*The Reaction of the Aquopentamminechromium(III) Complex Ion in Aqueous Solution. I. Substitution Reaction of a Coordinated Water with a Chloride Ion**

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Garrick[1] and Adell[2] have investigated a substitution reaction of aquopentamminecobalt(III) ion in which a coordinated water molecule of the complex ion is replaced by a chloride ion[3]. They have reported that the reaction is of first order with respect to the complex ion and the chloride ion respectively, and that the reaction rate decreases markedly as ionic strength increases.

A similar substitution reaction occurs in the case of aquopentamminechromium (III) ion as well. On addition of hydrochloric acid to the aqueous solution of an aquopentamminechromium (III) complex salt, red crystals precipitate slowly. The

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* Presented at the Symposium on Coordination Compounds, held at Nagoya, November, 1957.

[1] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 486 (1937).

[2] B. Adell, *Z. anorg. u. allgem. Chem.*, **246**, 303 (1941).

[3] In Ref. 6b, the reaction of this type was called "anation reaction". This word will be used in this paper for convenience.

absorption spectrum of a solution of the crystallines is identical with that of chloropentamminechromium(III) complex ion. The fact shows that the following substitution reaction occurs in the solution containing aquopentamminechromium(III) complex ion and chloride ion.

$$[Cr(NH_3)_5OH_2]^{3+} + Cl^- \rightarrow [Cr(NH_3)_5Cl]^{2+} + H_2O \qquad (1)$$

Since aquopentamminechromium (III) complex ion is very similar to that of cobalt(III) in steric configuration, ionic size and charge, but different only in electronic configuration of the central metal ion, it is interesting to investigate whether this difference in electronic configuration may appear in the reactions of these two metal-ammine-complexes.

This paper presents a study of the substitution reaction in which a coordinated water molecule of aquopentamminechromium(III) complex ion is replaced by a chloride ion in aqueous solution. Furthermore, the influence of ionic strength on the aquation of chloropentamminechromium(III) complex ion is also reported.

Experimental

Materials. — Aquopentamminechromium (III) perchlorate was prepared by the method of Linhard et al.[4] and was purified by recrystallization from perchloric acid solution twice and then from warm water once.

Chloropentamminechromium(III) chloride was prepared according to the direction of Biltz[5]. The chloride was converted by treatment with perchloric acid into perchlorate, and the latter was purified twice by reprecipitation from cold perchloric acid solution.

Sodium chloride of reagent grade was used without further purification. Sodium perchlorate was prepared by neutralizing sodium hydroxide with perchloric acid both of which were of reagent grade. Absorbancies for solutions of sodium chloride and sodium perchlorate were both so small that they could be neglected practically. Their magnitudes for the solutions of unit molarity at 44000 cm^{-1}, where all rate measurements were carried out, were 0.015 and 0.020, respectively against water.

Measurements.—Experimental solutions were prepared as follows. The solution of aquo-complex salt ($10^{-3} \sim 10^{-2}$ M) which was acidified with perchloric acid was placed in a stoppered and brown-colored flask. The solution of sodium chloride ($10^{-2} \sim 1$ M) whose ionic strength was adjusted with sodium perchlorate was prepared. These two solutions were kept at a constant temperature in a thermostat, and were mixed together quickly; then at intervals of a few minutes, the amount of chloropentamminechromium(III) ion formed was determined spectrophotometrically.

The measurement of absorbancy was made with a Beckman Model DU photoelectric spectrophotometer using stoppered 10 mm. quartz cells. The temperature of the cell compartment was kept constant within ±0.1°C by circulating thermostated water.

The aqueous solution of aquopentamminechromium(III) perchlorate which was acidified with perchloric acid did not change so fast as its neutral solution. When the pH of the solution was lower than approximately 4, no changes in absorbancy nor pH were observed during the course of measurements.

The aquation rate of chloropentamminechromium(III) ion was followed also spectrophotometrically. After dissolving chloropentamminechromium(III) perchlorate in a solution containing appropriate amounts of perchloric acid and sodium perchlorate at an experimental temperature, the change in absorbancy at 44000 cm^{-1} was followed with a thermostated spectrophotometer.

Results

Apparent Molar Extinction Coefficients of Complex Cations. — In order to determine the rate of the formation of chloropentamminechromium(III) complex ion by the measurements of a change in ultraviolet absorption, the correct molar extinction coefficients of complex ions under the reacting condition must be known. Table I shows the temperature dependence of molar extinction coefficients of chloro and aquopentamminechromium (III) ions at 44000 cm^{-1} in aqueous solution containing no chloride ion. These molar extinction coefficients were more or less greater when chloride ion was added.

Fig. 1 shows the variations of molar extinction coefficients of chloro and aquopentamminechromium(III) ions with respect to chloride ion concentration. This increase in extinction coefficients caused with chloride ion may be attributed

TABLE I. MOLAR EXTINCTION COEFFICIENTS OF COMPLEX IONS $\tilde{\nu} = 44000$ cm^{-1}

Temp., °C	$[Cr(NH_3)_5OH_2]^{3+}$	$[Cr(NH_3)_5Cl]^{2+}$
26		1213
30	21.3	
35	22.2	1236
40	23.3	
45	25.1	1281
50	27.6	
53		1314

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[4] M. Linhard and W. Berthold, *Z. anorg. u. allgem. Chem.*, **276**, 173 (1955).

[5] H. Biltz and W. Biltz, "Laboratory Methods of Inorganic Chemistry", translated by W. T. Hall et al., 2nd Ed., John Wiley & Sons, Inc, New York (1928), p. 185.

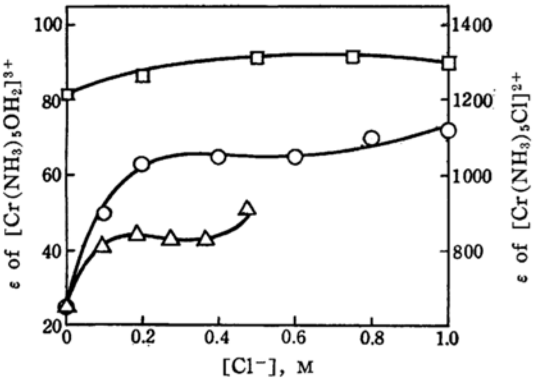

Fig. 1. The change in molar extinction coefficients of complex ions at 44000 cm^{-1} with the chloride ion concentration:
□, $[Cr(NH_3)_5Cl]^{2+}$ (20∼23°C);
○, $[Cr(NH_3)_5OH_2]^{3+}$ (45°C);
△, $[Cr(NH_3)_5OH_2]^{3+}$ (45°C, at constant ionic strength).

to the formation of outer sphere association complexes[6] between complex cations and chloride ion. Furthermore, since the formation of the association complex generally depends on the ionic strength of solution[7], the apparent extinction coefficient of a complex ion varies on addition of sodium perchlorate[8] to the solution containing chloride and complex ions. Extinction coefficients of complex ions under various conditions were obtained by extrapolating the absorbancies with regard to the time zero. On the estimation of the molar extinction coefficient of chloropentamminechromium(III) ion under reacting conditions, the small effect of ionic strength mentioned above was neglected. The magnitudes were determined from the data of Table I and Fig. 1, assuming that the temperature dependence of extinction coefficient of outer sphere association complex was similar to that of free complex ion.

The solution of chloropentamminechromium(III) ion obeys the Beer's law strictly where no chloride ion exists, and also satisfies it fairly well even in chloride solution.

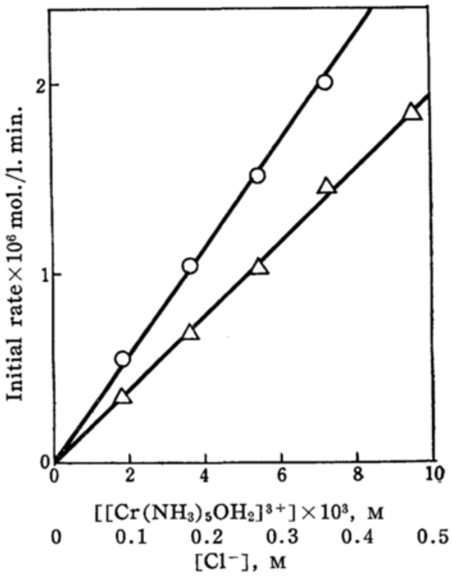

Fig. 2. The first order tests with each of two reactants at 45°C:
○, $[Cr(NH_3)_5OH_2]^{3+}$; △, Cl^-.

The Rate of Formation of Chloropentamminechromium(III) Ion. — It is shown in Fig. 2 that the initial rates of the formation of chloropentamminechromium(III) ion in the solution of the constant ionic strength are proportional to the concentrations of aquo-complex cation and chloride ion, respectively. Accordingly the rate constants of the anation reaction 1 were calculated by the usual method based on Eq. 2, being regarded as a second order reaction. To obtain more correct values of the anation rate, a reverse reaction, that is, an aquation of chloropentammine-complex ion, was taken into account according to the method of Garrick[1].

$$\frac{d[[Cr(NH_3)_5Cl]^{2+}]}{dt} = \overrightarrow{k}_2[[Cr(NH_3)_5OH_2]^{3+}][Cl^-] \qquad (2)$$

As is shown in Table II, the reaction

TABLE II. TEST FOR THE EFFECT OF HYDROGENE ION ON THE RATE OF ANATION REACTION OF $[Cr(NH_3)_5OH_2]^{3+}$ WITH Cl^- AT 45°C

$[HClO_4]$, mol./l.	Ionic strength, ω	$\overrightarrow{k}_2 \times 10^3$, l./mol. min.
0	0.510	1.55
0.49*	0.500	1.48
0.095	0.625	1.27
0.009	0.630	1.26
0.001	0.631	1.31

* HCl was used.

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[6] a. M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).
b. Many other works are summarized and surveyed in the following book: F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", John Wiley & Sons, Inc., New York (1958), p. 376.

[7] a. F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **78**, 15 (1956).
b. T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 552 (1954).

[8] Perchlorate ion itself is considered to have hardly any ability of association.

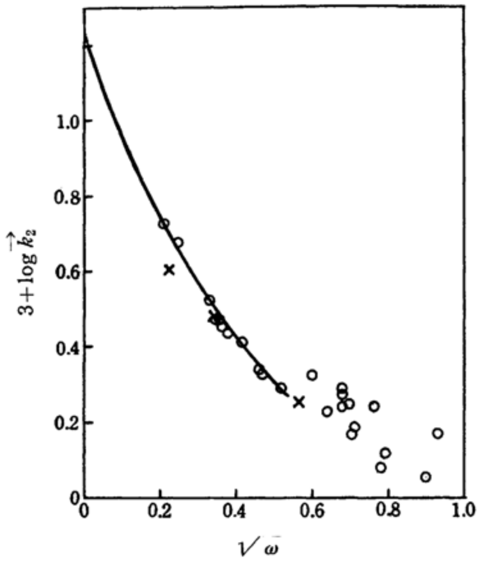

Fig. 3. Influence of ionic strength on the rate of anation:
○, $[Cr(NH_3)_5OH_2]^{3+}$—Cl^- at 45°C;
×, $[Co(NH_3)_5OH_2]^{3+}$—Cl^- 1) at 25°C, rate scale is for $4+\log\overrightarrow{k}_2$. The curve represents Eq. 3.

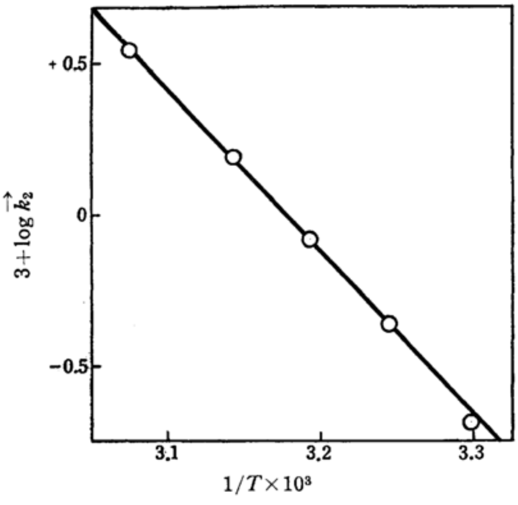

Fig. 4. Arrhenius plot of the anation reaction of $[Cr(NH_3)_5OH_2]^{3+}$ with Cl^- ($\omega=0.52\pm0.01$).

rates are independent of hydrogen ion concentrations so far as the solutions are acidic.

The reaction rate decreases remarkably with increasing ionic strength of solution. The influence is particularly significant in the lower ionic strength region. In Fig. 3, logarithms of rate constants measured at 45°C are plotted against the square root of the ionic strengths in molarity scale, which are calculated from the initial composition of solutions. Observed rates fluctuate markedly in a higher ionic strength region, whereas below a $\sqrt{\omega}$ of about 0.4, experimental results show a good regularity that can be reproduced by Eq. 3. The rate constant at infinite dilution at 45°C was evaluated to be 1.7×10^{-2} l. mol^{-1} min^{-1}.

$$\log\overrightarrow{k}_2=-1.77-\frac{3.09\sqrt{\omega}}{1+1.36\sqrt{\omega}} \qquad (3)$$

The results obtained at 30, 35, 40, 45 and 52°C ($\omega=0.52\pm0.01$) give a good Arrhenius plot (see Fig. 4), leading to the value of 24.6 kcal. mol^{-1} for the experimental activation energy, and 1.2×10^{14} l. mol^{-1} min^{-1} for the frequency factor.

Aquation of Chloropentamminechromium (III) Ion.—In order to obtain more correct rate constants of anation reaction 1 it is necessary to take the rate of the aquation[9] into account. Accordingly we were obliged to determine the rate of aquation of chloropentamminechromium(III) ion under various conditions. The results obtained are summarized in Table III.

The influence of ionic strength on the aquation is quite different from that on the anation reaction. In lower ionic strength region, the reaction rate rather increases with increasing ionic strength; then the rate decreases gradually and the gradient of the relation is steepest about $\omega=0.4$, and after that the decrease in rate becomes gradual again. It was observed that the aquation rate was independent of perchloric acid concentration from

TABLE III. RATE CONSTANTS OF AQUATION REACTION OF $[Cr(NH_3)_5Cl]^{2+}$

Temp., °C	$[HClO_4]$, mol./l.	Ionic strength, ω	$\overleftarrow{k}_A\times10^3$, min^{-1}
25			0.58*
26.2	0.00086	0.002	0.589
26.2	0.086	0.087	0.598
35	0.00086	0.002	1.91
35	0.0086	0.009	1.94
35			1.9*
45	0.00086	0.002	5.41
45	0.00082	0.089	5.45
45	0.001	0.263	5.32
45	0.001	0.502	4.67
45	0.00086	0.912	4.31
53.2	0.001	0.002	14.3

* Taken from Ref. 9.

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9) Freundlich et al. had studied this aquation, but their data were not sufficient to use for this purpose; H. Freundlich and H. Pape, *Z. physik. Chem.*, **86**, 458 (1914).

10^{-4} M to 10^{-1} M. The experimental activation energy and the frequency factor calculated from the temperature dependence of aquation rate were 22.8 kcal. mol^{-1} and 2.6×10^{13} min^{-1}, respectively. When the transmission coefficient is assumed to be unity, the activation entropy is calculated as -7 e. u.

Discussion

It is shown in Fig. 1 that the absorbancy of aquopentamminechromium(III) ion changes markedly with the concentration of chloride ion. The formation of outer sphere association complex, $[Cr(NH_3)_5 \cdot OH_2]^{3+} \cdot Cl^-$, ought to be thought for the reason of this absorbancy change, as was indicated by Linhard⁶⁾ in the case of hexamminechromium(III) ion and chloride ion.

The anation reaction 1 is experimentally shown to be of second order and the rate constant varies with the ionic strength of solution as is reproduced by the Brönsted-Bjerrum-Christiansen type Eq. 3^6b)^, which is the kinetic equivalent of the Debye-Hückel equation. The slope of the line in Fig. 3 is -3.09 at infinite dilution. This value is in good agreement with what is expected from a term $2Az_+z_-$ 10) in the Debye-Hückel equation. But it can not be concluded that the anation is a bimolecular reaction. Because these results may also be explained by the following unimolecular path through the outer sphere association complex.

$$[Cr(NH_3)_5OH_2]^{3+} + Cl^- \rightarrow [Cr(NH_3)_5OH_2]^{3+} \cdot Cl^- \quad \text{(fast)}$$

$$[Cr(NH_3)_5OH_2]^{3+} \cdot Cl^- \rightarrow [Cr(NH_3)_5Cl]^{2+} + H_2O \quad \text{(slow)}$$

The formation constant of the outer sphere association complex is about 10^2 under these experimental conditions11), therefore, a considerable amount of association complex exists in solution. If the reaction proceeds through such an outer sphere association complex, the rate-determining step is not the process of bimolecular association, but the following unimolecular process in which central chromium(III) ion releases a coordinated water molecule.

It is noteworthy that the reaction rate varies regularly according to the Debye-Hückel equation in spite of the considerable formation of the association complex. Moreover, its formation is also found to vary roughly according to the Debye-Hückel equation11). These facts indicate that the path through a simple five coordinated intermediate is less probable. In other words, the outer sphere association complex releases its coordinated water molecule more easily than the free complex ion. In the water exchange of hexaquochromium(III) complex ion, Plane et al.12) have found that various anions speed up the reaction. The fact is also explicable by assuming a higher lability of outer sphere association complex. On the other hand, the results of anation reaction for cobalt(III) complex ion obtained by Garrick1) seem rather extraordinary from the viewpoint of a gradual slope as is shown in Fig. 3, which is about -1. This gradualness may be explained by assuming an inert association complex and the contribution of another path which has a simple five coordinated intermediate13) in this case.

The effect of ionic environment on the aquation of chloropentamminechromium (III) ion is quite different from that on the anation reaction. The Brönsted-Bjerrum equation predicts a linear dependence of $\log \overleftarrow{k}_A$ ($\overleftarrow{k}_A$ is the rate constant of aquation) upon ionic strength ω14) when the Hückel's empirical term is taken into account in the expression of activity coefficients. Though only sodium perchlorate and perchloric acid were used to adjust ionic strength, the dependence was not linear even in the lower ionic strength region. It seems that perchlorate ion may also have some specific effects on the aquation.

Summary

The substitution reaction of aquopentamminechromium(III) ion in which a coordinated water molecule is replaced by a chloride ion was investigated spec-

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10) A denotes 0.4343 $e^3(2\pi N)^{1/2}/(10\varepsilon kT)^{3/2}$, and approximately equals 0.53 for aqueous solution at 45°C, z_+ and z_- are the ionic charges of reactants.

11) Result presented by the present author at the Symposium on Coordination Compounds, held in Tokyo, November, 1958. The details will appear elsewhere.

12) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952); J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954).

13) F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

14) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes", McGraw-Hill Book Co., New York (1941), p. 441.

trophotometrically. The reaction proceeds according to the second order rate law, $d[[Cr(NH_3)_5Cl]^{2+}]/dt=\overrightarrow{k_2}[[Cr(NH_3)_5OH_2]^{3+}]\cdot[Cl^-]$, and the rate constant varies regularly with the ionic strength of solution according to the Debye-Hückel type equation. The formation of outer sphere association complex in the solution was detected from the change in ultraviolet absorption. From these results the rate-determining process of this reaction was inferred to be a unimolecular process through the outer sphere association complex. The experimental activation energy and the frequency factor of this reaction were determined to be 24.6 kcal. mol^{-1} and 1.2×10^{14} l. mol^{-1} min^{-1} ($\omega\sim0.52$), respectively.

The aquation of chloropentamminechromium(III) ion was also studied in the solutions of various ionic strengths and the reaction rate was found to vary to some extent with ionic environment.

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