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Kinetics and Mechanism of the Aquation and Base Hydrolysis of the Nitratopentaamminecobalt(III) Ion and Related Complexes

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The kinetics of aquation of $Co(NH_3)_5NO_3^{2+}$ in acidic perchlorate media of ionic strength $I = 0.12\ M$ are first order in complex concentration and are represented over the temperature range 0–59° by $\Delta H_1{}^*{}_{25} = 24.34$ kcal mol^{-1}, $\Delta S_1{}^*{}_{25} = 1.9$ cal deg^{-1} mol^{-1}, and $\Delta C_p{}^* = -20$ cal deg^{-1} mol^{-1}. Base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ is strictly first order in $[OH^-]$ up to 0.2 M at least, and first order in [complex]; the kinetic data are represented by $\Delta H_2{}^* = 28.8$ kcal mol^{-1} and $\Delta S_2{}^* = 43$ cal deg^{-1} mol^{-1}, from 2 to 35° at $I = 0.12\ M$ in perchlorate media. In either reaction, the Co–O bond is the one which is broken in the transition state. Linear relationships of unit slope exist between the free energy of activation and the standard free energy change of reaction in both aquation and base hydrolysis of complexes of the type $Co(NH_3)_5X^{2+}$. A dissociative mode of activation common to both types of reaction is indicated.

In connection with our continuing investigations of the systematics of kinetic parameters for substitution reactions of transition metal complexes, we have reassessed the existing data on the kinetics and equilibria of aquation and base hydrolysis of complexes of the acidopentaamminecobalt(III) series. These data are extensive, but in the case of $Co(NH_3)_5NO_3^{2+}$ there has been no reported investigation of the kinetics of base hydrolysis, and there is some disagreement in the literature concerning the activation energy for the aquation reaction.

The aquation of $Co(NH_3)_5NO_3^{2+}$ has been studied previously at 15 and 20°,[5] at 25°,[6,7] and between 35 and 50°,[8] but the Arrhenius activation energy reported[6] for the 15–25° range is greater (24.8 kcal mol^{-1}) than that for the 35–50° bracket[8] (23.4 kcal mol^{-1}), with similar uncertainties in the entropy of activation, $\Delta S_1{}^*$. We have sought to determine whether this is a real effect arising from a strongly negative heat capacity of activation, $\Delta C_p{}^*$, of ~ -70 cal deg^{-1} mol^{-1}; Chan[9] has attributed similar discrepancies between the published activation energies for the aquation of $Co(NH_3)_5Cl^{2+}$ to a $\Delta C_p{}^*$ of -49 cal deg^{-1} mol^{-1}, which is large enough to cause concern about the validity of comparing mean values of ΔH^* and ΔS^* for reactions of this type. It is also desirable to determine whether the slight inverse acid concentration dependence reported by Kuroda[8] represents a parallel hydroxide ion dependent pathway in aquation or is simply a "medium" (ionic strength) effect.

We have also determined activation parameters for the very rapid base hydrolysis of $Co(NH_3)_5NO_3^{2+}$. It will be shown that this reaction probably proceeds by the "conjugate base" (SN1CB) mechanism[10,11] outlined in mechanism A, below. This is now favored by most workers in the field as the mechanism operative in the analogous reactions of other $Co(NH_3)_5X^{n+}$ complexes; alternative proposals (mechanisms B and C) which have been put forward[12,13] cannot easily be reconciled with our experimental observations.

(A) Conjugate-base mechanism[10,11]

$$Co(NH_3)_5NO_3^{2+} + OH^- \rightleftharpoons (NH_3)_4Co(NH_2)NO_3^{+} + H_2O \xrightarrow{\text{slow}} (NH_3)_5CoOH^{2+} + NO_3^-$$

(B) Electron-transfer mechanism[12]

$$Co^{III}(NH_3)_5NO_3^{2+} + OH^- \xrightarrow{\text{slow}} Co^{II}(NH_3)_5NO_3^{+} + \dot{O}H \xrightarrow{\text{rapid}} Co^{II}(NH_3)_5^{2+} + NO_3^- \xrightarrow{+\dot{O}H} Co^{III}(NH_3)_5OH^{2+}$$

(C) SN2 mechanism[13]

$$Co(NH_3)_5NO_3^{2+} + OH^- \longrightarrow \{HO—Co(NH_3)_5—NO_3\}^{+*} \longrightarrow Co(NH_3)_5OH^{2+} + NO_3^-$$

Experimental Section

Materials.—Nitratopentaamminecobalt(III) nitrate was prepared by the standard method[14] and its authenticity was checked by its visible spectrum[15] in solution and by microanalysis for N and H. It was converted to the perchlorate salt as previously described.[16] Baker Analyzed perchloric acid (72%) was used without further purification and was employed in making pure $LiClO_4 \cdot 3H_2O$.

Aquation of $Co(NH_3)_5NO_3^{2+}$.—Reaction mixtures were prepared from the appropriate quantities of the complex $LiClO_4 \cdot 3H_2O$ and aqueous $HClO_4$, and the reaction was followed spectrophotometrically at 300 nm using a Cary Model 15 spectrophotometer. The sampling procedure was chosen according to the temperature.

(a) Runs at 0.00° were carried out using sealed Pyrex am

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poules of solution in well-mixed ice-water slush in a large dewar vessel; ampoules were withdrawn and opened as necessary.

(b) For experiments up to 15°, the solution was contained in stoppered vessels immersed in a thermostated bath (±0.01°), and samples were pipetted out periodically.

(c) For experiments at 25°, the solution was contained in the optical cell, which was kept in a thin polyethylene bag immersed in a thermostat. The cell was removed periodically and quickly cleaned prior to taking optical absorbance readings.

(d) At temperatures greater than 25°, the reaction was followed spectrophotometrically *in situ*, the optical cell being contained in a block (Cary Model 1540750) which was thermostated from an external circulating water bath. The solution containing the inert electrolytes was brought to thermal equilibrium in the cell in the block, and a predetermined quantity of the solid complex was introduced from a prewarmed hypodermic syringe (connected to the cell with a Teflon needle) by dissolving it in the solution which was flushed quickly into the syringe and back to the cell. This permitted the filling of the cell with reaction mixture with the minimum of premature aquation and a negligible disturbance of the solution temperature. The temperature of the cell was monitored continuously during a run, using an Atkins thermistor–thermometer in conjunction with a Beckman Ten-Inch recorder. The thermistors were checked against precision mercury thermometers, which were also used to measure the temperature in methods a–c above, and the mercury thermometers were calibrated against a Leeds–Northrup platinum resistance thermometer, which was referred to a water triple-point cell.

Base Hydrolysis of $Co(NH_3)_5NO_3^{2+}$.—The kinetics of the slower hydrolyses were followed spectrophotometrically, either *in situ* in the thermostated optical cell after rapid mixing of the NaOH and $Co(NH_3)_5NO_3^{2+}$ solutions (method I), or else by withdrawing aliquots from a thermostated reaction mixture, quenching them rapidly with dilute $HClO_4$, and measuring the optical density at leisure (method II). The faster reactions were studied using a Durrum–Gibson stopped-flow spectrophotometer (method III). In one experiment using method III the usual NaOH solution was replaced by one which was 1 *M* in hydrogen peroxide, 0.1156 *M* in NaOH, and 0.084 *M* in $LiClO_4$; some decomposition of the H_2O_2 occurred before mixing with the solution of the complex, but it was nevertheless established that no detectable hydrolysis of $Co(NH_3)_5NO_3^{+2}$ occurred within 60 sec of mixing, at 25°, whereas a similar experiment without H_2O_2 resulted in 50% hydrolysis of the complex in 1 sec. Prolonged exposure of the complex to H_2O_2 resulted in general redox decomposition of both reagents.

Aquation of $Co(NH_3)_5NO_3^{2+}$ in the Presence of Iodide Ion.—A deoxygenated solution, 0.003 *M* in $[Co(NH_3)_5NO_3][ClO_4]_2$ and 0.01 *M* in $HClO_4$, with NaI and $LiClO_4$ to make a total ionic strength of 0.119 *M*, was thermally equilibrated in a tightly stoppered cell in the thermostated cell holder (25°) of the Cary Model 15 spectrophotometer, and the kinetics of aquation of the complex was followed at 300 nm. Charge-transfer spectra, due to the ion pairs $\{Co(NH_3)_5NO_3,I\}^+$ and (particularly) $\{Co(NH_3)_5OH_2,I\}^{2+}$, limited meaningful kinetic results to those experiments for which $[I^-]$ was 10^{-1} *M* or less; at higher $[I^-]$, the fall in optical density due to aquation of $Co(NH_3)_5NO_3^{2+}$ was offset by a rise in absorbance due to $\{Co(NH_3)_5OH_2,I\}^{2+}$ formation.

Aquation of $Co(NH_3)_5NO_3^{2+}$ in the Presence of Chloride Ion.—A solution was made, 0.003 *M* in complex, 0.100 *M* in KCl (Baker Analyzed), and 0.01 *M* in HCl, and the kinetics of aquation were studied at 25.0°, as with iodide ion (above).

Position of Bond Breaking during Alkaline Hydrolysis of $Co(NH_3)_5NO_3^{2+}$.—The chloride salt $[(NH_3)_5CoNO_3]Cl_2$ was used because its greater solubility required the use of less ^{18}O-enriched water per sample. The salt was prepared by adding the appropriate amount of tetraphenylarsonium chloride to a saturated solution of $[Co(NH_3)_5NO_3][ClO_4]_2$ in water at room temperature. The precipitate of tetraphenylarsonium perchlorate was removed by filtration and the filtrate cooled in an ice bath. The product which crystallized from the cooled solution was cooled, washed with methanol, and dried under vacuum.

The alkaline hydrolysis was carried out by dissolving 0.12 g of $[Co(NH_3)_5NO_3]Cl_2$ in 15 ml of 1.58% ^{18}O-enriched water (Bio-Rad Laboratories). Sodium hydroxide (5 *M*) was added rapidly from a syringe to the well-stirred solution of cobalt(III) complex. The hydrolysis was studied in 0.17, 0.33, and 0.67 *M* sodium hydroxide. After 30 sec the reaction solution was poured into an equal volume of cold 45% hydrobromic acid. The acid served to quench the reaction and also to precipitate the product as $[Co(NH_3)_5OH_2]Br_3$. The latter salt was collected, washed with water and methanol, and dried under vacuum for 24 hr.

Isotopic composition of the water in $[Co(NH_3)_5OH_2]Br_3$ was determined by heating the salt for 6 hr under vacuum and collecting the water released. This water was equilibrated with carbon dioxide of normal isotopic composition for 1 week in a sealed tube at ambient temperature. The equilibrated CO_2 was then vacuum distilled through two Dry Ice–acetone traps into a sample tube suitable for attachment to the mass spectrometer.

The isotopic composition of the solvent was obtained by taking an aliquot from the reaction solution just before quenching and vacuum distilling the water into a break-seal tube suitable for equilibration with CO_2. The equilibration and subsequent handling were done as described above.

The isotopic composition of the CO_2 was determined on a CEC Model 21-614 low-resolution mass spectrometer equipped with a Honeywell Electronik 15 recorder. The average intensity ratio of the 46 to 44 mass peaks from three scans was used to determine the ratio $R = C^{16}O^{18}O:C^{16}O^{16}O$. The ratio *R* was reproducible to ±2%.

Results

The aquation of $Co(NH_3)_5NO_3^{2+}$ in acidic solution was found to be accurately pseudo first order in complex concentration over at least three half-periods, and the first-order rate coefficients k_1 were representative of the optical absorbance measurements to within better than 0.5% standard deviation in all cases. Duplicate rate coefficients were within 1%. The rate coefficients k_1 were independent of $[H^+]$ at constant temperature and ionic strength in perchlorate media (Table I), although k_1 decreased slightly as the ionic strength *I* was increased.

For acidic solutions of constant ionic strength, the k_1 data (Table II) gave what would normally be considered to be a linear plot of $\log (k_1/T)$ *vs.* $1/T$°K over their 59° range in temperature, but in fact careful inspection of the plot showed a distinct curvature (convex upward). A nonlinear least-squares program[17] was therefore used with an IBM 360 System Model 50 computer to fit the data to the equation

$$\log k_1 = [(T_0\Delta C_p^* - \Delta H_0^*)/2.303RT] + [(\Delta C_p^* R) + 1]\log T + [(\Delta S_0^* - \Delta C_p^*)/2.303R] - [(\Delta C_p^* \log T_0)/R] + \log (\kappa/h)$$

Here, T_0 is a reference temperature (which we have chosen to be 25.00°), ΔH_0^* and ΔS_0^* are the enthalpy and entropy of activation at T_0, ΔC_p^* is the heat capacity of activation (assumed constant over the experimental temperature range), κ is Boltzmann's constant, and *h* is Planck's constant. If ΔC_p^* is treated as a free parameter, the data of Table II give $\Delta H_0^* = 24.34 \pm 0.06$ kcal mol^{-1}, $\Delta S_0^* = 1.9 \pm 0.2$ cal

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Table I

Pseudo-First-Order Rate Coefficients (k_1) for the Aquation of $Co(NH_3)_5NO_3^{2+}$ at 25.00°[a]

$[HClO_4]$, *M*	$[LiClO_4]$, *M*	*I*, *M*	10^5k_1, sec^{-1}
0.0100	0.100	0.119	2.38
0.0100	0.300	0.319	2.19
0.0500	0.550	0.609	2.04
0.0800	0.520	0.609	2.09
0.100	0.500	0.609	2.05
0.200	0.400	0.609	2.05
0.400	0.200	0.609	2.06
0.600	. . .	0.609	2.02

[a] Complex concentration 3.00×10^{-3} *M*.

Table II

Rate Coefficients (k_1) for the Aquation of $Co(NH_3)_5NO_3^{2+}$ in $HClO_4$–$LiClO_4$ Solutions at Ionic Strength 0.119 *M*[a]

Temp, °C	10^5k_1, sec^{-1}	Temp, °C	10^5k_1, sec^{-1}
0.00	0.0492	40.45	18.0
10.60	0.276	43.75	29.1
14.65	0.518	45.03	34.9
19.41	1.030	46.81	42.7
25.01	2.39	48.89	51.6
34.25	8.21	50.60	63.2
34.88	9.05	53.80	93.8
39.48	16.80	58.71	159.0

[a] Complex concentration 3.00×10^{-3} *M*; $[HClO_4] = 0.010$ *M*.

Table III

Bimolecular Rate Coefficients (k_2) for the Base Hydrolysis of $Co(NH_3)_5NO_3^{2+}$

Temp, °C	Method[a]	Electrolyte	*I*, *M*	$[OH^-]$, *M*	k_2, M^{-1} sec^{-1}
0.00	II	$NaClO_4$	1.00	0.0385	0.0750
				0.0909	0.0763
				0.150	0.0758
				0.200	0.0770
2.0	I	$NaNO_3$	0.10	0.0167	0.199
				0.0197	0.190
				0.0330	0.210
				0.0400	0.200
16.8	I	$NaNO_3$	0.10	0.0065	3.15
				0.0100	3.15
				0.0136	3.00
17.0	I	$NaClO_4$	1.00	0.025	1.68
				0.030	1.67
				0.050	1.71
20.55	III	$LiClO_4$	0.119	0.058	5.5
25.00	III	$LiClO_4$	0.119	0.0196	11.5
				0.0391	11.7
				0.058	12.0
				0.066	11.6
				0.080	11.3
				0.096	12.3
25.0	I	$NaClO_4$	1.00	0.00667	5.71
				0.00833	5.61
				0.0100	5.68
				0.0143	5.70
				0.0167	5.93
30.15	III	$LiClO_4$	0.119	0.066	31.5
35.20	III	$LiClO_4$	0.119	0.066	67.1

[a] See Experimental Section.

deg^{-1} mol^{-1}, and $\Delta C_p^* = -20 \pm 7$ cal deg^{-1} mol^{-1}, with a slight improvement in the fit of the data over that obtained by assuming $\Delta C_p^* = 0$. Higher absolute accuracy in k and in the temperature measurements would yield a more certain value of ΔC_p^*, but the improvement in ΔH_0^* and ΔS_0^* would be trivial. The values of k as recalculated from eq 1 fall within 2.1% of the experimental values, on the average; this is poorer than the reproducibility of the kinetic experiments, so that the main source of error is probably temperature measurement (especially where thermistors had to be used) but is reasonable in view of the width of the temperature range.

The kinetics of hydrolysis of $Co(NH_3)_5NO_3^{2+}$ in alkaline solution were accurately second order (first order in complex and in hydroxide ion concentrations) at pH >12. Since hydroxide ion was in large excess over complex, the reaction was pseudo first order in complex at any given $[OH^-]$. The data are summarized in Table III, from which it will be seen that the second-order rate coefficients k_2 are reproducible to within 5% at worst. The k_2 values for $I \approx 0.1$ *M* gave a good Arrhenius plot, despite the disparity in experimental techniques and slight differences in *I*, and it was found using a nonlinear least-squares digital computer program[17] that the apparent ΔH^* is 28.83 ± 0.04 kcal mol^{-1} and ΔS^* is 43.1 ± 1.4 cal deg^{-1} mol^{-1} over the range 2–35.2° at $I = 0.1$ *M*.

Aquation of $Co(NH_3)_5NO_3^{2+}$ in the presence of 1.00×10^{-5} and 1.00×10^{-3} *M* iodide ion at 25.00°, $I = 0.12$ *M*, gave first-order rate coefficients $k_1 = 2.40 \times 10^{-5}$ and 2.36×10^{-5} sec^{-1}, respectively; these are virtually identical with the value $k_1 = 2.39 \times 10^{-5}$ sec^{-1} obtained when perchlorate was the only anion present. By way of contrast, the pseudo-first-order rate constants for hydrolysis in the presence of 10^{-5} and 10^{-3} *M* hydroxide ion under the same conditions are 1.17×10^{-4} and 1.17×10^{-2} sec^{-1}, respectively. Aquation in the presence of 0.100 *M* KCl and 0.01 *M* HCl proceeded with first-order kinetics over at least one half-period of the reaction, giving $k_1 = 2.60 \times 10^{-5}$ sec^{-1} at 25.0° (an 8% acceleration as compared with the corresponding $HClO_4$–$LiClO_4$ medium); production of $Co(NH_3)_5Cl^{2+}$ was negligible in the time span of the experiment, though a calculated infinite-time absorbance reading was necessary.

The results of the ^{18}O tracer study are conveniently presented in terms of the mass 46 to 44 ratio (R) of the CO_2 samples. The values for the solvent R_{sol} from the 0.17, 0.33, and 0.67 *M* sodium hydroxide solutions are 0.0308, 0.0290, and 0.0278. The corresponding values for $[Co(NH_3)_5OH_2]Br_3$, R_{aquo}, are 0.0296, 0.0285, and 0.0270, respectively. Carbon dioxide of normal isotopic abundance gave a ratio R_0 of 0.00408.

The fraction of Co–O bond breaking is given by $(R_{aquo} - R_0)/(R_{sol} - R_0)$ and equals 0.955, 0.950, and 0.966 for the 0.17, 0.33, and 0.67 *M* sodium hydroxide samples, respectively. These values indicate that the hydrolysis occurs with greater than 95% Co–O bond breaking. It is quite possible that the small differences between R_{sol} and R_{aquo} are due to traces of normal water introduced during the analysis of $[Co(NH_3)_5OH_2]Br_3$ and to some $[Co(NH_3)_5OH_2]Cl_3$ impurity in the $[Co(NH_3)NO_3]Cl_2$ and that the bond breaking is 100% Co–O.

Discussion

Bond Fission in $Co(NH_3)_5NO_3^{2+}$.—The incorporation of H_2O^{18} into the cobalt(III) residue in both aquation and base hydrolysis of $Co(NH_3)_5NO_3^{2+}$ shows unambiguously that it is the Co–O and not the O–N bond which is being broken. This is in spite of the fact that the activation enthalpy for these reactions is significantly greater than that for the reaction of HNO_3 with H_2O^{18} solvent ($\Delta H^* = 21.5$ kcal mol^{-1}).[18] Thus, the nitrato complex generates an anion (NO_3^-) in the transition state of hydrolysis and can therefore be included in a general discussion of hydrolysis of $Co(NH_3)_5X^{2+}$ species.

Activation Parameters.—The measured value of ΔC_p^* (~ -20 cal deg^{-1} mol^{-1}) for the aquation of $(NH_3)_5CoNO_3^{2+}$, though only approximate, cannot by itself account for the differences between the activation energies reported in the existing literature.[6,8] These discrepancies can be ascribed to uncertainties in activation energies arising because the temperature ranges covered by previous workers were too narrow.

The numerical magnitude of ΔC_p^* is as expected for a hydrolysis reaction in which a very polar solute (a divalent cation, in this case) develops further polarity in the transition state. For solutes of *low* polarity (such as simple alkyl halides), the solvent–solvent interactions of liquid water are believed to be somewhat enhanced by the presence of ground-state solute molecules but broken during the ionogenic solvolysis reaction in favor of solute–solvent interactions, thus causing a marked decrease in the heat capacity of the system (which originates primarily in the water–water interactions);[19] typically, one finds $\Delta C_p^* \approx -50$ cal deg^{-1} mol^{-1} for such reactions. Clearly, a decidedly less negative ΔC_p^* is to be expected on this basis when the solute is polar and disrupts water–water interactions even in the ground state. Indeed, Parboo and Robertson[20] found ΔC_p^* values within the range -10 to -30 cal deg^{-1} mol^{-1} for the aquation of other typical members of the series $Co(NH_3)_5X^{2+}$, so that Chan's value[9] of -49 cal deg^{-1} mol^{-1} for X = Cl seems unusually high. In general, then, we conclude that one may justifiably compare mean ΔH^* and ΔS^* values for related reactions of this type even if the data have been obtained over somewhat different temperature ranges, unless these ranges lie at opposite ends of the normal liquid range of water.

Free-Energy Relations.—The existence of a linear free energy relationship (LFER), between log k_2 for the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ and the negative logarithm of the "stability constant" Q for the formation of $Co(NH_3)_5X^{(3-n)+}$ from X^{n-} and $Co(NH_3)_5OH_2^{3+}$ (or $Co(NH_3)_5OH^{2+}$, if Q is multiplied by the protolysis constant quotient K_{H_2O}/K_{aquo}), is demonstrated in Figure 1. The relevant data have been collected in Table IV. The slope of the representative straight line is 1.0, just as for the analogous aquation reaction.[21,22] It follows that there must also be a linear relationship of unit slope between log k_1 and log k_2, and this strongly suggests that the mode of activation is the same in both aquation and base hydrolysis.

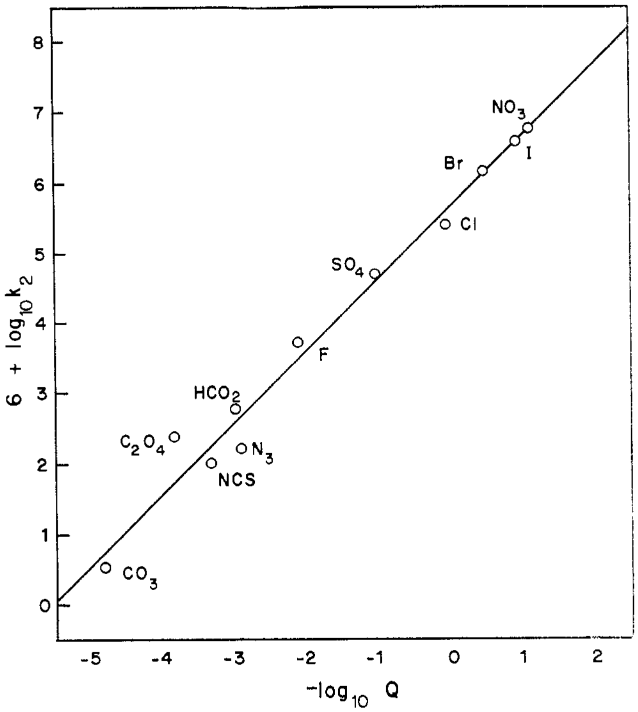

Figure 1.—Plot of log (rate coefficient) *vs.* log (equilibrium quotient) for the base hydrolysis of $Co(NH_3)_5X^{2+}$ ions at 25°. The origin of these data is given in Table IV.

Mechanisms of Reaction.—The fact that the rate of aquation of $Co(NH_3)_5NO_3^{2+}$ is unaffected by added chloride or iodide ions, in concentrations in which hydroxide ion would catalyze hydrolysis by many orders of magnitude, is strong evidence against the electron-transfer mechanism (B) of base hydrolysis. Similarly, the rate of aquation of chlorine-36-labeled $Co(NH_3)_5Cl^{2+}$ is virtually the same in the presence of 0.1 *M* chloride ion as in the presence of the same concentrations of nitrate or perchlorate ions,[23] whereas 0.1 *M* hydroxide ion would produce a 40,000-fold acceleration of hydrolysis. Since both chloride and iodide ions are better reducing agents[24] than hydroxide, it seems most improbable that base hydrolysis of $Co(NH_3)_5X^{2+}$ could proceed *via* reduction of Co(III) to Co(II) by oxidation of OH^- to OH. In the same way, one would expect[24] HO_2^- to be a much more effective reducing agent than OH^-, yet addition of excess H_2O_2 to an alkaline reaction mixture (thereby converting most of the OH^- to HO_2^-) resulted in a *decrease* of several-

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TABLE IV
SECOND-ORDER RATE COEFFICIENTS k_2 FOR THE BASE HYDROLYSIS AND FORMATION QUOTIENTS Q FOR $Co(NH_3)_5X^{(3-n)+}$ IN AQUEOUS PERCHLORATE MEDIA AT 25°

X^{n-}	Q, M^{-1}	I, M	k_2, M^{-1} sec^{-1}	I, M
NO_3^-	0.08	1.0[a]	5.72	1.0[b]
I^-	0.12	1.0[c]	3.7	1.0[c]
Br^-	0.35	1.0[a]	1.40	1.0[e]
Cl^-	1.11	1.0[a]	0.25	1.0[e]
SO_4^{2-}	11.0	1.0[f]	4.9×10^{-2}	1.0[g]
F^-	~100	0.12[h]	5.1×10^{-3}	0.12[d]
N_3^-	8.3×10^2	0.5[i]	1.6×10^{-4}	0.5[j]
HCO_2^-	9.7×10^2	1.0[k]	5.8×10^{-4}	1.0[l]
$-NCS^-$	2.7×10^3	0.5[m]	1.0×10^{-4}	0.5[n]
$HC_2O_4^-$	7.1×10^3	1.0[o]	2.45×10^{-4}	1.0[p]
CO_3^{2-}	6.6×10^4	1.0[q]	3.3×10^{-6}	1.0[q]

[a] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6,** 1027 (1967). [b] This work. [c] R. G. Yalman, *Inorg. Chem.*, **1,** 16 (1962). [d] By extrapolation of data of S. C. Chan, K. Y. Hui, J. Miller, and W. S. Tsang, *J. Chem. Soc.*, 3207 (1965). [e] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7,** 174 (1968). [f] From data of A. Haim and H. Taube, *ibid.*, **2,** 1199 (1963), with correction for ionic strength difference. [g] L. L. Po and R. B. Jordan, *ibid.*, **7,** 526 (1968). [h] W. E. Jones and T. W. Swaddle, unpublished work. [i] Reference 22. [j] From data of G. C. Lalor and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1560 (1963), using the relationship $\log k(25°) = -3.52 - 2.0I^{1/2} + 1.60I$. [k] R. B. Jordan, unpublished work. [l] R. B. Jordan, Ph.D. Thesis, University of Chicago, 1965. [m] From data of ref 7. [n] From data of D. L. Gay and G. C. Lalor, *J. Chem. Soc., A*, 1179 (1966). [o] C. Andrade and H. Taube, *Inorg. Chem.*, **5,** 1087 (1966). [p] N. S. Angerman and R. B. Jordan, *ibid.*, **6,** 1376 (1967). [q] D. J. Francis and R. B. Jordan, *J. Am. Chem. Soc.*, **89,** 5591 (1967); T. P. Das Gupta and G. M. Harris, *ibid.*, **90,** 6360 (1968).

thousandfold in the rate of hydrolysis of $Co(NH_3)_5NO_3^{2+}$, and the same is true[25] of the hydrolysis of $Co(NH_3)_5Cl^{2+}$.

A further piece of evidence against the electron-transfer mechanism of base hydrolysis is the implication of the free energy relationships that the mode of activation in both aquation and base hydrolysis is essentially the same. It would be hard to understand why the energetics of electron transfer from OH^- to $Co(NH_3)_5X^{2+}$ should be so obviously related to those of aquation—unless the aquation of Co(III) complexes proceeds by electron transfer from H_2O to the complexes, which seems most unlikely.[26]

The SN2 mechanism (C) of base hydrolysis, in which OH^- would make a direct nucleophilic attack on the cobalt atom, does not explain why OH^- is far more effective in bringing about substitution than are I^-, Cl^-, and even the powerful nucleophile HO_2^- (compare Pearson and Edgington[25]), nor is thiocyanate[7] an effective nucleophile against $Co(NH_3)_5NO_3^{2+}$.

The conjugate-base mechanism (A), on the other hand, is fully consistent with all of our experimental observations and is supported by the existence of the LFER (Figure 1). The acidity of the ammine protons within the series $Co^{III}(NH_3)_5X^{2+}$ is probably only very slightly dependent upon the identity of X,[27] so that, in comparing kinetic data for aquation and base hydrolysis, one is in effect comparing the aquations of $Co(NH_3)_5X^{2+}$ and $Co(NH_3)_4(NH_2)X^+$, if mechanism A is valid for all X. The fact that both series of reactions yield an LFER of unit slope can be taken to mean that the mode of activation is closely similar in either series, and we can argue, after Langford,[21] that the departing ligand X is only very weakly bonded to Co in the transition state, *i.e.*, that the activation process is strongly dissociative (SN1 or I_d), in all cases considered in Figure 1.

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(25) R. G. Pearson and D. N. Edgington, *J. Am. Chem. Soc.*, **84,** 4607 (1962).

(26) If the 199-nm absorption band of aqueous $[Co(NH_3)_5OH_2][ClO_4]_3$ is due to water-to-complex electron transfer, as suggested by W. E. Jones and T. W. Swaddle, *Can. J. Chem.*, **45,** 2647 (1967), then the energy requirements of such a process exceed 140 kcal mol^{-1}, which is very much in excess of the observed activation energies for aquation.

(27) From the data of ref 11, pp 184–186.