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Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

Kinetics of Hydrogen Phosphate Catalyzed Chelate Ring Opening in (Ethylenediamine)nickel(II)

RITA A. READ and DALE W. MARGERUM*

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The rate of dissociation of $Ni(en)^{2+}$ in acid is first order in the nickel complex and depends upon the acidity and phosphate concentration. At 25.0 °C ($\mu = 2.0$ ($NaClO_4$)) the chelate-ring-opening step has a rate constant of 0.13 s^{-1} for the solvent and is also general-acid catalyzed with the following rate constants ($M^{-1}\ s^{-1}$): H_3O^+, 0.044; H_3PO_4, 0.71; $H_2PO_4^-$, 1.23; HPO_4^{2-}, 11.7. The greater effect exhibited by the weaker acids and the failure of a noncoordinating acid (2,6-lutidinium ion) to accelerate the rate indicate that coordination of the acid species to the metal complex enhances the proton-transfer rate.

Introduction

The dissociation rate of (ethylenediamine)nickel(II), $Ni(en)^{2+}$, has been characterized in neutral, acidic, and highly acidic solutions.[1-3] The first-order dissociation rate constant, k_d, is highly pH dependent as shown in Figure 1. In neutral solution, the rate-determining step is the loss of the singly coordinated ethylenediamine from nickel as outlined in Figure 2 (III → IV). Between pH 8 and pH 5, an increase in the k_d value occurs as a result of protonation of the free amine group after the chelate ring is opened. The k_d value increases by a factor of 15 over this pH range and then reaches a plateau around pH 4.5 as the rate-determining step shifts to the chelate ring opening (Figure 2, II → III). Below pH 1.5, the k_d value increases again with increasing acidity. This increase is unexpected because the chelated ethylenediamine has no site to add a proton. We have proposed previously that acids accelerate the ring opening of the polyamine chelate complexes by direct protonation of the nitrogen donor while the donor is still within the first coordination sphere.[1,4] Acid attack at the amine nitrogen occurs prior to or during solvent replacement of the donor.

Below pH 2, carboxylic acids also increase the dissociation rate of $Ni(en)^{2+}$ by protonating the amine group within the first coordination sphere and accelerating chelate ring opening.[1] However, the weaker carboxylic acids more effectively catalyze the chelate ring opening. This reversal of the usual trend of general-acid behavior is attributed to the increased ability of weaker carboxylic acids to associate with the metal complex and to transfer a proton to the donor that is in the first coordination sphere.

In the present work, additional tests are made of the hypothesis that coordinating acids are effective in accelerating chelate ring opening by using the phosphoric acids, H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-}. Once again, weaker acids are more effective catalysts, and a large effect is seen even at pH 6. Noncoordinating acids, however, do not enhance chelate ring opening.

Experimental Section

Reagents. Phosphate solutions below pH 1 were prepared from standarized solutions of H_3PO_4 and $HClO_4$. Solutions of pH 1–2 were prepared from solid $NaH_2PO_4{\cdot}H_2O$ and standardized solutions of H_3PO_4 and $HClO_4$. Solid $NaH_2PO_4{\cdot}H_2O$ and $Na_2HPO_4{\cdot}7H_2O$ were added to give a 2.33 ratio of $[H_2PO_4^-]$ to $[HPO_4^{2-}]$ for the pH 6 solutions. The ionic strength was controlled by addition of standardized $NaClO_4$ solution or solid $LiClO_4{\cdot}3H_2O$.

At an ionic strength, μ, of 2.0 and at 25 °C, the value of the first acid dissociation constant, pK_1, is 1.76, interpolated from values at various ionic strengths.[5] The value for the second dissociation constant, pK_2, is 6.36 at ionic strength 2.0 and at 25 °C.[5]

Reagent grade 2,6-lutidine (Aldrich) was purified by distilling twice at reduced pressure. The ionic strength of the lutidine solutions ($\mu = 0.5$) was controlled by addition by standardized $NaClO_4$ solution, and the pH was adjusted to 5.0 by using a Corning Model 476051 combination-glass electrode thermostated at 25.0 ± 0.1 °C and an Orion Model 601 research pH meter. The H^+ concentration was calculated from a potentiometric titration at ionic strength 0.5 and at 25.0 ± 0.1 °C.

Preparation and standardization of the $Ni(en)^{2+}$ solution have been described previously.[1]

The H_3O^+ and phosphate dependences were determined at ionic strength 2.0 to avoid solubility problems and at 4.0 to compare with previous work. Both $LiClO_4$ and $NaClO_4$ were used to identify medium effects. The lutidine dependence was measured at ionic strength 0.5 because the solubility of the lutidinium salt is decreased at higher ionic strength.

Kinetics Measurements. The kinetics of the hydrogen phosphate catalyzed $Ni(en)^{2+}$ dissociation were followed by using a Durrum stopped-flow spectrophotometer interfaced[6] to a Hewlett-Packard Model 2108 M-Series computer. Absorbance of $Ni(en)^{2+}$ at 370 nm was measured for 4 half-lives of each decay. Pseudo-first-order conditions were maintained, and excellent first-order kinetics were observed except when the most concentrated phosphate solutions were used. Small deviations from first-order kinetics during the initial portion of these reactions were attributed to decreased mixing efficiency caused by increased viscosity of the phosphate solutions. Linear and nonlinear regression analyses of the data gave values for the initial absorbance (A_0), the final absorbance (A_∞), and the pseudo-first-order rate constant (k_{obsd}) as defined by eq 1 and 2. The values of k_{obsd} reported are the average of at least four runs.

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

$$-\frac{d[Ni(en)^{2+}]}{dt} = k_{obsd}[Ni(en)^{2+}] \qquad (2)$$

The reaction of $Ni(en)^{2+}$ in the presence of the 2,6-lutidinium ion was a reversible dissociation and was essentially a relaxation experiment using stopped-flow techniques. The lutidine concentration was at least tenfold greater than the $Ni(en)^{2+}$ concentration so that a pseudo-first-order rate constant, k_{obsd}, was obtained. This rate constant is the sum of the forward and reverse rate constants as shown in eq 3–5.

$$k_{obsd} = k_d + k_f([Ni^{2+}] + [en]) \qquad (3)$$

$$Ni(en)^{2+} \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Ni^{2+} + en \qquad (4)$$

$$K' = k_d/k_f \qquad (5)$$

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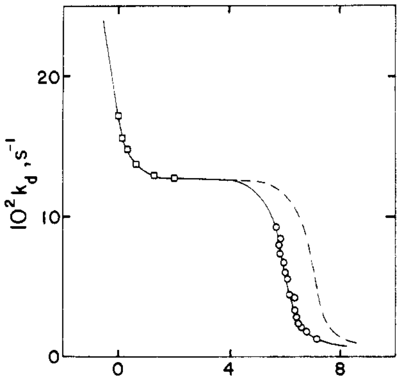

Figure 1. pH dependence for the dissociation rate constant of $Ni(en)^{2+}$ at 25 °C: (□) data from the present work at $\mu = 2.0$ ($NaClO_4$); (○) data from ref 3 at $\mu = 0.1$ ($NaClO_4$). The dashed line represents the shift in k_d expected at $\mu = 2.0$.

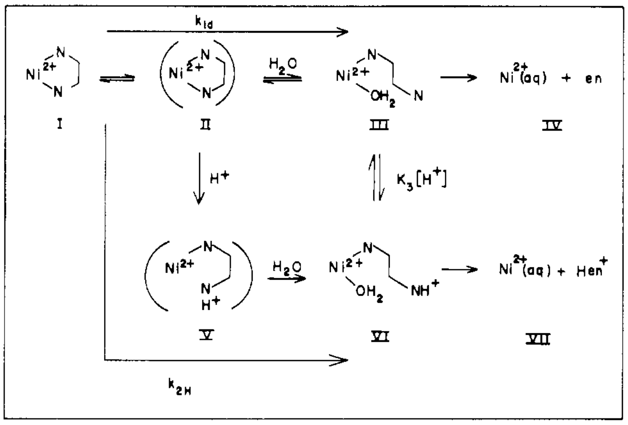

Figure 2. Mechanism for the acid-catalyzed dissociation of $Ni(en)^{2+}$.

The decomposition rate constant, k_d, was resolved with use of the conditional stability constant, K', calculated from the formation constant for $Ni(en)^{2+}$ ($10^{7.47}$, $\mu = 0.5$, 25 °C)[7] and the acid dissociation constants for ethylenediamine ($10^{7.31}$ and $10^{10.04}$, $\mu = 0.5$, 25 °C).[7]

Results

The observed rate constant for the phosphate-catalyzed decomposition of $Ni(en)^{2+}$ at low pH is the sum of the rate constants for H^+ and the various hydrogen phosphate species.

$$k_{obsd} = k_{1d} + k_{2H}[H^+] + k_1[HPO_4^{2-}] + k_2[H_2PO_4^-] + k_3[H_3PO_4] \quad (6)$$

The rate constant for the uncatalyzed dissociation is k_{1d}, and the H_3O^+ rate constant is k_{2H}.[1] The general-acid rate constants for the singly, doubly, and triply protonated phosphate species are given by k_1, k_2, and k_3, respectively. These rate constants were evaluated by measuring k_{obsd} as a function of $[H^+]$ or the total phosphate concentration, $[PO_4]_T$, and applying a linear least-squares regression.

Intercepts of the k_{obsd} vs. $[H^+]$ plots give values for k_{1d} while intercepts of the k_{obsd} vs. $[PO_4]_T$ plots correspond to $k_{1d} + k_{2H}[H^+]$. The slopes of the hydrogen ion dependences give values for k_{2H}.

General-acid rate constants for the individual phosphate species are evaluated from the slopes of the phosphate dependences. At pH values below zero, H_3PO_4 is the only significant phosphate species present so the slope of the phosphoric acid dependence is equal to k_3. In the pH range of 0–2, H_3PO_4 and $H_2PO_2^-$ are the major contributing species. Use of the acid dissociation constant, K_1, allows k_{obsd} to be expressed in terms of $[PO_4]_T$ as in eq 7. The general-acid rate

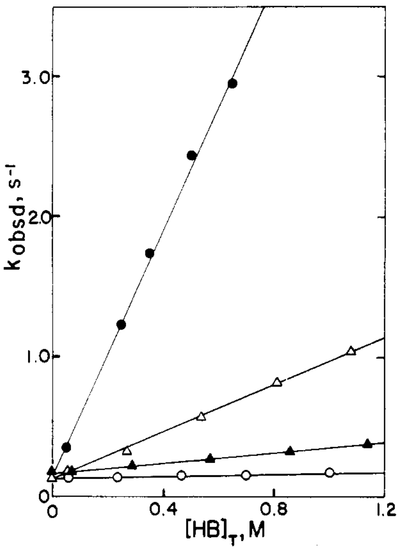

Figure 3. Comparison of rate constants for the dissociation of $Ni(en)^{2+}$ in the presence of H_3O^+ and phosphate ($[Ni(en)^{2+}] = 5.00 \times 10^{-3}$ M; $\mu = 2.0$ ($NaClO_4$–$HClO_4$); 25 °C): (●) phosphate, $[H^+] = 1.0 \times 10^{-6}$ M; (△) phosphate, $[H^+] = 0.01$ M; (▲) phosphate, $[H^+] = 1.00$ M; (○) H_3O^+ only.

$$k_{obsd} = k_{1d} + k_{2H}[H^+] + \left(\frac{k_3[H^+] + k_2K_1}{[H^+] + K_1} \right)[PO_4]_T \quad (7)$$

constants, k_3 and k_2, are calculated from the slopes of two k_{obsd} vs. $[PO_4]_T$ plots at different H^+ concentrations. Similarly, at pH 6, $H_2PO_4^-$ and HPO_4^{2-} are the predominant species and $[H^+]$ is small so k_{obsd} is given by eq 8. The slope of the phosphate dependence at pH 6, k_2 from calculations at lower pH, and K_2 are used to calculate k_1.

$$k_{obsd} = k_{1d} + \left(\frac{k_2[H^+] + k_1K_2}{[H^+] + K_2} \right)[PO_4]_T \quad (8)$$

Values of k_{1d} and k_{2H} for the dissociation of $Ni(en)^{2+}$ at ionic strength 2.0 in $LiClO_4$ and $NaClO_4$ were determined by varying $[H^+]$ over the range 0.05–1.0 M with no phosphate present (Table I, Figure 3). Values at ionic strength 4.0 in $LiClO_4$ and $NaClO_4$ were measured previously.[1] In all cases, first-order dependences are observed. The values of both rate constants are independent of ionic strength or medium (Table II).

General-acid rate constants for the phosphate species were determined at ionic strength 2.0 in $LiClO_4$ and in $NaClO_4$ by varying the total phosphate concentration from 0.05 to 1.0 M and maintaining $[H^+]$ constant with $HClO_4$. In $LiClO_4$, phosphate dependences were measured with 1.0 and 0.1 M $[H^+]$ (Table I) while in $NaClO_4$ dependences were measured at 1.0, 0.01, and 1.0×10^{-6} M $[H^+]$ (Table I, Figure 3). First-order phosphate dependences are observed in all cases. Values for the rate constants are shown in Table II. In both ionic media the general-acid rate constants increase as the acid strength decreases: $k_{2H} < k_3 < k_2 < k_1$. The increase from k_3 to k_2 is larger in $NaClO_4$ (0.171 ± 0.004 to 1.23 ± 0.01 $M^{-1}\ s^{-1}$) than in $LiClO_4$ (0.216 ± 0.004 to 0.78 ± 0.01 $M^{-1}\ s^{-1}$), indicating some medium effect due to the Na^+ ion.[1,8,9]

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Table I. Kinetic Data for the H_3O^+- and Phosphate-Catalyzed Dissociation of $Ni(en)^{2+}$ [a]

$[H_3O^+]$, M	$[\text{phosphate}]_T$, M	k_{obsd}, s^{-1}
$\mu = 2.0$ ($NaClO_4$-$HClO_4$)		
0.0581		0.129 ± 0.003
0.232		0.137 ± 0.001
0.465		0.148 ± 0.004
0.697		0.156 ± 0.003
1.00		0.1716 ± 0.0009
1.00		0.171 ± 0.001
1.00	0.0714	0.175 ± 0.006
1.00	0.286	0.216 ± 0.001
1.01	0.572	0.272 ± 0.006
1.01	0.857	0.332 ± 0.005
1.02	1.14	0.38 ± 0.01
0.0100		0.127 ± 0.001
0.00999	0.0541	0.18 ± 0.01
0.00999	0.270	0.33 ± 0.02
0.0100	0.540	0.574 ± 0.006
0.0100	0.811	0.81 ± 0.01
0.00999	1.08	1.04 ± 0.04
1.01×10^{-6}	0.0499	0.348 ± 0.005
1.00×10^{-6}	0.250	1.230 ± 0.006
1.01×10^{-6}	0.350	1.74 ± 0.02
1.00×10^{-6}	0.500	2.44 ± 0.04
1.00×10^{-6}	0.649	2.95 ± 0.04
$\mu = 2.0$ ($LiClO_4$-$HClO_4$)		
0.0581		0.131 ± 0.002
0.232		0.140 ± 0.002
0.465		0.155 ± 0.001
0.697		0.163 ± 0.002
1.00		0.178 ± 0.003
1.00		0.179 ± 0.002
1.00	0.0714	0.196 ± 0.002
1.00	0.286	0.238 ± 0.006
1.01	0.572	0.301 ± 0.007
1.01	0.857	0.37 ± 0.01
1.02	1.14	0.438 ± 0.009
0.100		0.134 ± 0.002
0.0999	0.0463	0.135 ± 0.004
0.0997	0.231	0.186 ± 0.003
0.0999	0.463	0.250 ± 0.003
0.0999	0.694	0.320 ± 0.004
0.0997	1.04	0.45 ± 0.01
0.0100		0.130 ± 0.002
0.00998	0.0541	0.159 ± 0.006
0.0100	0.270	0.291 ± 0.004
0.00999	0.540	0.488 ± 0.008
0.00998	0.811	0.68 ± 0.03
0.00999	1.08	0.94 ± 0.03
$\mu = 4.0$ ($NaClO_4$-$HClO_4$)		
2.00		0.201 ± 0.006
2.00	0.143	0.227 ± 0.006
2.00	0.572	0.332 ± 0.002
2.01	1.14	0.516 ± 0.009
2.01	1.43	0.60 ± 0.03
2.02	2.00	0.74 ± 0.03
$\mu = 4.0$ ($LiClO_4$-$HClO_4$)		
2.00		0.212 ± 0.001
2.00	0.143	0.243 ± 0.005
2.01	0.714	0.390 ± 0.009
2.01	1.14	0.52 ± 0.03
2.01	1.43	0.62 ± 0.01
2.02	2.14	0.81 ± 0.02

[a] $[Ni(en)^{2+}]_{ini} = 5.00 \times 10^{-3}$ M; 25.1 ± 0.2 °C; $\lambda = 370$ nm.

The general-acid rate constant was also determined for phosphoric acid at ionic strength 4.0 in $LiClO_4$ and $NaClO_4$ by varying $[H_3PO_4]$ from 0.1 to 2.0 M with $[H^+]$ held constant at 2.0 M (Tables I and II). First-order dependences are observed, and the rate constants are 0.284 ± 0.006 $M^{-1}\ s^{-1}$ in $LiClO_4$ and 0.296 ± 0.009 $M^{-1}\ s^{-1}$ in $NaClO_4$. The value of k_3 is independent of ionic medium at ionic strength 4.0 but is 50% larger than at ionic strength 2.0 (Table II).

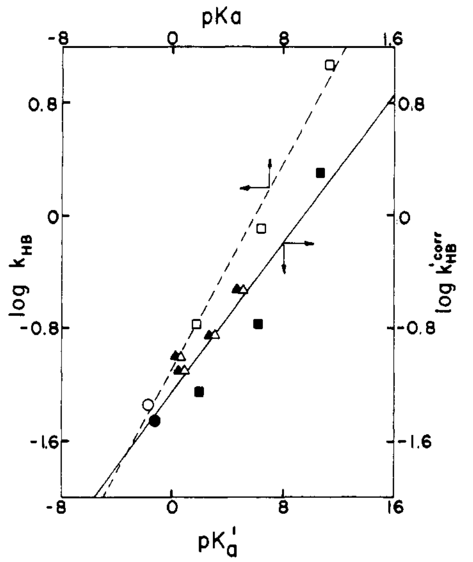

Figure 4. Linear free energy relationship between general-acid rate constants and acid dissociation constants: (○, ●) H_3O^+, $\mu = 2.0$ ($NaClO_4$-$HClO_4$); (□, ■) phosphate species, $\mu = 2.0$ ($NaClO_4$-$HClO_4$); (△, ▲) carboxylic acids, $\mu = 4.0$ ($NaClO_4$-$HClO_4$). Open symbols and dashed line are uncorrected; closed symbols and solid line are corrected for electrostatic and statistical factors.

Values of k_{obsd} for the reversible $Ni(en)^{2+}$ dissociation were determined as a function of the total 2,6-lutidine concentration over the range 0.05–0.25 M at pH 5 and ionic strength 0.5 in $NaClO_4$ (Table III). The dissociation rate constant, k_d, was evaluated at each concentration. The value of k_d is 0.13 s^{-1} and does not increase with lutidine concentration. This value agrees well with the value of $k_{1d} + k_{2H}[H^+] = 0.126 \pm 0.001\ s^{-1}$ calculated from the H^+ dependence at ionic strength 2.0 in $NaClO_4$.

Discussion

An increase of almost 1 order of magnitude occurs between each of the general-acid rate constants in the series k_{2H}, k_3, k_2, k_1 at ionic strength 2.0 in $NaClO_4$. The order of effectiveness in catalyzing the $Ni(en)^{2+}$ dissociation is $H_3O^+ < H_3PO_4 < H_2PO_4^- < HPO_4^{2-}$. Thus, the weakest acid is the best catalyst. The series of acetic and chloroacetic acids also exhibits a reversal of the usual general-acid behavior.[1]

A linear relationship (eq 9) exists between the logarithm

$$\log k_{HB} = 0.18\text{p}K_a - 1.10 \qquad (9)$$

of the general-acid rate constants, k_{HB}, and the acid dissociation pK_a values for H_3O^+ and the hydrogen phosphate species (Table IV, Figure 4). These acids range in charge from 1+ to 2− so the electrostatic contributions to the reaction rate must be considered even though the differences will be diminished by the high ionic strength. The values of k_{HB} can be corrected for electrostatic interactions by using a variation of the Debye–Hückel–Brønsted–Davies equation, which estimates the electrostatic attraction or repulsion as a function of ionic strength.[11] The correction is given by eq 10, where k_{HB}^{cor}

$$\log k_{HB}^{cor} = \log k_{HB} + 1.02 Z_A Z_B \left(\frac{\mu^{1/2}}{1 + \mu^{1/2}} - 0.2\mu \right) \qquad (10)$$

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(10) Bell, R. P. "The Proton in Chemistry"; Cornell University Press: Ithaca, NY, 1973; p 200.

(11) Perlmutter-Hayman, B. *Prog. React. Kinet.* **1971**, *6*, 239–67.

Table II. Rate Constants for the H_3O^+- and Phosphate-Catalyzed Dissociation of $Ni(en)^{2+}$ (25 °C)

μ	k_{1d}, s^{-1}	k_{2H}, M^{-1} s^{-1}	k_3, M^{-1} s^{-1}	k_2, M^{-1} s^{-1}	k_1, M^{-1} s^{-1}
2.0[a]	0.1265 ± 0.0008	0.044 ± 0.001	0.171 ± 0.004	1.23 ± 0.01	11.7 ± 0.1
2.0[b]	0.129 ± 0.001	0.050 ± 0.002	0.216 ± 0.004	0.78 ± 0.01	
4.0[a]	0.108 ± 0.008	0.056 ± 0.009	0.296 ± 0.009		
4.0[b]	0.115 ± 0.001	0.0486 ± 0.0008	0.284 ± 0.006		

[a] $NaClO_4$-$HClO_4$. [b] $LiClO_4$-$HClO_4$.

Table III. Kinetic Data for the Dissociation of $Ni(en)^{2+}$ in the Presence of 2,6-Lutidine[a]

[2,6-lutidine], M	$-\log [H^+]_{ini}$[b]	$-\log [H^+]_{final}$[c]	K',[d] M	k_{obsd}, s^{-1}	k_d, s^{-1}
0.05	4.72	5.41	8.6	0.233 ± 0.007	0.21
0.10	4.68	5.35	6.5	0.17 ± 0.02	0.16
0.20	4.72	5.15	2.6	0.138 ± 0.005	0.13
0.25	4.71	5.11	2.2	0.135 ± 0.002	0.13

[a] $[Ni(en)^{2+}]_{ini} = 5.00 \times 10^{-3}$ M; λ = 370 nm; 25.0 ± 0.1 °C. [b] $-\log [H^+]$ of lutidine solution before mixing. [c] $-\log [H^+]$ of Ni^{2+} solution after dissociation. [d] Conditional stability constant of $Ni(en)^{2+}$ at $-\log [H^+]_{final}$.

Table IV. Acid Dissociation Constants and General-Acid Rate Constants for H_3O^+, Phosphates, and Carboxylic Acids

acid	pK_a	k_{HB}, s^{-1}	pK'[a]	$\log k'_{HB}{}^{cor}$[b]
H_3O^+	−1.74[c]	0.044	−1.26	−1.46
H_3PO_4	1.76[d]	0.171	1.94	−1.24
$H_2PO_4^-$	6.36[e]	1.23	6.18	−0.77
HPO_4^{2-}	11.25[e]	11.7	10.65	0.31
CH_3COOH	5.01[f]	0.30[g]	4.71	−0.52
$ClCH_2COOH$	3.02[f]	0.141[g]	2.72	−0.85
$Cl_2CHCOOH$	0.87[h]	0.08[g]	0.57	−1.10
Cl_3CCOOH	0.66[h]	0.10[g]	0.36	−1.00

[a] See eq 11. [b] See eq 10 and 11. [c] Reference 10. [d] Calculated from values in ref 5. [e] Reference 5. [f] Reference 17. [g] Reference 1. [h] Reference 7.

corresponds to the value expected for a neutral species and k_{HB} is the value measured at high ionic strength. The values of $k_{HB}{}^{cor}$ for $H_2PO_4^-$ and HPO_4^{2-} fall along the same line as the values for H_3PO_4, CH_3COOH, $ClCH_2COOH$, $Cl_2CHCOOH$, and Cl_3CCOOH.

Since the phosphate species are polyprotic acids, a statistical correction must also be applied to the linear relationship. The approach suggested by Brønsted[12,13] corrects both k_{HB} and K_a for the number of equivalent protons (p) in the acid and the number of equivalent basic sites (q) in the conjugate base (eq 11). The values corrected for both the statistics and electrostatics are shown in Figure 4 and listed in Table IV. Least-squares treatment gives the corrected parameters in eq 12. Although some scatter is introduced by the corrections, the trend is unchanged. The fact that the relationship is linear implies that all of the species are reacting by the same mechanism even with 13 orders of magnitude difference in acid strength.

$$\frac{k_{HB}}{p} = G_a\left(\frac{qK_a}{p}\right)^{\alpha} \qquad (11)$$

$$\log k'_{HB}{}^{cor} = 0.13pK_a' - 1.3 \qquad (12)$$

The slope of the linear free energy relationship is opposite that of a typical Brønsted plot, which suggests that the catalytic activity is inversely proportional to the acid strength. Thus, it is necessary to demonstrate that conjugate acids rather than bases are the reactive species. We have shown previously that neither 2,6-lutidine nor the acetate ion catalyzes ring opening. At pH 6, the PO_4^{3-} concentration is 10^{-6} times the HPO_4^{2-} concentration, which means that the rate constant for PO_4^{3-} attack on $Ni(en)^{2+}$ would have to be 12×10^6 M^{-1} s^{-1} (10^6 times larger than k_1) to produce the observed rate. This value is the product of K and k' as defined by eq 13. Values for K are not available for the Ni^{2+}–PO_4^{3-} complex, but K is 120 M^{-1} (μ = 0.1, 25 °C) for the Ni^{2+}–HPO_4^{2-} complex.[13] This estimate for K requires that k' be 10^5 s^{-1}, which is unreasonably large for chelate ring opening. Furthermore, other bases such as acetate and chloroacetate anions have been shown ineffective in catalyzing the $Ni(en)^{2+}$ ring opening whereas their conjugate acids are catalysts.[1] Therefore, PO_4^{3-} is not likely to be the reactive species. Similarly, it is unreasonable to assign the rate constants resolved for H_3PO_4 and $H_2PO_4^-$ to their conjugate bases under the conditions used.

$$Ni(en)^{2+} + PO_4^{3-} \overset{K}{\rightleftharpoons} [O_3P\text{–}O\text{–}Ni(en)]^- \xrightarrow{k'} \text{products} \qquad (13)$$

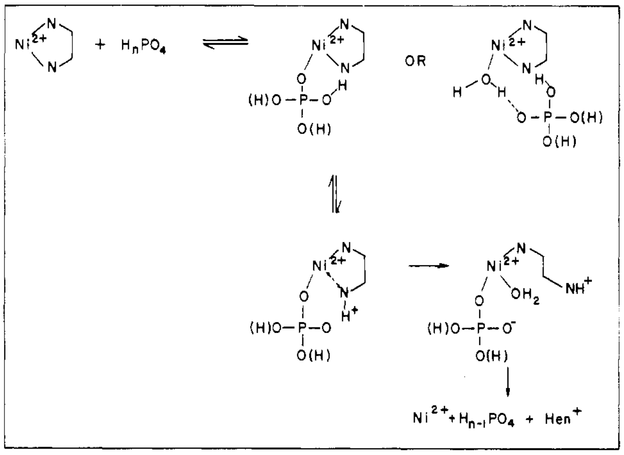

Figure 5. Chelate ring opening in $Ni(en)^{2+}$ assisted by coordinated hydrogen phosphate.

The correlation between the hydrogen phosphate and carboxylic acid linear free energy relationships and the reversal of the normal dependence of general-acid rate constants on acid strength suggest that the phosphate species are acting as coordinating general acids as was proposed for the carboxylic acids.[1] Coordination of the phosphate species to the nickel complex could occur via the unprotonated oxygens. The interaction may be direct coordination to the nickel or may be a hydrogen-bonded outer-sphere association (Figure 5). For the phosphate species, the two types of interaction are not kinetically distinguishable, but both would facilitate proton transfer to the nitrogen donor of the ethylenediamine. In both types of association, the rate of proton transfer becomes a function of the ability of the acid to coordinate to the complex and, therefore, is dependent on the same factors that decrease acid strength. Due to their coordinating ability, the $H_2PO_4^-$ and HPO_4^{2-} ions also show increased general-acid catalysis in the protonation of Cu(II) and Ni(II) peptide complexes.[14-16]

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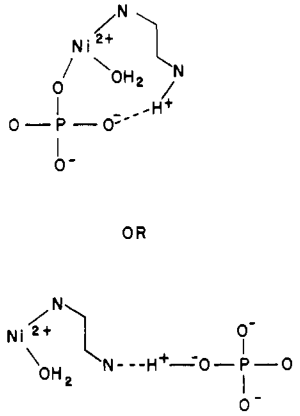

Figure 6. Proposed stabilization of the protonated, ring-opened $Ni(en)^{2+}$ by hydrogen bonding to phosphate.

The acid strength of the 2,6-lutidinium ion is comparable to that of $H_2PO_4^-$, but it has no ability to coordinate to the complex. The pK_a of 2,6-lutidine is 6.90 at ionic strength 0.5.[7] For this acid dissociation constant, the linear free energy correlation (eq 12) predicts the general-acid rate constant to be 0.4, which would correspond to an increase in rate of 230% over the concentration range studied. Instead, no enhancement of the $Ni(en)^{2+}$ dissociation occurs with increasing lutidinium ion concentration at pH 5. Thus, coordination of a general acid to the $Ni(en)^{2+}$ complex is required for a weak acid to be catalytically effective. Furthermore, the conjugate base, 2,6-lutidine, is similar in base strength to HPO_4^{2-} but is ineffective in catalyzing the dissociation.

At pH values of 5 and below the rate-determining step in the dissociation of Ni(II) polyamine complexes is chelate ring opening. At pH values above 5, in the absence of coordinating acids, the rate-determining step shifts to the dissociation of the singly coordinated ethylenediamine. This process is 15 times slower than chelate ring opening.[1-3] However, the dissociation rate at pH 6 with hydrogen phosphate is much faster than chelate ring opening, which suggests that $H_2PO_4^-$ and HPO_4^{2-} catalyze the ring opening. Thus, even at higher pH, a coordinating general acid can protonate one nitrogen donor of a polyamine chelate while it is within the first coordination sphere and shift the rate-limiting step to chelate ring opening.

At pH 5, absorbance changes indicate that the $Ni(en)^{2+}$ dissociation is incomplete with lutidine present. Resolution of the forward and reverse rate constants requires that the data be treated as in a relaxation experiment. Thus, the dissociation should be also be reversible at pH 6. In the presence of phosphate, however, the dissociation is essentially complete at pH 6. The HPO_4^{2-} ion coordinates to $Ni(aq)^{2+}$ with a stability constant of $10^{2.08}$ M^{-1} ($\mu = 0.1$, 25 °C).[5] This coordination shifts the conditional stability constant for $Ni(en)^{2+}$ to allow greater than 99% dissociation at pH 6.

The intercept of the phosphate dependence at pH 6 and ionic strength 2.0 in $NaClO_4$ is 0.15 ± 0.06 s^{-1}. This value agrees well with the value of 0.126 ± 0.001 s^{-1} for the uncatalyzed chelate ring opening rate constant k_{1d}, predicated from the H^+ dependence. This rate constant is much larger than the dissociation rate constant of 0.008 s^{-1} (25 °C) measured above pH 7 by Taylor, Stepien, and Rorabacher.[3]

Two explanations can be proposed for a larger than expected rate constant at pH 6. First, the shape of the pH profile is determined, in part, by the acid association constant of the singly coordinated ethylenediamine, K_3 (Figure 2). Figure 1 shows the effect of increasing K_3 by factor of 10. Large increases in K_3 are expected as the ionic strength is changed from 0.1, where the pH profile has been determined, to 2.0, where the phosphate rate constants have been measured. The log K_H value for H_2en^{2+} increases from 7.08 ($\mu = 0.1$) to 7.69 ($\mu = 2.0$).[7] Similarly, the repulsion between Ni^{2+} and the protonated nitrogen (Figure 2, structure VI) is expected to be diminished at higher ionic strength.

Second, once the protonated, singly coordinated ethylenediamine is formed, it may be stabilized relative to the unprotonated form by hydrogen bonding to the conjugate base of the phosphate (Figure 6). This stabilization has the same effect on the pH profile as an increase in the K_3 value. Both effects probably contribute to the unexpectedly large intercept in the phosphate dependence.

It probably should be emphasized again that the fully chelated ethylenediamine has no site to add a proton. A novel aspect of the hydrogen phosphate catalyzed chelate ring opening is the ability of the amine group to accept a proton prior to its removal from the first coordination sphere of nickel. Acid-catalyzed reactions in which the leaving ligand has readily available electron pairs to accept a proton are commonplace. However, it is interesting that in some of these reactions weak acids with coordinating groups are much more effective than H_3O^+. This is the case, for example, in the aquation reactions of $Cr(H_2O)_5OOCCH_3^{2+}$ and $Cr(H_2O)_5N_3^{2+}$, where the relative reactivity of HSO_3^- compared to H_3O^+ is 125 and 348, respectively.[18] We suggest that a coordinating-acid transition state, such as that proposed for the hydrogen phosphate reactions, may occur frequently in this and in other acid-catalyzed substitution reactions.

Conclusions

Phosphoric acid and the hydrogen phosphate anions accelerate the loss of ethylenediamine from $Ni(en)^{2+}$ by catalyzing the chelate ring opening step, even at pH 6. The order of catalytic effectiveness is $H_3O^+ < H_3PO_4 < H_2PO_4^- < HPO_4^{2-}$. The general-acid rate constants and acid dissociation equilibrium constants for the phosphate species and the carboxylic acids show a linear free energy correlation, but the weakest acid is the most effective because it has the greatest ability to coordinate. In contrast, a noncoordinating acid causes no acceleration of the $Ni(en)^{2+}$ dissociation. Thus, weak acids with coordinating ability can dramatically increase the rate of chelate dissociation by protonation of a basic donor atom while it is still within the first coordination sphere of the metal ion. The chelate dissociation step can be catalyzed even in neutral solution.

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Registry No. H_3PO_4, 7664-38-2.

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