SOME SCRAMBLING REACTIONS OF TETRAMETHYLTIN

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INTRODUCTION

Except for the essentially random exchange of several halogens and pseudohalogens on tetrahedrally bonded tin[1], there has been little quantitative or semiquantitative work in the equilibria or kinetics of reactions involving the scrambling of substituents on tin. In the study reported here, proton nuclear magnetic resonance (NMR) was employed to obtain quantitative information concerning tin scrambling reactions and the exchangeable substituents were chosen to be methyl groups and chlorine atoms since non-random equilibria are expected[2] for this pair of substituents. While the work described herein was underway, two papers were published[3] which described related studies carried out from the preparative rather than the physical point of view. Our work is consistent with these publications as well as with two other more recent papers[12] dealing with the preparative applications of alkyl transfer from tin to germanium.

EXPERIMENTAL SECTION

Reagents and reactions

The tetramethyltin was procured from Metallomer Laboratories, P.O. Box 152, Maynard, Mass., and the germanium tetrachloride from the Chemical Procurement Laboratories, College Point, N.Y. The latter was carefully redistilled under anhydrous conditions, with only the middle fraction being retained. The tin and silicon tetrachlorides were CP reagents from Fisher Scientific Company and the carbon tetrachloride was Baker and Adamson spectrochemical grade. All reagents showed no hydrogen-containing impurities (< 1 %) by proton NMR analysis; and fresh bottles were used in all cases, except for the redistilled germanium tetrachloride.

Mixing of reagents was carried out under carefully dried nitrogen in a glove box in which the reagent bottles and other vessels were allowed to stand so as to lose the readily desorbed water before being opened. 0.30 *M* solutions of the various reagents in CCl_4 were prepared by transferring calculated volumes of the reagents to standard flasks within the glove bag, checking the amount of the reagents by weighing, and then adding the carbon tetrachloride, again within the glove bag. Desired ratios of tetramethyltin with the different tetrahalides were obtained by proportioning these solutions into 5 mm sample tubes, using 1 cc hypodermic syringes graduated to 0.01

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cc. The over-all compositions are reported in terms of a composition ratio $R = [4(CH_3)_4Sn]/[(CH_3)_4Sn + MCl_4] = CH_3/(\text{total Sn} + Ge + Si)$, where M stands for the Sn, Ge, or Si introduced as its tetrachloride. The mixtures of neat liquids were prepared by direct weighing of the ingredients.

The samples were mixed in 5 mm precision-bore NMR tubes, which were put into the dry bag while still hot from the drying oven. After placing tight-fitting plastic stoppers on the filled tubes, they were removed from the dry bag, cooled in dry ice, and sealed with a torch.

Physical measurements

A Varian A-60 NMR spectrometer running at 60.000 Mc was employed in these studies, using a sweep rate of 0.5 or 0.1 cps (giving identical results) at the greatest available sweep width (50 cycles for the entire scale). The chemical shifts and spin–spin splitting constants for the tin compounds agreed with those values[4,5] which are reported, as did the chemical shifts for the compounds of silicon[5] and germanium[2]. The NMR assignments of the products of the reaction of tetramethyltin with silicon tetrachloride were verified by adding small amounts of the proton-containing materials suspected to be formed. The following species were added and found to increase the area of a peak already present: CH_3Cl, $(CH_3)_4Sn$, $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$, and CH_3SiCl_3 (not much present in most of the reaction mixtures). The compounds $CHCl_3$ and CH_2Cl_2 were added but found not to be present.

In the kinetic studies, samples were held at various temperatures from 0° to 150°. The 0° and 37° runs were carried out by mixing the precooled reagents in a tube kept in the thermostated probe of an A-60 NMR spectrometer and making a series of successive sweeps across the magnetic field during the reaction. Runs at higher temperatures were carried out in thermostated forced-draft drying ovens, with the samples being removed and cooled to room temperature for the NMR analysis.

Equilibrium measurements were made on the supercooled melts of $(CH_3)_4Sn$ with $SnCl_4$ after heating at 175°. Sn–H spin–spin splitting due to the ^{115}Sn isotope was observed in these melts in addition to the spin–spin splitting[5] due to ^{117}Sn and ^{119}Sn. For each of the molecular species, the Sn–H coupling constants across the methyl carbon atom decrease by the same amount when going from ^{119}Sn to ^{117}Sn as when going from ^{117}Sn to ^{115}Sn. This follows from the fact that the ratio of nuclear magnetic moments for ^{119}Sn to ^{117}Sn is 1.0462 and for ^{117}Sn to ^{115}Sn is 1.0895.

RESULTS AND INTERPRETATION

Kinetics of the $(CH_3)_4Sn$ vs. $SnCl_4$ reaction

In the temperature range from 0 to 50°, there is one predominant reaction, which is shown in equation (1):

$$(CH_3)_4Sn + SnCl_4 \longrightarrow (CH_3)_3SnCl + CH_3SnCl_3 \tag{1}$$

A typical rate curve for this reaction, using a 1:1 mole ratio of the starting ingredients, is presented in Fig. 1, from which it can be seen that the over-all process goes substantially to completion and is kinetically complex. The curve for the decrease in tetramethyltin with time consists of an anomalous preliminary section which is concave to the origin, followed by a final section which has the general shape associated with the usual chemical reaction. The anomalous first part of the curve becomes less prominent and finally disappears as the temperature is raised or the concentration is lowered. Thus, at a temperature of *ca.* 35° and an over-all concentration of 0.3 moles/l or, alternatively, at 0° and 0.05 moles/l, this anomalous section can no longer be seen and the rate curve exhibits the usual shape, with a slope corresponding to that of the first part of the reaction.

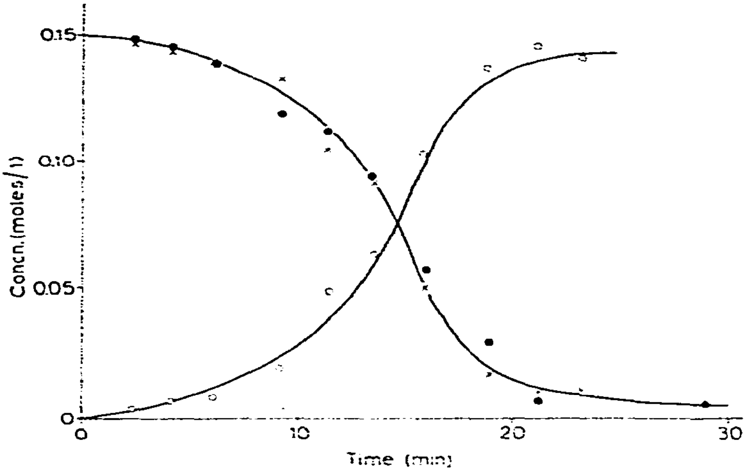

Fig. 1. Rate of exchange at 0° of one methyl group of tetramethyltin with a chlorine atom of tin tetrachloride. (●, ×), $(CH_3)_4Sn$ and $SnCl_4$; (○), $(CH_3)_3SnCl$ or CH_3SnCl_3.

It is unlikely that the first portion of the curve represents an induction period associated with a chain reaction since, for this kind of chemistry, such behavior is not expected at temperatures in the neighborhood of 0°. We have chosen to interpret tentatively this initial slow portion of the rate curve in terms of solvent polarity magnified by preferential solvation of the tin compounds by each other rather than by the carbon tetrachloride (*i.e.* the presence of tin association complexes undergoing rapid exchange*). With such preferential solvation, formation of an activated complex involving charge separation will be greatly aided by the presence of the polar products of reaction (1) (dipole moments, μ, of *ca.* 2.3) in the immediate neighborhood of the activated complex rather than only the nonpolar reagents ($\mu = 0$). Be this as it may, in considering the over-all reaction occurring at much higher temperatures, the second or fast part of the rate curve of Fig. 1 should be used for the rate of the reaction of equation (1). A second-order rate constant lying somewhere in the range of 300 to 800 l/mole-h fits this part of the rate curve at 0°. Comparison of the data taken between 0° and 37° leads to an activation energy of 3.5 to 5 kcal/mole for the reaction of equation (1), with the exact numerical value depending on the mathematical treatment used for the anomalous portion of the rate curve.

At all concentrations and temperatures studied, the reaction of equation (1) is completed before any further reactions are seen. Study of these further reactions

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* Evidence for preferential association is found in the heat of solution of *ca.* 3 kcal/mole for trace amounts of $(CH_3)_3SnBr$ dissolved in $(CH_3)_4Sn$. See ref. 7.

was nearly all done at 120° in order to have reasonably convenient periods of time between analyses. For various over-all mole ratios of the starting materials, the changes with time of the relative concentrations of the five species having the formula $(CH_3)_nSnCl_{4-n}$, with $n = 0, 1, 2, 3$, or 4, superficially appeared to be very different for the set of reactions subsequent to that of equation (1). However, the observed differences in the rate curves for different values are explained by the following analysis.

For the equimolar amounts of the reactants (*i.e.*, for $R = CH_3/Sn = 2$), the observed reaction is that of equation (2), since the fast reaction of equation (1), which is finished so quickly that it was not observed at 120°, gives the trimethyl and monomethyl compound in equal amounts with essentially no other products at this composition.

$$(CH_3)_3SnCl + CH_3SnCl_3 \rightleftharpoons 2(CH_3)_2SnCl_2 \qquad (2)$$

No anomalous effects were observed in this reaction which could be fitted reasonably well to a reciprocal concentration plot of the type used for simple second-order processes. The rate constant was 0.1 l/mole-h at a concentration of 0.30 *M* and 120°.

For $R > 2$, there is an excess of tetramethyltin over that needed for the reaction of equation (1). Following the nearly instantaneous reaction of equation (1), the resulting mixtures of $(CH_3)_4Sn$, $(CH_3)_3SnCl$, and CH_3SnCl_3 were seen to undergo further reaction to give an increase in $(CH_3)_3SnCl$ plus some $(CH_3)_2SnCl_2$, depending on the exact *R* value. The data could be explained by the reaction of equation 3 followed by further reaction according to equation 4 as the amount of $(CH_3)_2SnCl_2$ built up.

$$(CH_3)_4Sn + CH_3SnCl_3 \rightleftharpoons (CH_3)_3SnCl + (CH_3)_2SnCl_2 \qquad (3)$$

$$(CH_3)_4Sn + (CH_3)_2SnCl_2 \rightleftharpoons 2(CH_3)_3SnCl \qquad (4)$$

For $R < 2$, there is an excess of tin tetrachloride, and equation 5 becomes important after the completion of the reaction of equation (1), with equation (6) coming into play as the amount of $(CH_3)_2SnCl_2$ builds up.

$$(CH_3)_3SnCl + SnCl_4 \rightleftharpoons (CH_3)_2SnCl_2 + CH_3SnCl_3 \qquad (5)$$

$$(CH_3)_2SnCl_2 + SnCl_4 \rightleftharpoons 2CH_3SnCl_3 \qquad (6)$$

The twelve interactions corresponding to the forward-and-backward reactions of equations (1)–(6) represent the total number of chemically nontrivial exchange processes whereby a single methyl group on one of the molecules taken from the class $(CH_3)_nSnCl_{4-n}$ may be exchanged for a single chlorine atom on another. Analysis of the data indicated that an initially slow period or other gross kinetic anomalies are not present in the forward reactions of equations (2)–(6). Some qualitative experiments carried out at different temperatures indicated that the activation energies for this set of reactions [equations (2)–(6)] are quite large (> 10 kcal).

Equilibrium in the system $(CH_3)_4Sn$ vs. $SnCl_4$

Data thought to represent equilibrium conditions were obtained for the neat liquids and in solution at a concentration of 0.3 *M*. These data, along with points taken from two published[3] rate curves, are in agreement that the equilibrium constants of the form of equations (7)–(9) are very small. However, the numerical values for the equilibrium constants obtained from these three sets of data did not agree well. Although the disagreement might be due to a diminution in the amount of association complexes with decreasing concentration, it was more likely attributable to incomplete equilibration. Therefore, only the data for the neat liquids—the data we consider to be the most reliable—are presented in Table 1. The values of the corresponding equilibrium constants are shown in equations (7)–(9):

TABLE I

EQUILIBRATION OF $(CH_3)_4Sn$ WITH $SnCl_4$
Neat liquids, 17 h at 175°.

R = CH₃/Sn		*Percentage[a] of total Sn as*				
From ingredients	*By NMR*	$(CH_3)_4Sn$	$(CH_3)_3SnCl$	$(CH_3)_2SnCl_2$	CH_3SnCl_3	$SnCl_4$
0.95	1.00		0.3 (0.0)	17.5 (17.3)	64.5 (65.4)	17.7 (17.3)
2.00	1.97	—	0.3 (0.3)	96.6 (96.4)	3.1 (3.3)	
2.03	1.98	—	0.5 (0.4)	96.8 (97.2)	2.7 (2.4)	—
2.95	2.97	3.3 (3.6)	90.5 (89.8)	6.2 (6.6)		—

[a] Values in parentheses calculated from the constants of equations (7)–(9) using the *R* value corresponding to the NMR measurements.

$$K_1 = [(CH_3)_4Sn][(CH_3)_2SnCl_2]/[CH_3SnCl_3]^2 = 3 \times 10^{-3} \qquad (7)$$

$$K_2 = [(CH_3)_3SnCl][CH_3SnCl_3]/[(CH_3)_2SnCl_2]^2 = 1 \times 10^{-4} \qquad (8)$$

$$K_3 = [(CH_3)_2SnCl_2][SnCl_4]/[(CH_3)_3SnCl]^2 = 7 \times 10^{-2} \qquad (9)$$

Kinetics of the $(CH_3)_4Sn$ vs. $GeCl_4$ reaction

Substitution of germanium tetrachloride for tin tetrachloride in the reaction with tetramethyltin led to a considerable diminution in the rate of the initial reaction [which was similar to that of equation (1)]. The kinetic data are exemplified by Fig. 2. Such data can be adequately explained in terms of the two sets of reactions described in equations (10) and (11), respectively:

$$(CH_3)_4Sn + (CH_3)_nGeCl_{4-n} \longrightarrow (CH_3)_3SnCl + (CH_3)_{n+1}GeCl_{3-n} \qquad (10)$$

$$(CH_3)_3SnCl + (CH_3)_nGeCl_{4-n} \longrightarrow (CH_3)_2SnCl_2 + (CH_3)_{n+1}GeCl_{3-n} \qquad (11)$$

From the kinetic curves, it appears that the rates of methylation by tetramethyltin[12] and by trimethyltin chloride are in the order:

$$\text{Slow} \longleftarrow (CH_3)_2GeCl_2 < GeCl_4 < (CH_3)_3GeCl \text{ or } CH_3GeCl_3 \longrightarrow \text{fast} \qquad (12)$$

The reaction between tetramethyltin and germanium tetrachloride was estimated from data at several temperatures to have a small activation energy (< *ca.* 5 kcal).

The rate of exchange between tetramethyltin and germanium tetrachloride was so slow that equilibrium was never achieved even though the reaction was followed for a period of several months at 120°. However, from the long-term rate data, it appeared that methyl groups could be transferred *away from* the germanium, albeit very slowly. After very long heating times, formation of either perchloropolygermanes or perchlorocarbons from reaction with the CCl_4 solvent was deduced from the presence of a methyl chloride resonance in the NMR spectra.

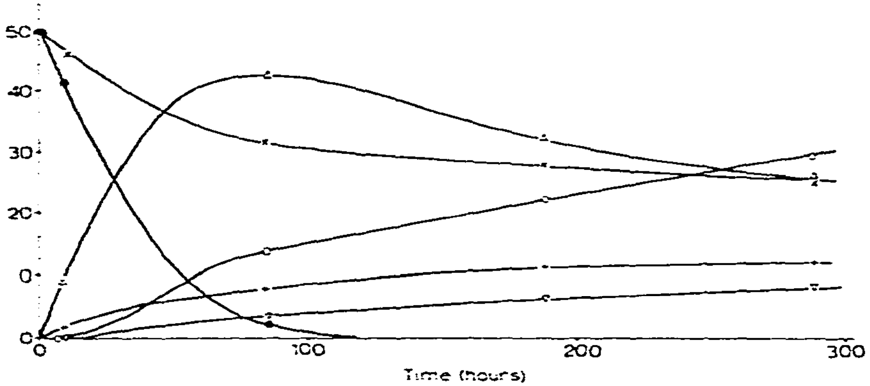

Fig. 2. Course of the reaction between equimolar amounts of tetramethyltin and germanium tetrachloride at 120°. (●), $(CH_3)_4Sn$; (△), $(CH_3)_3SnCl$; (O), $(CH_3)_2SnCl_2$; (×), $GeCl_4$; (+), $(CH_3)_4Ge$; (▽), $(CH_3)_2GeCl_2$.

Kinetics of the $(CH_3)_4Sn$ vs. $SiCl_4$ reaction

Substitution of silicon tetrachloride for germanium tetrachloride in the reaction with tetramethyltin causes such a large diminution in the rate of the simple substituent-exchange process that this reaction is observed only with great difficulty. Instead, a reaction leading to the formation of methyl chloride now becomes the prominent one. Kinetic data were obtained for this latter process [presumably described by equation (13)] in the sealed-tube studies:

$$(n\text{-}1)(CH_3)_4Sn + nSiCl_4 \longrightarrow (n\text{-}1)(CH_3)_3SnCl + (n\text{-}1)CH_3Cl + Si_nCl_{2n+2} \qquad (13)$$

Equilibrium was, of course, not observed in this system even after many months at 120°. However, after several months at 150°, it was found that a good part of the methyl groups had been transferred to the methyl chloride. The methyl chloride thus formed does not volatilize immediately on opening the sealed tube at room temperature. However, immersion of a rod into the liquid produces bubble fomation immediately and the methyl chloride NMR peak is seen to decrease greatly in area. At 120°, the stoichiometry shows that the methyl groups initially bonded to the tin end up attached to chlorine atoms which are substantially all derived from the silicon tetrachloride. At 150°, an appreciable amount of this chlorine also comes from the CCl_4 solvent. The compounds of the type Si_nCl_{2n+2} shown in equation (13) could not be directly assayed by NMR, of course; rather, they have been postulated on the basis of the material balance. Likewise, the stoichiometric requirements indicate that the CCl_4 solvent must form perchlorocarbons, C_nCl_{2n+2}, from a slow reaction with tetramethyltin. Of course, mixed perchloro compounds based on both chlorine and silicon could also result.

The reaction whereby over a period of months at 150° $(CH_3)_2SnCl_2$ and CH_3Cl are formed with concomitant build-up of colored compounds [polychlorosilanes(?)] is slower by a factor of *ca.* 20 than the reaction of equation (13). The analogous reaction of CCl_4 appears to be severalfold slower than that of $SiCl_4$. Finally, after many months of heating at 150°, small amounts of all of the mixed methylsilicon halides, particularly $(CH_3)_3SiCl$, are seen to be formed, according to the NMR spectra.

DISCUSSION

The free energies of formation of the mixed methyltin chlorides from the end-member compounds—tetramethyltin and tin tetrachloride—may be calculated from the equilibrium constants of equations (7)–(9). The difference between this free energy and that corresponding to statistically random sorting of the methyl groups with the chlorine atoms is an approximate measure of the enthalpy of the reaction[6]. Accordingly, $\Delta H = -7$ kcal/mole for formation of CH_3SnCl_3 from $(CH_3)_4Sn$ and $SnCl_4$, and from the same reagents, the respective ΔH values for $(CH_3)_2SnCl_2$ and $(CH_3)_3SnCl$ are -9 and -7 kcal/mole. For comparison, it should be noted that Skinner *et al.*[7] report $\Delta H = -10.8$ kcal/mole as measured calorimetrically for the formation of $(CH_3)_3SnBr$ from $(CH_3)_4Sn$ and $SnBr_4$.

In the series of reactions described by equations (1)–(6), the activated complex exhibiting the smallest heat of formation from the reactants is the one corresponding to equation (1). This is in agreement with the correlation[8] of fast rates (and concomitant low activation energies) with high heats of reaction* in a "series of similarly constituted reactants".

Thus, the equilibrium and kinetic results in the $(CH_3)_4Sn$ *vs.* $SnCl_4$ system are qualitatively interpretable in terms of the lower energies of the mixed compounds. These lower energies may be attributed to electron-correlation effects[10] on which further theoretical work is underway in our laboratory. Also related to such electron-correlation effects is the successive decrease in reaction rates when changing the atom M from tin to germanium to silicon in the following reaction:

$$(CH_3)_4Sn + MCl_4 \longrightarrow (CH_3)_3SnCl + CH_3MCl_3 \qquad (14)$$

The reaction rates for equation (14) were found to decrease by approximately 10^4 when going from tin to silicon. Such a successive stepwise decrease is expected when proceeding upward to a second-row element in a given period of the Periodic Table[11].

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* This correlation was first proposed by Polanyi; see ref. 9.

SUMMARY

By means of proton nuclear magnetic resonance, exchange of methyl groups with chlorine atoms has been studied in mixtures of tetramethyltin with the tetrachlorides of either tin, germanium, or silicon in 0.3 M CCl_4 solution. After several weeks at 120°, equilibrium was reached in the all-tin system with respect to scrambling of the methyl groups and chlorine atoms. Equilibrium constants for this system are given for the neat liquids at 175°. After several months in the range of 120–150°, the system involving germanium had only partially equilibrated with respect to scrambling of methyl and chloro groups between the tin and the germanium. In the case of the system involving silicon, initial reaction between tetramethyltin and silicon chloride led to the formation of $(CH_3)_3SnCl$ and CH_3Cl.

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