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The Kinetics of Aquation of *cis*-Dichloro-bis-(ethylenediamine)-chromium(III) Ion[1]

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The kinetics of acid hydrolysis of *cis*-$[\mathrm{Cr\ en_2Cl_2}]^+$ has been studied at *p*H 1.0 at three temperatures and under various conditions of added electrolytes by a procedure which employs a chloride concentration cell to measure chloride release. The pseudo first-order rate constant for the loss of one chloride is given by $k_1 = 9.65 \times 10^{11} \exp(-21{,}100/RT)$ sec.$^{-1}$, and $\Delta S^{\ddagger} = -5.72$ e.u. A value for the specific rate constant for the loss of a second chloride has been estimated. Results of studies on the change in optical rotation of *l*-*cis*-$[\mathrm{Cr\ en_2Cl_2}]^+$ are interpreted in terms of an initial aquation without loss of optical activity followed by racemization of the chloroaquo product. Analogies with the corresponding cobalt complexes suggest that complexes of the two metals follow similar mechanisms during acid hydrolysis. A suggestion is made as to why chromium(III) complexes resemble cobalt(III) complexes so closely.

Introduction

A large amount of kinetic data has accumulated in the literature on simple substitution reactions in octahedral complexes of the types: (I) $[\mathrm{MA_5X}]^{+2 \text{ or } +1}$ and (II) $[\mathrm{MA_4YX}]^{+1 \text{ or } +2}$ where M has been Co(III), Cr(III) or Ir(III) for type (I) and M has been Co(III) and, in a few cases, Cr(III) for type (II). The A represents a non-replaceable ligand and may be monodentate or polydentate, including N- and/or C-substituted polyamines. The X and Y, with X being the replaceable group, may be $\mathrm{F^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NCS^-}$, $\mathrm{NO_2^-}$, $\mathrm{NO_3^-}$, $\mathrm{N_3^-}$, $\mathrm{CO_3^=}$, $\mathrm{HCO_3^-}$, $\mathrm{OCH_3^-}$, $\mathrm{C_2H_3O_2^-}$, $\mathrm{OH^-}$ or $\mathrm{H_2O}$.

The three types of substitution reactions which have been studied are: (1) aquation, or replacement by water in neutral or acid solution; (2) hydrolysis, or replacement by hydroxide ion in basic media; and (3) anation, or substitution of X by another anion.[3]

Although kinetic studies on complex ions were reported as early as 1911,[4] it has been only recently that the emphasis in the study of the kinetics has been on the elucidation of the mechanism by which substitution reactions occur.

Practically all of the recent work on complexes of types (I) and (II) has been concerned with the complexes of cobalt(III). These have been studied mainly by Basolo, Pearson and co-workers,[5] Taube and co-workers,[6] and by Ingold, Nyholm and Tobe[7] in aqueous solution, and by Brown, Ingold and Nyholm[8] in absolute methyl alcohol.

Relatively few kinetic experiments[9] have ever been carried out on chromium(III) complexes of type (I) and only three have concerned complexes of type (II).[9b,e,g]

Experiments by Adamson and Wilkins[9c] on the rates of aquation and exchange in the $[\mathrm{Cr(NH_3)_5NCS}]^{+2}$ and $[\mathrm{Co(NH_3)_5NCS}]^{+2}$ ions led them to suggest that different mechanisms for substitution may be operating for the two metals. Furthermore, the difference in electronic configuration existing between cobalt(III) and chromium(III),[10] coupled with the invariably greater rates of aquation found for chromium(III) complexes as compared with the analogous cobalt(III) complexes, might lead one to suspect a difference in mechanism. Therefore, the purpose of the work reported in this paper was to further compare the chemistry of cobalt(III) and chromium(III) complex ions. The compound chosen for study was *cis*-$[\mathrm{Cr\,en_2Cl_2}]\mathrm{Cl{\cdot}H_2O}$. The reasons for this choice are: (1) the complex is readily prepared and reasonably stable for long periods of time (months) if kept in a desiccator in the dark; (2) the corresponding cobalt(III) complex has been thoroughly studied[5,11]; (3) the complex undergoes aquation at a rate which can be followed conventionally; and (4) the complex is easily resolved into its optical isomers, allowing studies of racemization.

The aquation reaction, which has been studied, in 0.10 *N* acid solution, takes place in two steps which may be written

$$\textit{cis}\text{-}\underset{\mathrm{A}}{[\mathrm{Cr\ en_2Cl_2}]^+} + \mathrm{H_2O} \xrightarrow{k_1} \textit{cis}\text{-}\underset{\mathrm{B}}{[\mathrm{Cr\ en_2Cl(H_2O)}]^{+2}} + \mathrm{Cl^-} \quad (1)$$

$$\textit{cis}\text{-}[\mathrm{Cr\ en_2Cl(H_2O)}]^{+2} + \mathrm{H_2O} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \textit{cis}\text{-}\underset{\mathrm{C}}{[\mathrm{Cr\ en_2(H_2O)_2}]^{+3}} + \mathrm{Cl^-} \quad (2)$$

That the aquation proceeds stepwise has been shown in this study by both conductivity and kinetic measurements, although salts containing

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[1] This article is based upon part of a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1957.

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[3] F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

[4] A. B. Lamb and J. W. Marden, THIS JOURNAL, **33**, 1873 (1911).

[5] F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952); R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953); G. Basolo, B. D. Stone, J. G. Bergman and R. G. Pearson, *ibid.*, **76**, 3079 (1954); R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955); R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709, 2673 (1956); F. Basolo, W. R. Matoush and R. G. Pearson, *ibid.*, **78**, 4883 (1956); A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

[6] A. C. Rutenberg and H. Taube, *J. Chem. Phys.*, **20**, 825 (1952); H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953); F. A. Posey and H. Taube, *ibid.*, **79**, 255 (1957).

[7] C. K. Ingold, R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956); R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956); S. Asperger and C. K. Ingold, *ibid.*, 2862 (1956).

[8] D. D. Brown, C. K. Ingold and R. S. Nyholm, *ibid.*, 2674 (1953); D. D. Brown and C. K. Ingold, *ibid.*, 2680 (1953); D. D. Brown and R. S. Nyholm, *ibid.*, 2696 (1953).

[9] H. Freundlich and R. Bartels, *Z. physik. Chem.*, **101**, 177 (1922); H. Freundlich and H. Pape, *ibid.*, **86**, 458 (1914); A. Adamson and R. G. Wilkins, THIS JOURNAL, **76**, 3379 (1954); C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955); D. M. Grant and R. E. Hamm, THIS JOURNAL, **78**, 3006 (1956); M. Ikuta, H. G. McAdie and W. MacF. Smith, *Can. J. Chem.*, **34**, 1361 (1956); R. E. Hamm, THIS JOURNAL, **75**, 609 (1953).

[10] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[11] J. P. Mathieu, *Bull. soc. chim. France*, **3**, 2121, 2156 (1936).

ion B never have been isolated. As will be shown, reaction 1 proceeds at a rate approximately 10 times that of reaction 2, so that no serious interference is caused by reaction 2 in the study of reaction 1. The diaquo cation (C) is stable only in strongly acid solution and has been shown to retain the *cis* configuration.[12] It will revert to the *cis*-dichloro cation only on standing for several days in a concentrated hydrochloric acid solution or upon evaporation of a concentrated hydrochloric acid solution.[13] Therefore, under the conditions of the experiments reported here, it is reasonable to assume that equilibrium is not established either in reaction 1 or 2 and that in any case, an equilibrium in reaction 1 would lie far toward the right. Indeed, the experimental data allow an approximation of k_2 to be made.

Experimental

Preparation of Compounds.—*cis*-[Cr en_2Cl_2]Cl·H_2O was prepared according to the method described by Rollinson and Bailar.[14] The recrystallization procedure was modified as follows. The impure salt was dissolved quickly in water (4 ml. for each gram of salt) which had been acidified with several drops of concentrated hydrochloric acid and the solution was heated to about 65°. The solution was filtered rapidly into ice-cold concentrated hydrochloric acid (1.5 ml. for each gram of salt used) and the filtrate was cooled to −5° in an ice-salt mixture. The red-violet needles which came out were collected on a sintered glass funnel, washed well with alcohol and ether, and then dried in a vacuum desiccator. Equivalent conductance at zero time, Λ_{700} = 103, which is in the correct range for a uni-univalent salt containing a complex cation.[15] *Anal.* Calcd. for [Cr en_2Cl_2]Cl·H_2O: C, 16.19; H, 6.12; N, 18.88. Found: C, 16.14; H, 6.03; N, 18.40. The complex salt, *cis*-[Cr en_2Cl_2]Cl·H_2O, was resolved into its optical isomers by a modification of the method of Werner.[16] To a freshly prepared solution of [Cr en_2Cl_2]Cl·H_2O (12.0 g., 0.0404 mole) in 200 ml. water at 19° was added ammonium *d*-α-bromocamphor-π-sulfonate (22.5 g., 0.0687 mole) with vigorous stirring. The solution was kept at 19°. After several minutes the sulfonate salt separated. It was filtered and washed with alcohol and ether (10.0 g., 89.5% diastereoisomer), and was then dissolved in concentrated HCl in the ratio of 4 ml./g. To this solution was added two volumes of alcohol, which precipitated fine, dark-red crystals. These crystals were filtered, washed well with alcohol and ether, and dried in a vacuum desiccator. The yield was 3.85 g. or 71.8%. The observed rotation for a 0.075% solution was +0.235; $[\alpha]^{25}D$ +314. *Anal.* Calcd. for *l*-*cis*-[Cr en_2Cl_2]Cl·H_2O: C, 16.19; H, 6.12; N, 18.88; Cr, 17.28. Found: C, 16.44; H, 6.12; N, 18.50; Cr, 17.54. All other reagents were commercially available materials of reagent grade, and were used without further purification.

Kinetic Measurements.—Preliminary determinations of the rate of loss of chloride from *cis*-[Cr $en_2Cl_2]^+$ were made by titrating the ionic chloride potentiometrically with silver nitrate after the reaction had been quenched by running the aliquot being analyzed into an ice-cold 1:1 ethanol-water mixture. The results indicated that the reaction is too fast to follow conveniently by a titration technique. Therefore, a more rapid and, at the same time, a more accurate means of following the loss of chloride, was sought.

The method finally adopted was to employ a concentration cell composed of two Ag–AgCl electrodes. The cell design appears in Fig. 1. The Ag–AgCl electrodes were prepared by plating silver from a $KAg(CN)_2$ bath onto platinum plates having an area of 1 cm.², followed by anodization of the plates in a 1.0 *M* hydrochloric acid-bath at a current of 25 ma. for 10 min. Electrodes prepared in this way were stable for several months and never had an asymmetry potential greater than 0.2 mv. Between runs they were stored in 0.05 *M* hydrochloric acid in the dark. The cell was immersed in a constant temperature bath controlled to within ±0.05°. A Rubicon K-2 potentiometer and Leeds and Northrup galvanometer were employed for the potential measurements. A stock solution of standard chloride ion concentration of 0.0100 *M* was prepared from NaCl and either 0.100 *M* $HClO_4$ or 0.100 *M* HNO_3.

For runs not involving added electrolytes, the procedure was as follows: 50 ml. of standard chloride solution was placed in Vessel A. A weighed amount of complex was dissolved in 50.0 ml. of 0.100 *M* acid (either $HClO_4$ or HNO_3, but the same as was used to prepare the standard solution) which previously had been brought to the proper temperature. This solution of the complex was placed in Vessel B and the solutions from both A and B were allowed to flow into the corresponding cell compartments with the pinch clamps closed over the Tygon tubing (see Fig. 1). The clamps were released after the compartments were filled and junction was thereby made in the center bulb. All of this required just under one minute from the time the solution of the complex was prepared. The rate of chloride production in the compartment containing the complex was then continuously and readily followed by observing the change in cell potential.

The 0.100 *M* acid present in each solution served a twofold purpose. First, it prevented any reaction of hydroxyl ion from interfering with normal aquation of the complex, and second, it eliminated concern over a junction potential in the cell.

To be sure that no chloride ion transfer occurred from one cell compartment to the other during the time of a normal run, standard chloride solutions of differing concentrations were allowed to run into the cell compartments and the potential was measured periodically. No change in potential occurred over a period of time equal to that of a normal kinetic run.

The runs which involved added electrolytes were carried out in the same way except that a weighed amount of the material whose effect upon the rate of aquation was to be determined was added to 50.0 ml. of the standard solution and to 50.0 ml. of the solution of the complex to produce the desired concentration.

The run in "strong light" was made with a 60-watt bulb approximately one foot from the cell.

Racemization Measurements.—Measurements of change in optical rotation of *l*-*cis*-[Cr en_2Cl_2]Cl·H_2O were made in a 10 cm. jacketed polarimeter tube maintained at 21.9 ± 0.1°. The polarimeter used is a Schmidt and Haensch No. 9143. Measurements were made at the sodium-D line or approximately 5890 Å. Solutions were 0.005 *M* (0.148%) in complex and 0.100 *M* in $HClO_4$ or HNO_3. At this concentration, precision is initially poor due to the high absorbancy of yellow light by the solution. This absorbancy decreases fairly rapidly so that readings after about 20–25 minutes are more precise. The rotatory dispersion curve of this complex[17] indicates that the rotatory power is highest at a wave length of approximately 5490 Å. However, at this wave length practically all light is absorbed by the complex solution, which is red-violet in color. At the red end of the spectrum (about 6000 Å.) very little light is absorbed by the solution, but the rotatory power is small and the eye is not very sensitive to changes in light intensity. Hence, the sodium-D line was a compromise choice.

Results and Discussion

The measured potential of the concentration cell was converted to a chloride concentration by means of the relation

$$E = 2.303 \frac{RT}{nF} \log_{10} \frac{a}{x}$$

where E is the measured potential, a is the fixed standard chloride concentration, and x is the chloride concentration in the solution of the com-

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[12] P. Pfeiffer, *Z. anorg. Chem.*, **58**, 228 (1908).

[13] P. Pfeiffer, *ibid.*, **56**, 261 (1907).

[14] C. L. Rollinson and John C. Bailar, Jr., "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 200.

[15] H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1955, pp. 106, 108, 111.

[16] A. Werner, *Ber.*, **44**, 3132 (1911).

[17] J. P. Mathieu, *Bull. soc. chim.*, **3**, 476 (1936).

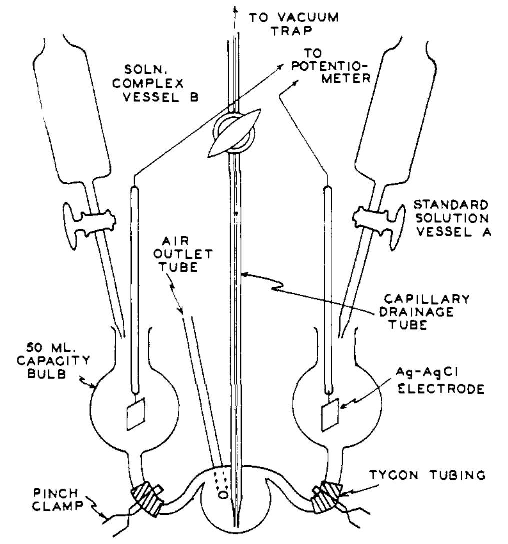

Fig. 1.—Concentration cell for measuring rate of chloride ion production.

plex at any time. The conditions at early reaction times may be represented as

$$\underset{(c - x_1)}{[\mathrm{Cr\ en_2Cl_2}]^+} + \underset{c}{\mathrm{Cl_a}^-} + \mathrm{H_2O} \xrightarrow{k_1} \underset{x_1}{[\mathrm{Cr\ en_2ClH_2O}]^{+2}} + \underset{c}{\mathrm{Cl_a}^-} + \underset{x_1}{\mathrm{Cl_b}^-} \qquad (3)$$

At later times reaction (4) also must be considered

$$\underset{(x_1 - x_2)}{[\mathrm{Cr\ en_2ClH_2O}]^{+2}} + \underset{c}{\mathrm{Cl_a}^-} + \underset{x_1}{\mathrm{Cl_b}^-} + \mathrm{H_2O} \xrightarrow{k_2} \underset{x_2}{[\mathrm{Cr\ en_2(H_2O)_2}]^{+3}} + \underset{c}{\mathrm{Cl_a}^-} + \underset{x_1}{\mathrm{Cl_b}^-} + \underset{x_2}{\mathrm{Cl_c}^-} \qquad (4)$$

The quantity measured experimentally is $(c + x_1 + x_2) = (\mathrm{Cl}^-)$, but at early times $x_2 \sim 0$ and the value measured is $\sim (c + x_1)$. Hence, the concentration of $[\mathrm{Cr\ en_2Cl_2}]^+$ left at any time is given by $(c - x_1)$ or $(2c - [\mathrm{Cl}^-])$, where c is the initial concentration. Plots of log $(c - x_1)$ *vs.* time were found to be linear up to a time representing about 60% completion of reaction 3. A sample plot appears in Fig. 2. Thus, it is seen that reaction 3 is pseudo first order. The positive deviations from linearity were assumed to arise from the slower reaction indicated by eq. 4. Thus, at times greater than about 40 minutes x_2 begins to become significant and therefore account must be taken of the fact that what is really plotted is $(c - x_1 - x_2)$. By extrapolating the straight line to longer times and taking the difference between the value for the projected first-order decomposition and the actual value observed, a measure of x_2 is obtained, *i.e.*, $(c - x_1 - x_2) - (c - x_1) = -x_2$. Using the standard equation[18] for the series first-order reactions

$$\underset{(a - x_1)}{\mathrm{A}} \xrightarrow{k_1} \underset{(x_1 - x_2)}{\mathrm{B}} \quad ; \quad \underset{(x_1 - x_2)}{\mathrm{B}} \xrightarrow{k_2} \underset{x_2}{\mathrm{C}}$$

which is

$$(x_1 - x_2) = a \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

it was possible by the method of successive approximations to obtain a value for k_2 from known or measured values of a, k_1, x_1, x_2 and t.

The specific rate constant, k_1, for reaction 3 is given in Table I for the conditions specified. In most cases duplicate runs agreed within ± 2%, with ± 3% being the maximum discrepancy. The rate constant, k_2, for reaction 4 is also included, but its value should be considered less accurate due to the method by which it was obtained.

TABLE I

RATES OF ACID HYDROLYSIS OF *cis*-$[\mathrm{M\ en_2Cl_2}]^+$ IN 0.10 M $\mathrm{HNO_3}$

Complex	Temp., °C.	Ionic strength	k_1, sec.$^{-1}$ × 10^4	k_2, sec.$^{-1}$ × 10^5
cis-$[\mathrm{Cr\ en_2Cl_2}]^+$	20.0	0.105	1.60	1.0
	20.0	.155[a]	1.57	..
	25.0	.105	3.30	2.8
	30.0	.105	5.88	..
cis-$[\mathrm{Co\ en_2Cl_2}]^+$	25	.105	2.5[b]	
	25	.022[d]	1.2[c]	
	30	.022[d]	2.15[c]	
	25.0	.105	1.76[e]	

[a] 0.05 M $\mathrm{NaClO_4}$. [b] Value obtained by Pearson, *et al.*[5d] [c] Values obtained by Mathieu.[11] [d] 0.012 M $\mathrm{HNO_3}$ and 0.01 M complex used. [e] See Discussion.

Several rate constant values for the cobalt complex are included and, as is seen, agreement among the several values is poor. Conductivity measurements were used by Mathieu[11] in obtaining the low value; spectrophotometric measurements were used by Pearson, *et al.*,[5d] in obtaining the high value; the intermediate value was obtained in our

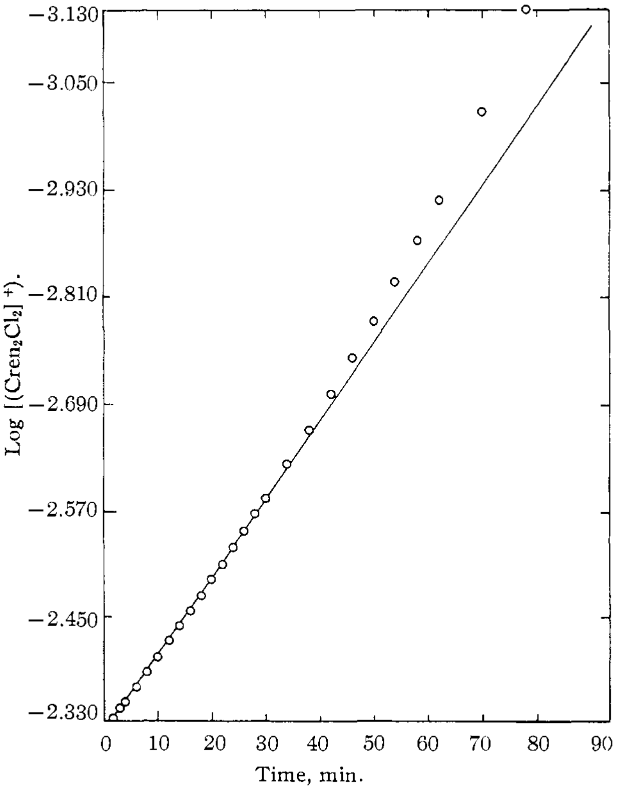

Fig. 2.—First-order rate plot for acid hydrolysis of *cis*-$[\mathrm{Cren_2Cl_2}]^+$.

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[18] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153.

concentration cell. The latter measurements were not as precise as was expected, due to interaction between the cobalt complex and the Ag–AgCl electrode, preventing the rapid establishment of equilibrium conditions between solution and electrode. Thus, meaningful readings could not be taken for at least ten minutes after the solution of the complex was placed in the cell, and experimental scattering was increased. The chromium complex did not affect the electrodes in this manner. No further study of this phenomenon was made. However, as expected, the chromium complex aquates faster than the corresponding cobalt complex.

The thermodynamic data for reaction 3, which were obtained from a linear Arrhenius plot of log k *vs.* $1/T$ are: $\Delta E^{\ddagger} = 21.1$ kcal., $\Delta H^{\ddagger} = 20.5$ kcal., $\Delta F^{\ddagger}_{298°} = 22.2$ kcal., $\Delta S^{\ddagger} = -5.72$ cal./deg. and log $Z = 11.98$. Corresponding values for the acid hydrolysis of the cobalt complex, *cis*-[Co en$_2$Cl$_2$]$^+$, are[11]: $\Delta E^{\ddagger} = 22.25$ kcal., $\Delta H^{\ddagger} = 21.6$ kcal., and log $Z = 14.02$. The energy required to form the activated complex is therefore similar for both metals, but is slightly lower in the case of chromium, as is expected.

Table II records the rate of acid hydrolysis at 25.0° and a pH = 1.0 (obtained with HClO$_4$) under various conditions of concentration and added electrolyte. Several conclusions can immediately be drawn. The presence or absence of light (no. 2) has no apparent effect on the reaction studied, as is apparently the case for some cobalt complexes.[7a] Variation in ionic strength (nos. 7, 8) appears to have no effect on the aquation reaction; this is in line with Mathieu's results with the cobalt complex.[11] However, chloride ion and sulfate ion (nos. 9–14) in concentrations 10-fold or greater over complex concentration appear to accelerate the aquation reaction. This can be accounted for by assuming ion-pair formation between anion and dichloro cation. If this is indeed the case, it constitutes additional support for an S$_N$1 or dissociation type mechanism. Thus, an ion pair [Cr en$_2$Cl$_2$]$^+$–SO$_4^=$ would induce an easier breaking of the Cr–Cl bond and at the same time would tend to prevent attack by the negative end of a water dipole which is necessary for the S$_N$2 mechanism. However, the aquation of *cis*-[Cr en$_2$Cl$_2$]$^+$ is not as greatly affected by the presence of sulfate ion as are the aquations of [Cr(NH$_3$)$_5$Cl]$^{+2}$ [9f] and [Co(NH$_3$)$_5$Cl]$^{+2}$.[19] This result was expected since the latter ions are doubly charged whereas the dichloro cation is singly charged.

TABLE II

RATES OF ACID HYDROLYSIS OF *cis*-[Cr en$_2$Cl$_2$]$^+$ UNDER VARIOUS CONDITIONS AT 25.0° AND pH 1.0 (HClO$_4$)

No.	Concn. of complex, $M \times 10^3$	Added electrolyte or other condition	Ionic strength	k_1, sec.$^{-1}$ $\times 10^4$
1	5.00	....	0.105	3.30
2	5.00	60 watt bulb 1 foot away	.105	3.27
3	5.00	Optically active form	.105	3.38
4	6.00	....	.106	3.22
5	4.00	....	.104	3.47
6	2.50	....	.102	3.58
7	5.00	0.05 *M* Mg(ClO$_4$)$_2$	.255	3.18
8	5.00	.05 *M* Ni(ClO$_4$)$_2$	.255	3.20
9	5.00	.05 *M* NaCl	.115	3.63
10	5.00	.010 *M* Na$_2$SO$_4$	.135	3.30
11	5.00	.025 *M* Na$_2$SO$_4$	.180	3.28
12	5.00	.050 *M* Na$_2$SO$_4$	.255	3.57
13	5.00	.075 *M* Na$_2$SO$_4$	.330	3.68
14	5.00	.100 *M* Na$_2$SO$_4$	.405	4.03

The slight variation in rate observed with a change in initial concentration is not at present understood and requires further study.

A study of the change in optical rotation of *l-cis*-[Cr en$_2$Cl$_2$]$^+$ has been made and the data may be interpreted in a manner similar to that used to treat data obtained with the corresponding cobalt complex.[20] Thus, in a plot of log α *vs.* t, an initial straight portion is joined to a final straight portion by a curved line. As Mathieu[20] has shown for the cobalt salt, the initial straight line yields a k value close to the acid hydrolysis constant, k_1, and the final straight line yields a specific rate constant for racemization of the species being formed by the first process, which in this case is *l-cis*-[Cr en$_2$Cl H$_2$O]$^{+2}$. If k_2 (Table I) is compared with k_r (Table III), it is seen that the optically active chloroaquo cation racemizes at a faster rate than it loses chloride. This is similar to what has been observed[20] in the case of the analogous cobalt complex and indicates that a different mechanism is operating to produce racemization than is operating to produce further aquation. A similar treatment has been given for the change in rotation of *d-cis*-[Co en$_2$ F$_2$]$^+$.[5f] Table III records the rates of acid hydrolysis, mutarotation and racemization for the above compounds. It appears that the initial change in rotation is due mainly to the formation of the optically active chloro-aquo compound, which then undergoes racemization.

It would seem from this work that the ions *cis*-[Co en$_2$Cl$_2$]$^+$ and *cis*-[Cr en$_2$Cl$_2$]$^+$ are not very different in their behavior, at least toward acid hydrolysis and optical change. This observation suggests that the two metal complexes follow a similar mechanism during the course of acid hydrolysis. Although the purpose of this work was not to attempt to decide upon a mechanism, the results would seem to favor for the chromium complex the S$_N$1 mechanism suggested by Basolo, Pearson, *et al.*,[5] for the acid hydrolysis of cobalt complexes.

If the assumption is true that both cobalt(III) and chromium(III) are using 3d^{2}4s4p^3 hybrid orbitals in their complex compounds, then the remaining three 3d orbitals are filled in cobalt and half-filled in chromium. It may well be that the strong similarity found between cobalt(III) and chromium(III) complexes is related to this fact. The similarity in reactivity between elements having the same orbital set either empty, half-filled, or filled has been noted before in both the transition and inner transition elements. Such orbital arrangements seem always to lead to greater stability than would otherwise be predicted. Thus it is suggested here that the filled orbitals in the cobalt complexes and the half-filled orbitals in the chro-

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(19) F. J. Garrick, *Trans. Faraday Soc.*, **34**, 7088 (1938).

(20) J. P. Mathieu, *Bull. soc. chim.*, **4**, 687 (1937).

TABLE III

RATES OF ACID HYDROLYSIS, MUTAROTATION AND RACEMIZATION GIVEN IN k (SEC.$^{-1}$)

Initial compd.	(Acid)	Temp., °C.	k_1, acid hydrolysis	k_m, mutarotation	k_r, racemization
l-*cis*-[Co en_2Cl_2]$^{+a}$	0.012	30	2.15×10^{-4}	5.37×10^{-4}	6.13×10^{-5}
d-*cis*-[Co en_2F_2]$^{+b}$	.001	25	6.0×10^{-6}	8.2×10^{-6}	3×10^{-8}
	.1	25	5×10^{-5}	10.3×10^{-5}	6.5×10^{-6}
l-*cis*-[Cr en_2Cl_2]$^{+}$	.1	22	2.30×10^{-4}	2.28×10^{-4}	1.48×10^{-4}
	.1	25	3.30×10^{-4}	3.30×10^{-4}	2.0×10^{-4}

[a] Values from Mathieu.[20] [b] Values from Basolo, *et al.*[5f]

mium complexes are in part responsible for (1) the general non-labile characteristics found for cobalt and chromium complexes as compared with other first row transition metal complexes, (2) the strong similarity of cobalt and chromium complexes in ease of substitution-type reactions, and (3) the ease with which Cr(II) goes to Cr(III) in systems which can form d^2sp^3 hybrid-orbital complexes with Cr(III).

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Pyridine: Experimental and Calculated Chemical Thermodynamic Properties between 0 and 1500°K.; a Revised Vibrational Assignment[1]

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From studies by low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry, values were obtained for the entropy, heat capacity and heat of formation of pyridine in the ideal gaseous state. The calorimetric values of entropy and heat capacity served as guides in revising the vibrational assignments for pyridine and several deuteropyridines. The revised assignment for pyridine and molecular structure data were used in computing values of the thermodynamic functions at selected temperatures between 0 and 1500°K. Values of the heat, free energy and equilibrium constant of formation were calculated at the same selected temperatures. The experimental investigations provided the following information: values of heat capacity for the solid (13–224°K.), the liquid [$C_{satd} = 33.633 - 9.1446 \times 10^{-2}T + 3.8478 \times 10^{-4}T^2 - 3.3430 \times 10^{-7}T^3$, cal. deg.$^{-1}$ mole^{-1} (240–347°K.)], and the vapor [$C_p^\circ = -8.262 + 10.608 \times 10^{-2}T - 5.4662 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (374–500°K.)]; the heat of fusion [1978.6 cal. mole^{-1}] at the triple point [231.49°K.]; the entropy of the liquid at 298.16°K. [42.52 cal. deg.$^{-1}$ mole^{-1}]; the vapor pressure [$\log_{10} p(\text{mm.}) = 7.04162 - 1374.103/(t + 215.014)$, (67–153°)]; the heat of vaporization [$\Delta Hv = 13077 - 10.201\ T - 4.7941 \times 10^{-3}T^2$, cal. mole^{-1} (346–388°K.)]; the second virial coefficient in the equation of state, $PV = RT\ (1 + B/V)$, [$B = -15–84.5 \exp(950/T)$, cc. mole^{-1} (346–500°K.)]; and the standard heat of formation of the liquid at 298.16°K. [23.89 kcal. mole^{-1}].

Thermodynamic investigations of organic nitrogen compounds were begun recently in this Laboratory as part of American Petroleum Institute Research Project 52. The objective is to provide comprehensive thermodynamic data for nitrogen compounds that are important in petroleum technology. This paper is the first of a projected series on cyclic nitrogen compounds. Results are reported for pyridine, a compound important in theoretical considerations concerning molecular structure as well as in practical considerations as an industrial chemical. Some thermodynamic data for pyridine have been reported previously,[2] but many of the basic data are not of the accuracy that can be obtained by present-day methods.

The experimental part of this investigation consisted of measurements of thermodynamic properties by the methods of low temperature calorimetry, comparative ebulliometry, flow calorimetry and combustion calorimetry. Descriptions of the experiments and detailed results are given in the Experimental part of the paper. For convenience, the most important experimental results—values of the entropy, heat capacity and heat of formation for the ideal gaseous state—are collected in Table I. The entropy and heat capacity data served as guides in revising the vibrational assignment for pyridine and as checks on thermodynamic properties calculated by the methods of statistical

TABLE I

OBSERVED AND CALCULATED MOLAL THERMODYNAMIC PROPERTIES OF PYRIDINE IN THE IDEAL GASEOUS STATE

	Entropy, S°, cal. deg.$^{-1}$			Heat capacity, Cp°, cal. deg.$^{-1}$	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
346.65	70.65	70.65	374.20	23.79	23.79
366.11	71.86	71.89	397.20	25.23	25.24
388.40	73.27	73.30	420.20	26.65	26.65
			450.20	28.43	28.40
			500.20	31.12	31.21

Heat of formation, $\Delta Hf^\circ_{298.16}$ (obsd.) = 33.50 kcal.

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(1) (a) This investigation was performed as part of American Petroleum Institute Research Project 52 on "Nitrogen Constituents of Petroleum," which is conducted at the University of Kansas in Lawrence, Kansas, and at the Bureau of Mines Experiment Stations in Laramie, Wyoming, and Bartlesville, Oklahoma. (b) Presented at 130th American Chemical Society Meeting, Atlantic City, N. J., September, 1956.

(2) (a) C. H. Kline and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944); (b) D. P. Biddiscombe, E. A. Coulson, R. Handley and E. F. G. Herington, *J. Chem. Soc.*, 1957 (1954); (c) E. F. G. Herington and J. F. Martin, *Trans. Faraday Soc.*, **49**, 154 (1953) [and references cited there]; (d) G. S. Parks, S. S. Todd and W. A. Moore, THIS JOURNAL, **58**, 398 (1936); (e) J. N. Pearce and H. M. Bakke, *Proc. Iowa Acad. Sci.*, **38B**, 450 (1929).