Polarographic Study of the Hydrolysis of the Halopentammine-Chromium(III) Ions[1]

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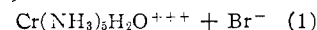
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Some of the optical and polarographic properties of the aquo- and halopentamminechromium(III) salts are described. Polarographic techniques for following the hydrolysis reactions of the halopentamminechromium(III) ions have been developed and as a result it was possible to examine the kinetics of the hydrolysis at any pH with chromium solutions as dilute as 10^{-4} M. The rate of hydrolysis is first order in chromium concentration and is independent of pH in the range 1 to 10. The rate constants for hydrolysis are 5.6×10^{-4}, 6.2×10^{-3} and 6.0×10^{-2} min.$^{-1}$ for the chloro, bromo and iodo complexes at 25°. Above a pH of about 11.5 the rate increases linearly with increasing hydroxyl ion concentration. The second order rate constants for the complexes at high pH are 0.11, 4.3 and 220 l. mole^{-1} min.$^{-1}$.

In recent years the kinetics of substitution reactions of metal complexes have been extensively studied[3] as a means of elucidating some factors which are important in the solution chemistry of inorganic compounds. Since numerous cobalt complexes can be readily prepared and since their substitution reactions are slow enough to be followed by conventional methods, cobalt complexes have been studied in greater detail than those of any other metal. By analogy with tetrahedral substitution reactions, the reactions at octahedral centers have been assigned to the classifications S_N1 or S_N2[4] depending upon whether the rate determining step is unimolecular or bimolecular. An S_N1 reaction ought to obey first order kinetics with the rate being dependent upon the displaced group whereas an S_N2 reaction ought to obey second order kinetics with the rate being dependent upon the displacing group. In actual practice the situation is not so clear cut but the weight of evidence indicates that the acid hydrolysis of cobalt complexes is S_N1[5] in character.

The substitution reactions of chromium complexes which have been studied are similar to those of cobalt in following pseudo first order kinetics. Hamm and Schull[6] proposed an S_N1 CB[7] mechanism for the base hydrolysis of the dichlorotetraquochromium (III) ion. Since the chemistry of chromium (III) in aqueous solution is complicated by olation,[8] it is possible that such reactions could have some effect on the rate of hydrolysis. Consequently a study of a series of complex ions in which all the coördination positions, except the one which is of interest, are occupied by non-labile ligands would eliminate this complication. This specification is met by the halopentamminechromium (III) ions. Extensive studies comparable to those carried out for cobalt[2] have not

been reported for the chromium (III) complexes. However, a few studies[9-12] of the hydrolytic removal of a labile group from chromium (III) complexes have appeared in the literature. Adamson and Wilkins[12] obtained evidence that in acid solution the thiocyanato cobalt complexes hydrolyzed by an S_N1 mechanism while those of chromium hydrolyzed by an S_N2 mechanism.

Freundlich and Bartels,[9] in 1922 found the reaction to be

$$Cr(NH_3)_5Br^{++} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{+++} + Br^- \quad (1)$$

to be first order in chromium with a rate constant of 3×10^{-3} min.$^{-1}$ at 25°.

The present study was undertaken to further investigate the hydrolytic removal of halogen from $Cr(NH_3)_5 X^{++}$ where X is Cl, Br or I.

Experimental

Preparation of Halopentamminechromium (III) Salts.— Aquopentamminechromium (III) nitrate ammonium nitrate double salt was prepared by reacting hydrated potassium chromium (III) sulfate with ammonia and ammonium nitrate at 60°. The $[Cr(NH_3)_5H_2O]$ $(NO_3)_3 \cdot NH_4NO_3$ was dissolved in dilute ammonia solution and reacted with an excess of concentrated hydrochloric, hydrobromic or hydiodic acid in a modification of procedures which have been described.[13]

Anal. Calcd. for $[Cr(NH_3)_5Cl]$ Cl_2: Cr, 21.4; NH₃, 35.0; Cl, 43.7. Found: Cr, 21.1; NH₃, 34.1; Cl, 43.7.

Anal. Calcd. for $[Cr(NH_3)_5Br]$ Br₂: Cr, 13.8; NH₃, 22.6; Br, 63.6. Found: Cr, 13.8; NH₃, 22.4; Br, 63.2.

Anal. Calcd. for $[Cr(NH_3)_5I]$ I₂: Cr, 10.0; I, 73.6. Found: Cr, 10.0; I, 73.7. The analysis for chromium was by redox titration involving standard ferrous sulfate after oxidation of the chromium to the chromate. Bromo- and iodo- complexes were oxidized by ammonium persulfate using a silver catalyst; while the chloro complex was oxidized by hydrogen peroxide in sodium hydroxide solution with a nickel salt as catalyst. Total halogen was determined in a boiled aqueous solution of the complex by conductance titration with silver nitrate. Ammonia was determined by the Kjeldahl method.

Chloropentamminechromium (III) perchlorate was prepared by precipitation from a saturated aqueous solution of $[Cr(NH_3)_5Cl]$ Cl₂ by the addition of concentrated perchloric acid, cooling to 0° and filtering. The salt was purified by repeating the above procedure.

Anal. Calcd. for $[Cr(NH_3)_5Cl]$ $(ClO_4)_2$: Cr, 14.0; Cl, 9.60. Found: Cr, 14.1; Cl, 9.50.

A solution containing bromopentamminechromium (III) ion free of ionic bromide was prepared by ion exchange. Bromopentamminechromium (III) bromide was dissolved

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(2) International Nickel Company Fellow 1960–1961.

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

(4) Ref. 3, page 91 to 96.

(5) R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(6) R. E. Hamm and C. M. Schull, *J. Am. Chem. Soc.*, **73**, 1240 (1951).

(7) R. G. Pearson, R. E. Meeker and F. Basolo, *ibid.*, **78**, 709 (1956).

(8) J. A. Laswick and R. A. Plane, *ibid.*, **81**, 3564 (1959).

(9) H. Freundlich and R. Bartels, *Z. physik. Chem.*, **101**, 177 (1922).

(10) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79**, 4285 (1957).

(11) R. G. Pearson, R. A. Munson and F. Basolo, *ibid.*, **80**, 504 (1958).

(12) A. W. Adamson and R. G. Wilkins, *ibid.*, **76**, 3379 (1954).

(13) T. Moeller, Editor, "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 132.

in ice cold 0.1M perchloric acid and absorbed on a short column of hydrogen form Amberlite IR120 cation exchange resin. The ionic bromide was washed through with additional 0.1 M perchloric acid and then the $Cr(NH_3)_5Br^{++}$ was eluted with 2.5 M perchloric acid.

Rate studies at low pH were carried out in perchloric acid or perchloric acid–sodium perchlorate mixtures and at very high pH sodium hydroxide or sodium hydroxide–sodium perchlorate mixtures. For other pH regions buffers were prepared by neutralizing sufficient perchloric acid solution with the appropriate amine, to give a final solution 0.1 M in perchlorate salt and then excess amine was added to give the required pH. The amines used were aniline and pyridine for pH 4 to 6, 2-aminopyridine for pH 6 to 8, ammonia for pH 8 to 10 and diethylamine for pH 10 to nearly 12.

Technique of Measurement.—The spectra of the halopentamminechromium (III), aquopentamminechromium (III) and hydroxopentamminechromium (III) ions in solution were obtained with a Cary Model 14 Recording Spectrophotometer. The absorption maxima were: $Cr(NH_3)_5$ H_2O 360 and 479 mμ; $Cr(NH_3)_5Cl^{++}$, 375 and 512 mμ; $Cr(NH_3)_5Br^{++}$, 378, 468 and 523 mμ; $Cr(NH_3)_5OH^{++}$, 399 and 507 mμ; $Cr(NH_3)_5I^{++}$, 471 and 528 mμ. The molar extinction coefficients at these absorption maxima were: $Cr(NH_3)_5H_2O^{+++}$, 29 and 34; $Cr(NH_3)_5Cl^{++}$, 39 and 36; $Cr(NH_3)_5Br^{++}$, 41, 25 and 38; $Cr(NH_3)_5OH^{++}$, 41 and 43, $Cr(NH_3)_5I^{++}$, 40 and 40. Thus, the spectra show that the absorption maxima shift to shorter wave lengths during the course of hydrolytic removal of halogen from the halo complexes. Accordingly it was possible to use the absorption spectra to follow the course of hydrolysis by observing the change in optical density at a specific wave length. There is considerable overlapping of the absorption curves of the halo and aquo complexes and as a result the change in optical density was small. Furthermore the effect on optical density of subsequent reactions of the hydrolyzed product could have been large. In near neutral and alkaline solutions, for instance, the aquo complex hydrolyzes further to precipitate basic chromium salts. In the pH region in which such precipitation occurs, the spectrophotometric method is not valid.

Solutions of the complexes were examined polarographically using a Leeds and Northrup type E Electrochemograph. The half wave potentials of the bromo and iodo complexes were sufficiently more positive than that of the aquo complex that the rate of disappearance of these complexes could be followed polarographically. For instance in a series of polarograms obtained during the hydrolysis of a solution of $[Cr(NH_3)_5Br](ClO_4)_2$ only the polarographic wave (at about -0.5 v.) corresponding to the one electron reduction of $Cr(NH_3)_5Br^{++}$ was present initially. As hydrolysis proceeded two new polarographic waves appeared. One at $+0.15$ volts was the bromide oxidation wave and was due to the release of the bromide ion from the complex during the reaction. The second of these at about -0.9 volts was due to the reduction of $Cr(NH_3)_5H_2O^{+++}$. When the logarithm of ($i_{d\infty}-i_{dt}$), where $i_{d\infty}$ is the diffusion current after complete reaction and i_{dt} is the diffusion current at any time t, for the bromo complex, the aquo complex or the bromide ion, was plotted against time a straight line was obtained. The rate constant obtained from the first order plot was the same in each case. Under these conditions any one of the three polarographic waves could be used for following the kinetics of the hydrolysis reaction in solutions as dilute as $10^{-4}M$. With appropriate modifications the kinetics of the hydrolysis of chloro-, bromo- and iodopentammine-chromium (III) complexes could be followed polarographically at any pH. Under conditions where the spectrophotometric method was applicable, the results agreed with those obtained polarographically. In general, for bromide and iodide hydrolysis studies the decrease in diffusion current due to the reduction of the $Cr(NH_3)_5Br^{++}$ or $Cr(NH_3)_5I^{++}$ was followed. In solutions of higher pH the $Cr(NH_3)_5H_2O^{+++}$ could not be used to follow the reaction because it was being continuously removed from solution by subsequent hydrolytic reactions leading to precipitation. It was also more convenient to use $[Cr(NH_3)_5Br]$ Br_2 or $[Cr(NH_3)_5I]$ I_2 rather than the perchlorate salt as the starting material. Since the half wave potentials for $Cr(NH_3)_5Cl^{++}$ and $Cr(NH_3)_5H_2O^{+++}$ are nearly the same[14] neither of these reduction waves could be used for following the hydrolysis of the chloro complex.

For these studies the change in the chloride diffusion current was measured at $+0.4$ volts vs. saturated calomel electrode. A saturated sulfate half cell was used as the source of potential and diffusion current was obtained by short circuiting a Scalamp galvanometer between the sulfate half cell and the dropping mercury electrode according to a technique previously described.[15] Therefore the perchlorate salt was used for hydrolysis studies of $Cr(NH_3)_5Cl^{++}$. That this method was a valid technique for measurement of rate constants was confirmed by a few runs followed spectrophotometrically. For instance, values of 5.70×10^{-3} min.$^{-1}$ and 5.75×10^{-3} min.$^{-1}$ were obtained for the chloro complex by the spectrophotometric and polarographic techniques respectively in 0.1 M perchloric acid at $45°$.

Kinetic Measurements.—Techniques for making measurements of rates of reaction with half times of only a fraction of a minute had to be developed since the hydrolysis rates were fast in studies involving high temperatures, highly alkaline solutions or the iodo complex. The technique involved removing samples from the rapidly reacting mixture, quenching the reaction and making the polarographic measurements rapidly enough[16] so that there was less than 5% reaction during the time required for measurement. Furthermore, care was taken that the fraction of reaction during measurement was approximately the same for each sample and then the slope of the first order plot was not affected.

Since more than a trace of gelatine used as maximum suppressor seriously distorts the chromium reduction waves, a flexible[17] salt bridge which is terminated by a porous (not sintered) glass plug was used instead of the usual gelatine or agar plug.

Procedure.—A solution of the appropriate pH and salt concentration was thermostatted to within $0.1°$ of the desired temperature with light excluded to avoid possible photochemical effects. Finely powdered chromium salt was then added and the solution agitated to dissolve the salt quickly. After appropriate time intervals 5 or 10 ml. samples were withdrawn for analysis and added to enough perchloric acid to neutralize any base present and to leave the solution about 0.1 M in excess acid. A measured trace of gelatine was added as maximum suppressor, the solution was bubbled free of dissolved air and the polarograms were run. In studies involving the bromide or chloride complex at either $25°$ or $45°$ the polarograms were run at $25°$, while for those at $0°$ the polarograms were run at $0°$. In all studies of the iodo complex the polarograms were run at $0°$.

Results

It was desirable to determine the effect of pH on the reaction rate over the entire pH range. This effect could be best studied in buffered solutions and since it is known that anions[18-20] can affect the rate of reaction in an unpredictable way it was necessary to prepare a series of buffers in which only a single kind of anion was present. Consequently recourse was had to a series of amine-perchlorate buffers. To expose any possibility of an effect characteristic of a particular buffer, they were made up so that the highest pH of one buffer system overlapped with the lowest pH of the next buffer system. The rates in 0.01 M perchloric acid with 0.09 M lithium, sodium, potassium, ammonium, anilinium, pyridinium, 2-aminopyridinium or diethylammonium perchlorates were identical within the limits of the precision with which the measurements were made. In the various buffer solutions free base was present, but this appears to have had no effect since the rate was constant over the pH range 1 to 10. It was con-

(14) J. A. Friend and P. W. Smith, J. Phys. Chem., 63, 314 (1959).

(15) W. E. Harris, J. Chem. Ed., 35, 408 (1958).

(16) In preparation.

(17) D. N. Hume and W. E. Harris, Ind. Eng. Chem., Anal. Ed., 15, 465 (1943).

(18) P. J. Garrick, Trans. Faraday Soc., 34, 1088 (1938).

(19) M. Ikuta, H. G. McAdie and W. M. Smith, Can. J. Chem., 34, 1361 (1956).

(20) H. Taube and F. A. Posey, J. Am. Chem. Soc., 75, 1463 (1953).

cluded that neither the free bases nor the cations associated with these buffers affected the hydrolysis reactions. For example, the result at pH 8 in Fig. 1 was obtained from separate runs using 2-aminopyridine buffer in one and ammonia buffer in the other.

It is apparent from the data obtained that the reaction leading to hydrolytic removal of halogen from the halopentamminechromium (III) complexes can be divided into two portions on the basis of its pH dependence. Figure 1 and the data of Table I illustrate that the reaction is pH inde-

TABLE I

RATE CONSTANTS FOR HYDROLYSIS OF THE HALOPENTAMMINECHROMIUM (III) IONS AT HIGH AND LOW pH IN 0.1 M PERCHLORATE SOLUTIONS

Reactant	$Cr(NH_3)_5Cl^{++}$	$Cr(NH_3)_5Br^{++}$	$Cr(NH_3)_5I^{++}$
k_1 (pH 1-10) min.$^{-1}$	5.6×10^{-4b}	6.2×10^{-3c}	6.0×10^{-2b}
k_1 (previous work[a])	4.8×10^{-4b}	3×10^{-3b}	10^{-2d}
k_b 1. mole^{-1} min.$^{-1}$	0.11^e	4.3^e	220^b

[a] Ref. 9; [b] 25.0°; [c] 25.3°; [d] 0.0°.

pendent over the range 1-10 and that the rate is linearly dependent upon the hydroxide ion concentration above pH 11.5. In the pH range 1 to 10 where the rate remains constant, the rate law

$$\text{rate} = k_1 [\text{complex}]$$

is followed. The data of Table I show that the rates of hydrolysis increase in the order chloro, bromo and iodo. The decrease in rate shown in Fig. 1 which was observed at pH less than one was greater than can be accounted for by the normal electrolyte effect.[21] It appears to be specifically associated with the hydrogen ion but the reason for this is not clearly understood. Above a pH of about 11.5 the reaction obeys the rate law,

$$\text{rate} = k_b [\text{complex}][\text{OH}^-]$$

This expression is valid even in 1 M sodium hydroxide if the effect of electrolyte is taken into account as shown in Fig. 1. The second order rate constants again increase in the order chloro, bromo, iodo as shown in Table I.

Selbin and Bailar[10] have observed that the concentration of complex in solution affects the rate. The results of experiments at two different pH values and with three different concentrations of complex varying over two orders of magnitude are shown in Table II. It can be concluded from

TABLE II

RATE CONSTANT FOR HYDROLYSIS OF $Cr(NH_3)_5Br^{++}$ AS A FUNCTION OF CONCENTRATION OF THE COMPLEX

M	$k_1 \times 10^3$ min.$^{-1}$ 0.1 M HClO$_4$	$pH = 9^a$
10^{-4}	6.5	6.2
10^{-3}	6.2	6.1
10^{-2}	6.2	6.1

[a] NH_4^+ –NH_3 buffer at $pH = 9$. $NH_4ClO_4 = 0.1$ M.

these data that the rate constant is substantially independent of the initial chromium concentration. The rates of reaction were measured as a function
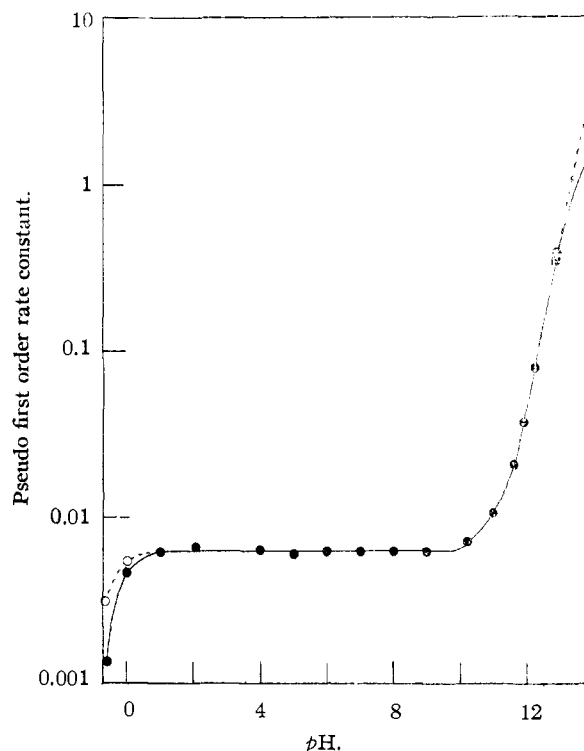
(21) In preparation.

Fig. 1.—Effect of pH on the rate constant for hydrolysis of $Cr(NH_3)_5Br^{++}$ at 25.3°. All solutions in the pH range 1 to 13 were 0.1 M in electrolyte. Above pH 13 and below pH 1, the open circles and dotted lines represent the data corrected for the additional electrolyte necessarily present.

of temperature over the ranges 0 to 25° for the iodo, 0 to 45° for the bromo and 0 to 60° for the chloro. Activation energies and frequency factors calculated from these data are shown in Table III. Estimated precision for these data is ± 0.3 kcal. for the activation energies.

TABLE III

ACTIVATION ENERGIES AND FREQUENCY FACTORS FOR HYDROLYSIS OF HALOPENTAMMINECHROMIUM (III) COMPLEXES IN 0.1 M PERCHLORATE SOLUTIONS

Reactant	$Cr(NH_3)_5Cl^{++}$	$Cr(NH_3)_5Br^{++}$	$Cr(NH_3)_5I^{++}$
Activation energy, pH 1 to 10,[a] kcal.	22.4	21.5	21.4
Activation energy, pH 11.5+, kcal.	26.7	26.3	26.8
Frequency factor, pH 1 to 10, min.$^{-1}$	1×10^{13}	4×10^{13}	3×10^{14}
Frequency factor, pH 11.5+, 1. mole^{-1} min.$^{-1}$	5×10^{17}	8×10^{18}	2×10^{19}

[a] Since this paper was written, it has come to the attention of the authors that A. Vlcek (*Discussions Faraday Soc.*, 26, 164 (1958)) has also measured activation energies at low pH. The values reported here are in agreement with those of Vlcek.

Discussion

The data presented in Fig. 1 show that the hydrolysis of the halopentamminechromium (III) complexes proceeds by two mechanisms which differ in their pH dependencies. At pH less than 10 the reaction obeys first order or pseudo first

order kinetics with dependence only on the concentration of the complex. Above $pH = 11.5$ second order kinetics are obeyed with linear dependence on the concentration of both the complex ion and the hydroxide ion. Thus, the chromium system follows the pattern, i.e., pH independent and pH dependent portions, which is now well established for the cobalt (III) system.[22] However, it is apparent that the pH dependent reaction begins to contribute importantly at a much higher pH (10) for chromium than for cobalt (5). In the chromium as in the cobalt system the rate constants increase as the leaving group is varied from chloride to bromide to iodide. The increase occurs regardless of whether it is the pH independent first order reaction or the pH dependent second order reaction. This would, of course, be expected regardless of the mechanism by which the halide ion is liberated provided bond breaking contributes to the rate determining step. Bond breaking contributes to the rate determining step of all except the hypothetical S_N2 lim mechanism.[22] It is surprising, then, to observe that the activation energy for the reaction is essentially independent of the halide being removed. Table III shows that the activation energy at pH 10 is about 22 kcal. and at pH 11.5 about 26.7 kcal. The variation in rate of hydrolysis as the halide is varied appears to originate in the pre-exponential factors. Rationalization of these observations can be obtained, without invoking an S_N2 lim intermediate, in terms of solvation in the activated complex.

In considering the solvolytic removal of halogen from a metal complex ion according to a reaction represented by equation II there will be seven principal energy terms to be considered.

$$Cr(NH_3)_5X^{++} + H_2O \longrightarrow Cr(NH_3)_5H_2O^{-++} + X^- \quad (II)$$

(1) bond rupture
(2) bond formation e.g: specific interaction of a solvent molecule with the metal ion of the complex
(3) solvation of the reactant complex ion
(4) solvation of the entering solvent molecule
(5) solvation of the product complex ion
(6) solvation of the product anion
(7) energy necessary to reorganize the ion to produce the transition state.

In a closely related series of complexes such as is being considered here, it is likely that the only terms that will differ significantly as X is varied are (1) and (6). Estimates of the values of these two terms are shown in Table IV for an analogous

TABLE IV

Energy Terms Contributing to Bond Rupture in MnX

| Anion	Anion solvation energy, $(E_s),^a$ kcal.	Energy of bond rupture, $(E_D),^b$ kcal. $MnX^+ \rightarrow$ $Mn^{++} + X^-$	$E_D - E_s$
F	−122.6	152	29
Cl	−88.7	146	57
Br	−81.4	141	60
I	−72.1	129	57

^{a} Ref. 25. ^{b} Bond dissociation energies from T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publication, London 1954; ionization potentials and electron affinities from T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952.

(22) Ref. 3.

ion (manganese (II)), since Cr X bond energies are not presently available.

The data in Table IV show that rupture of an MnX bond does not depend upon the strength of the bond when the reaction is carried out in aqueous solution. Solvation of the anion just compensates for the differences in bond strength through the sequence chloride to bromide to iodide. That this cancellation is a general phenomenon and not a coincidence based upon the choice of the model system is evident from values of the enthalpy of dissociation of the complexes $CrCl_2^+$, $CrBr_2^+$ and $ZnCl^+$, $ZnBr^+$, ZnI^- in aqueous solution as compiled by Bjerrum, Schwarzenbach and Sillen.[23] The enthalpies are 10.1 and 11.6 kcal. for the chloro- and bromochromium (III) complexes and 0 kcal. for each of the zinc complexes. If the transition state for the hydrolysis reaction corresponds to about the same charge separation in the case of each of the chloro-, bromo- and iodo-complexes, then the relative contributions of anion solvation and bond rupture ought to be the same in each of the three complexes. If this effect is able to compensate for change in bond strength in the formation of the separated ions, then it ought also to compensate in the process involving charge separation which leads eventually to the separated ions. As a consequence the small variation in the energy of activation which was observed ought not to be surprising. This argument would suggest that the solvent is an active participant in the transition state.

However, as pointed out above the rate of hydrolysis does vary with the nature of the halogen. It is shown by the data in Table III that this variation is primarily due to differences in the pre-exponential factors through the series of complexes. If the frequency factors are taken to be constant and to have values typical of gas phase reactions (10^{13} sec.$^{-1}$ for unimolecular and 10^{11} sec. for bimolecular[24]), then the differences in rates are correlatable in terms of a variation in the entropy of activation. For the chloro-, bromo- and iodopentamminechromium (III) complexes these values are 0, +2.8 and +6.8 e.u., respectively, if the reaction is unimolecular and +9.2, +11.9 and +15.8 e.u., respectively, if the reaction is bimolecular. Thus, it would seem that the variation in the entropy of activation is characteristic of the complexes which are being considered regardless of the mechanism by which reaction occurs. However, an estimate of the gas phase entropies of bond rupture show no variation as the breaking bond varies from chloro to bromo to iodo. This indicates that the trend in entropy values observed in the reaction cannot be primarily associated with the rupture of the chromium to halogen bond. It might then be found that the variation is related indirectly to bond rupture. Such an indirect relation would be found in terms of the orienting effect of the polar transition state upon the solvent sheath. The energy associated with this interaction has already been found necessary

(23) Stability Constants, Part II, Inorganic Ligands, The Chemical Society London, 1958.
(24) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

in explaining the invariance of the energy of activation from one halo complex to another. The reorientation of the solvent around the reacting complex must then be a real effect. The variable portion of this effect must be associated with the leaving group since it would appear to be the only variable within the system. If this is a correct assumption, then the differences in the entropy of activation between the complexes ought to roughly parallel the differences in the thermodynamic entropies of the reactions corresponding to I. Latimer and Jolly[25] have suggested a procedure for the estimation of the thermodynamic entropy of any reaction of this type. In general form this reaction is rewritten

halogen (bound) + $H_2O_{(1)}$ ⟶

$$H_2O(\text{bound}) + \text{halide (aq)} \quad \text{(III)}$$
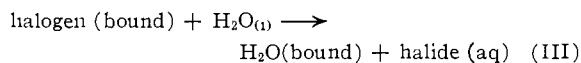
Values that have been estimated[26] for the various entropy terms in III are 9.4 e.u. for bound water, 21 e.u. for free bromide, 16.7 for free water and 9 for bound bromide. These values lead to a calculated value for ΔS_I for reaction 1 of +4.7 e.u. A similar treatment applied to the hydrolysis of the chloro and iodo complexes leads to values of +0.8 and 7.2 e.u., respectively. These values have

(25) W. M. Latimer and W. L. Jolly, J. Am. Chem. Soc., **75**, 1548 (1953).

(26) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., New York, N. Y., 1952.

approximately the same relationship to one another as do the entropies of activation for the hydrolysis reaction. The principal difference between the thermodynamic entropies of the reaction leading to the replacement of halogen by water in the complex is the entropy of formation of the various halide ions in solution (Cl⁻, 15 e.u., Br⁻, 21 e.u.; I⁻ 27 e.u.).[27] A correlation between the entropy of activation for the hydrolysis reaction and the thermodynamic entropy of hydration of the ion seems to be reasonable on the basis of this data. The relative order and magnitudes of these values is not greatly different from that observed between the entropies of activation for the three complexes. Such considerations as these indicate very strongly that the solvent sheath is a direct participant in both the pH independent and the pH dependent reactions. Furthermore the similarity of the variation of the entropy terms in the two reactions which behave so differently to changes in the pH indicates that both have transition states which interact with the solvent sheath in the same way. There is however, no indication as to whether a single solvent molecule is specifically involved in the transition state. It is not possible then to assign these reactions on the basis of the observations reported in this paper to either of the S_N1 or S_N2 classifications.

(27) W. M. Latimer, K. S. Pitzer and C. M. Slansky, J. Chem. Phys., **7**, 108 (1939).

[Contribution from the Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa]

# cis-Dichlorodiammineplatinum(II). Acid Hydrolysis and Isotopic Exchange of the Chloride Ligands[1]

By John W. Reishus and Don S. Martin, Jr.

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The acid hydrolysis of cis-[Pt(NH₃)₂Cl₂] has been studied at 25 and 35°   For the first acid hydrolysis

$$cis\text{-}[Pt(NH_3)_2Cl_2] + H_2O \longrightarrow cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$
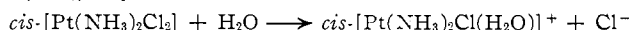
the equilibrium constant, K_1, is 3.3 × 10⁻³ mole/l. and the rate constant, k_1, is 2.5 × 10⁻⁵ sec.⁻¹ at 25°. There is no significant direct exchange between the chloride ligands of cis-[Pt(NH₃)₂Cl₂] and Cl⁻. For the second acid hydrolysis

$$cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \longrightarrow cis\text{-}[Pt(NH_3)_2(H_2O)_2]^{++} + Cl^-$$
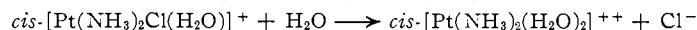
the equilibrium constant K_2 is 4 × 10⁻⁵ mole/l., at 25°. The exchange of chloride with cis-[Pt(NH₃)₂Cl(H₂O)] occurs at a rate which is chloride-independent and is characterized by a first order rate constant, $k_2 = 3.3 × 10^{-5}$ sec.⁻¹ at 25°. It appears likely that this exchange also occurs by only an acid hydrolysis mechanism.

Introduction

When the compound which was originally designated by Werner[2a] as cis-[Pt(NH₃)₂Cl₂] is dissolved in H₂O, the solution possesses the very low conductivity of a non-electrolyte. However, an increase in the conductivity of its solutions has been noted by a number of investigators.[2-4] Jensen[5] proposed that the increase in conductivity

(1) Contribution No. 924. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
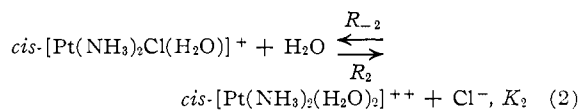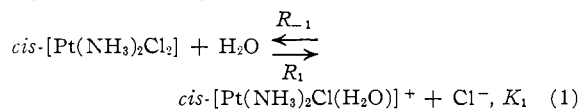
(2) (a) A. Werner, Z. anorg. Chem., **3**, 267 (1893). (b) A. Werner and A. Miolati, Z. physik. Chem., **12**, 49 (1893).

(3) H. D. K. Drew, F. W. Pinkard, W. Wardlaw and E. G. Cox, J. Chem. Soc., 988 (1932).

(4) D. Banerjea, F. Basolo and R. G. Pearson, J. Am. Chem. Soc., **79**, 4055 (1957).

(5) K. A. Jensen, Z. anorg. Chem., **229**, 252 (1936).

of the solutions upon aging can be explained in terms of acid hydrolysis or aquation of the chloride ligands according to

$$cis\text{-}[Pt(NH_3)_2Cl_2] + H_2O \underset{R_1}{\overset{R_{-1}}{\rightleftarrows}}$$
$$cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-, K_1 \quad (1)$$

$$cis\text{-}[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \underset{R_2}{\overset{R_{-2}}{\rightleftarrows}}$$
$$cis\text{-}[Pt(NH_3)_2(H_2O)_2]^{++} + Cl^-, K_2 \quad (2)$$

The R's are the rates for the indicated reactions and the K's are the equilibrium constants. In the present work, the rate expressions assumed to apply are