$$\underset{\mathbf{2}}{RuX_2(HL)(L)} \underset{HClO_4}{\overset{NEt_3}{\rightleftarrows}} \underset{\mathbf{4}}{RuX_2(L)_2^-} \qquad (2)$$

species **4** does have a voltammetric response on the negative side (showing that ruthenium(III) is more stable in **4** than in **2**) of that of **2** (Figure 4), but the cathodic peak is very flat, and the corresponding anodic response is relatively weak. The detailed nature of the process involved has not been investigated.

The electronic spectrum of **4** was determined in acetonitrile in a few cases (Figure 2, Table II). The ~1000-nm LMCT band characteristic of **2** shifts slightly to lower energy on deprotonation. On the other hand the ~570-nm band shifts to higher energy. Addition of perchloric acid to **3** brings back the original spectrum of **2**. These experiments clearly establish the presence of a proton in **2**. The facile protonation–deprotonation reaction (eq 2) is a characteristic feature of these hydrogen-bonded complexes. The $RuX_2(HB)(B)$ complexes behave similarly. Attempts to isolate **4** in the form of salts is currently in progress.

**(c) Chemical Reduction of 2 and Further Characterization of 3.** The conversion **2** → **3** (eq 1) can be brought about in acetonitrile by chemical reducing agents like hydroquinone and hydrazine. Hydroquinone ($H_2q$) was found to be a particularly convenient reducing agent for rapid and quantitative conversion of **2** to **3**. Excess of hydroquinone is required to complete the reduction, suggesting the presence of an equilibrium process (eq 3). Perchloric acid pushes equilibrium

$$\underset{\mathbf{2}}{2RuX_2(HL)(L)} + H_2q \rightleftharpoons \underset{\mathbf{3}}{2RuX_2(HL)(L)^-} + q + 2H^+ \qquad (3)$$

**3** to the left. On addition of excess acid, $H_2q$ no longer reduces **2**, but q is found to oxidize **3** to **2**.

Solutions of **3** are green, and both the electrochemically and chemically produced species have identical spectra (Figure 2, Table II). These spectra are quite different from those of the ruthenium(III) analogue (**2**). These are characterized by an intense band near 680 nm with a slight shoulder at ~500 nm. This band is believed to be due to metal ($t_{2g}$) → ligand ($\pi^*$) charge-transfer (MLCT) transition. MLCT transition is of common occurrence in ruthenium(II) complexes of conjugated ligands.[32,33] However, the band position in the present complexes is unusually low in energy. The MLCT band shifts to higher energy in the order Br > Cl. This order is opposite to that of the LMCT band of **2** (vide supra) as expected.

**E. Other Complexes.** We have attempted to prepare the iodo species $RuI_2(HL)(L)$ following a method similar to (NaI used instead of LiBr) that used for making the bromo complexes. Iodine-containing species thus obtained do not appear to be pure complexes, and full characterization is awaited. Some of the products show a strong EPR signal at 2.00 suggesting the presence of some free radicals. However, cyclic voltammetric data of the products in acetonitrile does show that the species $RuI_2(HL)(L)$ is most probably present to measurable extents. $E°_{298}$ values for couple 1 are as follows: $HL^1$, 0.55 V; $HL^3$, 0.50 V; $HL^4$, 0.53 V. The results are consistent with the expected (vide supra) order of $E°_{298}$ I > Br > Cl in **2**. Previously we have briefly reported diamagnetic pink ruthenium(II) complexes of the type $RuX_2(HL)_2$ prepared in absolute ethanol under nitrogen. These were given a tentative *trans*-$RuCl_2$ structure since a strong $\nu_{RuCl}$ was observed. We have now found that this stretch is actually due to contamination by the ruthenium(III) species $RuX_2(HL)(L)$. $RuX_2(HL)_2$ probably has a *cis*-$RuX_2$ structure. The system is under investigation. Arylazo oxime smoothly displaces halogen from *cis*-$Ru(bpy)_2Cl_2$ producing $Ru(bpy)_2(L)^+$ which can be readily protonated to $Ru(bpy)_2(HL)_2^+$. Further reports on such a system will be made in due course.

**Acknowledgment** is made to the Department of Science and Technology, New Delhi, for financial support. Thanks are due to Dr. J. G. Mohanty of Hyderabad University for EPR spectra.

**Registry No.** $RuCl_2(HL^1)(L^1)$, 78128-51-5; $RuCl_2(HL^1)(L^1)^-$, 78128-52-6; $RuBr_2(HL^1)(L^1)$, 78128-53-7; $RuBr_2(HL^1)(L^1)^-$, 78128-54-8; $RuCl_2(HL^2)(L^2)$, 78149-26-5; $RuCl_2(HL^2)(L^2)^-$, 78128-55-9; $RuBr_2(HL^2)(L^2)$, 78128-56-0; $RuBr_2(HL^2)(L^2)^-$, 78149-27-6; $RuCl_2(L^2)_2^-$, 78128-57-1; $RuCl_2(HL^3)(L^3)$, 78128-58-2; $RuCl_2(HL^3)(L^3)^-$, 78128-59-3; $RuBr_2(HL^3)(L^3)$, 78149-19-6; $RuBr_2(HL^3)(L^3)^-$, 78149-20-9; $RuCl_2(HL^4)(L^4)$, 78128-60-6; $RuCl_2(HL^4)(L^4)^-$, 78128-61-7; $RuBr_2(HL^4)(L^4)$, 78128-62-8; $RuBr_2(HL^4)(L_4)^-$, 78128-63-9.

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# Kinetics of Acid-Catalyzed Chelate Ring Opening in Nickel(II) Polyamine Complexes

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The rates of dissociation of $Ni(en)^{2+}$ and $Ni(en)_3^{2+}$ increase linearly with acid concentration at pH values below 1.5. The $H_3O^+$ rate constants are 0.056 and 19 $M^{-1}\ s^{-1}$ (25 °C), respectively. In addition, general-acid catalysis of the $Ni(en)^{2+}$ dissociation by acetic and mono-, di-, and trichloroacetic acids occurs. Contrary to the usual behavior of general acids, the rate constants for these acids decrease as the acid strength increases: $CH_3COOH$, 0.30 $M^{-1}\ s^{-1}$; $ClCH_2COOH$, 0.141 $M^{-1}\ s^{-1}$, $Cl_2CHCOOH$, 0.08 $M^{-1}\ s^{-1}$; $Cl_3CCOOH$, 0.10 $M^{-1}\ s^{-1}$. The dissociation of $Ni(en)_3^{2+}$ exhibits no general-acid catalysis under the same conditions. A slight acceleration of the dissociation of $NiNH_3^{2+}$ occurs with $H_3O^+$ and acetic acid at high concentrations, but this increase is small relative to the uncatalyzed aqueous dissociation rate. These results indicate that the dissociation of chelate complexes is accelerated by protonation of the donor while it is still within the first coordination sphere. Acid attack occurs prior to or during solvent separation of the metal and amine donor. The unusual general-acid effect for $Ni(en)^{2+}$ reflects the ability of the carboxylic acids to associate with the metal complex and to transfer a proton to a donor that is in the first coordination sphere.

## Introduction

Chelate dissociation is much slower than the analogous reaction of monodentate ligand complexes. However, acid can accelerate the dissociation by several orders of magnitude. After one donor is replaced by a solvent molecule, acid assists the dissociation of a polyamine chelate complex by protonating the partially coordinated intermediate and stabilizing it relative to the fully coordinated form.[1] Thus, the ring-opening step

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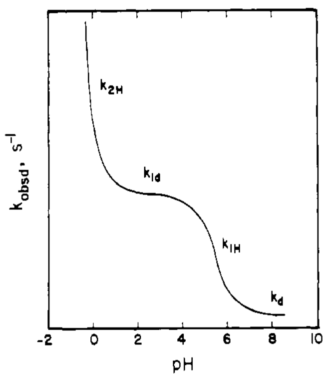

**Figure 1.** pH dependence for the dissociation of $Ni(en)^{2+}$; a composite of the present data (25 °C) and data from ref 7 (0.6 °C).

becomes rate determining at high acid concentrations.

Wilkins and co-workers have observed this phenomenon for a series of nickel(II) and copper(II) diamine complexes in moderately acidic media.[2-8] In particular, the dissociation of the (ethylenediamine)nickel(II) complex, $Ni(en)^{2+}$, was accelerated by a factor of 20 when the pH was lowered from 7.3 to 4. This pH dependence is designated by the rate constant $k_{1H}$ in Figure 1 and the water dissociation pathway (pH above 7.3) is represented by the rate constant $k_d$. Between pH 4 and 1.5, a limiting rate was observed with the rate constant given by $k_{1d}$. At pH values lower than 1.5, the rate again increased linearly with the acid concentration. The rate constant is $k_{2H}$. The highly acidic region was only cursorily treated, and it was suggested that, in high concentration, $H_3O^+$ aids the first bond rupture by competing for the nickel–nitrogen bonding electrons.[7]

Similar pH dependences have been observed for several other diamine chelate complexes of nickel(II).[8] Childers and Wentworth reported that acid concentrations of 0.5–5.0 M significantly increased the dissociation rate of Ni(*cis*,*cis*-1,3,5-tach)$^{2+}$.[9]

These few examples of acceleration of chelate complex dissociation in acid have generally received little attention. It has commonly been accepted that the only way in which acid could assist the dechelation of a polyamine complex was by protonation of a donor after solvent separated it from the metal.[10] However, Margerum and Cayley have proposed a mechanism to explain the low pH behavior.[1] According to the proposed mechanism, protonation can occur in solutions of high acid concentration before or during the solvation of the metal ion, thereby enhancing the dissociation rate. The purpose of this study has been to test this mechanism by investigating the specific- and general-acid dependences of the $Ni(en)^{2+}$ dissociation at low pH. The dissociations of $Ni(en)_3^{2+}$ and $NiNH_3^{2+}$ have also been studied for comparison.

## Experimental Section

**Reagents.** Solutions of $Ni(ClO_4)_2$, $NaClO_4$, and $LiClO_4$ were prepared by neutralization of the respective metal carbonates with $HClO_4$ followed by filtration and boiling to remove $CO_2$. $NaClO_4$ was diluted to the desired volume; $Ni(ClO_4)_2$ and $LiClO_4$ were collected as crystals, air dried, and dissolved to give solutions of the desired concentration. Standardization was accomplished by EDTA titration for $Ni(ClO_4)_2$, by microanalytical chlorine analysis for $LiClO_4$, and by gravimetric analysis for $NaClO_4$. An $NH_4NO_3$ solution was prepared from the solid and standardized by titration for ammonia. Stock solutions of $HClO_4$, $HNO_3$, and the carboxylic acids were standardized against NaOH with phenolphthalein indicator. Distilled pyridine was standardized with $HClO_4$ and bromocresol green indicator. Acid solutions used for kinetic measurements were prepared from these stock solutions.

Ethylenediamine was purified by distilling it twice at reduced pressure. A stock solution of the amine was prepared by weight and used without standardization. The $Ni(en)^{2+}$ and $Ni(en)_3^{2+}$ solutions ($10^{-2}$ M) were prepared from aqueous stock solutions of $Ni(ClO_4)_2$ and ethylenediamine. The stoichiometries of the complexes were controlled by adjusting the metal:ligand ratio (1.03:1 for $Ni(en)^{2+}$, 1:3.55 for $Ni(en)_3^{2+}$) and the pH (pH 6 for $Ni(en)^{2+}$, pH 9 for $Ni(en)_3^{2+}$).[11,12] The ionic strength was maintained at $\mu = 4.0$ with $NaClO_4$ or $LiClO_4$. The $NiNH_3^{2+}$ was prepared by addition of an aqueous ammonia solution to a 100% excess of $Ni(NO_3)_2$ solution. The ionic strength ($\mu = 2.0$) and pH were adjusted with $NH_4NO_3$.

**Kinetic Measurements.** The kinetics of the acid-catalyzed dissociations of the nickel complexes were followed at 25.0 ± 0.5 °C with the use of a Durrum stopped-flow spectrophotometer interfaced to a Hewlett-Packard Model 2115A computer.[13] Absorbance vs. time data were collected for 3–4 half-lives of each reaction at 370, 520, and 650 nm for the $Ni(en)^{2+}$, $Ni(en)_3^{2+}$, and $NiNH_3^{2+}$ studies, respectively. Pseudo-first-order conditions were maintained by using at least a tenfold excess of acid in each run. Good first-order kinetics were observed in all cases. Treatment of the data by linear and nonlinear regression analyses gave values for the pseudo-first-order rate constant ($k_{obsd}$), the initial absorbance ($A_0$), and the final absorbance ($A_\infty$) as defined by eq 1 and 2.

$$A = (A_0 - A_\infty)e^{-k_{obsd}t} + A_\infty \qquad (1)$$

$$-d[NiL^{2+}]/dt = k_{obsd}[NiL^{2+}] \qquad (2)$$

## Results

The stoichiometric equation for chelate complex dissociation at low pH is given in eq 3. Below pH 4, the water dissociation

$$NiL^{2+} + 2H^+ \rightarrow Ni(aq)^{2+} + H_2L^{2+} \qquad (3)$$

pathway with rate constant $k_d$ and the protonation pathway with rate constant $k_{1H}$ do not contribute to the observed rate. In this pH range, the observed rate constant, $k_{obsd}$, is expressed as the sum of several rate constants as shown in eq 4. The

$$k_{obsd} = k_{1d} + k_{2H}[H^+] + k_{2HB}[HB] \qquad (4)$$

individual rate constants were evaluated by measuring $k_{obsd}$ as a function of the acid concentration and applying a linear least-squares regression to fit the data. In this treatment, with no general acid present, the intercept and slope correspond to $k_{1d}$ and $k_{2H}$, respectively. With general acid present, the observed rate constant is expressed in terms of the total general-acid concentration, $[HB]_T$, as in eq 5. For plots of $k_{obsd}$

$$k_{obsd} = k_{1d} + k_{2H}[H^+] + \left(\frac{k_{2HB}[H^+]}{[H^+] + K_a}\right)[HB]_T \qquad (5)$$

vs. $[HB]_T$ at constant $[H^+]$, the intercept is $k_{1d} + k_{2H}[H^+]$ and the slope is $k_{2HB}[H^+]/([H^+] + K_a)$. For a monodentate complex, the corresponding dissociation, specific-acid, and general-acid rate constants are $k_d$, $k_H$, and $k_{HB}$, respectively.

**$Ni(en)^{2+}$.** Values of $k_{1d}$ and $k_{2H}$ for the dissociation of $Ni(en)^{2+}$ were evaluated by using $k_{obsd}$ for $[H^+]$ over the range 0.05–2.0 M with no general acids and the intercepts of the $k_{obsd}$

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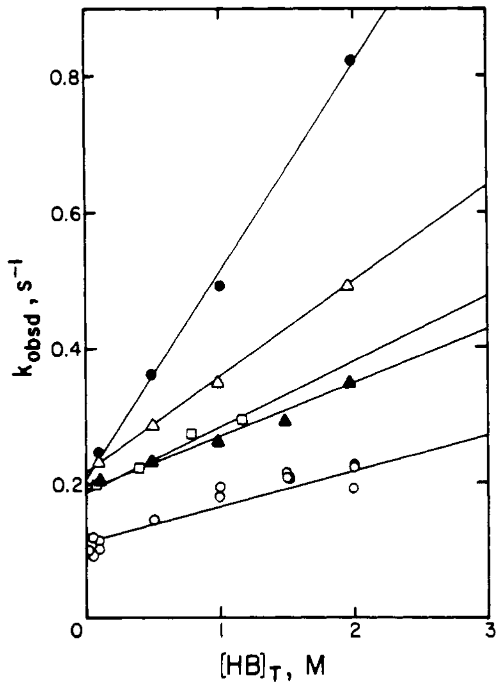

**Figure 2.** Comparison of rate increases for the dissociation of $Ni(en)^{2+}$ in the presence of $H_3O^+$ and several general acids ($\mu$ = 4.0 ($NaClO_4$–$HClO_4$); 25 °C): ○ $H_3O^+$; ● $CH_3COOH$, $[H^+]$ = 1.74 M; △ $ClCH_2COOH$, $[H^+]$ = 1.74 M; ▲ $Cl_2CHCOOH$, $[H^+]$ = 2.00 M; □ $Cl_3CCOOH$, $[H^+]$ = 2.00 M.

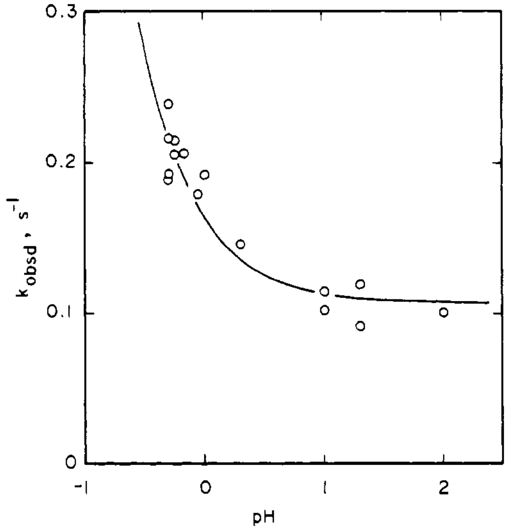

**Figure 3.** pH Dependence of the $Ni(en)^{2+}$ dissociation ($\mu$ = 4.0 ($NaClO_4$–$HClO_4$); 25 °C).

vs. $[HB]_T$ plots when general acids were present (Table I, Figures 2 and 3). The values obtained for $k_{1d}$ (0.108 ± 0.008 $s^{-1}$) and $k_{2H}$ (0.056 ± 0.006 $M^{-1}$ $s^{-1}$) indicate that there is indeed a substantial increase in the rate of dissociation of $Ni(en)^{2+}$ in concentrated acid (Figure 3). These results confirm the earlier work of Ahmed and Wilkins who obtained $k_{1d} = 6.3 \times 10^{-3}$ $s^{-1}$ and $k_{2H} = 4.3 \times 10^{-3}$ $M^{-1}$ $s^{-1}$ (0.6 °C, $\mu$ = 2 ($KNO_3$–$HNO_3$)).[7] Also, their calculated value of $k_{obsd}$, 0.145 $s^{-1}$, at 25 °C and 0.2 M acid[7] is in good agreement with our value of 0.119 $s^{-1}$ at 0.2 M $HClO_4$. More recently, $k_{obsd}$ was determined to be 0.17 ± 0.015 $s^{-1}$ at 25 °C in 0.5 M HCl.[14] Our value of 0.136 $s^{-1}$ (0.5 M $HClO_4$) is lower, but the difference may be attributed to medium effects.

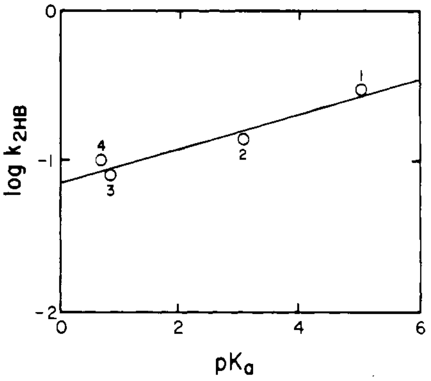

**Figure 4.** Relationship between the general-acid rate constants and the $pK_a$ values for acetic acid and the chloroacetic acids: 1, $CH_3COOH$; 2, $ClCH_2COOH$; 3, $Cl_2CHCOOH$; 4, $Cl_3CCOOH$.

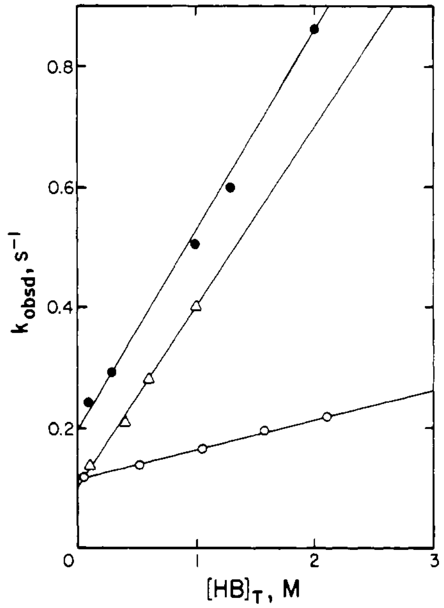

**Figure 5.** Comparison of rate increases for the dissociation of $Ni(en)^{2+}$ in the presence of $H_3O^+$ and acetic acid in $LiClO_4$ medium, ($\mu$ = 4.0 ($LiClO_4$–$HClO_4$); 25 °C; cf. Figure 3): ○ $H_3O^+$; ● $CH_3COOH$, $[H^+]$ = 2.00 M; △ $CH_3COOH$, $[H^+]$ = 0.105 M.

The general-acid rate constants, $k_{2HB}$, were determined for acetic acid and the chloroacetic acids by varying the total general-acid concentration over the range 0.1–2.0 M while maintaining $[H^+]$ constant at 1.7 or 2.0 M with $HClO_4$ (Table I). For all of the acids, the values of $k_{obsd}$ increase linearly with $[HB]_T$ (Figure 2). The values obtained for $k_{2HB}$ are tabulated in Table II. These results demonstrate that general-acid catalysis does occur and, in fact, enhances the rate of $Ni(en)^{2+}$ dissociation to a greater extent than specific-acid catalysis. Thus, the values of $k_{2HB}$ are greater than $k_{2H}$ for all of the acids in this series. Furthermore, the catalytic effectiveness of the carboxylic acids increases with decreasing acid strength as shown in the linear correlation between log $k_{2HB}$ and $pK_a$ (Figure 4).[15]

To determine if the general-acid rate constants depend on $[H^+]$, we measured the $k_{2HB}$ values for acetic and chloroacetic acids (Table I) with $[H^+]$ constant at 0.1 M as well as at 1.7 M. For both acids, $k_{2HB}$ decreased about 30% when the $[H^+]$ was lowered from 1.7 to 0.1 M (Table II). This decrease was thought to be an ionic environment effect due to the large

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(15) The rate constants for di- and trichloroacetic acids are inverted with respect to the trend, but this is attributed to larger uncertainties in $pK_a$ and $k_{2HB}$. These two acids are still significantly less effective catalysts than monochloroacetic and acetic acids.

**Table I.** Kinetic Data for the Dissociation of $NiL^{2+}$ in Acid

| $NiL^{2+}$ | acid | $[HB]_T$, M | $[H^+]$, M | $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|
| $Ni(en)^{2+\,a}$ | $H_3O^+$ | | 0.0500 | 0.119 ± 0.001 |
| | | | 0.500 | 0.143 ± 0.001 |
| | | | 0.990 | 0.179 ± 0.004 |
| | | | 1.48 | 0.206 ± 0.004 |
| | | | 2.00 | 0.22 ± 0.01 |
| | $CH_3COOH$ | 0.0995 | 1.74 | 0.244 ± 0.005 |
| | | 0.498 | | 0.358 ± 0.005 |
| | | 0.995 | | 0.489 ± 0.001 |
| | | 1.99 | | 0.820 ± 0.001 |
| | $CH_3COOH$ | 0.0995 | 0.0988 | 0.123 ± 0.003 |
| | | 0.498 | | 0.198 ± 0.004 |
| | | 0.696 | | 0.235 ± 0.004 |
| | | 0.995 | | 0.301 ± 0.002 |
| | $ClCH_2COOH$ | 0.0980 | 1.74 | 0.228 ± 0.008 |
| | | 0.490 | | 0.282 ± 0.009 |
| | | 0.980 | | 0.347 ± 0.008 |
| | | 1.96 | | 0.490 ± 0.007 |
| | $ClCH_2COOH$ | 0.0980 | 0.0988 | 0.125 ± 0.003 |
| | | 0.490 | | 0.159 ± 0.007 |
| | | 0.686 | | 0.179 ± 0.002 |
| | | 0.980 | | 0.21 ± 0.02 |
| | $Cl_2CHCOOH^b$ | 0.0986 | 2.00 | 0.204 ± 0.007 |
| | | 0.493 | | 0.23 ± 0.02 |
| | | 0.986 | | 0.26 ± 0.03 |
| | | 1.48 | | 0.29 ± 0.03 |
| | | 1.97 | | 0.35 ± 0.01 |
| | $Cl_3CCOOH$ | 0.0775 | 2.00 | 0.1938 ± 0.0003 |
| | | 0.388 | | 0.222 ± 0.005 |
| | | 0.775 | | 0.271 ± 0.006 |
| | | 1.16 | | 0.288 ± 0.006 |
| | $C_5H_5NH^+$ | 0.00923 | 1.98 | 0.205 ± 0.007 |
| | | 0.0923 | 1.99 | 0.208 ± 0.008 |
| | | 0.138 | 1.99 | 0.206 ± 0.001 |
| | | 0.185 | 2.00 | 0.202 ± 0.007 |
| $Ni(en)^{2+\,c}$ | $H_3O^+$ | | 0.0523 | 0.119 ± 0.003 |
| | | | 0.523 | 0.139 ± 0.002 |
| | | | 1.05 | 0.166 ± 0.002 |
| | | | 1.57 | 0.192 ± 0.002 |
| | | | 2.09 | 0.217 ± 0.004 |
| | $CH_3COOH$ | 0.0994 | 2.00 | 0.243 ± 0.001 |
| | | 0.298 | | 0.290 ± 0.006 |
| | | 0.994 | | 0.505 ± 0.003 |
| | | 1.29 | | 0.599 ± 0.006 |
| | | 1.99 | | 0.86 ± 0.01 |
| | $CH_3COOH^d$ | 0.100 | 0.105 | 0.136 ± 0.004 |
| | | 0.400 | | 0.21 ± 0.01 |
| | | 0.601 | | 0.282 ± 0.008 |
| | | 1.00 | | 0.401 ± 0.004 |
| $Ni(en)_3{}^{2+\,e}$ | $H_3O^+$ | | 0.0523 | 71 ± 10 |
| | | | 0.523 | 75 ± 12 |
| | | | 1.05 | 90 ± 13 |
| | | | 1.57 | 97 ± 5 |
| | | | 2.09 | 109 ± 9 |
| | $CH_3COOH$ | 0.0996 | 1.97 | 103 ± 18 |
| | | 0.498 | | 85 ± 8 |
| | | 0.996 | | 91 ± 12 |
| | | 1.39 | | 86 ± 13 |
| $NiNH_3{}^{2+\,f}$ | $H_3O^+$ | | 0.249 | 5.9 ± 0.1 |
| | | | 0.498 | 6.03 ± 0.02 |
| | | | 0.747 | 6.14 ± 0.09 |
| | | | 0.996 | 6.31 ± 0.09 |
| | $CH_3COOH$ | 0.498 | 0.936 | 6.73 ± 0.07 |
| | | 0.598 | | 6.83 ± 0.04 |
| | | 0.797 | | 7.02 ± 0.08 |
| | | 0.996 | | 7.30 ± 0.09 |

[a] $[Ni(en)^{2+}] = 5.00 \times 10^{-3}$ M; $\mu = 4.0$ ($NaClO_4$-$HClO_4$); 25.4 °C; $\lambda = 370$ nm. [b] 24.5 °C. [c] $[Ni(en)^{2+}] = 5.00 \times 10^{-3}$ M; $\mu = 4.0$ ($LiClO_4$-$HClO_4$); 25.3 °C; $\lambda = 370$ nm. [d] 25.6 °C. [e] $[Ni(en)_3{}^{2+}] = 4.94 \times 10^{-3}$ M; $\mu = 4.0$ ($NaClO_4$-$HClO_4$); 25.0 °C; $\lambda = 520$ nm. [f] $[NiNH_3{}^{2+}] = 5.10 \times 10^{-2}$ M; $\mu = 2.0$ ($NH_4NO_3$-$HNO_3$); 25.0 °C; $\lambda = 650$ nm.

**Table II.** Rate Constants for the Dissociation of $NiL^{2+}$ in Acid (25 °C)

| $NiL^{2+}$ ($\mu$) | acid | $pK_a$ | $k_{1d}$, $s^{-1}$ | $k_{2HB}$, $M^{-1}\ s^{-1}$ |
|---|---|---|---|---|
| $Ni(en)^{2+}$ (4.0 ($NaClO_4$-$HClO_4$)) | $H_3O^+$ | | 0.108 ± 0.008 | 0.056 ± 0.006 |
| | $CH_3COOH^a$ | $5.01^b$ | | 0.30 ± 0.01 |
| | $CH_3COOH^c$ | | | 0.198 ± 0.006 |
| | $ClCH_2COOH^a$ | $3.02^b$ | | 0.141 ± 0.002 |
| | $ClCH_2COOH^c$ | | | 0.097 ± 0.004 |
| | $Cl_2CHCOOH^d$ | $0.87^e$ | | 0.08 ± 0.01 |
| | $Cl_3CCOOH^d$ | $0.66^e$ | | 0.10 ± 0.01 |
| | $C_5H_5NH^{+\,d}$ | $5.15^f$ | | <0.05 |
| $Ni(en)^{2+}$ (4.0 ($LiClO_4$-$HClO_4$)) | $H_3O^+$ | | 0.115 ± 0.001 | 0.0486 ± 0.0008 |
| | $CH_3COOH^d$ | $4.52^f$ | | 0.33 ± 0.01 |
| | $CH_3COOH^c$ | | | 0.30 ± 0.01 |
| $Ni(en)_3{}^{2+}$ (4.0 ($NaClO_4$-$HClO_4$)) | $H_3O^+$ | | 68 ± 2 | 19 ± 2 |
| | $CH_3COOH^d$ | $5.01^b$ | | <10 |
| $NiNH_3{}^{2+}$ (2.0 ($NH_4NO_3$-$HNO_3$)) | $H_3O^+$ | | *h* | *i* |
| | $CH_3COOH^g$ | $4.41^b$ | | 1.13 ± 0.05 |

[a] $[H^+] = 1.7$ M. [b] Reference 27, pp 364, 374. [c] $[H^+] = 0.1$ M. [d] $[H^+] = 2.0$ M. [e] Martell, A. E., Smith, R. M., Eds. "Critical Stability Constants"; Plenum Press: New York, 1974; Vol. II, pp 18–19. [f] Sillen, L. G., Martell, E. A., Eds. "Stability Constants of Metal Ion Complexes"; The Chemical Society: London, 1971; Supplement No. 1; pp 250, 359. [g] $[H^+] = 0.94$ M. [h] $k_d = 5.76 \pm 0.02$. [i] $k_H = 0.54 \pm 0.03$.

difference in the mean acitivty coefficients of $HClO_4$ and $NaClO_4$.[10,16] Therefore, $k_{1d}$, $k_{2H}$, and $k_{2HB}$ for acetic acid were also measured under the same conditions as previously described except $LiClO_4$ was used to maintain the ionic strength (Table I). Statistically the same values were obtained for $k_{1d}$, $k_{2H}$, and $k_{2HB}$ ($[H^+] = 2.0$ M) in the $LiClO_4$ medium as in $NaClO_4$ (cf. Figures 3 and 5, Table II). In $LiClO_4$, the value of $k_{2HB}$ for acetic acid with $[H^+] = 0.1$ M did not decrease significantly from that seen at $[H^+] = 2.0$ M (Figure 5). Since $k_{2HB}$ is independent of $[H^+]$ in the presence of $LiClO_4$, the apparent dependence on $[H^+]$ in $NaClO_4$ is attributed to a medium effect rather than a mechanistic effect.

The effect of the pyridinium ion, $Hpy^+$, on the $Ni(en)^{2+}$ dissociation was investigated by varying $[Hpy^+]_T$ from 0.01 to 0.2 M with $[H^+] = 2.0$ M (Table I). The concentration range was limited by solubility, but over the accessible range, $k_{2HB} < 0.05\ M^{-1}\ s^{-1}$, assuming that a 5% rate increase is detectable.

**$Ni(en)_3{}^{2+}$.** The acid-assisted dissociation of $Ni(en)_3{}^{2+}$ to $Ni(en)_2{}^{2+}$ was studied by varying the $[H^+]$ from 0.05 to 2.1 M to obtain values for $k_{1d}$ and $k_{2H}$ (Table I). These rate constants are 68 ± 2 $s^{-1}$ and 19 ± 1 $M^{-1}\ s^{-1}$, respectively. In 0.5 M $HClO_4$, the combined rate constant is 78 $s^{-1}$, which is in excellent agreement with 77 $s^{-1}$ reported for 0.5 M HCl (25 °C).[14] The combined rate constant is 72 $s^{-1}$ in 0.2 M $HClO_4$. A larger value of 86.6 $s^{-1}$ (0.2 M $HNO_3$, 25 °C) was reported by Ahmed and Wilkins, who also observed a decrease in rate when the acid concentration was increased to 1.0 M.[17] The data presented in Table I clearly show an acceleration at the higher acid concentrations. However, the dissociation rate for $Ni(en)_3{}^{2+}$ is not enhanced by acid over the range from pH 6 to 0.5 M acid because the ring-closure step and the dissociation of the monodentate intermediate proceed at similar rates.[18] Thus, in moderately acidic solution, the $H^+$ depen-

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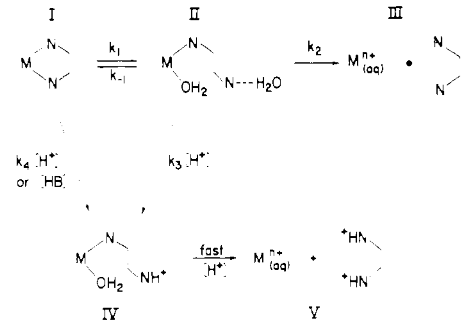

**Figure 6.** Proposed mechanism for the acid dissociation reactions of metal polyamine complexes.

**Table III.** Summary of Measured Rate Constants Defined in Terms of the Rate Constants for Individual Steps in the Dissociation of Ni(II) Polyamine and Ammine Complexes (25 °C; Cf. Figures 1 and 6)

| measd rate const | mechanistic rate const | $Ni(en)^{2+}$ | $Ni(en)_3^{2+}$ | $NiNH_3^{2+}$ |
|---|---|---|---|---|
| $k_d$, $s^{-1}$ | $(k_1/k_{-1})k_2$ | $6 \times 10^{-4}$ [a] | 47[b] | 5.76 |
| $k_H$, $M^{-1}$ $s^{-1}$ | | | | 0.54 |
| $k_{1d}$, $s^{-1}$ | $k_1$ | 0.108 | 68 | |
| $k_{1H}$, $M^{-1}$ $s^{-1}$ | $(k_1/k_{-1})k_3$ | $2 \times 10^3$ [a] | ~0[c] | |
| $k_{2H}$, $M^{-1}$ $s^{-1}$ | $k_4$ | 0.056 | 19 | |

[a] 0.6 °C. Calculated from data in ref 7. [b] Calculated from resolved rate constants in ref 18. [c] Reference 18.

dence is insignificant and $k_{1H}$ is not measurable.

The effect of acetic acid on the dissociation of $Ni(en)_3^{2+}$ to $Ni(en)_2^{3+}$ was measured for $[HB]_T$ over the range of 0.1–1.4 M with $[H^+]$ held constant at 2.0 M (Table I). The data are somewhat scattered, but the trend is toward a slight decrease in rate with increasing general-acid concentration. With the assumption that a 10% rate increase in 1.0 M acid could be detected, the upper limit for $k_{2HB}$ is 10 $M^{-1}$ $s^{-1}$.

**$NiNH_3^{2+}$.** The dissociation of $NiNH_3^{2+}$ has been studied at low pH to determine if an acceleration similar to that observed for the chelate complexes occurs. The values of $k_d$ and $k_H$ were evaluated by varying $[H^+]$ from 0.2 to 1.0 M (Table I). The results are $k_d = 5.76 \pm 0.02$ $s^{-1}$ and $k_H = 0.54 \pm 0.03$ $M^{-1}$ $s^{-1}$. The value of $k_d$ is in excellent agreement with the value of 5.8 $s^{-1}$ ($\mu = 2.0$ ($NaNO_3$–$HNO_3$), $[H^+] = 0.2$ M, 25 °C) previously reported by Melson and Wilkins, who concluded that the rate was independent of $[H^+]$.[19] Later values of 5.0 $s^{-1}$ ($\mu = 0.1$ ($NH_4NO_3$), 30 °C)[20] and 7.1 $s^{-1}$ ($\mu = 1.0$ ($NH_4ClO_4$), 25 °C)[21] for the dissociation of $NiNH_3^{2+}$ at neutral pH support that conclusion.

The general-acid effect on the $NiNH_3^{2+}$ dissociation was investigated for acetic acid concentrations of 0.5–1.0 M with 0.9 M $H^+$ (Table I). A small rate increase was observed with $k_{HB} = 1.13 \pm 0.05$ $M^{-1}$ $s^{-1}$.

## Discussion

**Specific-Acid Catalysis.** A modification of the mechanism proposed by Margerum and Cayley[1] to explain the entire pH profile of the $Ni(en)^{2+}$ dissociation is shown in Figure 6. The measured rate constants are summarized in Table III and are defined in terms of the mechanistic rate constants. The water dissociation pathway is represented by the sequence I → II → III, and the overall rate constant for this pathway is $k_d$. The $H^+$ dependence between pH 4 and 7.3 has the rate constant $k_{1H}$ and is accounted for by the pathway I → II → IV → V. The ring opening with solvent replacement (I → II) becomes rate determining around pH 4 with the limiting rate constant $k_{1d}$. Between pH 1.5 and, 4 the ring opening (I → II) to form species II is the rate-limiting step.

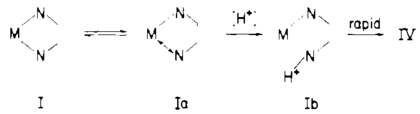

**Figure 7.** Possible intermediate steps in the protonation reaction of Ni(II) polyamine complexes in concentrated acid.

**Table IV.** Dissociation and Protonation Rate Constants for $NiL^{2+}$ Complexes and Ratios Representing the Relative Importance of the Two Pathways

| $NiL^{2+}$ | $k_{1d}$, $s^{-1}$ | $k_{2H}$, $M^{-1}$ $s^{-1}$ | $k_{2H}/k_{1d}$, $M^{-1}$ | $k_{2HOAc}/k_{1d}$, $M^{-1}$ |
|---|---|---|---|---|
| $Ni(en)^{2+}$ | 0.108 | 0.056 | 0.52 | 2.78 |
| $Ni(en)_3^{2+}$ | 68 | 19 | 0.28 | <0.15 |
| $NiNH_3^{2+}$ | 5.76 | 0.54 | 0.09 | 0.20 |
| $Ni(en)^{2+}$ [a] | $6.3 \times 10^{-3}$ | $4.3 \times 10^{-4}$ | 0.68 | |
| Ni(*rac*-2,3-diaminobutane)$^{2+}$ [b] | $6.9 \times 10^{-4}$ | $3.4 \times 10^{-4}$ | 0.49 | |
| Ni(*meso*-2,3-diaminobutane)$^{2+}$ [b] | $6.0 \times 10^{-3}$ | $4.0 \times 10^{-3}$ | 0.66 | |
| Ni(*trans*-1,2-diaminocyclohexane)$^{2+}$ [b] | $1.6 \times 10^{-5}$ | $6.5 \times 10^{-4}$ | 0.40 | |
| Ni(1,3-diaminopropane)$^{2+}$ [b] | $9.2 \times 10^{-3}$ | $3.4 \times 10^{-4}$ | 0.04 | |
| Ni(1,3-diamino-2,2-dimethylpropane)$^{2+}$ [b] | $5.2 \times 10^{-3}$ | $6.4 \times 10^{-4}$ | 0.12 | |
| Ni(*cis,cis*-1,3,5-tach)$^{2+}$ [c] | $1.3 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | 1.07 | |

[a] Calculated from data in ref 7. [b] Calculated from data in ref 8. [c] Calculated from data in ref 9.

The measured rate constant at low pH, $k_{2H}$, corresponds to $k_4$ for the mechanism shown in Figure 6. However, $H_3O^+$ would not be expected to attack the nitrogen donor in species I directly because no electron pairs are available. Figure 7 is an expanded version of the proposed pathway in which one nitrogen donor is dissociated from nickel without its replacement by a solvent molecule. The important aspect of this model is that no water molecule has replaced the amino group subsequent to its effective dissociation to produce an intermediate (Ia) in which the metal ion has a reduced coordination number. Thus, the chelate ring has not been opened sufficiently to move the nitrogen donor out of the first coordination sphere of the metal ion. In this situation, the amino group is weakly basic and susceptible to protonation to form species Ib which undergoes rapid chelate ring opening and metal ion solvation. Species Ia may not be a true intermediate but may be an activated or virtual intermediate with a lone pair available on the nitrogen.

This mechanism is supported by the following evidence. (1) As the pH is lowered from 1.5, the dissociaton rates of $Ni(en)^{2+}$ and of other nickel(II) chelate complexes[8,9] are accelerated from the limiting rates that are attributed to ring opening (I → II). Thus, at high concentration, $H_3O^+$ assists in the ring-opening step. (2) General-acid catalysis at low pH has been observed for $Ni(en)^{2+}$, indicating that direct proton transfer occurs during the rate-determining step. General-acid catalysis would not be possible if the equilibrium between species I and IV were rapid. (3) A similar effect has been reported for the protonation of metal peptide complexes. Direct proton transfer to the deprotonated peptide nitrogen occurs simultaneously with metal–peptide nitrogen bond weakening or rupture,[22-26] although in this case an additional

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lone pair of electrons is available at the peptide nitrogen.

If the donor is unrestricted and able to move easily out of the first coordination sphere, the presence of acid has little effect. However, if the movement of the donor away from the metal ion is hindered in some way, acid can enhance the rate of dissociation. The factors which affect the relative importance of the solvent-separation pathway and the protonation pathway are of interest here. The ratio $k_{2H}/k_{1d}$ represents the relative rate of dissociation by the solvation and the protonation pathways. The values of these ratios are tabulated in Table IV. The ratios are relatively large for the complexes containing five-membered chelate rings compared to the ratio for $NiNH_3^{2+}$. Both enthalpic and entropic effects influence the relative importance of the two pathways. It has been suggested that the larger activation energies of 5–6 kcal/mol and the slower dissociation rates of chelate complexes compared to analogous monodentate complexes are due to the angular expansion of bonds necessary for ring opening.[1] These effects are reflected in the smaller value of $k_{1d}$ for $Ni(en)^{2+}$ (0.108 $s^{-1}$) compared with the value of $k_d$ for $NiNH_3^{2+}$ (5.76 $s^{-1}$). The restrictions imposed by the chelate ring help to hold the donor in the first coordination sphere, making it more susceptible to acid attack than the monodentate donor which has neither the enthalpic nor entropic restrictions of the chelate ring to prevent it from moving smoothly out of the first coordination sphere.

The dissociation of $NiNH_3^{2+}$ is also accelerated by concentrated acid, suggesting that it may proceed via a transition state similar to species Ia for the chelate complex. However, for $NiNH_3^{2+}$, the ligand may be trapped by a cage formed of solvent molecules in the second coordination sphere. The effect of the solvent cage is a less important factor in determining the relative rates of the solvent-separation and protonation pathways than is the effect of the chelate ring. The smaller value of $k_H/k_d$ for $NiNH_3^{2+}$ (0.09 $M^{-1}$) compared with the value of $k_{2H}/k_{1d}$ (0.52 $M^{-1}$) for $Ni(en)^{2+}$ emphasizes this difference.

The ratios, $k_{2H}/k_{1d}$, for the six-membered chelate complexes are much smaller than the values for five-membered chelate complexes. Ring size has little effect on the decomposition rate constant, $k_{1d}$,[1] so the difference in the ratios is attributed to the smaller values of $k_{2H}$ for the six-membered rings (Table IV). The ring strain introduced by the angular expansion may be less for the more flexible six-membered rings than for five-membered rings. Consequently, ring opening may be easier for the six-membered rings, making the protonation pathway less important. However, for Ni(*cis*,*cis*-1,3,5-tach)$^{2+}$, the protonation pathway becomes important because the rigid structure of the ligand hinders ring opening.

**General-Acid Catalysis.** A summary of the general-acid rate constants for the dissociations studied is given in Table II, and values for the ratio $k_{2HOAc}/k_{1d}$ are given in Table IV. Comparison of these ratios for the dissociations of $Ni(en)^{2+}$ and $NiNH_3^{2+}$ shows the same trend as the $k_{2H}/k_{1d}$ ratios. Presumably the same ligand effects that make $H_3O^+$ catalysis important for chelate complexes also make general-acid catalysis important.

Weak acids are more effective than $H_3O^+$ in accelerating the $Ni(en)^{2+}$ dissociation, indicating that they react in a way that makes proton transfer more efficient. As the strength of the acids decreases, the catalytic effectiveness would normally be expected to decrease, but this is not the case. The reversal of the usual rate trend with acid strength cannot be accounted for by anion (conjugate base) coordination. If the stability constants for complexation of the metal by the conjugate bases of the general acids are no larger than that for the formation of Ni(acetate)$^{2+}$,[27] the concentration of acetate-containing complexes cannot exceed $10^{-6}$ M at the pH and general-acid concentrations used here. Instead, we suggest that the general acids coordinate to the complex in such a way that the proton can be more readily transferred to the donor. Similar enhanced general-acid catalysis of metal–peptide nitrogen bond breaking has been observed with other coordinating acids such as $HC_2O_4^-$, $H_2PO_4^{2-}$, $HCO_3^-$, $H_2trien^{2+}$, and $H_2O$.[23-26,28,29]

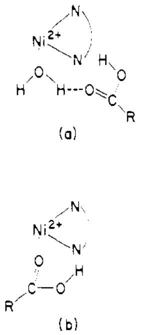

**Figure 8.** Possibilities for general-acid coordination to $Ni(en)^{2+}$ ion: (a) via hydrogen bonding to a bound $H_2O$ molecule; (b) via direct interaction with the nickel ion.

For the carboxylic acids, coordination could be accomplished via hydrogen bonding of the carbonyl oxygen to a coordinated water molecule or via direct coordination to the nickel ion (Figure 8). Molecular models show that either of these configurations brings the acidic hydrogen in proximity to the amine nitrogen. The rate of proton transfer would not depend so much on acid strength as on the ability of the acid to coordinate. The inductive effects that weaken the acid enhance the coordinating ability by placing greater electron density on the carbonyl oxygen. Thus, the coordinating ability of the carboxylic acids increases as their acidity decreases.

The ability of the carboxylic acids to act as coordinating general acids is supported by the following results. (1) The pyridinium ion has a p$K_a$ comparable to that of acetic acid but has no lone pairs of electrons available to participate in coordination. If the pyridinium ion were acting in the same manner as the carboxylic acids, an acceleration of about 30% would be expected over the concentration range studied. However, the increase is less than 5%, indicating that general-acid catalysis of the $Ni(en)^{2+}$ dissociation by noncoordinating general acids is relatively ineffective. (2) The $Ni(en)_3^{2+}$ complex has neither open coordination positions nor coordinated water molecules. Although the $Ni(en)_3^{2+}$ dissociation is catalyzed significantly by $H_3O^+$, the ratios of $k_{2HOAc}/k_{1d}$ for $Ni(en)^{2+}$ (2.78) and for $Ni(en)_3^{2+}$ (<0.15) indicate that general-acid catalysis is much less important for the latter. Both of these results are consistent with the proposal that either an open coordination site or a coordinated water molecule is necessary for weaker acids to effectively assist the ring opening. Although the two types of interaction are kinetically indistinguishable, the fact that hydrogen bonding between the proton of a coordinated amine in $Ni(en)_3^{2+}$ and the general acid is not kinetically significant suggests that direct coordination of the carboxylic acid to the nickel ion is the predom-

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inant kinetic pathway for the coordinating general acids.

## Conclusions

Acids can accelerate the ring opening of polyamine chelate complexes of nickel(II) by direct protonation of the nitrogen donor while the donor is still within the first coordination sphere. Acid attack at the amine nitrogen occurs prior to or during solvent replacement of the donor. The relative importance of the protonation and the solvent-separation pathways is controlled by those factors which prevent the donor atom from moving smoothly out of the first coordination sphere. The effect of the chelate ring is greater than that of a solvent cage.

Although the effect of coordinating general acids has been observed in other situations, it is unique that the effect occurs for a series of uncharged carboxylic acids. It is also important that these acids can, at high concentration, assist the ring opening of nickel(II) polyamine complexes.

**Acknowledgment.** This investigation was supported by Public Health Service Grant No. GM-12152 from the National Institute of General Medical Sciences.

**Registry No.** $Ni(en)^{2+}(aq)$, 15615-30-2; $Ni(en)_3{}^{2+}$, 15390-99-5; $NiNH_3{}^{2+}(aq)$, 18042-21-2; $CH_3COOH$, 64-19-7; $ClCH_2COOH$, 79-11-8; $Cl_2CHCOOH$, 79-43-6; $Cl_3CCOOH$, 76-03-9; $C_5H_5NH^+$, 16969-45-2.

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# Kinetics of the Acid-Catalyzed Dissociation of Nickel(II) Triglycine

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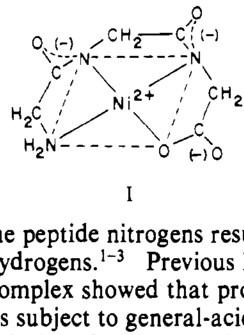
As the concentration of acid increases, more than one proton assists the rate of dissociation of the doubly deprotonated triglycine nickel(II) complex, $Ni(H_{-2}G_3)^-$. The observed first-order rate constant equals $k_{H_2O} + k_H[H^+] + k_{H,H}[H^+]^2 + (k_{HB} + k_{H,HB}[H^+])[HB]$, where HB is a general acid. The $k_{HB}$ and $k_{H,HB}$ rate constants increase with the acid strength of HB, but the Brønsted $\alpha$ value decreases as the acid strength increases. The values for the $H_3O^+$ rate constants are $k_H = 9.5 \times 10^4$ $M^{-1}$ $s^{-1}$ and $k_{H,H} = 1.1 \times 10^8$ $M^{-2}$ $s^{-1}$. A modified Marcus theory of proton transfer is used to fit the Brønsted plot for the single-proton pathway. A large $W_R$ term is required, and this is attributed to the need to solvate the nickel ion in the reaction complex. Mixed complexes in which ligands block axial coordination by solvent are not general-acid catalyzed.

## Introduction

Triglycine (glycylglycylglycine, $G_3$) forms a yellow, square-planar complex (structure I) with nickel(II) in which



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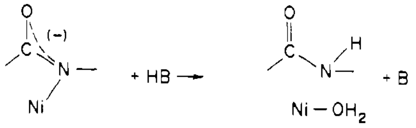
coordination of the peptide nitrogens results in ionization of the two peptide hydrogens.[1-3] Previous kinetic studies with the $Ni(H_{-2}G_3)^-$ complex showed that proton transfer to the peptide nitrogen is subject to general-acid catalysis.[3-6] The resulting Brønsted plots for the reaction in Scheme I are unusual. Although they resemble the behavior of Eigen's plots[7] for normal acids and bases and include a transition of the $\alpha$ value from 1 to 0, they differ from Eigen's plots in that the $H_3O^+$ rate constant is many orders of magnitude below the diffusion-controlled limit.

In the present work, we extend the study of general-acid catalysis with $Ni(H_{-2}G_3)^-$ to include a series of acids with $pK_a$ values between those of acetic acid ($pK_a = 4.64$) and $H_3O^+$ ($pK_a = -1.74$) (Figure 1). The present studies had to be carried out in higher concentrations of acid than used before, and two additional terms were found for the rate of acid decomposition of $Ni(H_{-2}G_3)^-$. One term exhibited a $[H^+]^2$ dependence and the other a $[H^+][HB]$ dependence. The behavior of the Brønsted plot with general acids can be accounted for by use of a modified[8,9] Marcus theory,[10,11] in which the intrinsic proton barrier ($\lambda/4$) is small, but a substantial input of work ($W_R$) is needed in order to form the reaction complex prior to proton transfer. The reaction complex differs from an encounter complex in that the $W_R$ term is much larger. This work appears to be associated with the need to solvate the nickel(II). The behavior of coordinating ligands such as $\alpha$-picoline, which block axial solvation of the nickel, support this explanation.

Scheme I. Direct Protonation of the Peptide Nitrogen



## Experimental Section

Nickel(II) perchlorate was prepared from nickel(II) carbonate and perchloric acid. Stock solutions were standardized by EDTA titration using murexide indicator. Nickel(II) triglycine solutions (($(2-4) \times 10^{-3}$ M) were prepared just prior to each set of experiments. The chromatographically pure triglycine (Sigma Chemical) was added in a 2:1 mole ratio to a nickel(II) perchlorate solution. The bright yellow $Ni(H_{-2}G_3)^-$ complex formed as the pH of the solution was

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