Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Kinetics of Aquonickel(II) Ion Reacting with Ethylenediamine. Evidence of the Internal Conjugate Base Effect and Intramolecular Hydrogen Bonding

RICHARD W. TAYLOR, HENRYK K. STEPIEN, and D. B. RORABACHER*

Received March 23, 1973 AIC30233Y

The formation and dissociation kinetics of the 1:1 complex formed between aquonickel(II) ion and ethylenediamine (en) have been studied using both the stopped-flow and temperature-jump techniques. Both methods exhibit interfering signals near neutral pH and above, which complicate data analysis. The combined results indicate that, for the reversible rate equation $d[Ni(en)^{2+}]/dt = k_1[Ni^{2+}][en] + k_2[Ni^{2+}][Hen^+] - k_{-1}[Ni(en)^{2+}] - k_{-2}[H^+][Ni(en)^{2+}]$, the "best" rate constant values at 25° and 0.1 M ionic strength are $k_1 = 3.5 \times 10^5\ M^{-1}\ sec^{-1}$, $k_2 = 1.8 \times 10^2\ M^{-1}\ sec^{-1}$, $k_{-1} = 8 \times 10^{-3}\ sec^{-1}$, and $k_{-2} = 4.5 \times 10^4\ M^{-1}\ sec^{-1}$. The anomalously large value of k_1, which is nearly 100 times larger than the corresponding value for the 1:1 nickel–ammonia complex, is interpreted as arising from the internal conjugate base (ICB) effect and its implications are discussed. By contrast, the k_2 value is approximately one-third the anticipated value, a factor attributed to intramolecular hydrogen bonding in the monoprotonated ligand species.

Introduction

In 1966[1] we first called attention to the fact that multidentate ligands containing the ethylenediamine moiety exhibit anomalously large complex formation rate constants in their reactions with aquonickel(II) ion relative to the values predicted by the Eigen dissociative mechanism.[2-4] To explain this behavior we proposed an internal conjugate base (ICB) mechanism as a modification of the normal dissociative mechanism in which outer-sphere hydrogen bonding leads to an acceleration in the complex formation rate.

As illustrated in Figure 1 for an octahedrally aquated metal ion, the *normal* dissociative mechanism involves the diffusion-controlled formation of an outer-sphere complex (ion pair) between the reacting metal ion and ligand, during the lifetime of which a metal–solvent coordinate bond may rupture with the concomitant rapid insertion of the outer-sphere ligand into the available inner-sphere site. For a wide variety of ligands, the observed substitution rate constant, $k_M{}^L$, appears to be independent of ligand nucleophilicity.[5] Thus, for *normal* dissociative behavior

$$k_M{}^L = K_{os}k^{M-S}/p \qquad (1)$$

where K_{os} can be estimated from diffusion equations,[6] k^{M-S} is presumed to approximate the specific solvent-exchange rate constant for the same solvated metal ion species, and p is introduced to account for apparent steric hindrance effects[6] (including ligand conformational effects).

In the proposed ICB mechanism, the anomalously rapid complex formation rates of multidentate ligands containing ethylenediamine have been attributed to the formation of a hydrogen bond between a coordinated water molecule and a strongly basic amine nitrogen donor atom in the outer sphere[1] (Figure 2). As a result, the outer-sphere complex is presumed to be stabilized (*i.e.*, K_{os} increases) and the possibility exists that the remaining inner-sphere solvent molecules may be labilized (*i.e.*, k^{M-S} may increase) as a result of the partial hydroxide character imparted to the water molecule involved in the hydrogen bond. Since the hydrogen-bonded ligand donor atom cannot simultaneously form a coordinate bond to the metal ion, only a multidentate ligand appears capable of exhibiting an ICB effect due to the requirement that the hydrogen bond must be intact at the point of the rate-determining step (k^{M-S}).[1,7]

The kinetic data which formed the basis for the original ICB proposal were limited to the complex formation reactions of $Ni(H_2O)_6{}^{2+}$ with just three ligand species:[1] ethylenediamine (en), monoprotonated triethylenetetramine (Htrien$^+$), and 2,2′-ethylenediaminobis(2-methyl-3-butanone)dioximine (EnAO). Of these, only the latter two had been measured directly,[8,9] the formation rate constant for the Ni–en system having been estimated[1,8,10] from a kinetic study of the dissociation of the $Ni(en)(H_2O)_4{}^{2+}$ complex carried out at 0°.[11] As discussed later, this estimation procedure is very inexact, however, and no great confidence could be placed in the value thus generated.

In the intervening years since the original postulation of the ICB mechanism, a few additional examples of enhanced complex formation rate constants have been reported for multidentate amine ligands reacting with $Ni(H_2O)_6{}^{2+}$ [12-15] or $NiZ(H_2O)_x{}^{2+}$ [16,17] (where Z represents 1,10-phenanthroline or ethylenediamine). Virtually all of these systems have also involved ligands containing the ethylenediamine moiety. The presence of substituents on the ligand (or of

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(7) An alternate formulation of the ICB mechanism has been suggested by recent related studies on hydrogen-bonding effects upon solvent-exchange reactions in which the same coordinated solvent molecule involved in the hydrogen bond is conceived to be the leaving group with a neighboring donor atom on the ligand swinging into the available site: J. Vriesenga, personal communication; *cf.* F. R. Shu and D. B. Rorabacher, *Inorg. Chem.*, 11, 1496 (1972).

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(9) R. K. Murmann, *J. Amer. Chem. Soc.*, 84, 1349 (1962).

(10) It should be noted that, in ref 1, the formation rate constant for 0° (log $k_{Ni}{}^{en}$ = 4.6) was inadvertently listed in place of the 25° estimate (log $k_{Ni}{}^{en}$ = 5.3).

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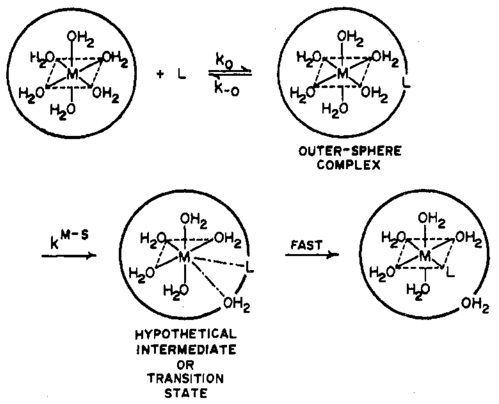

Figure 1. Schematic representation of the Eigen dissociative mechanism for a labile, octahedrally solvated metal ion MS_6, reacting with a ligand, L. The solid circle surrounding the solvated metal ion represents the next adjacent layer of solvent molecules (outer sphere). Bonding between the metal ion and the incoming ligand is presumed to be minimal at the point of the transition state in view of the relative constancy of the substitution rate constants with ligands of varying nucleophilicity.

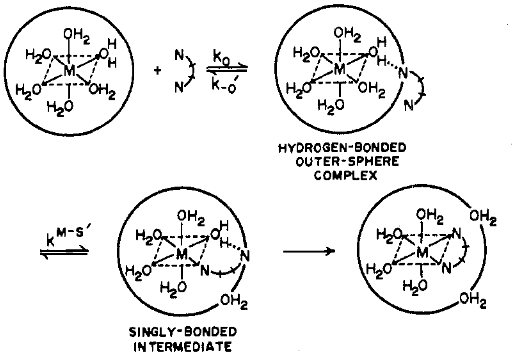

Figure 2. Schematic representation of the proposed internal conjugate base (ICB) mechanism for an octahedrally solvated metal ion, such as $Ni(H_2O)_6{}^{2+}$ (*cf.* Figure 4 of ref 1). The hydrogen bond formed between en and a coordinated water molecule is presumed to accelerate complex formation by decreasing k_{-0}, and, perhaps, increasing k^{M-S} relative to the values normally anticipated for these processes.

other ligands on the metal ion) has presumably introduced steric factors into these systems affecting the evaluation of the exact magnitude of the ICB rate enhancement. Thus a direct experimental determination of the formation rate constant for $Ni(en)(H_2O)_4{}^{2+}$ has remained a high-priority project. But an accurate direct measurement has proven difficult to obtain.

In a very limited stopped-flow study on the Ni(II)-en system, Cassatt and Wilkins obtained a rate constant for the monoprotonated en ligand but failed to resolve out a corresponding value for the unprotonated species.[18] In another study involving high concentrations of ligand, Jones and Margerum used the temperature-jump technique to obtain kinetic data for the substitution of a third en ligand on $Ni(en)_2(H_2O)_2{}^{2+}$ but recorded no information on the formation of the 1:1 complex.[16]

During the past 8 years, we have conducted three independent studies (by each of the three authors) on the acid-independent formation kinetics of the $Ni(en)^{2+}$ complex. As reported in the current paper, these have included both the the stopped-flow (study II) and temperature-jump (studies I and III) techniques covering a variety of reactant concentrations over a total pH range from 4.98 to 7.15 (and above). In all cases experimental interferences have been encountered at higher pH values where the kinetic contribution of the unprotonated ligand species becomes dominant. However, from the cross checks provided by the three studies, it has been possible to determine a reasonably accurate rate constant value for unprotonated en reacting with $Ni(H_2O)_6{}^{2+}$.

As anticipated from the ICB mechanistic proposal[1] and our earlier study on substituted en ligands,[13] the reaction involving the unprotonated en ligand exhibits one of the largest formation rate constants ever observed for aquonickel(II) ion—in support of the previously estimated values. As an additional point of interest, the rate constant obtained for the monoprotonated ligand species, Hen^+, is significantly lower than previously reported values[18] and suggests the presence of intramolecular hydrogen bonding in this species.[6,13]

Experimental Section

Reagents. $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, reagent grade) was used as the source of Ni(II) ion in study I while $Ni(ClO_4)_2 \cdot 6H_2O$ was used for studies II and III, the preparation, purification, and standardization for the latter having been previously described.[19] Ethylenediamine (en) was purified by fractional distillation, either under vacuum (bp 28° at 15 Torr) or at atmospheric pressure (bp 115-116°) over calcium hydride. The purified en showed no detectable impurities *via* gas chromatographic analysis.[13] Stock solutions were standardized by potentiometric acid-base titrations.

Ionic strength was controlled with reagent grade KNO_3 (study I: $\mu = 0.3\ M$) or $NaClO_4$ (studies II and III: $\mu = 0.1\ M$), solutions of the latter being filtered before use. Acid-base indicators (for monitoring the relaxation effects) were of unspecified grade and used as obtained. All other chemicals were reagent grade and used without further purification. Doubly distilled or distilled, deionized water was used to prepare all solutions. pH measurements were made as previously described,[1,19] an activity coefficient value of 0.796 being applied to calculate hydrogen ion concentration values for the 25° data at $\mu = 0.1\ M$.

Kinetic Measurements. Study II utilized an Aminco-Morrow stopped-flow mixing device mounted on a Beckman DU-2 monochromator with modified signal detection as previously described.[20] Studies I and III utilized double-beam[1] and single-beam,[19] Joule-heating, temperature-jump relaxation spectrometers, respectively. All three instruments were thermostated at 25 ± 0.4° or better.

Following preliminary studies at 365 and 230 nm, the major portion of the stopped-flow study was conducted at 225 nm to permit the use of sufficiently low en concentrations to minimize 1:2 complex formation while optimizing pH control. A borate-mannitol buffer[8,20] was used which, under the conditions used, restricted the pH decrease during reaction to within 0.04-0.06 unit, the average pH value being reported.

The temperature-jump studies were carried out with unbuffered solutions utilizing coupled acid-base indicators. Blank tests on solutions containing all reaction components except en showed no detectable relaxation effects in the observable time range (>10 μsec). However, similar solutions containing all components except Ni(II) showed a small relaxation effect (2-3 mV amplitude, 1 V = 100% relative transmittance) having a lifetime of approximately 1-2 sec. A similar effect was reported by Kirschenbaum and Kustin[21] at pH >6.0 in their study on the Cu(II)-en system and appears to arise from an unexplained interaction between the ligand and indicator. As a result of the small amplitude and long lifetime of this effect, however, it tended to merge with the convection curves normally encountered with our experimental relaxation curves and could not be discretely detected when all reactants were present. Thus, except as attempts were made to resolve out separate relaxation effects in conjunction with study III, this blank relaxation effect was not accorded further consideration.

The relaxation curves from study I were evaluated by matching against a standard series of logarithmic decay curves as previously described,[1] the greatest weight being placed on initial portions of the curve to minimize errors from convection and occasional small

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contributions from a slower second relaxation effect (distinguishable from convection and the blank effect) at higher pH values. For study III, where conditions were broadened to include a more thorough observation of this second relaxation effect, a curve-fitting routine obtained from Professor Daniel Leussing of The Ohio State University[22] was applied to all relaxation curves. The form of the expression to be adjusted is given by

$$A_t = A_\infty + \sum_{i=1}^{n} A_i e^{-t/\tau_i} \qquad (2)$$

where A_t is the absorbance (in arbitrary units) at any time t, A_∞ is the final equilibrium absorbance, A_i is the absorbance amplitude of each of the individual exponentials, and τ_i is the individual relaxation time. For successful convergence of the five parameters in this equation, it was necessary to supply at least 50 and preferably 75–100 points for each curve. While convergence was optimized by including points close to the establishment of final equilibrium, care was exercised in practice to avoid the inclusion of convection effects.

Results

Protonation and Stability Constants. For the relaxation studies, equilibrium concentrations of all species were calculated using a modified version of a program developed by Perrin and Sayce.[23] Since, under the experimental conditions required to obtain satisfactory relaxation data, the concentrations of some species are quite low, it was found to be important to utilize equilibrium constants determined under conditions identical to those used in the kinetic study.

Of the available literature data,[24] we have chosen to utilize the 25° values of Nasanen and coworkers which include ionic strength corrections.[25] The appropriate values, along with calculated values for 15 and 35°, are listed in Table I where the concentration constants are defined as (charges omitted)

$$K_{H1}^{c} = [HL]/[H][L] \qquad (3)$$

$$K_{H2}^{c} = [H_2L]/[H][HL] \qquad (4)$$

$$K_1 = [ML]/[M][L] \qquad (5)$$

$$K_2 = [ML_2]/[ML][L] \qquad (6)$$

$$K_3 = [ML_3]/[ML_2][L] \qquad (7)$$

In these equations L, HL, and H_2L represent the unprotonated, monoprotonated, and diprotonated species of en, respectively, M represents the aquonickel(II) ion, and ML, ML_2, and ML_3 represent the respective Ni(II)-en complexes. Table I also contains the protonation constants for the indicators used to monitor the relaxation measurements

$$K_{In}^{c} = [HIn]/[H][In] \qquad (8)$$

Stopped-Flow Kinetics. For the stopped-flow kinetics (study II), the concentration ratio of total Ni(II) (C_M) to total en (C_L) was maintained at approximately 10:1 to ensure that only the 1:1 complex would be formed in significant concentrations. Variations in reactant concentrations were deterred by the limitations of adequate buffer control and detectable absorbance change. Under the conditions used the reaction did not proceed to 100% completion but obeyed the reversible mixed second- and first-order equation

Table I. Protonation and Stability Constants Used for the Nickel(II)–Ethylenediamine System

	$\mu = 0.1\,M$			$\mu = 0.3\,M$	
	15°	25°	35°	25°	Ref
log K_{H1}^{c}	10.26	9.96	9.68	10.02	*a, b*
log K_{H2}^{c}	7.28	7.08	6.89	7.22	*a, b*
log K_1	7.55	7.35	7.16	7.41	*a, c*
log K_2	6.41	6.21	6.02	6.28	*a*
log K_3	4.33	4.15	3.98	4.23	*a*
log K_{In}^{c}(BTB)		6.96			*d*
log K_{In}^{c}(CPR)		6.05			*d*
log K_{In}^{c}(BCG)		4.58			*d*

[a] 25° values from ref 25. [b] 15 and 35° values calculated using $\Delta H_{H1} = -11.9$, $\Delta H_{H2} = -7.8$ kcal mol^{-1}: T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 2304 (1954). [c] 15 and 35° values calculated using $\Delta H_1 = -7.9$, $\Delta H_2 = -7.8$, $\Delta H_3 = -7.2$ kcal mol^{-1}: F. A. Cotton and F. E. Harris, *J. Phys. Chem.*, 59, 1203 (1955). [d] D. B. Rorabacher and E. Marczewski, unpublished results; BTB = Bromothymol Blue; CPR = Chlorophenol Red; BCG = Bromocresol Green.

$$d[ML]/dt = k_f[M][\Sigma L] - k_d[ML] \qquad (9)$$

where k_f and k_d represent the observed formation and dissociation rate constants, respectively, and $[\Sigma L]$ represents the total concentration of all species of uncomplexed ligand

$$[\Sigma L] = C_L - [ML] = [L] + [HL] + [H_2L] \qquad (10)$$

The observed rate constants were obtained by computer plot of the integrated form of eq 9 as previously described.[12] The resulting values of k_f and k_d obtained in two separate 25° data sets are listed in Table II. Data from a limited temperature study are also included.

At pH >6.80, anomalous stopped-flow curves were frequently observed in which the transmittance decreased below the equilibrium value and then increased back to an apparent final equilibrium. This behavior, illustrated in Figure 3, tended to become accentuated with increasing pH and increasing en concentration. This latter observation suggests the significant formation of an intermediate or subsequent higher complex formation. However, the occasional absence of this phenomenon (as for the data of pH 7.12 and 7.15 listed in Table II) would tend to discount such explanations. The interference could not be resolved on the basis of the data obtained and runs exhibiting such behavior were disregarded in the data analysis.

As with the substituted diamines,[13] both the unprotonated and monoprotonated forms of ethylenediamine may react with Ni(II) such that eq 9 may be expanded to the form

$$d[ML]/dt = k_1[M][L] + k_2[M][HL] - k_{-1}[ML] - k_{-2}[H][ML] \qquad (11)$$

which, after combination with eq 9, yields

$$k_f[\Sigma L]/[L] = k_1 + k_2K_{H1}^{c}[H] \qquad (12)$$

and

$$k_d = k_{-1} + k_{-2}[H] \qquad (13)$$

A plot of eq 12 is shown for the 25° data in Figure 4 where the data at low pH (<5.9) are observed to tail off and are not included in the regression analysis.

Temperature-Jump Kinetics. As a result of the anomalous behavior observed in the stopped-flow data above pH 7 and

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(23) D. D. Perrin and I. G. Sayce, *Talanta*, 14, 833 (1967).

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Table II. Study II: Experimental Stopped-Flow Kinetic Data for the Reaction of Nickel(II) with Ethylenediamine at $\mu = 0.1\ M$ ($NaClO_4$)

pH	$k_f, M^{-1}\ sec^{-1}$	$10^2 k_d$, sec^{-1}	$10^{-3}[\Sigma L]/[L]$ (calcd)
Data Set 1: 25°, $C_M = 14.97$ mM, $C_L = 1.57$ mM			
7.15	296	1.30	1.68
7.12	266	1.29	1.87
6.79	113, 112	1.92, 1.91	6.43
6.71	87.3, 76.4	2.06, 1.79	8.83
6.58	51.0, 49.0, 50.6	2.05, 1.96, 2.03	14.98
6.45	41.9	2.92	25.9
6.36	32.9, 31.6, 30.2	3.39, 3.26, 3.12	38.0
6.19	24.6, 25.5	5.39, 5.59	79.9
6.11	16.7, 15.1	5.25, 4.75	113.5
6.00	14.3, 13.0	7.12, 6.46	176.8
5.87	9.00, 8.74	8.52, 8.28	332
Data Set 2: 25°, $C_M = 14.47$ mM, $C_L = 1.55$ mM			
6.60	57.9, 63.2	2.00, 2.31	13.78
6.48	42.0, 41.1, 42.6	2.36, 2.34, 2.49	22.8
6.19	21.5, 22.4	4.27, 4.56	79.9
6.02	14.5, 13.3, 13.9	6.33, 5.73, 5.97	169.3
5.83	7.49, 7.08, 7.32	7.64, 7.18, 7.42	397
5.77	6.06, 6.16	7.89, 7.90	521
5.71	5.79, 5.13	9.80, 8.70	682
Data Set 3: 15°, $C_M = 14.47$ mM, $C_L = 1.55$ mM			
6.77	23.8, 21.1, 22.6	1.31, 1.16, 1.24	19.6
6.62	11.7, 12.8, 13.0	1.21, 1.34, 1.36	36.9
6.37	7.23, 7.70, 7.50	2.25, 2.40, 2.34	111.0
6.15	3.61, 3.73	3.01, 3.11	290
5.95	1.69, 1.65, 1.74	3.58, 3.37, 3.46	711
5.88	1.05	2.98	983
5.79	0.465	1.98	1472
Data Set 4: 35°, $C_M = 14.47$ mM, $C_L = 1.55$ mM			
6.86	322, 331	4.12, 4.25	1.86
6.73	214, 208, 204	4.35, 4.20, 4.08	3.01
6.50	117.8, 116.9	5.84, 5.78	7.41
6.30	62.8, 80.2, 70.5	7.22, 9.23, 8.13	16.93
6.13	49.1, 49.1	11.68, 11.70	35.0
6.06	43.0, 39.3	13.64, 12.44	47.4
5.99	29.4, 36.6, 32.5	12.65, 15.73, 13.93	64.0

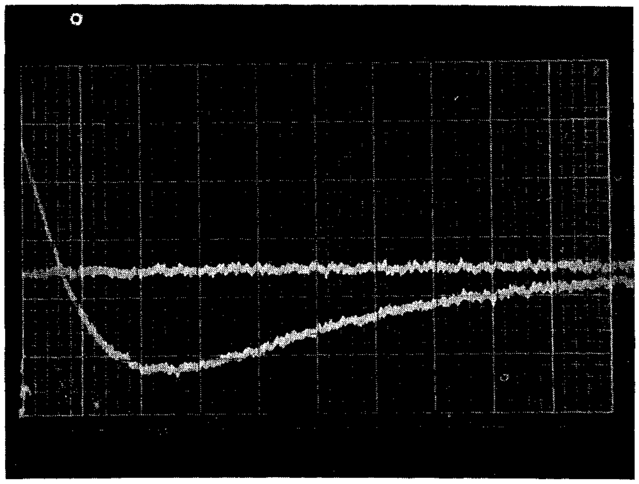

Figure 3. Oscilloscopic recording of anomalous stopped-flow transmittance changes as frequently observed for the Ni(II)–en reaction at higher pH in study II. The illustration shown represents the most exaggerated case of such behavior observed in this study. The horizontal line represents the final equilibrium transmittance value. Conditions: pH 7.22 $[Ni^{2+}] = 1.59 \times 10^{-2}\ M$, $[en] = 3.06 \times 10^{-3}\ M$, horizontal sweep rate 500 msec cm^{-1}, λ 230 nm.

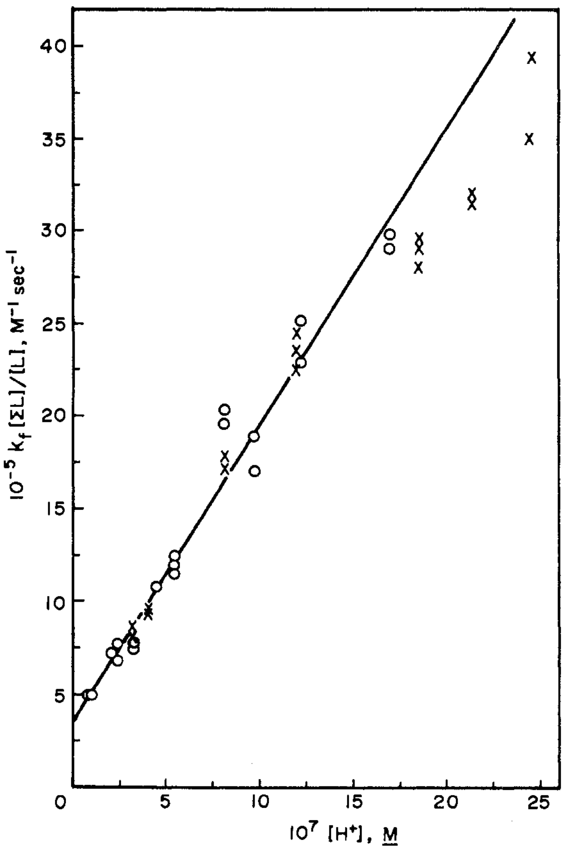

Figure 4. Resolution of the formation rate constants for Ni(II) reacting with unprotonated and monoprotonated ethylenediamine from stopped-flow data (study II) at 25°; plot of eq 12: ○, data set 1; X, data set 2.

the inability of varying the reactant concentrations significantly, it was deemed essential to obtain independent kinetic measurements on the Ni(II)–en system. Accordingly, two independent temperature-jump studies were included as part of this investigation. In study I primary emphasis was placed upon varying reactant concentrations while still maintaining a large excess of Ni(II). Since an apparent (small) second relaxation was observed in this study at a higher pH value, study III was undertaken with the specific aim of evaluating this second relaxation by utilizing a lower excess metal ion concentration and a more sophisticated mathematical approach (eq 2).

Under conditions utilized in the two temperature-jump studies, the absorbance change accompanying the Ni(II)–en equilibrium shift induced by the temperature increase was too small to permit effective monitoring of the relaxation effects. Therefore, as with our earlier studies on the Ni(II)–NH_3 system,[1,19] the desired reaction was coupled to an acid-base indicator dye. When only the 1:1 complex is significant, this system may be described by the coupled reactions (charges omitted)

$$M + L \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} ML \tag{14}$$

$$M + HL \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} ML + H \tag{15}$$

$$H + L \overset{K_{H_1}{}^c}{\rightleftarrows} HL \tag{16}$$

$$H + HL \overset{K_{H_2}{}^c}{\rightleftarrows} H_2L \tag{17}$$

$$H + In \overset{K_{In}{}^c}{\rightleftarrows} HIn \tag{18}$$

Since the proton-exchange reactions (eq 16–18) are rapid relative to the complexation steps, the following expression may be generated relating the relaxation time, τ, to the experimentally accessible variables

$$1/\tau = \{k_1 + k_2K_{\mathrm{H1}}\overline{\mathrm{H}}\}A \tag{19}$$

where

$$A = \frac{\overline{M}}{1 + \alpha + \beta} + \overline{\mathrm{L}} + \frac{1}{K_1} \tag{20}$$

The expressions for $\alpha = \partial\mathrm{HL}/\partial\mathrm{L}$ and $\beta = \partial\mathrm{H_2L}/\partial\mathrm{L}$ may be derived from eq 3-8 and material balance relationships to yield[26]

$$\alpha = \overline{\mathrm{H}}\{1/K_{\mathrm{H1}} + \overline{\mathrm{L}}(1 + 2K_{\mathrm{H2}}\overline{\mathrm{H}})/ (1 + 2K_{\mathrm{H2}}\overline{\mathrm{H}}\overline{\mathrm{L}} + C + D)\}^{-1} \tag{21}$$

$$\beta = \overline{\mathrm{H}}^2\{1/K_{\mathrm{H1}}K_{\mathrm{H2}} + 2\overline{\mathrm{L}}(1 + 2K_{\mathrm{H2}}\overline{\mathrm{H}})/ K_{\mathrm{H2}}(1 - K_{\mathrm{H1}}\overline{\mathrm{L}} + C + D)\}^{-1} \tag{22}$$

where

$$C = K_{\mathrm{In}}\overline{\mathrm{In}}/(1 + K_{\mathrm{In}}\overline{\mathrm{H}}) \tag{23}$$

$$D = \mathrm{OH}/(K_{\mathrm{s}} + \mathrm{H}) \tag{24}$$

(In the above expressions, concentration brackets have been omitted for simplicity and the barred quantities represent final equilibrium concentrations.)

As indicated in the Experimental Section, a second slower relaxation effect, presumed to derive from the 1:2 complex, was particularly in evidence in study III at high pH and/or high ligand concentration (the amplitude reaching nearly two-thirds that of the faster relaxation effect under optimum conditions) and was separated out in the manner indicated by eq 2. Each of the relaxation times obtained is presumed to represent a complex of two interactive relaxations.[27] Due primarily to overlap of the slower relaxation effect with the convection curve, however, the relaxation time characteristic of this effect could not be resolved under the conditions used. Thus, only the curves exhibiting one observable relaxation effect were included in the data resolution.

Even for the solutions exhibiting a single relaxation curve, a second relaxation time was separated out mathematically by the approach indicated in eq 2. Under such conditions, the two resolvable τ values were separated by 15-20-fold or more and the larger value was nearly constant suggesting that it may simply represent an experimental tailing effect arising primarily from convection. The smaller τ value (representative of the faster, dominant relaxation) was then treated as arising only from the 1:1 complex—a presumably valid assumption considering the large separation in the two relaxation times. In fact, it was confirmed that the same τ values could be obtained by resolving the observed relaxation curves on the basis that only a single relaxation effect was represented, thus supporting the treatment accorded to study I where larger C_M:C_L ratios were utilized.

The resolved relaxation data for the two temperature-jump studies are listed in Tables III and IV. Plots of the data from both studies are shown in Figure 5.

Table III. Study I: Experimental Relaxation Data for the Nickel(II)–Ethylenediamine System at 25°, $\mu = 0.3\ M$ (KNO$_3$)

pH	C_M, mM	C_L, mM	10^5A, M	τ^{-1}, sec^{-1}	$10^{-5}/\tau A$, M^{-1} sec^{-1}
6.80	1.5	0.71	0.18[a]	3.5	19.4
6.80	10.0	2.82	1.31[a]	17.5	13.4
6.80	19.9	7.1	2.42[a]	37.0	15.3
6.80	29.9	7.1	4.03[a]	54.0	13.4
6.80	39.8	9.9	5.32[a]	100	18.8
6.80	49.8	7.1	6.87[a]	60.0	8.7
6.80	59.8	14.1	8.05[a]	155	19.3
6.80	69.7	14.1	9.55[a]	105	11.0
6.80	79.7	7.1	10.39[a]	110	10.6
6.80	88.6	28.2	11.11[a]	200	18.0
6.40	10.0	2.42	0.59[a]	11.3	19.2
6.40	19.9	4.2	1.17[a]	19.0	16.2
6.40	29.9	7.1	1.71[a]	~45	~26
6.40	39.8	7.1	2.39[a]	53.0	22.2
6.40	59.8	14.1	3.39[a]	72.0	21.2
6.40	89.6	21.2	5.06[a]	115	22.7
6.00	19.9	2.12	0.47[b]	15.0	31.9
6.00	29.9	2.12	0.69[b]	21.0	30.4
6.00	49.8	4.1	1.19[b]	37.0	31.1
5.60	10.0	1.41	0.08[c]	7.2	90.0
5.60	19.9	4.2	0.20[b]	16.0	80.0
5.60	29.9	7.1	0.30[c]	23.0	76.7
5.60	49.8	11.3	0.50[c]	31.0	62.0
5.60	49.8	5.6	0.51[b]	29.0	56.9
5.60	79.7	7.1	0.81[b]	44.0	54.3
5.60	89.6	7.1	0.91[b]	48.0	59.3
5.60	99.6	14.1	1.00[c]	52.0	52.0

[a] Indicator: $2.00 \times 10^{-5}\ M$ Bromothymol Blue. [b] Indicator: $2.50 \times 10^{-5}\ M$ Bromocresol Green. [c] Indicator: $5.00 \times 10^{-5}\ M$ Bromocresol Green.

Table IV. Study III: Experimental Relaxation Data for the Nickel(II)–Ethylenediamine System at 25°, $\mu = 0.1\ M$ (NaClO$_4$)

pH	C_M, mM	C_L, mM	10^5A, M	τ^{-1}, sec^{-1}	$10^{-5}/\tau A$, M^{-1} sec^{-1}
6.91[a]	9.5	4.4	1.47	12.6	8.6
6.61[a]	9.5	4.4	0.885	12.9	14.5
6.61[b]	19.0	4.4	2.23	16.7	7.5
6.29[c]	21.1	11.0	0.97	16.6	17.1
6.29[c]	31.7	4.4	1.94	25.9	13.3
5.91[c]	10.6	4.4	0.283	7.7	27.4
5.91[c]	21.1	16.6	0.416	9.0	21.6
5.91[c]	21.1	11.0	0.497	15.7	31.6
5.91[c]	31.7	4.4	0.893	18.9	21.3
5.58[c]	21.1	16.6	0.264	13.5	51.1
4.85[d]	31.7	33.1	0.078	(26.9)	(345)

[a] Indicator: $3.50 \times 10^{-5}\ M$ Bromothymol Blue. [b] Indicator: $2.00 \times 10^{-5}\ M$ Bromothymol Blue. [c] Indicator: $1.50 \times 10^{-5}\ M$ Chlorophenol Red. [d] Indicator: $1.35 \times 10^{-5}\ M$ Bromocresol Green.

Discussion

The resolved rate constants obtained in the separate studies are listed in Table V along with available literature values. Included are approximate rate constant values from our limited stopped-flow studies carried out at approximately 15 and 35°,[28] the constants at 15° being particularly poor due to a marked deviation of the data obtained at lower pH.

The marked differences between the 25° k_1 values obtained from the stopped-flow (study II) and temperature-jump (studies I and III) data, as listed in Table V, require comment. As evidenced by the plot in Figure 5, the temperature-jump data obtained in study I were not highly reproducible. We note, however, that, with the possible exception of the data at pH 5.60, there is no evidence of a trend in the relaxation times with concentration over a 10-50-fold variation in A (Table III). Thus, we have concluded that the poor precision was primarily a function of random experimental error inherent in the method as applied to this

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(26) F. P. Cavasino, *J. Phys. Chem.*, **69**, 4380 (1965).

(27) M. Eigen and L. DeMaeyer in "Technique of Organic Chemistry," Vol. VIII, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Part II, 2nd ed, Interscience, New York, N. Y., 1963, p 895 ff; G. G. Hammes and J. I. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962); D. N. Hague, "Fast Reactions," Wiley-Interscience, London, 1971.

(28) These temperature values are those of the thermostating bath and may not be representative of the actual temperature in the stopped-flow cell: *cf.* P. K. Chattopadhyay and J. F. Coetzee, *Anal. Chem.*, **44**, 2117 (1972).

Table V. Resolved Rate Constant Values for the Nickel(II)-Ethylenediamine System

T, °C	μ, M	$10^{-5}k_1$, M^{-1} sec^{-1}	$10^{-2}k_2$, M^{-1} sec^{-1}	$10^{2}k_{-1}$, sec^{-1}	$10^{-4}k_{-2}$, M^{-1} sec^{-1}	Method[a]	Ref
25	0.3	12 ± 3	1.66 ± 0.21	4.7	6.8	TJ	Study I
25	0.1	7 ± 2	1.35 ± 0.15	3.1	5.5	TJ	Study III
25	0.1	3.5 ± 0.2[b]	1.79 ± 0.03[b]	0.8[b]	4.5[b]	SF	Study II
~15[28]	0.1	(~2-3)	(~0.6)	(~0.7)	(~3)	SF	Study II
~35[28]	0.1	~3	~3.2	~2	~9	SF	Study II
25	0.3		5.9[c]			SF	Cassatt[18]
25	0.3		6.7[c]			SF	Melson[d]
25	?	2-6		0.5		Calcd[e]	5a, 5c, 8, *f*

[a] TJ = temperature-jump; SF = stopped-flow. [b] Preferred values (see text). [c] Presumed to be in error due to a failure to account for the kinetic contribution of the unprotonated ligand species (see text). [d] G. Melson, Ph.D. Dissertation, University of Sheffield, 1962 (cited in ref 18). [e] Estimated values calculated from 0° dissociation data.[11] [f] T. S. Turan, Ph.D. Dissertation, Wayne State University, 1969, Appendix C.

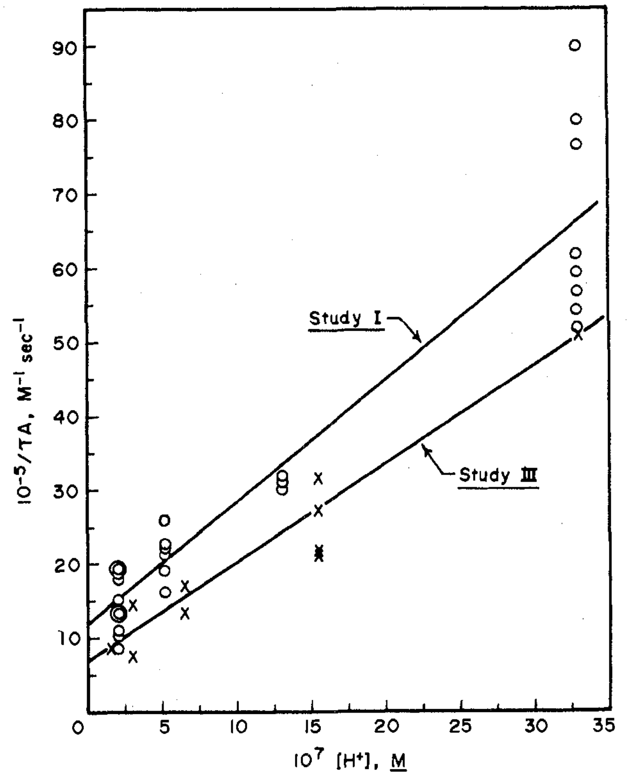


Figure 5. Resolution of the formation rate constants for Ni(II) reacting with unprotonated and monoprotonated ethylenediamine from temperature-jump relaxation data at 25°; plot of eq 28: ○, study I; ×, study III.

system and was not a result of interference from higher complexes.

The stopped-flow data obtained in study II show very good precision above pH 5.9 (Figure 4). Unfortunately, as noted earlier, the limiting considerations of adequate buffer control and detectable absorbance change did not permit a significant variation in reactant concentrations in this study. However, by comparison to the concentration levels utilized in study I, it is evident that no interference should be encountered from a 1:2 complex *for the conditions utilized in the stopped-flow study.*

Study III was initiated to investigate further the conditions under which the formation of a 1:2 complex becomes kinetically significant and, if possible, to evaluate the kinetic parameters associated with this species. Whereas we were unsuccessful in the latter aspect, presumably due to the interference of convection, we were able to confirm conclusively that the 1:2 complex, or other feasible species, should not be significant interferences *under the conditions of the stopped-flow study.* Thus, we conclude that the rate constants obtained from the stopped-flow study (study II) are the most reliable values available.

In view of the greater precision of the data obtained in study II, an attempt was made to obtain activation parameters for the several rate constants using the stopped-flow technique, particular interest being centered on the temperature dependence of the k_1 value. As indicated by the data in Table V, no temperature dependence could be observed within the limits of experimental error. In view of the apparent temperature dependence of k_1 as estimated from dissociation rate data,[11] however, this latter observation may simply reflect, once again, the inherent difficulties in obtaining an accurate value for k_1 rather than being indicative of $\Delta H_1^{\ddagger} \approx 0$. Thus, it was not deemed fruitful to pursue this matter further in view of the present limitations in data precision. By contrast, the data for k_2 indicate a $\Delta H_2^{\ddagger}$ value of 9-13 kcal mol^{-1} which is in the normal range for Ni(II) formation reactions.[5]

Formation Rate Constant with Unprotonated Ethylenediamine. As noted in the Introduction, all of the rate constant values found in the literature for the reaction of unprotonated ethylenediamine (en) with aquonickel(II) ion are estimates derived from the 0° dissociation study of Ahmed and Wilkins.[11] The estimation procedure involves (a) an extrapolation of their experimental dissociation rate constants to a limiting high pH value (presumed to represent k_{-1} at 0°), (b) an extrapolation of this k_{-1} value to 25° using an activation energy of 20.5 kcal mol^{-1},[11] and (c) a calculation of $k_1 = K_1k_{-1}$. Primarily due to the inexactness of step (a), various authors, using the same basic assumptions, have estimated 25° k_1 values of 1.8×10^5,[8] 4.0×10^5,[5c] and 6×10^5 [29] M^{-1} sec^{-1}. Moreover, the activation energy value of 20.5 kcal mol^{-1} relates specifically to the opening of the chelate ring[11] (as determined in highly acidic solutions) and may not be representative of k_{-1}. Therefore, in view of the several potential sources of error in the estimation procedure, the close correlation between these earlier estimates for k_1 and our experimentally obtained value of 3.5×10^5 M^{-1} sec^{-1} is unexpected.

As a closely correlated system, we have recently studied the kinetics of aquonickel(II) reacting with *N,N*-diethylethylenediamine (*N,N*-Et$_2$en) at 25°.[13] For this system, reliable kinetic data were obtained at higher pH values yielding a more precise, but nearly identical, value of $k_1 = 3.4 \times 10^5$ M^{-1} sec^{-1}. As measured by Nasanen, *et al.*,[25,30] en and *N,N*-Et$_2$en have essentially identical $K_{\mathrm{H}1}$ values suggesting that they should exhibit identical ICB effects. Yet, the latter ligand appears to act only as an unidentate ligand.[13] On the basis of statistical considerations, therefore, it might be anticipated that en (having two reactive sites) should exhibit a k_1 value twice that found for *N,N*-Et$_2$en,

(29) T. S. Turan, Ph.D. Dissertation, Wayne State University, 1969, Appendix C.

(30) R. Nasanen, P. Merilainen, and M. Koskinen, *Suom. Kemistilehti B*, **36**, 9 (1963).

if enthalpic contributions are comparable as is normally assumed for a dissociative mechanism. The fact that a twofold difference is not observed suggests that this latter point may merit further investigation.

The Internal Conjugate Base Effect. The rate constant values obtained for the reactions of aquonickel(II) ion reacting with unprotonated en and *N,N*-Et_2en are two of the largest values ever obtained for this metal ion species being nearly 100-fold larger than the corresponding value with ammonia.[1] As described in the Introduction, we have ascribed this enhanced rate behavior to the ICB effect (Figure 2) in which, within the context of eq 1, we assume that either the value of K_{os} or the value of k^{M-S} or both are increased as a result of the proposed hydrogen-bond formation in the outer-sphere complex[1,13] (Figure 2).

In view of the slight steric hindrance involved in these diamine ligands,[13] the actual ICB effect in these reactions must be even larger than 100-fold. Adopting the convention of treating these ligands as "a donor atom with a tail,"[6] the steric factor, p, in eq 1 which is applicable to en should be in the vicinity of 2.5-5.[6,31] Within this same context, the center-to-center distance in the outer-sphere complex as applied to the theoretical calculation of K_{os} can be assumed to remain constant for NH_3 and en.[6] Thus, the observed ICB effect is approximately

$$\frac{k_{Ni}^{en}}{k_{Ni}^{NH_3}}\left(\frac{p}{2}\right)=\frac{3.4\times10^5}{4.6\times10^3}\left(\frac{5}{2}\right)=2\times10^2 \qquad (25)$$

where the factor of 2 represents the presumed statistical factor arising from the presence of two donor atoms in en.

The question which now arises is: Can an ICB effect of this magnitude by reasonably accounted for by increases in the values of K_{os} and k^{M-S} as effected by the proposed hydrogen-bond formation? In terms of the K_{os} value, it must be presumed that the formation rate constant of the outer-sphere complex, k_0, is unaffected by subsequent hydrogen bonding, remaining at the diffusion limit (*i.e.*, $k_0 = 6\times10^9\ M^{-1}\ sec^{-1}$ for a neutral ligand[20]). Thus, any alteration in the value of K_{os} must be reflected in the outer-sphere dissociation rate constant, k_{-0}.

Studies on proton-exchange reactions in aqueous medium have shown that intramolecular hydrogen bonding can slow down such reactions by factors of 10^3 or more relative to the "normal" diffusion-controlled processes, the decrease being attributed to the breaking of the hydrogen bond.[32,33] Whereas, in the proton-transfer reactions, a portion of this factor may arise from rotational barriers, a 200-fold decrease in the value of k_{-0} as applied to the dissociation of the outer-sphere complex does appear to be within the realm of feasibility.[34]

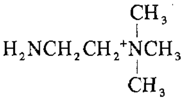
As noted in the original ICB proposal,[1] the formation of an outer-sphere hydrogen bond between en and a coordinated water molecule could impart a partial hydroxide character to the water molecule involved. Inner-sphere hydroxide has been observed to labilize the remaining coordinated water molecules for several other metal ions by up to 1000-fold,[1] most of these reports involving trivalent cations. Although there is no direct evidence of hydroxide labilization on Ni(II), inner-sphere labilization by unidentate ligands has been observed with $Ni(H_2O)_5Cl^+$ [35] and with $Ni(NH_3)(H_2O)_5^{2+}$ [36] yielding increases in the value of k^{M-S} amounting to about four- and sevenfold, respectively. A larger labilizing effect might be achieved with hydroxide, but these increases may well be representative of the inner-sphere effects to be anticipated with a hydrogen-bonded water.

Thus, we conclude that a 200-fold enhancement in the formation rate constant can be accounted for within the framework of the ICB mechanistic proposal *with the major contribution most likely arising in the K_{os} term.*

Formation Rate Constant with Monoprotonated Ethylenediamine. In contrast to the variability in k_1 values, the listing in Table V reveals excellent agreement among k_2 values obtained in our three separate studies. This undoubtedly results from the fact that the k_2 values are derived primarily from data in the lower pH regions which are presumably less affected by the experimental interferences previously described for pH >6.8. Moreover, over most of the pH region for which successful data were obtained, the k_2 term in eq 12 is dominant leading to a more precise evaluation of this constant.

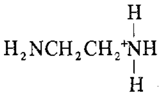
We note with particular interest that our values for k_2 are less than one-third the value previously reported by Cassatt and Wilkins.[18] Examination of their raw data for 25°, which consists of only *three* kinetic runs, reveals excellent agreement in the experimental k_f values with those obtained by us at comparable pH. In resolving their kinetic data, Cassatt and Wilkins used protonation constant values for en ($\log K_{H1} = 10.5$, $\log K_{H2} = 7.5$) which appear to be too large in view of other recent studies,[25] thus tending to increase the apparent value of k_2.[37] Furthermore, these authors ignored any contribution of the unprotonated ligand species to the observed rates[38] leading to a further increase in their resolved k_2 value. Therefore, we conclude that their reported k_2 value is erroneously large and presume that the correct value is in the vicinity of $k_2 = 1.8\times10^2\ M^{-1}\ sec^{-1}$ (Table V).

In a recent kinetic study on Ni(II) reacting in several solvent compositions with *N,N,N*-trimethylethylenediammonium ion (tmen⁺),[6] which may be considered an analog of Hen⁺,



$H_2NCH_2CH_2{}^{+}N(CH_3)_3$

tmen$^+$



$H_2NCH_2CH_2{}^{+}NH_3$

Hen$^+$

we obtained a rate constant value of $k = 5.0\times10^2\ M^{-1}\ sec^{-1}$ for Ni-tmen complex formation in aqueous solution at 25°. In view of the extensive discussion presented in that paper on the effects of various conformational and

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(31) D. B. Rorabacher and C. A. Melendez-Cepeda, *J. Amer. Chem. Soc.*, 93, 6071 (1971).

(32) M. Eigen, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, 3, 161 (1959).

(33) M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, *Progr. React. Kinet.*, 2, 285 (1964).

(34) As a point of interest, it should be noted that if, in fact, the value of K_{os} can increase by 200-fold, the applicability of the steady-state approximation to the outer-sphere complex could be jeopardized in many experimental situations. We note, however, that the experimental conditions used in our studies are safely within the limits of the steady-state assumption even under the most adverse circumstances. Of related significance is the observation that, in the case of Cu(II)-en, k^{M-S} is sufficiently large that the decrease in k_{-0} accompanying hydrogen bonding appears to cause the reaction to become diffusion controlled (*cf.* ref 20).

(35) S. F. Lincoln, F. Aprile, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, 7, 929 (1968).

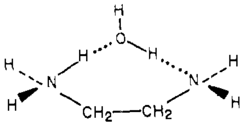
(36) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, 92, 798 (1970).

(37) Applying Cassatt and Wilkins' protonation constant values to our stopped-flow data yields $k_2 = 3.9\times10^2\ M^{-1}\ sec^{-1}$ and $k_1 = 1.2\times10^6\ M^{-1}\ sec^{-1}$. (Note the significant enhancement in the latter value.)

(38) The application of our protonation constants indicates that the rate contribution of unprotonated en becomes dominant in eq 11 above pH 6.8 while the use of Cassatt and Wilkins' protonation constants indicates that this phenomenon occurs above pH 7.0.

rotomeric ligand isomers upon complex formation rates,[6] we now suggest that the threefold lower formation rate constant observed for Hen^+ relative to $tmen^+$ is explainable in the terms that a significant fraction of the Hen^+ species is intramolecularly hydrogen bonded[13] (in a "gauche-in" conformation[6]) and is thus unreactive toward the metal ion.

One might suspect that internal hydrogen bonding would affect the protonation rate constants of the ligand, as has been found in comparing salicylic acid to phenol,[33] and might thus be reflected in abnormal protonation equilibrium constants. However, in the case of salicylic acid the proton is shared directly between two atoms of the same molecule, whereas in the case of Hen^+ the proton may be shared *via* a bridging water molecule



Such an arrangement would not affect the protonation rate constant since, as Eigen has pointed out,[32] the proton has direct access to the defect proton in the bulk solvent *via* the proton-jump mechanism.

Thus, we do not imply that either the process of rupturing an intramolecular hydrogen bond or the final loss of the proton from the ligand itself has any influence upon the rate of Ni(II) reaction with Hen^+. Rather, the existence of intramolecular hydrogen bonding shifts the conformational equilibria of the Hen^+ species such that, at any specific time, a smaller fraction of the protonated ligand is in a conformation favorable for coordinate bond formation to the metal ion.[6]

Conclusions

The formation rate constant for unprotonated ethylenediamine reacting with $Ni(H_2O)_6^{2+}$ is found to be about 200 times larger than would be anticipated on the basis of a normal dissociative mechanism. In attributing this enhancement to outer-sphere *intermolecular* hydrogen bonding between a donor atom of the ligand and a coordinated water molecule in terms of the internal conjugate base (ICB) effect, it is inferred that the principal accelerating factor is an increase in the outer-sphere equilibrium constant, K_{os}, as the result of a decrease in the rate constant for the diffusion of the two reactants apart, k_{-0}.

In the case of the monoprotonated ligand species, an apparent retardation in the formation rate constant is attributed to the influence of *intramolecular* hydrogen bonding in decreasing the fraction of ligand which is in a reactive conformation.

Acknowledgments. This work was supported in part by the National Institute of General Medical Sciences under Grant GM-12596. Portions of the work were also assisted by the following support: National Institutes of Health postdoctoral fellowship (D. B. R., 1964-1965), National Science Foundation undergraduate research participation grant (H. K. S., 1969), National Science Foundation graduate traineeship (R. W. T., 1970-1972). The authors also express their gratitude to Professor Manfred Eigen for making available the facilities of the Max Planck Institut fur physikalische Chemie, Gottingen, Germany (study I), and to Professor Daniel Leussing of The Ohio State University for consultations regarding the utilization of his computer program for the resolution of relaxation data (study III).

Registry No. Ni^{2+}, 14701-22-5; ethylenediamine, 107-15-3.

Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

The Relative Stabilities of Some Platinum(II) Carbonyl Complexes

FREDERICK PESA, LEN SPAULDING, and MILTON ORCHIN*

Received October 18, 1973 AIC30765E

Equilibrium constants, K_{eq}, for the reaction $(n\text{-}C_4H_9)_4N^+[(CO)PtCl_2(X)]^- + 4\text{-Zpy} \rightleftharpoons (n\text{-}C_4H_9)_4NX + (CO)PtCl_2(4\text{-Zpy})$, where X = Cl, Br, or I and 4-Zpy is a 4-substituted pyridine with Z = $COCH_3$, CO_2CH_3, H, C_2H_5, CH_3, or $C(CH_3)_3$, were determined in chloroform solution by infrared measurements of the CO bands. As expected, the more electron releasing Z is, the larger K_{eq} is, independent of X; the effect of changing Z is much greater than that of changing X.

Introduction

We have shown earlier[1] that if the infrared spectra of the complexes 1,3-dichloro-2-carbonyl-4-(4-Z-pyridine)platinum(II), $(CO)PtCl_2(4\text{-Zpy})$, are determined in acetonitrile (or acetone) solution using KBr cells, the solvent dissolves sufficient bromide ion to displace the pyridine, and a mixture of two carbonyl species is produced, giving rise to two readily distinguishable CO bands in the ir spectrum. We have also reported earlier[1] that the relative intensity of the two bands in acetone depends on the nature of Z; the more electron withdrawing Z is, the greater is the intensity (concentration) of the bromide complex. This displacement reaction seemed to us to merit separate investigation.

We wish to report now the results of a limited study on the equilibrium competition between bromide (and other halides) and 4-substituted pyridines (4-Zpy) for a site on the platinum in the reaction

$$\underset{\mathbf{1}}{[(n\text{-}C_4H_9)_4N]^+[(OC)PtCl_2(X)]^-} + 4\text{-Zpy} \rightleftharpoons (n\text{-}C_4H_9)_4NX + \underset{\mathbf{2}}{(OC)PtCl_2(4\text{-Zpy})} \qquad (1)$$

where X = Cl, Br, or I and Z = $C(CH_3)_3$, CH_3, C_2H_5, H, CO_2CH_3, or $COCH_3$. These equilibrium studies on carbonyl complexes of Pt(II) complement those previously reported

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(1) L. Spaulding, B. Reinhardt, and M. Orchin, *Inorg. Chem.*, 11, 2092 (1972); T. Weil, M. Rycheck, and M. Orchin, *ibid.*, 8, 1002 (1969).