Table IV. Rate Constants for Aquation of Species $Cr(OH_2)_5S^{3-s}$ in Aqueous Solution

Species	Medium	Temp, °C	10^6k, sec^{-1}	10^6k, sec^{-1} at 298.2°
$Cr(OH_2)_6^{3+}$	$I = 0.7$ *M*; ClO_4^-	27	3.3	2.4[a]
$Cr(OH_2)_5(OHCH_3)^{3+}$	0.10 *M* $HClO_4$ 0.13 *M* $NaClO_4$	30.0	11.0	5.2–5.6[b,c]
$Cr(OH_2)_5(OHC_2H_5)^{3+}$	4.42 *M* $HClO_4$	39.6	21.6	2.6–3.3[b]
$Cr(OH_2)_5Cl^{2+}$	1.0 *M* $HClO_4$			0.277[d]
$Cr(OH_2)_5Br^{2+}$	1.0 *M* $HClO_4$			4.6[e]
$Cr(OH_2)_5I^{2+}$	1.0 *M* $HClO_4$			84.1[d]

[a] J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954). This is $k/6$ to correct for the statistical factor. [b] Extrapolated to 25° assuming $\Delta H^{\ddagger} = 24.0$ and 27.0 kcal mole^{-1} to give range of values listed. [c] Extrapolated to aqueous medium from measurements in water–methanol solutions. [d] Extrapolated from values at other temperatures (T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965)). These are values for rate law term which is zero order in hydrogen ion. [e] Extrapolated from values at other temperatures (F. A. Guthrie and E. L. King, *Inorg. Chem.*, **3**, 916 (1964)). These are values for rate law term which is zero order in hydrogen ion.

chromium(III) ion and hexaaquochromium(III) ion. This comparison, which is only semiquantitative because of differences in reaction media and uncertain extrapolations to a common temperature, is given in Table IV. Also included are values for aquation of the chloro, bromo, and iodo species. The rates of loss of neutral solvent molecules are very similar; in the O^{18} exchange the chromium(III)–oxygen bond is broken, and, in the reactions in which methanol and ethanol are replaced by water, it is assumed that it is the chromium(III)–oxygen bond, and not the carbon–oxygen bond, which is broken. As might be expected, there is much wider variation in the rates of aquation of the three halo complexes.

Nuclear Magnetic Resonance Studies of Exchange in Stannylamines[1]

E. W. Randall, C. H. Yoder, and J. J. Zuckerman[2]

Contribution No. 570 from the Materials Science Center, Cornell University, Ithaca, New York.

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Abstract: The three-bond Sn–N–C–H couplings have been used to investigate exchange processes occurring in stannylamines which involve breakage of the Sn–N bond. We report the first temperature-induced change of spectra for these compounds. On the premise that the temperature required to produce a given rate of exchange (in these cases, *ca.* 250 sec^{-1}) is an index of the difficulty of inducing exchange, the data for $R_nSn[NR'R'']_{4-n}$ (where R = CH_3, C_2H_5, *n*-C_4H_9, and C_6H_5; R′ = R″ = CH_3 or C_2H_5; and R′ = CH_3, R″ = C_2H_5) can be accommodated by a simple model where exchange is favored by either a decrease in number, *n*, or in size of the attached groups, R, on tin, and by a decrease in size of the groups on nitrogen. The effect of addition of free amine or ammonium sulfate as a catalyst has been investigated, and it is concluded that, if any intermediate of the exchange reaction is also necessary for the related reaction of transamination, then the formation of this intermediate cannot be rate determining. In the isotopomeric N-trimethylstannylaniline-N^{14} and -N^{15} pairs, both the exchange and transamination are slower than *ca.* 120 sec^{-1}.

It has previously been reported that the three-bond Sn–N–C–H couplings, $J(Sn^{117}\text{–}H)$ and $J(Sn^{119}\text{–}H)$, which are present[3,4] in the room-temperature proton magnetic resonance spectra of stannyldiethylamines, $R_nSn[N(C_2H_5)_2]_{4-n}$ (where R = CH_3, C_6H_5; $0 \leqslant n \leqslant 3$), are absent in the case of the methylstannyldimethylamines, $(CH_3)_nSn[N(CH_3)_2]_{4-n}$, presumably because of a fast exchange process.[4] Low-temperature (−50°) spectroscopy on trimethylstannyldimethylamine, however, failed to slow down the postulated exchange.[5] Other workers have similarly noted the absence of satellites in the cases $(CH_3)_3SnN(CH_3)_2$, *n*-$Bu_2Sn[N(CH_3)_2]_2$, and *n*-$BuSn[N(CH_3)_2]_3$, but once again no corroboratory evidence has been adduced for the exchange hypothesis. We now report nmr work at various temperatures on both methyl- and ethylamine derivatives of tin which was undertaken to test this hypothesis. Furthermore, a

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[1] A preliminary report of this work was presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] Author to whom inquiries should be addressed.

[3] M. R. Kula, C. G. Kreiter, and J. Lorberth, *Chem. Ber.*, **97**, 1294 (1964).

[4] J. Lorberth and M. R. Kula, *ibid.*, **97**, 3444 (1964).

[5] J. Lorberth and M. R. Kula, *ibid.*, **98**, 520 (1965).

[6] J. Lee and J. Dyer, personal communication, 1965.

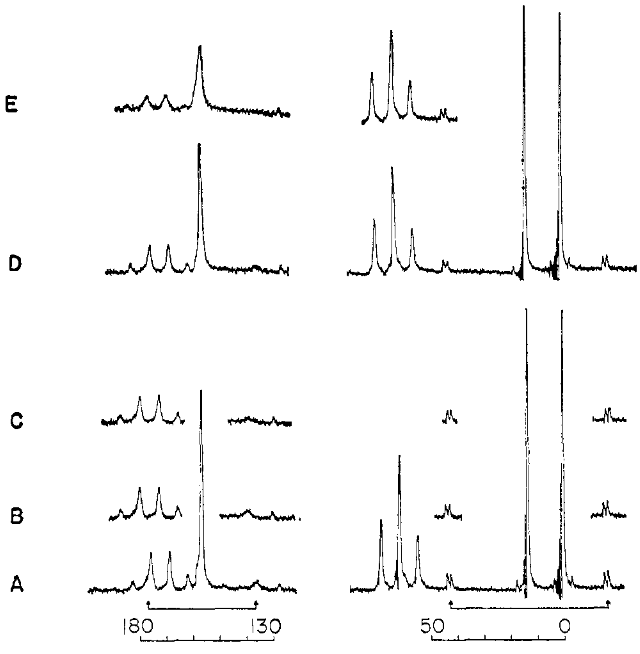

Figure 1. Proton magnetic resonance spectra of dimethylbis(methylethylamino)stannane at 60 Mcps at (A) 40°, (B) 60°, (C and D) 80°, (E) 100°. The small peak at 128 cps is an impurity. The satellites of the methyl-Sn and N-methyl lines are shown by arrows.

simple model is suggested into which the available results fit, and this model is tested.

Previous investigations[7] of transamination reactions involving not only tin, but also silicon and germanium, are pertinent to the discussion of exchange in amine derivatives of elements in group IV. Consequently, we have briefly studied the effects of addition of amines and of ammonium sulfate (a catalyst for transamination) on the nmr spectra of some of the stannylamines reported here.

Experimental Section

Apparatus. The nmr data were obtained with a Varian Model A-60 spectrometer with temperature-regulating accessories. Chemical shifts and coupling constants were determined by the audio side-band technique using a Hewlett-Packard (Model 200 AB) audio oscillator and a Model 521C electronic counter. The temperature in the magnetic gap was determined from peak separations in ethylene glycol or methanol, using calibration data furnished by Varian Associates.

The assignments for most of the aminostannanes were checked on a Varian Model HA 100 spectrometer.

Preparations. Dimethylbis(dimethylamino)stannane. An attempt to prepare this compound by lithioamination of dimethyldichlorostannane resulted in a rather complex mixture of compounds which appeared from the nmr spectrum to be various methyldimethylaminostannanes. Transamination of dimethylbis(diethylamino)stannane with excess dimethylamine in a sealed tube gave the desired product on distillation *in vacuo*. The chemical shifts of this material were identical with those reported.[5]

Dimethylbis(diethylamino)stannane. Prepared by the procedure of Jones and Lappert.[8] Nmr parameters for this material are reported elsewhere.[3]

Dimethylbis(methylethylamino)stannane. This material was obtained by lithioamination of the chlorostannane with the lithium salt of methylethylamine. The nature of the product was established by its proton magnetic resonance spectrum (see Figures 1 and 2). Trimethyl-, triethyl-, and tri-*n*-butylstannyldimethylamines were kindly supplied by Dr. M. F. Lappert and were examined without further purification.

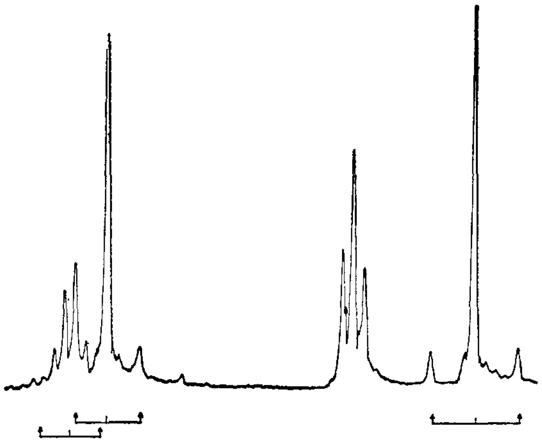

Figure 2. Proton magnetic resonance spectrum of the low-field N-methyl and N-methylene features of dimethylbis(methylethylamino)stannane at 100 Mcps and approximately 35°. The tin satellites are shown by arrows.

Results

The coupling constants are summarized in Table I. Chemical shifts (±0.5 cps) are given below in cps downfield from tetramethylsilane at 60 Mcps.

Dimethylbis(methylethylamino)stannane. The proton resonance spectra of dimethylbis(methylethylamino)stannane show peaks in the methyl-Sn region (δ 13.0 cps) with satellites due to Sn^{117} and Sn^{119}, in the N-methyl (δ 157 cps) and N-methylene (δ 175.5 cps) regions each with satellites, and in the methyl region (δ 62 cps) of the N-ethyl group without satellites (Figures 1A and 2). These results are in accordance with the chemical formulation and the previously reported spectroscopic behavior of related compounds.[3-5] The satellites for the methyl-Sn group could be clearly resolved into the components due to Sn^{119} and Sn^{117}, respectively, at 60 Mcps (difficulty with resolution was experienced on the HA 100 spectrometer due to the use of a micro cell), whereas the satellites on the N-methyl and N-methylene groups were not resolved. The nature of these peaks was satisfactorily established as arising from spin-spin coupling by comparison of the spectra at 60 and 100 Mcps (Figures 1A and 2). At 40° a slightly larger line width is obtained for the N-methyl resonance than for the methyl-Sn line, whereas at about −68° the line widths are approximately equal. The satellites of the N-methyl line are also slightly narrowed at the low temperature. Heating the sample stepwise to 100° caused broadening of the N-methyl satellites relative to the methyl-Sn satellites (see Figures 1A-D). Between 80 and 100° the N-methyl satellites were no longer observable.

Triethyl(dimethylamino)stannate. The ethyl region is a complex A_3B_2 pattern even at 100 Mcps with "first-order" satellite bands clearly resolved into Sn^{117} and Sn^{119} components. The N-methyl region at 38° also exhibits resolvable satellites. Coalescence of the N-methyl satellites occurs at 90°, and the collapsed line can no longer even be detected at 130°, whereas the methyl-Sn satellites show little change with temperature. The N-methyl line itself is also affected by heating the sample; it is broadened by about a factor of 2 to pro-

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[7] C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 4831 (1966).

[8] K. Jones and M. F. Lappert, *J. Chem. Soc.*, 1944 (1965).

Table I. ($Sn^{117,119}$-N-C-H) Couplings[a]

R	R′	R′′	Sn[NR′R′′]$_4$	RSn[NR′R′′]$_3$	R$_2$Sn[NR′R′′]$_2$	R$_2$Sn[NR′R′′]
CH_3	CH_3	CH_3	. . .	ns^{4}	ns$^{4\,b}$	ns^{4,5}
	CH_3	C_2H_5	. . .	. . .	41.0^{b,c}	. . .
	C_2H_5	C_2H_5	49.8^{2}	47.0^{2}	45.5,^{2} 43.4, 45.2^{b}	44.4^{2}
C_2H_5	CH_3	CH_3	. . .	. . .	. . .	34.8, 36.2^{b}
	C_2H_5	C_2H_5	. . .	43.7^{3}	40.8^{3}	38.8^{3}
n-C_4H_9	CH_3	CH_3	. . .	ns^{5}	ns^{5}	35.0, 36.5;^{5} 35.3, 36.7^{b}
	C_2H_5	C_2H_5	. . .	43.3^{3}	40.0^{3}	38.2^{3}
C_6H_5	CH_3	CH_3	. . .	44.0, 45.7^{5}	43.5, 44.9^{5}	. . .^{6,d}
	C_2H_5	C_2H_5	. . .	47.5^{2}	. . .	45.2^{2}

[a] Single numerals refer to an average of the Sn^{117} and Sn^{119} couplings. ns = satellites not observed. [b] This investigation. [c] Methyl and methylene couplings the same to ± 0.5 cps. [d] Solution (in CCl_4) too dilute for satellite observation.

duce a line width of approximately 3 cps at 130°. This line width was judged relative to the strongest sharp line in the A_3B_2 region which remained sharp at 130° and which provided a check on instrumental resolution (see Figure 3). Addition of a small amount (<0.1 g) of ammonium sulfate to the sample had no effect on the spectrum at any temperature studied.

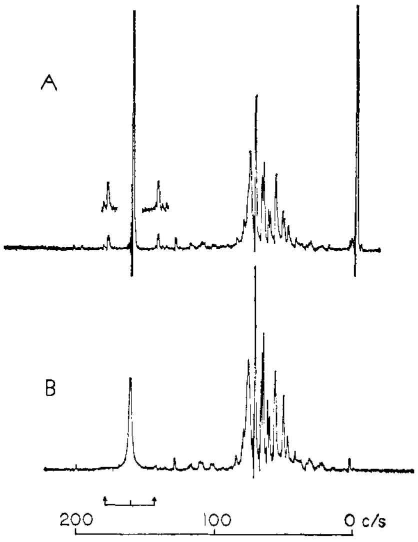

Figure 3. Proton magnetic resonance spectra of triethyldimethylaminostannane at 60 Mcps and (A) 40°, (B) 140°.

Tri-*n*-butyl(dimethylamino)stannane. The *n*-butyl region (two complex groups of lines at δ 55 and 85 cps) was not investigated further. The N-methyl satellites were easily identified since they are resolved into Sn^{117} and Sn^{119} components at 38°. They are broadened as the temperature is raised, but they are still clearly visible at 150° and detectable at 170°.

The chemical shifts for the neat liquid (N-dimethyl group, 155-7 cps; trimethyl-Sn group, 8.1 cps) differed slightly from the values[3] (161.3 and 11.3 cps, respectively) for solution in carbon tetrachloride.

Trimethyl(dimethylamino)stannane. This sample showed no Sn^{117} or Sn^{119} satellites for the N-methyl peak even at −68°. Addition of approximately 25% of dimethylamine by volume to the sample produced one broad N-methyl line (line width 7 cps) intermediate in shift (148 cps from tetramethylsilane) between the shifts for the sharp N-methyl lines of the separate components (155.5 and 129 cps). Cooling the sample to −40° resulted in two broad lines (width about 7 cps) with a separation of approximately 19 cps.

Dimethylbis(diethylamino)stannane. The pure compound showed tin satellites at 100° even in the presence of ammonium sulfate. Mixtures with either diethylamine or dimethylamine showed no evidence of exchange of alkylamino groups even at 110°. A slow reaction was, however, observed in the case of dimethylamine, which produced a single peak at δ 159 cps ascribed to the N-methyl peak of dimethylbis(dimethylamino)stannane, and a 1:3:3:1 quartet centered at 155 cps assignable to diethylamine. This reaction was successfully used as a preparation for dimethylbis(dimethylamino)stannane (*vide supra*). The observation of separate lines for dimethylamine and its dimethylstannyl derivative precludes rapid exchange for this pair in contrast to the result for trimethyldimethylaminostannane.

Discussion

The observation by Lorberth and Kula that the three-bond (Sn-N-C-H) spin-spin coupling between tin and hydrogen is approximately 40 cps provides an elegant method of investigating the relative rates of exchange processes involving breakage of the Sn-N bond. For rates of exchange greatly in excess of $2\pi \times 40$ sec^{-1}, *i.e.*, approximately 250 sec^{-1}, the Sn^{117} and Sn^{119} satellites will not be observed.

One difficulty in employing temperature variation to change the rate is the small broadening of the satellite lines which may be expected on raising the temperature of the sample because of the quadrupole relaxation effect of the ^{14}N nuclei on the protons to which they are coupled. This broadening is not expected to be more than a factor of 3 since the probable magnitude of the ^{14}N-C-H coupling should be of the order of only 1 cps or less from comparison with other systems. This point may be conveniently checked by observation of the central line as opposed to the satellite lines, since this too should broaden by this mechanism. Such broadening is observed but is small as expected and cannot account for the failure to observe satellites in the reported instances.[9] Furthermore, it is possible to ascribe

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(9) Work is in progress to check these assertions by synthesis and examination of the ^{15}N-substituted isotopomers.

this broadening to the exchange of amino groups between Sn^{117}, Sn^{119}, and other, zero-spin, tin nuclei.[10] A broadening produced in this way is expected to be small (as observed) provided the sites are chemically equivalent, *i.e.*, characterized by the same shift.

The disappearance of the Sn^{117} and Sn^{119} satellites at high temperature (150°) for triethyl(dimethylamino)stannane is the first reported temperature-induced change of spectra for the stannylamines. It may be rationalized on the basis of an exchange process as postulated by Lorberth and Kula[4] for the trimethyldimethylaminostannane. The rate of exchange is so rapid for the trimethylstannyl compound that cooling it to $-68°$ gives no evidence of satellites. Furthermore, we may conclude from the fact that the proton line due to the N-methyl group in triethyl(dimethylamino)stannane does not shift with temperature that the exchange is between equivalent sites (as defined above).

We have shown that tri-*n*-butyl(dimethylamino)stannane also is induced to exchange by elevating the temperature, and that the temperature required is higher than for the triethyl analog. Thus, the following sequence is established for the ease of exchange (on the simple premise that the temperature required to produce a given exchange rate, in this case approximately 250 sec^{-1}, is an index of the difficulty of inducing exchange): $n\text{-}Bu_3SnN(CH_3)_2 < Et_3SnN(CH_3)_2 < Me_3SnN(CH_3)_2$.

Furthermore, it is reported that, whereas satellites are observed for Bu_3SnNMe_2 at room temperature, the compounds $n\text{-}Bu_2Sn[N(CH_3)_2]_2$ and $n\text{-}BuSn[N(CH_3)_2]_3$ do not exhibit satellites under these conditions.[5] Thus, the sequence $n\text{-}Bu_3SnN(CH_3)_2 < n\text{-}Bu_2Sn[N(CH_3)_2]_2$, $n\text{-}BuSn[N(CH_3)_2]_3$ is established. If these sequences can be generalized for $R_nSn(NR_2)_{4-n}$, then it can be stated that the ease of exchange of amine groups is favored by either a decrease in the number, *n*, or in the size of the alkyl groups, R, on tin.

For the diethylaminomethylstannanes as opposed to the dimethylamino analogs, Lorberth and Kula have already shown that satellites are observed at 32°, so that it is known that the nature of the group on nitrogen also affects the rate of exchange. The extent of the differential is very marked: the compound bis(diethylamino)dimethylstannane proved so inert that heating to 140° did not induce exchange, even in the presence of ammonium sulfate which might have been expected to act as catalyst for this exchange because of its efficiency in promoting transaminations.

The proposition that the steric requirements at nitrogen are important for the exchange process was tested by the synthesis and the spectroscopic investigation of bis(methylethylamino)dimethylstannane which is expected to undergo exchange with facility between the bis(diethyl) and bis(dimethyl) analogs. Using the temperature index as before this consequence is realized.

A reaction of stannylamines related to the exchange reaction discussed above in requiring the making and breaking of an Sn–N bond is the transamination reaction. For bis(diethylamino)dimethylstannane and diethylamine, both processes were too slow to measure (slower than $\sim 250\ sec^{-1}$). For bis(diethylamino)dimethylstannane and dimethylamine, the same statement may be made. The pair dimethylamine and bis(dimethylamino)dimethylstannane, however, shows a differentiation—the exchange being faster than the transamination (separate resonance for the N-methyl groups but no satellites for the aminostannane). The fastest reactions (rates $>250\ sec^{-1}$ at 40° approximately), both exchange and transamination, were observed for dimethylaminotrimethylstannane and dimethylamine. The transamination, however, is frozen at $-40°$, whereas the exchange is still fast at $-68°$.

We may thus conclude that if any intermediate of the exchange reaction is necessary for the transamination, the formation of this intermediate is not the rate-determining step.

In the case of the N-anilinotrimethylstannane-N^{14} and -N^{15} isotopomers in the presence of aniline,[11] tin satellites have now been observed in the proton spectrum for the NH group although the separate Sn^{119} and Sn^{117} satellites are not resolved. The average coupling is 20 ± 1 cps. Thus, both the exchange and the transamination are here slower than $120\ sec^{-1}$.[12]

Acknowledgments. Our work is supported by the Advanced Research Projects Agency. We are indebted to the National Science Foundation for a predoctoral fellowship to C. H. Yoder, and to Dr. M. F. Lappert for donation of several samples.

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(10) We are grateful to a referee for pointing this out.

(11) E. W. Randall, J. J. Ellner, and J. J. Zuckerman, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

(12) E. W. Randall and J. J. Zuckerman, unpublished results.