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REACTIONS OF $(CH_3)_3SnM(CH_3)_3$ (M = Si; Ge) WITH CHLOROTRIMETHYLSTANNANE AND DICHLORODIMETHYLSTANNANE IN METHANOL SOLUTION

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Summary

The reactions of $(CH_3)_3SnM(CH_3)_3$ for $M = Si$ and Ge with $(CH_3)_3SnCl$ or $(CH_3)_2SnCl_2$ in methanol follow the same path as the corresponding reactions of $(CH_3)_6Sn_2$, and involve $Sn-CH_3$ cleavage at essentially the same rate. Complications arise from reaction of HCl generated by $(CH_3)_3MCl$ solvolysis with the intermediate dimethylstannylene, but not through its reaction with the substrates.

Introduction

Kinetic and product composition studies [1,2,3,4] for the reactions of hexamethylstannane, $(CH_3)_3SnM(CH_3)_3$ ($M = Sn$), in methanol solution with chlorotrimethylstannane, chlorotrimethylplumbane and dichlorodimethylstannane have revealed that the first step in these reactions is the cleavage of a $Sn-CH_3$ bond to yield an intermediate which readily dissociates to form dimethylstannylene (or some equivalent species), and that the latter is the source of some further products, including "polymeric dimethyltin" by Sn–Cl insertion reactions. Typically, for example:

$$\begin{array}{ll} (CH_3)_3MSn(CH_3)_3 + (CH_3)_3SnCl \xrightarrow{1} & (CH_3)_3MSn(CH_3)_2Cl + (CH_3)_4Sn \\ (M = Sn) & \qquad\qquad\downarrow\uparrow \\ & (CH_3)_3MCl + (CH_3)_2Sn \\ & \qquad\qquad\downarrow\uparrow \\ & \qquad\frac{1}{n}[(CH_3)_2Sn]_n \end{array} \tag{1}$$

The measured rate of reaction is that of step 1, and this has been compared with the corresponding rates for the reactions of t-butyltrimethylstannane ($M = C$), for which the product of reaction 1 does not dissociate, and tetramethylstannane. Similar comparisons have been made for the corresponding reactions with chlorotrimethylplumbane and dichlorodimethylstannane. It is clearly of interest to complete the comparison by the inclusion of M = Si and Ge and, amongst other features, to examine whether the intermediates $(CH_3)_3MSn(CH_3)_2Cl$ might isomerise to $(CH_3)_3SnM(CH_3)_2Cl$, and serve as sources of dimethylsilylene and dimethylgermylene.

Unfortunately, the products $(CH_3)_3MCl$ (M = Si,Ge) are rapidly solvolysed in methanol solution to yield HCl which is also reactive in these systems. This causes complications which had to be investigated before further progress could be made. The preceding paper [5] describes the investigations.

Experimental

The preparation, purification and storage of all the reagents and solvents employed in these studies; and the methods of product analysis and kinetic study by ^1H NMR spectroscopy have been described previously [4,5].

Mass spectra were recorded by Mr.G. Macfarlane at 70 eV on an A.E.I. MS 920S instrument.

Results and Discussion

Reaction of $(CH_3)_3SnCl$ with $(CH_3)_3SiSn(CH_3)_3$

Figure 1 shows the ^1H NMR spectrum of the reaction mixture from $(CH_3)_3SiSn(CH_3)_3$, initially 0.118 *M*, containing $(CH_3)_3SiCl$ (0.022 *M*), with $(CH_3)_3SnCl$, initially 0.276 *M*, in methanol after 7 h. The resonances are labelled as in Table 1 of the preceding paper [5]. At this stage the solution has just developed the characteristic yellow colouration of "polymeric dimethyltin" but its precipitation has not yet commenced. At no stage is there any evidence for $(CH_3)_6Sn_2$ arising from Sn–Si cleavage. A typical analysis of the soluble product mixture substantially later in the reaction, when precipitation had occurred, is given in Table 1 in terms of the changes in concentrations of the various observable species. The quantity of tetramethylstannane present (F in F, J) was determined from a comparison of the $^{119,117}Sn$ satellites of its resonance relative to those of chlorotrimethylstannane (C). Throughout the reaction the total Si content remains essentially constant, whereas the CH_3 and Sn contents fall by amounts in 2/1 ratio corresponding to "$(CH_3)_2Sn$" given in Table 1. There is also an increase in Cl content as determined by the total for $(CH_3)_3SnCl$ and "$(CH_3)_3SiCl$". But the latter represents both $(CH_3)_3SiCl$ and $(CH_3)_3SiOCH_3$ arising by solvolysis, so that the increased Cl content can be ascribed to HCl produced and made observable as the products of its reactions.

Two alternative allocations of the individual changes in composition are presented in Table 1. For case I it is assumed that the initial reaction 1 with M = Si is followed by "polymer" formation, thus:

$$(CH_3)_3MSi(CH_3)_2Cl \xrightarrow{d} (CH_3)_3MCl + (CH_3)_2Sn$$

$$n(CH_3)_2Sn + (CH_3)_3MSi(CH_3)_2Cl \xrightarrow{i} (CH_3)_3M[Sn(CH_3)_2]_{n+1}Cl$$

and that HCl generated by the rapid solvolysis of $(CH_3)_3SiCl$ also reacts with the substrate, in accordance with our previous findings [5], by both Sn–M (path A) and Sn–CH_3 (path B) cleavage (any $(CH_3)_3SiH$ formed is also presumed to have been

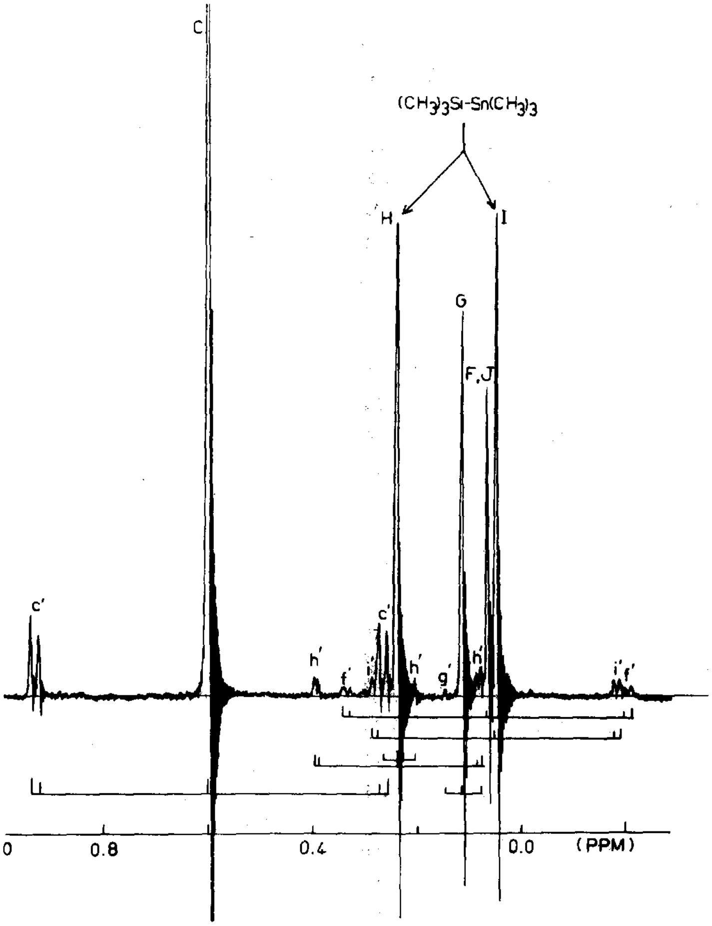

Fig. 1. ^1H NMR spectrum of reaction mixture: $(CH_3)_3SiSn(CH_3)_3$ (0.12 M)+$(CH_3)_3SnCl$ (0.28 M) after 7 h.

TABLE 1

ANALYSIS OF PRODUCTS OF $(CH_3)_3SnSi(CH_3)_3$ [a] + $(CH_3)_3SnCl$ [b] REACTION (1300 min)

	Observed change	I [c]				II [c]				
		a	b	c	Overall	a	d	e	f	Overall
$(CH_3)_3SnSi(CH_3)_3$	-0.09_8 M	-0.06_6	-0.02	-0.01_5	-0.10	-0.08	-0.02	.	.	-0.10
$(CH_3)_3SnCl$	-0.04_4	-0.06_5	$+0.02$	.	-0.04_5	-0.08	$+0.02$	$+0.02$	.	-0.04
$(CH_3)_3SiX$	$+0.09_7$	$+0.06_5$	$+0.02$	$+0.01_5$	$+0.10$	$+0.08$	$+0.02$	.	.	$+0.10$
$(CH_3)_4Sn$	$+0.06_5$	$+0.06_5$	.	.	$+0.06_5$	$+0.08$	.	-0.01	.	$+0.07$
"$(CH_3)_2Sn$"	$+0.08$	$+0.06_5$	.	$+0.01_5$	$+0.08$	$+0.08$	$+0.02$	.	-0.04	$+0.06$
$(CH_3)_2SnCl_2$	0?	.	.	.	0	.	-0.02	-0.01	$+0.04$	$+0.01$
HCl	?	.	-0.04	-0.01_5	-0.05_5	.	.	.	-0.08	-0.08

[a] Initial concentration 0.118 M with 0.022 M $(CH_3)_3SiCl$. [b] Initial concentration 0.276 M. [c] Change in composition due to substrate reaction with $(CH_3)_3SnCl$ (a); with HCl (b) path A; (c) by path B, A/B ~ 60/40; with $(CH_3)_2SnCl_2$ (d); due to $(CH_3)_4Sn$+$(CH_3)_2SnCl_2$ (e) and with $(CH_3)_2Sn$+2HCl (f).

completely decomposed by the HCl). Although the overall changes in composition are satisfactorily reproduced by this analysis, i.e. the correct consumption of $(CH_3)_3SnCl$ and HCl (~ 0.06 *M* suggested by the change in Cl content) and production of $(CH_3)_3SiX$ and "$(CH_3)_2Sn$" none of which were not employed in the development of the analysis, there are serious problems leading us to suggest the alternative II. The major problem is that while the $(CH_3)_3SnCl$ remains ca. 0.2 *M*, a substantially lower HCl concentration appears to have competed in 0.035/0.065, i.e. ~ 1/2, ratio with it in reaction with the substrate. The observed rate constants for $(CH_3)_3SnCl$, 5.3×10^{-5}, see below, and for HCl 1.7×10^{-5} M^{-1} s^{-1} [5] show this cannot be so. Furthermore, on the basis of the behaviour in the $(CH_3)_3SiSn(CH_3)_3$ + $(CH_3)_2SnCl_2$ reaction described below, it seems likely that $(CH_3)_3SiH$ if formed would survive in this reaction mixture.

Since there is an additional reaction consuming the substrate (beyond that accounted for by $(CH_3)_4Sn$ production) which is faster than that with HCl, and there is some process by which $(CH_3)_3SnCl$ is regenerated, we suggest that $(CH_3)_2SnCl_2$, eq. 2, is responsible

$$\underset{(M = Si)}{(CH_3)_3MSn(CH_3)_3} + (CH_3)_2SnCl_2 \xrightarrow{2} (CH_3)_3MSn(CH_3)_2Cl + (CH_3)_3SnCl \qquad (2)$$

despite our inability to observe it in this system. A satisfactory analysis is presented in Table 1 as case II. The relative rates of consumption of substrate by $(CH_3)_3SnCl$, average concentration ca. 0.25 *M*, and $(CH_3)_2SnCl_2$ of ca. 4/1 could be achieved, based upon the observed rate constant for the latter of 5×10^{-4} M^{-1} s^{-1}, if its concentration were ca. 0.008 *M*. In view of the fact that its resonance would be broadened by rapid exchange processes, such a low concentration might well be unobservable and we have assumed in the analysis that it may be present (It is taken into account as "missing" $(CH_3)_2Sn$).

The nature of the Si-containing products shows that the $(CH_3)_3Si$ groups remain intact throughout, and that no products arise from dimethylsilylene.

Analyses of the reaction mixture at earlier times gave kinetic data which are illustrated in Fig. 2. First order treatment, ln S vs. t where $S = [(CH_3)_3SiSn(CH_3)]_t$ appropriate to an essentially constant $[(CH_3)_3SnCl]$ of 0.265 *M* (a), or second order treatment, $\ln[S/(S + R_0 - S_0)]$ vs. t, where $R_0 = [(CH_3)_3SnCl]_0$ (b) show the same behaviour. The first period, 0 to 160 min (~ ca. 20% reaction) was taken to represent the initial reaction with $k_{obs} = 5.3 \times 10^{-5}$ M^{-1} s^{-1}, and the subsequent increased apparent rate constant (1.3×10^{-4} M^{-1} s^{-1}) arises from the incursion of the $(CH_3)_2SnCl_2$ process and the regeneration of $(CH_3)_3SnCl$.

A sample of "dimethyltin polymer" was collected from the reaction of $(CH_3)_3SiSn(CH_3)_3$, 0.17 *M*, and $(CH_3)_3SnCl$, 0.30 *M*, and found by mass spectral examination, see Table 2, to consist as expected, mainly of repeated $(CH_3)_2Sn$ units with one Si and perhaps one Cl only as end groups.

Reaction of $(CH_3)_2SnCl_2$ with $(CH_3)_3SiSn(CH_3)_3$

Aside from any intrinsic interest, a knowledge of the reactivity of the $(CH_3)_3SiSn(CH_3)_3$ towards $(CH_3)_2SnCl_2$ was required to substantiate our explanation of the $(CH_3)_3SnCl$ reaction above. As Fig. 3 illustrates some additional and important features were revealed.

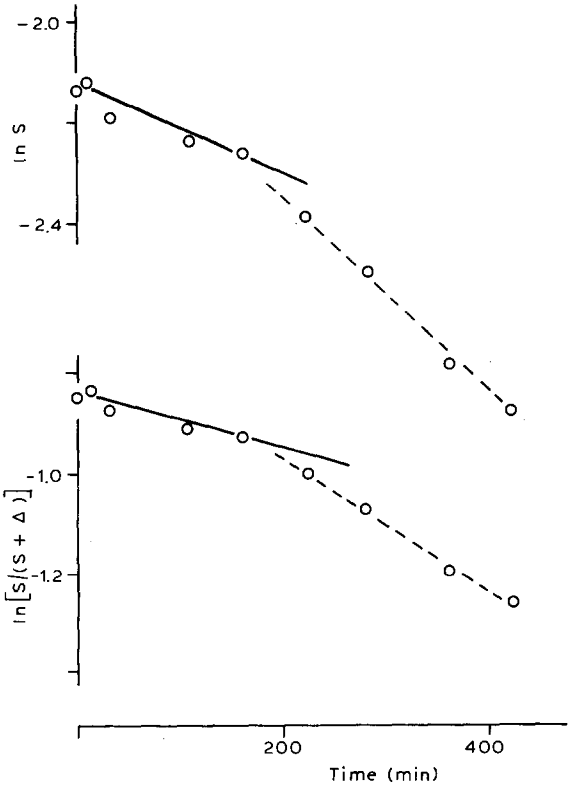

Fig. 2. Kinetic plots for $(CH_3)_3SnCl + (CH_3)_3SiSn(CH_3)_3$ (a) first order plot, $S = [(CH_3)_2SiSn(CH_3)_3]$ (b) second order plot, $\Delta = [(CH_3)_3SnCl]_0 - [(CH_3)_3SiSn(CH_3)_3]_0$.

After 150 min 70% of the substrate had been consumed to yield a complex mixture of products, most of which could be identified and their concentrations determined. The resonance of $(CH_3)_4Sn_2Cl_2$ was observed to be broad, and in a separate experiment (FX-100) its line width relative to that of cyclohexane was monitored at 12 min intervals during 96 min of reaction. The broadening factor of 1.28 (± 0.03) corresponding to k_{-3} 0.25 s^{-1} was found to be precisely the same as that previously determined [4] to arise from the rapid exchange process (eq. 3). (N.B.

$$(CH_3)_2SnCl_2 + (CH_3)_2Sn \underset{-3}{\overset{3}{\rightleftharpoons}} (CH_3)_4Sn_2Cl_2 \tag{3}$$

broadening of the resonance of $(CH_3)_2SnCl_2$ is inconsequential in the present system when its concentration is quite large, in contrast with the behaviour when its concentration is small) The concentration of $(CH_3)_4Sn$ was again deduced from the heights of its satellites relative to those of $(CH_3)_3SnCl$ and checked against the total CH_3, Sn and Si content of the system. There may be a small loss of CH_3 and Sn corresponding to "$(CH_3)_2Sn$", but its estimation is within experimental uncertainty.

Of particular importance are the new resonances labelled L, M and K in Fig. 3. The doublet (L,M) at 0.69 ppm (^3J(H,H) 0.8 Hz) is assigned to chlorodimethylstannane, $(CH_3)_2SnHCl$, and the resonance K is one half of the doublet (K,K′) at 0.01 ppm (^3J(H,H) 3.7 Hz) of trimethylsilane. These were confirmed by examination of the product from the reaction of $(CH_3)_3SiH$ (0.53 M) with $(CH_3)_2SnCl_2$ (0.23 M) in methanol. Initially $(CH_3)_3SiCl$ and $(CH_3)_2SnHCl$ are formed, in what appears to be an equilibrium process, but this is perturbed by the solvolysis of $(CH_3)_3SiCl$ and destruction of $(CH_3)_2SnHCl$. This can, however, be prevented by maintaining the system at low temperature. A notable feature is that $(CH_3)_3SiH$ is decomposed at only a moderate rate by the HCl generated through $(CH_3)_3SiCl$ solvolysis, and there is no evidence of $(CH_3)_6Si_2$ formation.

Table 3 summarises the analysis of the system which arises from a sequence of reactions following the initial reaction 2, and the dissociation of $(CH_3)_3SiSn(CH_3)_2Cl$. Thus:

$$(CH_3)_2Sn + (CH_3)_2SnCl_2 \rightleftharpoons (CH_3)_4Sn_2Cl_2 \tag{3}$$

TABLE 2

MASS SPECTRUM OF YELLOW POLYMER EX $(CH_3)_3SnCl/(CH_3)_3SiSn(CH_3)_3$

m/e	Probable ion	Relative intensity
644	$(CH_3)_7Sn_4SiCl^+$	1.8
629	$(CH_3)_6Sn_4SiCl^+$	0.9
614	$(CH_3)_5Sn_4SiCl^+$	3.6
524	$(CH_3)_7Sn_3SiCl^+$	18.4
509	$(CH_3)_6Sn_3SiCl^+$	4.7
494	$(CH_3)_5Sn_3SiCl^+$	19.1
472	$C_6H_{16}Sn_3Si^+$	4.8
446	$(CH_3)_6Sn_3{}^+$	19.0
442	$C_4H_{10}Sn_3Si^+$	20.6
431	$(CH_3)_5Sn_3{}^+$	19.0
428	$C_3H_8Sn_3Si^+$	25.4
415	$C_4H_{11}Sn_3{}^+$	47.5
390	$C_6H_{17}Sn_2SiCl^+$	32.4
386	$(CH_3)_8Sn_2Si^+$	34.2
376	$(CH_3)_5Sn_2SiCl^+$	30.0
372	$C_7H_{22}Sn_2Si^+$	19.5
363.5	$(CH_3)_7Sn_5Si^{2+}$	23.6
360	$C_4H_{11}Sn_2SiCl^+$	24.9
348.5	$(CH_3)_5Sn_5Si^{2+}$	12.7
346	$(CH_3)_3Sn_2SiCl^+$	44.9
333	$(CH_3)_4Sn_2Cl^+$	26.3
331	$(CH_3)_2Sn_2SiCl^+$	18.6
318	$(CH_3)_3Sn_2Cl^+$	19.0
317.5	$CHSn_5Si^{2+}$ (?)	9.4
316	$CH_3Sn_2SiCl^+$	17.8
310	$C_3H_8Sn_2Si^+$	4.7
237	$C_6H_{17}SnSi^+$	2.3
236	$C_6H_{16}SnSi^+$	3.6
207	$C_4H_{11}SnSi^+$	7.2
185	$(CH_3)_2SnCl^+$	71.8
165	$(CH_3)_3Sn^+$	100.0
155	$SnCl^+$	17.9
150	$(CH_3)_2Sn^+$	13.3
135	CH_3Sn^+	26.7
121	HSn^+	6.7
120	Sn^+	22.4

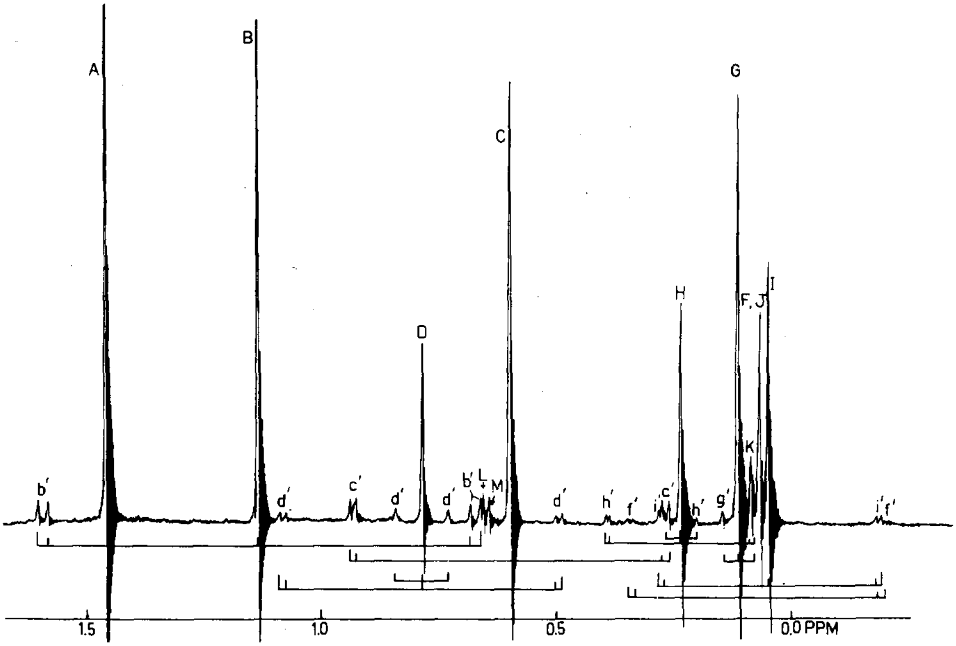

Fig. 3. ^1H NMR spectrum of reaction mixture: $(CH_3)_3SiSn(CH_3)_3$ (0.22 M)+$(CH_3)_2SnCl_2$ (0.345 M) after 150 min.

$$(CH_3)_2Sn + HCl \rightarrow (CH_3)_2SnHCl \tag{4}$$

$$(CH_3)_2SnHCl + HCl \rightarrow (CH_3)_2SnCl_2 + H_2 \tag{5}$$

$$(CH_3)_2SnHCl + (CH_3)_3SiCl \rightleftharpoons (CH_3)_2SnCl_2 + (CH_3)_3SiH \tag{6}$$

The observed yields of $(CH_3)_3SnCl$ and $(CH_3)_3SiX$ were not employed in the development of the analysis, and these are satisfactorily reproduced. The calculated

TABLE 3

ANALYSIS OF PRODUCTS OF $(CH_3)_3SnSi(CH_3)_3 + (CH_3)_2SnCl_2$ REACTION (150 min)

	Observed change	a[a]	b	c	d	e	f	Overall
$(CH_3)_3SnSi(CH_3)_3$	-0.12_3 M	-0.01	-0.11_5	.	.	.	.	-0.12_5
$(CH_3)_2SnCl_2$	-0.11_3	.	-0.11_5	-0.04_5	$+0.02$	.	$+0.02_5$	-0.11_5
$(CH_3)_3SiX$	$+0.10_6$	$+0.01$	$+0.11_5$	.	-0.02	.	.	$+0.10_5$
$(CH_3)_3SnCl$	$+0.10_8$	-0.01	$+0.11_5$					$+0.10_5$
$(CH_3)_4Sn_2Cl_2$	$+0.0.4_7$[b]	.	.	$+0.04_5$	.	.	.	$+0.04_5$
$(CH_3)_4Sn$	$+0.01_0$	$+0.01$	.	.	.	.	.	$+0.01$
$(CH_3)_2SnHCl$	$+0.01_9$	.	.	.	-0.02	$+0.04$	.	$+0.02$
$(CH_3)_3SiH$	$+0.02_2$				$+0.02$			$+0.02$
$(CH_3)_2Sn$	?	$+0.01$	$+0.11_5$	-0.04_5	.	-0.04	-0.02_5	$+0.01_5$
HCl	?	.	.	.	.	-0.04	-0.05	-0.09

[a] Change in composition due to substrate reaction with $(CH_3)_3SnCl$ (a), with $(CH_3)_2SnCl_2$ (b), due to $(CH_3)_2Sn + (CH_3)_2SnCl_2 \rightarrow (CH_3)_4Sn_2Cl_2$ (c), reduction of $(CH_3)_3SiX$ by $(CH_3)_3SnHCl$ (d), $(CH_3)_2Sn + HCl \rightarrow (CH_3)_2SnHCl$ (e) and $(CH_3)_2Sn + 2HCl \rightarrow (CH_3)_2SnCl_2$ (f). [b] Correction with broadening applied.

yield of "$(CH_3)_2Sn$" is probably too large, since the solution is at best pale yellow (but distinctly yellow after 20 h) and no "polymer" is precipitated. On the other hand the calculated requirement of HCl (0.09 M) can be provided by the $(CH_3)_3SiCl$ formed (0.105 M) and present initially (0.01 M), although its concentration can never be large.

Reaction 4 must be quite rapid to compete with reaction (3), whose rate constant, k_3, must be at least 10^2 M^{-1} s^{-1} on the basis of the known value of k_{-3} and the maximum estimated concentration of dimethylstannylene. Reactions 5 and 6 are much slower, as evidenced by the observable chlorodimethylstannane, and presumably both $(CH_3)_2SnHCl$ and $(CH_3)_3SiH$ are protected by the low HCl concentration. No resonances were seen that could be assigned to $(CH_3)_3SiSn(CH_3)_2Cl$, but these could well be obscured by signals from various other species. Furthermore if its dissociation were reversible then line broadening would be expected to render it unobservable.

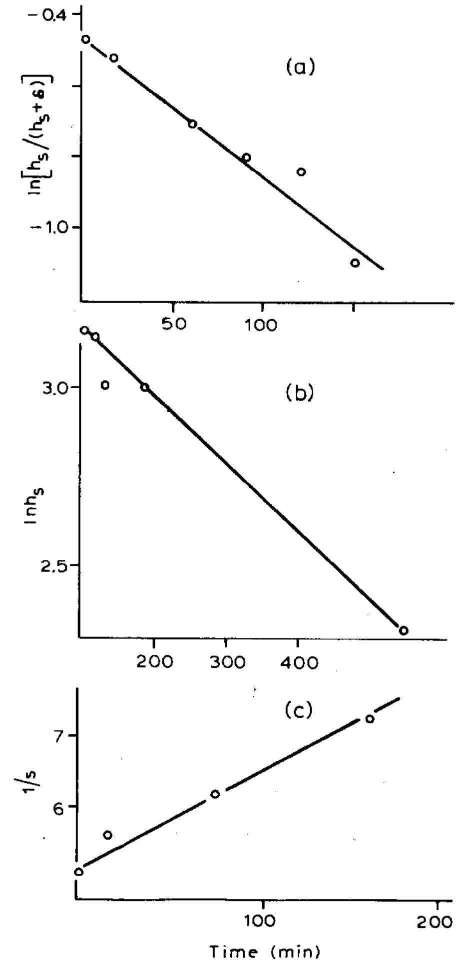

Fig. 4. Kinetic plots for: (a) $(CH_3)_2SnCl_2 + (CH_3)_3SiSn(CH_3)_3$; second order treatment; (b) $(CD_3)_3SnCl$ (0.52 M)+$(CH_3)_3GeSn(CH_3)_3$ (0.25 M); first order treatment; (c) $(CH_3)_2SnCl_2$ (0.194 M)+ $(CH_3)_3GeSn(CH_3)_3$ (0.197 M); second order treatment.

At much later times in the reaction (several days) all the substrate has reacted and, because of the presence of excess of $(CH_3)_2SnCl_2$, the $(CH_3)_4Sn$ has been consumed, and the composition is completely accounted for by $(CH_3)_2SnCl_2$, $(CH_3)_4Sn_2Cl_2$ and $(CH_3)_3SnCl$ with $(CH_3)_3SiX$, $(CH_3)_6Si_2O$ and some $(CH_3)_3SiH$. There is no precipitate and no yellow colouration.

The second order kinetic treatment for this system up to 150 min is illustrated in Fig. 4a. Substrate consumption is dominated by its reaction with $(CH_3)_2SnCl_2$, and the observed value of k_2 is $4.8 \times 10^{-4}\ M^{-1}\ s^{-1}$.

Reaction of $(CH_3)_3SnCl$ with $(CH_3)_3GeSn(CH_3)_3$

Figure 5 illustrates the ^1H NMR spectrum of the reaction mixture initially 0.352 M $(CH_3)_3GeSn(CH_3)_3$ and 0.409 M $(CH_3)_3SnCl$ after 30 h in methanol solution. A similar reaction conducted in CD_3OD solution yields $(CH_3)_3GeD$, whose spectrum (T′) is shown inset. This confirms the identification of the doublet (T) as trimethylgermane and verifies the source of the proton in the Ge–H bond.

Analysis of the reaction mixture at this stage (91% reaction) shows that there is a negligible loss of Ge, but a substantial loss of CH_3 and Sn in ratio 2/1, and the system corresponds to:

$$\begin{array}{lcl} (CH_3)_3GeSn(CH_3)_3 & + & (CH_3)_3SnCl \\ \quad -0.32_0M & & \quad -0.06_4M \end{array}$$

$$\begin{array}{lllllll} \rightarrow \text{“}(CH_3)_3GeCl\text{”} & + & (CH_3)_3GeH & + & (CH_3)_4Sn & + & \text{“}(CH_3)_2Sn\text{”} \\ \quad 0.28_6M & & \quad 0.03_6M & & \quad 0.19_0M & & \quad 0.19_5M \end{array}$$

Once again the composition can be accounted for, case I, in terms of competing reactions with $(CH_3)_3SnCl$ and with HCl, from $(CH_3)_3GeCl$ solvolysis, following paths A/A′/B = 30/50/20 as observed for HCl alone [5] but this requires $(CH_3)_3SnCl$/HCl reaction = 0.19/0.13 which is unacceptable. The alternative, case II, has $(CH_3)_3SnCl/(CH_3)_2SnCl_2$ reaction in this ratio, and this would be possible were $(CH_3)_2SnCl_2$ present at an average concentration of ca. 0.01 M. In this case the production of trimethylgermane is ascribed to reduction by the invisible $(CH_3)_2SnHCl$. Again the expected broadening of the small $(CH_3)_2SnCl_2$ resonance would prevent its detection, and the magnitude of the $(CH_3)_3SnCl$ resonance (C) may obscure any $(CH_3)_2SnHCl$. These analyses are summarised in Table 4.

A sample of yellow polymer was obtained under similar reaction conditions and its mass spectrum (Table 5) supports its identification as $(CH_3)_3Ge[Sn(CH_3)_2]_nCH_3$.

Reaction of $(CD_3)_3SnCl$ with $(CH_3)_3GeSn(CH_3)_3$

In the preceding experiment the large resonance, C, for $(CH_3)_3SnCl$ obscures an interesting part of the spectrum, but when $(CD_3)_3SnCl$ is employed two peaks, N at 0.62 ppm and 0 at 0.50 ppm (see Fig. 6), which remain in ratio 2/3, can be discerned. These are assigned to the intermediate $(CH_3)_3GeSn(CH_3)_2Cl$. They agree satisfactory with the resonances assigned by Shaw and Allred [6] to this species (in C_6D_{12}), and with those of the corresponding trifluoroacetoxy derivative observed by us [5]. It may be noted that this is the only $(CH_3)_3MSn(CH_3)_2X$ species we have been able to observe for X = Cl, and the most stable X = $OCOCF_3$ species was found to be that with M = Ge.

Not only can the Sn–Ge cleavage process yielding $(CH_3)_6Sn_2$ be shown to be

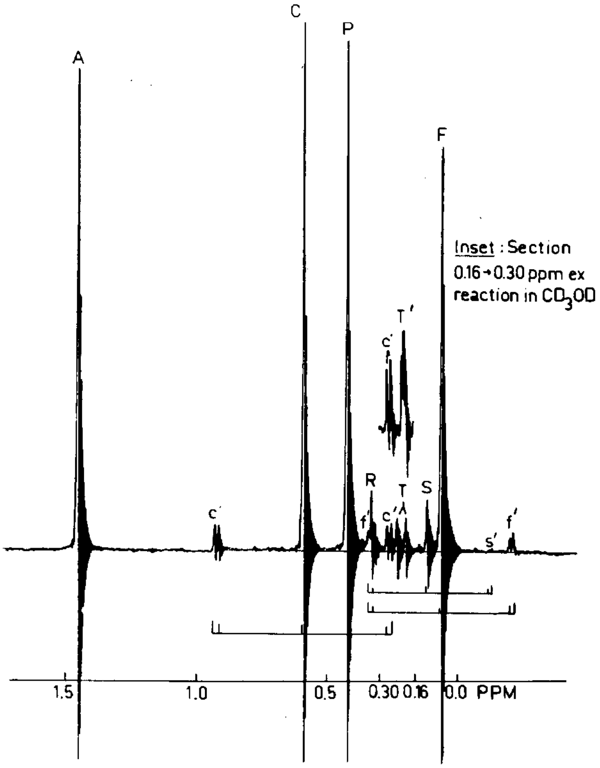

Fig. 5. ^{1}H NMR spectrum of reaction miuxture: $(CH_3)_3GeSn(CH_3)_3$ (0.35 M)+$(CH_3)_3SnCl$ (0.47 M) after 30 h.

unimportant, but the alternative process:

$$(CH_3)_3GeSn(CH_3)_3 + (CD_3)_3SnCl \rightarrow (CH_3)_3GeSn(CD_3)_3 + (CH_3)_3SnCl$$

does not take place, since the corrected peak heights for the substrate remain in 1/1

TABLE 4

ANALYSIS OF PRODUCTS OF $(CH_3)_3GeSn(CH_3)_3 + (CH_3)_3SnCl$ REACTION (30 h)

	I [a]					II [a]				
	a	b	c	d	Overall	e	f	g	h	Overall
$(CH_3)_3GeSn(CH_3)_3$	$-0.19M$	-0.04	-0.06_5	-0.02_5	-0.32	-0.13	.	.	.	-0.32
$(CH_3)_4Sn$	$+0.19$	.	.	.	$+0.19$	.	.	.	.	$+0.19$
$(CH_3)_3SnCl$	-0.19	$+0.04$	$+0.06_5$	.	-0.08_5	$+0.13$	.	.	.	-0.06
"$(CH_3)_3GeCl$"	$+0.19$	.	$+0.06_5$	$+0.02_5$	$+0.28$	$+0.13$	-0.03_5	.	.	$+0.28_5$
$(CH_3)_3GeH$	.	$+0.04$	.	.	$+0.04$	.	$+0.03_5$	.	.	$+0.03_5$
"$(CH_3)_2Sn$	$+0.19$	.	.	$+0.02_5$	$+0.21_5$	$+0.13$	.	-0.12_5		$+0.19_5$
HCl	.	-0.04	-0.13	-0.02_5	-0.19_5	.	.	-0.12_5	-0.08_5	-0.21
$(CH_3)_2SnCl_2$	0?	.	.	.	.	-0.13	$+0.03_5$	.	$+0.08_5$	$+0.01$
$(CH_3)_2SnHCl$	0?	.	.	.	.	.	-0.03_5	$+0.12_5$	-0.08_5	$+0.00_5$

[a] Change in composition due to substrate reaction with $(CH_3)_3SnCl$ (a); with HCl (b) Path A; (c) Path A'; (d) Path B, A/A'/B = 30/50/20; with $(CH_3)_2SnCl_2$ (e); reduction of $(CH_3)_3GeCl$ by $(CH_3)_2SnHCl$ (f), due to $(CH_3)_2Sn + HCl \rightarrow (CH_3)_2SnHCl$ (g) and $(CH_3)_2SnHCl + HCl \rightarrow (CH_3)_2SnCl_2$ (h).

TABLE 5

MASS SPECTRUM OF YELLOW POLYMER EX $(CH_3)_3SnCl/(CH_3)_3GeSn(CH_3)_3$

m/e	Probable ion	Relative intensity
490	$(CH_3)_4Sn_3Ge^+$	0.5
475	$(CH_3)_3Sn_3Ge^+$	1.0
460	$(CH_3)_2Sn_3Ge^+$	4.0
445	$CH_3Sn_3Ge^+$	1.6
400	$(CH_3)_6Sn_2Ge^+$	4.8
369	$C_4H_{11}Sn_2Ge^+$	4.2
328	$(CH_3)_6Sn_2{}^+$	29.8
325	$CH_3Sn_2Ge^+$	33.6
313	$(CH_3)_5Sn_2{}^+$	16.1
298	$(CH_3)_4Sn_2{}^+$	5.2
297	$C_4H_{11}Sn_2{}^+$	19.7
283	$(CH_3)_3Sn_2{}^+$	13.6
268	$(CH_3)_2Sn_2{}^+$	7.2
267	$(CH_3)_5SnGe^+$	6.4
253	$CH_3Sn_2{}^+$	5.9
251	$C_4H_{11}SnGe^+$	24.6
237	$(CH_3)_3SnGe^+$	25.8
185	$(CH_3)_2SnCl^+$	46.5
165	$(CH_3)_3Sn^+$	100.0
150	$(CH_3)_2Sn^+$	45.6
135	CH_3Sn^+	51.5
121	HSn^+	9.4
120	Sn^+	23.4

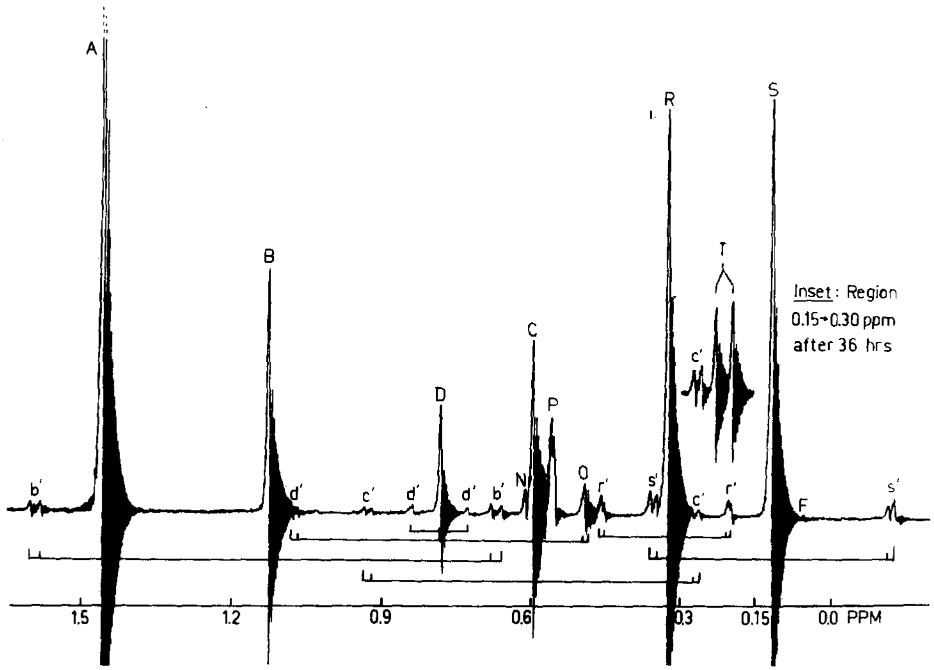

Fig. 6. ^1H NMR spectrum of reaction mixture: $(CH_3)_3GeSn(CH_3)_3 + (CH_3)_2SnCl_2$ after 160 min.

ratio throughout the reaction. Thus the situation for M = Ge, and presumably M = Si, is the same as that for M = Sn, for which it was deduced that no $(CH_3)_3SnSn(CD_3)_3)_3$ was generated from the absence of CD_3 groups in the "dimethyltin polymer" [3]. We confirmed this latter conclusion by examining the ^2H NMR spectra during reactions. Resonances arising from $(CD_3)_3SnCl$, 0.60 ppm with $J(^{119}Sn-^2H)$ 12.8 Hz, and $(CD_3)_3SnCH_3$, 0.06 ppm with $J(^{119}Sn-^2H)$ 7.8 Hz, are observed, but no resonance at 0.21 ppm for hexamethyldistannane.

The system follows satisfactory first order behaviour up to 60% reaction and $\ln[S]_t$ vs. t, see Fig. 4b, for essentially constant reagent 0.52 M gives $k = 3.0 \times 10^{-5}$ M^{-1} s^{-1}.

The composition of the reaction mixture after 220 min can be accounted for in terms of reactions of $(CD_3)_3SnCl$ and $(CH_3)_2SnCl_2$ both yielding $(CH_3)_3GeSn(CH_3)_2Cl$, most of which dissociates. The dimethylstannylene formed is largely converted into chlorodimethylstannane, which reduces some chlorotrimethylgermane, and, is converted via dichlorodimethylstannane into $(CH_3)_4Sn_2Cl_2$ (see Table 6).

The change in $(CD_3)_3SnCl$ concentration is of course unobservable, and the "tetramethylstannane" initially produced is taken to be $CH_3Sn(CD_3)_3$. There was initially present some protium species (ca. 10%) in the $(CD_3)_3SnCl$, which appear as small broad multiplets (t for CH_2D and q for CHD_2?) and a small sharp singlet, presumably for $CH_3(CD_3)_2SnCl$. At 220 min careful spectral examination reveals two singlets with 0.002 ppm separation in 2/3 ratio. We take the lower field resonance to be $(CH_3)_3SnCl$ (2/3), arising from substrate reaction with $(CH_3)_2SnCl_2$ and the higher field resonance to be $CH_3(CD_3)_2SnCl$ (3), initially present and arising from $CH_3Sn(CD_3)_3/(CD_3)_3SnCl$ exchange, $k = 7 \times 10^{-5}$ M^{-1} s^{-1} [1].

After 15 h of reaction there are three resonances in the chlorotrimethylstannane region, with separations of 0.004 and 0.001 ppm corresponding to $(CH_3)_3SnCl$, $(CH_3)_2(CD_3)SnCl$ and $CH_3(CD_3)_2SnCl$ in 1/1/1.5 ratio. In the tetramethylstan-

TABLE 6

ANALYSIS OF PRODUCTS OF $(CH_3)_3GeSn(CH_3)_3 + (CD_3)_3SnCl$ REACTION (220 min)

	Observed change	a[a]	b	c	d	e	f	g	Overall
$(CH_3)_3GeSn(CH_3)_3$	$-0.06_0 M$	-0.04_5	-0.01_5	.	.	.	.	.	-0.06
$CH_3Sn(CD_3)_3$	$+0.04_4$	$+0.04_5$	.						-0.04_5
$(CH_3)_3GeSn(CH_3)_2Cl$	$+0.01_1$	$+0.04_5$	$+0.01_5$	-0.05	.	.	.	.	$+0.01$
$(CH_3)_3GeCl$	$+0.03_7$	.	.	$+0.05$	-0.01	.	.	.	$+0.04$
$(CH_3)_3GeH$	$+0.01_1$	.	.	.	$+0.01$	.	.	.	$+0.01$
$(CH_3)_2SnHCl$	0	.	.	.	-0.01	.	-0.02	$+0.03$	0
$(CH_3)_2SnCl_2$	0	.	-0.01_5	.	$+0.01$	-0.01_5	$+0.02$	.	0
$(CH_3)_4Sn_2Cl_2$	$+0.01_4$	.	.	.	.	$+0.01_5$	.	.	$+0.01_5$
"$(CH_3)_2Sn$"	0	.	.	$+0.05$	.	-0.01_5	.	-0.03	$+0.005$
$(CH_3)_3SnCl$	?	.	$+0.01_5$	.	.	.	.	.	$+0.01_5$
$(CD_3)_3SnCl$	?	-0.04_5	.	.	.	.	.	.	-0.04_5
HCl	?	.	.	.	.	.	-0.02	-0.03	-0.05

[a] Change in composition due to substrate reaction with $(CD_3)_3SnCl$ (a), with $(CH_3)_2SnCl_2$ (b), decomposition of $(CH_3)_3GeSn(CH_3)_2Cl$ (c), reduction of $(CH_3)_3GeCl$ by $(CH_3)_2SnHCl$ (d), due to $(CH_3)_2SnCl_2 + (CH_3)_2Sn$ (e), reaction $(CH_3)_2SnHCl + HCl \rightarrow (CH_3)_2SnCl_2$ (f) and $(CH_3)_2Sn + HCl \rightarrow (CH_3)_2SnHCl$ (g).

TABLE 7

ANALYSIS OF PRODUCTS OF $(CH_3)_3GeSn(CH_3)_3 + (CH_3)_2SnCl_2$ (160 min)

	Observed change	b[a]	c	e	f,g	Overall
$(CH_3)_3GeSn(CH_3)$	$+0.06_0\,M$	-0.06	.	.	.	-0.06
$(CH_3)_2SnCl_2$	-0.06_8	-0.06	.	-0.03	$+0.02$	-0.07
$(CH_3)_3SnCl$	$+0.05_8$	$+0.06$	.	.		$+0.06$
$(CH_3)_3GeSn(CH_3)_2Cl$	$+0.00_8$	$+0.06$	-0.05	.		$+0.01$
$(CH_3)_3GeX$	$(+0.05)$	.	$+0.05$	.		$+0.05$
$(CH_3)_4Sn_2Cl_2$	$+0.03_2$	.		$+0.03$		$+0.03$
"$(CH_3)_2Sn$"	?	.	$+0.05$	-0.03	-0.02	0
HCl	?	.	.	.	-0.04	-0.04

[a] See Table 6.

TABLE 8

ANALYSIS OF PRODUCTS OF $(CH_3)_3GeSn(CH_3)_3 + (CH_3)_2SnCl_2$ (7 h)

	Observed change	a[a]	b	c	d	e	f	g	Overall
$(CH_3)_3GeSn(CH_3)_3$	$-0.18_3\,M$	-0.01	-0.17	.	.	.	.	.	-0.18
$(CH_3)_2SnCl_2$	-0.17_6	.	-0.017	.	$+0.04$	-0.06	$+0.01_5$	.	-0.17_5
$(CH_3)_3SnCl$	$+0.15_6$	-0.01	$+0.17$	.	.	.	.	.	$+0.16$
$(CH_3)_4Sn$	$+0.00_9$	$+0.01$	.	.	.	.	.	.	$+0.01$
$(CH_3)_3GeSn(CH_3)_2Cl$	0	$+0.01$	$+0.17$	-0.18	.	.	.	.	0
"$(CH_3)_3GeX$"	$+0.14_1$	.	.	$+0.18$	-0.04	.	.	.	$+0.14$
$(CH_3)_3GeH$	$+0.04_1$	.	.	.	$+0.04$	.	.	.	$+0.04$
$(CH_3)_4Sn_2Cl_2$	$+0.06?$	.	.	.	.	$+0.06$	.	.	$+0.06$
"$(CH_3)_2Sn$"	$(+0.075?)$	.	.	$+0.18$	.	-0.06	.	-0.05_5	$+0.06_5$
$(CH_3)_2SnHCl$	0	.	.	.	-0.04	.	-0.01_5	$+0.05_5$	0
HCl	.	.	.	.	.	.	-0.01_5	-0.05_5	-0.07

[a] See Table 6.

nane region there are four resonances, separated by 0.003, 0.004 and 0.003 ppm, which can be assigned to $(CH_3)_4Sn$, $(CH_3)_3SnCD_3$, $(CH_3)_2Sn(CD_3)_2$ and $CH_3Sn(CD_3)_3$ in 1/1.5/3.4/10 ratio.

Reaction of $(CH_3)_2SnCl_2$ with $(CH_3)_3GeSn(CH_3)_3$

The reaction between this substrate, 0.197 *M*, and dichlorodimethylstannane, 0.194 *M*, follows second order kinetics (equal reactant concentrations) with $[S]^{-1}$ vs. t, see Fig. 4c, yielding $k = 2.15 \times 10^{-4}\ M^{-1}\ s^{-1}$, and is in most respects the simplest system so far described.

The composition of the reaction mixture at 160 min, see Fig. 6, is well represented in Table 7 by the expected reactions, and no "polymeric dimethyltin" is in evidence at this stage. After 7 h, when most of the reactants have been consumed, there is polymer formation, since the latter stages of reaction are dominated by $(CH_3)_3SnCl$. These and other expected features lead to the analysis given in Table 8.

Conclusions

Despite the complications arising from the solvolyses of $(CH_3)_3MCl$ in methanol solution, the reactions of $(CH_3)_3MSn(CH_3)_3$ for M = Si; Ge with both $(CH_3)_3SnCl$

TABLE 9

STATISTICALLY CORRECTED RATE CONSTANTS (IN M^{-1} s^{-1} FOR ~ 30°C/METHANOL SOLUTIONS) FOR CLEAVAGE OF $Sn-CH_3$ BONDS

Substrate	Reagent				
	$(CH_3)_3SnCl$	(k_{rel}) [b]	$(CH_3)_2SnCl_2$ [d]	(k_{rel}) [b]	HCl
$(CH_3)_3SnSn(CH_3)_3$ (a)	$1.67(\pm0.05)\times10^{-5}$[3]	(0.93)	$4.0(\pm0.2)\times10^{-5}$[4]	(1.3)	3×10^{-6}[5]
$(CH_3)_3SnGe(CH_3)_3$ (b)	1.0×10^{-5}	(0.55)	3.6×10^{-5}	(1.2)	2×10^{-6}[5]
$(CH_3)_3SnSi(CH_3)_3$ (b)	1.8×10^{-5}	(1.0)	8.0×10^{-5}	(2.6)	2×10^{-6}[5]
$(CH_3)_3SnC(CH_3)_3$ (b)	$7.7(\pm0.4)\times10^{-7}$[3]	(0.04)	$1.0(\pm0.1)\times10^{-6}$[4]	(0.03)	–
$(CH_3)_4Sn$ (c)	$1.8(\pm0.1)\times10^{-5}$[3]	(1.0)	$3.1(\pm0.2)\times10^{-5}$[4]	(1.0)	–

[a] Statistical correction to k_{obs} for number of equivalent sites (a) 1/6 (b) 1/3 (c) 1/4 (d) 1/2. [b] Relative to $(CH_3)_4Sn$.

and $(CH_3)_2SnCl_2$ closely resemble those observed with hexamethyldistannane, i.e. M = Sn. The measured rate of reaction is that for $Sn-CH_3$ bond cleavage, and this takes place at quite similar rates for the individual $Sn-CH_3$ groups of these substrates and for the tetramethylstannane, as shown by the statistically corrected data given in Table 9. While a deactivating steric effect is evident in the case of M = C, none of the other $(CH_3)_3M$ groups show any significant activating nor deactivating effects. The rates of HCl cleavage of the $Sn-CH_3$ bonds are also similar.

The complications in the systems with M = Si; Ge, arising from HCl generated by solvolysis, do not appear to arise from the reaction of this species with the substrate itself, since this process is too slow. Rather, they arise from its reaction with the dimethylstannylene which is obtained from the initially formed $(CH_3)_3MSn(CH_3)_2Cl$, observable only in the case of M = Ge. Stepwise formation of $(CH_3)_2SnHCl$ and $(CH_3)_2SnCl_2$ provides opportunity for reduction of $(CH_3)_3MCl$ to $(CH_3)_3MH$, and so an additional mode of substrate decomposition.

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