, the contribution of the k_0-term to the total rate may be assumed to be small, because the value of the concentration product, $[ROH_2^{3+}][HCrO_4^-][H^+]$, is very small. The values of k_{-1}, k_{-2}', and k_{-4} were estimated tentatively by applying the least squares treatment to the values of k_r in this pH range, and obtained to be 2.29 ± 0.02, 0.08 ± 0.10, and −0.01 ± 0.08, respectively. It may be assumed the value of k_{-4} is relatively small. Thus, the k_{-4}-term was removed from the rate law 10, and the least squares treatment was applied to the whole of the k_r data. The values of k_{-0}, k_{-1} and k_{-2}' were $(1.74 \pm 0.18) \times 10^5$, 2.30 ± 0.09, and 0.02 ± 0.07, respectively. The observed values of k_r were reproduced well with the use of these rate constants.

The rate constants thus analyzed are summarized in Table V, along with the equilibrium constants for individual paths which were calculated by using these rate constants.

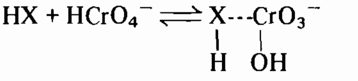
Sullivan *et al.* have studied this reaction in a more acidic region ($[H^+] = (1, 5, 10, \text{and } 50) \times 10^{-4}$ M), other experimental conditions being as follows: 25 °C, $I = 0.25$ M, $[Cr(VI)] = 4.49 \times 10^{-4}$ M, [Aqua complex] $= (0.167 \sim 2.083) \times 10^{-2}$ M. The kinetic results were analyzed as a function of $[H^+]$ to give the relations:

$$k_f = (2.18 \pm 0.92) \times 10^{-2} + (63.8 \pm 3.6) \times [H^+]$$

$$k_r = (0.80 \pm 0.20) + (1.68 \pm 0.38) \times 10^{-4}\ [H^+]^{-1}.$$

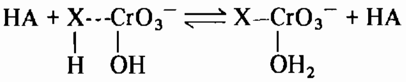
The values of k_f and k_r for the reaction (1) were plotted in Figs. 5 and 6 with solid triangles.

Haight [3] has analyzed the results obtained by Woods and Sullivan [2] and demonstrated that they are consistent with the general mechanism for substitution on the tetrahedral hydrogen chromate ion [14]. The general mechanism has been expressed as:



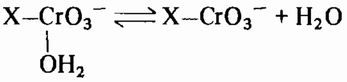
$$HX + HCrO_4^- \rightleftharpoons \underset{H}{X}\cdots\underset{OH}{CrO_3^-}$$

(a)



$$HA + \underset{H}{X}\cdots\underset{OH}{CrO_3^-} \rightleftharpoons X{-}\underset{OH_2}{CrO_3^-} + HA$$

(b)



$$X{-}\underset{OH_2}{CrO_3^-} \rightleftharpoons X{-}CrO_3^- + H_2O$$

(c)

where HX is the acidic substrate and where HA is an acid or base catalyst, or solvent. An assumed rate determining proton transfer from HX or from acid catalyst to $HCrO_4^-$ would require that the rate constant for the reaction between $HCrO_4^-$ and the acidic species HX depends on the acidity of HX and HA, and the general acid catalysis should be observed.

Some results obtained in this work are consistent with this mechanism: (1) the value of k_{-1}, 2.3 M^{-1} s^{-1}, for the reaction between $HCrO_4^-$ and $[Co(OH_2)(NH_3)_5]^{3+}$ compares well with 2 M^{-1} s^{-1} [14] for the condensation of $HCrO_4^-$ with $HCrO_4^-$. The acidity of $HCrO_4^-$ is nearly identical with that of $[Co(OH_2)(NH_3)_5]^{3+}$. (2) catalysis by phosphate and acetate buffers and the aqua complex has been observed. (3) the proton catalyzed path between $[Co(OH_2)(NH_3)_5]^{3+}$ and $HCrO_4^-$ has the rate constant which is comparable to the rate constants ($(1 \sim 7) \times 10^5$ M^{-2} s^{-1}) found for the condensation reactions of $HCrO_4^-$ with NCS^-, $HCrO_4^-$, $H_2PO_4^-$, and $H_2PO_3^-$ [14].

Many studies have been carried out on the hydrolysis reactions of pentaamminecobalt(III) complex with oxoanion ligands. In Table VI the rate constants are listed for the elementary processes of the hydrolysis and the anation reactions. In all the reactions shown in Table VI, except for the hydrolysis of pentaamminephosphatocobalt(III) complexes, it has been established that the substitution occurs at oxoanion center, that is, the reaction proceeds through the fission of a bond between the bridging oxygen and the central atom of the oxoanions [1]. The rate constant for the hydrolysis of $RPO_4H_2^{2+}$ at 25 °C is calculated to be 2.25×10^{-7} s^{-1} from the value of 1.57×10^{-5} s^{-1} at 60 °C by using $\Delta H^{\ddagger}$

TABLE V. The Analyzed Rate Constants for Reaction (1).

Reactions	k_f (s^{-1})	k_r (M^{-1} s^{-1})	M (*K*)
$RCrO_4H^{2+} + H_2O + H^+ \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^- + H^+$	151 ± 5	$(1.74 \pm 0.18) \times 10^5$	1.2×10^3
$RCrO_4H^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ROH_2^{3+} + HCrO_4^-$	$(2.2 \pm 0.4) \times 10^{-3}$	2.30 ± 0.09	1.1×10^3
$RCrO_4^+ + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ROH^{2+} + HCrO_4^-$	$<3.6 \times 10^{-7}$	0.022 ± 0.073	6.2×10^4

TABLE VI. The Hydrolysis Reactions of Pentaamminecobalt(III) Complex with Oxoanion-ligands and the Anation Reactions of Pentaammineaquacobalt(III) with Oxoanions[a].

Reactions	*T* (°C)	*I* (M)	k_f (s^{-1})	k_r ($M^{-1} s^{-1}$)	Refs.
$RPO_4 + OH^- \longrightarrow$	60	1	4.0×10^{-4}		[15]
$RPO_4 + H_2O \longrightarrow$	60	1	2.0×10^{-6}		[15]
$RPO_4H^+ + H_2O \longrightarrow$	60	1	1.05×10^{-6}		[15]
$RPO_4H_2^{2+} + H_2O \longrightarrow$	60	1	1.57×10^{-5}		[15]
$RPO_4H_3^{3+} + H_2O \longrightarrow$	60	1	1.50×10^{-4}		[15]
$RAsO_4H^+ + H_2O \rightleftharpoons ROH_2^{3+} + HAsO_4^{2-}$	22	1	2.90×10^{-5}	1.1×10^{-1}	[7]
$RAsO_4H_2^{2+} + H_2O \rightleftharpoons ROH_2^{3+} + H_2AsO_4^-$	22	1	4.08×10^{-4}	1.2×10^{-2}	[7]
$RAsO_4H_2^{2+} + H_2O + H^+ \rightleftharpoons ROH_2^{3+} + H_3AsO_4$	22	1	6.70×10^{-1}		[7]
$RMoO_4^+ + H_2O \rightleftharpoons ROH^{2+} + HMoO_4^-$	25	1		6.6×10^4	[16]
$RMoO_4^+ + H_2O + H^+ \rightleftharpoons ROH_2^{3+} + HMoO_4^-$	25	1		3.2×10^5	[16]
$RCrO_4^+ + H_2O \rightleftharpoons ROH^{2+} + HCrO_4^-$	25	0.01	$<3.6 \times 10^{-7}$	2.2×10^{-2}	This work
$RCrO_4H^{2+} + H_2O \rightleftharpoons ROH_2^{3+} + HCrO_4^-$	25	0.01	2.2×10^{-3}	2.3	This work
$RCrO_4H^{2+} + H_2O + H^+ \rightleftharpoons ROH_2^{3+} + HCrO_4^- + H^+$	25	0.01	1.5×10^2	1.7×10^5	This work

[a] R: $Co(NH_3)_5$.

of 97.4 kJ mol^{-1} given for this process [15]. This value is significantly smaller than those for the other processes shown in the Table, which reflects the difference of the mechanism between both cases.

Table VI shows that (1) the reactivity of $HMoO_4^-$ in the anation reaction is very large, (2) the hydrolytic reactivity of pentaammine complexes coordinated with oxoanion ligands increases with the increasing degree of protonation of the oxoanion ligands, and (3), in the anation reaction, ROH_2^{3+} is more reactive towards oxoanions than is ROH^{2+}.

Table VII shows the rate constants of the oxygen exchange reactions between oxoanions and water, which may be considered to be a measure of a lability of oxygen atoms of oxoanions in the reaction of the oxoanion in solution. If the bond-breaking between the bridging oxygen and the central atom of the oxoanion is involved in the rate determining step of the hydrolysis reaction, a parallelism should be observed between the rate constant of the hydrolysis reaction of the complex with oxoanion and that of the oxygen exchange reaction with water. However, it is difficult to find any parallelism from the data shown in Tables VI and VII.

TABLE VII. The Oxygen Exchange Reactions between Oxoanions and Water.

Reactions	*T* (°C)	k (s^{-1})	Refs.
$ROH_2^{3+} + H_2{}^{18}O \rightleftharpoons$	25	5.9×10^{-6}	[17]
$H_2PO_4^- + H_2{}^{18}O \rightleftharpoons$	100	4×10^{-6}	[18]
$HAsO_4^{2-} + H_2{}^{18}O \rightleftharpoons$	30	1.2×10^{-5}	[19]
$H_2AsO_4^- + H_2{}^{18}O \rightleftharpoons$	30	1×10^{-4}	[19]
$MoO_4^{2-} + H_2{}^{18}O \rightleftharpoons$	5	5.4×10^{-2}	[20]
$HCrO_4^- + H_2{}^{18}O \rightleftharpoons$	25	2.4×10^{-3}	[21]

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