The Oxygen Exchange Reaction of Pentaamminechromatocobalt(III) Ions with Water

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The oxygen exchange reaction of pentaamminechromatocobalt(III) ions with water in the presence of the concurrent hydrolysis of the complex ions has been studied at 0 and 25 °C in the pH-range 6.0–8.0. The results were interpreted by a set of concurrent mechanisms: 1) $RHCrO_4^{2+} + RCrO_4^+ \rightleftharpoons RCr_2O_7R^{4+} + OH^-$, *2)* $RHCrO_4^{2+} + HCrO_4^- \rightleftharpoons RCr_2O_7^+ + H_2O$, *3)* $RCrO_4^+ + HCrO_4^- \rightleftharpoons RCr_2O_7^+ + OH^-$, *and 4)* $RCrO_4^+ + H_2O \rightarrow ROH^{2+} + HCrO_4^-$, $HCrO_4^- + H_2^{18}O \rightleftharpoons HCrO_3^{18}O^- + H_2O$, $ROH^{2+} + HCrO_3^{18}O^- \rightarrow RCrO_3^{18}O^+ + H_2O$ *(R stands for* $(NH_3)_5Co\cdot$*). The Cr–O bond is broken in the hydrolysis of the chromato complex at pH 6.7.*

Introduction

The oxygen exchange reaction of oxoanion ligand in metal complexes has so far received limited attention. Apart from the exchange reaction of the bridging oxygen atom, the exchange reaction of the terminal oxygen atoms of the oxoanion ligands bears close similarity to those of free oxoanions in their rates and mechanisms [1]. We have studied the oxygen exchange reaction between chromate ions and water under the following conditions: 25 °C, pH 7–12, [Cr(VI)] = 0.075 mol dm^{-3}, I = 0.2 and 1 mol dm^{-3}, and proposed the uncatalyzed and acid catalyzed oxygen exchanges of hydrogen-chromate ions with water as additional rate terms to the kinetic law proposed by Holyer and Baldwin [2]. In this paper we report a study of the oxygen exchange reaction of pentaamminechromatocobalt(III) ion with water, which in its mechanism is in part analogous to that of the oxygen exchange of chromate ions [2, 3].

Experimental

Materials

Pentaamminechromatocobalt(III) chloride 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. It was analyzed as follows: the sample was decomposed by boiling with a solution of sodium hydroxide (0.3 *M***). The ammonia evolved was absorbed in a solution of boric acid and titrated by hydrochloric acid. The oxide of cobalt was removed, the filtrate being determined spectrophotometrically for chromate ions at 373 nm. The H- and N-contents were determined by elemental analyses. The results are as follows. Found: H, 5.52; N, 22.31; NH_3, 26.30; CrO_4, 36.99%. Calcd. for $[CoCrO_4(NH_3)_5]Cl\cdot H_2O$: H, 5.47; N, 22.34; NH_3, 27.16; CrO_4, 37.01%. The molar extinction coefficient of the chromato complex at the absorption maximum (540 nm) was evaluated as 167.9 ± 1.4 from the slope of the Beer-Lambert plots. This value is slightly larger than the published data of 138 [5], and is considered to be better (in our plots, each value of the absorbance was corrected for the change of absorbance due to the hydrolysis of chromato complex by extrapolation to the time zero). The IR spectra of the complex agreed well with the published data [6].

Water enriched in oxygen-18 was obtained from a fractionating column and purified as usual. All other chemicals were of reagent grade and used without further purification.

The Acid Dissociation Constant of Pentaamminechromatocobalt(III) Chloride

The equilibrium constant for the reaction,

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

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$$[CoHCrO_4(NH_3)_5]^{2+} \rightleftharpoons [CoCrO_4(NH_3)_5]^{+} + H^{+}$$

was determined potentiometrically. A weighed amount of the chromato complex was dissolved in a fixed quantity of water containing a definite amount of sodium hydroxide or hydrochloric acid. The operations were carried out under a nitrogen atmosphere in a thermostated cell, and the pH of the solution was measured with a Radiometer PHM 26 pH meter. Owing to the concurrent hydrolysis of the complex, $[CoCrO_4(NH_3)_5]^+ + H_2O \rightleftharpoons [CoOH(NH_3)_5]^{2+} + H^+ + CrO_4^{2-}$, the pH of the solution changes with time. Therefore the change of the pH was followed for a while, and extrapolated to zero time. The titration curve was constructed from a set of such measurements with varied acidities. The result is $pK_a = 4.44$ at 25 °C.

Oxygen Exchange between the Chromato Complex and Water

The reaction was started by dissolving a weighed amount of the chromato complex in oxygen-18 water. The pH of the solution was adjusted by the addition of a solution of sodium hydroxide or hydrochloric acid. The reaction was run at 25 °C under a nitrogen atmosphere. The change of the pH due to the hydrolysis of the complex was compensated by the addition of a solution of sodium hydroxide with a pH-stat device (a Radiometer PHM 26 pH meter coupled with an automatic titrator TTT11 and an automatic burette ABU 12). The concentrations of the reactants and the ^{18}O-content of the solution did not change appreciably with addition of the sodium hydroxide solution. After appropriate time intervals aliquots of the solution were poured into a tube containing a small amount of potassium iodide, and precipitated as iodide. The precipitate was washed with water, ethanol and diethyl ether, dried at 80 °C for an hour, and converted into carbon dioxide by the guanidinium chloride method. The isotopic analysis of the carbon dioxide was made on a Hitachi model RMS-I mass spectrometer. The rate of the oxygen exchange of the chromato complex was calculated by the formula:

$$R(M\,s^{-1}) = -\frac{1}{t} \cdot \frac{[\text{Complex}]\,[H_2O]}{3\,[\text{Complex}] + [H_2O]} \cdot \ln\left(1 - \frac{O_0 - O_t}{O_0 - O_\infty}\right),$$

where O_0, O_t, and O_∞ are the ^{18}O-contents of the chromato complex at times 0, t, and infinity, respectively, and where [Complex] and $[H_2O]$ are the molar concentrations of the pentaamminechromatocobalt(III) chloride and water, respectively. Preliminary experiments have shown that three of the four oxygen atoms of the chromato complex are exchangeable. Owing to the decomposition of the complex during a long period of reaction and especially in a solution of higher pH, it was difficult to obtain accurate values of $^{18}O_\infty$ from the analysis of the chromato complex, and these were calculated from the ^{18}O-content of water distilled from the solution at exchange equilibria.

Results and Discussion

The Position of Bond Breaking in the Hydrolysis of the Chromato Complex

Solid pentaammineaquacobalt(III) chloride was dissolved in an isotopically equilibrated solution of sodium chromate in oxygen-18 water, and the solution was allowed to reach the anation equilibrium at 25 °C and pH 6.7. In this time interval the oxygen exchange of the aqua complex is negligible [7]. After the attainment of the anation equilibrium, which was checked spectrophotometrically, the chromato complex was precipitated as iodide, and its oxygen-18 content was analyzed as described above. The results showed that the chromato complex contains 2.6 atoms of oxygen-18 per molecule (mean of three measurements).

It may be concluded that the bond breaking in the hydrolysis of the chromato complex occurs at the Cr–O bond. The result is in accord with that of the exchange reaction, which shows that only three oxygen atoms of the chromato complex are exchangeable. As to the reaction of pentaamminecobalt(III) complexes, it has been ascertained by 18-O tracer study that As–O and C–O bond breaking occurs in the hydrolysis of arsenato- [8] and carbonato- [9] complexes and the Co–O bond is intact in the formation of nitrito complex [10] from the aqua complex. It has been also suggested that the substitution occurs at the central atom of oxoanion in the complexation of aqua complex with molybdate [11], and hydrogen-selenite [12] from the rapid complexation, because the inert cobalt(III)–oxygen bond does not need to break and the reaction is expected to proceed very rapidly. The substitution mechanism at oxoanion centers cited above is in marked contrast to that for the dimethylphosphato- [13], and oxalato- [14] systems where the substitution on cobalt(III) predominates, and hydrolysis occurs very slowly.

Effect of the Concurrent Hydrolysis on the Rate of the Oxygen Exchange of the Chromato Complex

In the procedure described above the oxygen exchange of the chromato complex is studied under the concurrence of its hydrolytic reaction. A study of the hydrolysis of the chromato complex in the same conditions as those used for the oxygen

TABLE I. The Effect of the Hydrolysis on the Rate of the Oxygen Exchange of the Chromato Complex at 25 °C.

pH	$R/10^{-7}$ M s^{-1} Measured under the concurrence of the hydrolysis	$R'/10^{-7}$ M s^{-1} Measured after the attainment of the hydrolytic equilibrium	Degree of hydrolysis (%)
6.40	19.4 ± 0.7	19.1 ± 0.5	15
7.11	4.61 ± 0.15	4.22 ± 0.24	24
7.50	2.07 ± 0.10	1.69 ± 0.14	28

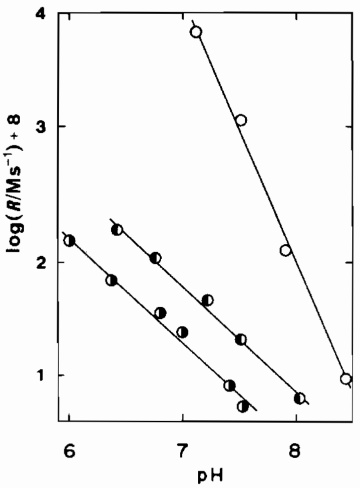

Fig. 1. A plot of log R against pH. ◑: 0 °C, [Chromato complex] = 5.0 × 10^{-3} M; ◐: 25 °C, [Chromato complex] = 4.5 × 10^{-3} M; ○: 25 °C, [Cr(VI)] = 4.5 × 10^{-3} M.

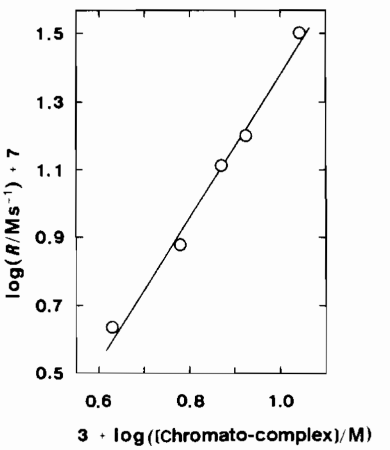

Fig. 2. The dependence of the exchange rate on [Chromato complex]. (25 °C, pH 7.2).

exchange studies (25 °C, [Chromato complex] = 4.5 × 10^{-3} M) has shown that the half-periods of the hydrolysis and the oxygen exchange reaction are 4 and 27 min at pH 6.4, 45 and 112 min at pH 7.2, and 6.1 and 14.0 h at pH 8.0, respectively*. The degree of hydrolysis at equilibrium is 15% at pH 6.4 and 38% at pH 8.0. These results suggest that the hydrolysis might affect the rate of the oxygen exchange reaction, and a slight sigmoid character has been observed on Mckay plots of the exchange reaction.

In order to estimate the effect of the hydrolytic reaction on the exchange reaction, the reaction has been studied with systems in the hydrolytic equilibrium, and the observed rates were compared with those obtained under the concurrence of the hydrolytic reaction. The chromato complex was dissolved in normal water containing an appropriate amount of sodium hydroxide, and the solution was allowed to reach the hydrolysis equilibrium at 25 °C. After the attainment of the equilibrium, which was ascertained spectrophotometrically, the exchange reaction was initiated by adding oxygen-18 water (*ca.* 5%) to the solution, and studied as described above. The addition of the oxygen-18 water did not change appreciably the hydrolysis equilibrium and other experimental conditions.

The results are shown in Table I, where R′ was calculated by using equilibrium concentrations of chromato complex, $[\text{Chromato complex}]_{eq}$. These results show that the effects of the concurrent hydrolysis on the rate of the exchange reaction is within *ca.* 22% of the total rate in our experimental condition (pH 6.0–8.0), and further studies were done with the simpler method.

Dependence of the Rate of Oxygen Exchange of the Chromato Complex on the pH and Concentration of the Complex

Figure 1 shows the plot of log R against pH at 0 °C and 25 °C. The concentration of the chromato complex is 5.0 × 10^{-3} M at 0 °C and 4.5 × 10^{-3} M at 25 °C. The slopes of the straight lines obtained by the least square fits of the data are 0.93 ± 0.06 for 0 °C and 0.94 ± 0.05 for 25 °C. The apparent activa-

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*The results of the hydrolysis reaction of pentaamminechromatocobalt(III) complex will be published in a separate paper.

TABLE II. The Effect of the Addition of Pentaammineaquacobalt(III) Ions on the Rate of Oxygen Exchange of the Chromato Complex.

pH	[Chromato complex]	[Aqua complex]	R
	10^{-3} *M*	10^{-3} *M*	10^{-6} *M* s^{-1}
6.42	4.5		1.94
6.42	4.5	8.9	0.793
7.18	7.9		1.46
7.18	7.9	7.1	0.743
7.18	8.1	13.3	0.528

tion energy of the oxygen exchange of the chromato complex at pH 7.4 is calculated to be 39.9 kJ/mol, which is considerably higher than that of the oxygen exchange of the chromate ions (25.5 kJ/mol at pH 7.4).

The pH dependence of the oxygen exchange of chromate ions in the same condition (25 ℃, [Cr(VI)] = 4.5 × 10^{-3} *M*) is also shown in Fig. 1. The oxygen exchange of the chromate ions is about 10^2 times faster than that of the chromato complex at pH 7 and about 10 times faster at pH 8. The pH dependence of the exchange rate is approximately second order for the exchange reaction of chromate ions and first order for that of the chromato complex.

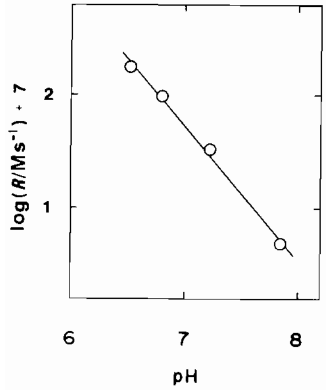

Fig. 3. The pH dependence of the exchange rate of the chromato complex in the presence of added chromate ions. (25 ℃, [Chromato complex] = [Cr(VI)] = 4.5 × 10^{-3} *M*).

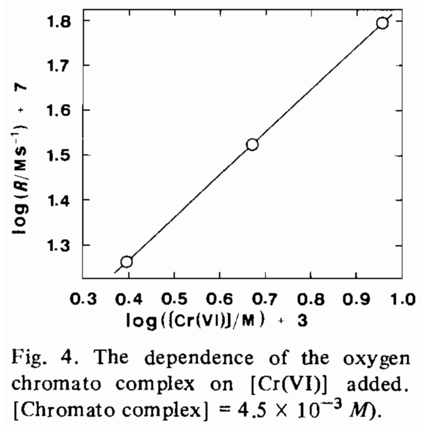

Fig. 4. The dependence of the oxygen exchange rate of chromato complex on [Cr(VI)] added. (25 ℃, pH 7.22, [Chromato complex] = 4.5 × 10^{-3} *M*).

The dependence of the exchange rate on the concentration of the chromato complex is shown in Fig. 2, and calculated to be 2.11 ± 0.07 from the slope of the curve (25 ℃, pH 7.2, [Chromato complex] = 4.28 × 10^{-3} ~ 1.103 × 10^{-2} *M*). These results may be interpreted by a mechanism:

$$[Co(NH_3)_5CrO_4]^+ + H^+ \rightleftharpoons [Co(NH_3)_5HCrO_4]^{2+}$$

$$[Co(NH_3)_5CrO_4]^+ + [Co(NH_3)_5HCrO_4]^{2+} \rightleftharpoons$$

$$[Co(NH_3)_5CrO_3 \cdot O \cdot O_3Cr(NH_3)_5Co]^{4+} + OH^- \quad (1)$$

The Effect of the Addition of Pentaammineaquacobalt(III) and Chromate Ions on the Exchange Rate of the Chromato Complex

The addition of the aqua complex retards the rate of the oxygen exchange of the chromato complex (Table II).

The addition of chromate ions, on the other hand, accelerates the rate of oxygen exchange of the chromato complex. The pH dependence of the exchange rate of the chromato complex in the presence of excess chromate ions is shown in Fig. 3 (25 ℃, [Chromato complex] = [Cr(VI)] = 4.5 × 10^{-3} *M*). The slope of the straight line is 1.20 ± 0.03. Figure 4 shows the dependence of logR on log[Cr(VI)] (25 ℃, pH 7.22, [Chromato complex] = 4.5 × 10^{-3} *M*). The concentration of the added chromate was between 2.1 × 10^{-3} and 9.0 × 10^{-3} *M*. Since, by the addition of chromate ions, the hydrolysis equilibrium is shifted to the left and the effect of hydrolysis is reduced to the minimum, $[Cr(VI)]_{added}$ may be used as the effective concentration of chromate ions. The slope of the straight line in Fig. 4 is 0.95 ± 0.00. The rate of oxygen exchange of the chromato complex in the presence of added chromate ions changes with the first power of [Cr(VI)].

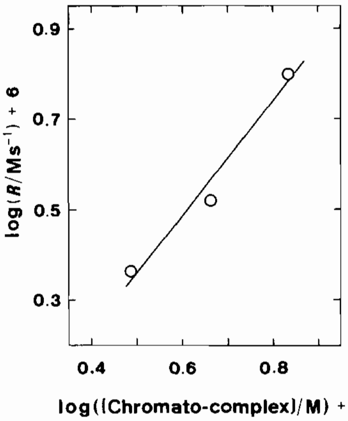

Fig. 5. The dependence of the oxygen exchange rate on [Chromato complex] in the presence of added chromate ions. (25 °C, pH 7.22, [Cr(VI)] = 4.7 × 10^{-3} *M*).

The dependence of the exchange rate at 25 °C and pH 7.22 on [Chromato complex] in the presence of the added chromate ions (4.65 × 10^{-3} *M*) is shown in Fig. 5. The concentration of the chromato complex was varied from 3.1 × 10^{-3} *M* to 6.8 × 10^{-3} *M*. (Further increase in the concentration of the chromato complex leads to the formation of the insoluble chromate of the chromato complex.) The slope of the straight line is 1.25 ± 0.20. In contrast to the exchange reaction without the added chromate, the exchange rate of the chromato complex with added chromate ions shows the nearly first-order dependence on [Chromato complex].

The above results with added chromate, the nearly first-order dependence of the exchange rate on [Chromato complex] and [Cr(VI)] may be interpreted by the reactions:

$$[Co(NH_3)_5HCrO_4]^{2+} + HCrO_4^- \rightleftharpoons [Co(NH_3)_5Cr_2O_7]^+ + H_2O \qquad (2)$$

$$[Co(NH_3)_5CrO_4]^+ + HCrO_4^- \rightleftharpoons [Co(NH_3)_5Cr_2O_7]^+ + OH^- \qquad (3)$$

and

$$[Co(NH_3)_5HCrO_4]^{2+} + CrO_4^{2-} \rightleftharpoons [Co(NH_3)_5Cr_2O_7]^+ + OH^- \qquad (3')$$

which is kinetically equivalent to reaction 3. The chromato complex exists for the most part in the form $[CoCrO_4(NH_3)_5]^+$ at pH 7.2 (pK_a = 4.44 at 25 °C). Since the order of the exchange rate with respect to the complex is slightly larger than 1, the exchange reaction occurs to some extent through the reaction,

$$[Co(NH_3)_5HCrO_4]^{2+} + [Co(NH_3)_5CrO_4]^+ \rightleftharpoons [Co(NH_3)_5CrO_3 \cdot O \cdot O_3Cr(NH_3)_5Co]^{4+} + OH^-. \qquad (1)$$

Mechanism of the Exchange Reaction

Accordingly, the oxygen exchange of the chromato complex without added chromate proceeds through reactions 1 to 3, with the equilibria,

$$[CoCrO_4(NH_3)_5]^+ + H_2O \rightleftharpoons [CoOH(NH_3)_5]^{2+} + HCrO_4^- \qquad (4)$$

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^-$$

$$[CoCrO_4(NH_3)_5]^+ + H^+ \rightleftharpoons [CoHCrO_4(NH_3)_5]^{2+}.$$

Addition of the aqua complex shifts the eequilibrium 4 to the left, and retards the exchange reaction 2 and 3.

Oxygen exchange through a series of reactions:

$$[CoCrO_4(NH_3)_5]^+ + H_2O \longrightarrow [CoOH(NH_3)_5]^{2+} + HCrO_4^-$$

$$HCrO_4^- + H_2^{18}O \rightleftharpoons HCrO_3^{18}O^- + H_2O \qquad (5)$$

$$[CoOH(NH_3)_5]^{2+} + HCrO_3^{18}O^- \xrightarrow{k_f} [CoCrO_3^{18}O(NH_3)_5]^+ + H_2O$$

may be possible especially in alkaline solutions, where the degree of hydrolysis of the chromato complex becomes appreciable. The contribution of path 5 to the total oxygen exchange rate of chromato complex with added chromate ions is estimated to be less than 5% at pH 6.5 and 7.2 by using the anation rate constant of chromate ion to aqua complex, k_f and equilibrium concentrations of chromate ion and aqua complex. The values of k_f and the equilibrium constant of hydrolysis reaction at pH 6.5 and 7.2 were obtained as 2.84 and 0.14 M^{-1} s^{-1}, and 7.6 × 10^{-5} and 2.0 × 10^{-4} *M*, respectively. Furthermore, it may be inferred that its role would be relatively unimportant in our experimental conditions, because it is incompatible with the result that the rate of the oxygen exchange reaction is retarded by the addition of the aqua complex, but accelerated in the presence of the excess chromate. It is also inconsistent with the second-order dependence of the exchange rate on the concentration of the chromato complex.

Analysis of the Exchange Rate

The rate equation may be written as:

TABLE III. The Rate Constants of the Condensation of Pentaamminechromatocobalt(III) Ions and Chromate Ions at 25 °C.

Reactions^a	Rate Constants/M^{-1} s^{-1}	Lit.
$RHCrO_4^{2+} + RCrO_4^+ \longrightarrow$	10	This work
$RHCrO_4^{2+} + HCrO_4^+ \longrightarrow$	100	This work
$RCrO_4^+ + HCrO_4^- \longrightarrow$	0.8 ± 0.1	This work
$HCrO_4^- + HCrO_4^- \longrightarrow$	5 ± 1	[3]
$HCrO_4^- + CrO_4^{2-} \longrightarrow$	10^{-3}	[3]

^{a}R; $(NH_3)_5Co$.

$$R = k_1[RHCrO_4^{2+}][RCrO_4^+] + k_2[RHCrO_4^{2+}][HCrO_4^-] + k_3[RCrO_4^+][HCrO_4^-]$$
$$= k_1[RHCrO_4^{2+}][RCrO_4^+] + (k_3 + k_2[H^+]/K')[RCrO_4^+][HCrO_4^-] \qquad (6)$$

where k_1-term corresponds to the reaction 1, k_3-term to reactions 3 and 3′, and k_2-term to the reaction, 2, and

$$K' = [RCrO_4^+][H^+]/[RHCrO_4^{2+}].$$

The concentrations of the ionic species were calculated using pK_a values of 4.44 and 6.49 for the dissociation constants of the chromato complex and hydrogen chromate ion, respectively, and log K_d = 1.53 for the dimerization constant of the hydrogenchromate ions.

The results in the presence of added chromate were chosen for the analysis, because in this case the hydrolytic equilibrium of the chromato complex is shifted considerably to the left, and the effect of the hydrolysis is reduced to the minimum.

Using eqn. 6, the data on [Cr(VI)] dependence (Fig. 4) and [Chromato complex] dependence (Fig. 5) were treated by the method of the least squares. The results obtained are $(k_3 + k_2 \cdot [H^+]/K') = 0.92 \pm 0.01\ M^{-1}\ s^{-1}$, and $k_1 = 14 \pm 1\ M^{-1}\ s^{-1}$ from the data on [Cr(VI)] dependence, and $(k_3 + k_2 \cdot [H^+]/K') = 0.70 \pm 0.21\ M^{-1}\ s^{-1}$ and $k_1 = 34 \pm 15\ M^{-1}\ s^{-1}$ from the data on [Chromato complex] dependence. The agreement of the values of the rate constants from two sets of independent experiments is satisfactory. The former set of the values is preferable, because of their smaller standard deviation values.

Rearrangement of eqn. 6 yields

$$\frac{R - k_1[RHCrO_4^{2+}][RCrO_4^+]}{[RCrO_4^+][HCrO_4^-]} = k_3 + k_2\frac{[H^+]}{K'}$$

The left-hand side of the above equation were calculated for the data on the pH-dependence (Fig. 3) using the values of the rate constants obtained above, and plotted against [H$^+$] in Fig. 6. Neglecting the plot at pH 7.84, where the effect of the hydrolysis becomes appreciable, the least-squares treatment of the data yields $k_2 = (1.3 \pm 0.2) \times 10^2\ M^{-1}\ s^{-1}$, and $k_3 = 0.78 \pm 0.08\ M^{-1}\ s^{-1}$.

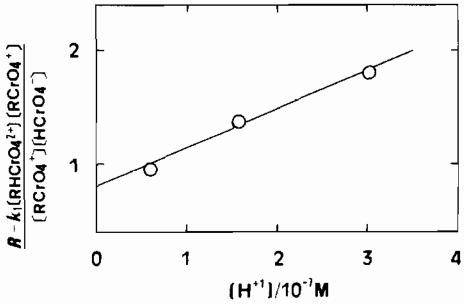

Fig. 6. A plot of $(R - k_1[RHCrO_4^{2+}][RCrO_4^+])/[RCrO_4^+]$-$[HCrO_4^-]$ against [H$^+$].

The results are summarized in Table III, together with the corresponding rate constants of the dimerization of chromate [3]. As shown in the table, the rate constants of the condensation reaction of $HCrO_4^-$ with $(NH_3)_5CoCrO_4^+$ and $HCrO_4^-$ are 0.8 and 5 M^{-1} s^{-1}, respectively. The effect of replacement of $(NH_3)_5Co$·group for H of the chromate ions on the rate of their condensation reaction cannot be estimated from the table, because the replacement changes the charge type of the reaction. Apparently the replacement exerts a retarding effect on the rate of condensation reactions. This trend may be interpreted by the fact that vibrational frequencies of the Cr–O bond increase on coordination of CrO_4^{2-} to cobalt to form the Co–O–Cr bond [6].

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