tentials are dependent on the nature of substituents on the biuret ligand probably due to electron donating or withdrawing through the delocalized $\pi$-electron system which overlaps with the Co $3d_{xz}$ orbital.

**Registry No.** $KCo(bi)_2$, 38637-46-6; $KCo(3\text{-}Ph(bi))_2 \cdot 2DMSO$, 38637-47-7; $Bu_4NCo(3\text{-}Ph(bi))_2$, 38637-48-8; $Bu_4NCo(bi)_2 \cdot H_2O$, 38637-49-9; $KCo(3\text{-}Pr(bi))_2(1\text{-}Pr(bi)H_2)_2$, 36472-84-1; $KCo(3\text{-}Pr(bi))_2 \cdot 2H_2O$, 38637-51-3; $KCo(3\text{-}Pr(bi))_2 \cdot 2DMSO$, 38637-52-4; $KCo(en(bi)_2)$, 38637-53-5; $KCo(o\text{-}phen(bi)_2)$, 38637-54-6; $Bu_4NCo(en(bi)_2)$, 38637-55-7; $Bu_4NCo(o\text{-}phen(bi)_2) \cdot CHCl_3$, 38637-56-8; $KCo(3\text{-}Pr(bi))_2(NH_3)_2$, 31282-33-4; $KCo(3\text{-}Pr(bi))_2(C_3H_7NH_2)_2$, 31282-34-5; $KCo(3\text{-}Pr(bi))_2(pyrrolidine)_2$, 31249-56-6; $KCo(3\text{-}Pr(bi))_2(pyridine)_2$, 31240-71-8.

**Acknowledgment.** The investigations were supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research. We wish to thank Mr. J. Diersmann for performing the analyses, Dr. C. P. Keijzers for providing the computer program for the Huckel calculations, and Professor L. L. van Reijen for giving us the opportunity to perform magnetic measurements below 150°K. We thank Dr. P. van der Put for help with the interpretation of magnetic data.

---

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

# Kinetics of the Nickel(II)-2-(4-Dimethylaminophenylazo)pyridine Reaction in Pyridine and in Pyridine-Nitromethane

HERBERT L. FRITZ and JAMES H. SWINEHART*

*Received November 3, 1972*

The following reaction between nickel(II) and 2-(4-dimethylaminophenylazo)pyridine (DPAP) in pyridine and in pyridine-nitromethane solvents has been studied

$$Ni^{2+} + DPAP \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} NiDPAP^{2+}$$

The rate constants (25°) and activation parameters in various solvents are as follows (solvent, $k_3$, $\Delta H_3^\ddagger$, $\Delta S_3^\ddagger$, $k_{-3}$, $\Delta H_{-3}^\ddagger$, $\Delta S_{-3}^\ddagger$): pyridine, $1.7 \times 10^4\ M^{-1}\ sec^{-1}$, 13.7 kcal/mol, 6 eu, 12 $sec^{-1}$, 15 kcal/mol, −4 eu; 6.20 $M$ pyridine in nitromethane, $5.0 \times 10^3\ M^{-1}\ sec^{-1}$, 11.1 kcal/mol, −4 eu, 20 $sec^{-1}$, 10 kcal/mol, −21 eu; 0.125 $M$ pyridine in nitromethane, $3.5 \times 10^5\ M^{-1}\ sec^{-1}$, 9 kcal/mol, −3 eu, · · · , · · · , · · · . The data are consistent with either the Bennetto-Caldin or Eigen-Wilkins mechanisms but not with a mechanism involving a reactive five-coordinate intermediate.

## Introduction

Nickel(II) complexation reactions in aqueous solutions have been widely studied. Two review articles by Kustin and Swinehart[1] and by Wilkins[2] summarize the available data for these reactions. The mechanism for these reactions can be written as

$$Ni(H_2O)_6{}^{2+} + L^{n-} \overset{K_1}{\rightleftarrows} Ni(H_2O)_6{}^{2+},L^{n-} \qquad (1)$$

$$Ni(H_2O)_6{}^{2+},L^{n-} \xrightarrow{k_1} Ni(H_2O)_{6-p}L^{2-n} + pH_2O$$

where $Ni(H_2O)_6{}^{2+},L^{n-}$ is an ion pair. The ion pairing constant $K_1$ can be calculated from an equation derived by Fuoss[3] and by Eigen.[4] Since temperature-jump and stopped-flow kinetic experiments provide data for the product $K_1k_1$, $k_1$ can be determined. When $L^{n-}$ is a water molecule, mechanism 1 becomes the generalized equation for solvent exchange

$$Ni(H_2O)_6{}^{2+} + H_2O^* \overset{k_2}{\rightleftarrows} Ni(H_2O)_5(H_2O^*)^{2+} + H_2O \qquad (2)$$

Nmr line broadening studies have been used to determine the value of $k_2$ in the above reaction.[5] In many Ni(II) aqueous complexation reactions,[2] $k_1$ has been calculated to be approximately equal to $k_2$. This more than coincidental agreement between $k_1$ and $k_2$ has been interpreted to mean that the rate-determining step in mechanism 1 is the elimination of a bonded water molecule from the first solvation sphere of the solvated Ni(II) ion.[1,2]

To determine the effect the solvent has on complexation reactions, these reactions must be studied in different solvents. Until recently, most complexation reactions have been studied in aqueous solvents. Research on nonaqueous complexation reactions has been done in three major areas. Nmr line broadening techniques have been used to determine the rates of solvent exchange for solvated metal cations in both pure- and mixed-solvent systems.[6-29] Nmr techniques have

---

(1) K. Kustin and J. H. Swinehart, "Inorganic Reaction Mechanism," J. O. Edwards, Ed., Wiley, New York, N. Y., 1970, pp 107-157.

(2) R. G. Wilkins, *Accounts Chem. Res.*, 3, 408 (1970).

(3) R. M. Fuoss, *J. Amer. Chem. Soc.*, 80, 5059 (1958).

(4) M. Eigen, *Z. Phys. Chem. (Frankfurt am Main)*, 1, 176 (1954).

(5) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **44**, 4103 (1966).

(6) T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, 2, 349 (1967).

(7) T. R. Stengle and C. H. Langford, *Annu. Rev. Phys. Chem.*, 19, 193 (1968).

(8) R. G. Pearson and R. D. Lainer, *J. Amer. Chem. Soc.*, 86, 765 (1964).

(9) J. W. Brievogel, Jr., *J. Phys. Chem.*, 73, 4203 (1969).

(10) L. S. Frankel, *J. Mol. Spectrosc.*, 29, 273 (1969).

(11) W. L. Purcell and R. S. Marianelli, *Inorg. Chem.*, 9, 724 (1970).

(12) N. A. Matwiyoff and S. V. Hooker, *Inorg. Chem.*, 6, 1127 (1967).

(13) J. F. O'Brien and W. L. Reynolds, *Inorg. Chem.*, 6, 2110 (1967).

(14) D. K. Ravage, T. R. Stengle, and C. H. Langford, *Inorg. Chem.*, 6, 1252 (1967).

(15) N. A. Matwiyoff, *Inorg. Chem.*, 5, 788 (1966).

(16) J. S. Babiec, Jr., C. H. Langford, and T. R. Stengle, *Inorg. Chem.*, 5, 1362 (1966).

also been used to determine solvent-exchange rates for solvated metal cations which contain some unexchangeable ligands in the first solvation sphere.[30,31] Relaxation and stopped-flow techniques have been used to study the kinetics of metal ion-ligand complexation reactions in nonaqueous solvents.[32-41]

Many nonaqueous Ni(II) complexation reactions have already been studied. The results of these studies do not always conform to the mechanism proposed for aqueous systems. Bennetto and Caldin[32-36] studied nickel(II)-bipyridyl complexation reactions in several solvents. In these studies, the second-order rate constants were not equal to the ion-pairing constant multiplied by the rate of solvent exchange. Consequently, these results in nonaqueous solvents do not fit the proposed mechanism for aqueous solvents. Langford and Tsiang[39] and Frankel[28] have done other studies of nonaqueous Ni(II) complexation reactions. The results of these studies also do not correspond to the proposed aqueous mechanism. These workers have proposed a mechanism involving a five-coordinate intermediate for Ni(II) complexation reactions in nonaqueous solvents.

The study of a nonaqueous Ni(II) complexation reaction in pyridine and in pyridine-nitromethane solvents, 0.125 and 6.20 *M* pyridine in nitromethane, is reported in this paper. One reason for studying Ni(II) complexation reactions in these solvents is that the nature of the solvated Ni(II) cation has been reported.[42] Knowledge of the composition of the solvation spheres of cations is important in understanding the effects of bulk solvent and mixed coordination spheres on metal ion complexation reactions. 2-(4-Dimethylaminophenylazo)pyridine (DPAP) was chosen as the ligand because a protonation-deprotonation equilibrium is not involved in complexation, the molecule is neutral and consequently "inert" electrolytes do not form ion pairs with it, 1:1 complexes form with Ni(II), and spectral changes on complexation are large.

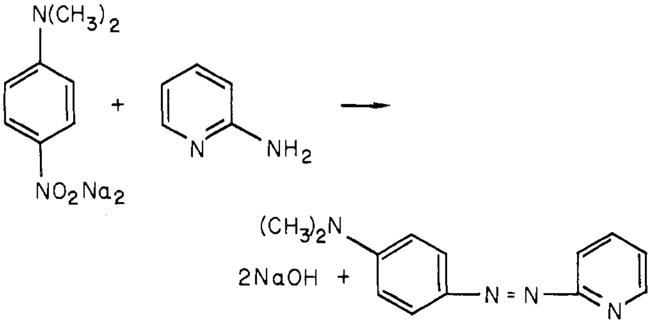
## Experimental Section

**Reagents and Solutions.** Reagent grade pyridine (py) was dried over barium oxide and distilled in a distillation apparatus protected from the atmosphere with calcium chloride drying tubes. The boiling point of the dried pyridine was 115.2°. Reagent grade spectroquality nitromethane (nm) was dried over Drierite and distilled in a one-piece distillation apparatus under reduced pressure (50-100 Torr). The water content of the solutions used was determined by the Karl Fischer method. The lowest attainable water concentration was 0.002 *M*.

**Bis(tetrafluoroborato)tetrakis(pyridine)nickel(II).** $Ni(py)_4(BF_4)_2$ was prepared according to the synthesis devised by Rosenthal and Drago.[42] Seven grams of $Ni(BF_4)_2\cdot 6H_2O$ (Alfa Inorganics) and 50 ml of 2,2-dimethoxypropane were stirred for 16 hr in a tightly sealed flask. Twenty-five milliliters of freshly distilled pyridine was then added to the mixture causing a pale blue precipitate to form slowly. The product was isolated in a dry nitrogen glove box, washed repeatedly with small portions of anhydrous ether, and dried *in vacuo* for 12 hr at 25°. *Anal.* Calcd for $C_{20}H_{20}N_4B_2F_8Ni$: C, 43.78; H, 3.67; N, 10.21. Found: C, 43.69; H, 3.73; N, 10.01.

This compound was stored in a desiccator and the purity was checked periodically by recording the spectrum of a solution of $Ni(py)_4(BF_4)_2$ in 6.2 *M* pyridine in nitromethane. The extinction coefficient at 605 nm is 15 $M^{-1}$ $cm^{-1}$ which is identical with the value reported by Rosenthal and Drago.[42]

**2-(4-Dimethylaminophenylazo)pyridine (DPAP).** DPAP was prepared by a method first published by Faessinger and Brown[43]



Clean dry sodium (2.4 g) was added to 4-nitrodimethylaniline (8.3 g) dissolved in 70 ml of dry toluene which was under nitrogen. The mixture was warmed to initiate the reaction. (Cooling was later necessary to control the reaction.) After the reaction had subsided, the reaction mixture was refluxed for 1 hr. To this refluxing solution, 4.7 g of 2-aminopyridine was added and refluxing was continued under nitrogen for another hour. The solvent was removed under vacuum and the crude solid product was dissolved in 200 ml of 25% acetic acid. After the addition of 500 ml of water, the solution was filtered to remove solid impurities. The remaining purple solution was neutralized with ice-cold 20% sodium hydroxide causing a red precipitate to form. This precipitate was recrystallized twice from petroleum ether (bp 95-115°). The solid yellow-orange product had a melting point identical with the reported melting point for the cis isomer, 108-109°. *Anal.* Calcd for $C_{13}H_{14}N_4$: C, 69.00; H, 6.24; N, 24.76. Found: C, 68.98; H, 6.29; N, 24.68.

Solutions used for equilibrium and kinetic measurements were prepared from stock solutions of $Ni(py)_4(BF_4)_2$ and DPAP. The pyridine-nitromethane solutions had pyridine concentrations of 0.125 *M* (1% pyridine-99% nitromethane by volume) and 6.20 *M* (50% pyridine-50% nitromethane by volume). The concentration of pyridine in the 0.125 *M* pyridine in nitromethane solution was in at least tenfold excess over the Ni(II) concentration. All solutions were protected from atmospheric water and were periodically monitored for water content using the Karl Fischer method.

**Instruments.** Visible and ultraviolet spectra were recorded with a Cary 14 recording spectrophotometer. All kinetic runs were made on a stopped-flow instrument manufactured by the Durrum Instrument Co. The temperature control on the stopped-flow apparatus was accurate to ±0.2°. The stopped-flow instrument provided a continuous-analog voltage signal from the photomultiplier tube and also provided an external trigger. The external trigger was usually used to trigger a storage oscilloscope but could be used to initiate any data storage system. Figure 1 is a schematic representation of the data storage device used in conjunction with the stopped-flow instrument. In the system diagrammed in Figure 1, the external trigger is used to

---

(17) L. S. Frankel, *Inorg. Chem.*, **10**, 2360 (1971).

(18) M. L. Yount and S. S. Zumdahl, *Inorg. Chem.*, **10**, 1212 (1971).

(19) D. G. Howard, *Diss. Abstr. B*, **31**, 4561 (1971).

(20) J. P. Hunt, F. Klanberg, and H. W. Dodgen, *Inorg. Chem.*, **2**, 478 (1963).

(21) A. L. Van Geet, *Inorg. Chem.*, **7**, 2026 (1968).

(22) H. Glaeser, H. W. Dodgen, and J. P. Hunt, *Inorg. Chem.*, **4**, 206 (1965).

(23) W. L. Rice and B. B. Wayland, *Inorg. Chem.*, **7**, 1040 (1968).

(24) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 2686 (1964).

(25) L. S. Frankel, *Inorg. Chem.*, **10**, 814 (1971).

(26) S. Thomas and W. L. Reynolds, *J. Chem. Phys.*, **46**, 4164 (1967).

(27) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 2579 (1969).

(28) L. S. Frankel, *Chem. Commun.*, 1254 (1969).

(29) S. Blackstaffe and R. A. Dwek, *Mol. Phys.*, **15**, 279 (1968).

(30) L. L. Rusnak and R. P. Jordan, *Inorg. Chem.*, **10**, 2686 (1971).

(31) R. W. Kluiber, R. Kukla, and W. D. Horrocks, Jr., *Inorg. Chem.*, **9**, 1319 (1970).

(32) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. D*, 599 (1969).

(33) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2191 (1971).

(34) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2198 (1971).

(35) H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, 2207 (1971).

(36) H. P. Bennetto, *J. Chem. Soc. A*, 2211 (1971).

(37) G. Macri and S. Petrucci, *Inorg. Chem.*, **9**, 1009 (1970).

(38) C. T. Lin and J. L. Bear, *J. Phys. Chem.*, **75**, 3705 (1971).

(39) C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, **9**, 2346 (1970).

(40) R. G. Pearson and P. Ellgen, *Inorg. Chem.*, **6**, 1379 (1967).

(41) W. J. MacKellar and D. B. Rorabacher, *J. Amer. Chem. Soc.*, **93**, 4379 (1971).

(42) M. R. Rosenthal and R. S. Drago, *Inorg. Chem.*, **4**, 840 (1965).

(43) R. W. Faessinger and E. W. Brown, *J. Amer. Chem. Soc.*, **73**, 4606 (1951).

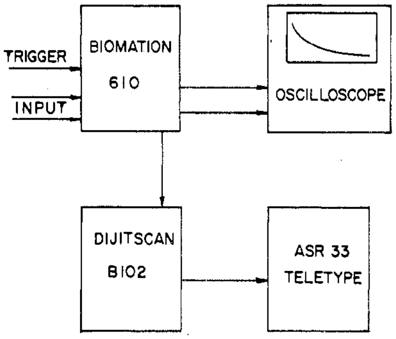


**Figure 1.** Electronic data gathering system.

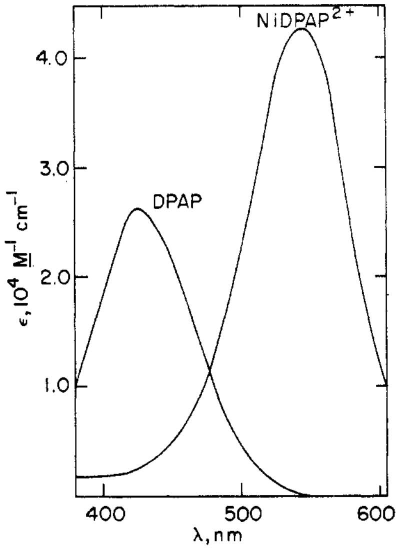


**Figure 2.** Spectra of DPAP and NiDPAP$^{2+}$ in 0.125 *M* pyridine in nitromethane.

trigger the Biomation 610 transient recorded (Biomation Corp., Palo Alto, Calif.). The Biomation 610 converts the analog data to digital form and stores the data. The Biomation 610 has its own time base generator and can convert and store 100 points in anywhere from 10 μsec to 5 sec. The memory section of this recorder is a constantly circulating 128-word, 6-bit MOS shift register memory. Once the data have been received and converted by the Biomation 610, the data are simultaneously available in several forms. First, the digitalized signal is converted to an analog signal with the aid of a smoothed digital to analog converter. In this form, the data are transferred to an oscilloscope and/or strip chart recorder. The digitalized data are available for output to a computer. An off-line technique is used to transfer the data to a PDP-8/I computer (Digital Equipment Corp., Maynard, Mass.) with an 8K work memory for analysis. The digitalized data from the Biomation 610 are transferred by means of a Model B102 Dijitscan interface (Pivan Data Systems, Chicago, Ill.) to an ASR 33 teletype (Teletype Corp.) which punches that data serial by bit and word in ASCII code on paper tape.

**Treatment of Data.** The stoichiometry of the complexes formed was determined by the method of Job.[44,45] In all cases the net reaction was

$$Ni^{2+} + DPAP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} NiDPAP^{2+} \qquad (3)$$

where $k_3$ ($M^{-1}$ sec$^{-1}$) and $k_{-3}$ (sec$^{-1}$) are rate constants for the forward and reverse reactions. The solvent and nature of the solvated cation are not included at this point in the discussion for simplicity. When the solvent was pyridine or 6.20 *M* pyridine in nitromethane, the observed pseudo-first-order rate constant ($k_{obsd}$ where $[Ni^{2+}] >> [DPAP]$) was equal to $k_3[Ni^{2+}] + k_{-3}$. This indicates that reversible first-order or pseudo-first-order kinetics are obeyed. Plots of $k_{obsd}$ *vs.* $[Ni^{2+}]$ yielded $k_3$ as the slope and $k_{-3}$ as the intercept. When the solvent was 0.125 *M* pyridine in nitromethane, the equilibrium position in reaction 3 was far on the side of NiDPAP$^{2+}$ and consequently the intercept $k_{-3}$ was zero within experimental error. In all cases, $k_{obsd}$ was independent of wavelength and kinetic runs were made at 550 nm. The slopes and intercepts of the best straight lines for plots were determined using a least-squares computer program. Activation parameters were calculated using the Eyring formalism.

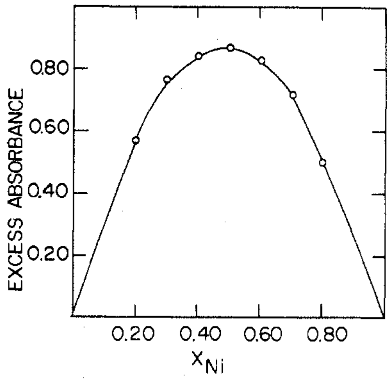


**Figure 3.** Job's plot for the Ni(II)-DPAP reaction in 6.20 *M* pyridine in nitromethane.

## Results

Figure 2 is a reproduction of the visible spectra of DPAP and the NiDPAP$^{2+}$ complex in 0.125 *M* pyridine in nitromethane. The free ligand has an extinction coefficient at 426 nm of $2.6 \times 10^4$ $M^{-1}$ cm$^{-1}$. In 6.2 *M* pyridine in nitromethane, the extinction coefficient at 428 nm is $2.3 \times 10^4$ $M^{-1}$ cm$^{-1}$. The spectrum of DPAP in pyridine has a maximum at 430 nm with an extinction coefficient of $2.3 \times 10^4$ $M^{-1}$ cm$^{-1}$. The spectrum of DPAP obeys Beer's law in pyridine, 6.20 *M* pyridine in nitromethane, and 0.125 *M* pyridine in nitromethane but does not obey Beer's law in pyridine-nitromethane solvents containing less than 0.125 *M* pyridine.

The complex has an absorbance maximum at 555 nm in all solvents. In 0.125 *M* pyridine in nitromethane, the extinction coefficient is $4.2 \times 10^4$ $M^{-1}$ cm$^{-1}$. It was impossible to obtain a spectrum of the complex without interference from uncomplexed ligand in 6.20 *M* pyridine in nitromethane and in pyridine because of equilibrium and solubility limitations.

Figure 3 is a reproduction of the Job's plot for NiDPAP$^{2+}$ in 6.20 *M* pyridine in nitromethane. The maximum at mole fraction of $Ni^{2+} = 0.50$ indicates that the ratio of Ni(II) to DPAP in NiDPAP$^{2+}$ complex is 1:1. Similar plots for the Ni(II)-DPAP reaction in pyridine and in 0.125 *M* pyridine in nitromethane show the complexes to be 1:1 complexes.

The kinetics of the Ni(II)-DPAP complexation reaction in pyridine, in 6.20 *M* pyridine in nitromethane, and in 0.125 *M* pyridine in nitromethane were studied by recording the change in absorbance at 555 nm as a function of time. The concentration of Ni(II) was at least 10 times the concentration of the DPAP in every kinetic run. All the kinetic plots are first-order over at least 4 half-lives. The pseudo-first-order rate constants from these plots were independent of the DPAP concentration.

Table I contains the kinetic data for the reaction of Ni(II) with DPAP in 6.20 *M* pyridine in nitromethane. These data are consistent with the rate law

$$\frac{d[NiDPAP^{2+}]}{dt} = k_3[Ni^{2+}][DPAP] - k_{-3}[NiDPAP^{2+}]$$

For any experiment in which $[Ni^{2+}] >> [DPAP]$, the observed rate constant is equal to $k_3[Ni^{2+}] + k_{-3}$. Figure 4 is a plot of $k_{obsd}$ *vs.* $[Ni^{2+}]$ for the data tabulated in Table I.

---

(44) W. R. Carmody, *J. Chem. Educ.*, **41**, 615 (1964).

(45) W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, **63**, 437 (1941).

**Table I.** Kinetics of the Ni(II)-DPAP Reaction in 6.20 *M* Pyridine in Nitromethane

| $10^3[Ni^{2+}]$, *M* | $10^6$[DPAP], *M* | Temp, °C | $[H_2O]$, *M* | $k_{obsd}$,[a] $sec^{-1}$ |
|---|---|---|---|---|
| 14.0 | 4.0 | 9.5 | 0.030 | 30.7 |
| 8.0 | 4.0 | 9.5 | 0.030 | 18.5 |
| 2.0 | 4.0 | 9.5 | 0.030 | 12.1 |
| 17.0 | 4.0 | 9.5 | 0.030 | 37.1 |
| 13.0 | 4.0 | 9.5 | 0.030 | 29.3 |
| 2.0 | 4.0 | 20.0 | 0.030 | 22.1 |
| 8.0 | 4.0 | 20.0 | 0.030 | 44.4 |
| 14.0 | 4.0 | 20.0 | 0.030 | 64.5 |
| 5.0 | 4.0 | 20.0 | 0.030 | 27.6 |
| 13.0 | 4.0 | 20.0 | 0.030 | 59.1 |
| 17.0 | 4.0 | 20.0 | 0.030 | 74.5 |
| 11.0 | 2.0 | 20.0 | 0.030 | 50.4 |
| 3.0 | 8.0 | 20.0 | 0.030 | 26.1 |
| 10.0 | 4.0 | 20.0 | 0.025 | 48.3 |
| 10.0 | 4.0 | 20.0 | 0.050 | 46.6 |
| 10.0 | 4.0 | 20.0 | 0.075 | 44.4 |
| 17.0 | 4.0 | 32.0 | 0.030 | 166 |
| 13.0 | 4.0 | 32.0 | 0.030 | 132 |
| 9.0 | 4.0 | 32.0 | 0.030 | 90.1 |
| 5.0 | 4.0 | 32.0 | 0.030 | 68.6 |
| 1.0 | 4.0 | 32.0 | 0.030 | 39.7 |
| 3.0 | 4.0 | 32.0 | 0.030 | 53.9 |
| 11.0 | 4.0 | 32.0 | 0.030 | 106 |
| 15.0 | 4.0 | 32.0 | 0.030 | 152 |

[a] Average of at least three experiments, ±5%.

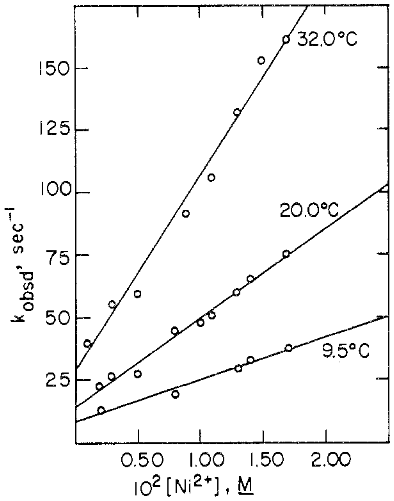


**Figure 4.** Plot of $k_{obsd}$ *vs.* $[Ni^{2+}]$ in 6.20 *M* pyridine in nitromethane at various temperatures.

**Table II.** Kinetics of the Ni(II)-DPAP Reaction in 0.125 *M* Pyridine in Nitromethane

| $10^4[Ni^{2+}]$, *M* | $10^6$[DPAP], *M* | Temp, °C | $[H_2O]$, *M* | $k_{obsd}$,[a] $sec^{-1}$ |
|---|---|---|---|---|
| 0.20 | 1.9 | 20.5 | 0.008 | 4.0 |
| 0.40 | 1.9 | 20.5 | 0.008 | 8.0 |
| 0.80 | 1.9 | 20.5 | 0.008 | 15.7 |
| 1.43 | 1.9 | 20.5 | 0.008 | 37.6 |
| 2.05 | 1.9 | 20.5 | 0.008 | 56.5 |
| 2.65 | 1.9 | 20.5 | 0.008 | 77.5 |
| 0.40 | 1.9 | 31.5 | 0.008 | 17.2 |
| 1.43 | 1.9 | 31.5 | 0.008 | 63.8 |
| 2.05 | 1.9 | 31.5 | 0.008 | 101 |
| 2.65 | 1.9 | 31.5 | 0.008 | 124 |
| 0.22 | 2.0 | 42.0 | 0.02 | 5.4 |
| 0.70 | 2.0 | 42.0 | 0.02 | 59.1 |
| 1.19 | 2.0 | 42.0 | 0.02 | 101 |
| 1.68 | 2.0 | 42.0 | 0.02 | 143 |
| 2.16 | 2.0 | 42.0 | 0.02 | 173 |

[a] Average of three experiments, ±10%.

**Table III.** Kinetics of the Ni(II)-DPAP Reaction in Pyridine

| $10^4[Ni^{2+}]$, *M* | $10^5$[DPAP], *M* | Temp, °C | $[H_2O]$, *M* | $k_{obsd}$,[a] $sec^{-1}$ |
|---|---|---|---|---|
| 2.0 | 0.75 | 16.0 | 0.003 | 7.2 |
| 4.0 | 0.75 | 16.0 | 0.003 | 9.7 |
| 6.0 | 0.75 | 16.0 | 0.003 | 10.8 |
| 8.0 | 0.75 | 16.0 | 0.003 | 12.4 |
| 10.0 | 0.75 | 16.0 | 0.003 | 14.2 |
| 2.0 | 1.00 | 20.8 | 0.004 | 13.0 |
| 4.0 | 1.00 | 20.8 | 0.004 | 15.8 |
| 6.0 | 1.00 | 20.8 | 0.004 | 17.0 |
| 8.0 | 1.00 | 20.8 | 0.004 | 20.1 |
| 10.0 | 1.00 | 20.8 | 0.004 | 23.5 |
| 2.0 | 0.75 | 25.5 | 0.005 | 15.9 |
| 4.0 | 0.75 | 25.5 | 0.005 | 18.9 |
| 6.0 | 0.75 | 25.5 | 0.005 | 21.6 |
| 8.0 | 0.75 | 25.5 | 0.005 | 28.7 |
| 10.0 | 0.75 | 25.5 | 0.005 | 30.0 |
| 2.0 | 1.00 | 30.5 | 0.004 | 24.8 |
| 4.0 | 1.00 | 30.5 | 0.004 | 28.6 |
| 6.0 | 1.00 | 30.5 | 0.004 | 34.3 |
| 8.0 | 1.00 | 30.5 | 0.004 | 36.9 |
| 10.0 | 1.00 | 30.5 | 0.004 | 48.0 |
| 2.0 | 0.75 | 36.0 | 0.005 | 39.2 |
| 4.0 | 0.75 | 36.0 | 0.005 | 47.6 |
| 6.0 | 0.75 | 36.0 | 0.005 | 58.7 |
| 8.0 | 0.75 | 36.0 | 0.005 | 64.5 |
| 10.0 | 0.75 | 36.0 | 0.005 | 71.6 |
| 6.0 | 0.38 | 36.0 | 0.005 | 57.6 |
| 6.0 | 0.38 | 36.0 | 0.025 | 52.3 |
| 6.0 | 0.38 | 36.0 | 0.045 | 47.6 |

[a] Average of three experiments, ± 5%.

**Table IV.** Rate Constants for the Ni(II)-DPAP Complexation Reaction

| Solvent | Temp, °C | $k_3$, $M^{-1}$ $sec^{-1}$ | $k_{-3}$, $sec^{-1}$ |
|---|---|---|---|
| 6.20 *M* pyridine in nitromethane | 9.5 | (1.7 ± 0.1) × $10^3$ | 7 ± 1 |
| | 20.0 | (3.5 ± 0.1) × $10^3$ | 14 ± 1 |
| | 32.0 | (7.9 ± 0.4) × $10^3$ | 28 ± 3 |
| 0.125 *M* pyridine in nitromethane | 20.5 | (2.7 ± 0.3) × $10^5$ | |
| | 31.5 | (4.8 ± 0.4) × $10^5$ | |
| | 42.0 | (8.3 ± 0.5) × $10^5$ | |
| Pyridine | 16.0 | (8.4 ± 0.3) × $10^3$ | 5.8 ± 0.3 |
| | 20.8 | (1.3 ± 0.1) × $10^4$ | 10.3 ± 0.5 |
| | 25.5 | (1.9 ± 0.2) × $10^4$ | 12 ± 1 |
| | 30.5 | (2.7 ± 0.3) × $10^4$ | 18 ± 2 |
| | 36.0 | (4.1 ± 0.2) × $10^4$ | 31.8 ± 0.3 |

The kinetics of the Ni(II)-DPAP complexation reaction in 0.125 *M* pyridine in nitromethane (Table II) are consistent with the rate law

$$\frac{d[NiDPAP^{2+}]}{dt} = k_3[Ni^{2+}][DPAP]$$

The kinetic data for the Ni(II)-DPAP complexation reaction in pyridine (Table III) are also consistent with the first rate law. All the kinetic plots are first-order over at least 4 half-lives when the $[Ni^{2+}] >> [DPAP]$.

Table IV contains the rate constants determined at several temperatures for the three kinetic systems studied. The activation parameters appear in Table V along with the rate constants at 25°.

The rate constants showed very little dependence on the concentration of water. An increase in the $[H_2O]$ from 0.025 to 0.075 *M* decreased the rate constants by about 10% for the Ni(II)-DPAP reaction in 6.20 *M* pyridine in nitromethane. The rate constants for the Ni(II)-DPAP reaction in pyridine decreased by 15% when the $[H_2O]$ was increased from 0.005 to 0.045 *M*. There was no change in the rate constants for the Ni(II)-DPAP reaction in 0.125 *M* pyridine in nitromethane between 0.002 and 0.008 *M* $H_2O$.

**Table V.** Activation Parameters for the Ni(II)-DPAP Complexation Reaction

| | 6.20 *M* pyridine in nitromethane | 0.125 *M* pyridine in nitromethane | Pyridine |
|---|---|---|---|
| $k_3(25°)$, $M^{-1}$ sec$^{-1}$ | $5.0 \times 10^3$ | $3.5 \times 10^5$ | $1.7 \times 10^4$ |
| $\Delta H_3^{\ddagger}$, kcal/mol | 11.1 ± 0.6 | 9 ± 1 | 13.7 ± 0.5 |
| $\Delta S_3^{\ddagger}$, eu | −4 ± 2 | −3 ± 4 | 6 ± 2 |
| $k_{-3}(25°)$, sec$^{-1}$ | 20 | | 12 |
| $\Delta H_{-3}^{\ddagger}$, kcal/mol | 10 ± 3 | | 15 ± 3 |
| $\Delta S_{-3}^{\ddagger}$, eu | −21 ± 7 | | −4 ± 8 |

## Discussion

Among others, Rosenthal and Drago[42] and Sharp, *et al.*,[46] have shown that hexacoordinate pyridinenickel(II) salts cannot be prepared in the solid state. Only complexes having the general formula $Ni(py)_4X_2$ can be prepared. If $X^- = BF_4^-$ or $ClO_4^-$, Ni(II) can be solvated in pyridine-nitromethane solutions as $Ni(py)_5nm^{2+}$ or $Ni(py)_6^{2+}$ according to the equilibrium

$$Ni(py)_5nm^{2+} + py \overset{K_4}{\rightleftharpoons} Ni(py)_6^{2+} + nm \qquad (4)$$

The equilibrium concentration quotient $[Ni(py)_6^{2+}]/[Ni(py)_5nm^{2+}][py]$ is 8.9 $M^{-1}$ at 28°[42] assuming nitromethane is the solvent. Therefore, 0.125 *M* pyridine in nitromethane contains 47.2% $Ni(py)_5nm^{2+}$ and 52.8% $Ni(py)_6^{2+}$, and 6.20 *M* pyridine in nitromethane contains 1.8% $Ni(py)_5nm^{2+}$ and 98.2% $Ni(py)_6^{2+}$. In pyridine, $Ni(py)_4(BF_4)_2$ dissolves to form $Ni(py)_6^{2+}$.[47] Our observations suggest that $K_4$ is nearly independent of temperature over the range used in this study.

Because solutions of DPAP in nitromethane containing less than 0.125 *M* pyridine do not obey Beer's law, a kinetic study of the Ni(II)-DPAP reaction in a nitromethane solvent with less than 0.125 *M* added pyridine was not feasible. The kinetics of the Ni(II)-DPAP complexation reaction in nitromethane containing 0.0125 *M* pyridine were not reproducible and indicated a second-order dependence for the ligand. A dimerization process, which is perhaps dependent on the water concentration, might account for these observations.

DPAP has been shown to function as a bidentate chelate.[48] Since the spectra of metal complexes in which DPAP is a chelate are similar to the spectrum of $NiDPAP^{2+}$ in pyridine and pyridine-nitromethane mixtures, DPAP is probably coordinated to Ni(II) through the pyridine nitrogen and one of nitrogens in the azo linkage.

Three mechanisms have been proposed to describe metal ion complexation reactions. Each of these mechanisms is briefly described and the expected behavior is compared with the data. The first mechanism was proposed by Eigen and Wilkins[49] to explain the correlation of ligand substitution rate constants with water-exchange rate constants for solvated metal cations. This mechanism is represented by the reactions

$$M(S)_m^{2+} + L \overset{K_{5a}}{\rightleftharpoons} M(S)_m^{2+},L \qquad (5a)$$

$$M(S)_m^{2+},L \xrightarrow{k_{5b}} M(S)_{m-n}L^{2+} + nS \qquad (5b)$$

The rate-determining step in the mechanism is the elimination of a solvent molecule from the first solvation sphere of the metal ion. When reaction 5a is a preequilibrium with respect to reaction 5b, the rate constant for complexation is equal to the ion-pairing constant, $K_{5a}$, multiplied by the rate constant for solvent exchange, $k_{5b}$. For a bidentate ligand such as DPAP, the rate-determining step need not be the elimination of the first solvent molecule from the coordination sphere.[2] The reaction could be sterically controlled, in which case the rate-determining step is the formation of the chelate and not the elimination of the first solvent molecule. The rate constant for sterically controlled substitution reactions cannot be predicted from the ion-pairing constant and the rate constant for solvent exchange. More kinetic data for complexation reactions of known monodentate and known bidentate ligands with Ni(II) in pyridine and in pyridine-nitromethane mixtures are needed to determine if DPAP reactions are sterically controlled or normal substitution reactions.

Some statements can be made about the applicability of the Eigen-Wilkins mechanism to Ni(II)-DPAP reactions in pyridine and in pyridine-nitromethane mixtures if normal substitution is assumed. Since the rate constants for the reactions

$$Ni(py)_6^{2+} + py^* \rightleftharpoons Ni(py)_5py^{*2+} + py$$

$$Ni(py)_5nm^{2+} + nm^* \rightleftharpoons Ni(py)_5nm^{*2+} + nm$$

have not been measured, it is difficult to test the applicability of the Eigen-Wilkins mechanism. However, some statements can be made concerning the applicability of this mechanism to the reported reactions. The average lifetime of pyridines on $Ni(py)_4Cl_2$ at 25° is $(4.4 \pm 0.6) \times 10^{-6}$ sec.[19] The rate constant for solvent exchange is then $2.3 \times 10^5$ sec$^{-1}$. The coordinated chlorides probably labilize the coordinated pyridine molecules in $Ni(py)_4Cl_2$. Therefore, $2.3 \times 10^5$ sec$^{-1}$ should be an upper limit on the rate constant for pyridine exchange in $Ni(py)_6^{2+}$.

The ion-pairing constant for the reaction of a neutral ligand with $Ni(py)_6^{2+}$ can be calculated using the equation[2]

$$\text{ion-pairing constant} = 4\pi Na^3/3000$$

where *a* is the distance of closest approach between the ligand and metal. A good estimate of *a* for $Ni(py)_6^{2+}$ is the sum of the Ni(II) ionic radius[50] and the length of a pyridine molecule. The structure of pyridine has been determined.[51] The length of a pyridine molecule is the sum of the van der Waals radii[52] of nitrogen and hydrogen plus the distance between the nitrogen nucleus and the para hydrogen nucleus. If 7.3 Å is used as the estimate for *a*, the ion-pairing constant for the reaction of $Ni(py)_6^{2+}$ with a neutral molecule is 1. Therefore, the first-order rate constant for solvent exchange should be numerically equal to the second-order rate constant for complexation of $Ni(py)_6^{2+}$ with a neutral ligand. The upper limit for the solvent-exchange rate constant at 25° is larger than the rate constants for complexation of $Ni(py)_6^{2+}$ either in pyridine or in 6.2 *M* pyridine in nitromethane. It is impossible to exclude the Eigen-Wilkins mechanism simply because the calculated upper limit second-order rate constant is larger than that observed. Application of the Eigen-Wilkins mechanism to the results in Table V would require that DPAP react much faster with $Ni(py)_5nm^{2+}$ than with $Ni(py)_6^{2+}$. It is likely that the coordinated nitromethane of $Ni(py)_5nm^{2+}$ exchanges more rapidly than the coordinated pyridines in both $Ni(py)_5nm^{2+}$ and $Ni(py)_6^{2+}$.[41] If one con-

---

(46) D. H. Brown, R. H. Nuttall, J. McAvoy, and D. W. A. Sharp, *J. Chem. Soc. A*, 892 (1966).

(47) R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970).

(48) I. M. Klotz and W. C. L. Ming, *J. Amer. Chem. Soc.*, **75**, 4159 (1953).

(49) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, No. 49, 55 (1965).

(50) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 49th ed., Chemical Rubber Co., Cleveland, Ohio, 1968, p F152.

(51) B. Bak, L. Hansen-Hygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, **2**, 361 (1958).

(52) Reference 50, p D107.

siders that only $Ni(py)_5nm^{2+}$ reacts with DPAP, corrected values of the rate constant for the formation of the $Ni(DPAP)^{2+}$ can be calculated by dividing $k_3$ from Table V for 6.20 *M* pyridine- and 0.125 *M* pyridine-nitromethane solutions by 0.018 and 0.472, respectively. These values are $2.8 \times 10^5$ and $7.4 \times 10^5$ $M^{-1}$ $sec^{-1}$, respectively. Since the ion-pairing constants vary slightly with solvent, the agreement between the observed rate constants is fairly good and it is not possible to discount the Eigen-Wilkins mechanism on the basis of this calculation. The proposal that the Ni(II)-DPAP reaction proceeds by the reaction of $Ni(py)_5nm^{2+}$ in both solvent systems is weakened by the fact that the enthalpies of activation are not the same, 11.1 ± 0.6 and 9 ± 1 kcal/mol in 6.2 and 0.125 *M* pyridine, respectively.

The second mechanism, which has been postulated for $Ni(DMSO)_6{}^{2+}$ complexation reactions,[39] is represented by the mechanism

$$Ni(DMSO)_6{}^{2+} \rightleftarrows Ni(DMSO)_5{}^{2+} + DMSO$$

$$Ni(DMSO)_5{}^{2+} + L \rightarrow Ni(DMSO)_5L^{2+}$$

The activation entropies for reactions conforming to this mechanism should be large positive numbers owing to the dominant contribution to the entropy from the formation of a five-coordinate intermediate. The entropies of activation for the complexation reactions listed in Table V are not large positive numbers. If $Ni(py)_5nm^{2+}$ is the primary Ni(II) reactant and the process

$$Ni(py)_5nm^{2+} \rightleftarrows Ni(py)_5{}^{2+} + nm$$

results in the formation of the five-coordinate intermediate, the formation of this intermediate should be enhanced by lowering the concentration of nitromethane. In fact the rate constant in 0.125 *M* pyridine is larger than in 6.20 *M* pyridine, which is contrary to the expected observation. However, if a process

$$Ni(py)_6{}^{2+} \rightleftarrows Ni(py)_5{}^{2+} + py$$

produces the intermediate, the rate constant for the formation of the complex corrected for the concentration of $Ni(py)_6{}^{2+}$ present should increase as the solvent changes from pyridine to 6.20 *M* pyridine to 0.125 *M* pyridine. The rate constants in this order are $1.7 \times 10^4$, $5.0 \times 10^3$, and $6 \times 10^5$ $M^{-1}$ $sec^{-1}$, which is again contrary to the expected behavior. Thus, a mechanism involving a five-coordinate intermediate appears unlikely.

The third mechanistic interpretation of metal ion complexation reactions has been proposed by Bennetto and Caldin.[33,34] This mechanism adequately describes solvent and ligand substitution reactions in water and in nonaqueous solvents. The Eigen-Wilkins mechanism is only rigidly applicable to complexation reactions in water.[33] Bennetto and Caldin[33,34] proposed that three different solvent environments play important roles in the complexation process. The Eigen-Wilkins mechanism implies that the free energy of activation for a complexation reaction is due to the breaking of a metal-solvent bond and to the free energy of formation for the ion pair. In the Bennetto-Caldin model for an ion plus molecule reaction, the breaking of a metal-solvent bond and the changes in the surrounding solvent structure contribute to the free energy of activation. The three solvent regions in the Bennetto-Caldin model are the primary solvation sphere of the metal cation, the bulk solvent, and the intermediate disordered region between the bulk solvent and the primary solvation sphere. Movement of a solvent molecule or ligand molecule from one region to another region is accompanied by concerted movements of other solvent molecules in other regions.

Bennetto and Caldin showed that there is a linear correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for all Ni(II) solvent-exchange and ligand-substitution reactions. Figure 5 is a reproduction of part of this plot.[34] The points marked with squares and error flags represent activation parameters determined in this work. The complexation studies reported in this work fit the Bennetto-Caldin model reasonably well. The linear correlation of $\Delta H^\ddagger$ values with $\Delta S^\ddagger$ values reported here is a line parallel to but displaced from the line determined by Bennetto and Caldin. (See Figure 5.) This displacement might be due to characteristics which are specific to pyridine and nitromethane but which are not present in the solvents studied by Bennetto and Caldin. DPAP is quite different from the bipyridyl ligand which was used by Bennetto and Caldin.[33,34] Bipyridyl would be expected to interact with solvent molecules differently from the way in which DPAP interacts with solvent molecules. This ligand difference may explain why the line defined by the activation parameters reported in this paper does not coincide with the line deter-

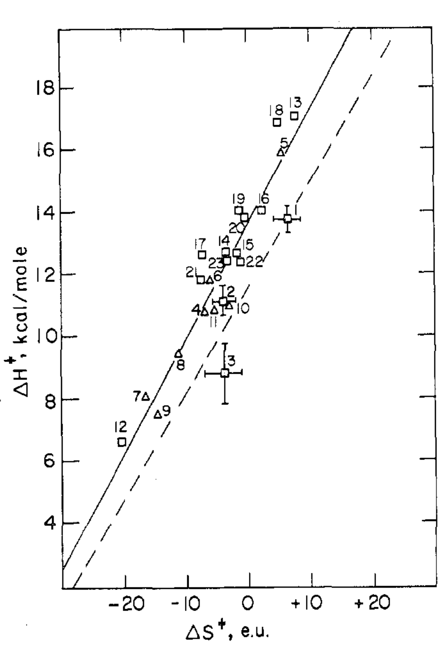


**Figure 5.** Plot of $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ for Ni(II) exchange (△) and complexation (□) reactions.

| Reaction | Solvent | Ref |
|---|---|---|
| 1. $Ni(py)_6{}^{2+}$ + DPAP | py | This work |
| 2. $Ni(py)_6{}^{2+}$ and $Ni(py)_5nm^{2+}$ + DPAP | 6.20 *M* py in nm | This work |
| 3. $Ni(py)_6{}^{2+}$ and $Ni(py)_5nm^{2+}$ + DPAP | 0.125 *M* py in nm | This work |
| 4. $Ni(H_2O)_6{}^{2+}$ + $H_2O$ | $H_2O$ | 5 |
| 5. $Ni(CH_3OH)_6{}^{2+}$ + $CH_3OH$ | $CH_3OH$ | 24 |
| 6. $Ni(CH_3CN)_6{}^{2+}$ + $CH_3CN$ | $CH_3CN$ | 14 |
| 7. $Ni(DMSO)_6{}^{2+}$ + DMSO | DMSO | 26 |
| 8. $Ni(DMF)_6{}^{2+}$ + DMF | DMF | 16 |
| 9. $Ni(DMMP)_6{}^{2+}$ + DMMP | DMMP | 10 |
| 10. $Ni(NH_3)_6{}^{2+}$ + $NH_3$ | $NH_3$ | 22 |
| 11. $Ni(EtOH)_6{}^{2+}$ + EtOH | EtOH | 9 |
| 12. $Ni(CH_3CN)_6{}^{2+}$ + bipy | $CH_3CN$ | 33 |
| 13. $Ni(MeOH)_6{}^{2+}$ + bipy | MeOH | 33 |
| 14. $Ni(DMF)_6{}^{2+}$ + bipy | DMF | 33 |
| 15. $Ni(H_2O)_6{}^{2+}$ + bipy | $H_2O$ | 33 |
| 16. $Ni(D_2O)_6{}^{2+}$ + bipy | $D_2O$ | 33 |
| 17. $Ni(DMSO)_6{}^{2+}$ + bipy | DMSO | 33 |
| 18. $Ni(Et(gly))_6{}^{2+}$ + bipy | Et(gly) | 33 |
| 19. $Ni(DMMP)_6{}^{2+}$ + bipy | DMMP | 33 |
| 20. $Ni(H_2O)_6{}^{2+}$ + terpy | $H_2O$ | 33 |
| 21. $Ni(DMSO)_6{}^{2+}$ + terpy | DMSO | 33 |
| 22. $Ni(H_2O)_6{}^{2+}$ + 4,4'-$Me_2$bipy | $H_2O$ | 33 |
| 23. $Ni(H_2O)_6{}^{2+}$ + 4,4'-$Cl_2$bipy | $H_2O$ | 33 |

mined by Bennetto and Caldin. Furthermore, the Ni(II)-py bond could have a different energy from other Ni-solvent bonds. This energy difference could account for the apparent displacement of the activation parameter plot. One of the premises of the Bennetto-Caldin theory is that the enthalpy for the solvent-metal dissociative step is much the same from one solvent to another. This would seem to indicate that the composition of the primary solvation sphere of the metal ion is of little consequence in determining the overall activation parameters for the complexation reaction. Instead, the bulk solvent composition is probably very important. This model requires that many solvent molecules be involved in the activated complex. The concerted movements of these solvent molecules influence the activation parameters and the rate constants for complexation reactions.[34] Bennetto and Caldin proposed that the enthalpy of the metal-solvent dissociation step is much the same from one solvent to another and that the entropy change is small for this step. Any differences in activation parameters and in rate constants for metal ion complexation reactions in different solvents are a result of solvent properties.[34] Consequently, the different activation parameters for the Ni(II)-DPAP reaction in pyridine, in 6.20 *M* pyridine in nitromethane, and in 0.125 *M* pyridine in nitromethane can be interpreted using the Bennetto-Caldin model. The bulk solvent characteristics could account for the different activation parameters. The nitro group in nitromethane is free to rotate around the carbon-nitrogen bond, $\Delta H_{\mathrm{rot}} = 0$.[53] Nitromethane molecules are thus able to reorient quite easily while pyridine molecules are only able to reorient through motion of the entire molecule. The enthalpy and entropy of activation for a metal ion complexation reaction in solvents containing large amounts of pyridine should be higher than the corresponding activation parameters for the same reaction in solvents containing large amounts of nitromethane because pyridine is "stiffer" than nitromethane. The experimental values are in agreement with the predicted results.

The overall results of this work are consistent with the mechanism proposed by Bennetto and Caldin. The results do not exclude the Eigen-Wilkins mechanism, but a mechanism involving a five-coordinate intermediate is ruled out. The five-coordinate intermediate mechanism is not applicable to the reactions reported in this work for two reasons. First, the activation parameters for the reaction do not conform to those expected for the formation of a five-coordinate intermediate. Second, the solvent effects on the observed rate constants are not those expected for the formation of the five-coordinate intermediate $\mathrm{Ni(py)_5}^{2+}$ from $\mathrm{Ni(py)_5nm}^{2+}$ or $\mathrm{Ni(py)_6}^{2+}$. The applicability of the Eigen-Wilkins mechanism cannot be evaluated without a better knowledge of solvent-exchange rate constants for $\mathrm{Ni(py)_6}^{2+}$ and $\mathrm{Ni(py)_5nm}^{2+}$. The bimolecular rate constant for the reaction of $\mathrm{Ni(py)_6}^{2+}$ with DPAP is less than the upper limit established for the rate constant for pyridine exchange at $\mathrm{Ni(py)_6}^{2+}$.[19] The Bennetto-Caldin model is a reasonable mechanism for the Ni(II) complexation reactions studied in this work. The variations in activation parameters for these reactions can be fit into the general relationship[34] of $\Delta H^\ddagger$ to $\Delta S^\ddagger$ proposed for this mechanism.

**Registry No.** $\mathrm{Ni(py)_4(BF_4)_2}$, 15530-21-9; DPAP, 38894-49-4; $\mathrm{NiDPAP^{2+}}$, 38894-50-7; $\mathrm{Ni(py)_6}^{2+}$, 20037-72-3; $\mathrm{Ni(py)_5nm}^{2+}$, 38894-52-9.

**Acknowledgment.** The authors acknowledge support of this work through a grant (PRF-2177-A3,5) from the Petroleum Research Fund administered by the American Chemical Society. H. L. F. was the recipient of an NDEA fellowship and a University of California Regents fellowship during the course of this work.

[53] D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969, p 41.

---

Contribution from the Department of Chemistry,
Oregon State University, Corvallis, Oregon 97331

# Coordination and Oxidation-Reduction in Copper(I) and -(II) Chloride-Triethylphosphine-Triethylchlorophosphonium Chloride (Triethyldichlorophosphorane) Systems[1]

DARRELL D. AXTELL[2] and JOHN T. YOKE*

*Received November 27, 1972*

Triethylphosphine is oxidized by copper(II) chloride above −45°, according to the following equations: $\mathrm{(C_2H_5)_3P + 2CuCl_2 \rightarrow (C_2H_5)_3PCl^+[Cu_2Cl_3^-]}$; $(2n + 1)\mathrm{(C_2H_5)_3P + 2CuCl_2 \rightarrow (C_2H_5)_3PCl_2 + 2(CuCl}\cdot n\mathrm{P(C_2H_5)_3)}$, $n = 1, 3$. These products have been identified by comparison with complexes in copper(I) chloride-triethylphosphine-triethylchlorophosphonium chloride systems, using $^1$H and $^{31}$P nmr spectra, infrared spectra, and phase studies. Chlorocuprate(I) salts with the triethylchlorophosphonium cation are additional examples of room-temperature fused salts.

## Introduction

The reduction of copper(II) chloride by triethylphosphine was reported by Jensen[3] to give the known[4] copper(I) complex, $\mathrm{CuCl\cdot P(C_2H_5)_3}$, presumably tetrameric by analogy to the iodide.[5] The oxidation product has not been characterized, although tertiary phosphine oxides have been obtained

---

(1) Presented in part at the 27th Northwest Regional Meeting of the American Chemical Society, Corvallis, Oreg., June 1972. Taken from the Ph.D. dissertation of D. D. A., Oregon State University, 1973.

(2) NSF Trainee, 1967-1971.

(3) K. A. Jensen, *Z. Anorg. Allg. Chem.*, 229, 282 (1936).

(4) A. E. Arbuzov, *Zh. Russ. Fiz.-Khim. Obshchest.*, 38, 293 (1906).

(5) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1503 (1936).