tion of an external reference is appreciably different than if the reference is internal. It is for these reasons as well as those discussed by Tiers that ^{19}F nmr data should be reported in a truly interconvertible system of units such as ϕ values.

Safety Precautions. Although no explosions of bis(perfluoroalkyl) trioxides have been observed during the course of this work, the same safety precautions previously described[22] for fluoroxy compounds have been observed.

Fluorination of Sodium Trifluoroacetate. A 2.1-g (15.6 mmoles) sample of finely divided dry sodium trifluoroacetate in a monel sintered-plate reactor was treated with 0.30 mole of fluorine under the following conditions: 4% F_2, 15 min; 20% F_2, 1 hr; 34% F_2, 2 hr. The temperature of the reactor gradually increased from 17 to 22°. The volatile products condensed in the liquid oxygen trap (9.3 mmoles) were analyzed by gas chromatography after work-up by standard vacuum line procedures. Approximately 4% of CF_3OOOCF_3 was found together with smaller amounts of $CF_3OOOC_2F_5$. Yields of CF_3OOOCF_3 were generally 1–5%.

Bis(perfluoromethyl) Trioxide. Bis(perfluoromethyl) trioxide was purified by gas chromatography at $-30°$. Its retention time was found to be approximately 60 relative to fluorotrichloromethane. Elemental analyses were obtained on a sample of chromatographed CF_3OOOCF_3. A molecular weight determination on this material gave a value of 187 (calcd, 186).

Anal. Calcd for $C_2F_6O_3$: C, 12.9; F, 61.3. Found: C, 13.0; F, 60.4.

Perfluoromethyl Perfluoroethyl Trioxide. Perfluoromethyl perfluoroethyl trioxide was purified by gas chromatography at 0°. Its retention time was found to be approximately 150 relative to fluorotrichloromethane. Elemental analyses were obtained on a sample of chromatographed $CF_3OOOC_2F_5$. Unfortunately the sample was then contaminated by a small amount of $CFCl_3$. A quantitative measurement of the amount of $CFCl_3$ in the sample was made by both infrared and mass spectroscopy. The two determinations were in good agreement and the calculated values for $C_3F_8O_3$ are adjusted for the 4 wt % $CFCl_3$ present. A molecular weight determination on this sample gave a value of 234; calcd (cor), 232.

Anal. Calcd for $C_3F_8O_3$ (cor): C, 15.0; F, 62.4. Found: C, 15.0; F, 62.0.

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Kinetics of Ligand Exchange by Nuclear Magnetic Resonance Complete Line-Shape Techniques. I. Exchange of 2-Picoline with Dichlorobis(2-picoline)cobalt(II)

Steven S. Zumdahl[1] and Russell S. Drago

Contribution from the William A. Noyes Laboratory, University of Illinois, Urbana, Illinois. *Received February 20, 1967*

Abstract: The exchange kinetics of excess 2-picoline with dichlorobis(2-picoline)cobalt(II) in acetone-d_6 were investigated by nuclear magnetic resonance computerized, complete line-shape techniques. Exchange rates were measured between -39 and $-60°$, and in this region it was found that $1/\tau_M = K_2$[2-picoline]. The Arrhenius activation energy for K_2 is $E_a = 5.3 \pm 0.3$ kcal/mole.

In recent years many studies have been conducted on the exchange kinetics of inorganic complexes *via* nuclear magnetic resonance.[2,3] Most of these studies have involved octahedral complexes in aqueous solution or in the free ligand as solvent.[4-9] Thus, there was no opportunity to definitively study, in a relatively inert solvent, the role of the free ligand in the exchange mechanism. Also, these studies have almost exclusively employed line-broadening methods to obtain the exchange rates.

Very little is known about the exchange kinetics of tetrahedral complexes. When this study was begun, no nmr exchange studies had been conducted on this type of system.[10] Thus, it was of interest to us to study the exchange reactions of tetrahedral complexes in a relatively inert solvent where the concentration of free ligand could be varied. An additional purpose of this work was to test the feasibility of using computerized, complete line-shape techniques to evaluate the exchange rates for paramagnetic systems where the signals are broad and the signal-to-noise ratio is usually not favorable due to limited complex solubility. Application of the line-shape method is desirable, since it appears to be inherently more accurate than line-broadening techniques.[11] Also, the former method is more versatile, since it is applicable over the entire temperature range in which the exchange rate influences the signal shape.

With these goals in mind we chose $Co(2\text{-pic})_2Cl_2$, which has been previously characterized,[12,13] for ex-

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change studies. The reaction studied is

$$\mathrm{Co(2\text{-}pic)_2Cl_2} + \text{2-pic*} \rightleftharpoons \mathrm{Co(2\text{-}pic)(2\text{-}pic^*)Cl_2} + \text{2-pic}$$

where 2-pic is 2-methylpyridine.

Experimental Section

Materials. 2-Methylpyridine was obtained from the J. T. Baker Co. and was distilled (bp 128°) prior to use. Acetone-d_6 (99.5% isotopic purity) was obtained from Columbia Organic Chemicals Co. $\mathrm{Co(2\text{-}pic)_2Cl_2}$ was prepared as previously reported[13] and recrystallized from ethanol.

Anal. Calcd for $\mathrm{Co(2\text{-}pic)_2Cl_2}$: C, 45.6; H, 4.4; N, 8.9; Co, 18.6. Found: C, 45.6; H, 4.5; N, 8.6; Co, 18.4.

Nmr Spectra. The nmr spectra were obtained on a Varian A56/60A spectrometer equipped with a Varian Model V-6040 variable-temperature controller. The temperature could be held constant to within at least ±1°. The temperature was monitored by use of a YSI Model 42SL thermistor thermometer whose accuracy is ±0.5°.

Great care was taken to obtain undistorted, pure absorption signals and to avoid machine-broadening effects. To reduce noise problems the experimental intensities were obtained from the average of three scans.

Results and Discussion

Line-Shape Program. The line-shape program used in this study consists of a main program, SHAPE 4, for least-squares fitting of the theoretical and experimental curves; a subroutine, LADDAB, which calculates the theoretical line shapes; and a subroutine, PLOT, which plots the experimental and theoretical spectra by means of an IBM CalComp plotter.

SHAPE 4 is a modified version of the curve-fitting program used by Jonas, *et al.*[14] LADDAB calculates a theoretical spectrum using a line-shape function for an AB system similar to that derived from the Bloch equations by Gutowsky and Holm[15] but more general because of the inclusion of both transverse relaxation times.[16]

The input parameters for the line-shape calculation are the difference in chemical shift between sites A and B in the absence of exchange, the transverse relaxation times for both sites, the mole fraction of nuclei in each site, an estimated value of the exchange rate, and an experimental spectrum.

The calculation procedure is as follows. An experimental spectrum is presented to the computer as a series of digitized absorption intensities measured at arbitrary frequency intervals. This spectrum is normalized by the computer. LADDAB, using the input parameters, then calculates 200 normalized, theoretical spectra corresponding to small increments in the rate between five times the input rate and one-fourth the input rate. The theoretical spectrum which shows the smallest sum of squared deviations in intensity from the experimental spectrum is then printed out along with the corresponding exchange rate. Also, the experimental spectrum and best theoretical spectrum are plotted by the CalComp plotter.

Solutions. Solutions for the exchange study were prepared by dissolving $\mathrm{Co(2\text{-}pic)_2Cl_2}$ and excess 2-picoline in acetone-d_6. The electronic spectra of these solutions were essentially the same as for $\mathrm{Co(2\text{-}pic)_2Cl_2}$ dissolved in pure 2-picoline. (It has been demonstrated previously[12] that these complexes do not add ligand to form $\mathrm{CoL_4X_2}$ in the presence of excess 2-picoline.) Also, plots of the observed shift of the fast-exchange-averaged proton signals *vs.* mole fraction of free ligand (P_L) showed linear behavior for all five types of protons at 34° over a concentration range from $P_L = 0.45$ to 0.95. Therefore, we conclude that no serious decomposition of the complex occurs in acetone in the presence of excess ligand. However, to ensure against any dissociation of 2-picoline from the complex, all rate studies were conducted using solutions containing a large concentration of excess 2-picoline.

Isotropic Shift. To obtain the magnetic shift between the protons in the complexed ligand and free ligand sites it is necessary to evaluate the paramagnetic isotropic shift.

Preliminary nmr studies of neat 2-picoline showed that only the 2-methyl protons are not spin-spin coupled with the other protons in the system. Thus, the 2-methyl protons were chosen for line-shape study since they comprise a simple AB exchange system.

Nmr studies of deuterioacetone solutions of $\mathrm{Co(2\text{-}pic)_2Cl_2}$ containing excess 2-picoline showed that no separation of the free and coordinated ligand signals occurred at temperatures down to −60°. Also, it was shown that fast exchange conditions (*i.e.*, $1/\tau_M \gg \Delta\omega_M$, where τ_M is the mean lifetime of a coordinated ligand, and $\Delta\omega_M$ is the isotropic shift between coordinated and free ligand protons) prevailed down to approximately −25°. This was demonstrated by plotting the log of the line width at half-height for the averaged methyl peak *vs.* the reciprocal of the absolute temperature. This plot was linear down to ∼−25°. Below −25° the signal began to show exchange-broadening effects.

Thus, at temperatures above −25° the equation[17]

$$\nu_{\mathrm{obsd}} = P_M\nu_M + P_L\nu_L \tag{1}$$

is applicable, where ν_{obsd} is the observed shift of the fast-exchange-averaged peak from some reference, ν_M and ν_L are the chemical shifts for the complexed and free ligand protons from the reference, and P_M and P_L are the mole fractions of complexed and free ligand protons, respectively.

Thus, to obtain ν_M and ν_L one can plot ν_{obsd} *vs.* P_L and evaluate the intercepts at $P_L = 0$ and $P_L = 1$, respectively. In order to obtain the isotropic shift in the temperature region where exchange is significant, mole fraction plots were made at several temperatures in the fast-exchange region, and ν_M was evaluated at each temperature. $\nu_L - \nu_M$ was then plotted *vs.* $1/T$°K as shown in Figure 1. The resulting plot shows the expected Curie law behavior in the fast-exchange temperature region. Values of the isotropic shift in the exchange-controlled region can be obtained by extrapolation of the straight line into the lower temperature region.

Transverse Relaxation Times. Also necessary for the AB line-shape calculation is the knowledge of the transverse relaxation times, T_{2M} and T_{2L}, for both

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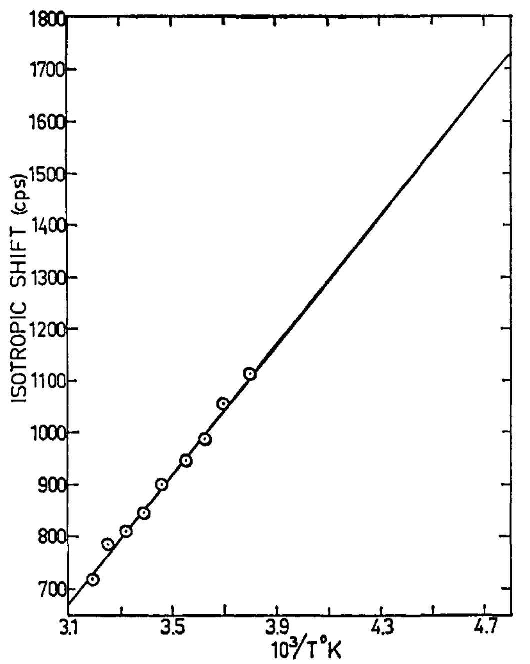

Figure 1. Plot of the isotropic shift ($\nu_L - \nu_M$) for the 2-methyl protons *vs.* $10^3/T$°K.

magnetic sites. In order to evaluate these parameters we used the equation[17]

$$(\Delta\nu_{1/2})_{\text{obsd}} = P_M(\Delta\nu_{1/2})_M + P_L(\Delta\nu_{1/2})_L \tag{2}$$

which is applicable in the fast-exchange region. In this equation $(\Delta\nu_{1/2})_{\text{obsd}}$ is the observed line width (cps) at half-maximum intensity for the fast-exchange-averaged signal, $(\Delta\nu_{1/2})_M$ and $(\Delta\nu_{1/2})_L$ are the line widths at half-height for protons in the coordinated and free ligand sites, respectively, in the absence of exchange, and P_L and P_M are as defined above.

In order to obtain $(\Delta\nu_{1/2})_M$ and $(\Delta\nu_{1/2})_L$, a plot of $(\Delta\nu_{1/2})_{\text{obsd}}$ *vs.* P_L is constructed, and the intercepts at $P_L = 0$ and $P_L = 1$ are evaluated. This procedure was carried out for the 2-methyl proton signal at several temperatures in the fast-exchange region. Plots were then made of log $(\Delta\nu_{1/2})_L$ and log $(\Delta\nu_{1/2})_M$ *vs.* $1/T$. It was found that the error (±0.5 cps) in obtaining $(\Delta\nu_{1/2})_L$ from the mole fraction plots represented a significant percentage of $(\Delta\nu_{1/2})_L$ whose magnitude is 3–5 cps. This made impossible an accurate extrapolation to lower temperatures. To eliminate this difficulty, the following procedure was used to fit the points for log $(\Delta\nu_{1/2})_L$ *vs.* $1/T$. The temperature dependence of the transverse relaxation time for protons on the ligand in the bulk solvent was assumed to be the same as for protons on the coordinated ligand. This is reasonable, since the same mechanism very likely determines both T_{2M} and T_{2L} (see below). This has been observed previously.[5] The position of the line was determined by fitting (2) using the known values of $(\Delta\nu_{1/2})_{\text{obsd}}$ and $(\Delta\nu_{1/2})_M$ for several solutions at several temperatures in the fast-exchange region. The results appear in Figure 2. It can be seen that the above procedure gives a good fit of the observed data for $(\Delta\nu_{1/2})_L$. These plots can be extrapolated to lower temperatures to obtain T_{2M} and T_{2L} in the exchange-controlled region since

$$1/T_2 = \pi(\Delta\nu_{1/2}) \tag{3}$$

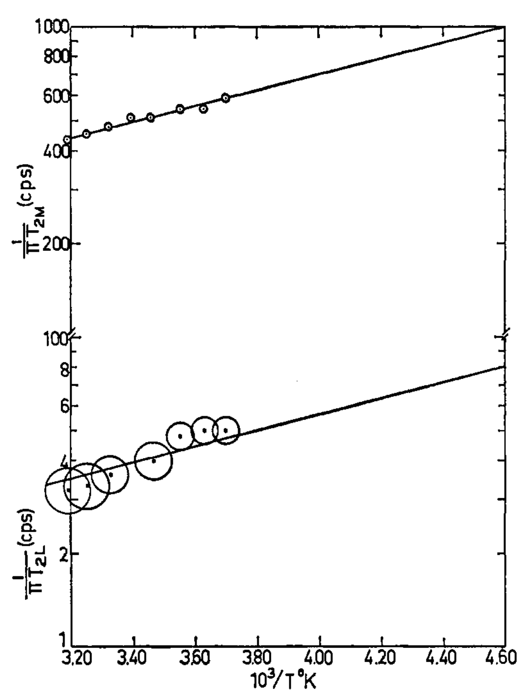

Figure 2. Plots of log ($1/\pi T_{2L}$) and log ($1/\pi T_{2M}$) *vs.* $10^3/T$°K where L and M refer to the free and coordinated 2-methyl ligand protons, respectively.

It is interesting to note that the apparent activation energy of $1/T_{2M}$ is −1.2 kcal/mole. As explained by Luz and Meiboom,[5] this indicates that the correlation time which controls T_{2M} and T_{2L} is τ_s, the electron relaxation time.

Estimation of the Exchange Rate. The estimated exchange rate is submitted to the program as $1/\tau$ where $\tau = P_L\tau_M = P_M\tau_L$. Here τ_L and τ_M refer to the mean lifetimes of a ligand in the bulk solvent and the primary coordination sphere of the metal ion, respectively.

To estimate τ for this system the following equation[11,18] was used

$$\tau = \frac{\Delta\nu_{1/2}'}{P_LP_M4\pi(\Delta\nu_M)^2} \tag{4}$$

where $\Delta\nu_M$ is the isotropic shift between the free and complexed ligand sites, and $\Delta\nu_{1/2}'$ is the difference between the observed line width at half-height and the fast-exchange line width at half-height from (2). Equation 4 is valid for systems near very fast exchange.

Rate Studies. To study the kinetics of the exchange of excess 2-picoline with $Co(2\text{-pic})_2Cl_2$, several solutions were prepared in deuterioacetone ranging from 1.6 to 3.6 *M* in 2-picoline and holding the complex concentration constant at 0.09 *M*. The nmr spectrum of the 2-methyl protons was observed for each of these solutions at temperatures ranging from −39 to −60°.

τ_M values were then obtained from each spectrum using the line-shape program as described above with one exception. It was found that the small errors present in the extrapolated isotropic shift values caused a slight mismatching of the centers of the calculated and experimental spectra. This led to large errors in τ_M. Therefore, a two-parameter variation (τ and $\Delta\nu_M$) was necessary. The value of τ_M for each experimental

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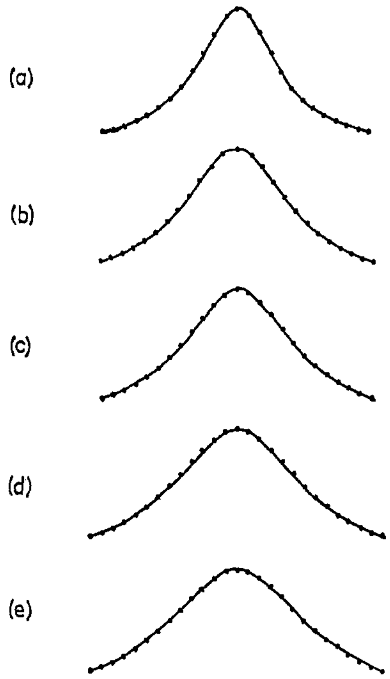

Figure 3. Comparison of experimental (solid line) and theoretical (dots) nmr spectra at $T = -44°$. All solutions are 0.09 *M* in $Co(2\text{-pic})_2Cl_2$ and contain the following concentrations of excess 2-picoline: (a) 3.54 *M*, (b) 2.64 *M*, (c) 2.40 *M*, (d) 2.11 *M*, (e) 1.85 *M*.

spectrum was taken from the theoretical spectrum which gave the best least-squares fit. Typical results are shown in Figure 3 where the normalized experimental spectra (solid lines) are shown with a few representative points of the normalized calculated spectra for several solutions at −44°. The fit of the theoretical and experimental spectra was very good.

Examination of the resulting τ_M values showed that a plot of $1/\tau_M$ *vs.* the free ligand concentration, [L], resulted in a straight line passing through the origin within experimental error for each temperature studied. Also, it was observed that changing the concentration of complex while holding [L] constant produced no change in τ_M. Thus, τ_M can be represented as

$$1/\tau_M = K_2[L] \qquad (5)$$

which is characteristic of second-order kinetics.

An Arrhenius activation energy was calculated for K_2. The plot is shown in Figure 4. The points at each temperature were calculated by use of (5) for a series of ligand concentrations. A least-squares analysis of the data gives $E_a = 5.3 \pm 0.3$ kcal/mole at the 90% confidence level. At 234°K this corresponds to $\Delta H^{\ddagger} = 4.8$ kcal/mole and $\Delta S^{\ddagger} = -14.5$ eu.

In conclusion, it is interesting to note that the second-order kinetics found in the present study agree with

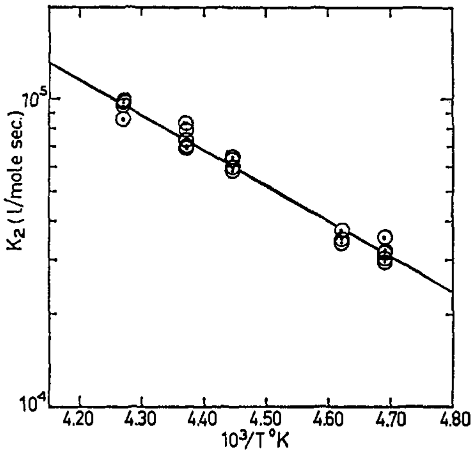

Figure 4. Arrhenius activation energy plot. Log K_2 is plotted *vs.* $10^3/T$°K. Size of the circle indicates the average deviation.

the results obtained by Horrocks and Pignolet[10] in their recent note on the exchange kinetics of pseudotetrahedral Co(II) and Ni(II) complexes of triphenylphosphine. Thus, in all examples studied to date participation of the free ligand in the activated complex of the exchange mechanism is observed for this type of complex. This result should be contrasted to the proposal that exchange reactions of octahedral complexes proceed *via* a dissociative-type mechanism.[19,20]

Also, it is of interest to compare the exchange rates obtained from the line-width method (eq 4) and from the complete line-shape technique. We observed that the line-broadening method gave τ values which differ by 5 to 15% (usually toward smaller values of τ) from the values given by the complete line-shape method. These deviations probably result from errors in measuring the line widths for use in eq 4.

We feel that a significant result of this study is the demonstration that computerized, complete line-shape techniques can be effectively applied for exchange studies of paramagnetic complexes. To our knowledge this has not been done before. We feel that although the line-shape method is more time-consuming than line-broadening methods, it is superior for the study of the exchange reactions of paramagnetic complexes because of its greater accuracy and versatility.

Acknowledgment. The authors are grateful to Dr. J. Jonas for help with the computer program. Also, the authors thank the Chemistry Branch of the Atomic Energy Commission for partial support of this research through Contract No. AT(11-1)758.

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