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Thermodynamics of Metal Halide Coordination. II. $\Delta H°$ and $\Delta S°$ Values for Stepwise Formation of HgX_2 (X = Cl, Br, I) in Aqueous Solution at 8, 25, and 40°[1a]

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Received July 13, 1963

$\Delta H°$ and $\Delta S°$ values have been determined for the stepwise reaction at 8, 25, and 40° of X^- with Hg^{+2} to form $HgX_2(aq)$ (X = Cl, Br, I) and $HgX_2(s)$ (X = I). All data are valid in a solvent 0.10 *F* in $HClO_4$ and 0.40 *F* in $NaClO_4$. Relative Hg–X bond strengths in the gaseous phase and in aqueous solution are discussed. Trends in $\Delta H°$ and $\Delta S°$ values are discussed in terms of the thermodynamic quantities involved.

Introduction

Equilibrium constants and $\Delta G°$ values were reported in a previous communication[2] for the stepwise interaction at 7, 25, and 40° of X^- (X = Cl, Br, I) with Hg^{+2} to form HgX_2. The similar electronic structures of these ligands make them an interesting series to use for a study of the relative magnitudes of the thermodynamic quantities associated with complex ion formation by d^{10} metal ions in aqueous solution. $\Delta H°$ values as a function of temperature for the stepwise interaction of X^- with Hg^{+2} to form HgX_2 should be useful in better understanding the nature of the Hg–X bond. However, few heats for these reactions are available at any temperature, and none has been reported as a function of temperature.

Calorimetric heats have been reported for the stepwise reaction at 25° of Cl^- with Hg^{+2} to form $HgCl^+$ [3,4] and $HgCl_2$,[3] and for the stepwise interaction of Br^- and I^- with Hg^{+2} to form $HgBr^+$ and HgI^+.[4]

Calorimetric $\Delta H°$ data are reported here for the stepwise reaction at 8, 25, and 40° of X^- with Hg^{+2} to form HgX_2. $\Delta S°$ values are calculated from these and corresponding $\Delta G°$ values.

A thermometric titration procedure is used to obtain heats for the stepwise reaction of X^- with Hg^{+2}. The advantages of the thermometric titration procedure in determining heats for reactions involving simultaneous equilibria have been discussed.[5]

The standard state for the solute species in this study is a hypothetical 1 *M* solution in which the ionic strength, μ, is 0.5 *M*. The superscript degree sign when used with the thermodynamic quantities refers to the standard changes in these quantities with respect to this standard state.

Experimental

Materials.—Reagent grade NaCl (Baker and Adamson), NaBr (J. T. Baker Chemical Co.), NaI (Mallinckrodt), $HClO_4$ (Baker and Adamson), HgO (Baker and Adamson), and NaOH (Baker and Adamson) were used in the preparation of solutions for the enthalpy determinations. A standard stock mercuric perchlorate solution was prepared by dissolving a weighed amount of HgO in a standard perchloric acid solution. Standard NaCl, NaBr, and NaI solutions were prepared by dissolving weighed amounts of the salts in boiled distilled water. NaI solutions were prepared and stored under an atmosphere of nitrogen.

Procedure.—The thermometric titration equipment used in the heat determinations has been described.[5,6] All solutions to be titrated were mixed and subsequently equilibrated at the desired temperature for at least 48 hr. prior to use. The calorimeter environment temperatures used in the study (8, 25, and 40°) were maintained to ±0.1° during the course of a series of determinations at the given temperature. All data are valid for $\mu = 0.5$. Mercuric ion hydrolysis was minimized by having the solutions 0.1 *F* in $HClO_4$. The remainder of the ionic strength was made up primarily of $NaClO_4$.

Calculations.—Analysis of thermometric titration data has been described for several types of systems.[5,6] A typical thermometric titration curve obtained by titration of a Hg^{+2} solution with NaCl is shown in Fig. 1a. Assignment of heats of reaction to the correct species requires a knowledge of the equilibrium constants for the system. From these equilibrium constants and appropriate mass balance expressions, one obtains the species distribution shown in Fig. 1b. The total measured heat change can then be apportioned to the *n* species present by solving *n* simultaneous equations involving the total heat produced at each of *n* points on the curve, the percentage distribution of each of the *n* species at each point, and the *n* unknown heats of formation of the several species present. A sharp end point corresponding to stoichiometric HgX_2 formation was observed in each thermometric titration (Fig. 1a). Calculation shows that the concentrations of the Hg^{+2}, HgX^+, HgX_3^- and HgX_4^{-2} species at this end point (Fig. 1b) are negligible when compared to that of the HgX_2 species. Because of the stoichiometric formation of $HgX_2(aq)$ from HgX^{+2} and $2X^-$ the over-all heat, $\Delta H_{12}°$, for this reaction may be obtained directly from the thermometric tiration curve without use of consecutive equilibrium constants. $\Delta H_{12}°$ values are, therefore, known with greater certainty than are the consecutive heats of formation, since assignment of these latter heats is made using formation constants of limited accuracy. The appearance of this end point also provided evidence that the reaction between the sodium halide titrant and Hg^{+2} is rapid.

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(1) (a) Supported by the Atomic Energy Commission, Contract No. AT(04-3)-299; (b) to whom correspondence concerning this article should be addressed; (c) supported by a Public Health Service predoctoral fellowship (No. GF-17, 337) from the Division of Research Grants, Public Health Service.

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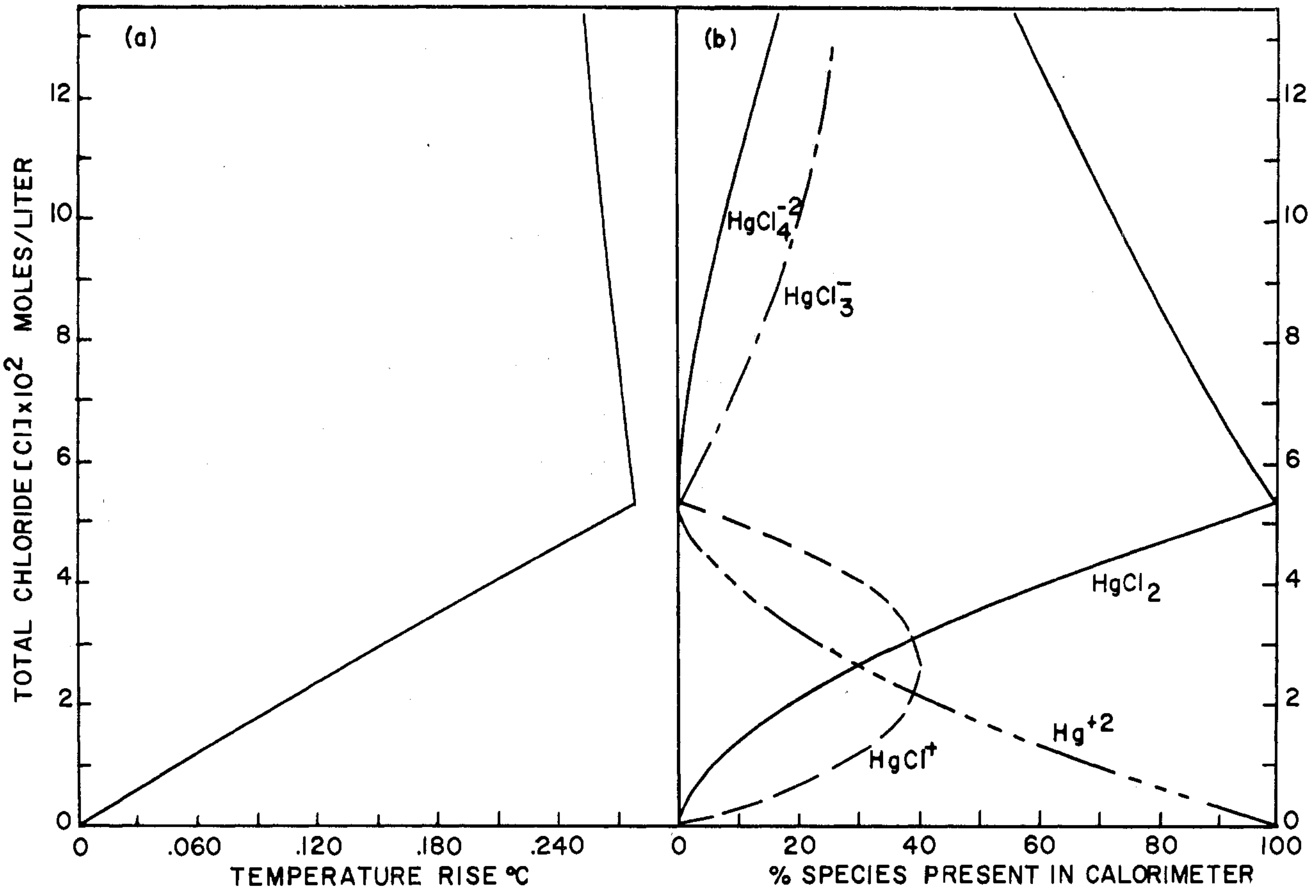

Fig. 1.—Correlation of temperature rise with per cent species present in calorimeter during the titration of Hg^{+2} with NaCl.

Individual ΔH values at a given total mercury concentration, $(Hg)_T$, were calculated from the average of 3 to 10 separate determinations ($\mu = 0.50$ in all determinations). At 25° five to ten sets of such determinations were made at various $(Hg)_T$ concentrations covering a range of $(Hg)_T$ concentrations from 1×10^{-3} to 2×10^{-2} *M* (in the case of HgI_2, the $(Hg)_T$ concentration was varied from 7×10^{-5} to 33×10^{-2} *M* in order to obtain as a final product both $HgI_2(aq)$ and $HgI_2(s)$). At 8 and 40° two to five sets of determinations were carried out through a $(Hg)_T$ concentration range of 1×10^{-3} to 1×10^{-2} *M*. $\Delta H°$ values reported in this study were calculated in each case by extrapolation of ΔH *vs.* $(Hg)_T$ concentration plots to $(Hg)_T$ concentration = 0 ($\mu = 0.50$). This extrapolated $\Delta H°$ value usually agreed closely with the average of the ΔH values, since there was little or no significant change in the ΔH values with $(Hg)_T$ concentration within the limits of error assigned these values.

All calculations were carried out on an IBM650 electronic computer.

HgI_2 Solubility.—Because of the low solubility of HgI_2 a precipitate appeared during the thermometric titrations at 8 and 25° before the stoichiometric HgI_2 end point was reached. Therefore, the solubility of HgI_2 was determined[2] in the solvent at 8, 25, and 40°. These solubility data allow calculation of $\Delta G°$ values at these temperatures for the reaction $HgI_2(s) = HgI_2(aq)$ and provide an independent determination (based on the varation of the equilibrium constant with temperature) of the $\Delta H°$ value for this reaction.

TABLE I

$\Delta H°$ VALUES AS A FUNCTION OF TEMPERATURE FOR THE STEPWISE ($\Delta H_1°$ AND $\Delta H_2°$) AND OVER-ALL ($\Delta H_{12}°$) REACTION OF X^- WITH Hg^{+2} TO FORM HgX_2

$\mu = 0.50$. Previous work is given in parentheses.

		—$-\Delta H°$ values, kcal./mole—		
Reaction	X^-	8°	25°	40°
$Hg^{+2}(aq) + X^-(aq) = HgX^+(aq)$ $(-\Delta H_1°)$	Cl^-	6.7_5	5.5 (5.9)[a] (4.8)[b]	5.6
	Br^-	11.1	10.2 (10.6)[b]	10.0
	I^-	18.9	18.0 (17.6)[b]	17.3
$HgX^+(aq) + X^-(aq) = HgX_2(aq)$ $(-\Delta H_2°)$	Cl^-	7.3	7.2_5 (6.9)[a]	6.9
	Br^-	11.5	11.0	11.4
	I^-	15.3	16.2	17.2
$HgX^+(aq) + X^-(aq) = HgX_2(s)$	I^-	22.6	23.1_5	23.6_5
$Hg^{+2}(aq) + 2X^-(aq) = HgX_2(aq)$ $(-\Delta H_{12}°)$	Cl^-	14.05	12.75 (12.80)[a]	12.50
	Br^-	22.60	21.23	21.40
	I^-	34.0	34.1_5	34.5
$Hg^{+2}(aq) + 2X^-(aq) = HgX_2(s)$	I^-	41.50	41.10	41.00

[a] Reference 3, $\mu = 0.5$. [b] Reference 4, $\mu = 0$.

Results

In Table I are presented $\Delta H°$ values determined in this study together with recently reported values for the stepwise ($\Delta H_1°$ and $\Delta H_2°$) and over-all ($\Delta H_{12}°$) reaction of $X^-(aq)$ with $Hg^{+2}(aq)$ to produce $HgX_2(aq)$ (also $HgX_2(s)$ in the case of HgI_2) at 8, 25, and 40° and $\mu = 0.50$. For reasons pointed out in the Experimental section, $\Delta H_{12}°$ values are more precise than are either the $\Delta H_1°$ or $\Delta H_2°$ values. The precision of the $\Delta H_{12}°$ data is estimated to be ±0.1 kcal./mole, while that of the $\Delta H_1°$ and $\Delta H_2°$ data is estimated to be

±0.2 kcal./mole. A detailed listing of all experimental ΔH values is available.[7]

$\Delta H_2°$ and $\Delta H_{12}°$ values for the formation of $HgI_2(aq)$ were obtained from the determinations carried out at $(Hg)_T$ concentrations less than 2×10^{-3} *M*, where no $HgI_2(s)$ precipitated. Combination of these data with corresponding data at higher $(Hg)_T$ concentrations where $HgI_2(s)$ precipitated gave values for the heat of the reaction $HgI_2(aq) = HgI_2(s)$. Values of -7.2 ± 0.5 and -6.9 ± 0.5 kcal./mole were obtained in this manner for the heats of the above reaction at 8 and 25°, respectively. These values agree well with those at 16, 25, and 32° (−7.6, −7.0, and −6.4 kcal./mole, respectively), calculated from the solubility data[2] by use of the second-law method.

$\Delta H°$ values in Table I were combined with $\Delta G°$ values[2] to obtain the $\Delta S°$ values which are given in Table II. $\Delta S°$ values at 25° were calculated using $\Delta G°$ values derived from equilibrium constants[2] taken from work reported by Sillén. The estimated uncertainty in $\Delta S°$ values is ±1.5 e.u. for the $\Delta S_1°$ and $\Delta S_2°$ values and ±1.0 e.u. for $\Delta S_{12}°$ values.

TABLE II

$\Delta S°$ VALUES AS A FUNCTION OF TEMPERATURE FOR THE STEPWISE ($\Delta S_1°$ AND $\Delta S_2°$) AND OVER-ALL ($\Delta S_{12}°$) REACTION OF X^- WITH Hg^{+2} TO FORM HgX_2; $\mu = 0.50$.

		$\Delta S°$ values, e.u.		
Reaction	X^-	8°	25°	40°
$Hg^{+2}(aq) + X^-(aq) = HgX^+(aq)$ ($\Delta S_1°$)	Cl^-	9.0	12.4 (11.9)[a]	12.2
	Br^-	4.0	7.1	7.9
	I^-	−5.3	−1.5	1.5
$HgX^+(aq) + X^-(aq) = HgX_2(aq)$ ($\Delta S_2°$)	Cl^-	4.7	5.3 (4.8)[a]	6.2
	Br^-	−0.6	1.1	−0.9
	I^-	−1.4	−4.2	−6.4
$HgX^+(aq) + X^-(aq) = HgX_2(s)$	I^-	−6.5	−8.6	−10.8
$Hg^{+2}(aq) + 2X^-(aq) = HgX_2(aq)$ ($\Delta S_{12}°$)	Cl^-	13.7	17.7 (16.7)[a]	18.4
	Br^-	3.4	8.2	7.0
	I^-	−6.7	−5.7	−4.9
$Hg^{+2}(aq) + 2X^-(aq) = HgX_2(s)$	I^-	−11.8	−10.1	−9.3

[a] $\Delta S°$ values at 25° calculated from $\Delta G°$ values derived from equilibrium constants determined in this laboratory.[2]

Discussion

The enthalpy values determined in the present study (Table I) for the formation at 25° in aqueous solution of $HgCl^+$ and $HgCl_2$ from Hg^{+2} and Cl^- agree well with those of Gallagher and King,[3] which also were determined at $\mu = 0.50$. The enthalpy values for the formation of HgX^+ at 25° reported by Malcolm, *et al.*,[4] are valid at $\mu = 0$, and, therefore, may be compared only qualitatively with the data in the present study. Calculation of the standard heats of formation of $HgX_2(s)$ from the elements in their standard states by use of a thermochemical cycle yields values of −54.4, −40.8, and −26.2 kcal./mole for $HgCl_2(s)$, $HgBr_2(s)$, and $HgI_2(s)$, respectively. The values used in the thermochemical calculations were taken from Table I (this paper), ref. 8, and Latimer.[9] These values agree well with the standard heats of formation given in ref. 8 (−55, −40.5, and −25.2 kcal./mole) for the formation of the corresponding compounds at 25°.

As previously mentioned,[2] $\Delta G°$ values for the stepwise and over-all formation of $HgX_2(aq)$ from $Hg^{+2}(aq)$ and $X^-(aq)$ are surprisingly unaffected by temperature. This constancy of the $\Delta G°$ values can be understood from the trends observed in the corresponding $\Delta H°$ and $\Delta S°$ values.

The following trends in $\Delta H°$ values can be seen from the data in Table I. (a) At a given temperature $-\Delta H°$ values increase in the order Cl, Br, I. This trend parallels the observed stability order ($\Delta G°$) in aqueous solution of the three ligands with mercuric ion. (b) $-\Delta H_2°$ values are greater than $-\Delta H_1°$ values for Cl and Br, but less for I; however, this anomaly disappears with increase in temperature. (c) The effect of temperature on $-\Delta H_1°$ and $-\Delta H_2°$ is more noticeable in the case of I than in Br and Cl, and the effect on $\Delta H_1°$ is opposite to that on $\Delta H_2°$ in the case of I.

By use of a thermodynamic cycle it is possible to calculate heats for the reaction $Hg^{+2}(g) + 2X^-(g) = HgX_2(g)$. Data for this calculation were taken from Table I of this paper (heats of formation of $HgX_2(aq)$ and heat of solution of $HgI_2(s)$) and the literature (heats of sublimation and solution of $HgCl_2(s)$ and $HgBr_2(s)$)[8-10] without attempting to correct the several thermochemical quantities to the same μ value. Such corrections would be expected to be small, as can be seen in Table I by the small variation of ΔH with μ (comparison of present results with those of ref. 4). Values of −608, −600, and −596 kcal./mole calculated for the formation of $HgCl_2(g)$, $HgBr_2(g)$, and $HgI_2(g)$, respectively, show the Hg–X bond strength to decrease in the order Hg–Cl, Hg–Br, Hg–I. The data in Table I show the opposite trend to exist in aqueous solution. This reversal in trend, as can be seen in the thermochemical cycle, is a result of the relative magnitudes of the heats of hydration of the halides, which becomes more positive in the order Cl^-, Br^-, I^-. Analysis of the heats of formation of metal dihalides in the gas phase shows the order of stability ($\Delta H°$) to be Cl > Br > I. Although mercury(II) dihalides also show this stability order, the Hg–I bond is more stable in comparison to the Hg–Cl and Hg–Br bonds than would be expected from electrostatic bonding alone. This extra stability undoubtedly arises from greater "total" covalency. Orbital overlap calculations are now being undertaken in an attempt to determine the relative amounts of σ and π bonding in the mercury(II) halides. $\Delta H°$ values calculated from thermochemical data[8,9] for the reaction of gaseous Hg and X atoms to form the gaseous HgX_2 are −106, −89, and −70 kcal./mole for the chloride, bromide,

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[7] J. D. Hale, Ph.D. Thesis, Brigham Young University, July, 1963.

[8] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500 (1952).

[9] W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solution," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

[10] O. Kubaschewski and E. L. L. Evans, "Metallurgical Thermochemistry," 3rd Ed., Pergamon Press, Inc., New York, N. Y., 1958.

and iodide, respectively, and, thus, show the same order of stability (ΔH°) as seen above for the reaction of the gaseous halide and mercuric ions.

The effect of temperature on $-\Delta H_1^\circ$ and $-\Delta H_2^\circ$ in the case of I can be explained by analysis of the heats of hydration of the products and reactants. The fact that $-\Delta H_1^\circ$ increases as temperature decreases indicates that the heat of hydration of the final product, $HgI^+(aq)$, is more temperature dependent than is that of the reactants. $-\Delta H_2^\circ$ decreases as temperature decreases because HgI^+ is now a reactant rather than a product in the reaction. Heats of hydration of $HgBr^+$ and $HgCl^+$ are affected to a lesser extent by temperature and consequently ΔH_1° and ΔH_2° for Br and Cl are not as temperature dependent. This trend is also apparent in ΔS_1° and ΔS_2° for the corresponding reactions. ΔH_{12}° shows little variation with temperature since the effects of the intermediate species are subtracted out in each case.

The following trends in ΔS° values are observed from the data in Table II. (a) At a given temperature, values of ΔS° decrease in the order Cl, Br, I. This trend parallels the solvent ordering effect of the halide ions. (b) ΔS_2° values are more negative at each temperature than are corresponding ΔS_1° values in the cases of Cl and Br. The ΔS_2° value in the case of I is more positive at 8°, but less positive at 25 and 40°, than is the ΔS_1° value. (c) The effect of temperature on $-\Delta S_1^\circ$ and $-\Delta S_2^\circ$ is more noticeable in the case of I than in that of either Cl or Br, and the effect on $-\Delta S_1^\circ$ is opposite to that on $-\Delta S_2^\circ$, especially in the case of I.

The ΔS° values for the stepwise and over-all formation of $HgX_2(aq)$ from $Hg^{+2}(aq)$ and $X^-(aq)$ may be divided into two quantities.[11] These are (a) the cratic portion, *i.e.*, that which deals with the number of particles involved in the reaction and is negative for the reactions under consideration since two particles combine to form one and (b) the unitary portion, *i.e.*, that which depends on the ordering ability that the products and reactants have toward the solvent. The unitary portion is positive in the reactions considered here since the reactants carry greater charge than do the products. The ΔS° values in Table II become more positive in the order I, Br, Cl as a result of the relative solvent ordering abilities of these halide ions, indicating an increasing importance of the unitary term in the above order.

At 25° the absolute ionic entropies ($S_{H^+}^\circ = 0$) of HgI^+, $HgBr^+$, and $HgCl^+$ calculated from data in Table II and the literature[9] are approximately the same, *i.e.*, 19, 21, and 20 e.u., respectively. Absolute entropies at 25° of $HgI_2(aq)$, $HgBr_2(aq)$, and $HgCl_2(aq)$ calculated in a similar manner are 41, 41, and 39 e.u., respectively.

From the trends observed in ΔH° and ΔS° it is apparent why ΔG° values are constant with temperature. ΔH° and ΔS° values are affected in the same manner by similar temperature dependent factors. Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, increases in ΔH° and ΔS° cancel the effect of each other.

Acknowledgments.—The authors gratefully acknowledge the assistance of Miss Judy Gates, Mr. Don Wrathall, and Mrs. Arlene Hill in solution preparation and analysis and in performing the thermometric titrations.

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The Mechanism of Substitution Reactions at Octahedral Sites. III.[1] Deuterium Isotope Effects in the Acid and Base Hydrolysis of Anionopentaamminechromium(III) Ions

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Received May 1, 1963

The hydrolysis of $Cr(NH_3)_5X^{+2}$, where X = Cl^-, Br^-, I^-, and SCN^-, has been examined in solvents containing varying proportions of H_2O and D_2O. For X = SCN^-, Cl^-, Br^-, and I^-, k_D/k_H takes on the values 0.43, 0.60, 0.95, and 1.51, respectively. The interpretation of these effects suggests a transition state which intimately involves one or more water molecules and is strongly polar but does not involve separated ions. In basic solution, the corresponding ratio of rate constants for the chloro complex is 1.37. The interpretation of these data suggests that the transition state for the base hydrolysis involves direct interaction and charge transfer between the hydroxide ion and the metal ion. The exchange of hydrogen between the solvent and the ammonia molecules of the solute has also been measured.

It has been shown previously[3] that the acid and base hydrolyses of halopentaamminechromium(III) ions follow essentially the same pattern as the cobalt(III) compounds with respect to their dependence on pH. Distinct regions are found in both systems. At low pH (<10 for Cr(III), <5 for Co(III)) the hydrolysis

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