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# Mechanisms of in Situ Macrocyclic Ligand Synthesis. 1. Kinetics and Mechanism of Formation of a Noncyclic Nickel(II) Complex[1]

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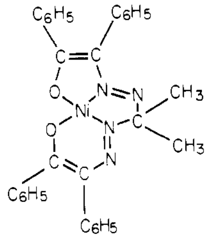
The rate of reaction of (1,2,8,9-tetraphenyl-3,4,6,7-tetraaza-5,5-dimethylnona-1,3,6,8-tetraene-1,9-dioxy)nickel(II) with 1,3-propanediamine has been studied in tetrahydrofuran–ethanol solution. It was found that the rate is first order in nickel complex, second order in 1,3-propanediamine, and first order in added base (hydroxide or ethoxide ion) concentration. The enthalpy of activation, $\Delta H^*$, is determined to be 32.4 ± 1.0 kJ mol$^{-1}$ and the entropy of activation, $\Delta S^*$, is −210 ± 30 J mol$^{-1}$ K$^{-1}$. A multistep mechanism for the reaction is proposed in which initial coordination of two molecules of amine is followed by nucleophilic attack of the deprotonated amine at a coordinated CO group of the ligand. The proposed mechanism is consistent with the kinetic template effect in which the metal ion orients the reactant molecules and acts as a center of positive charge for polarization of the reactants.

## Introduction

The development of procedures for the synthesis of complexes containing macrocyclic ligands has been an active area of research during the past several years. In general, there have been two approaches reported. The first involves a complexation reaction between a presynthesized macrocyclic ligand and the metal ion in solution whereas in the second approach, the macrocyclic ligand is synthesized in the presence of the metal ion.[3] The latter, in situ, synthesis has been widely used for the preparation of many synthetic and "classical" macrocycles such as porphyrins, corrins, etc., and the role of the metal ion in such in situ reactions has been the source of much discussion. Lindoy and Busch[4] described this role in terms of coordination template effects; if the directive influence of the metal ion controls the steric course of a sequence of stepwise reactions, then the kinetic template effect is considered to be operative. The first demonstration of this effect via a kinetics study was reported by Blinn and Busch for the reaction of (2,3-pentanedione bis(mercaptoethyliminato))nickel(II) with $\alpha,\alpha'$-dibromo-$o$-xylene.[5] This study indicated that the reaction occurs in two distinct steps, the first involving the attack at one of the coordinated mercaptide groups by a halide from the $o$-xylene followed by a second rapid ring-closure step. After the first mercaptide has reacted, the second mercaptide and halide are oriented such that the cyclization reaction proceeds rapidly. Although many other reactions that lead to complexes containing macrocyclic ligands by in situ processes have been described in the literature,[3] with the above exception, no study of the kinetics of in situ macrocyclic ligand synthesis has been reported. In view of the importance of complexes containing macrocyclic ligands with a set of $N_4$ donor atoms, we have initiated a program that is aimed at the determination of the kinetics and elucidation of mechanisms for reactions that lead to the in situ formation of such ligands. It is anticipated that knowledge of the mechanisms of these reactions should lead to a more complete understanding of the factors that control them and in particular should determine the role of the metal ion. With this information available, it is possible that new, improved synthetic procedures may be developed.

Condensation reactions between a nickel(II) complex containing a tetradentate ligand with an $N_2O_2$ donor set derived from benzil monohydrazone, **1**, abbreviated NiMMK, and some amines in the absence of a solvent have been previously described.[6] With ethylenediamine, en, a nickel(II) complex containing a 13-membered macrocyclic ligand, Ni(Me$_2$Ph$_4$-[13]tetraenatoN$_4$(N$_2$))[7] (**2**) was obtained whereas with 1,3-propanediamine, 1,3-pn, the complex obtained, abbreviated NiApSo, contains a noncyclic ligand in which only one of the coordinated CO groups of NiMMK has undergone reaction with the amine. Absorption spectra obtained during the course of the above reactions in tetrahydrofuran solution suggest that the formation of **2** from **1** and en occurs via a two-step process with the rates of both steps being comparable.[8] The two steps correspond to successive reaction of the two coordinated CO groups of NiMMK with one molecule of ethylenediamine. Since the rates of the two steps are comparable, a significant concentration of an intermediate in which only one coordinated CO group has condensed with one end of the ethylenediamine builds up during the reaction. This intermediate has an absorption spectrum that is similar to that of NiApSo and also to that of the product of the reaction between **1** and *unsym*-dimethylethylenediamine in which only one of the CO groups of **1** has undergone condensation. By investigating the reaction of NiMMK with 1,3-pn, we hope to gain some understanding of the mechanism of in situ macrocyclic ligand synthesis through the study of a reaction in which only the first step occurs.



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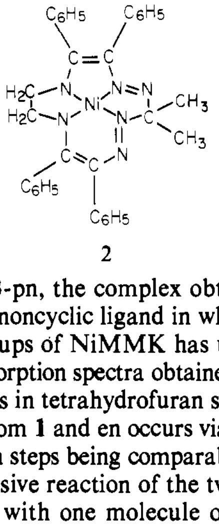

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(1) Abstracted from the Ph.D. Thesis of G.M.S., Michigan State University, and the M.S. Thesis of C.A.R., Virginia Commonwealth University.

(2) (a) La Salle College. (b) Virginia Commonwealth University.

(3) Melson, G. A. In "Coordination Chemistry of Macrocyclic Compounds"; Melson, G. A., Ed.; Plenum Press: New York, 1979; Chapter 2.

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(7) For the macrocyclic ligand abbreviation system used see ref 3, p 6.

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In this paper, we report a study of the kinetics of and propose a mechanism for the formation of NiApSo from NiMMK and 1,3-pn in tetrahydrofuran–ethanol solution and we discuss the factors that are important in controlling condensation reactions between amines and complexes with an $N_2O_2$ donor atom set.

## Experimental Section

**Materials.** (1,2,8,9-Tetraphenyl-3,4,6,7-tetraaza-5,5-dimethylnona-1,3,6,8-tetraene-1,9-dioxy)nickel(II), abbreviated as NiMMK (**1**), was prepared as previously reported[6] and recrystallized from 1-butanol. 1,3-Propanediamine (1,3-pn) was distilled from sodium hydroxide and stored under an atmosphere of dry $N_2$. Tetrahydrofuran, THF, was refluxed over and distilled from calcium hydride prior to use; it was then stored over molecular sieves (Linde 4A). Absolute ethanol was used without further purification. Ethanolic sodium hydroxide solutions were prepared by dissolving sodium hydroxide pellets (Mallinkrodt) in cold, degassed absolute ethanol in a Schlenk flask. The dissolution was allowed to occur under a flow of dry $N_2$ over a period of several hours; any remaining solid sodium hydroxide was removed by filtration and the solution stored in a Nalgene bottle in a refrigerator. Ethanolic sodium ethoxide solutions were prepared in a similar manner by dissolving sodium metal in cold absolute ethanol. The sodium hydroxide and ethoxide solutions were standardized by titration against potassium hydrogen phthalate with use of phenolphthalein as indicator. Biacetyl bis(benzoylhydrazone), DBH, was prepared by the method of Peckman and Bauer;[9] mp 280 °C (lit. 285 °C). Biacetyl bis(benzoylhydrazono))nickel(II), NiDB, was prepared by the procedure of Sacconi;[10] mp 262 °C dec (lit. 261–265 °C dec). Bis(1,3-propanediamine)(biacetyl bis(benzoylhydrazono))nickel(II) was prepared by a procedure similar to that described by Sacconi et al.[11] Anal. Calcd for NiDB·2(1,3-pn), $C_{24}H_{36}N_8O_2Ni$: C, 54.66; H, 6.88; N, 21.25. Found: C, 53.19; H, 6.88; N, 21.11.

**Kinetics Data.** A weighed quantity of NiMMK (approximately 0.08 g, $1.5 \times 10^{-4}$ mol) was dispensed into a 100-mL round-bottom flask that was equipped with a thermometer port, reflux condenser, and side arm fitted with a stopcock; the exit from the stopcock was sealed with a septum. Tetrahydrofuran was added to dissolve the NiMMK, and then the ethanolic base solution was added. A drying tube containing Drierite and Ascarite, for the absorption of water and carbon dioxide, respectively, was placed at the top of the condenser. After dry $N_2$ was passed through the system for approximately 30 s, the stirred solution was heated to reflux and the amine injected into the flask through the side arm. The final NiMMK concentration was approximately $3 \times 10^{-3}$ M. After the solution came to reflux again, usually within 30 s, the timer was started; aliquots were withdrawn from the side arm via a syringe fitted with a Chaney adapter, injected into cold ethanol in a volumetric flask, and diluted to 10 mL. The absorbance of the diluted solution (concentration of nickel complex $\sim 1 \times 10^{-4}$ M) was monitored at 340 and 390 nm by using either a Beckman DB-GT or Beckman MVII spectrometer. For kinetics data not obtained at reflux temperature, a thermostated oil bath was used; the reaction temperature was controlled to ±0.2 °C, and dry $N_2$ continually flowed over the solution to prevent decomposition of NiMMK. The rest of the procedure was identical with that used for obtaining data at reflux temperature.

All kinetics data were obtained under pseudo-first-order conditions ([1,3-pn] and [base] >> [NiMMK]) so that the absorbance of NiMMK could be used to determine the extent of reaction. The first-order rate equation

$$A_t - A_\infty = (A_0 - A_\infty)e^{-k_{\text{obsd}}t}$$

was used to fit the data with the KINFIT[12] program on the Michigan State University CDC 6500 or the Virginia Commonwealth University IBM 370/158 computer. In the above expression, $A_t$ is the absorbance of NiMMK at time $t$, with time expressed in seconds, $A_0$ is the initial absorbance, $A_\infty$ is the absorbance of the product, and $k_{\text{obsd}}$ is the pseudo-first-order rate constant. The equation was solved by an iterative method for $A_0$, $A_\infty$, and $k_{\text{obsd}}$. The experimentally observed and calculated values of $A_\infty$ agreed to better than 3%, and the standard deviation of the rate constant was less than 10%. Multiple runs were carried out at selected concentrations. The rate constants between different runs agreed to within 5%. Rate constants were calculated by using data obtained at both 340 and 390 nm, designated $k_{340}$ and $k_{390}$, respectively; agreement was generally within 5%. The average of these values is designated as $k_{\text{obsd}}$. The dielectric constant of each solution used in the kinetics experiments was obtained at 25 °C by using a Wissenschaftlich-Technische Werkstätten Type DM-01 dipole meter. The equation relating the dielectric constant of the solution, $D$, to the dipole meter reading, $M$, is

$$D = 0.5636M + 3.757$$

This equation is obtained by a least-squares analysis of four standard solutions: ethanol, $D$ = 24.3; tetrahydrofuran, $D$ = 7.23; methylene chloride, $D$ = 9.08; 1-propanol, $D$ = 20.1.

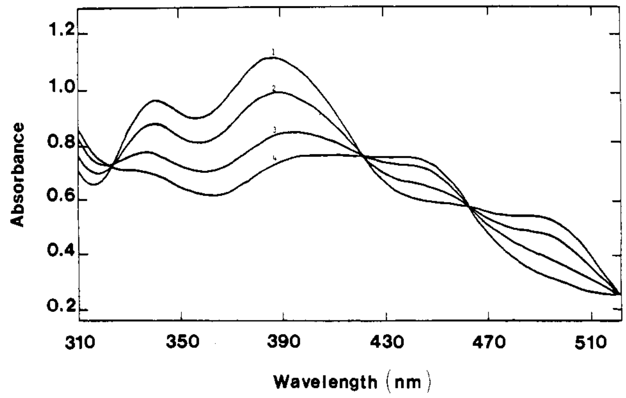

**Figure 1.** Absorption spectra obtained during reaction of NiMMK with 1,3-propanediamine.

Table I. Rate Constants as a Function of Added Base[a]

| $10^2$[base], M | $10^4k_{340}$, s$^{-1}$ | $10^4k_{390}$, s$^{-1}$ | $10^4k_{\text{obsd}}$, s$^{-1}$ |
|---|---|---|---|
| | (a) Hydroxide | | |
| 2.7 | 1.1 ± 0.1 | 1.1 ± 0.1 | 1.1 ± 0.1 |
| 4.5 | 2.0 ± 0.1 | 2.1 ± 0.1 | 2.1 ± 0.1 |
| 6.7 | 2.5 ± 0.2 | 2.7 ± 0.2 | 2.6 ± 0.2 |
| 9.0 | 3.0 ± 0.2 | 2.9 ± 0.2 | 3.0 ± 0.2 |
| | (b) Ethoxide | | |
| 1.2 | 0.54 ± 0.09 | 0.56 ± 0.07 | 0.55 ± 0.08 |
| 1.6 | 0.69 ± 0.06 | 0.70 ± 0.05 | 0.70 ± 0.06 |
| 1.8 | 0.83 ± 0.1 | 0.78 ± 0.1 | 0.81 ± 0.1 |
| 3.8 | 1.3 ± 0.1 | 1.3 ± 0.1 | 1.3 ± 0.1 |
| 6.0 | 2.1 ± 0.1 | 2.1 ± 0.1 | 2.1 ± 0.1 |
| 8.0 | 2.6 ± 0.1 | 2.6 ± 0.1 | 2.6 ± 0.1 |
| 9.5 | 3.4 ± 0.2 | 3.4 ± 0.2 | 3.4 ± 0.2 |
| 11.0 | 4.0 ± 0.2 | 4.2 ± 0.2 | 4.1 ± 0.2 |

[a] [NiMMK] = $3.0 \times 10^{-3}$ M; [1,3-pn] = $5.9 \times 10^{-1}$ M; temperature = 69.0 ± 0.2 °C.

## Results

The reaction of NiMMK (**1**) with 1,3-propanediamine does not proceed in solution in the absence of added base; however, in the presence of hydroxide or ethoxide ion the noncyclic product NiApSo is obtained as the exclusive product. A series of spectra obtained during the reaction in a tetrahydrofuran–ethanol solvent mixture at reflux temperature is shown in Figure 1; spectrum 1 corresponds to NiMMK and spectrum 4 to NiApSo. The detection of several isosbestic points in the series of spectra suggests that only two uniquely absorbing species are present in the reaction medium and that significant concentrations of intermediates or decomposition products do not occur during the course of the reaction. The reaction was followed by monitoring absorbance changes at 340 and 390 nm under pseudo-first-order conditions (see Experimental Section). Since the data fit the first-order expression, it is concluded that the rate of the reaction is first order in con-

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(9) Peckman, H.; Bauer, W. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 663.
(10) Sacconi, V. *Z. Anorg. Allg. Chem.* **1954**, *275*, 249.
(11) Sacconi, V.; Lombardo, G.; Paoletti, P. *J. Chem. Soc.* **1954**, 848.
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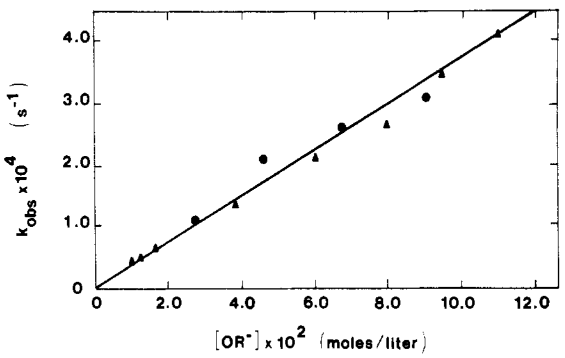

**Figure 2.** Dependence of rate constant on the concentration of added base: (●) $OH^-$; (▲) $OEt^-$.

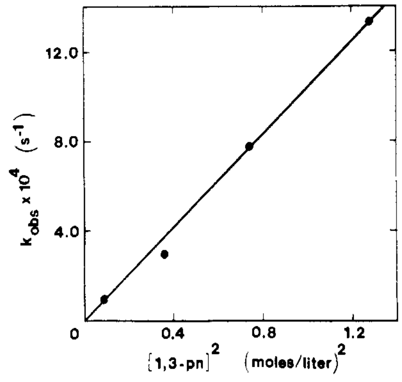

**Figure 3.** Dependence of rate constant on the concentration of 1,3-propanediamine.

**Table II.** Rate Constants as a Function of 1,3-Propanediamine Concentration[a]

| [1,3-pn], M | $10^4k_{\text{obsd}}$, $s^{-1}$ | [1,3-pn], M | $10^4k_{\text{obsd}}$, $s^{-1}$ |
|---|---|---|---|
| 0.30 | 0.95 ± 0.1 | 0.86 | 7.8 ± 0.4 |
| 0.60 | 2.9 ± 0.3 | 1.13 | 13.3 ± 0.8 |

[a] [NiMMK] = $3.0 \times 10^{-3}$ M; [$OH^-$] = $9.0 \times 10^{-2}$ M; temperature = 69.0 ± 0.3 °C.

**Table III.** Dependence of the Rate Constant on the Dielectric Constant of the Medium[a]

| $D$ | $10^2/D$ | $10^4k_{\text{obsd}}$, $s^{-1}$ | $-\ln k_{\text{obsd}}$ |
|---|---|---|---|
| 8.85 | 11.3 | 6.1 ± 0.3 | 7.4 |
| 9.34 | 10.7 | 4.2 ± 0.3 | 7.8 |
| 9.80 | 10.2 | 3.0 ± 0.2 | 8.1 |
| 10.53 | 9.5 | 2.0 ± 0.1 | 8.5 |
| 11.24 | 8.9 | 1.1 ± 0.1 | 9.1 |

[a] [NiMMK] = $3.0 \times 10^{-3}$ M; [$OH^-$] = $9.0 \times 10^{-2}$ M; [1,3-pn] = $5.9 \times 10^{-1}$ M; temperature = 69.0 ± 0.2 °C.

**Table IV.** Temperature Dependence of the Reaction Rate Constant[a]

| $T$, K | $10^3/T$, $K^{-1}$ | $10^4k_{\text{obsd}}$, $s^{-1}$ | $-\ln$ ($k_{\text{obsd}}/T$) |
|---|---|---|---|
| 341.5 | 2.928 | 7.7 ± 0.4 | 13.00 |
| 339.0 | 2.950 | 7.1 ± 0.6 | 13.08 |
| 336.5 | 2.972 | 6.5 ± 0.3 | 13.16 |
| 334.1 | 2.993 | 5.9 ± 0.3 | 13.25 |

[a] [NiMMK] = $3.0 \times 10^{-3}$ M; [$OH^-$] = $9.0 \times 10^{-2}$ M; [1,3-pn] = $8.9 \times 10^{-1}$ M.

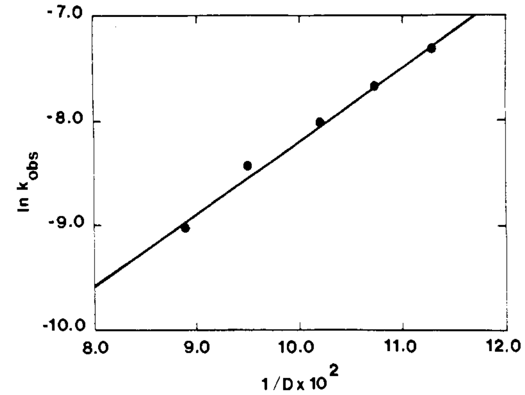

**Figure 4.** Dependence of rate constant on the dielectric constant of the medium.

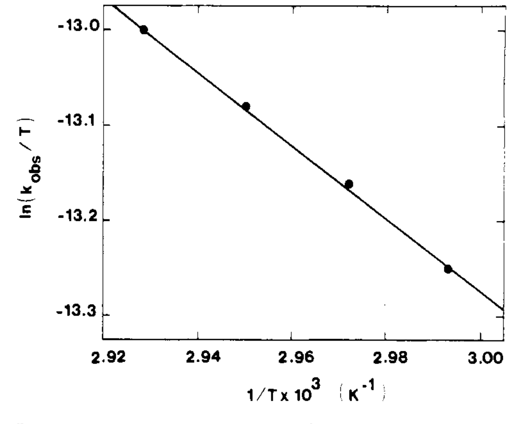

**Figure 5.** Temperature dependence of the rate constant.

centration of NiMMK. The order of the reaction with respect to the concentration of added hydroxide or ethoxide ion ($OR^-$, R = H, Et) was determined, and the rate constants are reported in Table I. The plot of log $k_{\text{obsd}}$ vs. log [$OR^-$] is a straight line with slope 0.97 ± 0.05. The plot of $k_{\text{obsd}}$ vs. [$OR^-$] is shown in Figure 2; it should be noted that the intercept is zero ($1.85 \times 10^{-5} \pm 1.1 \times 10^{-5}$ $s^{-1}$) in agreement with the observation that the reaction does not proceed in solution in the absence of added base. Both graphs indicate a first-order dependence of the reaction on the concentration of added base. The dependence of the reaction rate on the concentration of 1,3-propanediamine was determined, and rate constants are reported in Table II. The plot of log $k_{\text{obsd}}$ vs. log [1,3-pn] is a straight line with slope 1.98 ± 0.05 (intercept $-3.5 \times 10^{-5} \pm 4.4 \times 10^{-5}$ $s^{-1}$), and in Figure 3 it is shown that a plot of $k_{\text{obsd}}$ vs. $[1,3\text{-pn}]^2$ is a straight line. Both relationships confirm the second-order dependence of the reaction rate on 1,3-propanediamine concentration. The reaction is dependent on the nature of the solvent system; the rate decreases as the mole fraction of ethanol in the ethanol–tetrahydrofuran mixture increases. The mole fraction, $X$, of ethanol in the mixture was varied from 0.154 to 0.382. These extremes were dictated by the reaction conditions: below $X = 0.154$ sodium hydroxide precipitates from solution; above $X = 0.382$ significant decomposition of NiMMK occurs. The dielectric constant, $D$, was determined for each solution (see Experimental Section), data for $k_{\text{obsd}}$ and $D$ are given in Table III, and a plot of ln $k_{\text{obsd}}$ vs. $1/D$ is shown in Figure 4; the linear relationship is expected for the interaction of either two polar molecules or an ion and a polar molecule.[13] The temperature dependence of the reaction rate was determined, albeit over a limited temperature range. Below 60 °C, extensive decomposition of NiMMK occurs, and thus no reliable data could be obtained below this temperature. The upper limit, 69 °C, is a result of the solvent mixture employed; for an increase of the upper limit, a different solvent mixture must be used that would not allow the temperature dependence of the reaction rate to be determined under identical conditions. The data obtained are

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(13) Laidler, K.; Eyring, H. *Ann. N.Y. Acad. Sci.* **1940**, *39*, 303.

presented in Table IV, and Figure 5 shows a plot of ln ($k_{obsd}/T$) vs. $1/T$.[14] From this plot the enthalpy of activation for the reaction, $\Delta H^{\ddagger}$, is determined from the slope to be 32.4 ± 1.0 kJ mol$^{-1}$ and the entropy of activation, $\Delta S^{\ddagger}$, at 341.5 K, is calculated to be −210 ± 30 J mol$^{-1}$ K$^{-1}$. Although the reaction is expected to occur in a series of steps and individual $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for each step have not been determined (see Discussion), the large negative value of $\Delta S^{\ddagger}$ indicates the formation of a highly ordered intermediate during the course of the reaction.

## Discussion

The data presented in the Results section imply that the rate law for the reaction of NiMMK with 1,3-pn to form NiApSo can be expressed as

$$\text{rate} = \frac{d[\text{NiApSo}]}{dt} = \frac{-d[\text{NiMMK}]}{dt} = k[\text{NiMMK}][1,3\text{-pn}]^2[\text{OR}^-]$$

where R = H or Et for hydroxide or ethoxide ion, respectively. Because the rate constants for the hydroxide and ethoxide ion catalyzed reactions are the same within experimental error under similar conditions, we conclude that these bases serve the same function. Since a tetramolecular collision is highly improbable, we propose the mechanism

$$\text{NiMMK} + 2(1,3\text{-pn}) \rightleftharpoons \text{NiMMK}\cdot 2(1,3\text{-pn}) \quad k_1, k_{-1} \qquad \text{step I}$$

$$\text{NiMMK}\cdot 2(1,3\text{-pn}) \xrightarrow{\text{OR}^-} \text{NiApSo} \quad k_2 \qquad \text{step II}$$

If steady-state conditions are applied to NiMMK·2(1,3-pn), then

$$d[\text{NiMMK}\cdot 2(1,3\text{-pn})]/dt = 0 \tag{1}$$

which leads to

$$[\text{NiMMK}\cdot 2(1,3\text{-pn})] = \frac{k_1[\text{NiMMK}][1,3\text{-pn}]^2}{k_{-1} + k_2[\text{OR}^-]} \tag{2}$$

If step II is the slow, rate-determining step, then

$$\frac{d[\text{NiApSo}]}{dt} = \frac{-d[\text{NiMMK}]}{dt} = k_2[\text{NiMMK}\cdot 2(1,3\text{-pn})][\text{OR}^-] \tag{3}$$

and thus

$$\text{rate} = \frac{k_2k_1[\text{NiMMK}][1,3\text{-pn}]^2[\text{OR}^-]}{k_{-1} + k_2[\text{OR}^-]} \tag{4}$$

Dividing the numerator and denominator of the right-hand side of the above equation by $k_{-1}$ produces

$$\text{rate} = \frac{k_2K[\text{NiMMK}][1,3\text{-pn}]^2[\text{OR}^-]}{1 + (k_2/k_{-1})[\text{OR}^-]} \tag{5}$$

where $K = k_1/k_{-1}$, the equilibrium constant for the formation of the bis(1,3-propanediamine) adduct (step I). At low alkoxide ion concentration and where $k_2 << k_{-1}$, the rate law reduces to

$$\text{rate} = k_2K[\text{NiMMK}][1,3\text{-pn}]^2[\text{OR}^-] \tag{6}$$

which is the observed rate law, where $k_2K = k$.

Under pseudo-first-order conditions, where [1,3-pn] and [OR$^-$] are significantly greater than [NiMMK] and assumed to remain constant during the course of the reaction, then

$$\text{rate} = k_{obsd}[\text{NiMMK}] \tag{7}$$

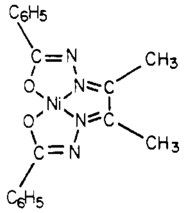
where

$$k_{obsd} = k_2K[1,3\text{-pn}]^2[\text{OR}^-] \tag{8}$$

It should be possible to determine the individual rate constants under special conditions. For example, at high [OR$^-$], eq 5 reduces to

$$\text{rate} = k_1[\text{NiMMK}][1,3\text{-pn}]^2 \tag{9}$$

i.e., the rate becomes independent of [OR$^-$], and $k_1$ may be obtained. However, with the concentrations of OR$^-$ used in this study, no "leveling effect" is observed for the [OR$^-$] dependence (see Figure 2). Concentrations of OR$^-$ greater than those used could not be obtained in the EtOH/THF solvent employed due to precipitation of the base and decomposition of NiMMK. In order to calculate $k_2$, it is necessary to determine the value of $K$ for the adduct (see eq 6). Bis(amine) adducts of NiMMK could not be prepared in our laboratory, and spectral changes that would indicate the formation of detectable concentrations of an adduct in solution were not observed. Absorption spectra of NiMMK display only dilution effects upon addition of amine, and the overall integrity of the spectrum remains unaltered; thus $K$ could not be determined. However, the above observations do not preclude the existence of the adduct as an intermediate. It was concluded earlier, from the series of spectra obtained under reaction conditions that show the presence of several isosbestic points, that only two uniquely absorbing species are present in solution. Although the presence of an isosbestic point is normally considered to show the existence of only two absorbing species, this interpretation is not necessarily true.[15] If an absorbing species is present in low concentration and equilibration of the species is rapid relative to the rate of the reaction, its presence will not affect the appearance of an isosbestic point. Thus, for the reaction of NiMMK with 1,3-pn, the adduct may be present in such a low concentration, i.e., it is a highly reactive intermediate, that it is unobservable under the experimental conditions. There are several reasons why the suggestion of the formation of a bis(1,3-propanediamine) adduct of NiMMK is reasonable. The kinetics data obtained in this study indicate a second-order dependence on the concentration of 1,3-pn, and the large negative $\Delta S^{\ddagger}$ value (~−210 J mol$^{-1}$ K$^{-1}$) is consistent with the formation of a highly ordered intermediate. Furthermore, bis(amine) adducts of nickel(II) complexes that are similar in structure to NiMMK have been prepared; these adducts undergo facile dissociation of the amine in solution. For example, the complex NiDB (3) forms adducts with various amines including pyridine, ethylenediamine, and 1,3-propanediamine. Although we were able to isolate the adduct NiDB·2(1,3-pn), it does not persist in solvents that are even relatively poor donors. When NiDB·2(1,3-pn) is dissolved in benzene, the solution obtained has an absorption spectrum in the visible region that is that of NiDB only. Addition of excess 1,3-pn results in a change in the absorption spectrum to one



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[14] Espenson, J. H. In "Chemical Kinetics and Reaction Mechanism"; McGraw-Hill: New York, 1981; p 121.

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that implies re-formation of the adduct. In a solvent system such as tetrahydrofuran–ethanol, such bis(amine) species would be more labile toward displacement of the amine because of the good donor properties of the solvent molecules.

In spite of the limitations of the rate constant calculations, the proposed two-step mechanism for the reaction of NiMMK with 1,3-pn remains reasonable. In the first step, the bis(1,3-propanediamine) adduct that is proposed concurs with the prediction that six-coordinated nickel(II) complexes are generally more favorable than five-coordinate species. The reactant 1,3-pn is thus oriented for reaction to occur with the ligand system. However, since the reaction does not occur in solution in the absence of added base, we conclude that the coordinated 1,3-pn is not a sufficiently strong nucleophile to react with the coordinated CO group of the ligand. It was concluded earlier, from the kinetics data, that the hydroxide and ethoxide ions serve the same function in these reactions. The second step is suggested to involve deprotonation of the coordinated amine by the base (it is well-known that coordination of an amine results in increased acidity of the hydrogens) followed by attack of this much stronger nucleophilic species at the carbon atom of a coordinated CO group of the ligand and the regeneration of the base to give the product NiApSo. We conclude that the rate-determining step in the overall mechanism is the nucleophilic attack by the deprotonated amine; the solvent-dependence data is consistent with an ion–molecule reaction. Deprotonation of the amine cannot be the rate-determining step because both bases (hydroxide and ethoxide) give identical rates under similar experimental conditions, yet they are of different nucleophilicity. The proposed second step in the mechanism is similar to that reported by Sargeson in papers dealing with reactions of coordinated nucleophiles.[16] In these reactions, a base-catalyzed facile intramolecular condensation between a ligand containing a reactive carbonyl center and a coordinated ammonia was described.

The study of the reaction of NiMMK with 1,3-pn has provided clear evidence for the presence of a kinetic template effect and demonstrates the role of the metal ion in reactions of this type. In addition to serving as a template for the orientation of reactant molecules by using available coordination sites, the metal ion also serves as a center of positive charge, which results in polarization effects of the reactants, which in turn allows the reaction to proceed. This study has also enabled us to formulate a mechanism that describes the initial condensation reaction in the in situ formation of macrocyclic ligands derived from the MMK ligand. The reaction of NiMMK with ethylenediamine to produce Ni($Me_2Ph_4$-[13]tetraenato$N_4(N_2)$) has been studied in THF–EtOH solution.[17] The kinetics data for the initial condensation reaction are similar to those reported here for the reaction of NiMMK with 1,3-pn, viz., rate $\propto$ [ethylenediamine]$^2$, [added base], and [NiMMK]. Under similar experimental conditions, the overall rate of the initial condensation reaction is similar to that observed for the reaction of NiMMK with 1,3-pn, indicating that the rate-determining step is similar in both systems. Small differences in the observed rates of reaction may be ascribed to differences in nucleophilic strengths of the deprotonated amines.

Subsequent papers in this series will report kinetics data and proposed mechanisms for several in situ macrocyclic ligand syntheses, probe the factors that are important in controlling the reactions, and, in particular, investigate the role of the metal ion.

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# Kinetics and Mechanism of the Dioxygen Uptake of the Four-Coordinate (X = Cl) and Five-Coordinate (X = I, SCN, $PPh_3$) Complexes Ir(cod)(phen)X

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The reaction of [Ir(cod)(phen)]Cl (cod = cycloocta-1,5-diene, phen = phenanthroline) with dioxygen in methanol solution was studied kinetically in the absence and presence of $SCN^-$ and $I^-$. The five-coordinate complexes IrX(cod)(phen) (X = I, SCN) are generated in solution on addition of NaI or NaSCN to an $Ir(cod)(phen)^+$ solution. The kinetic data obtained at normal and elevated pressures indicated that the five-coordinate complexes (X = I, SCN) are much more reactive toward dioxygen than the four-coordinate complex (X = Cl). An "end-on" oxidative addition of $O_2$ to IrX(cod)(phen) (X = I, SCN) is postulated.

## Introduction

The reactions of dioxygen with transition-metal complexes can be divided into two groups: (a) The first consists of reactions of dioxygen with metal complexes in which a one-electron metal-to-ligand transfer occurs to form an "end-on" bonded superoxide complex.[1,2] The principal oxidation states of the metals involved in these reactions normally differ by one unit, e.g., Fe(II,III), Co(II,III), and Cu(I,II). The mechanism of these reactions is most probably an "end-on" attack of dioxygen on the metal center. (b) The second group consists of reactions of dioxygen with metal complexes in which a two-electron metal-to-ligand transfer occurs.[3-5] These

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