TABLE VI

THE *trans* EFFECTS OF NH_3, Cl^-, AND H_2O IN SOME ELECTRON-TRANSFER REACTIONS

Reaction	k_t/k_c[a]			Mechanism	Ref
	NH_3	Cl^-	H_2O		
$Co(en)_2XOH^{n+} + Cr^{2+}$	1.1	...	3.3	Hydroxide bridge	*b*
$Co(en)_2XNCS^{n+}$ Cr^{2+}	1.2	...	30	Thiocyanate bridge	*c*
$Cr(en)_2XCl^{n+} + Cr^{2+}$	...	26	37	Chloride bridge	*d*
$Co(en)_2XCl^{n+} + Fe^{2+}$	3.7	20	520	Chloride bridge (?)	*e*
$Co(NH_3)_4XN_3^{n+} + Fe^{2+}$	...	...	68	Azide bridge (?)	*f*

[a] Ratio of rate constants (25°) of *trans* to *cis* complex. [b] Ref 5. [c] Ref 6. [d] This work. [e] Ref 4. [f] A. Haim, *J. Am. Chem. Soc.*, **86**, 2352 (1964).

stretching of the Co–O bond was important. It must be noted, however, that these arguments are based on rate comparisons. Now the assignment of a certain effect on the basis of rate comparisons presupposes an ability to predict what the rates would have been in the absence of such an effect. In the above discussion it was assumed that a simple relation between crystal field strength of the *trans* ligand and rate of reaction held. Although gross reactivity features would appear to obey such a relation, we must admit that, at the present stage of development of the subject, predictions of detailed reactivity orders may be uncertain. We conclude, therefore, that, although stretching of the metal–oxygen bond in reductions of *trans*-$Co(en)_2OH_2Cl^{2+}$ or $Cr(en)_2OH_2Cl^{2+}$ provides a not unreasonable rationalization of the observed trends in reactivity, this suggestion must be considered tentative until direct evidence (such as oxygen isotopic fractionation studies[28]) either supports or refutes the suggestion.

The activation parameters measured in the present work (see Table IV) do not provide much information. The higher rates for the *trans* complexes are associated with slightly lower enthalpies of activation, whereas the entropies of activation remain approximately constant in the series (−33 ± 3 eu) and lie in the range (−25 ± 10 eu) observed for other electron-transfer reactions of a similar type.[7,29]

It is useful to contrast the behavior of the chromium(II)-catalyzed aquations of $Cr(en)_2OH_2Cl^{2+}$ and $CrCl^{2+}$. In the former case no acid dependence is observed, whereas in the latter case the dominant reaction proceeds *via* an inverse hydrogen ion path. At first glance it would appear that these results are contradictory. However, they can be readily understood by considering the relative efficiencies of Cl^- and OH^- as bridges and the nature of the reactions under consideration. Using the rate constants for the Cr^{2+}–$CrOH^{2+}$ ($k = 0.7\ M^{-1}\ sec^{-1}$ at 25°[30]) and Cr^{2+}–$CrCl^{2+}$ ($k = 9\ M^{-1}\ sec^{-1}$ at 0°[22]) reactions as a measure of the efficiency of OH^- and Cl^- bridges, we would conclude[31] that $Cr(en)_2OH_2Cl^{2+}$ and $Cr(en)_2OHCl^+$ react at rates that do not differ by more than 10^2. However, at the lowest $[H^+]$ used, the hydroxo species is approximately 10^{-4} less abundant than the aquo species. Therefore, the inverse acid path would be approximately 10^{-6} smaller than the acid independent path and obviously was not detected. Of course, the same considerations apply to $CrCl^{2+}$ and $CrOHCl^+$, but in this case the inverse hydrogen ion path was readily detected. The difference in the two systems is that for $Cr(en)_2OH_2Cl^{2+}$ reaction *via* a chloride bridge results in a net consumption of the reactant, whereas for $CrCl^{2+}$ reaction *via* a chloride bridge does not bring about any net reaction and can only be detected by radioactive exchange studies.[22]

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(29) J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Am. Chem. Soc.*, **86**, 1019 (1964).

(30) A. Anderson and N. A. Bonner, *ibid.*, **76**, 3826 (1954).

(31) It is assumed that the $1/[H^+]$ path corresponds to reaction *via* a hydroxide-bridged transition state.

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The Kinetics of Formation and Dissociation of the Monoammine Complexes of the Divalent, First-Row, Transition Metal Ions

BY D. B. RORABACHER[1]

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The kinetics of formation and dissociation have been studied for the monoammine complexes of Co(II), Ni(II), and Zn(II) in aqueous solution using the temperature-jump relaxation method. The evaluated formation rate constants are shown to correspond to a mechanism involving the dissociation of water from the aquometal ion as the rate-determining step following the initial formation of an outer-sphere complex. To account for the much faster formation rates of the previously studied polyamine complexes, an internal conjugate base mechanism is proposed.

Introduction

In a previous paper[2] it was found that the formation rate constants for nickel polyamine complexes could be correlated with a mechanism involving the first nickel–nitrogen bond formation as the rate-determining step. However, a rate constant for the

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(2) D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, Jr., *Inorg. Chem.*, **2**, 667 (1963).

formation of the monoamminenickel(II) complex, calculated from the stability constant and a measured dissociation rate constant,[3] appeared to be much too small in comparison with the values for the polyaminenickel(II) complexes. Although, in the strictest sense, ammonia is not a member of the homologous series of polyamines included in the earlier study, it represents a lower limit to that series. Therefore, the contradictory behavior appeared to merit further investigation.

In the present study the temperature-jump relaxation method was utilized to measure the formation and dissociation kinetics of the monoammine complexes of the divalent transition metal ions in aqueous solution. The kinetic behavior of these reactions is compared with the behavior predicted by the general mechanism for metal–ligand complex formation as formulated by Eigen,[4] in which the formation of an outer-sphere complex between the aquometal ion and the ligand precedes the loss of a coordinated water molecule as the rate-determining step

$$\mathrm{M(H_2O)_6 + L \overset{K_{os}}{\rightleftharpoons} M(H_2O)_6\cdots L \xrightarrow{k^{M-H_2O}} ML(H_2O)_5 + H_2O} \quad (1)$$

As applied to the reactions studied in this work, M is a divalent transition metal ion, L is NH_3, K_{os} is the equilibrium constant for outer-sphere association, $M(H_2O)_6\cdots L$ is the outer-sphere complex, and k^{M-H_2O} is the rate constant for metal–water bond rupture.

As a result of the agreement found for the monoammine complex formation rates studied in the present work with mechanism 1, and also the previously noted discrepancy between the formation rate constants for the monoammine– and polyamine–nickel(II) complexes, it is concluded that the polyamines react abnormally fast with the aquated divalent transition metal ions. To account for this apparent deviation, a modification of the general mechanism (eq 1) is formulated wherein a basic donor atom of the reacting multidentate ligand forms a hydrogen bond to a coordinated water molecule, thereby stabilizing the outer-sphere intermediate and labilizing subsequent water loss. As a result, the multidentate ligand promotes its own coordination. This "internal conjugate base" (ICB) mechanism does not contradict the earlier interpretation of the reaction mechanism for multidentate ligands[2] but rather expands the detailed understanding of the first bond-formation step.

Experimental Section

Solutions.—All chemicals used were reagent grade. Solutions of Co(II), Ni(II), and Zn(II) were prepared from the respective hydrated nitrates and standardized by titration with EDTA. In the case of cobalt, concentrated (1.00 *M*) Co(II) solutions were prepared fresh each week and stored at pH 2–3 to protect against oxidation. Ammonium nitrate was used to maintain an ionic strength of 0.1 (for lowering the resistance of the solution) and, at the same time, provided the source of NH_3 in solution. The pH of the final solution was adjusted within ±0.01 unit of the desired pH by dropwise addition of concentrated NaOH and HNO_3 solutions. The change in volume during pH adjustment was negligible.

Temperature-Jump Method.—The theory of the temperature-jump method has been extensively treated elsewhere.[5] As applied in the current investigation, the basic principle involves discharging a capacitor charged to a high voltage through a solution in which the reactants and products are at equilibrium. The subsequent rapid temperature rise (in the present study, $\Delta T = 5°$) displaces the equilibrium position, and the reaction is monitored spectrophotometrically as equilibrium is reestablished at the new temperature. Since the equilibrium shift is small, the change in reactant concentrations is sufficiently small that the observed reaction may be treated as a linear relaxation process.

Resolution of the Data.—To improve the evaluation of the relaxation curves, a standard series of 25 logarithmic decay curves were prepared which were then matched with an enlarged projection of the photographic recording of the optical density change (as displayed on an oscilloscope screen) to determine the best fit. The value of the relaxation time was then evaluated from the parameters of the matching logarithmic curve and the oscilloscopic scan rate used. Errors in tracing and plotting the curves were thereby avoided and deviations in the relaxation curves could be readily detected.

Correction of Equilibrium Constants.—For use in the kinetic calculations, the protonation constants for NH_3 at the various temperatures, as determined by Bates and Pinching,[6] were adjusted to 0.1 ionic strength using the empirical correction factor reported by Bjerrum.[7] Values used for the stability constants of the monoammine and bisammine complexes were those determined by Bjerrum with empirical corrections for ionic strength and temperature.[7] The resultant values of all constants for $\mu = 0.1$ and the various experimental temperatures are summarized in Table I.

TABLE I

CORRECTED PROTONATION AND STABILITY CONSTANTS FOR $\mu = 0.1^a$

	11°	20°	30°	35°
log $K_{NH_4}{}^{NH_3}$	9.688	9.413	9.106	8.960
log $K_{NiNH_3}{}^{Ni}$	2.82	2.75	2.68	
log $K_{Ni(NH_3)_2}{}^{NiNH_3}$	2.27	2.20	2.13	
log $K_{CoNH_3}{}^{Co}$	2.09	2.05		1.97
log $K_{Co(NH_3)_2}{}^{CoNH_3}$	1.61	1.57		1.49
log $K_{ZnNH_3}{}^{Zn}$	2.34			
log $K_{Zn(NH_3)_2}{}^{ZnNH_3}$	2.41			

[a] $K_{NH_4}{}^{NH_3} = [NH_4{}^+]/[H^+][NH_3]$; $K_{M-NH_3}{}^{M} = [M\text{-}NH_3{}^{2+}]/[M^{2+}][NH_3]$, etc.

Results and Treatment of Data

For the present reversible systems the formation reactions were found to be second order and the dissociation reactions first order. The normal kinetic equation for these reactions is

$$-\frac{d[M]}{dt} = k_M{}^{NH_3}[M(H_2O)_6{}^{2+}][NH_3] - k^{M-NH_3}[M(NH_3)(H_2O)_5{}^{2+}] \quad (2)$$

which, for an uncoupled system, can be shown to yield the relaxation equation

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(3) G. A. Melson and R. G. Wilkins, *J. Chem. Soc.*, 4208 (1962).

(4) M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p 373.

(5) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," A. Weissberger, Ed., Vol. VIII, Part II, 2nd ed, Interscience Publishers, New York, N. Y., 1963.

(6) R. G. Bates and G. D. Pinching, *J. Res. Natl. Bur. Std.*, **42**, 419 (1949).

(7) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

$$\frac{1}{\tau} = k_M{}^{NH_3}(\bar{C}_M + \bar{C}_L) + k^{M-NH_3} \qquad (3)$$

where τ is the relaxation time and $\bar{C}_M$ and $\bar{C}_L$ represent the equilibrium concentrations of $M(H_2O)_6{}^{2+}$ and NH_3, respectively.

If the reaction is presumed to proceed by mechanism 1, two coupled relaxations would be expected—one relating to the formation and dissociation of the outer-sphere complex, and a second corresponding to loss of a water molecule from the inner coordination sphere of the metal ion. It is readily verified that the relaxation step involving the first process would be very rapid for the present case so that only the second relaxation, relating to metal–water bond rupture, should be observable. Taking into account coupling with the first process, the equation for the latter relaxation can be written in the form[8]

$$\frac{1}{\tau} = \frac{k^{M-H_2O}K_{os}(\bar{C}_M + \bar{C}_L)}{1 + K_{os}(\bar{C}_M + \bar{C}_L)} + k^{M-NH_3} \qquad (4)$$

Under the conditions utilized in this study $((\bar{C}_M + \bar{C}_L) \leqq 0.1\ M;\ K_{os} \approx 0.15)$, eq 4 reduces to eq 3. It is concluded, therefore, that observable relaxation data for the reactions studied should conform to eq 3 whether the reactions follow mechanism 1 or some other second-order reaction path (*e.g.*, a diffusion-controlled process or a bimolecular substitution mechanism). As a result, agreement between the experimental data and eq 3 cannot be taken as confirmatory evidence for a particular mechanism.

Since the spectrophotometric changes for the formation reactions of the monoammine complexes are small, it was necessary to couple these reactions with a pH indicator

$$M(H_2O)_6{}^{2+} + NH_3 \underset{k^{M-NH_3}}{\overset{k_M{}^{NH_3}}{\rightleftharpoons}} M(NH_3)(H_2O)_5{}^{2+} + H_2O \qquad (5)$$

$$H^+ + NH_3 \rightleftharpoons NH_4{}^+ \qquad (6)$$

$$H^+ + In^- \rightleftharpoons HIn \qquad (7)$$

where the equilibrium shift for reaction 7 resulted in an observable absorbance change.

Three coupled relaxations are expected for this system. Treatment of the data is considerably simplified if reactions 6 and 7 are very rapid compared to reaction 5 so that these reactions may be considered to be at equilibrium at all times. Reaction 6 has been studied independently[9] and a relaxation time of approximately 0.1 μsec is calculated for the conditions utilized in this work ($[NH_3] \approx 0.3$ mM). No rate constants are available for the protonation and acid dissociation of brom thymol blue, the indicator used to monitor all reactions for which successful data were obtained. However, rate constants for related sulfonephthaleins[10] suggest that a relaxation time as slow as 1 μsec or slightly more might be expected for reaction 7 due to the low concentration of indicator present in the reaction solution ($\Sigma In = 0.02$ mM; pH ≈ 7). These values indicate that the relaxation times for reactions 6 and 7 should be independent of the relaxation for reaction 5 in the case of the "slow" reacting Ni(II) and Co(II) systems ($\tau \geq 20$ and $\tau \geq 0.1$ msec, respectively).

Such independence could not be conclusively established for the Zn(II) system, for which relaxation times as short as 10 μsec were obtained. However, it was experimentally demonstrated that solutions containing ammonia and indicator, without metal ion, had relaxation times which were shorter than the resolution time of the instrument used ($\tau < 5\ \mu$sec). It was also found that small changes in the indicator concentration did not cause observable deviations in the zinc relaxation times. It was concluded, therefore, that the possible overlap of the relaxation curve for reaction 7 with that attributable to reaction 5 presented no greater interference than the more obvious limitation imposed by the resolution time of the instrument itself. Such a conclusion is supported by the observed agreement of the rate constants obtained with previous data.

Although it is concluded that the relaxation curves for the three reactions do not seriously overlap, the coupling of reaction 5 with reactions 6 and 7 necessitates a modification of eq 3 to the form

$$\frac{1}{\tau} = k_M{}^{NH_3}\left(\frac{\bar{C}_M}{1 + \alpha} + \bar{C}_L\right) + k^{M-NH_3} \qquad (8)$$

where

$$\alpha = \frac{K_H[H^+](K_i[In^-] + K_i[H^+] + 1)}{K_H[NH_3](K_i[H^+] + 1) + K_i([In^-] + [H^+]) + 1} \qquad (9)$$

In eq 9, K_H represents $K_{NH_4}{}^{NH_3}$, the protonation constant for ammonia, and K_i is the protonation constant of the indicator (for brom thymol blue, $\log K_i = 6.8$).

For the concentrations and pH utilized in the present study, α is considerably less than unity so that eq 8 also reduces to eq 3. Therefore, despite the possibility of four coupled relaxations (defined by eq 6 and 7, the formation of the outer-sphere complex, and the loss of water from the inner coordination sphere of the metal ion), only one relaxation process was detected in the observable range (1 sec $> \tau >$ 5 μsec), for which the relaxation time is defined by eq 3.

In all cases final pH adjustments were made on the solutions at 20°. For the relaxation measurements at other temperatures, the pH was significantly shifted as a result of the shift in the NH_3–$NH_4{}^+$ equilibrium. As substantiated by experimental measurements, the final pH at each temperature could be approximated by the relationship

$$^*[H^+] = \frac{K_H{}^*K_1}{^*K_HK_1}[H^+] \qquad (10)$$

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(8) M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 93 (1962).

(9) M. T. Emerson, E. Grunwald, and R. A. Kromhout, *J. Chem. Phys.*, **33**, 547 (1960).

(10) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. Reaction Kinetics*, **2**, 287 (1964).

where K_H, K_1, and $[H^+]$ represent the values for these parameters at 20° (K_1 represents $K_{MNH_3}{}^{M}$) and $*K_H$, $*K_1$, and $*[H^+]$ are the corresponding values at the final temperature reached following the temperature jump.

The values for $\bar{C}_M$ and $\bar{C}_L$ were calculated from the relationships

$$\bar{C}_L = \frac{[NH_4^+]}{*K_H*[H^+]} \approx \frac{(\Sigma NH_3)}{*K_H*[H^+]} \qquad (11)$$

$$\bar{C}_M = \frac{(\Sigma M)}{1 + *K_1\bar{C}_L + *K_1*K_2(\bar{C}_L)^2} \qquad (12)$$

where (ΣM) and (ΣNH_3) represent the total concentrations of metal ion and ammonia, respectively, and $*K_1$ and $*K_2$ represent the stability constants for the monoammine and bisammine complexes at the final temperature. In all cases $\bar{C}_M$ was much larger than $\bar{C}_L$ so that the third term in the denominator of eq 12 (representing the fraction of the total metal ion which is in the form of the bisammine complex) was generally negligible.

Cobalt.—The reaction of aquocobalt(II) ion with ammonia was studied at 11° over the pH interval from 6.70 to 7.55 with the total Co(II) concentration varied from 5.0 to 100 m*M*. In the range studied the observed relaxation time obeyed eq 3 and was independent of pH. Measurements were also made at 20 and 35° in the region of pH 7.

The experimental data are tabulated in Table II. Each τ value listed represents the median of 5–7 trials with a precision of ±10%. Plots of the reciprocal relaxation times against the sum of the equilibrium reactant concentrations for the three temperatures are shown in Figure 1, and the rate constants evaluated from these data, as well as the activation parameters, are listed in Table III.

Nickel.—The reaction between aquonickel(II) ion and ammonia was studied at 11, 20, and 30° in the region of neutral pH with the total concentration of nickel varied from 0.50 to 10.0 m*M* at each temperature. The experimental data are listed in Table II with each relaxation time representing the median value of 5–7 trials (precision = ±10%). Plots of the data are shown in Figure 2, and the evaluated rate constants and activation parameters are presented in Table III.

In the case of the 11° data, the relaxation times exceeded 0.25 sec for the lowest reactant concentrations studied, resulting in deviations in the relaxation curves due to temperature readjustment in the reaction cell. As a consequence, the value of k^{Ni-NH_3} for 11°, as determined from the intercept in Figure 2, was less accurately determined for this temperature.

Zinc.—The reaction between aquozinc(II) ion and ammonia was studied at 11° in the neutral pH region with the total zinc concentration varied from 1.00 to 10.00 m*M*. The rapidity of this reaction, as well as the small net equilibrium shift observed during relaxation, decreased the precision of the data and precluded accurate measurements at total zinc ion concentrations greater than 8 m*M* or at temperatures significantly above 11°. The relaxation times obtained for 11°, as listed in Table II, represent the median of 6–10 trials with a precision of ±25%. A plot of the data is shown in Figure 3, and the evaluated rate constants are given in Table III.

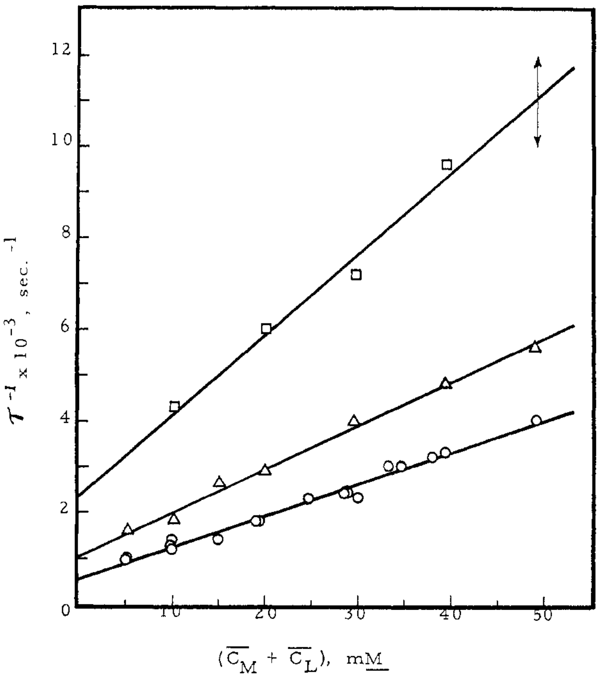

Figure 1.—Resolution of the formation and dissociation rate constants for monoamminecobalt(II) ion. Plot of eq 3: ○, 11° data; △, 20° data; □, 35° data.

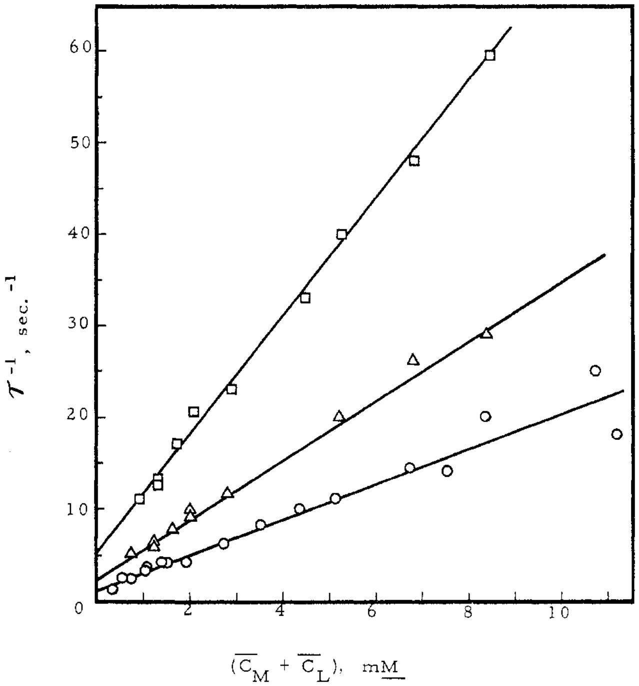

Figure 2.—Resolution of the formation and dissociation rate constants for monoamminenickel(II) ion. Plot of eq 3: ○, 11° data; △, 20° data; □, 30° data.

Manganese, Iron, and Copper.—Attempts to meas-

TABLE II

EXPERIMENTAL DATA FOR RECIPROCAL RELAXATION TIMES

Cobalt(II)

pH	$\overline{C_M}$, m$\underline{M}$	$\tau^{-1} \times 10^{-3}$, sec.$^{-1}$
(Temp. = 11°; $\overline{C_L}$ = 0.3 m$\underline{M}$)		
6.74	4.9[a]	0.95
7.19	4.8	1.0
7.19	9.6	1.25
6.69	9.9[a]	1.2
7.54	9.3[c]	1.4
7.19	14.7	1.4
7.54	18.6[c]	1.8
7.19	19.2	1.8
6.69	19.8[a]	1.75
7.19	24.5	2.3
7.54	27.9[c]	2.4
7.19	28.8	2.45
6.99	29.8[b]	2.3
7.54	32.6[c]	3.0
7.19	34.3	3.0
7.54	37.3[c]	3.2
7.19	38.6	3.3
7.19	49.0	4.0
(Temp. = 20°; $\overline{C_L}$ = 0.4 m$\underline{M}$)		
7.00	4.8	1.6
7.00	9.8	1.8
7.00	14.6	2.6
7.00	19.5	2.9
7.00	29.2	4.0
7.00	39.0	4.8
7.00	48.6	5.6
(Temp. = 35°; $\overline{C_L}$ = 0.5 m$\underline{M}$)		
6.63	9.7	4.3
6.63	19.5	6.0
6.63	29.2	7.2
6.63	38.9	9.6
6.63	48.6	10-12

Nickel(II)

pH	$\overline{C_M}$, m$\underline{M}$	τ^{-1}, sec.$^{-1}$
(Temp. = 11°; $\overline{C_L}$ = 0.35 m$\underline{M}$)		
6.74	0.23[a]	1.1
7.24	0.20	2.3
7.24	0.40	2.3
6.94	0.89[b]	3.2
7.24	0.80	3.2
7.24	0.80	3.6
7.24	1.06	4.1
7.24	1.20	4.1
7.24	1.60	4.4
6.94	1.78[b]	4.1
7.24	2.40	6.1
7.24	3.20	8.2
7.24	4.00	10.0
7.24	4.80	11.0
7.24	6.40	14.4
7.24	7.20	14
7.24	8.00	20
7.24	10.4	25
6.74	11.1[a]	18
(Temp. = 20°; $\overline{C_L}$ = 0.43 m$\underline{M}$)		
7.04	0.40	5.0
7.04	0.80	5.8
7.04	0.80	6.5
7.04	1.19	7.8
7.04	1.59	9.2
7.04	1.59	10.0
7.04	2.39	11.5
7.04	4.78	20
7.04	6.37	26
7.04	7.96	29
(Temp. = 30°; $\overline{C_L}$ = 0.53 m$\underline{M}$)		
6.83	0.40	11
6.83	0.79	12.5
6.83	0.79	13
6.83	1.19	17
6.83	1.58	20.5
6.83	2.37	25
6.83	3.95	33
6.83	4.74	40
6.83	6.31	48
6.83	7.90	60

Zinc(II)

pH	$\overline{C_M}$, m$\underline{M}$	$\tau^{-1} \times 10^{-4}$, sec.$^{-1}$
(Temp. = 11°; $\overline{C_L}$ = 0.47 m$\underline{M}$)		
7.36	0.63	1.8
7.36	1.26	2.3
7.36	2.54	2.8
7.36	3.17	3.1
7.36	3.81	3.0
7.36	3.81	3.2
7.36	5.06	3.6
7.36	5.06	4.0
7.36	6.34	3.8
7.36	6.34	4.0

[a] $\bar{C}_L = 0.11$ mM. [b] $\bar{C}_L = 0.18$ mM. [c] $\bar{C}_L = 0.7$ mM.

ure the kinetics of ammonia reacting with aquomanganese(II) and aquocopper(II) ions were unsuccessful—apparently due to the combination of rapid relaxation and a small net shift in the equilibrium. Aquoiron(II) solutions underwent oxidation to the +3 state, and the immediate precipitation of ferric hydroxide in the neutral solutions used made measurements impossible.

Discussion

Confirmation of Reaction Mechanism.—The agreement between the experimental relaxation times and eq 3, as shown by the plots in Figures 1, 2, and 3, confirms the fact that the formation of the monoammine complexes proceeds by a second-order reaction. If these reactions follow the general mechanism (eq 1) then the experimentally obtained formation rate constants, $k_M^{NH_3}$, can be equated to the corresponding rate constants for metal–water bond rupture, k^{M-H_2O}, by eq 13.

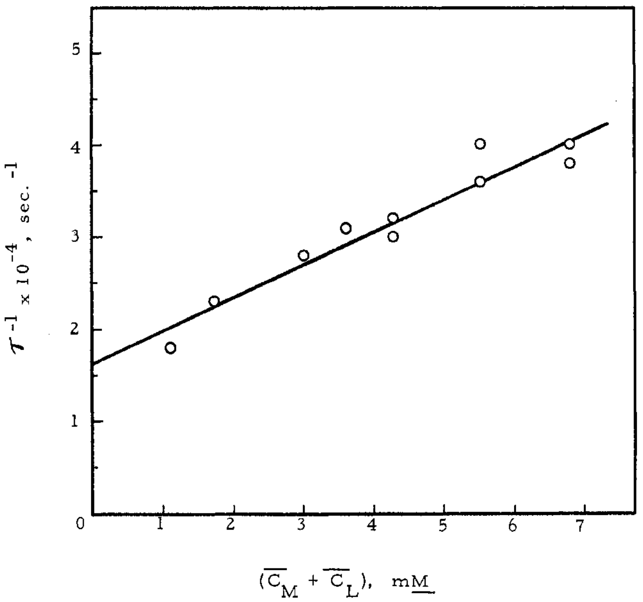

Figure 3.—Resolution of the formation and dissociation rate constants for monoamminezinc(II) ion at 11°. Plot of eq 3.

$$k_M^{NH_3} = K_{os}k^{M-H_2O} \quad (13)$$

This relationship can be tested as a means of confirming or repudiating the applicability of this mechanism if a suitable value can be calculated for the association constant, K_{os}.

In establishing the general applicability of mechanism 1 for metal–ligand complex formation, Eigen and most subsequent workers have focused attention on reactions involving negatively charged ligands. For such systems the reaction intermediate preceding water loss is a true "ion pair," and the value of the association equilibrium constant, K_{os}, can be calculated using an equation of the type derived by Fuoss[11] for ion-pair formation

$$K_{os} = \frac{4}{3}\pi a^3 N_A e^b \times 10^{-3} \quad (14)$$

where

$$b = \frac{z_A z_B e_0^2}{a\epsilon kT} \quad (15)$$

In these equations, a is the center-to-center distance (in cm) between the two reaction partners at the point of closest approach, N_A is Avogadro's number, z_A and z_B are the formal charges on the reacting species, e_0 is the electronic charge (in esu), ϵ is the dielectric

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(11) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958). The form of the equation shown is a modification of Fuoss' equation which, in the original version, was derived only for the case where $z_A = -z_B = 1$. A similar modification has been used by Eigen, *et al.*[10]

TABLE III

EVALUATED RATE CONSTANTS AND ACTIVATION PARAMETERS[a]

Rate constants	11°	20°	30°	35°	E_a, kcal/mole	log A	log $K_{M-NH_3}{}^{M}$ [b] (11° exptl value)
$k_{Co}{}^{NH_3}$	6.9×10^4	9.5×10^4	...	17.6×10^4	6.8	10	2.12
k^{Co-NH_3}	0.53×10^3	1.1×10^3	...	2.3×10^3	11	11	
$k_{Ni}{}^{NH_3}$	1.9×10^3	3.3×10^3	6.5×10^3	...	11	12	3.28
k^{Ni-NH_3}	1.1	2.3	5.0	...	14	11	
$k_{Zn}{}^{NH_3}$	3.6×10^6	...	...	...	...	...	2.35
k^{Zn-NH_3}	1.6×10^4	...	...	...	...	...	

[a] All formation rate constants in M^{-1} sec^{-1}; dissociation rate constants in sec^{-1}. [b] Compare to 11° literature values in Table I.

constant, k is the Boltzmann constant (in ergs), and T is the absolute temperature.

The constant for outer-sphere association between $M(H_2O)_6{}^{2+}$ and NH_3 could be calculated as the attraction between a dipositive ion and a negative dipole. However, the magnitude of the dipole moment for ammonia (1.48 D.) is less than the dipole moment for the solvent water (1.83 D.), so that the electrostatic attraction between the reaction partners should be ineffective in stabilizing the outer-sphere intermediate.

A more realistic approach would be to calculate the outer-sphere association constant for the case in which one of the reacting species is uncharged. From the form of eq 15 it is obvious that, as the charge on one of the species approaches zero, the exponential term approaches unity and eq 14 reduces to

$$K_{os} = \frac{4}{3}\pi a^3 N_A \times 10^{-3} = a^3 \times 2.52 \times 10^{21} \quad (16)$$

Equation 16 can be derived independently from the equations for the diffusion of two species to positions of nearest neighbors and their redissociation—a manifestation of the so-called "solvent cage effect." If the two species have *no electrostatic interaction*, the form of the equilibrium constant is identical with eq 16.[12]

For the aquated metal ions studied, models indicate that the value of a is between 3.5 and 5 A depending on the extent to which the ammonia molecule penetrates between the water molecules coordinated to the metal ion prior to the effective loss of one of the waters. Assuming a most probable value of 4 A for a, K_{os} is approximately equal to 0.15. (This value is in line with estimates made by previous workers, who, while not detailing the method of calculation, have utilized values of 0.3 and 0.1, respectively, for reactions involving the neutral ligands imidazole[13] and pyridine-2-azo-*p*-dimethylaniline.[14])

The resultant values calculated for k^{M-H_2O}, the rate constant for metal–water bond rupture, are listed in Table IV for Co(II), Ni(II), and Zn(II). Two sets of previously reported values are listed for comparison. The values of Swift and Connick were determined from nmr line-broadening measurements of O^{17}-labeled water exchanging in the inner coordination sphere of the metal ion,[15] while those reported by Eigen, Tamm, and Maass were obtained by sound absorption measurements of sulfate ion exchanging with coordinated water.[16] Both o fthese methods are independent of any calculation for prior outer-sphere association.

TABLE IV

VALUES FOR WATER LOSS RATE CONSTANT, k^{M-H_2O}(SEC^{-1})

Metal ion	This work (25°)	Swift and Connick (25°)	Eigen, *et al.* (20°)
Co^{2+}	8×10^5	11.3×10^5	3×10^5
Ni^{2+}	3×10^4	2.7×10^4	1×10^4
Zn^{2+}	2×10^7 [a]	...	3×10^7

[a] Calculated for 11°.

The close agreement between these two sets of values and the values calculated from the ammonia reactions studied in this work appears to confirm the fact that the formation of the monoammine complexes proceeds by mechanism 1.

Discrepancy between Formation Rate Constants for Monoamminenickel(II) and Polyaminenickel(II) Complexes: Proposed Internal Conjugate Base Mechanism.—In a previous study of the kinetics of nickel polyamine complexes,[2] it was noted that the formation rate constant for the monoamminenickel(II) complex—which was at that time calculated from an available dissociation rate constant and the stability constant—was approximately 50 times smaller than for the monoethylenediaminenickel(II) complex, whereas mechanism 1 would predict that the two reactions should proceed at nearly the same rate. The results of the investigation on the higher polyamine complexes of nickel showed that the experimental formation rate constants for these complexes were in agreement with the constant for ethylenediamine. However, as seen in the present work, the formation of monoamminenickel(II) proceeds at a rate to be expected on the basis of mechanism 1. Therefore, it must be presumed that the polyamine ligands react abnormally fast with the aquonickel ion.

This increase in the reaction rate constants of the polyamine ligands could be attributed to (a) a change in mechanism to either a classical bimolecular mechanism (involving a seven-coordinate intermediate) or a

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[12] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 500. In deriving the equilibrium equation, Benson has made an arithmetic error in obtaining $K_{os} = 8a^3N_A \times 10^{-3}$ (eq XV.2.16), which differs by a factor of two from eq 16.

[13] G. G. Hammes and J. I. Steinfeld, *J. Am. Chem. Soc.*, **84**, 4639 (1962).

[14] R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).

[15] T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

[16] M. Eigen and K. Tamm, *Z. Elektrochem.*, **66**, 107 (1962); M. Eigen and G. Maass, unpublished data.

conjugate base mechanism, or (b) an increase in $k^{\text{M-H}_2\text{O}}$ and/or K_{os}. A classical bimolecular mechanism, although recently suggested by Wilkins and coworkers to account for an enhancement in the rate of reaction of monoterpyridine complexes toward further substitution,[17] has not yet been substantiated as an important reaction path for formation reactions of the transition metal complexes. In fact, quite the opposite appears to be true.[18] Moreover, if such a mechanism were important for polyamine reactions, ammonia would be expected to proceed *via* the same mechanism, whereas it has been shown that ammonia appears to exchange with coordinated water by the unimolecular mechanism 1. Therefore, the classical bimolecular mechanism is considered unlikely.

Similarly, if the increased lability of hexaaquonickel(II) ion toward reaction with a polyamine could be attributed to a simple conjugate base effect, as elucidated by Basolo and Pearson,[19] the same mechanism should also be observed for ammonia since the protonation constant for ammonia ($\log K_{\text{NH}_4}{}^{\text{NH}_3} = 9.3$) is nearly the same as the first protonation constant for the polyamine ligands ($\log K_{\text{HP}}{}^{\text{P}} \approx 9.8$). However, the present study of ammonia reactions reveals no evidence for a conjugate base effect, and the normal conception of a conjugate base mechanism would not explain the fact that the enhanced formation rate constants appear to be peculiar to the multidentate ligands. Similar arguments can be used to refute other alternate mechanisms.

If both ammonia and the polyamine ligands are presumed to react *via* the unimolecular mechanism 1 then the enhanced reaction rates in the case of the polyamines must be attributable either to an increase in K_{os} or $k^{\text{M-H}_2\text{O}}$ or both. Since an unprotonated polyamine involves the same electrostatic considerations as does ammonia, the formation of the outer-sphere complex must proceed at approximately the same rate in both cases (a difference in the diffusion rates will cancel with the contribution of the same factor in the dissociation process).[12] However, the dissociation rate of this intermediate could be decreased if some means of stabilization were available. In the case of the polyamine ligands this could be achieved by hydrogen bonding between a nitrogen donor atom of the incoming polyamine and a hydrogen of one of the coordinated water molecules. This process is made feasible by the similarity in the two protonation constants[20]

$$\text{H}^+ + \text{polyamine} \rightleftharpoons \text{Hpolyamine}^+ \qquad \log k_{\text{HP}}{}^{\text{P}} = 9.8$$

$$\text{H}^+ + \text{Ni(H}_2\text{O)}_5\text{(OH)}^+ \rightleftharpoons \text{Ni(H}_2\text{O)}_6{}^{2+} \qquad \log K_{\text{Ni}}{}^{\text{Ni-H}} \approx 9$$

Although ammonia could also participate in this type of hydrogen bond, formation of the hydrogen bond would eliminate the potential ability of the same ammonia molecule to coordinate with the central metal ion. By contrast, hydrogen-bonded ethylenediamine, or one of the higher polyamines, contains an adjacent nitrogen donor atom within the same molecule which still has the ability to form a coordinate bond. Therefore, hydrogen-bond formation between the aquometal ion and the polyamine would effectively increase K_{os} while still promoting the desired reaction. This would account for the observation of enhanced formation rate constants only in the case of multidentate ligands.

Hydrogen-bond formation of the type postulated would be expected to impart at least a partial hydroxide ion character to the coordinated water molecule participating in the hydrogen bond. The results of studies involving Cr(III),[21] Fe(III),[22] Co(III),[23] and Cu(II)[24] indicate that monohydroxo complexes lose water molecules from the inner sphere at approximately 100 to 1000 times the rate observed for the corresponding hexaaquo metal ion species. The hydrogen-bonded intermediate might also be expected to undergo water loss at an enhanced rate, the degree of labilization being dependent upon the strength of the hydrogen bond formed. As a result, the net effect of this mechanism is that of an "internal conjugate base" (ICB), where the reacting multidentate ligand molecule promotes its own rate of coordination by increasing the values of both K_{os} and $k^{\text{M-H}_2\text{O}}$.

The proposed ICB mechanism, as shown in Figure 4 for ethylenediamine, can be broken down into five steps: (1) the formation of an outer-sphere complex, (2) the establishment of a hydrogen bond between a coordinated water molecule and a basic donor atom of the ligand, (3) loss of a labilized water molecule from the inner sphere with rapid substitution of a second donor atom from the same multidentate ligand molecule, (4) rupture of the original hydrogen bond, and (5) further bonding of the multidentate ligand by the normal reaction path which has been outlined previously.[2] It will be noted that the water lost in step 3 must be *cis* to the position of the hydrogen bond in order to promote the proposed mechanism. Ingold, Nyholm, and Tobe report that coordinated hydroxide labilizes both *trans* and *cis* water molecules in the case of Co(III).[25]

The fact that ammonia and the polyamines may not be sufficiently basic to completely remove a proton from a water molecule coordinated to hexaaquonickel(II) ion could explain the absence of a "normal" conjugate base mechanism since this mechanism has been reported only for the more acidic aquated metal ions. The failure of ammonia to react by a modified conjugate base mechanism, similar to the one proposed above, can be attributed to the requirement that two ammonia molecules would have to be in close proximity

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[17] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).

[18] See, *e.g.*, M. L. Tobe, *Record Chem. Progr.*, **27**, 79 (1966).

[19] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p 129 ff.

[20] L. G. Sillén and A. E. Martell, "Stability Constants," 2nd ed, Special Publication No. 17, The Chemical Society, London, 1964.

[21] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

[22] H. Wendt and H. Strehlow, *Z. Elektrochem.*, **66**, 228 (1962); R. E. Connick and C. P. Coppel, *J. Am. Chem. Soc.*, **81**, 6389 (1959).

[23] R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).

[24] D. W. Margerum, B. A. Zabin, and D. L. Janes, *Inorg. Chem.*, **5**, 250 (1966).

[25] C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

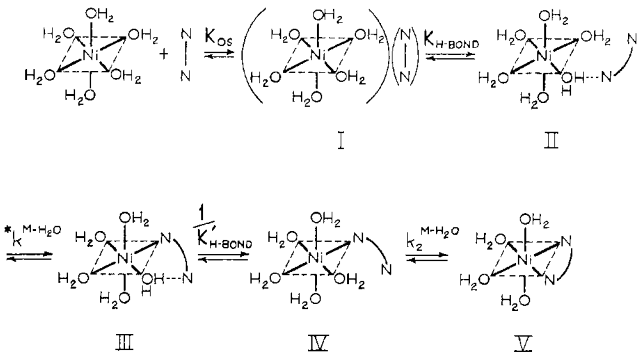

Figure 4.—Proposed "internal conjugate base" (ICB) mechanism using the reaction of hexaaquonickel(II) ion with ethylenediamine as a model: I, outer-sphere complex; II, hydrogen-bonded outer-sphere complex; III, single-bonded intermediate with hydrogen bond still intact; IV, normal single-bonded intermediate; V, normal double-bonded complex; K_{os} = equilibrium constant for outer-sphere association; K_{H-BOND} = stability constant for hydrogen-bond formation; $*k^{M-H_2O}$ = rate constant for enhanced metal–water bond rupture (rate-determining step); K'_{H-BOND} = stability constant for hydrogen bond formation in single-bonded complex; $k_2^{M-H_2O}$ = rate constant for metal–water bond rupture in single-bonded complex.

to the aquometal ion simultaneously (one ligand to form a hydrogen bond and a second to replace a water molecule in the inner sphere). This situation, which correlates to a termolecular collision (*i.e.*, a second bimolecular collision within the lifetime of the activated intermediate), is statistically unfavorable for dilute solutions (unless the activated intermediate were to have a very long lifetime). Therefore, it is concluded that only an *internal* conjugate base mechanism will be favored, and this mechanism will be observed only for multidentate ligands containing two strongly basic donor atoms in the structural relationship which allows one of the donor atoms to enter the first coordination sphere readily while a second is hydrogen bonded to a coordinated water molecule.

Support for the proposed mechanism is obtained from a comparison of the literature values for formation rate constants of nickel complexes in aqueous solution. The values listed in Table V reveal that all multidentate ligands with protonation constants less than 10^8 react at rates comparable to unidentate ligands, whereas those with protonation constants significantly above this value exhibit enhanced formation rate constants. Ligands in the latter category include the regular polyamines and a related ligand, 2,2′-ethylenediaminobis-(2-methyl-3-butanone) dioxime (EnAO).[26] All of these ligands have at least two amine nitrogens situated in positions favorable for chelate ring formation, thus meeting the requirements for the ICB mechanism. It is of particular interest that protonated species of the polyamines, having protonation constants no greater than 10^8 ($H_2(trien)^{2+}$, $H_2(tetren)^{2+}$, $H_3(tetren)^{3+}$), fail to exhibit enhanced formation rate constants even though two or more unprotonated nitrogen donor atoms are present.

Table V

Correlation of Nickel Complex Formation Rate Constants with Base Strengths of the Multidentate Ligands

Charge on ligand	Ligand	Log rate constant[a]	Log protonation constant[b]	Remarks
−2	SO_4^{2-}	4.2	Unidentate	
−2	H_2EDTA^{2-}	3.3	2.7	Abnormally slow
−2	Mal^{2-}	4.8[c]	5.6	
−2	$Oxal^{2-}$	4.9	4.0	
−1	SCN^-	3.7	Unidentate	
−1	$HOxal^-$	3.7	Unidentate[d]	
−1	$HMal^-$	3.5[c]	Unidentate[d]	
−1	Diglycine	4.3	8.2	Slightly fast
−1	Triglycine	3.9	8.1	
0	H_2O	4.4[e]	Unidentate	
0	NH_3	3.6[f]	Unidentate	
0	N_2H_4	3.4	Unidentate	
0	py	3.7	Unidentate	
0	IM	3.7	Unidentate	
0	Phen	3.5	5.0	
0	2-MePhen	2.7	5.3	Abnormally slow
0	5-MePhen	3.5[g]	5.3	
0	2-ClPhen	3.0[g]		
0	5-ClPhen	2.4[g]	4.2	Abnormally slow
0	$5\text{-}NO_2Phen$	3.2[g]	3.5	
0	dipy	3.2[g]	4.4	
0	terpy	3.1	4.3	
0	PAD	3.6	4.5	
0	EnAO	4.4[i]	8.5	Abnormally fast
0	en	4.6	10.0	Abnormally fast
+1	Hen^+	2.8	Unidentate[d]	
+1	$HEnAO^+$	0.6[i]	6.1	Abnormally slow
+1	$Htrien^+$	4.0[h]	9.2	Abnormally fast
+2	H_2trien^{2+}	2.0[h]	7.8	
+2	$H_2tetren^{2+}$	2.5[h]	8.1	
+3	$H_3tetren^{3+}$	0.5[h]	4.8	

[a] All rate constants in M^{-1} sec.$^{-1}$; unless otherwise noted, all values are from R. G. Wilkins and M. Eigen in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965. [b] Values taken from ref 20. [c] F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965). [d] Ligand resembles unidentate ligand at time of first bond formation since only one donor atom is unprotonated. [e] Rate constant in sec^{-1}. [f] This work. [g] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965). [h] Ref. 2. [i] Ref 26. The ligand abbreviations used are as follows: $EDTA^{4-}$ = ethylenediaminetetraacetate; Mal^{2-} = malonate; $Oxal^{2-}$ = oxalate; py = pyridine; IM = imidazole; Phen = 1,10-phenanthroline; dipy = dipyridine; terpy = terpyridine; PAD = pyridine-2-azodimethylaniline; en = ethylenediamine; trien = triethylenetetramine; tetren = tetraethylenepentamine; EnAO = 2,2′-ethylenediaminobis-(2-methyl-3-butanone) dioxime.

The proposed ICB mechanism should be applicable to other metal ions as well although data are almost nonexistent for ligands of the type which favor this mechanism reacting with metal ions other than nickel. However, at least one piece of supporting evidence is found in the case of tetramethylethylenediamine reacting with hexaaquocopper(II) ion, for which the calculated formation rate constant is approximately 100 times larger than the corresponding calculated rate constant with ammonia.[27]

Since promotion of the ICB mechanism requires that at least one donor atom have a basicity of the order of magnitude of the coordinated water molecules (or greater), it is expected that some ligands will react

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(26) R. K. Murmann *J. Am. Chem. Soc.*, **84**, 1349 (1962).

(27) R. G. Wilkins, *J. Chem. Soc.*, 4475 (1962).

by this mechanism with certain aquometal ions while failing to do so with others. This aspect is currently being investigated.

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The Volume of Activation in the Acid Hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$

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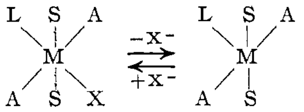
The volumes of activation for the acid hydrolysis of $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$ have been determined by measurement of the effect of hydrostatic pressure on the reaction rates. The values of ΔV^* are, respectively, -17 and -14 ml/mole with an error of approximately 2 ml in each. The effect of pressure on the equilibrium constants is too small for reliable measurement and the volumes of reaction are therefore nearly zero. It is inferred that, in the transition state, the formation of two Pt–OH_2 bonds is nearly complete, and the Pt–Cl bond is nearly intact.

Introduction

In recent years the measurement of activation volume has proved to be a useful tool in the study of reaction mechanisms.[1] The aquation reactions of platinum(II) complexes appear to be well suited to investigation by this method because their reaction rates lie in a convenient range, accurate kinetic and equilibrium data at ordinary pressure are already recorded, and a variety of types of evidence support the postulation of a mechanistic pathway.[2,3]

It has been shown in previous studies that the substitution reactions of platinum(II) complexes can be divided into two classes. One class includes the reactions of the poor nucleophilic reagents whose rates are first order in complex, zero order in reagent, and approximately the same for all substitutions on a given complex. The other class includes the good nucleophilic reagents whose rates are higher than those of the first and are first order in both complex and reagent. It is believed that the square-planar complexes of Pt(II) possess, in addition to the four strong bonds to ligands in the plane of the complex, two weak bonds to solvent molecules above and below the plane of the complex. In the mechanistic path postulated for the first class of reactions a five-coordinated intermediate (resembling either a square pyramid or trigonal bipyramid) is formed when two solvent molecules move in closer to the complex and help displace the leaving group, *viz.*[2,3]



(1)

Since the theory of platinum(II) substitution reactions imputes such an important role to the solvent in the rate-determining step, it seemed desirable to measure first the volume of activation in the hydrolysis of one of the complexes. Determination of kinetic order is unable to reveal any participation of solvent in the formation of the activated complex, but measurement of activation volume has revealed the bimolecular nature of several hydrolysis reactions of organic substrates.[4]

The volume of activation can be attributed either to a change in the volume of the molecules in the activated state or in the volume of the solvent provided a change in the electrical polarization accompanies the formation of the activated complex.[1] The acid hydrolysis (first aquation) of $Pt(NH_3)Cl_3^-$ which is described by the reaction

$$\mathrm{Pt(NH_3)Cl_3^- + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} Pt(NH_3)Cl_2(H_2O) + Cl^-} \qquad (2)$$

seemed best suited for a volume of activation study since the charge type of reactant and product ions is the same, and consequently the volume change due to solvent effects should be negligible. In the acid hydrolysis of $PtCl_4^{2-}$ described by the reaction

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(1) (a) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, pp 163–205; (b) S. D. Hamann, "Physico-Chemical Effects of Pressure," Butterworth and Co. Ltd., London, 1957; (c) S. D. Hamann, *Ann. Rev. Phys. Chem.*, **15**, 349 (1964); (d) E. Whalley, *Advan. Phys. Org. Chem.*, **2**, 93 (1964).

(2) R. G. Pearson, H. B. Gray, and F. Basolo, *J. Am. Chem. Soc.*, **82**, 787 (1960).

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp 186–190.

(4) (a) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959); (b) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964).