the absorption maxima from *trans* to *cis* isomer were only a few millimicrons; these shifts are in accord with the very small one found in the absorption maximum of the isomeric forms of $RuCl_2^+$.[21]

A word is in order regarding the assignment of formulas to the species designated as $RhCl_4^-$ and $RhCl_5^{2-}$. There is no question from the ion exchange experiments that the species given these formulations are anionic in character, and the absorption spectra (see Experimental) definitely eliminate the possibility that either is the $RhCl_6^{3-}$ complex. Both the order of elution and the positions of the absorption maxima argue for our assignment. On the basis that an anion of charge −1 would be held less tightly than one of −2 charge, the species coming off the anion resin column first was given the formula $RhCl_4^-$. Moreover, the assignment is consistent with the fact that the absorption maxima for this species occur at shorter wave lengths than do those of the second species off the column, to which the formula $RhCl_5^{2-}$ was given.

It should be mentioned that these two anionic complexes differ in spectra from those to which Kristjanson and Lederer[20] gave the same formulas. These investigators isolated their complexes by boiling a solution of rhodium(III) hydroxide in 6 *M* hydrochloric acid, passing the solution through a Dowex 2 (anion) resin, and eluting with hydrochloric acid. The "$RhCl_4^-$" species was reported to move with the eluting solvent as a yellow band and the "$RhCl_5^{2-}$" complex was described as being present on the resin as a very fast-moving orange-tan band. The spectra for these complexes reported by Kristjanson and Lederer correspond roughly to those attributed by us to $RhCl_2^+$ and $RhCl_3$. It is conceivable that the former workers failed to wash their resin column with water to remove positively charged and neutral species prior to elution with hydrochloric acid.

The various rhodium(III)–chloride species isolated in the investigation herein reported would appear to correspond to those separated by Lederer[26,27] in his study of the same system by paper chromatography, paper electrophoresis, and paper ion exchange chromatography. In his work, assignment of charge was based on comparisons of migration rates with those of similar ions of known charge.

The best values of formation constants were obtained for k_4, k_5, and k_6 (Table III). The few values which were determined for k_1, k_2, and k_3 would indicate that these constants are all of the same order of magnitude, 10^3, although it is probable that this value is a lower limit for k_1 and k_2. In many instances no values could be obtained for k_1, k_2, and k_3 because the calculated bound chloride concentrations were evaluated to be slightly greater than the total chloride concentrations. Frequently, the concentrations of a given chloro-complex came out to have negative values, which precluded calculation of meaningful formation constants.

Acknowledgment.—The generous advice of Drs. Robert E. Connick and Howard H. Cady on the application of the ion exchange technique to the system reported in this investigation is gratefully acknowledged. Special thanks are due to Paul Coulter for his invaluable assistance in writing the computer program used for the determination of the formation constants. W. C. W. acknowledges his indebtedness to the National Science Foundation for Coöperative Graduate Fellowships held during the period 1959–1962. The aid from the Petroleum Research Fund, administered by the American Chemical Society, for the purchase of a Cary Model 14 spectrophotometer also is greatly appreciated.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINNESOTA

Rate Constants for the Formation and Aquation of *cis*- and *trans*-$CrCl_2^{+}$[1]

BY HOWARD B. JOHNSON AND WARREN L. REYNOLDS

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The pseudo first order rate constants for the reactions *trans*-$CrCl_2^+ = CrCl^{+2} + Cl^-$ (1) and *cis*-$CrCl_2^+ = CrCl^{+2} + Cl^-$ (2) were determined at 25.0° in 1.0 *M* hydrochloric acid solutions and found to be 8.23×10^{-5} sec.$^{-1}$ and 4.25×10^{-5} sec.$^{-1}$, respectively. The activation energy for reaction 1 is 26.5 kcal./mole. Extinction coefficients for *trans*-$CrCl_2^+$, *cis*-$CrCl_2^+$, and $CrCl^{+2}$ in 1 *M* hydrochloric acid were determined at 450 and 635 mμ. In the presence of Cr^{+2} reaction 2 was observed to be very fast.

The rate of conversion of $CrCl_2^+$ to $CrCl^{+2}$ and Cl^- has been studied by a number of investigators[2-6] employing different methods. Recently, the *cis*- and *trans*-$CrCl_2^+$ isomers were separated and their spectra published.[7] It was shown that only the *trans*-$CrCl_2^+$

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[1] This is taken from a thesis presented by Howard B. Johnson to the Department of Chemistry of the University of Minnesota in partial fulfillment of the requirements for the M.S. degree.

[2] (a) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); (b) J. Olie, Jr., *Z. anorg. allgem. Chem.*, **51**, 29 (1906).

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species was produced when dark green chromium(III) chloride was dissolved in aqueous solutions. Since this salt was used to furnish the $CrCl_2^+$ ion the previous investigators studied the *trans*-$CrCl_2^+$ conversion to $CrCl^{+2}$ and Cl^- and the corresponding *cis*-$CrCl_2^+$ reaction has not been studied. In the work reported here the two reactions were studied in the same media so that rate constants could be compared.

The literature[7,8] values of the equilibrium constants for reactions 1 and 2 were checked. The rate constants

$$CrCl^{+2} + Cl^- \underset{k_{d,t}}{\overset{k_{a,t}}{\rightleftharpoons}} trans\text{-}CrCl_2^+;\ K_t \qquad (1)$$

$$CrCl^{+2} + Cl^- \underset{k_{d,c}}{\overset{k_{a,c}}{\rightleftharpoons}} cis\text{-}CrCl_2^+;\ K_c \qquad (2)$$

for formation of *cis*- and *trans*-$CrCl_2^+$ by the forward reactions in 1 and 2 were calculated from the appropriate equilibrium constants and rate constants for the reverse reactions.

During the investigation, it was found that the *trans* → *cis* isomerization occurred too rapidly at high Cl^- concentrations for isomerization to occur solely by reactions 1 and 2. Studies[9] of absorption spectra of chloroaquochromium(III) species in 12 M HCl have led to the conclusion that a species, probably $CrCl_3$, was present in these solutions. In the present work the

$$trans\text{-}CrCl_2^+ + Cl^- \underset{k_{3,t}}{\overset{k_{t,3}}{\rightleftharpoons}} CrCl_3;\ K_{3t} \qquad (3)$$

$$cis\text{-}CrCl_2^+ + Cl^- \underset{k_{3,c}}{\overset{k_{c,3}}{\rightleftharpoons}} CrCl_3;\ K_{3c} \qquad (4)$$

absorption spectra studies have been extended to include smaller HCl concentrations. As a result reactions 3 and 4 have been postulated as contributing to isomerization. It was not possible to make more definitive rate studies, by the methods used, to support or reject the proposed mechanism. The $CrCl_3$, which seems to be present at the high Cl^- concentrations necessary to study the isomerization reaction, rapidly formed $CrCl_2^+$ (mainly the *cis* isomer) when the reaction mixture was diluted in placing the *cis* and *trans* isomers on the exchange column and hence gave false determinations for the *cis* and *trans* concentrations in the reaction mixture.

Since Cr^{+2} has been observed[10,11] to catalyze the conversion of *trans*-$CrCl_2^+$ to $CrCl^{+2}$ and Cl^- the catalytic effect of Cr^{+2} on *cis*-$CrCl_2^+$ also was studied briefly.

Experimental

Reagents.—All solutions used in the work were prepared using reagent grade chemicals and de-ionized water. The Dowex-50-X12 resin (20–50 mesh) was treated as described by Hougen, Schug, and King.[12] Solutions of chromium(II) perchlorate were prepared by the method of Lingane and Pecsok.[13] Solutions of *trans*-$CrCl_2^+$ were prepared by dissolving recrystallized $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$.[8]

Solutions containing only *cis*-$CrCl_2^+$ were prepared by dissolving $[CrCl_3(H_2O)_3]$[14] in 0.001 M HCl and passing the solution through a Dowex-50-X12 column. Because the *cis*-$CrCl_2^+$ is not as easily eluted as the *trans*-$CrCl_2^+$, the later fractions[7] of eluent contained only *cis*-$CrCl_2^+$. A solution of 0.08 M HCl was used to separate the *trans*-$CrCl_2^+$ from the *cis*-$CrCl_2^+$.

Solutions of $CrCl^{+2}$ were prepared by passing *trans*-$CrCl_2^+$ solutions pre-aged 24 hr. through a Dowex-50-X12 column to separate the +2 species from the +1 and the +3 species.

Standard solutions of $AgNO_3$ and KSCN were used for the determination of Cl^-.

Analyses.—The Cl^- concentration was determined by the Volhard method and the chromium(III) concentration was determined iodometrically.

The concentrations of *cis*- and *trans*-$CrCl_2^+$ in a solution of $CrCl_2^+$ were calculated from the absorbances at 450 and 635 mμ employing the measured molar extinction coefficients. The extinction coefficients reported by King, Woods, and Gates[7] were used for $HClO_4$ solutions and the extinction coefficients reported here were used for 1 M HCl solutions.

Apparatus.—A Beckman DU spectrophotometer, with thermostated cell compartment, and a Bausch and Lomb Model 505 recording spectrophotometer were employed to measure absorbances. A 60-cm. ion-exchange column was used to separate the Cr^{+3}, $CrCl^{+2}$, and $CrCl_2^+$ species.

The following apparatus was used in the study of reactions involving Cr^{+2} ion. The reaction flask was a three-necked round-bottom flask of 125 ml. capacity. Purified H_2 or N_2 was released near the bottom of the reaction flask through a bubbler inserted in one neck of the flask. A Cr^{+2} solution of known concentration was kept in a reduced state in a separatory funnel containing amalgamated mossy zinc. A known volume of Cr^{+2} solution could be added to the reaction flask by means of a 1-ml. graduated buret sealed to the stem of the separatory funnel and passing through a stopper in a second neck of the flask. The third neck of the flask was connected to a water bubbler which kept the pressure inside the apparatus above atmospheric pressure.

Determination of the Formation Constants of *cis*- and *trans*-$CrCl_2^+$ and of the *cis–trans* Equilibrium Constant.—One-molar solutions of *trans*-$CrCl_2^+$ were made by dissolving the correct weight of $[Cr(H_2O)_4Cl_2]Cl\cdot 2H_2O$. Solutions containing equilibrium concentrations of *cis*- and *trans*-$CrCl_2^+$, $CrCl^{+2}$, and Cl^- were produced by allowing 1 M *trans*-$CrCl_2^+$ solution, containing 0.1 M $HClO_4$ and saturated with NaCl, to stand for 3 to 4 days. The *cis*- and *trans*-$CrCl_2^+$ concentrations were determined as described under Analyses after separation from $CrCl^{+2}$, Cl^-, and any Cr^{+3} present by ion exchange.

To reduce dissociation of the $CrCl_2^+$ species on the column, the time required for elution of the $CrCl_2^+$ species was reduced considerably by increasing the $HClO_4$ concentration of the eluent from 0.1 to 0.4 M. Also, the eluent was analyzed for *cis*- and *trans*-$CrCl_2^+$ in fractions as rapidly as it came from the column. Thus the initially collected portions of eluent did not have to wait while dissociation of $CrCl_2^+$ occurred before the final portions of the eluent could be collected and the whole eluent analyzed for *cis*- and *trans*-$CrCl_2^+$ contents. The absorption spectrum of the eluent indicated that complete separation of the $CrCl_2^+$ species from the more highly charged $CrCl^{+2}$ and Cr^{+3} species was achieved with 0.4 M $HClO_4$.

The equilibrium constants for reaction 1 and 2 were calculated from the known concentrations of $CrCl^{+2}$ and Cl^- and from the concentrations found for *cis*- and *trans*-$CrCl_2^+$ in the equilibrium mixture. The equilibrium constant, K(t/c), for *cis–trans* isomerization was calculated from the measured concentrations of the *cis* and *trans* isomers.

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The errors in the *cis*- and *trans*-$CrCl_2^+$ concentrations are rather large because an error of 0.001 in the absorbance readings at 450 and 635 mμ results in considerable error in the concentrations of the two species.

Determination of Extinction Coefficients in 1.0 *M* Hydrochloric Acid.—Solutions of *trans*-$CrCl_2^+$, *cis*-$CrCl_2^+$, and $CrCl^{+2}$ were prepared in 1.0 *M* HCl and the absorbances of the solutions measured. The concentration of the chromium species was determined iodometrically.

Determination of the Uncatalyzed Rate of Aquation of *trans*- and *cis*-$CrCl_2^+$.—The rate of the reverse reaction in (1) was measured by determining the concentrations of *trans*-$CrCl_2^+$ and $CrCl^{+2}$ in the *trans*-$CrCl_2^+$ and $CrCl^{+2}$ mixtures at various times with the Beckman DU spectrophotometer. The initial concentration of *trans*-$CrCl_2^+$ was approximately 0.02 *M* and the HCl concentration was 1.0 *M*. The reference cell contained the reaction medium minus the Cr(III). The rate of the reverse reaction in (2) was determined in an analogous manner. The initial *cis*-$CrCl_2^+$ concentration was varied between 0.005 and 0.02 *M*.

The Conversion of $CrCl_3$ to $CrCl_2^+$.—Solutions of $CrCl_3$ were prepared by dissolving $[Cr(H_2O)_4Cl_2]Cl$ in 12.0 *M* HCl as reported by Elving and Zemel[9] or by dissolving $[CrCl_3(H_2O)_3]$ salt. The $CrCl_3$ solutions in 12 *M* HCl were diluted with water to several different concentrations and the spectrum scanned repeatedly. The approach to equilibrium could be observed as the spectra changed with time.

The Aquation of *cis*- and *trans*-$CrCl_2^+$ in the Presence of Cr^{+2} Ion.—A solution of either *cis*- or *trans*-$CrCl_2^+$ was prepared and half of the solution was placed in the reactor used for reactions involving Cr^{+2} ion. Purified H_2 or N_2 then was bubbled through the solution for 20 min. or more before Cr^{+2} was added. After a specified length of time, H_2O_2 was added to oxidize the Cr^{+2}(aq) to Cr(III). The spectrum of the reaction mixture was compared with the spectrum of the solution to which Cr^{+2} had not been added. The species in the solutions were identified from the spectra.

Results and Discussion

Extinction Coefficients.—Extinction coefficients were determined for *trans*-$CrCl_2^+$, *cis*-$CrCl_2^+$, and $CrCl^{+2}$ in 1.0 *M* HCl at wave lengths at 450 and 635 mμ, the wave lengths for absorption maxima of both *cis*- and *trans*-$CrCl_2^+$. The molar extinction coefficient, ε, of each species was independent of Cr(III) concentration over the range from 3×10^{-3} to 3×10^{-2} *M*. The extinction coefficients and the number of determinations, *n*, are listed in Table I.

TABLE I

EXTINCTION COEFFICIENTS FOR *trans*- AND *cis*-$CrCl_2^+$ AND $CrCl^{+2}$

25.0 ± 0.1°, 1.0 *M* HCl

	ε (M^{-1} cm.$^{-1}$)		
Cr(III) species	450 mμ	635 mμ	*n*
trans-$CrCl_2^+$	22.0 ± 0.5	24.1 ± 0.5	4
cis-$CrCl_2^+$	25.7 ± 1.4	18.0 ± 1.2	8
$CrCl^{+2}$	15.8 ± 0.4	13.3 ± 0.3	4

The extinction coefficients of *trans*-$CrCl_2^+$ in 1 *M* HCl are the same as reported earlier[7] for *trans*-$CrCl_2^+$ in $HClO_4$. The extinction coefficients for *cis*-$CrCl_2^+$ and $CrCl^{+2}$ in 1 *M* HCl were about 10% lower than those reported[7,9] in perchloric acid solutions. These differences can be attributed to medium effects or there is a possibility that a small percentage of $CrCl_3$ may cause the difference in the case of *cis*-$CrCl_2^+$.

Formation Constants for *cis*- and *trans*-$CrCl_2^+$.—The data from which the equilibrium constants of (1) and (2) were calculated are given in Table II. Values for K_2, the second formation constant of $CrCl_2^+$, are given in column 3 of Table II. The average value of K_2 was $(3.4 \pm 0.5) \times 10^{-2}$ M^{-1}. All errors reported in this work are standard deviations. This value for K_2 is in good agreement with that (0.030) reported by Gates and King[8] for $(Cl^-) \cong 4.2$ *M*. The values for the *cis–trans* equilibrium constant, *K*(t/c), are given in column 4; the average value of 0.48 ± 0.04 agrees with the value 0.5 ± 0.2 reported by King, Woods, and Gates[7] for $\mu \sim 4$ at 30–95°.

Values of K_t and K_c, the second stepwise formation constants of *trans*- and *cis*-$CrCl_2^+$, are given in the last two columns; their average values were (1.1 ± 0.1) $\times 10^{-2}$ and (2.3 ± 0.4) $\times 10^{-2}$ M^{-1}, respectively.

The reported equilibrium constants neglect any $CrCl_3$ contribution. The $CrCl_3$ species dissociates rapidly to predominantly *cis*-$CrCl_2^+$ when the Cl^- concentration is reduced as it was when the solution was analyzed using ion-exchange methods. This could cause errors in the reported equilibrium constants.

The formation constants for $CrCl_3$ are not known and are very difficult to determine accurately. Serious attempts to estimate K_{3c} from the change of spectrum with change of Cl^- concentration yielded 0.2 M^{-1} as a very conservative estimate of the upper limit for K_{3c}, which is a factor of 30 greater than that assumed by Gates and King.[8] If the upper limit used by Gates and King is correct, the presence of $CrCl_3$ will not significantly affect results, but if the value of K_{3c} is greater than this, the reported values will have to be modified in the future.

It has been stated[7] that dissociation of $CrCl_2^+$ on the column is slow. The results obtained by us support this statement since the total $CrCl_2^+$ concentration did not seem to decrease significantly with length of time on the column. Furthermore, the ratio of *trans* to *cis* isomers did not change within experimental error with length of time on the column. When pure *trans*-$CrCl_2^+$ solutions were passed into the column only

TABLE II

SECOND FORMATION CONSTANTS OF *cis*- AND *trans*-$CrCl_2^+$

Room temperature, 1.0 *M* Cr(III), 5.4 *M* Cl^-, 0.1 *M* $HClO_4$, $\mu = 7$

10^2[*cis*-$CrCl_2^+$], *M*	10^2[*trans*-$CrCl_2^+$], *M*	10^2K_2, M^{-1}	*K*(t/c)	10^2K_1, M^{-1}	10^2K_c, M^{-1}
8.5	4.0	2.6	0.47	0.85	1.8
10.3	5.5	3.5	.53	1.2	2.3
10.2	5.0	3.3	.49	1.1	2.2
10.7	4.8	3.4	.45	1.1	2.3
12.5	5.5	4.1	.44	1.2	2.8
	Av.:	3.4 ± 0.5	0.48 ± 0.04	1.1 ± 0.1	2.3 ± 0.4

trans-$CrCl_2^+$ left the column, thus proving that isomerization did not occur in the column.

Rate of Aquation of *cis*- and *trans*-$CrCl_2^+$.—Data from typical experiments are plotted in Fig. 1 and 2. The reactions were first order with respect to the concentration of the chromium(III) species. The rate constant $k_{d,t}$ for the *trans* isomer obtained from the slope in Fig. 1 was 8.27×10^{-5} sec.$^{-1}$ at 25° for $\mu = 1$. The average rate constant for four such measurements was $(8.23 \pm 0.20) \times 10^{-5}$ sec.$^{-1}$ and is in fair agreement with the value of 7.0×10^{-5} sec.$^{-1}$ reported by Lamb and Fonda[3] for 0.01 M HCl and in poor agreement with Bjerrum's[2a] value of 4.5×10^{-5} sec.$^{-1}$. The average value for four measurements at 40.0° was $(7.27 \pm 0.2) \times 10^{-4}$ sec.$^{-1}$. Hence the Arrhenius activation energy and the entropy of activation are 26.5 kcal./mole and −9.3 cal./deg. mole, respectively. Using a value of 1.1×10^{-2} M^{-1} for the equilibrium constant of (1), one may calculate a value of 9.1×10^{-7} M^{-1} sec.$^{-1}$ for the formation rate constant $k_{a,t}$ of *trans*-$CrCl_2^+$. It must be noted that the value of the equilibrium constant employed is for $\mu = 7$. When a more accurate value of K_t for $\mu = 1.0$ is determined, a correction in $k_{a,t}$ should be made.

The rate constant, $k_{d,c}$, for conversion of *cis*-$CrCl_2^+$ to $CrCl^{+2}$ and Cl^- was the same within experimental error regardless of whether pure *cis*-$CrCl_2^+$ obtained in 0.08 M HCl by ion exchange and then made 1 M in HCl was used or whether a solution of *cis*-$CrCl_2^+$, *trans*-$CrCl_2^+$, and $CrCl_3$ obtained by dilution of a 12 M HCl solution of $CrCl_3$ to 1 M HCl was used. The rate of *cis*-$CrCl_2^+$ disappearance was independent of H^+ concentration over the range of $0.5 \leq [H^+] \leq 2.0$ M and of Cl^- concentration over the range $0.5 \leq [Cl^-] \leq 2.0$ M within the experimental error of 15% obtained when $[H^+]$ and $[Cl^-]$ were kept constant. The ionic strength was not maintained constant when $[H^+]$ and $[Cl^-]$ were varied, since the experimental error did not warrant it.

Since the *cis*-$CrCl_2^+$ aquation rate constant was not measurably dependent upon the Cl^- concentration, the possible aquation path *via* *cis*-$CrCl_2^+ \rightarrow CrCl_3 \rightarrow$ *trans*-$CrCl_2^+ \rightarrow CrCl^{+2}$ seems to be unimportant compared to the conversion of *cis*-$CrCl_2^+$ directly to $CrCl^{+2}$. The path *via* $CrCl_3$ had to be considered because the rate constant $k_{d,t}$ is greater than the corresponding rate constant, $k_{d,c}$, for *cis*-$CrCl_2^+$ and because it seemed likely that small amounts of $CrCl_3$ could be present in the 1 M HCl solutions.

When *trans*-$CrCl_2^+$ was originally present its initial concentration and that of *cis*-$CrCl_2^+$ were both determined at zero time from measured absorbances and the extinction coefficients listed in Table I. The *trans*-$CrCl_2^+$ concentration at all times, t, thereafter was calculated from its known rate of dissociation and the measured absorbances at 450 and 635 mμ were corrected for absorbance due to the *trans* isomer. The *cis*-$CrCl_2^+$ and $CrCl^{2+}$ concentrations were calculated from the corrected absorbances. The rate constant, $k_{d,c}$, obtained in these experiments was the same as that obtained when the pure *cis*-$CrCl_2^+$ solutions were used in the reaction medium.

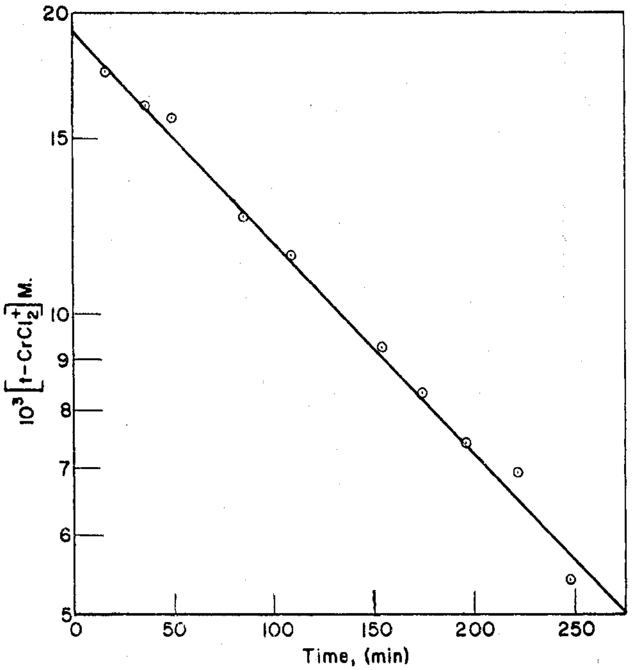

Fig. 1.—Log [*trans*-$CrCl_2^+$] *vs.* time: [*trans*-$CrCl_2^+$]$_0$ = 1.95×10^{-2} M, HCl = 1.0 M, μ = 1.0, 25 ± 0.1°.

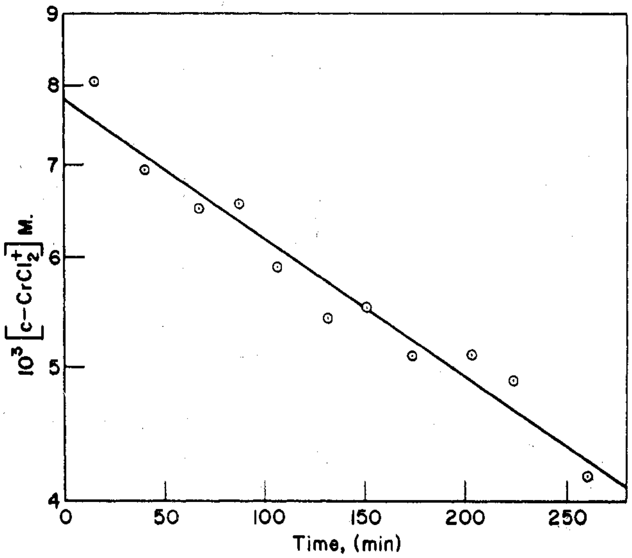

Fig. 2.—Log [*cis*-$CrCl_2^+$] *vs.* time: [*cis*-$CrCl_2^+$]$_0$ = 7.83×10^{-3} M, HCl = 1.0 M, μ = 1.0, 25 ± 0.1°.

Least squares values of $k_{d,c}$ were calculated from the data. The average rate constant for seven measurements was $(4.25 \pm 0.67) \times 10^{-5}$ sec.$^{-1}$. Using a value of 2.3×10^{-2} M^{-1} for the equilibrium constant of (2), one may calculate a value of 9.8×10^{-7} M^{-1} sec.$^{-1}$ for the formation rate constant $k_{a,c}$ of *cis*-$CrCl_2^+$. Again it must be noted that the value of the equilibrium constant employed is for $\mu = 7$.

The aquation rate constant for *cis*-$CrCl_2^+$ is approximately one-half that for *trans*-$CrCl_2^+$. Hence there is a small *trans* effect on this aquation reaction.

Formation and Aquation of $CrCl_3$.—When dark green chromium(III) chloride, which dissolves as *trans*-

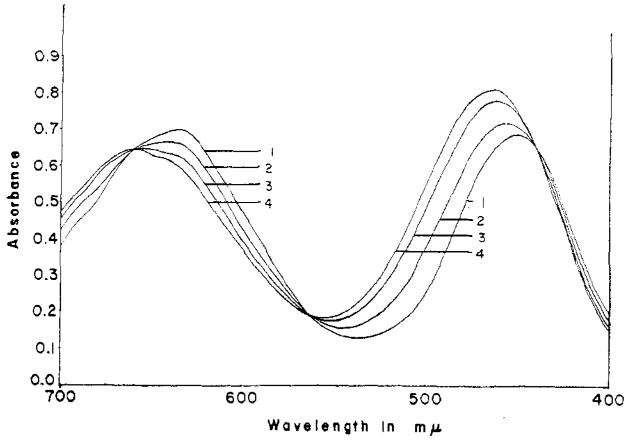

Fig. 3.—Absorption spectra at various times of *trans*-$CrCl_2^+$ dissolved in 0.1 M HCl + 11.9 M LiCl solution; [Cr(III)] = 2.71×10^{-2} M; $\mu = 12$; 25 ± 1°: 1, 6 min.; 2, 30 min.; 3, 60 min.; 4, 115 min.

$CrCl_2^+$, was dissolved in 12 M chloride solutions, the two maxima in the absorption spectrum of *trans*-$CrCl_2^+$ were observed to shift toward longer wave lengths. The absorption peak at the shorter wave length was observed to increase in height as compared to the same peak for *trans*-$CrCl_2^+$. The spectral shifts to the longer wave lengths, indicating formation of $CrCl_3$, were observed in 12 M HCl, 1.0 M HCl + 11 M LiCl, and 0.1 M HCl + 11.9 M LiCl solutions. For all practical purposes equilibrium was reached in 50 min. in 12 M HCl and 95 min. in both LiCl solutions. The final spectra did not change over a period of 4 days in the 12 M HCl and 6 days in the LiCl solutions. The spectra obtained in a 0.1 M HCl + 11.9 M LiCl solution are shown in Fig. 3. Virtually identical spectra were obtained in 1 M HCl + 11 M LiCl solutions. The spectra in LiCl solutions are slightly different from those in 12 M HCl solutions. An isosbestic point was observed at 565 mμ in the LiCl solutions and at 569 mμ in the HCl solutions. Apparently *trans*-$CrCl_2^+$ is converted to $CrCl_3$. Since $CrCl_3$ can dissociate to *cis*-$CrCl_2^+$ the latter also will be formed in the solution. However, the *cis* and *trans* isomers have equal extinction coefficients at these wave lengths[7] so the conversion of *trans*-$CrCl_2^+$ to $CrCl_3$ and *cis*-$CrCl_2^+$, *i.e.*, to two species rather than one, will not eliminate the isosbestic point.

The formation of $CrCl_3$ also was observed when the $CrCl_3$ salt was dissolved in 12 M HCl and when the HCl concentration of other chromium(III) chloride solutions was increased to 12 M by bubbling HCl into the solutions. The absorption spectrum of the 12 M HCl equilibrium solutions was the same regardless of starting compound.

The conversion of $CrCl_3$ to $CrCl_2^+ + Cl^-$ was followed by the shift of the absorption peaks toward shorter wave lengths after dilution of the 12 M HCl solutions to lower concentrations of HCl. The solutions appeared to reach a temporary equilibrium in 6–10 min. The solution contained a *cis*-to-*trans* ratio of approximately 6:1. Thus $CrCl_3$ dissociates more rapidly to *cis* than to *trans* assuming that the *cis*-to-*trans* ratio in equilibrium with $CrCl_3$ in the 12 M HCl solution was 2:1.

When $CrCl_3$ salt was dissolved in 0.1 M HCl the $CrCl_3$ was observed to dissociate rapidly into $CrCl_2^+$. The $CrCl_3$ dissociation appeared to be complete in 4 min. and was independent of initial concentration. Assuming the reaction was first order, a lower limit for the total rate constant for $CrCl_3$ conversion to $CrCl_2^+$ may be calculated as follows. From the spectra it is evident that at least 90% of the $CrCl_3$ dissociated in 4 min. Hence

$$k_{(CrCl_3 \rightarrow CrCl_2^+)} = (1/240) \ln (10/1) \simeq 0.01 \text{ sec.}^{-1}$$

This rate constant represents the sum of the rate constants for $CrCl_3$ conversion to *cis*- and *trans*-$CrCl_2^+$. But, as was stated earlier, *cis*-$CrCl_2^+$ is produced faster than *trans*-$CrCl_2^+$ from $CrCl_3$. Hence, the rate constant for the $CrCl_3$ dissociation to *cis*-$CrCl_2^+$ contributes the major portion of the rate constant.

When *trans*-$CrCl_2^+$ was dissolved in solutions of 6 M HCl and 1 M HCl saturated with NaCl, [Cl^-] ~ 6.0 M, the absorption peaks were observed to broaden. This indicated that both $CrCl_3$ and $CrCl^{+2}$ were forming since they shift the absorption peak in opposite directions. An attempt was made to study the *trans* to *cis* isomerization rate at these Cl^- concentrations. (A high Cl^- concentration is required so that measurable amounts of *trans* and *cis* will exist in equilibrium with $CrCl^{+2}$.) However, the measurements were rendered useless because of the presence of the $CrCl_3$ which dissociates rather rapidly to *cis* when the +2 and +1 species are separated on an ion-exchange column preparatory to a spectrophotometric determination of *cis* and *trans* concentrations.

From the preceding it is seen that $CrCl_3$ can be formed from *trans*-$CrCl_2^+$ in HCl + LiCl solutions and in 1 M HCl + saturated NaCl solutions. It also has been shown that $CrCl_3$ dissociates rapidly into predominantly *cis*-$CrCl_2^+$. Thus it has been shown that *trans*- to *cis*-$CrCl_2^+$ isomerization *via* $CrCl_3$ is a possible path at high Cl^- concentrations.

Cr^{+2}-Catalyzed Aquation of *cis*- and *trans*-$CrCl_2^+$.—When Cr^{+2} ion was added to *trans*-$CrCl_2^+$ or *cis*-$CrCl_2^+$ solutions the $CrCl_2^+$ conversion to $CrCl^{+2}$ was catalyzed. In several experiments Cr^{+2} ion was added to half of a *cis*-$CrCl_2^+$ solution while the other half was retained as a reference for spectrophotometric measurements. A minimum value for the rate constant of the Cr^{+2}-catalyzed conversion of *cis*-$CrCl_2^+$ to $CrCl^{+2}$ was obtained by allowing 1.35×10^{-4} M Cr^{+2} to be present in the *cis*-$CrCl_2^+$ solution for only 1 min. During this time approximately one half of the *cis*-$CrCl_2^+$ had disappeared from solution. If it is assumed that the catalyzed dissociation of *cis*-$CrCl_2^+$ is first order with respect to the concentrations of *cis*-$CrCl_2^+$ and Cr^{+2} then

$$k^*_{d,c} = \frac{\ln 2}{(60)(1.35 \times 10^{-4})} = 1 \times 10^2 \ M^{-1} \text{ sec.}^{-1}$$