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Mechanism of Dimethyl Sulfide Intermolecular Exchange and Trans–Cis Isomerization of $SnCl_4 \cdot 2Me_2S$. Variable-Pressure Proton NMR and Variable-Temperature Tin-119 Magnetization Transfer NMR Studies[1,2]

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Dichloromethane solutions of tin(IV) tetrachloride with an excess of dimethyl sulfide contain *trans*- and *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ isomers in dynamic equilibrium. Three exchange processes are possible: (i) an exchange between free and cis-coordinated $(CH_3)_2S$ with a rate constant k_c [*cis*-$SnCl_4 \cdot 2(CH_3)_2S + {}^*(CH_3)_2S \rightleftharpoons$ *cis*-$SnCl_4 \cdot 2(CH_3)_2S \cdot {}^*(CH_3)_2S + (CH_3)_2S$]; (ii) the analogous process on the trans isomer with a rate constant k_t; (iii) an inter- or intramolecular isomerization with a forward rate constant k_i [*trans*-$SnCl_4 \cdot 2(CH_3)_2S \rightleftharpoons$ *cis*-$SnCl_4 \cdot 2(CH_3)_2S$]. A combination of variable-temperature and -pressure ^1H NMR line-broadening and $^{119}Sn\{^1H\}$ NMR magnetization transfer experiments show that k_c is 10^4–10^5 times greater than k_i, which in turn is at least 1 order of magnitude greater than k_t, and yield the following kinetic parameters for i and iii, respectively: $k^{298} = 1.2 \times 10^7$ and 3.3×10^2 s^{-1}; $\Delta H^* = 66.6$ and 71.0 kJ mol^{-1}; $\Delta S^* = +114.3$ and $+41.7$ J K^{-1} mol^{-1}; $\Delta V_0^* = +38.4$ and $+12.2$ cm^3 mol^{-1}. The thermodynamic parameters are $K_{iso}^{298} = [trans]/[cis] = 0.86$, $\Delta H_{iso}^0 = +3.4$ kJ mol^{-1}, $\Delta S_{iso}^0 = +10.0$ J K^{-1} mol^{-1}, and $\Delta V_{iso}^0 = +3.2$ cm^3 mol^{-1}. The intermolecular $(CH_3)_2S$ exchange on the cis adduct (i) occurs via a dissociative limiting D mechanism as witnessed by the first-order rate law, the positive ΔS^*, and the very large positive ΔV^*. The trans to cis isomerization is assigned to an intramolecular twist mechanism proceeding via an expanded six-coordinate transition state in view of the relatively small, but clearly positive, activation volume.

Introduction

In recent years we have undertaken an extensive study of the substitution reaction mechanisms of labile, high oxidation state, octahedral metal halide adducts in inert solvents.[3,4] These reactions (eq 1) provide an appropriate basis for study, since they are common to many transition metals and are simple, proceeding in general via a single step.

$$MX_{6-n} \cdot nL + {}^*L \rightleftharpoons MX_{6-n} \cdot (n-1)L \cdot {}^*L + L \qquad (1)$$

The reactions of the adducts of tin(IV) tetrahalides with neutral Lewis bases are particularly interesting in this context, since they offer the possibility of observing both inter- and intramolecular exchange processes, and a large number of publications have appeared describing structural aspects of their chemistry.[5-8] Spectroscopic studies have shown[9-11] that octahedral $SnX_4 \cdot 2L$ adducts exist in general as either the cis or the trans form in the solid[12] but that the coexistence of both isomers in solution is not uncommon. Indeed, using vibrational[11] and NMR spectroscopy,[13] we have investigated the trans–cis isomerization reactions of these adducts in solution. Variable-temperature ^1H NMR studies have furnished the most detailed information on the kinetics and mechanism of the exchange reactions of $SnX_4 \cdot 2L$ adducts to date and show that, in the presence of excess ligand, three potential exchange reaction pathways are feasible.[14] These are as follows: (i) a ligand exchange between the free ligand and the ligand coordinated to the cis isomer

$$cis\text{-}SnX_4 \cdot 2L + {}^*L \overset{k_c}{\rightleftharpoons} cis\text{-}SnX_4 \cdot L \cdot {}^*L + L \qquad (2)$$

(ii) the analogous ligand exchange on the trans isomer

$$trans\text{-}SnX_4 \cdot 2L + {}^*L \overset{k_t}{\rightleftharpoons} trans\text{-}SnX_4 \cdot L \cdot {}^*L + L \qquad (3)$$

(iii) an intra- or intermolecular trans–cis isomerization

$$trans\text{-}SnX_4 \cdot 2L \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} cis\text{-}SnX_4 \cdot 2L \qquad (4)$$

Although ^1H NMR spectra of solutions of $SnX_4 \cdot 2L$ (X = Cl, Br; L= neutral Lewis base) have been published[14] and discussed[15] previously, it is worth describing the results obtained in some detail, since they lay the groundwork for the experiments detailed hereafter. Attention will be focused on one chemical system in particular, that of solutions of $SnCl_4$ and excess $(CH_3)_2S$ in CD_2Cl_2.

At temperatures of less than ca. 200 K, chemical exchange is slow in these solutions, and three main peaks are observed in the ^1H NMR spectrum. By comparison with results from vibrational spectroscopy, these are assigned,[14] in order of increasing frequency, to "free" $(CH_3)_2S$, to $(CH_3)_2S$ coordinated in the *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ adduct, and to $(CH_3)_2S$ coordinated in the *trans*-$SnCl_4 \cdot 2(CH_3)_2S$ adduct. When the temperature is increased, the signal of free $(CH_3)_2S$ and that of cis-coordinated $(CH_3)_2S$ broaden and eventually coalesce, leaving the signal of trans-coordinated $(CH_3)_2S$ unaffected. The reaction giving rise to this phenomenon is attributed to a ligand substitution reaction between cis-coordinated and free $(CH_3)_2S$. On the basis of the first-order rate law and positive entropy of activation measured for this process, a dissociative, D, mechanism has been proposed. At higher temperatures, well after the complete coalescence of the free and cis-coordinated signals, evidence of a second exchange reaction is provided by the broadening and coalescence of the two remaining ^1H NMR signals. This can be attributed to either the analogous ligand exchange on the trans adduct (reaction 3), to trans–cis isomerization (reaction 4), or indeed to a combination of both of these processes. ^1H NMR is not capable of distinguishing between these possibilities because of the rapid exchange between cis-coordinated and free $(CH_3)_2S$ at these temperatures. Nevertheless, since a positive activation entropy and a first-order rate law were also determined for the reaction at the trans site, the broadening of the trans-coordinated $(CH_3)_2S$ signal was tentatively attributed[14] to a ligand-exchange reaction between free and trans-coordinated $(CH_3)_2S$, also occurring via a dissociative, D, mechanism.

However, we have recently shown[15] this to be incorrect and have established, using tin-119 NMR magnetization transfer experiments, that at 285 K the broadening of the ^1H NMR signal of trans-coordinated $(CH_3)_2S$ is largely, or wholly, the result of a trans to cis isomerization reaction. It is clear that the observation

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(12) Although, in the case of $SnCl_4 \cdot 2THT$ (THT = tetrahydrothiophene) both isomers could be isolated.[11]
(13) Ruzicka, S. J.; Merbach, A. E. *Inorg. Chim. Acta* **1977**, *22*, 191-200.
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of a dominant trans–cis isomerization at one temperature does not, in itself, rule out the possibility of the occurrence of a trans-coordinated/free ligand exchange at other temperatures, and consequently in this work a series of variable-temperature ^{119}Sn NMR experiments have been performed. These experiments leave no doubt that the broadening of the trans-coordinated $(CH_3)_2S$ signal in ^1H NMR is due to a trans–cis isomerization over the temperature range studied and that the rate of trans-coordinated/free ligand exchange is at least 1 order of magnitude smaller. Thus, we have evidence of two distinct types of processes that are amenable to NMR analysis over two different, well-separated temperature ranges.

In an attempt to determine the mechanistic pathway of both processes and throw light on their transition-state structures, we have undertaken a variable-pressure ^1H NMR study. The effect of pressure on the rate of a chemical reaction is now widely accepted as a powerful tool of mechanistic analysis and is paramount in the diagnosis of dissociative and associative activation modes of exchange processes.[16,17] For example, in the case of the $SnCl_4{\cdot}2(CH_3)_2S$ adducts investigated, we expect an intramolecular trans–cis isomerization process to yield a small activation volume,[18,19] whereas a large ΔV^* value is expected for an intermolecular isomerization process characterized by an intermediate of reduced coordination number.

Experimental Section

Materials. Dichloromethane (Fluka, puriss. p.a.), dichloromethane-d_2 (Medipro, 99.8%), and dimethyl sulfide (Fluka, purum.) were stored in dark bottles over a 4-Å molecular sieve for several days before use. Tin(IV) tetrachloride (Fluka, purum.) was used without further purification. All samples were prepared by weight under an inert N_2 atmosphere (water concentration $\leq$0.5 ppm) by adding the reagents directly to the solvent. Consequently, concentrations are given in terms of molality, m, in mol kg^{-1}. Sealed 10-mm glass NMR tubes were used for ^{119}Sn variable-temperature work, and specially designed 5-mm NMR tubes[20] were used for ^1H variable-pressure experiments. Fresh samples were prepared for each series of experiments undertaken.

Samples for the ^{119}Sn NMR experiments were prepared in neat dichloromethane-d_2, while those for the ^1H NMR experiments were prepared from a 50:50 (w/w) mixture of CH_2Cl_2 and CD_2Cl_2, in order to provide a clear ^1H NMR signal for field shimming and inhomogeneity measurements. In all cases, the total concentration of the $SnCl_4{\cdot}2(CH_3)_2S$ adducts was 0.20 m and that of free $(CH_3)_2S$ was 0.12 m for the variable-temperature experiments and 0.20 m for the variable-pressure work.

NMR Measurements. All spectra were obtained on a Bruker CXP-200 spectrometer, operating in the FT mode at 74.545 MHz for ^{119}Sn and 200.044 MHz for ^1H NMR. In the case of the ^{119}Sn variable-temperature experiments, the temperature was measured by a substitution technique, using a Pt resistor.[21] The deuterium signal of the solvent was used as internal field/frequency lock. ^{119}Sn NMR chemical shifts are referenced to external tetramethyltin. The variable-pressure ^1H NMR experiments were performed with a homebuilt high-pressure probe, described in detail elsewhere.[20] The spectra were obtained without sample rotation, and the instrument was not field/frequency locked. The resulting resolution varied from less than 2 Hz in the best cases to ca. 5 Hz in the worst. ^1H NMR chemical shifts are quoted with respect to Me_4Si. The high-frequency positive convention is adopted throughout, signals occurring to high frequency of the reference being denoted as positive.

Data Treatment. The experimental data obtained from the ^{119}Sn NMR magnetization transfer experiments were fitted to the equations given by Led and Gesmar[22] using an iterative, nonlinear least-squares routine. The following parameters were iterated: the final intensities of both signals, their initial intensities, the isomerization rate constant, and the exchange-averaged longitudinal relaxation rate. The ratio of the signal line width was measured at each temperature and used as a constant in the iterations. Consequently, values of the isomerization rate constant, the relaxation rate, and the isomerization equilibrium constant were obtained from each set of experiments. The equations used describe the return to equilibrium of the magnetization after the selective inversion of one of the signals, under conditions of chemical exchange and in the absence of cross-relaxation.

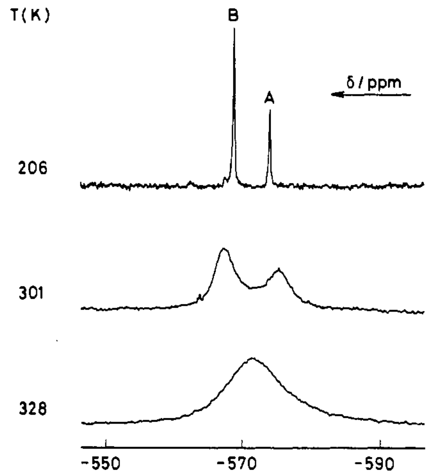

Figure 1. 74.5-MHz $^{119}Sn\{^1H\}$ NMR spectra of a CD_2Cl_2 solution 0.2 m in $SnCl_4{\cdot}2(CH_3)_2S$ and 0.12 m in $(CH_3)_2S$ at various temperatures. Peak A corresponds to the trans adduct and peak B to the cis adduct. The spectra at 206 and 301 K were recorded over a sweep width of 5 kHz, with 4K data points and 5-μs pulses (90° = 20 μs) with an acquisition time of 0.41 s and an interpulse delay of 1 s. The spectra required, respectively, 1278 and 30730 pulses. The spectrum at 328 K was recorded over a 10-kHz sweep width, with 4K data points and 73038 pulses of 5 μs with an acquisition time of 0.2 s and an interpulse delay of 0.5 s. A line broadening of 3 Hz has been applied to the spectrum recorded at 206 K and of 8 Hz to the two remaining spectra. Chemical shifts are quoted with respect to external tetramethyltin and are at 206 K: δ(*cis*-$SnCl_4{\cdot}2(CH_3)_2S$) = −569 and δ(*trans*-$SnCl_4{\cdot}2(CH_3)_2S$) = −574.

Rate constants were obtained from the variable-pressure ^1H NMR spectra with use of both the exchange probability matrices and the computer programs described earlier.[14]

The activation parameters ΔH^*, ΔS^* and ΔV^*, $\Delta\beta^*$ were determined by an iterative least-squares fitting procedure. The effects of pressure on the exchange rate constants were calculated by expression 5, where $\Delta\beta^*$ is the compressibility coefficient of activation.[23]

$$\ln k = \ln k_0 - (\Delta V_0^*/RT)P + (\Delta\beta^*/2RT)P^2 \qquad (5)$$

The isomerization reaction volue, ΔV_{iso}^0, was determined from the measured isomerization equilibrium constants, K_{iso}, with the compressibility term set to 0.

Results

Tin-119 NMR Spectroscopy. In principle, variable-temperature ^{119}Sn NMR spectroscopy should provide an excellent means of distinguishing between an isomerization and a free/coordinated ligand-exchange process, since the former will result in a chemical exchange contribution to the $^{119}Sn\{^1H\}$ NMR line widths, whereas the latter will not. Figure 1 shows three $^{119}Sn\{^1H\}$ NMR spectra as a function of temperature. Increasing the temperature results in a broadening of both signals. However, analysis reveals that the extent of line broadening is unrelated to the population of the trans and cis sites, P_t and P_c, and consequently cannot be the result of chemical exchange alone. For example, at 301 K, if chemical exchange were the only contribution to the line widths, $\Delta\nu_t^{1/2}$ and $\Delta\nu_c^{1/2}$, then $\Delta\nu_t^{1/2}P_t = \Delta\nu_c^{1/2}P_c$ would hold. This is clearly not the case, and at temperatures where the rate of an isomerization reaction would have an appreciable effect on the ^{119}Sn NMR spectrum, relaxation effects resulting from $^{119}Sn-^{35}Cl$ scalar coupling dominate the ^{119}Sn NMR line widths, prohibiting the determination of the isomerization exchange rate constants by ^{119}Sn NMR line-shape analysis. Nevertheless, proton-coupled ^{119}Sn NMR is useful for qualitative confirmation of the kinetic

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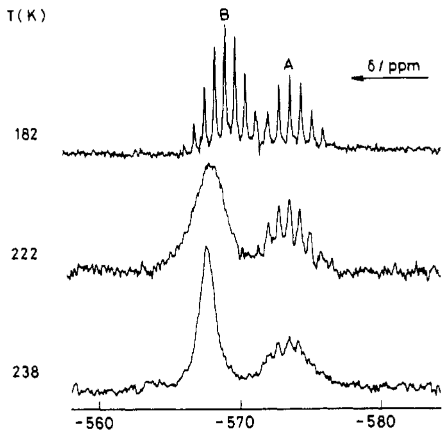

Figure 2. 74.5-MHz ^{119}Sn NMR spectra of a CD_2Cl_2 solution 0.20 *m* in $SnCl_4{\cdot}2(CH_3)_2S$ and 0.12 *m* in Me_2S at various temperatures. Peak A is that of *trans*-$SnCl_4{\cdot}2(CH_3)_2S$, peak B corresponding to *cis*-$SnCl_4{\cdot}2(CH_3)_2S$. The multiplet structure is the result of ^1H–^{119}Sn coupling ($^3J(^1H-^{119}Sn)$ = 54.1 Hz for the cis complex and 59.1 Hz for the trans). The spectrum at 182 K was recorded over a sweep width of 5 kHz, with 4K data points and an acquisition time of 0.41 s. A total of 3846 pulses of 5 μs (90° = 20 μs) were needed, at a repetition rate of 1.5 s. A line broadening of 2 Hz has been applied. The two remaining spectra were recorded over a 3-kHz sweep width, with 4K data points, giving an acquisition time of 0.68 s. 5-μs pulses at a repetition rate of 1.7 s were used, the spectrum at 222 K requiring 1328 and that at 238 K requiring 1425 pulses. A line broadening of 5 Hz has been applied to both spectra.

results obtained by ^1H NMR spectroscopy, as illustrated in Figure 2. The upper spectrum is recorded at a temperature at which all exchange processes are slow on the NMR time scale and exhibits two first-order multiplets, corresponding to the two $SnCl_4{\cdot}2(CH_3)_2S$ isomers. The multiplet structure (13 lines in theory) is the result of three-bond ^1H–^{119}Sn coupling. As the temperature is raised, the rate of $(CH_3)_2S$ exchange becomes significant and the ^1H–^{119}Sn coupling on the multiplet arising from the cis adduct collapses (middle spectrum) and eventually disappears (bottom spectrum), thus confirming that the rate of the cis-coordinated/free ligand exchange is indeed the greatest. It is clear, however, that the effects of ^{119}Sn–^{35}Cl scalar coupling impose a severe limitation in quantitative applications of ^{119}Sn NMR line-broadening analysis at higher temperatures.

Recently, we reported the results of a preliminary ^{119}Sn NMR magnetization transfer experiment on solutions of these adducts.[15] Modifications of the spin-saturation transfer techniques, originally described by Hoffmann and Forsén[24] in 1963, are becoming an accepted method of obtaining kinetic information from systems undergoing chemical exchange, although their quantitative applications are by no means widespread and have in general been limited to the more popular nuclei, in particular ^1H, ^{31}P, and ^{13}C.[25] In systems in which the longitudinal relaxation rate, $1/T_1$, is less than or equal to the exchange rate, it is possible to deduce the exchange rate between two sites by selectively saturating, or inverting, one site and monitoring the intensity of the signal of the other site, or both sites, as a function of the time between the inversion and monitoring pulses. The return of the magnetization to equilibrium is then governed by both the longitudinal relaxation rate of the exchanging species and the exchange rate between the sites.[22,26] In the experiments performed in this work, a selective 180° pulse is applied to the ^{119}Sn magnetization of the *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ adduct, using the so-called "1-2-1" pulse train.[27] After a variable time, *t*, a nonselective 90° pulse allows observation of both signals. The behavior of the magnetization as a function of *t* is analyzed on the basis of the McConnell equations,[28] as

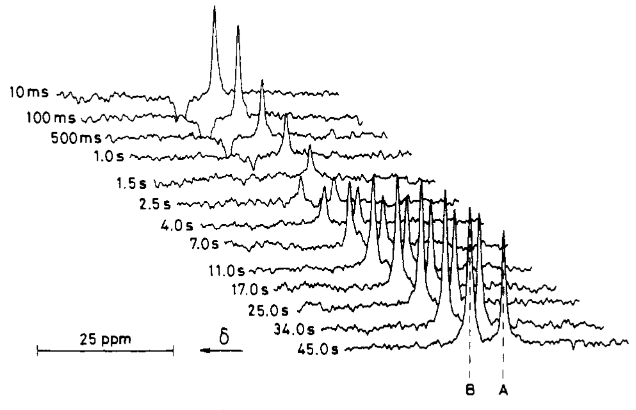

Figure 3. 74.5-MHz $^{119}Sn\{^1H\}$ NMR spectra of a 0.20 *m* $SnCl_4{\cdot}2(CH_3)_2S$ and 0.12 *m* $(CH_3)_2S$ solution in CD_2Cl_2 at 244.6 K, as a function of the time interval, *t*, between the end of the inversion pulse train and the observation pulse. The following pulse sequence was used: (−45°-D_1-90°-D_1-45°-*t*-90°-D_2)- where the delay D_1 was 1.1 ms, the 180° pulse was 42 μs, and the delay D_2 was 48 s. Each spectrum was recorded over a sweep width of 7463 Hz and required 75 pulses. 4K data points were acquired, giving an acquisition time of 0.27 s, and an exponential line-broadening function of 25 Hz has been applied to each spectrum. Peak A is that of the trans isomer and peak B that of the cis isomer.

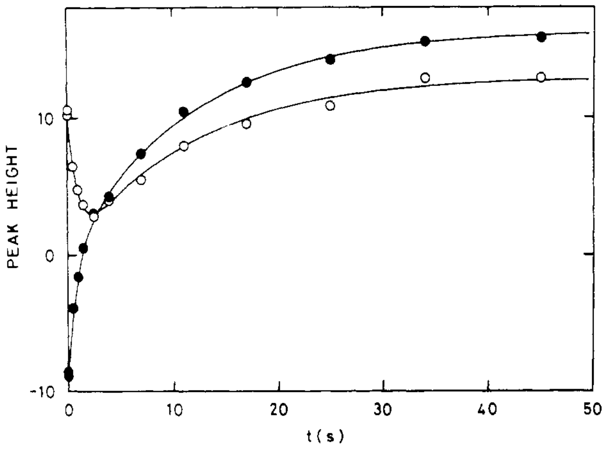

Figure 4. Plot of peak height (arbitrary units) against time for the spectra recorded at 244.6 K and shown in Figure 3: (○) trans; (●) cis. The peak heights were obtained by direct measurement from the spectra. The solid lines are generated by the equations given in ref 22 and are fitted to the experimental data by an iterative routine. Numerical analysis yields values of k_i of 0.66 ± 0.04 s^{-1}, an exchange-averaged value of $1/T_1(^{119}Sn)$ of 0.087 ± 0.005 s^{-1}, and an isomerization constant K_{iso} of 0.635.

described by Led and Gesmar.[22] Knowledge of the longitudinal relaxation rates, $1/T_1(^{119}Sn)$, of the species involved is an essential prerequisite for a successful magnetization transfer experiment, and consequently the ^{119}Sn longitudinal relaxation times were measured, by using the inversion recovery technique, at the extremes of the temperature range covered. Since $T_1(^{119}Sn)$ relaxation in $SnCl_4$ is dominated by the relatively inefficient spin-rotation mechanism and since T_1 is greater than T_2, the latter being governed by scalar coupling to the halogen[29] ($^1J(^{119}Sn-^{35}Cl)$ = 375 Hz), relaxation rates of the $SnCl_4{\cdot}2L$ adducts are expected to be both small and proportional to temperature. At the lowest temperature studied, 244.6 K, the measured $1/T_1(^{119}Sn)$ values from the cis and trans adduct signals are 0.081 and 0.069 s^{-1}, respectively. At the highest temperature, 290.7 K, these values are 0.24 and 0.22 s^{-1}.

Figure 3 shows the $^{119}Sn\{^1H\}$ NMR magnetization transfer spectra obtained at 244.6 K. The decrease in the intensity of the

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(29) (a) Sharp, R. R. *J. Chem. Phys.* **1972**, *57*, 5321–5330. (b) Sharp, R. R. *Ibid.* **1974**, *60*, 1149–1157. (c) Sharp, R. R.; Hawk, R. M. *Ibid.* **1974**, *60*, 1009–1017. $^1J(^{119}Sn-^{35}Cl)$ was quoted as 470 Hz in (a) but amended to 375 Hz in (c).

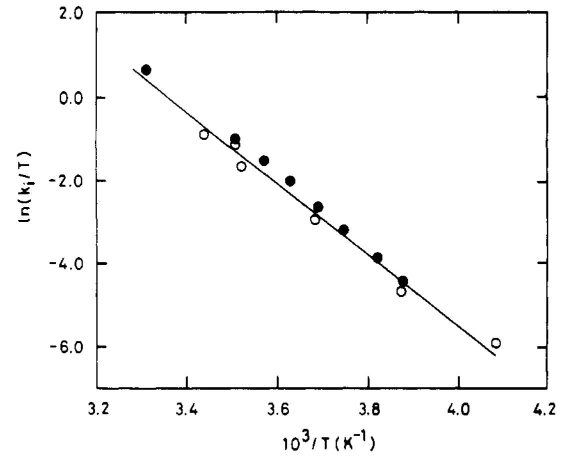

Figure 5. Plot of ln (k_i/T) data vs. reciprocal temperature for the trans to cis isomerization of $SnCl_4 \cdot 2(CH_3)_2S$ in CD_2Cl_2, as obtained from the ^{119}Sn NMR magnetization transfer (○) and from ^1H NMR line-shape analysis reported in ref 14 (●).

trans isomer signal as a function of the time between the inversion and observation pulses reveals that magnetization is being transferred between the two adducts, proving the existence of trans–cis isomerization. Numerical analysis (Figure 4) provides a value for the exchange rate constant, k_i, of 0.66 ± 0.04 s^{-1} and an exchange-averaged longitudinal relaxation rate, $1/T_1(^{119}Sn)$, of 0.087 ± 0.005 s^{-1}. This last value is in agreement with those given above, which must also be exchange averaged since k_i is much greater than the relaxation rate. Results from similar experiments performed at higher temperatures indicate that the exchange rate, k_i, is always much greater then $1/T_1(^{119}Sn)$. At 290.7 K, these values are 118 ± 14 and 0.15 ± 0.02 s^{-1}, respectively, demonstrating that magnetization transfer is an ideal method of quantifying the isomerization rate constant in these solutions. Indeed, under favorable conditions such as these magnetization transfer is capable of providing rate constants well outside the range amenable to line-shape analysis.[30]

Figure 5 shows the rate constant obtained from six ^{119}Sn NMR magnetization transfer experiments, plotted as a function of reciprocal temperature. Data from the original ^1H NMR line-shape analysis have also been included.[14] It should be noted that in ^1H NMR, because free $(CH_3)_2S$ and cis-coordinated $(CH_3)_2S$ are undergoing fast exchange in this temperature domain, the mean residence time of a ligand in the trans site, τ_t, must be expressed in terms of two possible exchange processes. Thus, eq 6 is applicable, where $\tau_{t\text{-}f}$ is related to the first-order rate constant for trans-coordinated/free ligand exchange by eq 7 (since at any one

$$1/\tau_t = (1/\tau_{t\text{-}f}) + (1/\tau_{t\text{-}c}) \qquad (6)$$

$$1/\tau_{t\text{-}f} = k_t/2 \qquad (7)$$

time only one of the two ligands contributing to the ^1H NMR signal is exchanging) and $\tau_{t\text{-}c}$ is related to the first-order rate constant for trans–cis isomerization by eq 8. The good agreement

$$1/\tau_{t\text{-}c} = k_i \qquad (8)$$

between the $1/\tau_t$ value from magnetization transfer and ^1H NMR line-broadening[31] experiments in Figure 5 shows that the $1/\tau_{t\text{-}f}$ term is insignificant compared to $1/\tau_{t\text{-}c}$ over the whole temperature range studied.

This result does not, however, permit the existence of direct-bound ligand-free ligand substitution on the trans adduct to be completely ruled out, although it indicates that the rate of any such reaction is too slow to contribute significantly to the line broadening observed in ^1H NMR and must be less than the experimental error associated with the line-broadening measurements. The numerical values of the activation parameters ΔH^* and ΔS^* for the trans to cis isomerization process are given in Table I.

Table I. Kinetic Parameters for the Exchange between Free Dimethyl Sulfide and *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ and for the Trans–Cis Isomerization and Thermodynamic Parameters for the Isomerization Equilibrium[a]

	cis free exchange	isomerization
k^{298}, s^{-1}	$(1.2 \pm 0.3) \times 10^7$ [b]	335 ± 39[e]
ΔG^*(298 K), kJ mol^{-1}	32.5 ± 0.2[b]	58.6 ± 0.1[e]
ΔH^*, kJ mol^{-1}	66.6 ± 1.3[b]	71.0 ± 2.6[e]
ΔS^*, J K^{-1} mol^{-1}	+114.3 ± 6.8[b]	+41.7 ± 9.7[e]
ΔV_0^*, cm^3 mol^{-1}	+38.4 ± 0.7[c]	+12.2 ± 0.7[c]
$10^2\Delta\beta^*$, cm^3 mol^{-1} MPa^{-1}	+13.9 ± 0.6[c]	+1.5 ± 0.6[c]
$K_{iso}{}^{298}$ (=[trans]/[cis])		0.86 ± 0.06[d]
$\Delta G_{iso}{}^0$(298 K), kJ mol^{-1}		+0.38 ± 0.07[d]
$\Delta H_{iso}{}^0$, kJ mol^{-1}		+3.4 ± 1.0[d]
$\Delta S_{iso}{}^0$, JK^{-1} mol^{-1}		+10.0 ± 6.8[d]
$\Delta V_{iso}{}^0$, cm^3 mol^{-1}		+3.2 ± 0.4[c]

[a] Reported errors are 1 standard deviation. [b] Measured by ^1H NMR line broadening.[14] [c] Measured by ^1H NMR line broadening. [d] Obtained from ^{119}Sn NMR magnetization transfer. [e] Calculated from a combination of the results from ^1H NMR line broadening, given in ref 14 (taking into account the factor of 2, see text), and ^{119}Sn NMR magnetization transfer.

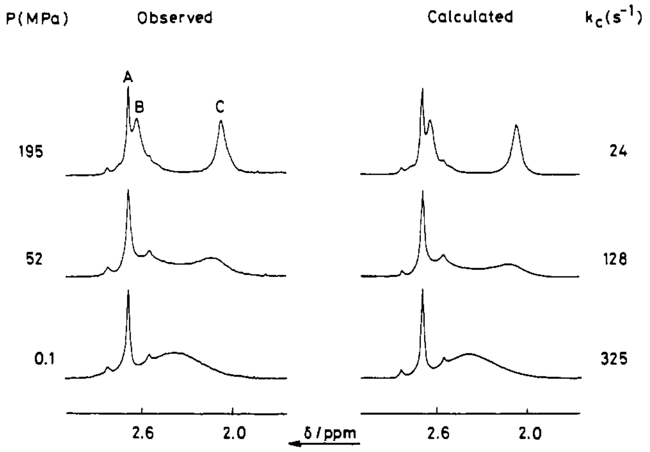

Figure 6. Observed and calculated 200-MHz ^1H NMR spectra, recorded at 223.6 K, illustrating the pressure dependence of the rate constant k_c for the ligand-exchange reaction between free dimethyl sulfide, peak C, and the *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ adduct, peak B. Peak A is the resonance of the *trans*-$SnCl_4 \cdot 2(CH_3)_2S$ adduct; the tin-119 and -117 satellites are also visible. The spectra were recorded over a sweep width of 1200 Hz, with 4K data points, giving an acquisition time of 1.7 s. Four 3-μs (22°) pulses were required, and an exponential line broadening of 0.6 Hz has been applied in each case. The solution used was 0.20 *m* in $SnCl_4 \cdot 2(CH_3)_2S$ and 0.20 *m* in $(CH_3)S$ in CD_2Cl_2/CH_2Cl_2. Chemical shifts and the $^3J(^1H-^{117/119}Sn)$ coupling constants are in agreement with those given in ref 14, and these values were used in the simulation above and in Figure 7.

Proton NMR Spectroscopy. For the ligand exchange between the free ligand and the ligand coordinated to the cis isomer (Eq 2), the pressure dependence of the exchange rate constant, k_c, has been determined at 223.6 and 225.1 K by ^1H NMR line-shape analysis at 200 MHz. Figure 6 shows the effect of pressure on the spectrum of a solution of both $SnCl_4 \cdot 2(CH_3)_2S$ adducts and free $(CH_3)_2S$ in a CD_2Cl_2/CH_2Cl_2 mixture at 223.6 K. Signals labeled A–C correspond to $(CH_3)_2S$ coordinated to the trans adduct, to $(CH_3)_2S$ coordinated to the cis adduct, and to free $(CH_3)_2S$, respectively. Increasing the pressure results in a decrease in the rate of ligand exchange on the cis adduct, as witnessed by the decrease in the widths of the peaks of the cis-coordinated and free ligands. Indeed, the effect is so pronounced that at high pressures the ^{117}Sn and ^{119}Sn satellites of the cis-coordinated signal are partially resolved. For the isomerization reaction (eq 4), the pressure dependence of the rate constant, k_i, was also determined

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(31) $1/\tau_t$ values from ^1H NMR line broadening are obtained from ref 14 by dividing the quoted k_t values by 2.

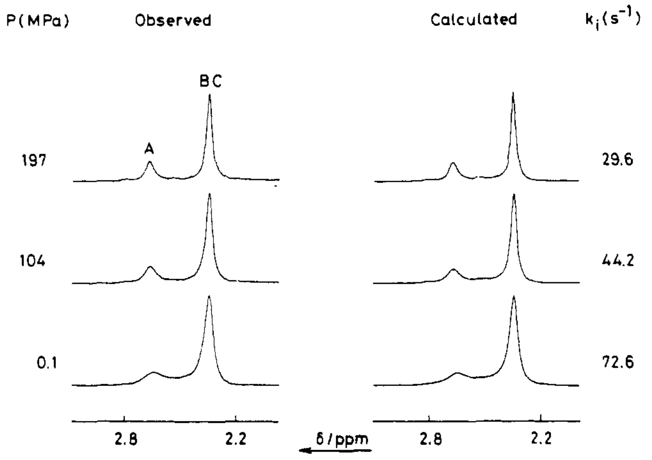

Figure 7. Observed and calculated ^1H NMR spectra, recorded at 200 MHz and at 282.9 K, showing the pressure dependence of the rate constant, k_i, for trans–cis isomerization of $SnCl_4{\cdot}2(CH_3)_2S$ adducts in CD_2Cl_2/CH_2Cl_2. The peak labeled A is due to the trans adduct, while peak BC arises from the coalesced signals of both the cis isomer and free dimethyl sulfide. These species are undergoing rapid chemical exchange at this temperature. The spectra were recorded over a sweep width of 1200 Hz and are the result of a single 3-μs (22°) pulse. 8K data points were required, giving an acquisition time of 3.4 s. An exponential line broadening of 0.6 Hz has been applied in each case. The solution used was 0.20 *m* in $SnCl_4{\cdot}2(CH_3)_2S$ and 0.20 *m* in $(CH_3)_2S$.

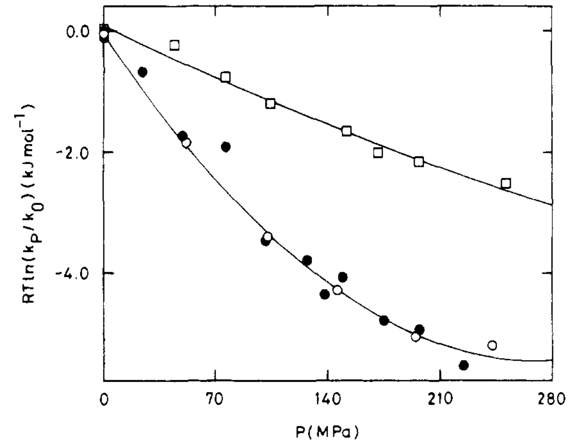

Figure 8. Plot of $RT \ln (k_p/k_0)$ vs. pressure for the ligand-exchange reaction between *cis*-$SnCl_4{\cdot}2(CH_3)_2$ and free $(CH_3)_2S$ at 225.1 K (●) and at 223.6 K (○) and the trans to cis isomerization rate between the $SnCl_4{\cdot}2(CH_3)_2S$ adducts at 282.9 K (□) in CD_2Cl_2/CH_2Cl_2.

by ^1H NMR. In principle, variable-pressure ^{119}Sn NMR magnetization transfer can yield the same information but requires far more spectrometer time. The pressure effect on the ^1H NMR spectra at 282.9 K is shown in Figure 7. Signal A arises from the trans-coordinated ligand while signal BC is due to the coalesced resonances of both the free ligand and the cis-coordinated ligand, which are undergoing rapid exchange at this temperature. Again, an increase in pressure is reflected by a decrease in the isomerization rate constant as reflected by the sharpening of the signals. However, it is apparent that the rate of isomerization is not as sensitive to pressure as is the ligand-exchange reaction on the cis adduct, and this is shown in Figure 8. Furthermore, the compressibility coefficient of activation $\Delta\beta^*$, is also very different for both reactions. The ligand-exchange reaction on the cis adduct displays a large $\Delta\beta^*$ as shown by the curvature on the $\ln (k_p/k_0)$ vs. pressure plot, whereas for the isomerization reaction $\Delta\beta^*$ is close to zero. Numerical values for ΔV^* and $\Delta\beta^*$ are given in Table I.

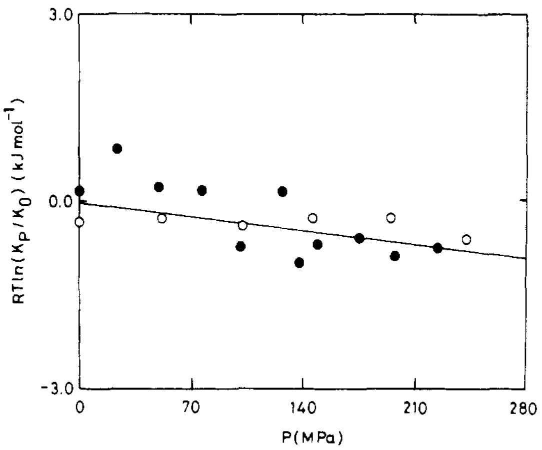

Figure 9. Plot of $RT \ln (K_0/K_p)$ vs. pressure for the isomerization equilibrium constant, K_{iso}, for *trans*- and *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ adducts at 225.1 K (●) and 223.6 K (○) in CD_2Cl_2/CH_2Cl_2.

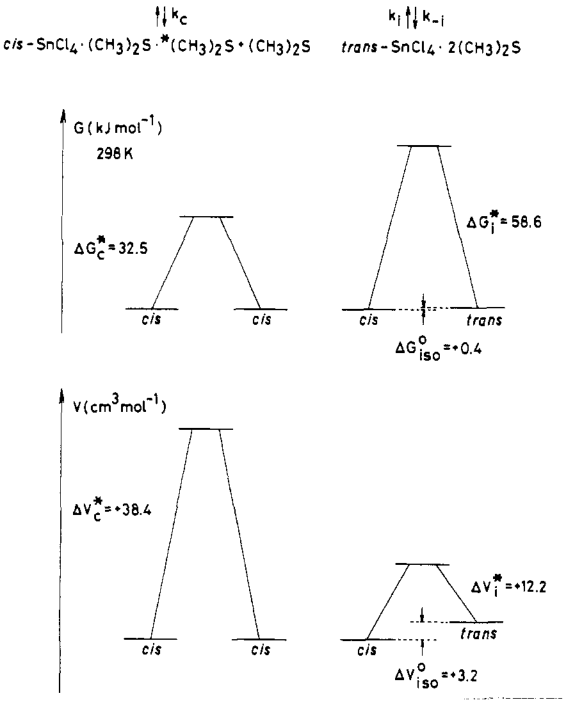

Figure 10. Volume, *V*, and free energy, *G*(298 K), reaction profiles for the ligand-exchange reaction between free $(CH_3)_2S$ and *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ and the isomerization reaction between the *trans*- and *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ adducts.

Isomerization Equilibrium. The small temperature dependence of the isomerization equilibrium constant, $K_{iso} = [trans\text{-}SnCl_4{\cdot}2(CH_3)_2S]/[cis\text{-}SnCl_4{\cdot}2(CH_3)_2S]$, was obtained from the ^{119}Sn NMR magnetization transfer experiments. The calculated values of the corresponding thermodynamics parameters are given in Table I and are in agreement with those reported previously from ^1H NMR measurements.[13] The volume of isomerization, ΔV_{iso}^0, was obtained from the change in the trans/cis adduct population ratio as a function of pressure from the ^1H NMR spectra at 223.6 and 225.1 K. These data are shown in Figure 9, and the ΔV_{iso}^0 value is reported in Table I.

Discussion

This study confirms that the fastest process in dichloromethane solutions of $SnCl_4{\cdot}2(CH_3)_2S$ with an excess of dimethyl sulfide is the free $(CH_3)_2S$ exchange on *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ (eq 2). Combined ^1H and ^{119}Sn NMR experiments have shown unambigously that the isomerization reaction between *trans*- and *cis*-$SnCl_4{\cdot}2(CH_3)_2S$ (eq 4) is 10^4–10^5 times slower and that the rate of direct free $(CH_3)_2S$ exchange on *trans*-$SnCl_4{\cdot}2(CH_3)_2S$ (eq 3) is too slow to be measured and is at least 1 order of magnitude smaller that the isomerization rate. This implies that there is little or no direct $(CH_3)_2S$ exchange on the trans isomer; rather, exchange proceeds through three elementary processes: isomerization to the cis isomer, very fast intermolecular $(CH_3)_2S$ exchange on that isomer, and finally return to the trans isomer. We now discuss in detail the mechanism of the reactions described by eq 2 and 4 in terms of the thermodynamic data and activation parameters given in Table I and pictured in the reaction profiles of Figure 10.

As suggested earlier, the first-order rate law and the large and positive value of ΔS^* imply a limiting D mechanism for the intermolecular $(CH_3)_2S$ exchange on the *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ adduct.[14] In this context the high-pressure data are particularly informative. The experimental volume of activation ΔV_0^* is usually considered to be the sum of an intrinsic contribution, ΔV_{int}^*, and of a solvation contribution, ΔV_{solv}^*.[23] The former results from changes in internuclear distances and bond angles within the reactants during the formation of the transition state, and the latter is mainly due to the electrostrictive effects. In many cases, the interpretation of the information provided by variable-pressure studies is clouded by the difficulty in estimating ΔV_{solv}^*, which may be considerable in a nonpolar solvent such as dichloromethane.[16,32] However, since the reactions studied here involve noncharged reactants, transition states, and products, electrostrictive changes are minimal and ΔV_0^* can be interpreted in a straightforward manner, in terms of ΔV_{int}^* alone. Indeed, the effect of pressure on the isomerization equilibrium is small, with $\Delta V_{iso}^0 = +3.2$ cm^3 mol^{-1}. Nevertheless, the small positive value is as expected: the cis adduct has a nonzero dipole moment, and consequently electrostriction will be more appreciable than on the trans isomer. This effect is also reflected in the small and positive ΔS_{iso}^0. It has also been shown that a good semiquantitative agreement exists between the volumes of activation for limiting dissociative (D) ligand (L) exchange reactions on $MX_5 \cdot L$ (M = Nb, Ta, Sb; X = halide; L = neutral Lewis base)[3,4,33] and the volume of the exchanging ligand within the first coordination sphere. For instance, for $NbCl_5 \cdot L$, the experimental ΔV_0^* for a rodlike ligand such as CH_3CN is +19.5 cm^3 mol^{-1} whereas for a sterically crowded donor group such as $(CH_3)_2O$ it is +28.7 cm^3 mol^{-1}. For the even bulkier donor group of the ligand $(CH_3)_2S$, a large ΔV_0^* is expected and a value of +38.4 cm^3 mol^{-1} is found for ligand exchange on *cis*-$SnCl_4 \cdot 2(CH_3)_2S$. This very large ΔV^* (thought to be the largest recorded for a simple dissociative step) and the large compressibility coefficient of activation, which was also found for $NbCl_5 \cdot (CH_3)_2O$, confirms the limiting D mechanism for the ligand exchange on the cis adduct. Proposals for the geometry of the five-coordinate intermediate $SnCl_4 \cdot (CH_3)_2S$ must be speculative, but it should be remembered that its geometry will be goverened by the condition that the reaction with an incoming $(CH_3)_2S$ ligand always leads to the cis isomer.

In the case of the *trans*- to *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ isomerization process a first-order rate law has also been observed. Accordingly, two extreme mechanistic pathways can be visualized.[34] Either isomerization occurs via an intermediate of reduced coordination number or an intramolecular rearrangement occurs. For the former, a ΔV_0^* as large as that measured for the D dimethyl sulfide exchange on the cis adduct would be required, whereas an intramolecular rearrangement has been assumed to show little or no pressure dependence.[18,19] The same is true for ΔS^*, which is expected to be large and positive for a D ligand exchange and near zero for an intramolecular rearrangement. The volume of activation and, to a less extent, the entropy of activation (due to its inherently less accurate determination[35]) clearly place the isomerization mechanism between these two limiting cases. Consequently, the intermolecular isomerization route involving a pentacoordinated intermediat can be immediately excluded. An expanded six-coordinate transition state, in which the Sn–Cl and Sn–S bonds lengthen somewhat to allow rearrangement, would be consistent with the relatively small and positive, but nonzero, values of both ΔV^* and ΔS^*. This implies an intramolecular, twist, process. In conclusion, tin-119 NMR magnetization transfer and high-pressure proton NMR experiments have allowed the exclusion of both a direct dimethyl sulfide exchange on *trans*-$SnCl_4 \cdot 2(CH_3)_2S$ and a dissociative intermolecular *trans*- to *cis*-$SnCl_4 \cdot 2(CH_3)_2S$ isomerization, respectively.

Acknowledgment. We thank M. J. Forster and Dr. P. J. Nichols for discussions and for their invaluable help with the numerical analysis and the Swiss National Science Foundation for financial support through Grant 2.024-0.83.

Registry No. *trans*-$SnCl_4 \cdot 2(CH_3)_2S$, 62182-06-3; *cis*-$SnCl_4 \cdot 2(CH_3)_2S$, 63038-92-6; $(CH_3)_2S$, 75-18-3.

Supplementary Material Available: Listings of isomerization rate constants (Table SI) and equilibrium constants (Table SII) as a function of temperature from tin-119 NMR magnetization transfer and rate constants for cis/free exchange (Table SIII), rate constants for isomerization (Table SIV), and isomerization equilibrium constants (Table SV) as a function of pressure from proton NMR (5 pages). Ordering information is given on any current masthead page.

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