

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO 80302

The Kinetics of the Exchange Reaction of 3-Picoline *N*-Oxide with Hexakis(3-picoline *N*-oxide)nickel(II)

BY MARK L. YOUNT AND STEVEN S. ZUMDAHL*

Received September 30, 1970

The exchange kinetics of 3-picoline *N*-oxide with hexakis(3-picoline *N*-oxide)nickel(II) have been studied in a solvent composed of 50% nitromethane-*d*₃ and 50% acetone-*d*₆ by volume. Kinetic parameters were obtained over the temperature region +50 to -60° by the use of nuclear magnetic resonance line width and complete line shape techniques. The concentration of free ligand was varied and the exchange rate was found to be independent of this concentration. Kinetic parameters obtained for Ni(3-*N*-picO)₆²⁺ are $1/\tau_M(25^\circ) = 5.4 \times 10^4 \text{ sec}^{-1}$, $\Delta H^\ddagger = 12.5 \pm 0.2 \text{ kcal/mol}$, and $\Delta S^\ddagger = 6.8 \pm 0.9 \text{ eu}$.

As part of a program designed to establish the mechanism¹⁻³ and to explore the factors^{4,5} such as ligand properties, solvent properties, and changes in crystal field stabilization energy which make potentially significant contributions to the kinetic parameters for the exchange reactions of octahedral complexes, we report here a study of the exchange of 3-picoline *N*-oxide (3-*N*-picO) with the corresponding octahedral Ni(II) complex in a solvent mixture composed of 50% nitromethane-*d*₃ and 50% acetone-*d*₆ by volume. To our knowledge this is the first detailed report on an exchange reaction of a purely octahedral complex under conditions where the free ligand concentration could be varied over a wide range.

The kinetic parameters have been obtained by both nmr line width and complete line shape techniques.

Experimental Section

Materials.—3-Picoline *N*-oxide was obtained from Aldrich Chemical Co., Inc., and was purified by several successive sublimations under vacuum. The absence of water was confirmed by infrared analysis. The complex [Ni(3-*N*-picO)₆](BF₄)₂ was prepared and purified by the methods of Herlocker, Drago, and Meek.⁶

Acetone-*d*₆ and nitromethane-*d*₃ were purchased from Mallinckrodt and Diaprep, Inc., respectively.

Solutions.—All solutions were prepared and handled in a drybox under a nitrogen atmosphere. In order to achieve the desired concentrations and still retain the ability to work at low temperatures, a solvent composed of 50% nitromethane-*d*₃ and 50% acetone-*d*₆ (by volume) was employed.

Nmr Spectra.—The nmr spectra were obtained using a Varian HA-100 spectrometer operated in the HA mode using benzene as the internal lock. The spectrometer is equipped with a standard temperature control system. Temperatures were obtained from the chemical shift of methanol below 45° and from ethylene glycol above 45°. Special efforts were taken to obtain symmetrical signals free of machine broadening.

Results

Electronic Spectra.—In order to establish the stability of the Ni(3-*N*-picO)₆²⁺ complex in the acetone-nitromethane solvent mixture the electronic spectrum was studied as a function of both the complex and the excess ligand concentrations. In the presence of excess ligand the complex gives a typical octahedral spectrum.⁶ Beer's law plots were made for the band at ~720 mμ (ε 11) in both nitromethane and in the 50:50 acetone-

nitromethane mixture. Linear plots passing through the origin were obtained for solutions containing 0.01–0.10 *M* complex where the ligand:complex concentration ratio was 10 or greater. Solutions where this ratio was less than 10 showed deviations from linearity presumably due to competition from the nitromethane for primary sphere coordination sites. All kinetic studies were made on solutions where the ligand:complex ratio was 10 or greater.

Nmr Studies.—In order to study the exchange kinetics of Ni(3-*N*-picO)₆²⁺ acetone-nitromethane solutions were made up in which the complex concentration was held constant at 0.10 *M* and the free ligand concentration was varied from 1.03 to 4.04 *M* in ~0.6 *M* increments. The nmr spectrum of the ligand methyl group was then studied at temperatures between +80 and -80°.

A plot of the log of the observed line width at half-height of the signal due to the ligand methyl protons, $(\Delta\nu_{1/2})_{\text{obsd}}$, vs. $10^3/T^\circ\text{K}$ for a typical solution is shown in Figure 1. (At temperatures below the coalescence point $(\Delta\nu_{1/2})_{\text{obsd}}$ represents the line width of the methyl signal for ligand molecules in the bulk solution.) Note that the variation of $\log(\Delta\nu_{1/2})_{\text{obsd}}$ is typical of that for a system where the ligand exchange is stopped at low temperatures and is in the fast-exchange limiting region⁷ at high temperatures. Specifically, for this complex ligand exchange is stopped below ~-60° and undergoes fast exchange above ~50°. Thus, between these temperatures the nmr signal shape is affected by the rate of ligand exchange and it is possible to get kinetic information in this region.

In order to obtain exchange rates (see below) using the line width method valid in the region near fast exchange or from the complete line shape method, the value of the chemical shift between methyl protons in the complexed and free ligand sites must be obtained at each temperature of interest in the exchange-controlled region. Since Ni(3-*N*-picO)₆²⁺ is a paramagnetic complex, large isotropic shifts, which should exhibit a marked temperature dependence, are expected for the complexed ligand protons. In order to ensure an accurate extrapolation into the exchange-controlled temperature region, values of the isotropic shift ($\Delta\nu$) have been obtained both in the region where exchange is stopped and in the fast-exchange limiting region. In the former temperature region $\Delta\nu$ can be measured directly. In the fast-exchange region the isotropic shift can be obtained from the equation⁷

$$\nu_{\text{obsd}} = P_M \nu_M + P_L \nu_L \quad (1)$$

where ν_{obsd} , ν_M , and ν_L are, respectively, the position of the observed methyl signal, the position of the signal due to methyl protons on the coordinated ligand in the absence of exchange, and the position of the methyl signal for ligand molecules in the bulk solvent (all referenced to the same internal standard). P_M and P_L are the mole fractions of coordinated and free ligand, respectively. In this study values of ν_M in the fast-exchange limiting region were calculated from eq 1 assuming that ν_L remains constant. The validity of this assumption is based on the fact that ν_L was observed to be constant for all solutions at all temperatures in the region where exchange is stopped.

(7) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., pp 218-225.

(1) For a review of much of the previous work see T. R. Stengle and C. H. Langford, *Coord. Chem. Rev.*, **2**, 349 (1967).

(2) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

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

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

(5) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 145.

(6) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

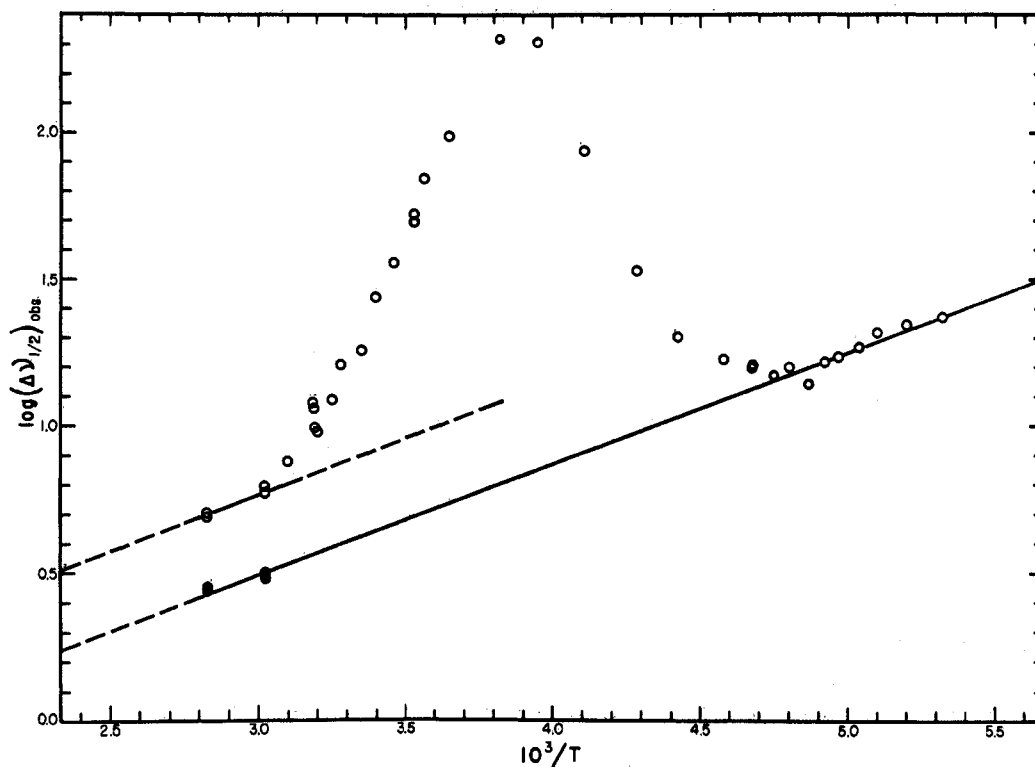


Figure 1.—Plot of the log of the observed line width for the ligand methyl protons vs. $10^3/T^\circ\text{K}$ for a solution containing 0.10 M complex and 1.03 molar excess of ligand. At temperatures below the coalescence point $(\Delta\nu_{1/2})_{\text{obs}}$ corresponds to the line width of the bulk ligand signal.

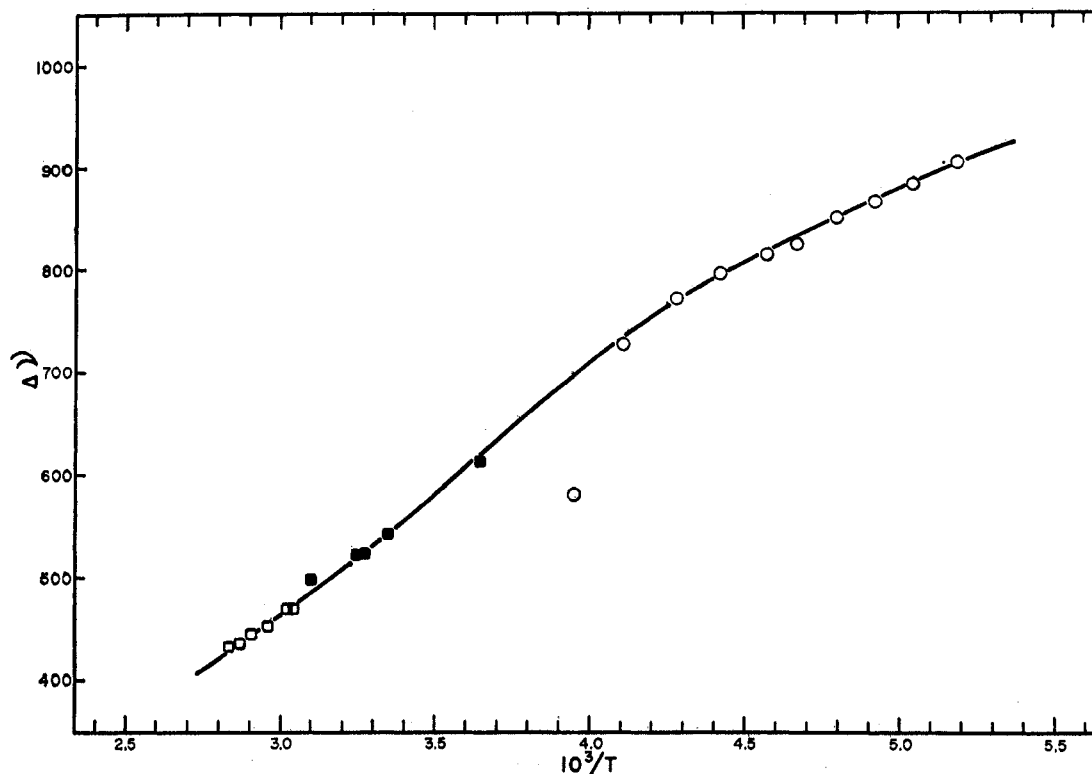


Figure 2.—Plot of the isotropic shift vs. $10^3/T^\circ\text{K}$ for a solution containing 0.10 M complex and 1.03 molar excess of ligand: \circ , measured directly from the spectrum; \square , obtained from eq 1; \blacksquare , obtained from the line shape calculations.

The isotropic shifts ($\nu_M - \nu_L$) for solutions containing 0.1 M $\text{Ni}(3\text{-}N\text{-picO})_6^{2+}$ and various representative concentrations of 3-picoline N -oxide are listed in Table I. Note that the observed shifts show a marked dependence on the solution composition. In addition the isotropic shifts show significant deviations from Curie law behavior as can be seen from Figure 2. The open

circles in the low-temperature region of Figure 2 represent the measured difference between the methyl signals due to the coordinated and free ligand sites. The open squares represent values of $\Delta\nu$ obtained in the fast-exchange region from eq 1. The closed squares are values of $\Delta\nu$ which were required to fit the complete nmr line shape (see below). Solutions containing

higher concentrations of free ligand exhibit very similar curvature. In view of the dependence of $\Delta\nu$ on the solution composition a plot analogous to Figure 2 for the determination of values of the isotropic shift in the exchange-controlled region was made for each solution. Possible reasons for the observed behavior of the isotropic shift will be discussed below.

TABLE I
VALUES OF THE OBSERVED ISOTROPIC SHIFT FOR
SOLUTIONS CONTAINING VARIOUS CONCENTRATIONS
OF EXCESS LIGAND

$10^3/T$, deg ⁻¹	Obsd isotropic shift, ^a Hz		
	a	b	c
2.87	437	444	451
3.04	470	482	492
4.67	825	845	860
4.80	851	869	889

^a The solutions each contain 0.1 *M* complex and the following concentrations of excess ligand: (a) 1.03 *M*; (b) 1.46 *M*; (c) 2.93 *M*. All shifts are upfield of the methyl signal of the uncoordinated ligand.

In addition to the isotropic shifts, values of the transverse relaxation rates characteristic of ligand protons in the coordinated and free ligand sites ($1/T_{2M}$ and $1/T_{2L}$, respectively) must be obtained in the exchange-controlled region in order to carry out a kinetic analysis on the nmr spectrum. To obtain this information the observed line widths of the methyl signal were measured in both the fast-exchange region and the region where exchange is stopped. In the fast-exchange region the transverse relaxation rates can be obtained from the equation⁷

$$(\Delta\nu_{1/2})_{\text{obsd}} = P_M(\Delta\nu_{1/2})_M + P_L(\Delta\nu_{1/2})_L = P_M\left(\frac{1}{\pi T_{2M}}\right) + P_L\left(\frac{1}{\pi T_{2L}}\right) \quad (2)$$

where $(\Delta\nu_{1/2})_{\text{obsd}}$ represents the width of the observed signal at half-height, P_M and P_L represent the mole fractions of ligand in the coordinated and free ligand sites, respectively, and $(\Delta\nu_{1/2})_M$ and $(\Delta\nu_{1/2})_L$ represent the line widths at half-height of the signals due to coordinated and bulk ligand. Values of $(\Delta\nu_{1/2})_L$ in the fast-exchange region were obtained from plots of $(\Delta\nu_{1/2})_{\text{obsd}}$ vs. P_L using data obtained from a series of solutions where P_L was varied from 0.6 to 0.9. In the region where exchange is stopped values of $(\Delta\nu_{1/2})_L$ were measured directly. Figure 1 shows the least-squares fit of the high- and low-temperature data for $(\Delta\nu_{1/2})_L$ for a solution containing 1.03 molar excess ligand. It was found that $(\Delta\nu_{1/2})_L$ was insensitive to solution composition within experimental error and the line shown in Figure 1 was used for the kinetic analysis of the data from all of the various solutions. The apparent activation energy for $1/T_{2L}$ is -1.54 kcal/mol which is in the range expected for a relaxation process controlled by electron spin relaxation.⁸

Values of $(\Delta\nu_{1/2})_M$ were measured directly in the low-temperature region and were obtained in the fast-exchange region by use of eq 2. These results were found to show, analogously to the isotropic shifts, that $1/T_{2M}$ increases slightly as the free ligand concentration is increased. In the region where exchange is stopped, an increase of 3–4 Hz is observed in $1/\pi T_{2M}$ for each ~ 0.6 *M* increase in the free ligand concentration. This difference decreases to less than 0.5 Hz per 0.6 *M* increase in free ligand in the fast-exchange temperature region.

The values of $\log(\Delta\nu_{1/2})_M$ obtained in both the high- and low-temperature regions when plotted vs. $1/T$ seem to lie on a straight line for each solution. However, the scatter in the low-temperature region due to experimental error in measuring the line widths makes it difficult to state this with certainty. For lack of a better procedure values of $1/T_{2M}$ in the exchange-controlled region (for use in the line shape calculations) were obtained by assuming linear behavior over the temperature range of interest. Owing to the dependence of $1/T_{2M}$ on the solution composition a separate plot was made for each solution from which kinetic data were obtained. The apparent activation energy for $1/T_{2M}$ was found to vary from ~ -1.6 kcal/mol at 1.03 molar excess ligand to ~ -2.0 kcal/mol at 4.04 molar excess ligand.

To obtain the rates of exchange in the present work three

different methods, none of which require special concentration conditions, have been used. One of the techniques^{8,9} involves measurement of the line broadening in the slow-exchange temperature region. The rate constant is obtained from the equation⁸

$$\frac{1}{\tau_M} = k = \pi[(\Delta\nu_{1/2})_M^{\text{obsd}} - (\Delta\nu_{1/2})_M] = \frac{P_L}{\tau_L P_M} = \frac{P_L \pi}{P_M} [(\Delta\nu_{1/2})_L^{\text{obsd}} - (\Delta\nu_{1/2})_L] \quad (3)$$

where τ_M is the mean lifetime of a ligand in the primary coordination sphere of the metal ion, $(\Delta\nu_{1/2})_M^{\text{obsd}}$ represents the observed line width at half-height of the signal due to coordinated ligand protons, and $(\Delta\nu_{1/2})_M$ represents the natural line width for this signal. The terms with L subscripts refer to analogous quantities for the signal due to ligand molecules in the bulk solvent. This equation is valid in the slow-exchange region up to the temperature at which the signals begin to overlap.

An additional line width technique^{9,10} which is valid in the region near the fast-exchange limit is given by the equation

$$\tau_M = \frac{\Delta\nu_{1/2}'}{P_L^2 P_M (4\pi) (\Delta\nu)^2} \quad (4)$$

where $\Delta\nu_{1/2}'$ is the difference between the observed line width at half-height and the fast-exchange line width at half-height from eq 2, and $\Delta\nu$ is the isotropic shift at the temperature of interest.

In order to supplement and check the validity of these line width methods, rates of exchange were also obtained by employing a computerized complete line shape calculation.¹¹ This method involves calculation of the complete nmr spectrum for a two-site exchange system as a function of the exchange rate. The exchange rate is varied until the calculated spectrum fits the experimental spectrum. In view of the non-Curie-law behavior of the isotropic shift, the value of $\Delta\nu$ was also varied to ensure exact matching of the experimental and calculated signal positions. This was done by fitting the experimental spectrum as a function of the exchange rate at values of $\Delta\nu$ systematically varied about the estimated value. This procedure also proved of value in obtaining accurate shifts for use in eq 4.

In analyzing the kinetic data the following expression for k was used

$$k = \frac{k'T}{h} \exp[-(\Delta H^\ddagger - T\Delta S^\ddagger)/RT] = \frac{1}{\tau_M}$$

The resulting activation enthalpy plot is shown in Figure 3.

The values for k given in Figure 3 were obtained from solutions containing 0.1 *M* Ni(3-*N*-picO)₆²⁺ and concentrations of free ligand varying from 1.03 to 4.04 *M*. Since the data points from the various solutions show no systematic trend but are randomly distributed around the least-squares line due to experimental error, no attempt was made to specify to which solution a given point corresponds. This was done to minimize confusion on the plot. The points in the low-temperature region ($10^3/T > 4.0$) which are indicated by circles were obtained by use of eq 3 from line width measurements on the bulk ligand signal. The points in the high-temperature region ($10^3/T < 3.6$) which are indicated by circles were obtained from eq 4 using values of $\Delta\nu$ obtained from plots corrected for the non-Curie-law behavior. The points indicated by diamonds were obtained by use of the complete line shape technique.

A least-squares analysis of these data gives the following kinetic parameters: $k(25^\circ) = 5.4 \times 10^4$ sec⁻¹, $\Delta H^\ddagger = 12.5 \pm 0.2$ kcal/mol, and $\Delta S^\ddagger = 6.8 \pm 0.9$ eu at 95% confidence limits. The scatter observed for the $\ln(k/T)$ values in the very low-temperature region is probably due to the large percentage error in measuring the exchange broadening in this region, which is on the order of 0.5–1 Hz, and to the greater difficulty in maintaining accurate temperature control at these temperatures. No values of k are reported at intermediate temperatures because of interference from isotopic impurities in the deuterated solvents.

In order to assess the significance of small errors in $\Delta\nu$, rates of exchange in the near fast-exchange region were calculated

(9) L. H. Piette and W. A. Anderson, *ibid.*, **30**, 899 (1959).

(10) A. Allerhard, H. S. Gutowsky, J. Jonas, and R. A. Meinzer, *J. Amer. Chem. Soc.*, **88**, 3185 (1966).

(11) S. S. Zumdahl and R. S. Drago, *ibid.*, **89**, 4319 (1967).

(8) Z. Luz and S. Meiboom, *J. Chem. Phys.*, **40**, 1058, 1066 (1964).

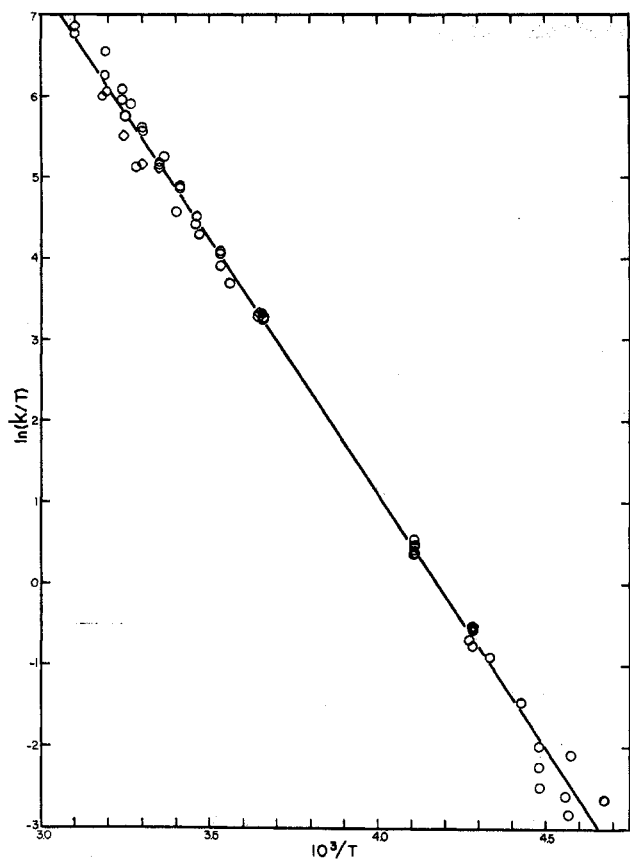


Figure 3.—Plot of $\ln(k/T)$ vs. $10^3/T^\circ\text{K}$: (a) \circ , in the region where $10^3/T > 4.0$, obtained using eq 3 and solutions containing 0.10 *M* complex and 1.03, 1.46, 2.21, 2.93, 3.41, and 4.04 molar excesses of ligand; (b) \circ , in the region where $10^3/T < 3.7$, obtained using eq 4 and solutions containing 0.10 *M* complex and 1.03, 1.46, and 2.93 molar excesses of ligand; (c) \diamond , obtained using the complete line shape calculation.

(eq 4) using the values of $\Delta\nu$ obtained assuming linear behavior in the intermediate temperature region. When these values were used, along with those from the slow-exchange method and the line shape method, to calculate ΔH^\ddagger , a difference of only $\sim 1\%$ was observed in ΔH^\ddagger . Thus small errors in estimating $\Delta\nu$ in the exchange region are not significant.

Discussion

From the results of the present work and from other recent studies^{3,12} it seems clear that exchange reactions involving neutral ligands with octahedral and pseudo-octahedral complexes of Ni(II) follow a rate law of the type

$$\text{rate} = nk[\text{complex}]$$

where n represents the coordination number of the exchanging monodentate ligand. Although, as has been suggested,¹² it is possible that this first-order rate law arises because of strong preferential solvation of the complex by the exchanging ligand, it seems that the results of the three ligand-exchange studies taken together strongly support a dissociative mechanism for the exchange reaction. Considering the variety of solvents and exchanging ligands used in these studies, it is unlikely that the ligand would preferentially solvate the complex in every case to such an extent to preserve first-order kinetics for an associative exchange mechanism. For example in the present study the CH_3 -

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

NO_2 :3-picoline *N*-oxide molar ratio was varied from ~ 1 in the most concentrated solution ($[\text{ligand}]/[\text{complex}] = 40$) to ~ 7 in the most dilute solution ($[\text{ligand}]/[\text{complex}] = 10$). It would be somewhat surprising to have the complex essentially completely solvated by the ligand under these greatly varying conditions. The conclusion that a dissociative mechanism is operative in these systems is also supported by the recent work of Langford and Tsiang.¹³

One of the most interesting results of this study concerns the dependence of the isotropic shift and the transverse relaxation rate for coordinated ligand protons on the composition of the solution. As the free ligand concentration is increased, increases in both $\Delta\nu$ and $1/T_{2M}$ are observed. These effects are outside experimental error and are quite reproducible.

One possible explanation for the dependence of $\Delta\nu$ on the solution composition is that the internal standard (benzene) does not compensate correctly for changes in bulk susceptibility. That this explanation is not correct is indicated by the fact that the position of the free ligand signal is not dependent on the solution composition and occurs at the expected frequency in all solutions in the temperature region where exchange is stopped. Also the fact that the line width shows a dependence on the solution composition indicates that other factors besides susceptibility are important.

Concentration-dependent isotropic shifts have been noted before particularly for systems involving ion-paired cations.^{14,15} Recently Wicholas¹⁶ has observed that the isotropic shifts for the complexes $\text{Fe}(\text{DP-SO})_6^{2+}$, $\text{Ni}(\text{DPSO})_6^{2+}$, and $\text{Co}(\text{DPSO})_6^{2+}$, where DPSO represents diphenyl sulfoxide, are a function of the complex concentration in chloroform. This behavior was attributed to ion pairing. To our knowledge changes in $\Delta\nu$ as a result of varying the excess ligand concentration have not been noted previously. Perhaps this is due to the fact that complexes of this type have not been studied under conditions where the free ligand concentration can be changed significantly.

Several possible explanations can be suggested to account for the dependence of $\Delta\nu$ and $1/T_{2M}$ on the solution composition. In view of the moderate to low dielectric constants of the solvents employed in this study it is possible that ion pairing is quite significant in the solutions used to obtain the kinetic data. It has been shown in previous studies^{17,18} that ion pairing can cause enough distortion in a normally isotropic complex to produce dipolar contributions to the isotropic shift. Although, to our knowledge, this type of behavior has not been demonstrated for octahedral Ni(II), this is a possible source of concentration dependence of the shifts. Also, it is possible that ion pairing may produce changes in the hyperfine coupling constant and thus alter the contact contribution to the shift.

Assuming that one type of ion pair is predominant in these solutions, the observed isotropic shift, $\Delta\nu_{\text{obsd}}$, can be expressed as $\Delta\nu_{\text{obsd}} = P_0\Delta\nu_0 + P'\Delta\nu'$, where P_0 and $\Delta\nu_0$ refer to the mole fraction and isotropic shift of the non-ion-paired complex with P' and $\Delta\nu'$ the anal-

(13) C. H. Langford and H. G. Tsiang, *ibid.*, **9**, 2346 (1970).

(14) J. C. Fanning and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 3987 (1968).

(15) D. W. Larson and A. C. Wahl, *Inorg. Chem.*, **4**, 1281 (1965).

(16) M. Wicholas, *J. Inorg. Nucl. Chem.*, **32**, 873 (1970).

(17) I. M. Walker and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6951 (1968).

(18) D. W. Larsen, *ibid.*, **91**, 2920 (1969).

ogous terms for the ion-paired species. This equation can be rewritten in terms of the ion-pair formation constant, K_0 , as

$$\Delta\nu_{\text{obsd}} = \Delta\nu_0 + \left(\frac{K_0[\text{BF}_4^-]}{K_0[\text{BF}_4^-] + 1} \right) \nu' \quad (5)$$

where ν' is defined as $\Delta\nu' - \Delta\nu_0$. On this basis an explanation for the dependence of $\Delta\nu_{\text{obsd}}$ on the free ligand concentration can be made in terms of a change in the solution dielectric constant which in turn changes the value of K_0 . Also, model calculations assuming that $\Delta\nu_0 = 400$ Hz and $\nu' = 150$ Hz at 25° show that values of $K_0 \approx 1$ and a heat of formation for the ion pair, ΔH , of ~ -3 kcal/mol or greater produce non-linearity in a plot of $\Delta\nu_{\text{obsd}}$ vs. $1/T$ of the type observed in Figure 2. It is very difficult to estimate values for K_0 and ΔH in the acetone-nitromethane solutions but in view of previous studies^{19,20} values of $K_0 \approx 1$ and $\Delta H \approx -3$ kcal/mol do not appear unreasonable.

Thus, it seems that an ion-pairing model can account for the changes in $\Delta\nu_{\text{obsd}}$ either by assuming that a dipolar contribution to the isotropic shift is induced in the ion pair or by assuming that the hyperfine coupling constant of the complex is altered in the ion pair.

The ion-pair model can also be used to explain the variation in $1/T_{2M}$ as the composition of the solution is changed in that ion pairing might be expected to alter the electron spin relaxation time. Model calculations with $\Delta H \approx -3$ kcal/mol and $K_0 \approx 1$ and assuming values of the line widths due to the free complex and the ion-paired complex at 25° to be 23 and 33 Hz, respectively, show that a plot of $\log(\Delta\nu_{1/2})_{\text{obsd}}$ vs. $1/T$ gives good linearity in the temperature region from $10^3/T = 2.5$ – 5.0 . This assumes that $(\Delta\nu_{1/2})_{\text{obsd}}$ is given by an expression analogous to eq 5. Thus these calculations support the assumption that $\log(\Delta\nu_{1/2})_M$ is linear

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

(20) A. Kowalak, K. Kustin, R. F. Pasternack, and S. Pertrucci, *J. Amer. Chem. Soc.*, **89**, 3126 (1967).

in the temperature range covered in this study. This assumption is further supported by the excellent agreement obtained between rates from the line shape technique and the two line width methods.

Finally, it is possible that the observed dependence of $\Delta\nu$ and $1/T_{2M}$ on the free ligand concentration may result from the presence of small amounts of nonoctahedral species produced by the insertion of nitromethane or tetrafluoroborate into the coordination sphere. However, in view of the results from the spectral studies and the fact that the rates obtained from all solutions agree very well at all temperatures, large amounts of such species (>3–4%) cannot be present. Also the fact that the plot of $\ln(k/T)$ vs. $1/T$ shows no apparent curvature over a 110° temperature range is not consistent with any significant decomposition of the octahedral complex. On the other hand, Frankel³ has observed that the activation enthalpies for exchange of DMSO with $\text{Ni}(\text{DMSO})_6^{2+}$ and $\text{Co}(\text{DMSO})_6^{2+}$ are the same in methylene chloride and nitromethane. He has interpreted this to mean that ion pairing does not significantly affect the ΔH^\ddagger for ligand exchange. On this basis the linear activation enthalpy plot obtained in this work is not inconsistent with the ion-pairing model discussed above.

Further studies on similar systems are now in progress to explore the concentration dependence of $\Delta\nu$ and $1/T_{2M}$ and to determine the significance of the donor strength of the ligand and the importance of solvation energies as contributions to the enthalpy of activation for exchange.

Acknowledgment.—The authors gratefully acknowledge the Research Corp. for the partial support of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Low-Spin Five-Coordinate Nickel(II) Complexes Containing a Macrocyclic Tetradentate Amine

By E. KENT BAREFIELD AND DARYLE H. BUSCH*

Received August 18, 1970

Catalytic reduction of the complex (II) prepared by condensation of $\text{Ni}(\text{tm})_3(\text{ClO}_4)_2$ (tm \equiv trimethylenediamine) and acetone leads to a low-spin five-coordinate complex containing ligand I and coordinated perchlorate. Nmr evidence indicates that only one ligand stereoisomer is formed in the reduction. Other low-spin five-coordinate complexes with bonded Cl^- , Br^- , and I^- have been prepared. These represent new examples of low-spin five-coordinate nickel(II) complexes, which are rather rare for ligands containing more than one nitrogen donor. Others are discussed. In donor solvents the equilibrium $\text{NiL}(\text{solvent})^{2+} \rightleftharpoons \text{Ni}(\text{L})^{2+} + \text{solvent}$ occurs and the concentration of the five-coordinate species is proportional to the donor strength of the solvent, $\text{DMSO} > \text{DMF} > \text{CH}_3\text{CN} \sim \text{H}_2\text{O} > \text{CH}_3\text{NO}_2$. These species are also low spin in electronic configuration.

Introduction

Since the first report of five-coordinate nickel(II) in complex molecules there has been a steady increase in the number of established examples. Five-coordinate

nickel(II) complexes approximate either of two distinct geometrical forms, square pyramidal or trigonal bipyramidal. Within these two geometrical types the metal ion may be either high spin ($S = 1$) or low spin ($S = 0$).