pounds. For the tellurium-rich composition, the phase diagram[7] indicates, in addition to the 132° α to β transformation temperature, structural transformations at 286, 425, and 465°. Also, a eutectic halt line at 351° is shown for Te compositions greater than Ag_3Te_2. As a check on our DTA data for Ag_2Te, a preparation was made with excess tellurium and a DTA curve was obtained for it. A strong endothermic peak was observed at 351° with weaker endothermic peaks also observed at 425 and 458°. Failure to observe the 132° peak and observation of the 351° eutectic halt line indicates that the composition was richer in tellurium than Ag_3Te_2. The observation of these DTA peaks on the tellurium-rich compositions supports the DTA observations made on the clean electrolytic preparation and confirms the result that the composition of these compounds is in the silver-rich portion of the homogeneity range.

CuTe.—The X-ray patterns obtained for the CuTe preparation which was dried at 120° and for compounds annealed at 200° were very complex and did not correspond to the orthorhombic pattern reported by Anderko and Schubert.[12] Heating the compounds above 250°, however, resulted in a structure change and the orthorhombic pattern reported by Anderko and Schubert was obtained. In addition, careful weighing indicated no weight change attendant with the structure change. These results give evidence for the existence of a low temperature CuTe phase below 250°.

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Halogen-Terminated Polydimethyltin Sulfides

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Mixtures of dimethyltin dihalide with trimeric dimethyltin sulfide were found by proton nuclear magnetic resonance (n.m.r.) to exhibit rapid interchange of halogen atoms for sulfur bridges. The rate was most rapid when the halogen atom was chlorine (average lifetime = *ca.* 10^{-4} sec.) and was slowest for iodine (average lifetime = *ca.* 10^{-2} sec.) in 1 *M* carbon tetrachloride solutions at room temperature. Because of slower rate of exchange for iodine, the equilibrium between the simple dihalide molecule and the end and middle units making up the complicated molecules based on Sn–S–Sn chains terminated with halogen atoms was determined for the case where the halogen is iodine and found to be close to that predicted for statistically random sorting of the iodine with bridging sulfur atoms on the dimethyltin moiety.

In other studies[1] carried out in this laboratory, it has been found that heating of mixtures of dihalodimethylsilanes with either cyclic dimethylsiloxanes or dimethylsilthians gives an equilibrium between the starting materials and the halogen-terminated dimethylsiloxane or dimethylsilthian chain molecules. In the case of the oxygen-bridged compounds, the chain–ring equilibrium is shifted completely to the chain species, within experimental error. On the other hand, in the case of the sulfur-bridged compounds, the rings predominate. In both cases, the time needed for equilibration was found to be in the order of magnitude of days at 200°.

In the study reported here, tin analogs were investigated by proton nuclear magnetic resonance (n.m.r.) in order to demonstrate the existence of the tin-based families of compounds and to obtain a measure of the physical parameters whereby they may be characterized (rate of equilibration, equilibrium constants, etc.).

Experimental

Reagents.—Dimethyltin dichloride, m.p. 105°, and dimethyltin dibromide, m.p. 75°, were obtained from Orgmet, Hampstead, N. H., and dimethyltin diiodide was prepared from dimethyltin dichloride and sodium iodide in acetone[2] and recrystallized from hexane, m.p. 45°. Dimethyltin oxide[3] and trimeric dimethyltin sulfide,[4] m.p. 149°, were prepared according to methods in the literature.

N.m.r. Measurements.—Proton n.m.r. spectra were obtained[1] on a Varian A-60 analytical spectrometer, with the samples being contained in precision 5-mm. o.d. tubes.

Equilibration.—Upon mixing and brief heating (*ca.* 1–2 min. above the melting point of the eutectic), the trimeric dimethyltin sulfide dissolved in the dimethyltin dihalide to give clear liquids, the viscosity of which decreased with increase in the composition parameter $R \equiv X/Sn$, where X = Cl, Br, or I.

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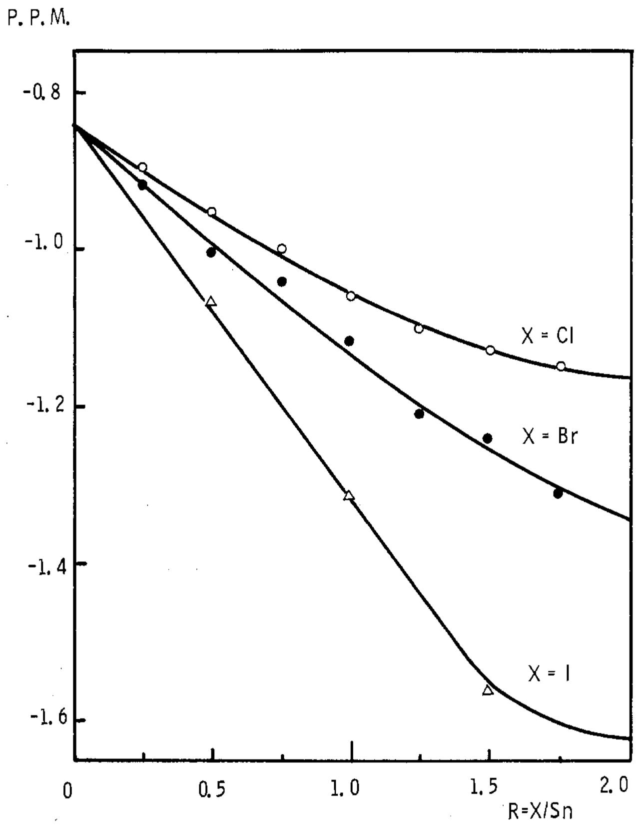


Fig. 1.—Proton n.m.r. chemical shift of the single unresolved resonance, in p.p.m. relative to tetramethylsilane, of equilibrated mixtures of $(CH_3)_2SnX_2$ *vs.* $(CH_3)_2SnS$. For X = Cl and Br measured as 10% solutions in CCl_4, for X = I as 1:1 CCl_4 solutions.

For the system $(CH_3)_2SnCl_2$ *vs.* $(CH_3)_2SnS$, equilibrated samples were generally found to crystallize within a few minutes after cooling to room temperature, except for compositions ranging from $R = 0.5$ to 1.0 which remained completely liquid for a few hours. Indeed, the composition having an R value of 0.75 did not exhibit any precipitate for about 24 hr. When dissolved in CCl_4, equilibrated mixtures containing dimethyltin dichloride and dimethyltin sulfide produced crystals of dimethyltin dichloride after a few hours standing at room temperature. All n.m.r. measurements were made on the single-phase liquid samples before any crystallization had occurred.

For the system $(CH_3)_2SnBr_2$ *vs.* $(CH_3)_2SnS$, equilibrated mixtures ranging in composition from $R = 0.25$ to 1.75 were readily supercooled at room temperature, with crystallization taking place only after several hours. For the system $(CH_3)_2SnI_2$ *vs.* $(CH_3)_2SnS$, it was found that, after equilibration, samples with $R = 0.6$ to 1.75 remained liquid at room temperature and did not crystallize at all.

Results and Discussion

When long-chain dimethyltin oxide was heated at elevated temperatures for several days with dimethyltin dihalide (120° for $(CH_3)_2SnBr_2$ and 200° for $(CH_3)_2SnCl_2$), it apparently dissolved only to a very small extent, leaving the greatest part of the solid oxide unreacted. However, trimeric dimethyltin sulfide was found to dissolve readily in dimethyltin dihalide upon heating above the melting point of the solid mixture.

N.m.r. Spectra.—Proton n.m.r. traces obtained on supercooled liquids made by melting various proportions of dimethyltin sulfide with dimethyltin dihalide or on their concentrated solutions in CCl_4 showed single, rather sharp resonance peaks. As seen in Fig. 1, the chemical shifts of these resonances varied approximately linearly with the relative amount of the two reagents. Table I lists the proton n.m.r. chemical shifts and coupling constants of the starting compounds. It is seen that the shielding of the hydrogens of the methyl groups bonded to tin in the compounds $(CH_3)_2SnX_2$ is decreased as X changes from Cl to Br and I. As is often the case with n.m.r., an increase in electronegativity of a coupled atom gives more rather than less shielding as indicated by simple-minded theory.

Table I

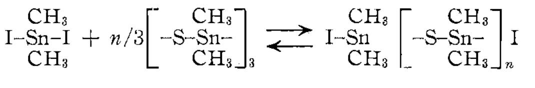
Chemical Shifts and Coupling Constants of Some Dimethyltin Compounds

	Chem. shift δ, p.p.m.	Coupling constants, c.p.s. $J_{Sn^{115}-H}$	$J_{Sn^{117}-H}$	$J_{Sn^{119}-H}$	$J_{C^{13}-H}$
$(CH_3)_2SnCl_2$	-1.157^a	60.8	67.3	70.5	137.8
$(CH_3)_2SnBr_2$	-1.378^b	58.7	63.7	66.6	137.2
$(CH_3)_2SnI_2$	-1.617^a	55.0	59.6	62.8	137.5
$(CH_3)_2SnS$	-0.858^a	57.3	59.3	62.2	131.3

[a] In 5% CCl_4 solution. [b] In 5% $CHCl_3$ solution.

Dilution of the equilibrated mixtures with carbon tetrachloride caused broadening of the observed single peaks for the systems involving either dimethyltin dichloride or dibromide. For the dimethyltin diiodide system, it was found that the single n.m.r. peak observed for the neat liquids and concentrated CCl_4 solutions could be resolved into three separate resonances at tenfold or greater dilution. Based on these observations, it appears that halogen and sulfur atoms bonded to the dimethyltin moiety undergo rapid exchange, with the exchange rate being diminished by increasing dilution.

Equilibria in the Systems $(CH_3)_2SnX_2$ *vs.* $(CH_3)_2SnS$.—In agreement with our previous approach,[1] the appearance of three separate resonance peaks upon dilution with CCl_4 of equilibrated samples of $(CH_3)_2SnI_2$ and $(CH_3)_2SnS$ is interpreted in terms of equilibria of the type



$$\underset{CH_3}{\overset{CH_3}{I{-}Sn{-}I}} + n/3\left[-S{-}\underset{CH_3}{\overset{CH_3}{Sn}}-\right]_3 \rightleftarrows I{-}\underset{CH_3}{\overset{CH_3}{Sn}}\left[-S{-}\underset{CH_3}{\overset{CH_3}{Sn}}-\right]_n I \quad (1)$$

involving the *neso* compound,[5] $(CH_3)_2SnI_2$; middle groups, $-S_{1/2}Sn(CH_3)_2S_{1/2}-$, which may appear in either rings or chains; and end groups, $I(CH_3)_2SnS_{1/2}-$. The upfield peak exhibited the same chemical shift as dimethyltin sulfide; the downfield peak had the same chemical shift as dimethyltin diiodide. From this information, as well as from material-balance calculations, the upfield peak was assigned to middle groups and the central peak (appearing at −1.275 p.p.m.) to end groups in the various compounds based on dimethyltin moieties, with bridging

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(5) The word *neso* refers to the smallest molecule in a family of compounds. It comes from νῆσος meaning "island" and has been employed for a number of years in silicate chemistry, *e.g.*, see G. W. Morey, "Encyclopedia of Chemical Technology," R. E. Kirk and D. Othmer, Ed., Interscience, New York, N. Y., 1st Ed., 1954, Vol. XII, p. 280.

by sulfur atoms and chain termination by iodine atoms. The downfield peak corresponded to the *neso* compound, $(CH_3)_2SnI_2$. Based on this assignment, the experimental data obtained from peak-area measurements of the n.m.r. spectra are presented in Table II. Using these data, the equilibrium between the various structure-building units in the system was calculated[6] to be

$$K = [\text{neso}][\text{middle}]/[\text{end}]^2 = 0.223 \qquad (2)$$

with a standard error of 0.013. The equilibrium constant, K, was used to obtain[6] the calculated values (given in parentheses in Table II) for the relative amounts of the various structure-building units participating in the equilibrium. The agreement between the experimental and calculated values is generally quite good, as can be observed by inspection of the table. Were the sorting of bridging sulfur and iodine atoms on the dimethyltin moiety completely random, the constant K in eq. 2 would have been 0.250. From the experimentally determined value of K, it is apparent that this equilibrium is close to the ideally random case, assuming no rings.

TABLE II

EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA (IN MOLE %) FOR THE SYSTEM $(CH_3)_2SnI_2$–$(CH_3)_2SnS$

R = I/Sn	$(CH_3)_2SnI_2$	Ends	Middles
0.25[a] (0.25)[b]	3.0	18.6	78.2
(0.25)[b]	3.6	17.7	78.6
	(1.4)[c]	(22.1)	(76.4)
0.50 (0.46)	6.8	32.7	60.4
(0.48)	6.8	34.3	58.8
	(5.9)	(38.3)	(55.9)
0.75 (0.73)	13.8	45.6	40.5
(0.74)	17.1	39.8	43.0
	(13.4)	(48.1)	(38.4)
1.00 (1.00)	23.2	53.6	23.1
(1.02)	26.0	49.9	23.9
	(24.3)	(51.4)	(24.4)
1.25 (1.25)	37.4	50.5	12.0
(1.24)	38.2	47.3	14.4
	(38.4)	(48.1)	(13.4)
1.50 (1.48)	52.2	43.8	3.8
(1.43)	51.3	40.3	8.3
	(55.8)	(38.3)	(5.9)
1.75 (1.73)	74.3	24.0	1.5
(1.70)	71.9	26.0	1.9
	(76.4)	(22.1)	(1.4)

[a] Value calculated from ingredients. [b] Value calculated from n.m.r. peak areas. [c] Values in parentheses are calculated for K = 0.223.

In the two systems involving dimethyltin dichloride and dimethyltin dibromide, dilution and/or cooling of equilibrated samples did not result in the resolution of the original single n.m.r. peak into multiple resonances so that equilibrium constants of the form of eq. 2 could be evaluated.

Colligative measurements in freezing benzene show a linear relationship between molecular weight and the composition parameter R, with the molecular weight decreasing from that of the trimeric dimethyltin sulfide to the appropriate monomeric *neso* compound. These results may be interpreted in two ways. The first and most likely explanation is that in these dilute solutions (0.5 g. of sample/10 ml. of benzene), all of the middle groups are present in the form of the trimeric ring and all of the end groups as the end–end chain compound. Alternatively, the exchange could be so fast (see below) that the colligative measurement determines only the molecular weight of parts of molecules caught in the act of interchange. However, it is unlikely that this could lead to a linear relationship for all three systems, which have quite different exchange rates.

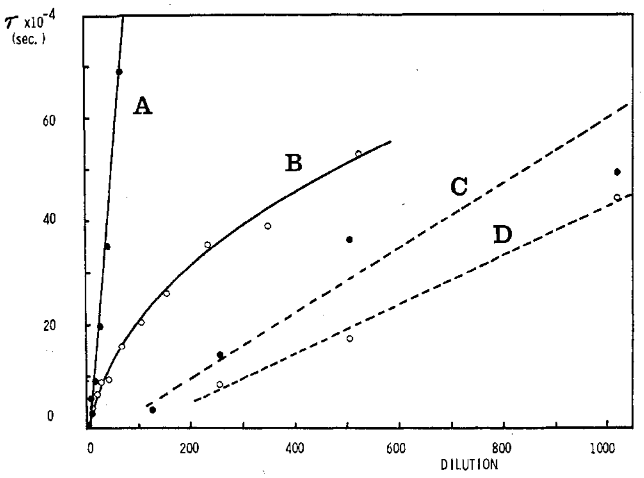

Fig. 2.—Average lifetimes, τ, in the systems $(CH_3)_2SnX_2$ *vs.* $(CH_3)_2SnS$ for various dilutions with CCl_4 (vol./vol.) as obtained from line broadening at 35°: A: X = Br, R = 0.5; B: X = Br, R = 1.5; C: X = Cl, R = 0.5; D: X = Cl, R = 1.5.

Rates of Exchange.—From the variation in line width[7] upon dilution with CCl_4, the average pre-exchange lifetimes of a given species in the systems $(CH_3)_2SnX_2$ *vs.* $(CH_3)_2SnS$ were estimated. Figure 2 shows a plot of the average pre-exchange lifetime as a function of dilution for the systems X = Cl and Br and the compositions R = 0.5 and 1.5. The curves indicate that for a given dilution, the exchange rates—which are inversely proportional to the average lifetimes—for the exchange of chlorine and sulfur are much greater than for the exchange of bromine and sulfur atoms attached to the dimethyltin moiety. In each system, the exchange rate is also seen to be the fastest for those compositions in which *neso* molecules and end groups predominate. It is estimated that in solutions 1 M with respect to Sn, the pre-exchange lifetime in the chlorine system ranges from 1×10^{-4} to 4×10^{-4} sec., and in the bromine system, from 3×10^{-4} to 10×10^{-4} sec.

The average rate of exchange of iodine and bridging sulfur atoms could be determined by two methods[7]: At dilutions ranging from 1:1 to 1:50, from the height of the saddle between neighboring peaks, and, at higher

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(7) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139 (1964). Also, for details, see J. W. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 220–225.

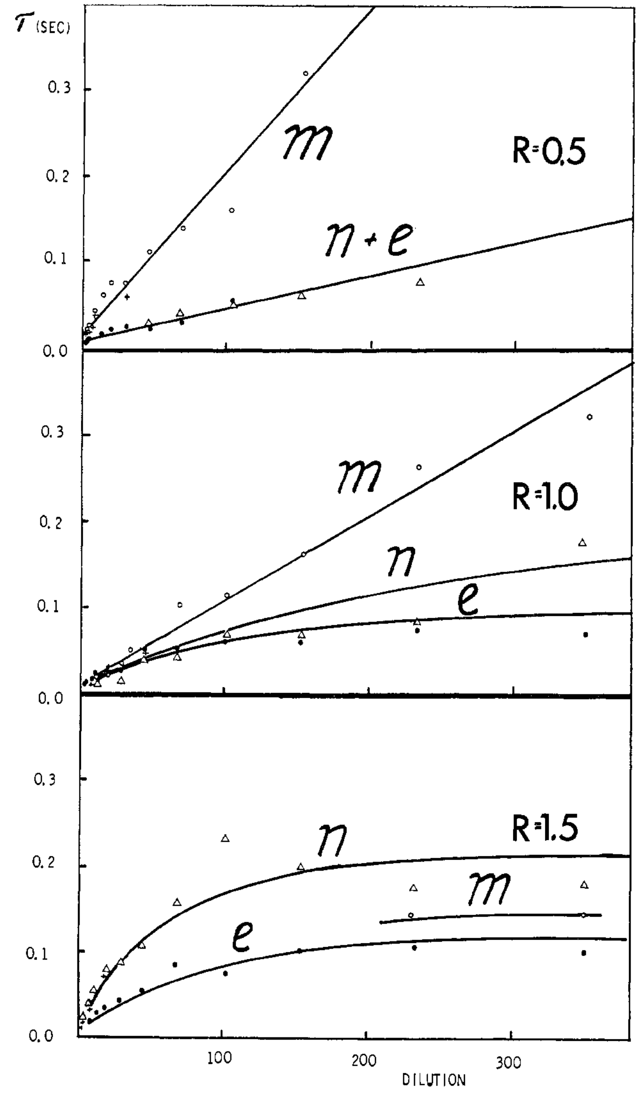

Fig. 3.—Average lifetimes, τ, in the system $(CH_3)_2SnI_2$ *vs.* $(CH_3)_2SnS$ for various dilutions with CCl_4 (vol./vol.) at 35°. The crosses represent data obtained from saddle-shaped resonances. All other points were obtained from line broadening, *n* = *neco*, *e* = end groups, *m* = middle groups.

dilutions, from the line width of the three separated resonances. The pre-exchange lifetimes at different dilutions are presented in Fig. 3 for the compositions $R = 0.5$, 1.0, and 1.5.

Linearity in Fig. 2 and 3 is consistent with a second-order rate of exchange. The observed curvature in some of the lines in these figures corresponds to a lesser decrease in rate with increasing dilution than would be expected for a second-order process. This is probably attributable to an increase with dilution in the ratio of the activity coefficients of the reactants over that of the activated complex.

The n.m.r. peak for pure dimethyltin diiodide is sharp at all concentrations (exhibiting a width of 1 c.p.s. rather than 0.5 c.p.s. due to slight quadrupole broadening by the iodine) because exchange of iodine between these like molecules does not result in a change in the chemical environment of the dimethyltin moiety. This means that the calculated pre-exchange lifetime in this case is infinite. As the value of R is decreased from 2 (corresponding to the pure dimethyltin diiodide), the calculated lifetime is found to decrease rapidly at first and then more slowly because of the continuing rise in the amount of end and middle groups with which the *neso* compound can exchange an iodine for a sulfur atom. Similar arguments apply to the lifetime of dimethyltin sulfide and middle groups.

Activation Energy of the Exchange Reactions.—From the variation in n.m.r. line width[7] with temperature, the activation energy of the exchange of halogen atoms and sulfur bridges was determined. For the 1 *M* solutions in CCl_4, the activation energy for the exchange process was found to be *ca.* 4 kcal. for the system in which the halogen is chlorine, *ca.* 2 kcal. for the bromine system, and also *ca.* 2 kcal. for the iodine system.

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Some Properties of *n*- and Isotetrasilane

BY SUDARSHAN D. GOKHALE AND WILLIAM L. JOLLY

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The two isomers of tetrasilane were prepared in an ozonizer-type electric discharge and isolated by gas chromatography. The isomers were identified, consistently, by their n.m.r. spectra, their infrared spectra, and their relative volatilities.

Introduction

Stock, *et al.*,[1] obtained normal tetrasilane from the products of the reaction of magnesium silicide with hydrochloric acid, but they were unable to isolate the branched-chain isomer. Fehér, *et al.*,[2] achieved a partial separation of the two isomers by fractional distillation and reported the boiling and freezing points, densities, and refractive indices of the isomers. Borer and Phillips[3] and Fehér and Strack[4] showed that the

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