Kinetic and Thermodynamic Studies of a Pentadentate Schiff Base Complex of Nickel(II)

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Abstract: The enthalpy of formation of the adduct of 4-methylpyridine (4-mepy) with bis(salicylidene-γ-iminopropyl)methylamine nickel(II) (abbreviated NiSDPT) was measured calorimetrically in the solvents methylene chloride and toluene. These enthalpies are compared with activation enthalpies for the exchange of 4-methylpyridine with the 4-methylpyridine adduct of NiSDPT (see reaction 1), measured in the same solvents

$$\text{NiSDPT(4-mepy)} + \text{4-mepy*} = \text{NiSDPT(4-mepy*)} + \text{4-mepy} \quad (1)$$

using nmr density matrix techniques. It has been found that in both solvents the activation enthalpy is substantially larger than the enthalpy of adduct formation, the difference being 3.0 kcal/mol in methylene chloride and 1.4 kcal/mol in toluene. By having both kinetic and thermodynamic data available, much has been learned about the details of the kinetic process. For example, the difference between the enthalpy of adduct formation and the activation enthalpy provides some of the best evidence to date for the existence of a stable intermediate in the dissociative pathway. The 1.6 kcal mol^{-1} discrepancy in the differences in the two solvents provides considerable information regarding the participation of solvent in the reaction mechanism. The kinetic studies yielded first-order exchange rate constants on the order of 10^7 sec^{-1} at 25°.

In recent years, this research group has shown that it is possible to correlate many measured enthalpies of interaction between acids and bases in poorly solvating solvents using a four-parameter equation of the form

$$-\Delta H = E_A E_B + C_A C_B \quad (2)$$

The parameters and their possible interpretation have been described in detail in other papers.[1] Attempts have been made in the literature to equate activation enthalpies for first-order dissociative processes to the strength of the bond being broken. If this is correct, such activation data should be amenable to incorporation into eq 2. With the accumulation of activation enthalpy data in the literature as a consequence of interest in nuclear magnetic resonance, this possible criterion of bond strength seemed worthy of further investigation. In the nmr experiment, exchange reactions of the following general form are often suitable for investigation

$$\text{AB} + \text{B*} = \text{AB*} + \text{B}$$

where A is an acid molecule and B and B* are identical basic molecules. For the particular situation where AB is a six-coordinate transition metal complex, A is a five-coordinate complex, and a first-order dissociative exchange mechanism is anticipated. If this is indeed the case, one might expect the enthalpy of activation to be equal to or slightly larger than the enthalpy, $-\Delta H^{\text{ad}}$, of the adduct formation reaction 3.

$$\text{A} + \text{B} = \text{AB} \quad (3)$$

This is made clear by the reaction coordinate diagram in Figure 1, which is expected to apply to the following mechanism for exchange.

$$\text{Step 1.} \quad \text{AB} = \text{A} + \text{B} \qquad \text{slow} \qquad \Delta H^1$$

$$\text{Step 2.} \quad \text{A} + \text{B*} = \text{AB*} \qquad \text{fast} \qquad -\Delta H^1$$

If free A were formed in step 1, one would certainly be justified in assuming that $\Delta H^{\text{ad}} = -\Delta H^1$, where ΔH^1 is the net enthalpy change associated with the dissociative step of the above mechanism (see Figure 1). The question is whether one can assume that ΔH^1 is equal to the activation enthalpy associated with step 1, $\Delta H^{\ddagger}$, which is obtained from a kinetic study. From Figure 1, this is seen to be the case when the quantity $\Delta H^{\text{diff}} = 0$, *i.e.*, when the depth of the potential well is zero. It is the aim of this study to determine, at least for the system under consideration, whether or not $\Delta H^1 \approx \Delta H^{\ddagger}$ and hence whether dissociative activation enthalpies are a good criterion for the strength of bonding.

The system studied was selected for several reasons. First, for nmr exchange studies, it is convenient to observe a set of protons which do not couple with other protons in the molecule under examination. The methyl protons of 4-methylpyridine are ideal in this respect. The methyl resonance is a sharp singlet at room temperature, with a width at half-height of approximately 1 Hz, indicating that if coupling with the ring protons does occur, it is so small as to be unimportant. The methyl resonance was used to obtain all of our kinetic data. Second, NiSDPT is an ideal acid molecule in two respects. In the first place, it has only one position available for coordination. Thus, in the absence of geometrical isomers,[2] there can be only one species of adduct present in solution. The question of solution structure will be discussed in more detail later. In the second place, the fact that the nickel complex is itself a stable five-coordinate species makes a pure dissociative pathway quite feasible. Since the proposed comparison of $-\Delta H^{\text{ad}}$ and $\Delta H^{\ddagger}$ is meaningful only for such a pathway, it is important to choose an acid for which dissociative activation is probable.

Finally, the solvents toluene and methylene chloride were chosen for their very low freezing points and because they are quite commonly used in acid–base work. Furthermore, they are slightly solvating solvents whose properties have been studied in the past and whose solvation contributions to the enthalpy of adduct for-

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[1] R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Amer. Chem. Soc.*, 93, 6014 (1971).

[2] G. N. LaMar and L. Sacconi, *J. Amer. Chem. Soc.*, 89, 2282 (1967).

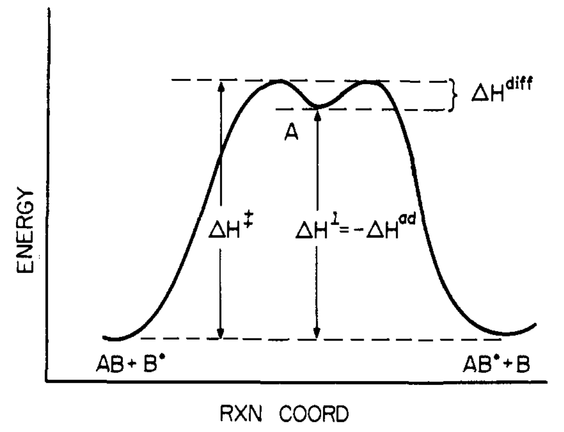


Figure 1. Reaction coordinate diagram for a general exchange reaction.

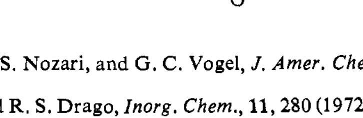
mation are predictable.[3,4] It was of interest to ascertain their contribution to the kinetic data.

An essential part of this research was to obtain highly precise activation enthalpies. This can only be accomplished if the activation plot from which the enthalpy is obtained covers a large temperature range. The simplest and most common method of obtaining rate constants and activation parameters from nmr data is to make use of the line width at half-height of the nmr signal of a particular set of protons in the so-called slow-exchange temperature region. Previous work in this laboratory has shown that this method often gives unreliable rate constants.[5] Moreover, the precision of the activation parameters is determined by the size of the temperature range covered. Since the slow-exchange region comprises only about half of the temperature region in which exchange affects the nmr spectrum, it is usually not possible to obtain precise activation parameters from that region alone, especially if the activation enthalpy is large. A much superior procedure is to employ either line-shape analysis or density matrix techniques, with which the entire temperature region of interest can be covered. Further, the fact that these latter techniques require the matching of not only the line width of the resonance, but also its chemical shift, provides an additional check on the reliability of the rate constants obtained. The density matrix approach enabled us to cover a range of 64° in one system and 43° in the other. These are quite substantial ranges of temperature and permit the determination of precise activation parameters.

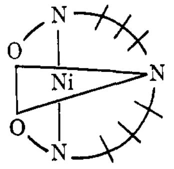
Experimental Section

1. **Preparation and Purification of Materials.** Bis(salicylidene-γ-iminopropyl)methylaminenickel(II) was prepared according to the method of Sacconi and Bertini.[6] *Anal.* Calcd: C, 60.64; H, 5.86; N, 10.61. Found: C, 60.50; H, 5.88; N, 10.63. The structure of the ligand follows.

$SDPT^{2-}$ =



The arrangement of the ligand about the nickel atom is as shown below.[7]



4-Methylpyridine was obtained from Eastman Organic Chemicals and was purified by distillation from calcium hydride or barium oxide at atmospheric pressure. The fraction boiling at 144° was collected and stored over Linde 4A molecular sieves in a desiccator containing Drierite. When stored over sieves, the 4-methylpyridine was found to be stable for a period of weeks as judged by the infrared spectrum.

Solvents for Calorimetric Measurements. Methylene chloride was stored over Drierite ($CaSO_4$) for 24 hr, then distilled at atmospheric pressure from CaH_2. All measurements were performed within 3 days after a distillation. Reagent grade toluene was stored over 4A sieves for 3 days and used without further purification.

Solvents for Nmr. Methylene chloride-d_2 and toluene-d_8 were used in the nmr studies. Reagent grade methylene chloride-d_2 was obtained from the Stohler Isotope Chemical Co. and was used without further purification. Reagent grade toluene-d_8 was obtained from Schwarz Bioresearch and was not purified further.

2. **Calorimetric Measurements.** The construction and operation of the calorimeter have been described elsewhere.[8] Pure 4-methylpyridine (4-mepy) was added by the syringe method[9] to solutions of NiSDPT in the appropriate solvent.

3. **Nmr Measurements.** Spectra (60 MHz) were run on a Jeolco C-60H high resolution nmr spectrometer. Temperature regulation was achieved by a VT-3 temperature controller, which held the temperature constant to within ±1.0°. Temperature measurement was achieved either with a YSI Model 42SL telethermometer, accurate to ±0.5°, or with a copper–constantan thermocouple, good to ±0.5°. The thermocouple was used exclusively for temperatures below −60°.

Spectra (100 MHz) were run on a Varian HA-100 nmr spectrometer equipped with a Model V6040 temperature controller. Temperature was measured using a copper–constantan thermocouple or a YSI Model 42SL telethermometer.

Preparation of Nmr Samples. NiSDPT(4-mepy) in Methylene Chloride. A stock solution of NiSDPT (3 ml) in methylene chloride-d_2 was prepared. Samples were then prepared by weighing the calculated amount of 4-mepy into a 1-ml flask, adding the desired amount of stock solution, and diluting to the mark with methylene chloride-d_2. The 1-ml solutions were then placed in nmr tubes, capped with pressure caps, and sealed by wrapping with parafilm. All work was performed in an N_2-filled glove bag. Samples were not degassed. No internal standard was added. Chemical shifts were measured relative to the residual hydrogen resonance of methylene chloride-d_2.

NiSDPT(4-mepy) in Toluene-d_8. A stock solution of NiSDPT in toluene could not be prepared due to the very poor solubility of the complex in this solvent. Solutions were prepared individually by weighing the desired amount of NiSDPT into a 1-ml volumetric flask, adding the correct amount of 4-mepy, and diluting to the mark with toluene-d_8. The solutions were placed in a desiccator for a day to allow maximum dissolution and were then transferred to nmr tubes, capped with pressure caps, and sealed by wrapping with parafilm. Benzene was added as an internal standard. All work was performed in an N_2-filled glove bag. Samples were not degassed.

4. **Line-Shape Calculations.** The density matrix computer program and the associated theory have been described in detail elsewhere.[10] For the systems described here, the subroutine for an AB spin system undergoing two-site exchange was used to calculate

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[3] R. S. Drago, M. S. Nozari, and G. C. Vogel, *J. Amer. Chem. Soc.*, 94, 90 (1972).

[4] M. S. Nozari and R. S. Drago, *Inorg. Chem.*, 11, 280 (1972).

[5] S. S. Zumdahl and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 4319 (1967).

[6] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

[7] P. L. Orioli, M. DiVaira, and L. Sacconi, *Chem. Commun.*, 300 (1966).

[8] G. C. Vogel, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1970.

[9] F. L. Slejko, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1972.

[10] R. L. Chiang, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1972.

the shape and position of the methyl resonance of free 4-mepy. Calculations were performed on an IBM 360 computer.

5. Description of Experimental Input Parameters. In order to perform a density matrix calculation, several experimental parameters must be specified which enter into the general density matrix line-shape equation. The parameters and their descriptions are listed below. All descriptions refer to the particular set of protons being observed, in this case the methyl protons of 4-mepy. ω_L = the chemical shift of the free ligand resonance in the absence of exchange relative to some internal standard. ω_M = the chemical shift of the corresponding coordinated ligand resonance in the absence of exchange relative to the same internal standard. T_{2L} = the transverse relaxation time of protons in the free ligand environment in the absence of exchange. T_{2M} = the transverse relaxation time of protons in the coordinated environment in the absence of exchange. P_L = the mole fraction of protons in the free environment. P_M = the mole fraction of protons in the coordinated environment. τ_L = the lifetime of a ligand in the free environment. τ_M = the lifetime of a ligand in the coordinated environment. The methods for experimentally determining ω_L, ω_M, T_{2L}, and T_{2M} have been described elsewhere,[10] so in the interests of brevity, they will only be sketched here.

The terminology and equations used in the nmr slow-exchange line-width approximation have been thoroughly described in the literature.[11] In order to extract rate constants from observed line widths of the bulk ligand by this technique, it is necessary only to know the transverse relaxation time, T_{2L}, which would prevail for the subject proton at the temperature of interest in the absence of chemical exchange. Once known, $1/T_{2L}$ may be subtracted from the reciprocal of the observed transverse relaxation time, $(1/T_2)_{obsd}$, to yield the rate constant, $1/\tau_L$, describing the departure of ligands from the bulk of the solution.[12] This may then be converted to the rate constant describing the departure of ligands from the coordination sphere of the metal, $1/\tau_M$, by multiplication by the ratio of mole fractions P_L/P_M. It has been generally observed that the log $1/\pi T_{2L}$ ($\pi(\Delta\nu_{1/2})_L = 1/T_{2L}$) has a linear reciprocal temperature dependence in the stopped-exchange region. This line may be easily extrapolated to any desired temperature to give the appropriate T_{2L} for use in the line-width calculation. The same approach may be used for density matrix calculations. Similar to the behavior for T_{2L}, log $1/\pi T_{2M}$ is generally also linear with $1/T$ in the stopped-exchange region, and data from this region may be extrapolated to any desired temperature to obtain a value of T_{2M} appropriate for the density matrix calculation of the spectrum at that temperature. Finally, the parameter $\Delta\omega_M = \omega_M - \omega_L$ is related to temperature in the stopped-exchange region through the Bloembergen equation.[13]

$$\frac{\Delta\omega_M}{\omega_0} = -\frac{Ag_{av}B_eS(S+1)}{g_N\beta_N 3kT} \tag{4}$$

Here A = the coupling constant in ergs, $\Delta\omega_M$ = the isotropic shift in Hz, ω_0 = the probe frequency in Hz, g_{av} = the g value for the complex being considered, g_N and β_N are constants characteristic of the nucleus being observed, and T = the temperature in degrees Kelvin. Again, values of $\Delta\omega_M$ appropriate to any temperature in the exchange-controlled temperature region can be obtained by extrapolation of stopped-exchange data.

The stopped-exchange region is obviously very important for determining the necessary computer input parameters involved in a density matrix calculation. It is possible in some cases to use the fast-exchange region to indirectly obtain the parameters T_{2L}, T_{2M}, and $\Delta\omega_M$; however, we feel that data determined in this way are not as reliable as data obtained from the stopped-exchange region, where direct measurement of the necessary parameters is possible.

Results

I. NiSDPT(4-mepy) in Methylene Chloride. Calorimetric Studies. The heats evolved were input to an IBM 1800 computer which calculated the best value of the enthalpy, $-\Delta H^{ad}$, and the equilibrium constant, K_{eq}, for the adduct formation reaction for each solution.[14] The calorimetric results are reported in Table I.

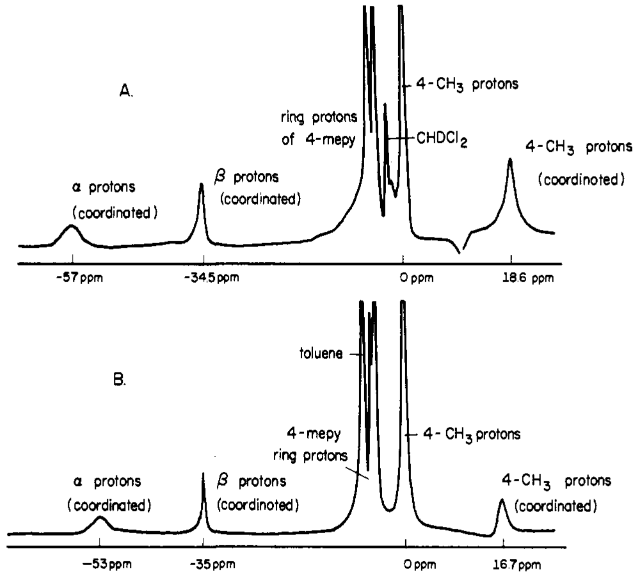

Figure 2. Stopped-exchange spectra in (A) methylene chloride and (B) toluene.

Table I. Calorimetric Results[a]

	$-\Delta H^{ad}$, kcal/mol	K, M^{-1}
1.	NiSDPT + 4-mepy in CH_2Cl_2	
	6.74 ± 0.03	13.68 ± 0.27
	6.67 ± 0.05	11.30 ± 0.16
	6.71 ± 0.04	11.42 ± 0.13
	6.78 ± 0.11	11.95 ± 0.32
Mean values	6.73 ± 0.05	12.09 ± 0.80
	ΔS^{ad} = −17.63 eu (calcd)	
2.	NiSDPT + 4-mepy in Toluene	
	10.28 ± 0.22	102.0 ± 10.8
	10.53 ± 0.12	106.7 ± 6.2
	10.40 ± 0.02	125.2 ± 1.3
	9.26 ± 0.02	128.2 ± 1.5
Mean values	10.12 ± 0.58	115.5 ± 13.1
	ΔS^{ad} = −24.52 eu (calcd)	

[a] An expanded Table I is given in the microfilm edition. See paragraph at end of paper regarding supplementary material.

Kinetic Studies. Preliminary scans on a solution containing 0.15 *M* NiSDPT and 0.30 *M* total 4-mepy showed that exchange could be stopped at *ca.* −100°. The line shape was affected by the exchange rate up to a temperature of −35°. Below *ca.* −80°, two resonances were observed for each type of 4-mepy proton (see Figure 2), one set due to the free base and one due to the coordinated base. For the methyl protons, the coordinated resonance was upfield from the free base resonance, whereas the ring protons of 4-mepy were shifted downfield upon coordination.

Following the preliminary scans, spectra were run on four solutions (for concentration details, see microfilm edition) at a series of temperatures between −112 and −35°. Below −112°, the solvent froze, and above −35°, the line shape was no longer affected by the rate process. The isotropic shift, $\Delta\omega_M$, for the methyl protons, was measured as a function of temperature in the stopped-exchange region (between −112 and −100°) and a plot of $\Delta\omega_M$ *vs.* $1/T$ was constructed. This is shown in Figure 3. The plot contains data from all four solutions, since the isotropic shift is independent of the concentration of either complex or

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

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

(13) N. Bloembergen, *J. Chem. Phys.*, 27, 595 (1957).

(14) R. M. Guidry and R. S. Drago, *J. Chem. Educ.*, submitted for publication.

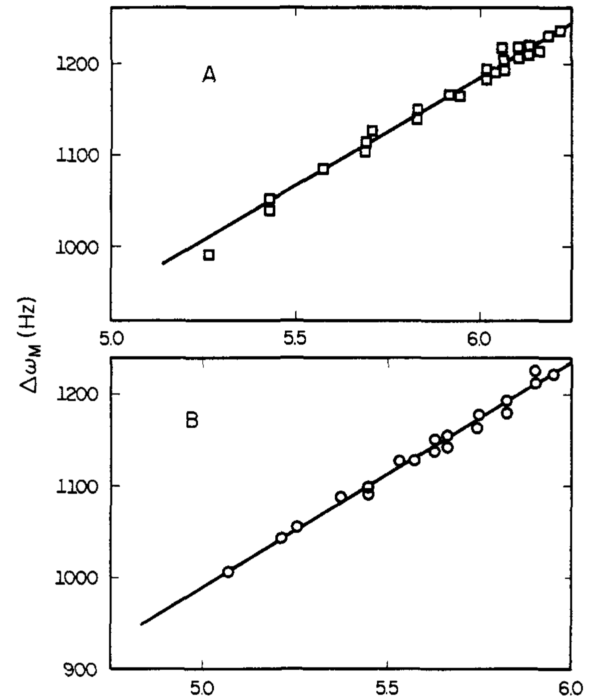

Figure 3. Isotropic shift ($\Delta\omega_m$) *vs.* $1/T$ for the methyl protons of 4-mepy in the stopped-exchange region: (A) methylene chloride; (B) toluene.

base. The line varies slightly from Curie law behavior in that there is a nonzero intercept of *ca.* −200 Hz. However, an intercept of this magnitude is not serious since it is nearly zero within experimental error.

Also in the stopped-exchange region, spectra were run of the coordinated-ligand methyl resonance to obtain T_{2M} as a function of temperature. These data can be seen plotted logarithmically in Figure 4. As for the isotropic shift, data from all solutions are included in this plot since T_{2M}, like $\Delta\omega_M$, is independent of the concentrations of NiSDPT and 4-mepy. Also plotted in Figure 4 is the complete line-width profile for the free-ligand methyl resonance of 4-mepy for solution 2. The various temperature regions are labeled in the figure. Unlike $\Delta\omega_M$ and T_{2M}, T_{2L} is inversely proportional to the molarity of NiSDPT. Accordingly, stopped-exchange T_{2L} data are plotted in Figure 4 for each solution individually.

Least squares analysis was performed on the stopped-exchange data for T_{2L}, T_{2M}, and $\Delta\omega_M$. The best lines were found to be

$$\Delta\omega_M = 2.316 \times 10^5(1/T) - 204.48 \text{ Hz}$$

$$\log 1/\pi T_{2M} = 355.40(1/T) - 0.3119$$

Solution 1. $\log/\pi T_{2L} = 435.96(1/T) - 1.6133$
Solution 2. $\log 1/\pi T_{2L} = 565.18(1/T) - 2.3979$
Solution 3. $\log 1/\pi T_{2L} = 533.28(1/T) - 2.2122$
Solution 4. $\log 1/\pi T_{2L} = 328.63(1/T) - 1.2130$

These equations were used to evaluate $\Delta\omega_M$, T_{2M}, and T_{2L} at temperatures in the kinetics-affected region, as described in the previous section.

Rate constants are obtained ultimately from density matrix calculations. The procedure used involves a comparison of experimental and calculated spectra for the free ligand methyl resonance of 4-mepy. Spectra are calculated for a variety of values of the quantity τ_L. The "correct" value of τ_L is taken as the value giving the calculated spectrum which best matches the experimental spectrum. Some sample fits are illustrated in Figure 5. Values of $1/\tau_M$ (which is related to the true rate constant for exchange) are calculated by the program from the value of τ_L, using the relationship

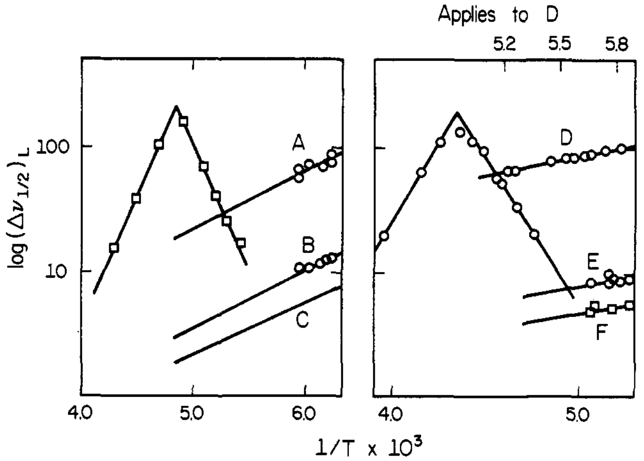

Figure 4. Line-width data (log of observed line width *vs.* $1/T$): methylene chloride, (A) $\log 1/\pi T_{2M}$, (B) $\log 1/\pi T_{2L}$ ([NiSDPT] = 0.0758 *M*), (C) $\log 1/\pi T_{2L}$ ([NiSDPT] = 0.0379 *M*); toluene, (D) $\log 1/\pi T_{2M}$ (upper scale), (E) $\log 1/\pi T_{2L}$ ([NiSDPT] = 0.0486 *M*), (F) $\log 1/\pi T_{2L}$ ([NiSDPT] = 0.0245 *M*).

$$P_M/\tau_M = P_L/\tau_L$$

P_M and P_L are the mole fractions of 4-mepy in the coordinated and free environments, respectively.

When density matrix calculations were performed for the four solutions at various temperatures in the kinetics-affected temperature region, it was found that the resulting rate constants fall on a common activation plot, shown in Figure 6. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ obtained from this plot are given in Table II. Also reported in the table is the value of the rate constant $1/\tau_M$, at 25°, obtained by extrapolation of the activation plot.

Table II. Kinetic Results[a]

1. NiSDPT(4-mepy) + 4-mepy* = NiSDPT(4-mepy*) + 4-mepy in methylene chloride-d_2
$\Delta H^{\ddagger} = 9.76 \pm 0.19$ kcal/mol[b]
$\Delta S^{\ddagger} = 6.00 \pm 0.11$ eu
$k = 1/\tau_M(25°) = (8.83 \pm 1.2) \times 10^6 \text{ sec}^{-1}$[c]
2. NiSDPT(4-mepy) + 4-mepy* = NiSDPT(4-mepy*) + 4-mepy in toluene-d_8
$\Delta H^{\ddagger} = 11.54 \pm 0.63$ kcal/mol
$\Delta S^{\ddagger} = 9.66 \pm 0.48$ eu
$k = 1/\tau_M(25°) = (2.77 \pm 0.45) \times 10^6 \text{ sec}^{-1}$

[a] An expanded Table II is given in the microfilm edition. [b] Error limits are 99% confidence limits on all parameters obtained from the slope or intercept of a plot. [c] Error limits on calculated rate constants are set at 15%. Experimental rate constants are accurate to within 10%, and an additional 5% is allowed for error in extrapolation of the experimental activation plot.

II. NiSDPT(4-mepy) in Toluene. Calorimetric Studies. Some difficulties were encountered in studying this system calorimetrically. To perform the calorimetric experiment, it is necessary to inject base into solutions of NiSDPT in the desired solvent. It is im-

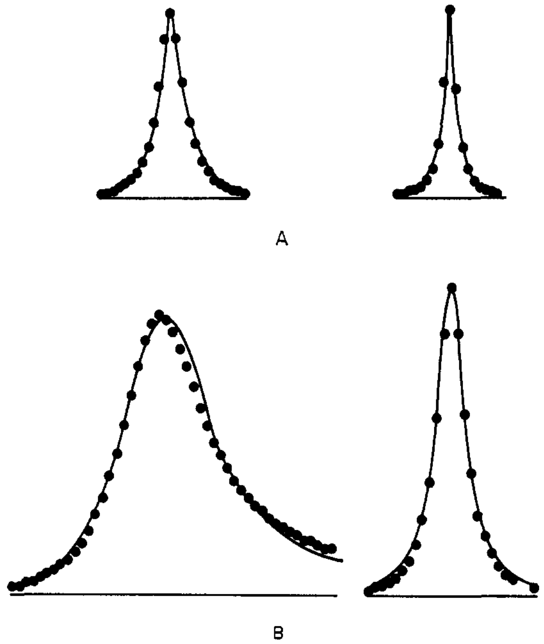

Figure 5. Density matrix fits of experimental spectra. Points are calculated, lines are experimental: (A) methylene chloride; (B) toluene.

possible to add NiSDPT to solutions of the base because it is a solid material and dissolves relatively slowly (>0.5 sec, the required time of mixing). It was found on attempting to prepare a ~0.01 *M* solution of NiSDPT in toluene that the acid forms a suspension which is nearly colloidal and which fails to dissolve upon long standing. The calorimetric results from such a "solution" are ambiguous because of potential enthalpy contributions from the solid phase.

To circumvent the solubility problem, solutions were prepared by adding toluene to a weighed excess of NiSDPT in a 250-ml volumetric flask. The solution was stirred for 2 hr to dissolve the maximum amount of NiSDPT and was then filtered through an ultra-fine fitted glass filter to remove undissolved solid. Two 100-ml aliquots were then taken for calorimetric studies and a 25-ml aliquot was analyzed for nickel. As a check on the analysis, the undissolved NiSDPT was dried and weighed to constant weight. This weight and the total sample weight were then used to calculate the concentration of NiSDPT, which agreed to within 1% with the microanalysis value.

It was found that the maximum attainable concentration of NiSDPT in toluene is ~0.005 *M*. Three injections (~0.2, 0.4 and 0.4 ml) of pure 4-mepy from a 1-ml syringe into 100 ml of a solution of this concentration serve to convert the complex almost completely to the adduct. The third injection is slightly endothermic and very close to the deflection observed when 4-mepy is injected into toluene. When the heat of solution makes the predominant contribution to the deflections (as was the case in the third injection), experimental uncertainty in the heat of solution can seriously affect the position of the $-\Delta H^{\text{ad}}$ *vs.* $1/K$ fit. It was found that the value of $-\Delta H^{\text{ad}}$ for the formation of the NiSDPT-(4-mepy) adduct in toluene is changed by as much as 1 kcal/mol when two sets of heat of solution data differing by 10% are used. Ordinarily, the way to eliminate this problem is to increase the acid concentration, thereby increasing the contribution to the deflections due to adduct formation. However, this is impossible in the system under discussion. Thus, the small experimental uncertainty in heat of solution and the unavoidable uncertainty in acid (NiSDPT) concentration (about 3%) couple to produce a fairly large uncertainty in the measured enthalpy of adduct formation on this system. The calorimetric results for several aliquots are reported in Table I.

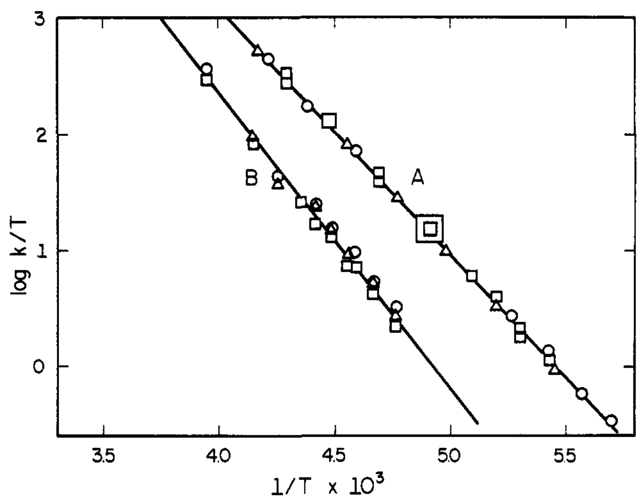

Figure 6. Activation plots (log k/T *vs.* $1/T$) for exchange reaction 1 in (A) methylene chloride and (B) toluene.

It is appropriate at this point to say a few words about an enthalpy reported on a similar system in ref 6. The authors report the value of ΔH^{ad} for the adduct formation reaction of NiSDPT and pyridine in benzene as -6.7 kcal/mol, measured using the spectrophotometric technique. It seems unreasonable that this enthalpy and ours should differ by 3.4 kcal/mol. However, the authors report that they used complex concentrations of 10^{-4} *M*. At the wavelength at which the complex absorbs most strongly (5850 Å), its molar extinction coefficient has the value 70 l./(mol cm) (we obtained a value of 75 l./(mol cm), in good agreement with the value reported in ref 6). Even with a 10-cm cell, the maximum attainable absorbance change (*i.e.*, assuming the adduct has $\epsilon = 0$ at 5850 Å, which it does not) would be 0.075 absorbance unit. Absorbance changes *actually* observed would be at most 0.02 absorbance unit. Since the Cary 14 is accurate to 0.002 unit, one could measure absorbance changes to at best 10% precision, which would ultimately lead to large error in the ΔH obtained from the slope of a van't Hoff plot over a limited temperature range. These considerations would seem to cast doubt on the accuracy of the reported enthalpy and we conclude that our number is more reliable.

Kinetic Studies. The techniques used to study this system were in general the same as those used in the solvent methylene chloride. However, due to solubility problems in toluene which have been already discussed, it was necessary to have at least tenfold excess free base in order to dissolve the adduct. As a result of this solubility difficulty, the range of mole fractions obtained in the solvent CH_2Cl_2 could not be attained, and line broadening effects were not nearly as pronounced as in methylene chloride.

In addition, it was observed that the width at half-height of the methyl resonance of free 4-mepy at any temperature in the kinetics-affected region increased noticeably as a function of time. Measured line widths increased by a factor of ~2 over a period of 3 weeks. However, the activation enthalpy proved to be independent of this broadening phenomenon, so we felt justified in ignoring it.

Preliminary nmr scans indicated that exchange could be stopped at about −80°. The line shape of the methyl resonance of free 4-mepy was affected by the exchange process up to a temperature of −20°. Below −60°, two resonances were observed for each type of 4-mepy proton, one due to coordinated 4-mepy and the other to free 4-mepy. The directions of the shifts are the same as those observed in CH_2Cl_2 (see Figure 2).

Isotropic shift ($\Delta\omega_M$) data for three solutions of differing complex and 4-mepy concentrations (for details, see microfilm edition), measured in the stopped-exchange region (between −85 and −100°) at a probe frequency of 60 MHz, is plotted against $1/T$(°K) in Figure 3. The plot is linear with a small negative intercept. T_{2M} data for these solutions were also measured at 60 MHz in the stopped-exchange region and are plotted logarithmically in Figure 4. Stopped-exchange T_{2L} data and spectra in the kinetics-affected region (−63 to −20°) were taken at a probe frequency of 100 MHz. The complete line-width profile for the methyl resonance of free 4-mepy for solution 2 is plotted in Figure 4. The best least squares fits for $\Delta\omega_M$, T_{2M}, and T_{2L} are reported below.

$\Delta\omega_M = 2.465 \times 10^5(1/T) - 243.3$
$\log 1/\pi T_{2M} = 307.3(1/T) + 0.2138$
$\log 1/\pi T_{2L} = 440.5(1/T) - 1.355$ for solutions 1 and 2
$\log 1/\pi T_{2L} = 504.2(1/T) - 1.9138$ for solution 3

Rate constants were obtained from the observed spectra by density matrix calculations in the same way as described for the previous system, with one difference. The spectra fitted in this case were 100-MHz spectra. To fit these, it was necessary to calculate appropriate isotropic shifts from those measured at 60 MHz by multiplying the latter by the factor $^5/_3$. Experimental justification for the use of corrected 60-MHz contact shifts to fit 100-MHz spectra was obtained as follows. In the temperature region after coalescence, the observed line width is related[12] to the isotropic shift through the following equation

$$\pi(\Delta\nu_{1/2})_{\text{obsd}} = (1/T_2)_{\text{obsd}} = P_M\tau_M(\Delta\omega_M)^2$$

where P_M, τ_M, and $\Delta\omega_M$ have the meanings already discussed. The ratio of the line width at 100 MHz to the line width at 60 MHz should be $(^5/_3)^2$ at any given temperature after coalescence. This is found experimentally and provides justification for the fitting procedure used.

It should be said that, in general, calculated and experimental spectra do not agree as well for this system as for the study in methylene chloride. Some sample fits are seen in Figure 5. There is more scatter in the activation plot (see Figure 6) than in the methylene chloride system, most likely due to the smaller mole fraction ranges attainable. However, the plot is still quite good. For this system as for the previous system, the rate constants for all three solutions fall on the same activation plot.

The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $k(25°)$ obtained from Figure 6 are given in Table II.

Discussion

Examination of the activation plots in Figure 6 shows that the rate constant for exchange at any temperature is independent of either the concentration of free 4-mepy or the concentration of the NiSDPT (4-mepy) adduct in both solvents studied. This result is consistent with the following rate law

$$\frac{-\mathrm{d}[\text{NiSDPT(4-mepy)}]}{\mathrm{d}t} = k[\text{NiSDPT(4-mepy)}]$$

where $k = 1/\tau_M$. Such a first-order rate law implies that the exchange reaction proceeds by a dissociative rather than an associative mechanism, as expected for an octahedral substitution process. However, there are two types of dissociative activation, both of which have been found for octahedral substitution.[15] These are shown below for the general ligand exchange reaction depicted in eq 5.

$$\text{MB} + \text{B*} = \text{MB*} + \text{B} \tag{5}$$

1. Pure dissociative

$$\text{MB} \xrightarrow{k_1} \text{M} + \text{B} \quad \text{slow}$$
$$\text{M} + \text{B*} \longrightarrow \text{MB*} \quad \text{fast}$$
$$\text{rate} = k_1[\text{MB}]$$

2. Dissociative interchange

$$\text{MB} + \text{B*} \overset{K_{\text{os}}}{\rightleftharpoons} \text{MBB*} \quad \text{fast equil}$$
$$\text{MBB*} \xrightarrow{k_1} \text{MB*} + \text{B} \quad \text{slow}$$
$$\text{rate} = \frac{k_1K_{\text{os}}[\text{M}]_T[\text{B*}]}{K_{\text{os}}[\text{B*}] + 1}$$

where $[\text{M}]_T = [\text{MB}] + [\text{MBB*}]$. The first mechanism involves the formation of a five-coordinate intermediate, followed by the rapid reaction of this intermediate with the incoming ligand to form the product. An exchange reaction following this path *must* show first-order kinetics, regardless of the concentration conditions involved. The second mechanism involves the initial rapid formation of an outer sphere complex, in which the incoming ligand B* can be considered to be weakly associated with the metal ion complex. The outgoing ligand and incoming ligand then exchange positions in the rate determining step and the products are formed. A reaction proceeding by this mechanism can exhibit either first- or second-order kinetics, depending upon the relative magnitudes of the terms in the denominator of the rate expression. If $K_{\text{os}}[\text{B*}] \gg 1$, the rate law becomes identical with that for the pure dissociative mechanism. If, however, $K_{\text{os}}[\text{B*}] \ll 1$, the rate law becomes

$$\text{rate} = k_1K_{\text{os}}[\text{M}]_T[\text{B*}]$$

and second-order kinetics is observed. For charged reactant species in aqueous solution, values of K_{os} usually[16] range between 0.1 and 4. It is reasonable that for systems in which the reactant species are un-

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

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

charged, as in this work, K_{os} would be at most 0.5 and probably smaller. This would be especially true in CH_2Cl_2, where the outer sphere complexation process would have to compete with the hydrogen bonding of 4-mepy to the solvent. In order that $K_{os}[B^*]$ be equal to 1, it would then be necessary that $[B^*]$ be 2 *M*. For the concentrations of free ligand used in this work (*i.e.*, at most 1 *M*), $K_{os}[B^*] < 1$ and second-order kinetics would be observed if the dissociative interchange mechanism were operative. The fact that strictly first-order kinetic behavior is found is good evidence for pure dissociative activation, as shown in mechanism 1.

Further, an examination of the enthalpies reported in Tables I and II shows that in both solvents, $\Delta H^{\ddagger} > -\Delta H^{ad}$, the difference being 3.0 kcal/mol in methylene chloride and 1.4 kcal/mol in toluene. These numbers are outside the range of experimental error. We have shown that the kinetic results substantiate a pure dissociative exchange mechanism. Thus we may assume, as proposed in the introduction, that $\Delta H^1 = -\Delta H^{ad}$ in Figure 1 (*i.e.*, the NiSDPT molecule is itself the five-coordinate intermediate), and therefore the quantity $\Delta H^{diff} = \Delta H^{\ddagger} - (-\Delta H^{ad})$ represents direct thermodynamic evidence for the presence of a relatively stable intermediate in the dissociative pathway. This in itself is a significant result in that there are few examples of such evidence for an intermediate species in octahedral substitution reactions.

Although there have been many claims made for the pure dissociative mechanism from nmr studies, we have recently shown[17] that these studies have been carried out under conditions where discrimination between the two mechanisms described above is not possible. This study thus constitutes one of the first experiments employing the nmr technique in which the two mechanisms have been distinguished.

The values of the first-order rate constants for exchange obtained by extrapolation of the activation plots in Figure 6 to 25° are even larger than the value of 2.8×10^6 sec^{-1} reported for the exchange of DMF between the bulk solution and the coordination sphere of some four-coordinate macrocyclic complexes[18] of nickel(II). In fact, the value of the rate constant in CH_2Cl_2 is the largest yet observed for nickel exchange. This is attributed to the reasonably good hydrogen bonding ability of CH_2Cl_2 and the decreased Lewis acidity of the nickel in the particular complex. The fact that a smaller rate constant is observed in toluene than in CH_2Cl_2 supports a hydrogen bonding contribution to the rate in the latter solvent. The poor Lewis acidity of the nickel complex is in part attributed to the steric repulsions expected between atoms of the pentadentate ligand when the nickel becomes octahedrally coordinated.

Before proceeding with a complete analysis of the energetics of exchange reaction 1, some comments will be made on the importance of the solution structure of NiSDPT. The problem is twofold: (1) is there more than one isomer of NiSDPT or its adduct in solution, and (2) do NiSDPT or its adduct have different structures in different solvents? The pmr data reported in ref 2 particularly and the visible absorption spectra in ref 6 are *fully consistent* with the presence of only one isomer in solution. The presence of more than one isomer would be evident in the temperature dependence of the pmr spectrum as non-Curie law behavior. This was not observed for the free acid.[2] The existence of more than one structure for the adduct of NiSDPT with pyridine (or 4-methylpyridine) is also convincingly ruled out by pmr and visible spectral data. Careful construction and consideration of both Courtauld and framework molecular models has convinced us beyond any final doubt that there is only one reasonable configuration for the adduct of NiSDPT with 4-mepy. Thus, the question of geometrical isomers does not complicate our interpretation.

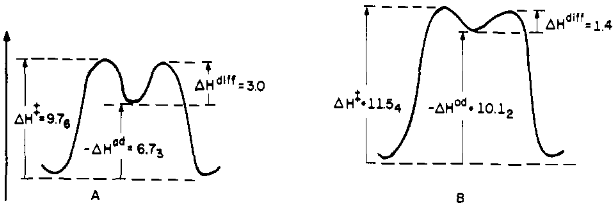

Figure 7. Reaction coordinate diagrams for reaction 1 in (A) methylene chloride and (B) toluene.

NiSDPT very probably has a slight solvent-dependent solution structure, for identical structures in two solvents would result only from identical solvation by those solvents. The impetus for a small structural change in going from one solvent to another arises from the different (specific or nonspecific) solvating properties of the solvents. The enthalpy for such small structural changes is included as a part of the solvation process since separation of this enthalpy contribution from solvation effects is impossible and meaningless in any real sense. The arguments which follow are *in no way* dependent upon a rigid solution structure for NiSDPT. However, ref 2 shows that if any structural change does occur with solvent variation, it is very slight, for the solution nmr spectrum of NiSDPT is nearly independent of the solvent dielectric constant over a range of 2.2 (CCl_4, benzene) to 39 (CH_3NO_2, CH_3CN). The pmr isotropic shift patterns are essentially identical in all solvents studied, and variations in shifts from one solvent to another are small (this is not true for the similar complex NiSalMeDPT, in which there is a methyl group on the amino nitrogen). Any differences in structure must indeed be small to cause such small effects in very sensitive paramagnetic pmr spectrum!

The proposed reaction coordinate diagrams for the exchange reaction 1 in the solvents CH_2Cl_2 and toluene are shown in Figure 7. They are consistent with mechanism 1, discussed earlier; the equality of ΔH^1 and $-\Delta H^{ad}$ has been employed in the figure.

Three sets of comparisons must be made in order to thoroughly explain the energetics of the exchange and adduct formation reactions: (1) the relation between $-\Delta H^{ad}$ values in the two solvents; (2) the relation between $\Delta H^{\ddagger}$ values in the two solvents; and (3) the relation between $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$ in a given solvent. These will be considered one at a time in the following discussion.

First, the difference between $-\Delta H^{ad}$ values in the two solvents is larger than anticipated. Toluene is a

[17] W. D. Perry, R. S. Drago, and N. K. Kildahl, submitted for publication.

[18] L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, 10, 2686 (1971).

low dielectric constant solvent, which in the absence of specific interactions is expected to be poorly solvating and to give enthalpies comparable to those found in cyclohexane or carbon tetrachloride. As shown in earlier work,[3,4,19] pyridines interact specifically with benzene, so enthalpies determined on systems involving pyridine-type donors in benzene or toluene must be converted to the cyclohexane analog by adding 0.9 kcal mol^{-1}. Accordingly, the solvation-corrected toluene enthalpy of adduct formation is 11.0 kcal mol^{-1}. It has also been shown that in methylene chloride with the base pyridine, the measured enthalpy is consistently 2.5 kcal mol^{-1} lower than that measured in CCl_4 or cyclohexane. According to this criterion, the enthalpy of formation of the NiSDPT(4-mepy) adduct in cyclohexane should be $6.7 + 2.5 = 9.2$ kcal mol^{-1}. The discrepancy in these two corrected enthalpies must be attributed to a breakdown in the ESP procedure.[3,4]

We attribute this breakdown to the acid rather than to the base, since 4-mepy is similar to pyridine, which has been shown to be well behaved toward several acids in regard to the solvent corrections described here. In contrast, no previous acid–base work has been done with NiSDPT, so its solvent interactions have not yet been elucidated. It has been shown[7] that the complex NiSDPT exists in the solid state as a distorted trigonal bipyramid. It has been shown[2] that this structure is favored in solution also, as long as the solvent is noncoordinating. Molecular models indicate that in forming the six-coordinate adduct with 4-mepy, it is necessary for considerable rearrangement of the complex to occur in order to accommodate the 4-mepy molecule in the first coordination sphere of the nickel. In the rearranged form, the aromatic rings of the SDPT ligand are much closer together than they are in the normal five-coordinate configuration. It is reasonable to expect that when rearrangement occurs with adduct formation, one or two weak hydrogen bonds between the hydrogens of methylene chloride and the aromatic rings of the SDPT species are destroyed as those rings are forced together; *i.e.*, there are specific interactions between methylene chloride and the acid which are destroyed when the adduct is formed. As pointed out in the literature, ESP will work only if specific interactions of the sort just described are of comparable magnitude in the adduct and free acid or base. In contrast, no such specific interactions with the complex are expected in toluene solvent. Hence, we find a 1.8-kcal/mol discrepancy in the corrected heats for the two solvents. The specific interaction of methylene chloride with the free acid will receive further support in our discussion of the kinetic parameters.

Second, we shall consider the relationship between the $\Delta H^{\ddagger}$ values in the two solvents. We found that $\Delta H^{\ddagger}$ for reaction 1 is 1.7 kcal/mol larger in toluene than in methylene chloride. This implies that the transition state is stabilized more relative to the adduct in CH_2Cl_2 than in toluene. Prior to interpreting the nature of this stabilization, we should return to our contention that the failure of ESP to work can be attributed to the specific interaction of methylene chloride with the free acid NiSDPT. The existence of this interaction receives support from entropy considerations. (See Tables I and II for the values of ΔS^{ad} and $\Delta S^{\ddagger}$.) The difference in the thermodynamic value of the entropy of adduct dissociation and the entropy of activation for dissociation is the entropy of dissociating the transition state into the free acid and base. These quantities have the values of +11.6 and +14.9 eu in methylene chloride and toluene, respectively. Thus, there is less ordering in going from the intermediate (free acid and base) to the transition state in CH_2Cl_2 than in toluene to the extent of 3.3 eu, which is consistent with the idea that hydrogen bonds between methylene chloride and the acid are broken during this process. Entropy changes due to breakup of the 4-mepy–toluene complex and the partial breakup of the 4-mepy–methylene chloride complex, also involved in going from the intermediate to the transition state in the respective solvents, are expected to be similar.

One additional piece of essential information can be obtained from $-\Delta S^{ad}$ (*i.e.*, the entropy of adduct dissociation) and $\Delta S^{\ddagger}$. The values of these quantities indicate that the majority of the rearrangement involved in adduct formation occurs in going from the separated acid and base to the transition state—the entropy involved in forming the adduct from the transition state is only about one-half the value involved in forming the transition state from the free acid and base. Thus, the transition state and the adduct are *structurally* similar, even though they are energetically quite different (as reflected in the values of $\Delta H^{\ddagger}$). This suggests a structure for the transition state which is like that of the adduct, but with a long nickel–pyridine bond. With this in mind, we attribute the 1.7 kcal/mol difference in activation enthalpies in toluene and methylene chloride as due to the formation of a partial hydrogen bond between the methylene chloride and the leaving 4-mepy in the transition state. The hydrogen bonding between methylene chloride and the NiSDPT moiety which is lost upon conversion of the free acid to complex is not expected to contribute to the activation enthalpy because the transition state and adduct have similar structures.

Next, we need to examine the relation between $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$ in each solvent. Viewing the intermediate in the reaction coordinate diagram as completely separated 4-mepy and NiSDPT and the transition state as only a partially separated adduct implies that any solvent–4-mepy interaction must be at least partially disrupted in the course of forming the transition state from the intermediate. In the toluene system, the 1.4 kcal/mol difference in $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$ includes as an upper limit 0.9 kcal/mol required to completely break up the 4-mepy–toluene complex. Subtracting this from 1.4 kcal/mol, we obtain 0.5 kcal/mol as the lower limit for the difference in $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$. This may be the energy required to overcome intramolecular and intermolecular rearrangement barriers which undoubtedly arise during adduct formation. However, since error limits on $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$ in toluene are about 0.6 kcal/mol, the 0.5 kcal/mol difference which remains after correcting for solvent–base interaction is within experimental error; *i.e.*, if we assume no interaction between 4-mepy and toluene in the transition state, $\Delta H^{\ddagger}$ and the solvent corrected $-\Delta H^{ad}$ are equal within experimental error. The 3 kcal/mol difference in $\Delta H^{\ddagger}$ and $-\Delta H^{ad}$ in CH_2Cl_2 must be considered in the light of the 1.7 kcal/mol difference of $\Delta H^{\ddagger}$ in

[19] J. A. Nusz, unpublished results.

toluene and CH_2Cl_2. If we assume that interaction between NiSDPT and solvent is similar in the adduct and transition state (an assumption which is supported by entropy considerations, as has been shown), then this latter difference of 1.7 kcal/mol can be attributed almost entirely to the incomplete destruction of the hydrogen bonding of methylene chloride to 4-mepy in forming the transition state. The maximum value of this H-bonding interaction is 2.5 kcal/mol;[19] thus, of the 3 kcal/mol required to go from the intermediate to the transition state in methylene chloride, 0.8 kcal/mol (2.5–1.7) may be attributed to destruction of 4-mepy–CH_2Cl_2 bonding. The ESP considerations discussed earlier allow us to attribute an upper limit of 1.8 kcal/mol to destruction of hydrogen bonds between the aromatic rings of NiSDPT and methylene chloride. Thus, all but 0.4 kcal/mol of the total difference between $-\Delta H^{ad}$ and $\Delta H^{\ddagger}$ in methylene chloride may be accounted for by specific interactions between the solvent and the acid and base species. This difference is again within the limits of experimental error, due to the error in the activation enthalpy in toluene; however, the possibility exists that rearrangement barriers, which undoubtedly exist, could be of this magnitude.

In this analysis, we have assumed no interaction of the toluene with 4-mepy in the transition state. Should such an interaction exist, this would require that the 4-mepy–methylene chloride interaction in the transition state be greater than 1.7 kcal/mol. Since the hydrogen bonding interaction is at most 2.5 kcal/mol and we do not wish to assume total 4-mepy–CH_2Cl_2 interaction in the transition state, the activation energy in toluene must be essentially solvent free.

Finally, it is interesting to compare the enthalpy of interaction of methyl cobaloxime and trimethyl phosphite[20] with the activation enthalpy for the exchange process

$$RCo(DH)_2(TMPP) + TMPP^* \longrightarrow RCo(DH)_2(TMPP^*) + TMPP$$

which has been measured in toluene.[21] The solvation corrected value of $-\Delta H^{ad}$ is found to be 19.7 kcal/mol, whereas $\Delta H^{\ddagger}$ has the value 22 ± 1 kcal/mol. In this system, solvation effects are expected to be minimal.

The potential 0.5 kcal/mol discrepancy in the NiSDPT system and the 2.3 ± 1 kcal/mol discrepancy in the methyl cobaloxime system certainly make questionable inferences about bond strength from activation enthalpies. If it can be demonstrated that these discrepancies are constant quantities which depend only on the acid when a series of different bases are studied, this quantity can be determined by a procedure recently reported for evaluating constant contributions to the enthalpy of adduct formation.[22] This remains to be demonstrated.

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Supplementary Material Available. Tables I and II in their expanded forms will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-6245.

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