Steric Effects on the Kinetics and Equilibria of Nickel(II)–Alkylamine Reactions in Aqueous Solution

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Abstract: The equilibria and kinetics of aquonickel(II) ion reacting with ammonia, methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, isopropyl-, and *tert*-butylamine have been investigated at 25°, $\mu = 1\ M$ by means of potentiometric titration procedures (including the determination of ligand protonation constants) and the temperature-jump relaxation method. Formation and dissociation rate constants for the 1:1 complexes, along with reliable equilibrium constants, were obtained only for the reactions involving (in order of decreasing formation rate constants) ammonia, methyl-, ethyl-, isopropyl-, and dimethylamine. The tenfold decrease observed in the formation rate constants parallels an increase in the bulk of the substituted alkyl groups. The twofold difference in dissociation rate constants, if significant, also appears to be of steric origin with no apparent inductive contribution.

In accord with the demonstrated applicability of the general dissociative mechanism, as proposed by Eigen, to a wide variety of substitution reactions involving octahedral metal–ligand complexes,[1,2] coordination chemists have been able to interpret even complicated multidentate ligand reactions in terms of the stepwise reaction processes involved.[2] Fundamental to placing such interpretations on a quantitative basis is the availability of independent experimental data on the formation and dissociation rates of the constituent metal–donor atom bonds as well as related intramolecular processes.

For metal ions with unfilled d orbitals, amine nitrogen is of prime importance as a donor atom in coordinating reagents. In an earlier paper we investigated the kinetics of three aquometal ions [Co(II), Ni(II), and Zn(II)] reacting with ammonia, the simplest nitrogen-containing ligand.[3] As a neutral compound of comparable size and structure to water, ammonia provides an ideal species for the theoretical interpretation of experimental results. Thus, when interpreted in light of the dissociative mechanism, the formation rate constants for the 1:1 ammonia complexes were found to be in excellent agreement with solvent-exchange data obtained from nuclear magnetic resonance measurements.

The application of the ammonia results to reactions involving larger ligands containing amine nitrogen groups[4,5] is complicated by the uncertain influence of steric and inductive effects resulting from substitution on the nitrogen atom. Thus, Melson and Wilkins, in using ammonia and aziridine as reference unidentate ligands, have indicated that the alkylamines would represent better systems for comparison.[5]

Previous attempts at studying the equilibria and kinetics of complex formation between transition metal ions and the alkylamines have been hampered by the limited extent to which such reactions occur in aqueous solution. The inherent difficulties are largely attributable to the fact that these compounds are generally much more basic than ammonia so that only a minute fraction of the unprotonated species is present in solution in pH regions where metal hydroxide precipitation is not a competing interference. Thus, available aqueous stability constant values for even methylamine complexes are limited to Ag(I), Cd(II), and Hg(II).[6]

In the current study a renewed effort has been made to evaluate steric and inductive effects in the reactions of aquonickel(II) ion with the unidentate alkylamines to form the 1:1 complex, *viz.*

$$\mathrm{Ni(H_2O)_6^{2+} + NR_3 \rightleftharpoons Ni(NR_3)(H_2O)_5^{2+} + H_2O} \qquad (1)$$

where NR_3 represents methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, isopropyl-, and *tert*-butylamine. Ammonia has also been restudied under corresponding conditions for purposes of comparison.

Despite the use of high ligand concentrations (1.0 *M*) and a sophisticated statistical treatment of the data, an attempt at determining the Ni(II) complex stability constants by means of potentiometric titrations yielded questionable results. However, a kinetic investigation utilizing the temperature-jump relaxation method, with the addition of a coupled indicator to increase the sensitivity of detection, has made it possible to determine both the formation and dissociation rate constants, along with iterated equilibrium constants for Ni(II) ion reacting with four of the alkylamines in addition to ammonia.

The results indicate that increasing alkyl substitution significantly decreases the formation rate constant of the 1:1 complexes, with an apparent slight increase in the dissociation rate constant. Whereas the former trend is readily attributable to steric effects, the latter trend is in apparent contradiction to anticipated inductive effects and is in distinct contrast to earlier studies which have indicated a direct relationship between the complex dissociation rate constants and the ligand acid dissociation constants for series of related ligands interacting with aquonickel(II) ion.[7,8]

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(2) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970), and references cited therein.

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Experimental Section

Reagents. $Ni(ClO_4)_2 \cdot 2H_2O$ was prepared by allowing reagent grade $NiCO_3$ and $HClO_4$ to react. The resultant salt and the commercially obtained NH_4ClO_4 and $NaClO_4$ (G. F. Smith Chemical Co., reagent grade) were recrystallized twice from saturated aqueous solution to remove metal ion impurities.

Methylamine hydrochloride ($MeNH_2 \cdot HCl$) (J. T. Baker Chemical Co.) was recrystallized from absolute methanol to remove green-colored impurities, washed with chloroform, and dried in a vacuum desiccator, mp 232° (lit. mp 231.8–233.4°).[9] In preparing solutions the free amine was liberated with aqueous NaOH, distilled (bp −6.3° [10]), and collected in 0° water. Diethylamine (Et_2NH) and triethylamine (Et_3N), obtained as anhydrous liquids (J. T. Baker Chemical Co.), were converted to the corresponding hydrochlorides in ethanol and crystallized in absolute ethanol:[9] mp 223–224 and 254.5°, respectively; lit. mp 223.5 and 254°, respectively.[9] The neutral amines were then regenerated as needed by adding excess NaOH and distilling (Et_3N forming an azeotrope with water which distilled at 75.8°). These solutions were kept under nitrogen atmosphere to deter oxidation[10] and used as rapidly as possible after generation, since concentrated aqueous solutions (~1 *M*) were found to decompose in less than 24 hr. For potentiometric titrations these amines were added to an acid solution immediately before titrating.

Isopropylamine (i-$PrNH_2$) and *tert*-butylamine (*tert*-$BuNH_2$) (J. T. Baker Chemical Co.) were purified by direct distillation and collected at 32 and 44°, respectively; lit. 33[11] and 44°,[9] respectively. Dimethylamine (Me_2NH), trimethylamine (Me_3N), and ethylamine ($EtNH_2$), obtained as anhydrous liquids in sealed vials, showed no impurities detectable by gas chromatography, and aqueous solutions were prepared directly as needed.

All other reagents were obtained in reagent grade (with the exception of the acid–base indicators) and used without further purification. Deionized distilled water was used to prepare all solutions.

Equilibrium and Kinetic Measurements. All pH measurements were made with a Corning Model 12 pH meter using glass and saturated calomel electrodes, the latter equipped with a KCl–agar bridge to prevent precipitation of $KClO_4$ at the junction. During potentiometric measurements, solutions were maintained at 25.0 ± 0.1° by inserting the vessel in a thermostated hollow brass jacket. The protonation constant values of the acid–base indicators used to monitor the relaxation rates were determined spectrophotometrically using a Beckman Acta V recording spectrophotometer.

All kinetic relaxation measurements were made using a single-beam, Joule-heating, temperature-jump spectrometer manufactured by Messanlagen Studiengesellschaft mbH, Goettingen, Germany, equipped with a Bausch and Lomb high-intensity grating monochromator. The final temperatures achieved were 25.0 ± 0.2° as calibrated by a thermistor. The relaxation spectra were displayed on a Tektronix Type 549 storage oscilloscope and subsequently recorded on 35-mm film. The relaxation times were then evaluated by matching the curves to standard exponential curves as previously described.[3] Under the conditions of measurement, the inauguration of convection within the cell following the heating discharge placed an upper time limit of approximately 1 sec on the observed relaxations. This, in turn, placed lower limits on the concentration levels for which interpretable data could be obtained for most systems included in this study and prevented measurement of two systems altogether.

The range of total nickel ion used for the relaxation measurements was varied from 1 to 7 m*M* for the NH_3 study, 5 to 50 m*M* for Me_2NH, and 10 to 100 m*M* for $MeNH_2$, $EtNH_2$, and i-$PrNH_2$. The total concentration of ligand for all studies was within the range 0.72–1.00 *M*, the concentration of the acid perchlorate salt added being varied in order to maintain 1 *M* ionic strength. The concentration of the free unprotonated ligand species was then primarily a function of the solution pH which was generally in the range 6.5–7.0.

Results

Determination of Protonation Constants. Initial kinetic studies on the Ni(II)–monoamine reactions, using conditions identical with those applied in the former ammonia study,[3] revealed that, in order to evaluate the formation rate constants satisfactorily *via* the temperature-jump method, relatively high reactant concentrations were required, resulting in a solution ionic strength greater than 0.1 *M*. Therefore, a constant ionic strength of 1.0 *M* was chosen for these experiments, necessitating the determination of new protonation constant values for all ligands studied. These values were determined from potentiometric titrations under nitrogen atmosphere of the basic amine solutions with standard perchloric acid ($\mu = 0.1$) or nitric acid ($\mu = 1.0$) using $NaClO_4$ (0.1 *M*) or KNO_3 (1.0 *M*) to maintain constant ionic strength.

The protonation constant values were calculated as concentration constants (M^{-1}) defined by the relationship

$$K_H^c = [HL^+]/[H^+][L] = \gamma_H[HL^+]/a_H[L] \qquad (2)$$

(γ_H and a_H representing the activity coefficient and activity, respectively, of the solvated hydrogen ion) using the Bjerrum $\bar{n}_H$ function[12] in such a way as to allow the inclusion of all experimental titration points as previously described.[13] To check the accuracy of these measurements, corresponding values were determined at 0.1 *M* ionic strength for comparison with available literature values.[14–17] All values for the nine ligands included in this study are listed in Table I.

Table I. Concentration Protonation Constants of the Aliphatic Monoamines at 25.0°

Amines	Log K_H^c [a] (μ = 1.0 *M*)	Log K_H^c [a] (μ = 0.1 *M*)	Lit. value (μ = 0.1 *M*)	Ref
NH_3	9.385	9.21[b]	9.245	14
$MeNH_2$	10.765	10.594	10.630	15
Me_2NH	10.912	10.735	10.788	15
Me_3N	9.983	9.802	9.800	15
$EtNH_2$	10.778	10.585	10.645	16
Et_2NH	11.111	10.920	10.940	16
Et_3N	10.815	10.767	10.67	17
i-$PrNH_2$	10.721	10.595		
tert-$BuNH_2$	10.716	10.633		

[a] Only the first two figures to the right of the decimal are significant. [b] Reference 13.

It is to be noted that, with the exception of Et_3N, all protonation constant values determined in this study at 0.1 *M* ionic strength are within 0.06 log unit of the corresponding literature values. Furthermore, the protonation constants appear to increase consistently on going from 0.1 to 1.0 *M* ionic strength by 0.18 ± 0.01 log

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unit, with the exception of the data for Et_3N, *i*-$PrNH_2$, and *tert*-$BuNH_2$.

Determination of Stability Constants. With the exception of NH_3, no stability constant values were available for the Ni(II)–amine complexes included in this study. In an attempt to determine the stepwise stability constants K_1, K_2, etc., potentiometric titrations of the protonated ligand were carried out with standard base solution in the presence of Ni(II) ion at 1.0 *M* ionic strength in the manner described by Bjerrum.[12] The titrimetric data were then resolved using a modification of a computer program written by Varga[18] involving matrix solutions of the Bjerrum $\bar{n}_L$ function.

For the Ni(II)–NH_3 system, the stability constant values obtained in this manner ($\log K_1 = 2.82$, $\log K_2 = 2.19$, $\log K_3 = 1.73$, $\log K_4 = 1.12$) were in excellent agreement with available literature values.[12] For all other systems, the high basicity of the ligands severely restricted the extent of complex formation observed prior to the precipitation of nickel hydroxide. As a result, the apparent stability constant values obtained were unreasonably large and totally inconsistent with the kinetic data. To circumvent this difficulty, the stability constant values of the 1:1 complexes were iterated simultaneously with the rate constants from the relaxation spectra.

Temperature-Jump Relaxation Measurements. In utilizing the temperature-jump relaxation method for studying the formation and dissociation kinetics of the Ni(II)–alkylamine systems, it was necessary to couple the desired reactions with an acid–base indicator

$$\mathrm{Ni(H_2O)_6{}^{2+} + L \underset{k^{Ni-L}}{\overset{k_{Ni}{}^{L}}{\rightleftharpoons}} NiL(H_2O)_5{}^{2+} + H_2O} \qquad (1a)$$

$$\mathrm{H^+ + L \overset{K_H}{\rightleftharpoons} HL^+} \qquad (3)$$

$$\mathrm{H^+ + In^- \overset{K_i}{\rightleftharpoons} HIn} \qquad (4)$$

where the absorbance change in reaction 4 was monitored. Such a system was previously described for the ammonia study[3] and shown to yield the relaxation equation

$$1/\tau = k_{\mathrm{Ni}}{}^{\mathrm{L}}([\overline{[\mathrm{Ni}^{2+}]}/(1 + \alpha)] + [\overline{\mathrm{L}}]) + k^{\mathrm{Ni-L}} \qquad (5)$$

where $[\overline{\mathrm{Ni}^{2+}}]$ and $[\overline{\mathrm{L}}]$ represent the equilibrium concentrations of uncomplexed species and α represents the rate of change in concentration of free unprotonated ligand relative to the change in concentration of uncomplexed Ni(II) ion, which can be related to the protonation constants for the ligand and the indicator (K_H and K_i, respectively) by the equation

$$\alpha = \frac{K_H[H^+](K_i[In^-] + K_i[H^+] + 1)}{K_H[L](K_i[H^+] + 1) + K_i([In^-] + [H^+]) + 1} \qquad (6)$$

Unlike the conditions prevailing in the earlier ammonia study,[3] the values of α were frequently significant and were included in resolving the data using eq 5. Since it was demonstrated in the previous study[3] that hydroxynickel species did not contribute to the kinetic behavior of the nickel–ammonia system at pH values well above those utilized in this work, this aspect was not investigated further.

Phenol red and bromothymol blue were used preferentially as the monitoring indicators (eq 4), the choice of indicator being made such that the log K_i values were about 0.5 unit larger than the pH values of the solution being measured. In this manner only about one-fourth of the indicator was present in the basic form which was then monitored at the visible wavelength of maximum absorption. The logarithmic K_i values for these two indicators were determined at 25.0°, $\mu = 1.0$ *M*, as 7.54 and 6.84 for phenol red and bromothymol blue, respectively. Under the conditions used for the relaxation measurements, both indicators exhibit very fast relaxations relative to the systems being studied, the rate constant for phenol red protonation having been reported previously[19] and the protonation reaction of bromothymol blue having been demonstrated to have a lifetime of less than a microsecond under the conditions used.[3]

In calculating the values of $[\overline{\mathrm{Ni}^{2+}}]$ and $[\overline{\mathrm{L}}]$ to utilize in eq 5 for resolving the rate constants, the protonation constants listed in Table I were utilized and an iteration procedure was used in the calculations until the value of K_1 converged with the resultant ratio of the resolved rate constants, $k_{\mathrm{Ni}}{}^{\mathrm{L}}/k^{\mathrm{Ni-L}}$. (Owing to the high basicities of the ligands involved, the contributions of K_2, K_3, etc., were never significant under the experimental conditions used.) For the nickel–ammonia complex, the stability constant obtained in this manner was in excellent agreement with the K_1 value obtained potentiometrically.

The plots of eq 5 resulting from this treatment are shown in Figures 1 and 2 for the reactions involving NH_3, $MeNH_2$, $EtNH_2$, *i*-$PrNH_2$, and Me_2NH. The systems involving Et_2NH and *tert*-$BuNH_2$ yielded nonexponential relaxation curves (possibly representing multiple relaxations) which were not resolvable on the basis of the available data. No relaxation was observed for Me_3N, while Et_3N appeared to relax too slowly (>1 sec) to be measured with the temperature-jump spectrometer used.

The resolved rate constants for the five systems for which significant kinetic data were obtained are listed in Table II. Also given are the iterated values for K_1

Table II. Resolved Rate Constants for the Ni(II)–Alkylamine Reaction Systems; 25°, $\mu = 1.0$ *M* ($HLClO_4$)

Ligand	$k_{\mathrm{Ni}}{}^{\mathrm{L}} \times 10^{-3}$, $M^{-1}\ \mathrm{sec}^{-1}$	$k^{\mathrm{Ni-L}}$, sec^{-1}	Iterated $\log K_1$
NH_3	4.48[a]	7.1[a]	2.80
$MeNH_2$	1.31	7.7	2.23
$EtNH_2$	0.865	13.3[b]	1.81
i-$PrNH_2$	0.605	16.8	1.56
Me_2NH	0.332	11.3	1.47

[a] Compare to $k_{\mathrm{Ni}}{}^{\mathrm{NH_3}} = 4.6 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$, $k^{\mathrm{Ni-NH_3}} = 3.4\ \mathrm{sec}^{-1}$ determined previously at 25°, $\mu = 0.1$ *M* (ref 3). [b] Also determined at $\mu = 0.1$ *M*: $k^{\mathrm{Ni-EtNH_2}} = 9.6\ \mathrm{sec}^{-1}$.

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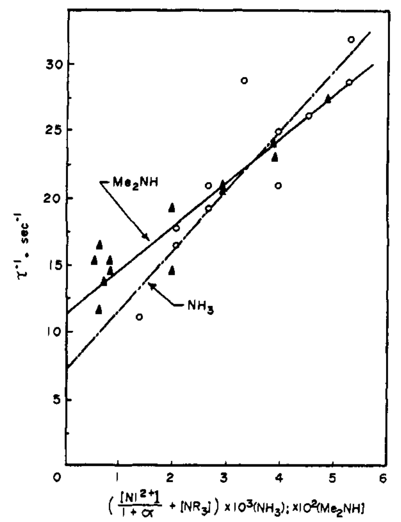

Figure 1. Resolution of the formation and dissociation rate constants for the 1:1 Ni(II)-alkylamine complexes: ○, NH_3; ▲, Me_2NH. Plot of eq 5. (Note the difference in abscissa scales for the two systems.)

obtained as described above. From an examination of the relaxation data, the formation rate constant values are presumed to be known to within ±10%, whereas the dissociation rate constants may be in error by as much as 50%.

Discussion

The Effect of N-Alkyl Substitution on Stability Constants. As has been observed by previous workers[15,20] in studying the basicity of the N-alkyl-substituted monoamines in water and other solvents, the reaction of these amines with Ni(II) ion cannot be simply interpreted in terms of the magnitude of the interaction between an acid and a base as might be anticipated if nucleophilicity were the sole determining factor. Thus, no direct correlation is immediately apparent between the stability constants and the protonation constants for these amines. Instead, the stability of the complexes decreases with increasing alkyl substitution which correlates with the values of *Dq* observed for the interaction of Ni(II) ion with primary amines.[21]

Investigations on the relative basicity of the substituted amines in nonaqueous solvents indicate that the order of basicity depends on the nature of the solvent.[20] In chloroform and chlorobenzene, for example, the relative trends in amine basicity are reported to be in the order primary < secondary < tertiary in conformance with the positive inductive effects of the substituted alkyl groups. Thus it appears that the order of basicity for the substituted amines in aqueous solution is strongly influenced by the solvent in an undetermined manner.

A comparison of the kinetically determined stability constants for the nickel–amine complexes as obtained in this work (Table II) with this "intrinsic" basicity of the amine ligands reveals an inverse relationship. This strongly suggests that steric effects are of primary importance.

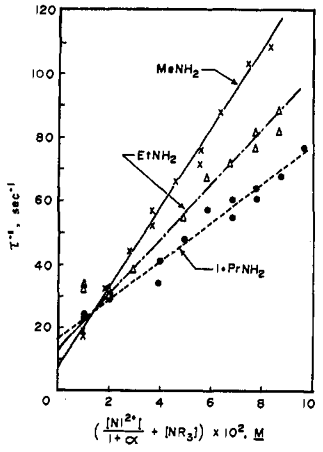

Figure 2. Resolution of the formation and dissociation rate constants for the 1:1 Ni(II)-alkylamine complexes: ×, $MeNH_2$; △, $EtNH_2$; ●, *i*-$PrNH_2$. Plot of eq 5.

Some authors[22] have related coordinating abilities to differences in permanent dipole moments of the molecule. It has been observed that the polarizability of the bonding electrons in the ligand molecule is decreased in all cases by alkyl substitution. The decrease in coordinating ability from NH_3 to primary amine to secondary amine to tertiary amine runs parallel to a decrease in the permanent dipole moment of the molecules. As noted in Table III, however, a comparison of methyl- and ethyl-substituted amines shows inconsistencies between the two groups, the ethyl-substituted ligands having lower coordinating ability despite higher dipole moments. This again suggests that steric effects are involved.

Table III. Variation of Dipole Moment with Alkyl Substitution on Aliphatic Monoamines

Ligand[a]	Permanent dipole × 10^{18}, esu	Ligand[a]	Permanent dipole × 10^{18}, esu
NH_3	1.49	$(C_2H_5)_2NH$	1.20
CH_3NH_2	1.23	$(CH_3)_3N$	0.6
$C_2H_5NH_2$	1.3	$(C_2H_5)_3N$	0.9
$(CH_3)_2NH$	0.96		

[a] Ability to coordinate decreases in going from the top to the bottom of this list.

The maximum coordination number shown by Ni(II) ion toward these amines does decrease with increasing degree of alkyl substitution on the nitrogen, as observed in the gas phase by Hatfield and Yoke[23] for the reaction of the ethylamines with the halides of calcium, cobalt(II), and zinc. On the basis of the foregoing observations, it is suggested that a direct correlation exists

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(20) R. G. Pearson and D. C. Vogelsong, *J. Amer. Chem. Soc.*, **80**, 1038 (1958).

(21) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

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between the stability constants of the nickel–amine complexes and the steric aspects of the substituent groups on the nitrogen donor atom.

In order to correlate the stability of the complexes to steric effects in a quantitative manner, one could use the function log $\bar{K}_{ML}$/log K_H as proposed by Bjerrum,[24] where $\bar{K}_{ML}$ represents the average stepwise stability constant of the complexes. Bjerrum proposed that a decrease in this ratio within a series of complexes for a particular metal ion indicates an increase in steric hindrance in the ligand. This approach assumes that, for a related series of substituted ligands, the protonation constants of the ligands are essentially unaffected by steric factors owing to the small size of the proton, while the stability constant of the complex is influenced much more strongly. It further assumes that any solvation effects are similar for the ligand reaction with a proton and nickel ion.

In the present study only the 1:1 complex was investigated in detail and only the first stability constant value, K_1, was consistently evaluated for all systems. The substitution of K_1 in place of $\bar{K}_{ML}$ in calculating the Bjerrum steric function has the effect of eliminating any ligand–ligand steric factors from this function so that only metal–ligand steric factors remain.

Values of log K_1/log K_H for the nickel–monoamine systems studied are listed in Table IV. This ratio exhibits a distinct decreasing trend with increasing alkyl substitution on the nitrogen donor atom which would appear to support the suggestions made in the preceding paragraphs indicating that steric factors do play a strong role in influencing the relative stability constant values. However, in view of the previously cited evidence of an undetermined solvent influence upon the relative basicities of the amines in aqueous solution, the basic premise incorporated in the Bjerrum steric function that the K_H values represent the relative basicities of the ligands is without apparent validity. Therefore, the trend in log K_1/log K_H values is of questionable significance.

Table IV. Calculated Steric Factors for Aquonickel(II) Ion Reacting with the Aliphatic Monoamines at 25.0° and μ = 1.0 *M*

Ligand	Log K_1/log K_H[a]	E_s (log [$k_{Ni}^{L}/k_{Ni}^{NH_3}$])
NH_3	0.30	0.00
$MeNH_2$	0.21	−0.53
$EtNH_2$	0.17	−0.71
i-$PrNH_2$	0.15	−0.87
Me_2NH	0.13	−1.13

[a] Values calculated using log K_1 values obtained kinetically (Table II).

It is concluded that the thermodynamic approach to the evaluation of steric effects, which has been utilized in several previous studies, is of limited value for the systems included in this work. By contrast, a comparison of the kinetic rate constants permits an examination of steric effects upon formation rate constants as distinguished from dissociation rate constants.

The Effects of N-Alkyl Substitution on the Kinetics. A theoretical value of the formation rate constant for Ni(II) ion reacting with ammonia based on the dissociative mechanism can be calculated from the relationship[2,3]

$$k_{Ni}^{L} = K_{os}k^{Ni-H_2O} \qquad (7)$$

where K_{os} represents the equilibrium constant for outer-sphere complex (ion pair) formation between the reacting partners, and k^{Ni-H_2O} represents the rate constant for nickel–water bond rupture—presumed to represent the rate-determining step.[1-3] Using a value of 4 Å for the center-to-center distance of closest approach in the outer-sphere complex, a value of K_{os} equal to 0.16 M^{-1} is obtained for 25°.[3] The value of k^{Ni-H_2O} has been determined by Swift and Connick[25] to be 2.7 × 10^4 sec^{-1} at 25°. Substituting these two values into eq 7, a calculated value of the formation rate constant, k_{Ni}^{L}, of 4.5 × 10^3 M^{-1} sec^{-1} results. This is in excellent agreement with the value of 4.6 × 10^3 M^{-1} sec^{-1} obtained by Rorabacher at μ = 0.1 *M*[3] and that of 4.48 × 10^3 M^{-1} sec^{-1} determined in this work at μ = 1.0 *M* (Table II).

If, for the aliphatic amines included in this study, it is assumed that the center-to-center distance of closest approach between the nitrogen donor atom and the aquonickel ion remains about the same as for ammonia, *i.e.*, K_{os} remains constant, the formation rate constants for Ni(II) reacting with all the amines should be about the same as the value obtained with ammonia *if steric effects are negligible*. However, the values shown in Table II indicate that the formation rate constants are decreasing with increasing alkyl substitution. This discrepancy from the expected theoretical value can be explained by observing that, in the calculation of the formation constant using eq 7, K_{os} does not take into account the fact that the ligand molecule must be properly oriented in the outer-sphere complex for bonding to occur at the time that the metal–water bond breaks. Otherwise only solvent exchange will take place with no substitution of the water molecule by the ligand.

To facilitate correlation of the values of the formation rate constants to steric effects, one can use the logarithmic ratio for the organic substituent effect, E_S,[26,27] defined as

$$E_S = \log (k/k_0) \qquad (8)$$

where k_0 is the reference rate constant for a given system without appreciable steric hindrance. Table IV lists the calculated E_S values for the systems studied, taking k_0 as $k_{Ni}^{NH_3}$ (equal to 4.5 × 10^3 M^{-1} sec^{-1}), the experimentally observed value of the formation rate constant for the nickel–ammonia system.

As observed for the trend in stability constants, among the primary amines the steric hindrance is greatest for the system with a branched alkyl group, *i.e.*, *i*-$PrNH_2$, the effect appearing to vary with both the size and number of alkyl groups substituted on the

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nitrogen donor atom. The magnitude of the apparent steric effects (amounting to 3-, 5-, 7.5-, and 13.5-fold for methyl, ethyl, isopropyl, and dimethyl substitution, respectively) reemphasizes the importance of using the alkylamines rather than ammonia as reference species in interpreting the kinetics of reactions involving larger chelating ligands.

Dissociation Rate Constants. The dissociation rate constants observed for $EtNH_2$ and i-$PrNH_2$ appear to be significantly larger than for NH_3. From molecular models it appears that formation of the nickel–nitrogen bond in $EtNH_2$ and i-$PrNH_2$ requires the carbon atoms in the alkyl group to be rotated away from the nickel ion, giving rise to less stable configurations, the effect being greater for i-$PrNH_2$ where crowding of the alkyl group is also involved. The instability of this configuration may then account for the increased dissociation rate constants observed. The increase in dissociation rate constant for Me_2NH is marginally significant but may represent crowding with neighboring inner-sphere solvent molecules.

As noted previously, these systems were originally studied at 0.1 M ionic strength. A value of k_d for $EtNH_2$ was obtained (Table II) under these conditions. This value of 9.6 sec^{-1} is smaller than the value of 13.3 sec^{-1} obtained at 1 M ionic strength. Variations in the k_d for NH_3 (3.8 sec^{-1}, $\mu = 0.1$ M;[3] 7.1 sec^{-1}, $\mu = 1.0$ M) at different ionic strength has also been observed. These trends are not understood on the basis of the dissociative mechanism but, if significant, may be indicative of hitherto unresolved bulk solvent effects which have been indicated in recent nonaqueous kinetic studies of nickel–amine reactions.[28,29]

In any event, the larger dissociation rate constants observed for the alkylamines relative to ammonia represent an inversion from the order anticipated on the basis of the inductive effects of the substituted alkyl groups. Thus it must be concluded that, for the 1:1 Ni–alkylamine complexes included in this study, inductive effects either (a) play a minor role in determining the relative dissociation rate constants or (b) are masked by the contributing steric and/or bulk solvent effects upon the dissociation rates.

Conclusions

As a consequence of the foregoing observations, the 1:1 alkylamine complexes with Ni(II) ion exhibit two features which are in sharp contrast to previous studies on related ligand complexes. (1) The inverse relationship between dissociation rate constants and ligand protonation constants, which has been previously reported for two series of related ligands with Ni(II) ion,[7,8] is not observed when ammonia is compared to the alkylamines. (2) The trend in complex stability constants does not parallel the dissociation rate constants[1,2] but is primarily dependent on the formation rate constants.

For the small alkyl groups included in this study, the formation rate constants are observed to decrease significantly as a function of the increasing bulk and number of alkyl groups substituted on the nitrogen donor atom. The magnitude of the observed trend indicates that extremely large steric effects are to be anticipated for secondary and tertiary nitrogen donor atoms substituted by bulky alkyl groups.[30]

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