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KINETICS OF INTERACTION OF NICKEL(II) WITH 2-PICOLYLMETHYLAMINE

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The kinetics of the reaction in aqueous solution between 2-picolylmethylamine, (PMA), and nickel(II) ions have been studied using the stopped-flow technique. Formation of the 1:1 complex is second-order in the pH range of 5 to 7. The rate constant for reaction of the neutral ligand form is $2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0° at an ionic strength of 0.3. This value is compared and contrasted with rates of substitution of water on nickel(II) ions by other ligands, and the rate enhancement may be explained by the internal conjugate base mechanism. Monoprotonated PMA reacts very much more slowly under identical conditions ($\sim 20 \text{ M}^{-1} \text{ s}^{-1}$). This value is consistent with expectation from earlier studies.

KEY WORDS: Nickel(II), 2-picolylmethylamine, stopped-flow kinetics, substitution mechanism.

INTRODUCTION

The reactivity of aliphatic diamines toward nickel(II) ions has been fully investigated¹⁻³ but different interpretations may be placed upon the results of those studies.^{3,4} Other work⁵ has shown that when nickel(II) ions react with an amine-ligand of mixed aliphatic and aromatic character, the complex formation rate constants, while enhanced from the values predicted on the basis of the Eigen-Wilkins mechanism,⁶ are quite consistent with the theoretical value obtained for diamines when that mechanism is amended to include stabilization of the outer sphere complex through hydrogen bonding (within the outer sphere complex) and water molecule labilization.⁷ The present kinetics study using the ligand, 2-picolylmethylamine, PMA, which is isomeric with 2-(2-aminoethyl)pyridine, AEP, extends the earlier work⁵ in an attempt to delineate further the refinements to the general mechanism of nickel(II) complex formation. Equilibrium data regarding the metal complex stability and ligand protonations that

are pertinent to choice of experimental conditions in a kinetics investigation are available.⁸

EXPERIMENTAL SECTION

Materials

2-Picolylmethylamine (K and K Laboratories, Plainview, N.Y.) was distilled under vacuum and converted to the dihydrochloride by dissolving the distillate in anhydrous diethyl ether and passing dry hydrogen chloride through the stirred solution. The white solid was filtered, washed with dry ether, and dried under vacuum over phosphorous pentoxide.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{N}_2\text{Cl}_2$: C, 43.10; H, 6.20; N, 14.36. Found: C, 42.5; H, 6.27; N, 14.12.

Reagent grade hydrated nickel perchlorate was used as a source of nickel ions. The concentration of stock nickel ion solutions was checked complexometrically. Other materials used were reagent grade commercial products.

Proton Dissociation Constants

The pK_a values of PMA were determined by a potentiometric method. The ligand salt was titrated

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with standard sodium hydroxide solution in a vessel thermostatted at 25.0° using an Accumet Model 320 pH meter. Ionic strength was maintained at 0.1 M with potassium perchlorate and the pH meter was calibrated using standard buffers. Values of 2.70 and 9.29 were obtained for pK_{a1} and pK_{a2} respectively. In the analysis of kinetics results (below) ultimately only the latter value is used. The values determined are not inconsistent with earlier determinations of the pK_a of PMA.⁹

Kinetics

The nickel complex of PMA absorbs more than a mixture of the ligand and its protonated forms in regions of the ultraviolet. Complex formation was monitored at 269 nm in a Durrum-Gibson stopped-flow spectrophotometer. In the pH range studied, 5–7, protons are liberated upon complex formation; consequently solutions were buffered (0.01 M cacodylate buffer). Ionic strength was maintained constant with 0.3 M sodium perchlorate. Reactions were run under pseudo-first-order conditions with nickel ion in large excess to ensure that only 1:1 complex is formed. The nickel ion concentration was generally in the range of 10–80 fold excess at higher pH values and 20–300 fold excess at lower pH values. Oscilloscope traces yielded excellent first-order rate plots, linear for at least 3 half-lives. At least four and usually six or seven replicate determinations were made for each set of conditions.

To test for overall second-order kinetics for complex formation, the pseudo-first-order rate constants were plotted against the total nickel ion concentration. The slope of such plots, which were

linear, yields the second-order formation rate constant, k_f .

All rate constants reported and quoted in this report are for 25°.

RESULTS AND DISCUSSION

In the pH range investigated, 5–7, the observed reaction is first order in ligand concentration since the kinetic traces yield excellent first-order plots. In the range of nickel ion concentration used, usually about 1.0–8.0 mM in the pH range 6–7 and 2.0–30 mM at lower pH, the linearity of plots of observed rate constant versus nickel ion concentration is evidence of a first-order dependence of the rate upon that species. Ligand concentrations were usually 0.10 mM but a few determinations were made using $[PMA] = 0.20$ mM. A wider pH range of study is prevented at the high end by interference from hydroxy species of nickel(II) and precipitation, and at the low end by lack of complex formation and acid dissociation. Table I is a compilation of the kinetic data obtained under the conditions specified. Only k_f values are reported; dissociation rate constants k_d measured as the intercept of plots of observed rate constants versus nickel ion concentration according to Eq. (1) are very small and are not accurately known. The value of k_f is sharply

$$k_{obs} = k_f[Ni^{2+}] + k_d \quad (1)$$

dependent upon pH from 7.0 down to about 6, but then becomes relatively pH independent with a further small decrease as pH 5 is approached.

The pK_a values of PMA, 9.3 for protonation of

TABLE I
Kinetic data for formation of $Ni(PMA)^{2+}$ at $\mu = 0.3$ M^a and 25°^b

$[Ni^{2+}]$ mM	pH ^c	k_f^d M ⁻¹ s ⁻¹	$[Ni^{2+}]$ mM	pH	k_f M ⁻¹ s ⁻¹
2.00–10.00	6.92	128	2.00–14.0	5.91	29.2
1.0 – 8.0	6.8	1.1×10^2	1.00– 8.00	5.83	30.0
3.0 –12	6.8	97	4.00–28.0	5.83	22.0
2.00–20.0	6.75	109	3.00–36.0	5.61	15.5
1.00– 8.00	6.58	87.1	6.00–24.0	5.51	12.0
1.00– 8.00	6.40	61.0	6.00–24.0	5.26	6.80
1.00– 7.00	6.28	47.5	3.00–18.0	5.20	7.99
4.00–28.0	6.11	40.1	6.00–32.0	4.99	4.30
1.00– 4.50	6.10	39.0			

^a Ionic strength made up to 0.3 M using sodium perchlorate.

^b In most runs $[PMA]_{TOTAL} = 0.10$ mM; in the remainder $[PMA]_{TOTAL} = 0.20$ mM.

^c pH measurement using an Orion 701 model pH meter.

^d Values of k_f determined as described in the Results section.

the secondary nitrogen and 2.7 for the protonation of the pyridine, allow an assessment of the ligand species present in solution in the kinetic studies.^{8,9} The predominant form is PMAH^+ , with much smaller amounts of the free ligand, PMA, and the diprotonated species, PMAH_2^{2+} present. For the purposes of initial analysis, reaction of all three ligand species is considered. It is unlikely, however, that PMAH_2^{2+} will react to a significant extent or at a rapid rate with nickel(II) ions. The rate of production of Ni(PMA)^{2+} may be written as:

$$\begin{aligned} d[\text{Ni(PMA)}^{2+}]/dt &= k_f[\text{Ni}^{2+}][\text{PMA}]_{\text{TOTAL}} \\ &= k_1[\text{Ni}^{2+}][\text{PMA}] + k_2[\text{Ni}^{2+}][\text{PMAH}^+] \\ &\quad + k_3[\text{Ni}^{2+}][\text{PMAH}_2^{2+}] \end{aligned} \quad (2)$$

where k_1 , k_2 , k_3 , are defined as the rate constants for formation of complex from nickel ions with the neutral ligand, the monoprotated ligand, and the diprotonated ligand respectively. The acid dissociation constants may be written as:

$$K_{a1} = [\text{H}^+][\text{PMAH}^+]/[\text{PMAH}_2^{2+}] \text{ and}$$

$$K_{a2} = [\text{H}^+][\text{PMA}]/[\text{PMAH}^+].$$

Assuming that equilibration between the ligand forms is very rapid compared with complex formation then substitution of K_{a1} and K_{a2} into Eq. (2) leads to:

$$\begin{aligned} k_f(1 + [\text{H}^+]/K_{a2} + [\text{H}^+]^2/K_{a1}K_{a2}) = \\ k_1 + k_2[\text{H}^+]/K_{a2} + k_3[\text{H}^+]^2/K_{a1}K_{a2} \end{aligned} \quad (3)$$

Eq. (3) does not yield an excellent fit to the data using values of $K_{a2} = 5.1 \times 10^{-10}$ and K_{a1} of 2.0×10^{-3} . This was to be expected since the value of k_f does not decline with decrease in pH in the systematic manner expected if the PMAH_2^{2+} specie reacts with nickel(II) ions. The best fit of Eq. (3) is achieved with $k_3 \rightarrow 0$ which is consistent with prediction of non-reactivity of PMAH_2^{2+} in this context. Eliminating the contribution of the diprotonated ligand from Eq. (2) leads to an equation similar to but of simpler form than (3):

$$k_f(1 + [\text{H}^+]/K_{a2}) = k_1 + k_2[\text{H}^+]/K_{a2} \quad (4)$$

The results plotted in the form of the left hand side of Eq. (4) versus $[\text{H}^+]/K_{a2}$ produce a good linear plot (correlation coefficient 0.96) for the data from pH 7.0 to 5.9, but as $[\text{H}^+]$ is increased, Eq. (4) becomes less suitable for fitting the data. It is conceivable that acid dissociation of the complex is responsible for the decrease in the value of k_f beyond that expected if Eq. (4) is descriptive over the whole pH range studied as the pH is lowered below 5.8.

Using the data that fit well to Eq. (4), k_1 may be estimated as $2.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25.0°C . This is in excess of the range of values ($\sim 1 - 6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) that prevails^{1,6,10} for substitution by a neutral diamine of coordinated water on aquated nickel(II). In fact the aromatic ligand 2,2'-bipyridine reacts with a constant corresponding to k_1 of $\sim 2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$,^{1,11} which is about one order of magnitude lower. The value of k_1 for PMA is in excess of the values determined at 25° for the isomeric 2-(2-aminoethyl)pyridine, AEP, ($k_1 = 9.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at an ionic strength of 0.1),⁵ and for the unsubstituted analog of PMA, 2-aminomethylpyridine, AMP, ($k_1 = 8.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at an ionic strength of 0.3).¹ The internal conjugate base (ICB) mechanism^{3,7} has been invoked to explain higher values of k_1 for nickel(II) complex formation than might be expected on the basis of the Eigen-Wilkins mechanism. The overall pathway of reaction is similar in either mechanistic scheme but the latter implies that the observed rate constant (k_f), a product of the equilibrium constant for metal ion-ligand outer sphere complex formation (K_0) and the rate constant for dissociation of a metal coordinated water molecule from the complex (k_0), should vary little with change in ligand.⁶ This is observed in many cases. The former mechanism effectively allows for ligand assistance in promoting the rate of complex formation. The outer sphere complex is stabilized through the formation of a hydrogen bond between an imminently coordinating nitrogen of the ligand of pK_a similar to that of $\text{Ni(H}_2\text{O)}_6^{2+}$ (or other metal ion in the general case) and a hydrogen atom of the metal specie, and subsequent labilization of coordinated water which accelerates first covalent bond formation through the second nitrogen donor atom. Consequently, a plausible explanation for enhanced values of k_f through increase in both k_0 and K_0 is available. The pK_{a2} value of 9.3 for the aliphatic nitrogen of PMA is in the range suggested for the operation of the ICB mechanism and the enhanced value of k_1 therefore is consistent with this mechanism. Comparison may be made of the reactivity of PMA with that of the similar ligands AEP and AMP whose enhanced rates of complex formation with nickel(II) ions have been suggested earlier to be consistent with the ICB mechanism. It is surprising at first glance that complex formation with PMA, which is somewhat sterically hindered by the methyl group on the aliphatic nitrogen atom, is faster (a factor of 3) than with the unsubstituted AMP. However, in both ligands the aliphatic nitrogen is the donor atom which has a pK_a value (8.6 in AMP and 9.3 in PMA) which makes it

amenable to hydrogen bond formation and stabilization of the outer sphere complex in the ICB scheme; and in the formation of the PMA complex the effect would manifest itself somewhat more than in the formation of the AMP complex because of the slightly higher pK_a value of PMA. Since first bond formation is presumably then through the pyridine nitrogen atom following rate determining water molecule loss, the possible steric effect of the methyl group is not detectable. Second covalent bond formation through chelate ring closure should be very rapid in both cases.⁶

The enhancement of the complex formation rate constant with PMA over that of the isomeric AEP may be rationalized as due to the difficulty involved in forming the first covalent bond which forms a temporary eight membered chelate system (the stabilizing hydrogen bond connects the other nitrogen to the aquo metal ion), as the $Ni(AEP)^{2+}$ complex is formed. In addition final closure of the six membered chelate ring may also be involved in overall retardation of the formation of $Ni(AEP)^{2+}$. It has been shown,⁵ previously, from an analysis of the rate constants of an $AMPH^+$ and $AEPH^+$ reacting with aqueous nickel(II) ions that a steric effect lowers the reactivity of AEP from that which might be expected for that ligand (pK_a 9.65) on the basis of the ICB mechanism.

The slope from use of Eq. (4) for the data from pH 5.9 to 7.0 yields a value of $19 M^{-1} s^{-1}$ for the reaction of $PMAH^+$ with nickel(II) ions (k_2). This is in the same general range as values for other similarly singly protonated ligands (k_2 of $35 M^{-1} s^{-1}$ and $7.3 M^{-1} s^{-1}$ for $AMPH^+$ and $AEPH^+$ respectively). The trend is reasonable in that the methyl group of $PMAH^+$ offers a measure of steric hindrance in its reaction, and therefore it is less reactive than $AMPH^+$. The reaction of $AEPH^+$ has earlier⁵ been suggested to be subject to a steric effect when

considering the five fold rate enhancement of $AMPH^+$ over $AEPH^+$. The uncertainty in k_2 for $PMAH^+$ does not justify further analysis of the significance of the value.

Mixed aliphatic aromatic diamines in their kinetics of reactions with aquo nickel(II) ions provide further support for the general tenets of the Eigen-Wilkins mechanism. Detailed refinement of the general scheme to explain deviations in kinetic parameters from predicted values can be performed using the ICB mechanism and steric considerations.

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