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REACTION OF HEXAMETHYLDITIN WITH DIMETHYLTIN DICHLORIDE

II *. RATE STUDIES AND MECHANISM

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Summary

Rate data for the concurrent reaction of hexamethylditin with dimethyltin dichloride and with two of the products of this reaction in methanol solution at 30°C have been analysed in terms of individual steps. Line-broadening phenomena in the system have been studied, providing evidence of the intermediacy of dimethyltin and its insertion into tin—chlorine bonds. A general mechanism for this and related reactions is presented.

Introduction

In the preceeding paper [1] we reported a detailed examination of the product composition and stoichiometry of the reaction of $(CH_3)_2SnCl_2$ with $(CH_3)_6Sn_2$ in methanol solution including the line broadening observed for $(CH_3)_2SnCl_2$ and the intermediate, $(CH_3)_4Sn_2Cl_2$. These preliminaries completed, kinetic data can now be presented, comparisons made with $(CH_3)_4Sn$ and $(CH_3)_3SnC(CH_3)_3$ and mechanistic conclusions drawn.

Experimental

Materials

Hexamethylditin, tetramethyltin and dimethyltin dichloride were prepared, purified and stored as previously described [1].

Trimethyl-t-butyltin was donated by Dr. D.C. McWilliam and was distilled under reduced pressure, b.p. 46—48°C/37 mmHg. It solidified on standing, m.p. 31°C (lit. [2] m.p. 31.5°C).

Dry methanol [1] was degassed before use.

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* For part I see ref. 1.

Kinetic measurements

Kinetic experiments were generally performed as follows. A 5 mm NMR tube was capped and weighed and ca. 0.5 ml of dry, degassed methanol containing 1—2% w/w cyclohexane added. (On some occasions the cyclohexane was added separately.) The cap was replaced and the tube reweighed. Appropriate quantities of reagents were added in turn and the tube weighed after each addition. Fine particles were removed by filtering the entire contents of the tube through a fine glass sinter into a second tube which was flushed with nitrogen before recapping; Standard NMR caps were used except in the study of very slow reactions or where gas was evolved. In such cases, polythene pressure caps were required. Initial concentrations were calculated from the weights of solvent and solutes added.

An appropriate region of the 100 MHz ^{1}H NMR spectrum (usually 150—200 Hz) was examined at regular intervals using the JEOL PS-100 or FX-100 spectrometers. CW spectra were recorded using a sweep rate of 2.2 Hz s^{-1} or 1.1 Hz s^{-1} at sweep widths of 1080 Hz and 540 Hz, respectively. Faster sweep rates were used for faster reactions but in general, the slight time lag incurred when recording different peaks in the same scan was not considered significant. Conditions were carefully adjusted to attain maximum signal-to-noise ratio while the r.f. power and modulation levels were maintained below saturation levels. Internal lock (on the methanol -OH resonance) was always used. FT spectra were generally recorded by pulsing every four minutes using three or four 45° pulses and 8K sampling points over a frequency range of 150—200 Hz. In these experiments, CD_3OD was always used as solvent and the ^{2}H resonance of the CD_3 group used for heteronuclear internal lock. For slow reactions, a constant-temperature bath was maintained at the probe temperature (30°C) and the tube placed in this bath between readings.

Peak height measurements with appropriate corrections were employed to determine concentrations as described in the previous paper [1].

Results and discussion

Reaction of dimethyltin dichloride with tetramethyltin

The reaction proceeded according to:

$$(CH_3)_2SnCl_2 + (CH_3)_4Sn \rightarrow 2(CH_3)_3SnCl$$

and second order plots for four experiments at varying initial concentrations of $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn$ were obtained using the integrated rate eq. 1.

$$\ln\left[\frac{1.5h_B{}^0 - h_c}{3h_F{}^0 - h_c}\right] = \left(\frac{B-F}{2}\right)k_{obs}t + \ln\frac{B}{F} \qquad (1)$$

where B, F are the initial concentrations of $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn$, respectively; $h_B{}^0$, $h_F{}^0$ the calculated initial peak heights of $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn$, respectively; and h_c is the height at time t of the $(CH_3)_3SnCl$ resonance. (All heights being referenced to internal cyclohexane standard.)

Linear regression data for four such plots are listed in Table 1 (all plots show good linearity).

The value of k_{obs} must be divided by a statistical factor of four to correct for

TABLE 1

RATE DATA FROM 2ND ORDER PLOTS FOR REACTION: $(CH_3)_2SnCl_2 + (CH_3)_4Sn$

$[(CH_3)_2SnCl_2]^0$ (*M*)	0.68 ± 0.01	0.70 ± 0.01	0.97 ± 0.02	0.21 ± 0.01
$[(CH_3)_4Sn]^0$ (*M*)	0.53 ± 0.01	0.59 ± 0.01	0.50 ± 0.01	0.37 ± 0.01
slope $\times 10^5$ (s^{-1})	1.68 ± 0.05	1.32 ± 0.02	5.9 ± 0.1	—1.30 ± 0.05
$k_{obs} \times 10^4$ (M^{-1} s^{-1})	2.24 ± 0.06	2.44 ± 0.03	2.51 ± 0.07	2.6 ± 0.1

the number of methyl groups attached to tin in $(CH_3)_4Sn$ and by a further factor of two to correct for the presence of two Cl atoms in $(CH_3)_2SnCl_2$.

The average value of the second order rate constant thus derived is: $k = 3.1$ $(\pm 0.2) \times 10^{-5}$ M^{-1} s^{-1}.

This reaction had previously been studied (using large excesses of $(CH_3)_4Sn$) by Plazzogna, Bresodola and Tagliavini [3]. The concentrations of reactants used by these authors were:

$[(CH_3)_4Sn]^0 = 3.0\text{—}6.5 \times 10^{-2}$ M

$[(CH_3)_2SnCl_2]^0 = 1.0\text{—}10.0 \times 10^{-4}$ M

and the average value of the pseudo first order rate constant obtained (after statistical correction) was 1.6×10^{-4} M^{-1} sec^{-1}, although it was noted that the rate constant decreased with increasing initial concentration of $(CH_3)_2SnCl_2$ (by ca. 10% over the range investigated). The discrepancy between this result and the value obtained in the present investigation may be explained by consideration of the likely extent of dissociation of $(CH_3)_2SnCl_2$ in the range of concentrations used.

It had been claimed [4] that, in hydroxylic solvents (S), $(CH_3)_2SnCl_2$ dissociates forming two solvent-coordinated cations.

$$(CH_3)_2SnCl_2 + xS \rightleftharpoons (CH_3)_2SnCl(S)(S)_{x-1}{}^{+} + Cl^{-}$$

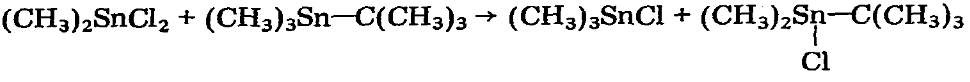
$$(CH_3)_2SnCl(S)(S)_{x-1}{}^{+} + S \rightleftharpoons (CH_3)_2Sn(S)_2(S)_{x-1}{}^{2+} + Cl^{-}$$

This led Plazzogna, Bresodola and Tagliavini to conclude that at low concentrations $(CH_3)_2SnCl_2$ would be largely dissociated, and hence the reacting species would be the cations $(CH_3)_2SnCl(S)(S)_{x-1}{}^{+}$ and $(CH_3)_2Sn(S)_2(S)_{x-1}{}^{2+}$. These conclusions were supported by the fact that the reaction rate exhibited a dependence on both solvent polarity and concentrations of added Cl^{-}.

The concentrations of $(CH_3)_2SnCl_2$ employed in the present study are several powers of ten greater than those of the previous study so that dissociation was not expected to be significant. The rate constant obtained is then a more appropriate measure of the reactivity of undissociated $(CH_3)_2SnCl_2$, predictably a considerably weaker electrophile than either of the cations.

Reaction of dimethyltin dichloride with trimethyl-t-butyltin

Examination of ^1H NMR spectra revealed a slow reaction, proceeding at least in the earlier stages via exclusive Sn—CH_3 cleavage.

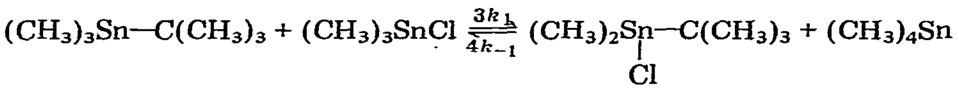


$$(CH_3)_2SnCl_2 + (CH_3)_3Sn\text{—}C(CH_3)_3 \rightarrow (CH_3)_3SnCl + (CH_3)_2\underset{\displaystyle Cl}{\underset{|}{Sn}}\text{—}C(CH_3)_3$$

A spectrum of a mixture of $(CH_3)_2SnCl_2$ (0.48 *M*) and $(CH_3)_3SnC(CH_3)_3$ (0.45 *M*) after 70 hours shows the resonances indexed in Table 2 (where a compound contains two distinct types of methyl group, italics are used to label those under consideration).

^{13}C NMR spectra were also recorded and the shifts and coupling constants for $(CH_3)_3Sn—C(CH_3)_3$ and $(CH_3)_2Sn(Cl)C(CH_3)_3$ are listed in Table 3.

Later in the reaction, a small amount of $(CH_3)_4Sn$ had been formed via:



$$(CH_3)_3Sn{-}C(CH_3)_3 + (CH_3)_3SnCl \underset{4k_{-1}}{\overset{3k_1}{\rightleftharpoons}} (CH_3)_2\underset{\mathrm{Cl}}{\underset{|}{Sn}}{-}C(CH_3)_3 + (CH_3)_4Sn$$

for which the following rate constants are known [5]:

$k_1 = 0.77 \times 10^{-6}\ M^{-1}\ s^{-1}$, $k_{-1} = 0.95 \times 10^{-5}\ M^{-1}\ s^{-1}$

The amount of $(CH_3)_4Sn$ present remains very small and this may be explained in two ways. Either the rate of reaction of $(CH_3)_3SnCl$ with $(CH_3)_3C—Sn(CH_3)_3$ is very much slower than that of $(CH_3)_2SnCl_2$ (and may thus be ignored in a kinetic analysis) or any $(CH_3)_4Sn$ thus formed is rapidly reconverted to $(CH_3)_3SnCl$ via:

$$(CH_3)_2SnCl_2 + (CH_3)_4Sn \xrightarrow{8k_2} 2(CH_3)_3SnCl\ (k_2 = 3.1 \times 10^{-5}\ M^{-1}\ sec^{-1})$$

The rate of reaction of $(CH_3)_3Sn—C(CH_3)_3$ with $(CH_3)_2SnCl_2$ could be satisfactorily determined by following the rate of appearance of $(CH_3)_3SnCl$. Second order plots were obtained using the integrated rate eq. 2.

$$\ln\left[\frac{1.5h_B{}^0 - h_C}{h_V{}^0 - h_C}\right] = (B - V)k_{obs}t + \ln\frac{B}{V} \qquad (2)$$

where *B*, *V* are the initial concentrations of $(CH_3)_2SnCl_2$ and $(CH_3)_3Sn—C(CH_3)$, respectively; $h_B{}^0$ the calculated initial height of $(CH_3)_2SnCl_2$; $h_V{}^0$ the calculated initial peak height for $(CH_3)_3Sn—C(CH_3)_3$, i.e. of either of the observable resonances; and h_C is the height at time *t* of $(CH_3)_3SnCl$.

The results from two experiments are listed in Table 4, and k_{obs} must be divided by a statistical factor of three to correct for the number of labile methyl

TABLE 2

^{1}H NMR SPECTRUM OF $(CH_3)_3SnC(CH_3)_3 + (CH_3)_2SnCl_2$ SYSTEM

Peak	Chemical shift	^2J(Sn—H) (Hz)	^3J(Sn—H) (Hz)	Identity
A	1.45			cyclohexane
B	1.13	89.2, 92.9		$(CH_3)_2SnCl_2$
C	0.60	64.7, 67.8		$(CH_3)_3SnCl$
F	0.06	not observable		$(CH_3)_4Sn$
V	—0.01	48.1, 52.0		$(\mathit{CH}_3)_3Sn—C(CH_3)_3$
W	1.03		61.6, 65.2	$(\mathit{CH}_3)_3C—Sn(CH_3)_3$
Y	0.56	54.0, 56.5		$(CH_3)_2\underset{\mathrm{Cl}}{\underset{\mid}{Sn}}—C(CH_3)_3$
Z	1.26		83.0, 87.0	$(\mathit{CH}_3)_3C—\underset{\mathrm{Cl}}{\underset{\mid}{Sn}}(CH_3)_2$

TABLE 3

^{13}C NMR PARAMETERS FOR $(CH_3)_3C{-}Sn(CH_3)_2X$ (X = Cl, CH_3)

Compound		Chemical Shift (ppm)	$^1J(Sn{-}C)$ (Hz)
$(CH_3)_3C{-}Sn(CH_3)_3$	$CH_3{-}C$	29.90	
	$CH_3{-}C$	21.78	
	$CH_3{-}Sn$	−12.38	283.2, 296.0
$(CH_3)_3C{-}\underset{\text{Cl}}{\underset{\vert}{Sn}}(CH_3)_2$	$CH_3{-}C$	30.40	
	$CH_3{-}C$	31.70	
	$CH_3{-}Sn$	−2.12	347.7, 355.5

groups in $(CH_3)_3Sn{-}C(CH_3)_3$ and two for the number of Cl atoms in $(CH_3)_2SnCl_2$. The value of the corrected second order rate constant thus obtained is:

$$k = 1.0\ (\pm 0.1) \times 10^{-6}\ M^{-1}\ s^{-1}$$

Dimethyltin dichloride/hexamethylditin system

Determination of the rate constant for the reaction of $(CH_3)_6Sn_2$ with $(CH_3)_2SnCl_2$ proved a matter of some difficulty. The consumption of $(CH_3)_6Sn_2$ in this system involves several consecutive competing second order reactions, thus precluding the use of any simple kinetic analysis. There is, for example, no product from reaction of $(CH_3)_6Sn_2$ with $(CH_3)_2SnCl_2$ which is not involved in a number of other processes, and hence none that could be used to monitor the reaction rate. An approach involving the use of integrated rate equations was devised, as set out below.

It is necessary to assume that, at least early in the reaction, $(CH_3)_6Sn_2$ is consumed only by reaction with $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$ and $(CH_3)_4Sn_2Cl_2$ in processes described by rate constants k_1, k_2 and k_3, respectively, i.e.

$$(CH_3)_2SnCl_2 + (CH_3)_6Sn_2 \xrightarrow{k_1} ....$$

$$(CH_3)_3SnCl + (CH_3)_6Sn_2 \xrightarrow{k_2} ....$$

$$(CH_3)_4Sn_2Cl_2 + (CH_3)_6Sn_2 \xrightarrow{k_3} ....$$

This assumption is valid if the concentrations of the homologues $(CH_3)_{2n+1}Sn_nCl$ and $(CH_3)_{2m}Sn_mCl_2$ ($n > 2$, $m > 3$) are small and if consumption of $(CH_3)_6Sn_2$ by $(CH_3)_2Sn$ is also unimportant, either because it does not insert into

TABLE 4

RATE DATA FROM 2ND ORDER PLOTS FOR REACTION: $(CH_3)_2SnCl_2 + (CH_3)_3SnC(CH_3)_3$

Experiment No.	1	2
$[(CH_3)_2SnCl_2]^0$ (M)	0.481 ± 0.002	0.525 ± 0.002
$[(CH_3)_3SnC(CH_3)_3]^0$ (M)	0.450 ± 0.002	0.395 ± 0.002
slope $\times 10^7$ (s^{-1})	1.97 ± 0.03	7.1 ± 0.2
$k_{obs} \times 10^6$ ($M^{-1}\ s^{-1}$)	6.4 ± 0.5	5.5 ± 0.3

Sn—Sn bonds or because its concentration is as yet too low.

If B, C, D and E are the concentrations at time t of $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$, $(CH_3)_4Sn_2Cl_2$ and $(CH_3)_6Sn_2$, respectively, (concentrations at $t = 0$ are B^0, C^0, D^0 and E^0), then the following differential rate equation may be written:

$$\frac{-\mathrm{d}E}{\mathrm{d}t} = k_1EB + k_2EC + k_3ED$$

and cast in the form of an integral equation:

$$\frac{-\mathrm{d}E}{E} = k_1B\mathrm{d}t + k_2C\,\mathrm{d}t + k_3D\,\mathrm{d}t$$

$$\therefore -\int_{t=t_1}^{t_2} \frac{\mathrm{d}E}{E} = k_1 \int_{t=t_1}^{t_2} B\,\mathrm{d}t + k_2 \int_{t=t_1}^{t_2} C\,\mathrm{d}t + k_3 \int_{t=t_1}^{t_2} D\,\mathrm{d}t$$

$$\therefore -[\ln E(t_2) - \ln E(t_1)] = k_1 \int_{t=t_1}^{t_2} B\,\mathrm{d}t + k_2 \int_{t=t_1}^{t_2} C\,\mathrm{d}t + k_3 \int_{t=t_1}^{t_2} D\,\mathrm{d}t$$

Setting:

$$I_\mathrm{B} = \int_{t=t_1}^{t_2} B\,\mathrm{d}t\ ,\ I_\mathrm{C} = \int_{t=t_1}^{t_2} C\,\mathrm{d}t\ ,\ I_\mathrm{D} = \int_{t=t_1}^{t_2} D\,\mathrm{d}t \text{ and } I_\mathrm{E} = \int_{t=t_1}^{t_2} E\,\mathrm{d}t$$

gives

$$\ln\left[\frac{E(t_1)}{E(t_2)}\right] = k_1I_\mathrm{B} + k_2I_\mathrm{C} + k_3I_\mathrm{D} \tag{3}$$

From the stoichiometric relationships previously established [1] one has $B = B^0 - D - \frac{1}{2}C$, and hence

$$\ln\left[\frac{E(t_1)}{E(t_2)}\right] = k_1[B^0(t_2 - t_1) - I_\mathrm{D} - \tfrac{1}{2}I_\mathrm{C}] + k_2I_\mathrm{C} + k_3I_\mathrm{D} \tag{4}$$

Another expression may be obtained by substituting the stoichiometric relationships $D = E^0 - E$ and $B = (B^0 - E^0) + E - \frac{1}{2}C$ giving:

$$\ln\left[\frac{E(t_1)}{E(t_2)}\right] = k_1[(B^0 - E^0)(t_2 - t_1) + I_\mathrm{E} - \tfrac{1}{2}I_\mathrm{C}] + k_2I_\mathrm{C} + k_3[E^0(t_2 - t_1) - I_\mathrm{E}] \tag{5}$$

These expressions are of varying utility. Expression 3 may be used whenever all concentrations may be measured over the integration range $t = t_1 \rightarrow t_2$. The line width of $(CH_3)_2SnCl_2$ must, then, be measured at each value of t to allow an accurate measure of its concentration. With this limitation, this expression may be used over the entire course of reaction. Expressions 4 and 5 may be used as long as the stoichiometric relations may be assumed to hold. A good estimate of the extent of their applicability for a particular set of data may be obtained by an inspection of the plot of D vs. $E - E^0$ as discussed previously [1]. These expressions are particularly useful as they do not require direct measurement of the concentration of $(CH_3)_2SnCl_2$ at any time except $t = 0$.

Concentrations for use in calculation of the integrals were derived from ^1H NMR peak heights. Integrals were evaluated by the use of Simpson's rule for numerical integration, i.e.

$$I = \int_a^b f(x)\,dx \sim \frac{h}{3}[f(x_0) + 4f(x_1) + 2f(x_2) + \ldots\ldots\ldots + 4f(x_{n-3}) + 2f(x_{n-2})$$

$$+ 4f(x_{n-1}) + f(x_n)]$$

where $x_0 = a; x_i = x_0 + ih$ $(i = 1, 2, \ldots n - 1)$

$x_n = b; h = \dfrac{b-a}{n}$ and n = odd, integer

In this analysis, $f(x_k)$ is the concentration of a particular species at a certain time and the nature of the function f is not precisely known. Concentration measurements must be taken at regular time intervals. Expressions used in this analysis are then of the form below (for the integral of $[(CH_3)_3SnCl]$).

$$I_C = \int_{t=t_1}^{t_2} C_{(t)}\,dt \sim \frac{\Delta t}{3}[C_{(t_1)} + 4C_{(t_2)} + 2C_{(t_3)} + \ldots + 4C_{(t_{n-3})} + 2C_{(t_{n-2})}$$

$$+ 4C_{(t_{n-1})} + C_{(t_n)}]\,.$$

where Δt = time increment in seconds between measurements

n = number of time intervals used (must be odd)

$C_{(t_i)}$ = value of concentration of $(CH_3)_3SnCl$ at time t_i $(i = 1, 2, \ldots n)$

t_i = i th time in seconds, $t_i = t_1 + (i - 1)\,\Delta t$

The values of fifteen integrals from eight experiments at varying initial concentrations of $(CH_3)_6Sn_2$ and $(CH_3)_2SnCl_2$ were calculated (for full details see ref. 6). Equations in k_1, k_2 and k_3 may be written in the generalized form of eq. 7.

$$\ln\left[\frac{E(t_1)}{E(t_2)}\right] = C_1k_1 + C_2k_2 + C_3k_3 \qquad (7)$$

with coefficients C_1, C_2 and C_3 being the terms in expressions 3, 4 or 5. The forms of these coefficients are summarized again in Table 5.

Whenever possible, integrals were evaluated over more than one time interval

TABLE 5

SUMMARY OF THE FORMS OF COEFFICIENTS C_1, C_2, C_3 IN INTEGRATED RATE EQUATIONS

Coefficient	Exp. 1	Exp. 2	Exp. 3
C_1	I_B	$B^0(t_2 - t_1) - I_D - \frac{1}{2}I_C$	$(B^0 - E^0)(t_2 - t_1) - I_E - \frac{1}{2}I_C$
C_2	I_C	I_C	I_C
C_3	I_D	I_D	$E^0(t_2 - t_1) - I_E$

to maximize the number of equations obtained. The values of these coefficients for the fifteen integrals evaluated, together with the corresponding values of $\ln[E(t_1)/E(t_2)]$ were employed and after averaging the estimates of C_1, C_2 and C_3 and rounding off, fifteen equations in k_1, k_2 and k_3 were obtained.

The determination of the best set of solutions to these equations is, however, not a straightforward matter. Solution of random sets of three equations in three unknowns by orthodox Gaussian reduction does not give meaningful results. Many solutions are either physically impossible (negative) or at variance by several orders of magnitude. The reason for this lies in the fact that the coefficients C_1, C_2 as C_3 as well as the quantity $\ln[E(t_1)/E(t_2)]$ are not absolute but experimentally determined quantities. Any solution to a set of three equations is determined by a complex expression in the twelve quantities, all with an associated experimental error.

Attention was turned to the use of a computer-based iterative technique using the direct-search sub-routine STEPIT [7]. STEPIT is a routine of wide applicability in "goodness of fit" analyses and approaches a problem in the following way:

Suppose the variables x_1—x_n determine a set of experimental data. A function called FOBJ, where FOBJ = $f(x_1, x_2, \ldots x_n)$, provides a measure of the difference between an experimentally determined result and a result calculated from x_1—x_n. The x_1—x_n are then varied between certain set limits and the values of x_1—x_n which produce the minimum value of the function FOBJ are determined by successively incrementing each variable. Thus, the values of x_1—x_n giving the best fit to experimental data may be found. This approach was applied to the problem at hand as follows.

The fifteen equations are written in the following way:

$$C_1(I)\,k_1 + C_2(I)\,k_2 + C_3(I)\,k_3 = D(I), I = 1\text{—}15$$

Then the "goodness of fit" of a particular set of solutions k_1, k_2 and k_3 will be determined by the sum of squares function, eq. 8

$$\mathrm{FOBJ} = \sum_{I=1}^{15} [D(I) - (C_1(I)\,k_1 + C_2(I)\,k_2 + C_3(I)\,k_3)]^2 \tag{8}$$

STEPIT was used to explore the interval

$$1.0 \times 10^{-10} < k_1, k_2, k_3 < 1.0 \times 10^{-1}\ M^{-1}\ \mathrm{s}^{-1}$$

to find the minimum value of this function. In this way, the following values for k_1, k_2 and k_3 were determined:

$k_1 = 4.84 \times 10^{-4}\ M^{-1}\ \mathrm{s}^{-1}$

$k_2 = 1.05 \times 10^{-4}\ M^{-1}\ \mathrm{s}^{-1}$

$k_3 = 3.26 \times 10^{-4}\ M^{-1}\ \mathrm{s}^{-1}$

The values of $D(I)$ given by these solutions, together with the experimentally determined values, are listed in Table 6.

The value of k_2, i.e. for reaction of $(CH_3)_3SnCl$ with $(CH_3)_6Sn_2$, had already been determined [5] as 1.00 (±0.03) × $10^{-4}\ M^{-1}\ \mathrm{s}^{-1}$. The value determined here

TABLE 6

VALUES OF $D(I)$ OBTAINED EXPERIMENTALLY AND CALCULATED FROM SOLUTIONS TO EQUATIONS I—XV BY ITERATIVE ANALYSIS

Equation	Values of $D(I)$		error (%)
	obs	calcd.	
I	0.939	0.919	—2.1
II	0.720	0.727	1.0
III	0.677	0.683	0.9
IV	0.320	0.312	2.5
V	1.830	1.835	0.3
VI	0.888	0.857	—3.5
VII	1.249	1.241	0.6
VIII	0.318	0.348	9.4
IX	0.399	0.351	—9.7
X	0.473	0.493	4.2
XI	0.385	0.404	—4.9
XII	0.752	0.757	0.7
XIII	0.623	0.644	3.4
XIV	0.480	0.522	8.8
XV	1.080	1.054	—2.4

($1.05 \times 10^{-4}\ M^{-1}\ s^{-1}$) is in excellent agreement with this known value, thus providing a useful check on the procedure.

The uncertainty of a result obtained from an iterative process of this nature is difficult to formally evaluate [8]. An estimate was made on the basis of the 'root mean square' percentage error of the calculated values of $D(I)$ listed in Table 6. This value (ca. 4.8%) was taken to approximate the errors of k_1, k_2 and k_3. To obtain the averaged rate constant for methyl cleavage (k), the values of k_{obs} must be divided by a statistical factor of twelve for both $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn_2Cl_2$. Thus,

for $(CH_3)_2SnCl_2$: $k_{\text{obs}} = 4.8\ (\pm 0.2) \times 10^{-4}\ M^{-1}\ s^{-1}$
$k = 4.0\ (\pm 0.2) \times 10^{-5}\ M^{-1}\ s^{-1}$
for $(CH_3)_4Sn_2Cl_2$: $k_{\text{obs}} = 3.3\ (\pm 0.1) \times 10^{-4}\ M^{-1}\ s^{-1}$
$k = 2.8\ (\pm 0.1) \times 10^{-5}\ M^{-1}\ s^{-1}$

Table 7 lists the values of k for reaction of both $(CH_3)_3SnCl$ and $(CH_3)_2SnCl_2$ with various substrates. The two values listed for reaction of $(CH_3)_3SnCl$ with $(CH_3)_6Sn_2$ arise from mechanisms involving insertion of $(CH_3)_2Sn$ into Sn—Cl or Sn—Sn bonds, respectively, (see discussion of mechanism below).

As expected, methyl cleavage of $(CH_3)_3SnR$ proceeds somewhat more rapidly with reagent $(CH_3)_2SnCl_2$ than with $(CH_3)_3SnCl$. Magnitudes of this rate enhancement for various substituents R are listed in Table 8. It was expected that all three enhancements would be similar, so that the rate constant derived on the basis of the 'Sn—Cl-insertion mechanism' for reaction of $(CH_3)_3SnCl$ with $(CH_3)_6Sn_2$ gives the more consistent result.

It was suggested previously [5] that this 'Sn—Cl-insertion mechanism' leading to polymer formation in the $(CH_3)_3SnCl/(CH_3)_6Sn_2$ system should be preferred since it gives rise to a $(CH_3)_6Sn_2$: $(CH_3)_4Sn$ reactivity ratio for $(CH_3)_3SnCl$

TABLE 7

AVERAGE RATES OF METHYL CLEAVAGE BY $(CH_3)_3SnCl$ AND $(CH_3)_2SnCl_2$

Reagent	Substrate	Rate Constant (M^{-1} s^{-1})	Ref.
$(CH_3)_3SnCl$	$(CH_3)_4Sn$	1.8 (±0.1) $\times 10^{-5}$	5
	$(CH_3)_3SnC(CH_3)_3$	0.77 (±0.04) $\times 10^{-6}$	5
	$(CH_3)_6Sn_2$	1.67 (±0.05) $\times 10^{-5}$ or 8.33 (±0.25) $\times 10^{-6}$	5
$(CH_3)_2SnCl_2$	$(CH_3)_4Sn$	3.1 (±0.2) $\times 10^{-5}$	
	$(CH_3)_3SnC(CH_3)_3$	1.0 (±0.1) $\times 10^{-6}$	
	$(CH_3)_6Sn_2$	4.0 (±0.2) $\times 10^{-5}$	

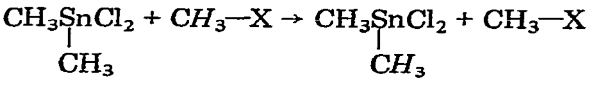
which is more consistent with that for $(CH_3)_3PbCl$ [9]. Ratios obtained are:

for $(CH_3)_3PbCl$ 1.4 (±0.4) : 1
for $(CH_3)_3SnCl$ 0.93 (± 0.09) : 1 (Sn—Cl-insertion mechanism)
or
0.47 (±0.05) : 1 (Sn—Sn-insertion mechanism)

Line-broadening phenomena

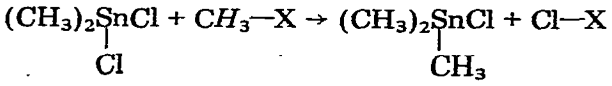
It has previously been established [1] that broadening of both the ^1H and ^{13}C resonances of $(CH_3)_2SnCl_2$ occurs in this system. Figure 1 shows a ^{119}Sn NMR spectrum of a $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ reaction mixture (ca. 0.2 M in CH_3OD) and is indexed in Table 9. Line broadening is again evident. A sealed capillary containing 0.13 M $(CH_3)_4Sn$ reference was added to the sample of which this spectrum was recorded and thus the resonance labelled F represents $(CH_3)_4Sn$ contained in the capillary as well as that produced in the reaction. (The fact that only one sharp resonance is observed establishes the validity of this and other ^{119}Sn chemical shift measurements made using a reference contained in an internal capillary). Line widths in the absence of broadening and accurate chemical shifts were determined for individual species.

It is clear that the ^{119}Sn resonance of $(CH_3)_2SnCl_2$ is, in addition to its ^1H and ^{13}C resonances, broader than its natural line width. This observation eliminates the possibility that the broadening is caused by a simple exchange of methyl groups with some methyl source X—CH_3, i.e.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{S}}nCl_2 + \mathit{CH_3}\text{—}X \rightarrow CH_3\underset{\displaystyle \mathit{CH_3}}{\underset{|}{S}}nCl_2 + CH_3\text{—}X$$

Such a reaction could conceivably broaden the ^1H and ^{13}C resonances but, as the Sn atom always sees the same environment, the ^{119}Sn resonance should remain unbroadened. There remain two types of exchange consistent with these NMR results, the first being 'exchange' of Cl for CH_3 via some electrophilic process, e.g.



$$(CH_3)_2\underset{\displaystyle Cl}{\underset{|}{S}}nCl + \mathit{CH_3}\text{—}X \rightarrow (CH_3)_2\underset{\displaystyle CH_3}{\underset{|}{S}}nCl + Cl\text{—}X$$

This would give rise to broadening of the ^1H, ^{13}C and ^{119}Sn resonances of

TABLE 8

REACTION OF $(CH_3)_2SnCl_2$ AND $(CH_3)_3SnCl$ WITH $(CH_3)_3SnR$ (RELATIVE RATES)

Substrate $(CH_3)_3SnR$ R =	$\frac{k(CH_3)_2SnCl_2}{k(CH_3)_3SnCl}$
CH_3	1.7 ± 0.2
$(CH_3)_3C$	1.3 ± 0.2
$(CH_3)_3Sn$	2.4 ± 0.2 (Sn—Cl insertion mechanism) or 4.8 ± 0.4 (Sn—Sn insertion mechanism)

$(CH_3)_2SnCl_2$ but should also broaden the $(CH_3)_3SnCl$ resonances; a phenomenon which is never observed. In addition, such processes are known to occur far too slowly to cause NMR broadening.

The reaction which immediately suggests itself as being responsible for broadening of the ^1H resonances of both $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn_2Cl_2$ is the reversible insertion of $(CH_3)_2Sn$ into $(CH_3)_2SnCl_2$:

$$(CH_3)_2Sn + (CH_3)_2SnCl_2 \rightleftharpoons (CH_3)_4Sn_2Cl_2$$

This process has been shown [1] to account for the rate of CD_3 transfer to $(CH_3)_4Sn_2Cl_2$ in the $(CD_3)_2SnCl_2$ + $(CH_3)_6Sn_2$ reaction and to be responsible for the decomposition of $(CH_3)_4Sn_2Cl_2$ in methanol solution [10].

A complete analysis of the variation of line width and concentration in this reaction system places rigorous demands on the ^1H NMR instrumentation em-

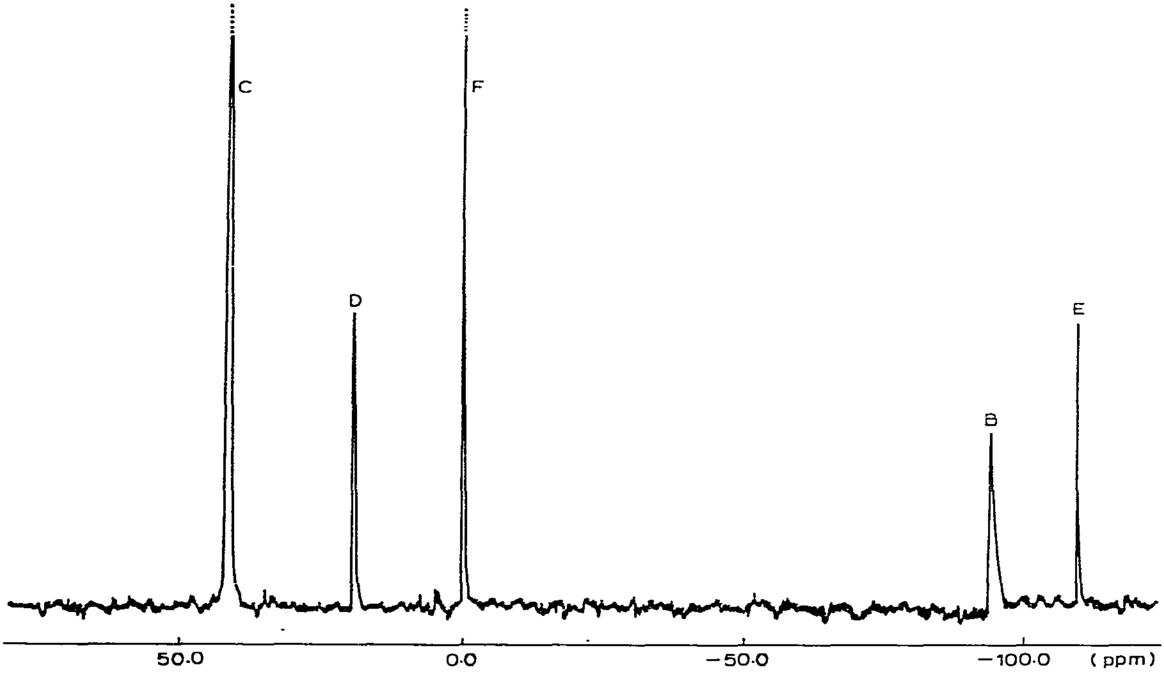


Fig. 1. ^{119}Sn NMR spectrum of reaction mixture: $(CH_3)_2SnCl_2$ + $(CH_3)_6Sn_2$.

TABLE 9

INDEX OF ^{119}Sn NMR SPECTRUM, FIG. 1

Peak	Chemical shift [b]	Line width (Hz)	Natural line width (Hz)	Identity
B	−94.0	33.8 [c]	26.3	$(CH_3)_2SnCl_2$
C	41.0	14.2	14.2	$(CH_3)_3SnCl$
D	19.0	9.6	?	$(CH_3)_4Sn_2Cl_2$
E	−109.2	3.5	3.5	$(CH_3)_6Sn_2$
F	0.0	3.8	3.8	$(CH_3)_4Sn$

[a] FT spectra at 37.146 MHz; 3000—4000 pulses and 16 K data points over 20,000 Hz (+292 to −247 ppm).
[b] In ppm relative to $(CH_3)_4Sn$. [c] This line width increases as reaction proceeds.

ployed. The "ideal" requirement for such an analysis is a set of spectra taken at regular intervals; spectra from which both the line width and height of every resonance therein may be satisfactorily measured. It is also necessary that, for each individual spectrum in the set, the time lag between recording of the various resonances be as small as possible.

In the earlier stages of this investigation, only continuous wave spectra were available, these being recorded on the JEOL PS-100 spectrometer. The direct measurement of line widths on this instrument could not be made with sufficient precision. Firstly, to obtain a reasonable measure of the line width of a peak greatly expanded spectra must be recorded, which places considerable demands on the field homogeneity and tuning of the CW instrument. Secondly, as the recording of spectra at the required expansion is necessarily very slow, a number of resonances cannot be swept quickly enough to allow the assumption that no appreciable change has occurred in the system during the sweep. An alternative method, particularly for continuous monitoring of the line width of the $(CH_3)_2SnCl_2$ resonance, is the comparison of its measured height with a height calculated from eq. 9, a relation derived from the stoichiometry of the reaction [1].

$$h_B\ (\text{calcd.}) = h_B{}^0 - \tfrac{1}{2}h_D - \tfrac{1}{3}h_C \qquad (9)$$

where h_B, h_C, h_D are the corrected heights of the $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$ and $(CH_3)_4Sn_2Cl_2$ resonances, respectively. Then, if a resonance of height h_B and width $W_B{}^{1/2}$ is broadened to width $W_B{}^{1/2\prime}$ and height $h_B{}'$, and assuming a consistent triangular shape of the peak,

$$h_B W_B{}^{1/2} = h_B{}' W_B{}^{1/2\prime}$$

$$\text{i.e.}\ \frac{W_B{}^{1/2}(\text{broadened})}{W_B{}^{1/2}(\text{unbroadened})} = \frac{h_B}{h_B{}'} = \frac{h_B{}^0 - \frac{1}{2}h_D - \frac{1}{3}h_c}{h_B\,(\text{measured})} \qquad (10)$$

Since only the heights of the various resonances need to be measured in this method, the considerable expansion of individual ^{1}H NMR spectra is unnecessary. Spectra could thus be conveniently obtained at appropriate time intervals (e.g. every 5 minutes). This method, however, fell foul of the very rigid requirements it places on the accuracy of peak height measurements. Even though a height-reproducibility of generally 95% could be obtained using the PS-100, inspection of eq. 10 reveals that it is very error sensitive. Four experimentally determined quantities are required, three of which are continuously varying and it was found in practice that the resultant error of the calculated ratio of widths was often of the order of 15—20%. These difficulties were alleviated, eventually, by the availability of the JEOL FX-100 Fourier Transform NMR spectrometer. The use of the FT technique offers many advantages in the study of kinetics by NMR. Firstly, all resonances in one spectrum are examined simultaneously and thus time-lag errors may be eliminated. A second and, in this case, more important advantage is offered by the "autostacking" facility of this FT instrument. This allows a series of spectra to be collected by pulsing at regular intervals and for these spectra to be automatically stored on a memory disc. Once stored on disc, spectra may subsequently be read back for measurement of all heights and also expanded and plotted to afford a direct and accurate measure of all line widths.

Spectra were generally recorded by pulsing every four minutes using 3 or 4 45° pulses and 8K sampling points over a frequency range of 150—200 Hz. The resonance of reference cyclohexane (of average width 0.30 Hz) was thus defined by some 25—30 transformed points. Two experiments were carried out at initial concentration ratios of $(CH_3)_2SnCl_2$ and $(CH_3)_6Sn_2$ of 2.15 : 1 and 0.62 : 1.

A selection of data from one of these experiments is given in Table 10, all widths being presented as the ratio of the measured width to that of the standard cyclohexane. (Note that the value for the width of $(CH_3)_2SnCl_2$ at t = 0 is the width recorded before the addition of $(CH_3)_6Sn_2$).

Several conclusions may be immediately drawn from these results, viz:

TABLE 10

LINE WIDTHS OF VARIOUS RESONANCES IN THE REACTION SYSTEM $(CH_3)_2SnCl_2$ (0.47 *M* + $(CH_3)_6Sn_2$ (0.22 *M*)

Time (min)	(CH_3) $(CH_3)_2SnCl_2$	$(CH_3)_4Sn_2Cl_2$	$(CH_3)_6Sn_2$	$(CH_3)_3SnCl$
0	1.00			
8	1.18	1.26	1.04	0.97
12	1.19	1.26	1.02	
16	1.23	1.34	1.00	1.02
20	1.25	1.32	1.02	
24	1.28	1.28	0.96	1.00
28	1.31	1.29	1.00	
32	1.33	1.30	0.92	0.98
36	1.35	1.31	0.93	
48	1.41	1.33	0.96	1.06
60	1.43	1.30	0.95	1.02
72	1.52	1.30	0.96	0.99
84	1.61	1.33	0.98	
100	1.77	1.32	0.99	0.98
108	2.06	1.37	0.98	
120	2.33	1.34	0.95	1.02
132	2.50	1.40	1.09	
156	2.61	1.30	0.99	
180	2.62		1.00	
188	2.71		0.95	
Average		1.31 ± 0.04	0.98 ± 0.04	1.00 ± 0.03

The $(CH_3)_3SnCl$ resonance remains unbroadened.

The $(CH_3)_6Sn_2$ resonance remains unbroadened.

The $(CH_3)_4Sn_2Cl_2$ resonance is broadened, but to a relatively constant extent throughout the course of reaction, i.e. by a factor of ca. 1.3.

The $(CH_3)_2SnCl_2$ resonance is broad from the outset of reaction and becomes broader as reaction proceeds.

As a check on the reliability of these results, separate 0.1 *M* solutions of $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$ and $(CH_3)_6Sn_2$ were each monitored for two days, during which time no line-broadening was observed in any case. A 0.1 *M* solution of $(CH_3)_4Sn_2Cl_2$ alone in methanol (see ref. 10) also shows line-broadening by a factor of 1.27, due to its decomposition, while in chloroform no broadening and no decomposition was observed. The second set of the experiments gave similar results with broadening by a relatively constant factor of 1.25.

Rate data from line width measurements

The line width of the $(CH_3)_4Sn_2Cl_2$ resonance (D) is given by the relation

$$W_D^{1/2} = (W_D^{1/2})^0 + \frac{(\tau_D^{-1})}{\pi}$$

where, $W_D^{1/2}$ is the observed width at half height of D; $(W_D^{1/2})^0$ is the width at half height of D in the absence of exchange; and τ_D^{-1} is the mean lifetime of methyl groups on $(CH_3)_4Sn_2Cl_2$, which is given by

$$\tau_D^{-1} = \frac{1}{D}\left(\frac{dD}{dt}\right) = k_{-6}$$

where k_{-6} is the rate constant for the presumed dissociation reaction of $(CH_3)_4Sn_2Cl_2$ (Scheme 1).

$$W_D^{1/2} = (W_D^{1/2})^0 + \frac{k_{-6}}{\pi} \qquad (11)$$

Equation 11 requires that the line width of $(CH_3)_4Sn_2Cl_2$ should be independent of its concentration and remain, as observed, constant throughout the course of reaction. As the natural line width of $(CH_3)_4Sn_2Cl_2$ in methanol cannot be measured, it is assumed identical to that of the cyclohexane reference (0.30 Hz). This is reasonable as the line widths of $(CH_3)_2SnCl$ (in the absence of exchange), of $(CH_3)_4Sn$, $(CH_3)_6Sn_2$, $(CH_3)_3SnCl$ and cyclohexane in methanol are all identical. Furthermore, the line width of $(CH_3)_4Sn_2Cl_2$ itself in chloroform is also the same as that of cyclohexane.

The average ratio of the width of the $(CH_3)_4Sn_2Cl_2$ resonance to that of cyclohexane in methanol was found to be 1.27 ± 0.03, hence $k_{-6} = 0.25$ (±0.02) s^{-1}.

Similarly, the line width of $(CH_3)_2SnCl_2$ (B) is given by

$$W_B^{1/2} = (W_B^{1/2})^0 + \frac{(\tau_B^{-1})}{\pi}$$

where

$$\tau_B^{-1} = \frac{1}{B}\left(\frac{dB}{dt}\right) = \frac{1}{B}(k_6BZ) = k_6Z$$

with B the concentration of $(CH_3)_2SnCl_2$ and Z the concentration of $(CH_3)_2Sn$.

Broadening of the $(CH_3)_2SnCl_2$ resonance is, then, not a first order process and the line width may well vary throughout the course of reaction. It should, furthermore, vary in the same way as the concentration of $(CH_3)_2Sn$ in solution. Variations in the $(CH_3)_2SnCl_2$ line width were studied for the two reactions with different initial concentrations of $(CH_3)_2SnCl_2$ and $(CH_3)_6Sn_2$. Concentration curves for these reactions are shown in Fig. 2 and 4., while plots of the $(CH_3)_2SnCl_2$ line width (measured as the ratio of the observed width to that of cyclohexane) versus time are shown in Figs. 3 and 5. By inspection of these plots, it may readily be seen that the broadening varies in much the same fashion in both systems. The line width increases throughout the course of reaction; rapidly at first, then much more slowly, then rapidly again during the later stages. In addition, it is clear that the broadening does not vary in a simple manner with respect to the concentration of any one of the species present in high concentration.

Analysis of the broadening of the $(CH_3)_2SnCl_2$ resonance is rendered very difficult by the fact that the concentration of $(CH_3)_2Sn$ is always small and cannot be measured directly. It is possible, however, to make various assumptions which allow the derivation of simple expressions for the concentration of $(CH_3)_2Sn$ in terms of known concentrations and the extent to which such assumptions allow prediction of the observed phenomena provides, at least, a check on the validity of the assumptions.

The most attractive assumption that could be made about the system is that the reaction

$$(CH_3)_2SnCl_2 + (CH_3)_2Sn \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} (CH_3)_4Sn_2Cl_2$$

is always at or near equilibrium, i.e. that equilibrium is established very early in the course of the overall reaction and that the slower processes which alter the concentrations of $(CH_3)_2SnCl_2$ and $(CH_3)_4Sn_2Cl_2$ serve only to slightly perturb the equilibrium which is always rapidly re-established. Given this assumption, then

$$k_6BZ = k_{-6}D$$

and hence

$$\Delta W_B{}^{1/2} = \frac{k_{-6}}{\pi W^{1/2}{}_{\text{ref}}} \frac{D}{B} \qquad (12)$$

where $\Delta W_B{}^{1/2} = (W_B{}^{1/2} - W^{1/2}{}_{\text{ref}})/W^{1/2}{}_{\text{ref}}$

Equation 12 requires that a plot of $\Delta W_B{}^{1/2}$ vs. D/B should be linear with slope $(k_{-6}/\pi W^{1/2}{}_{\text{ref}}) = 0.27$. Such plots for the two reactions studied are shown in Figs. 6 and 7. Both are distinctly non-linear and, although they feature relatively straight portions, the slopes of these are very different from eqn. 12. The broadening is always greater than predicted so that it must be concluded that the insertion/dissociation reaction never reaches equilibrium and, further, that the concentration of $(CH_3)_2Sn$ is not only always increasing but is always greater than required by the equilibrium condition.

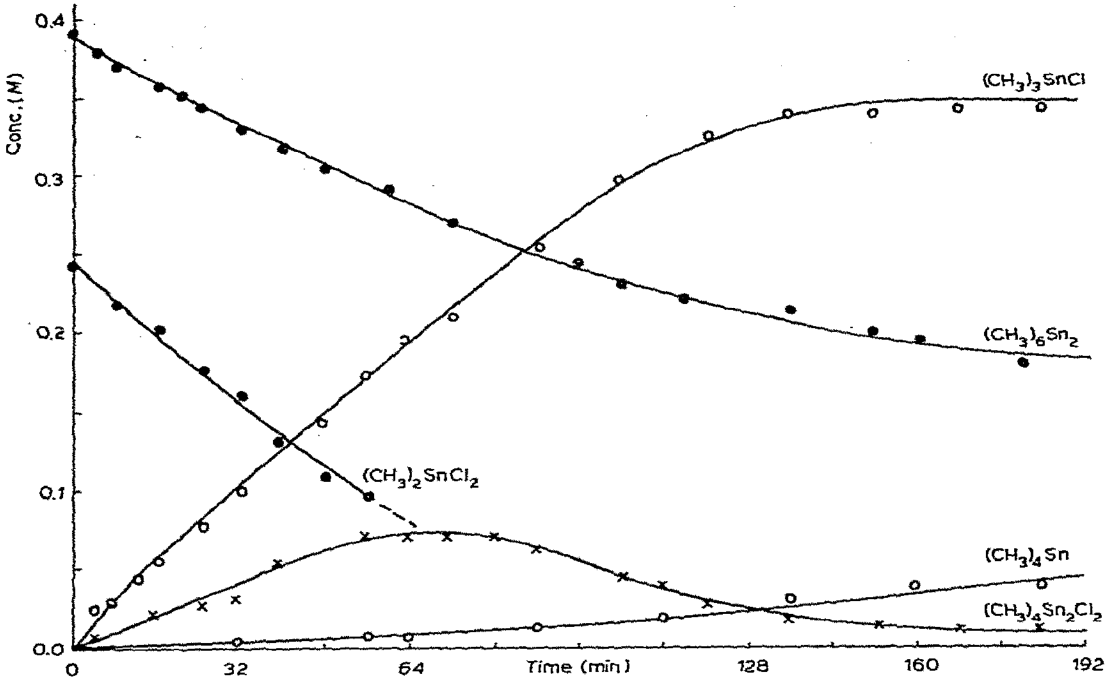


Fig. 2. **Concentration-time curves for reaction: $(CH_3)_2SnCl_2$ (0.24 *M*) + $(CH_3)_6Sn_2$ (0.39 *M*).**

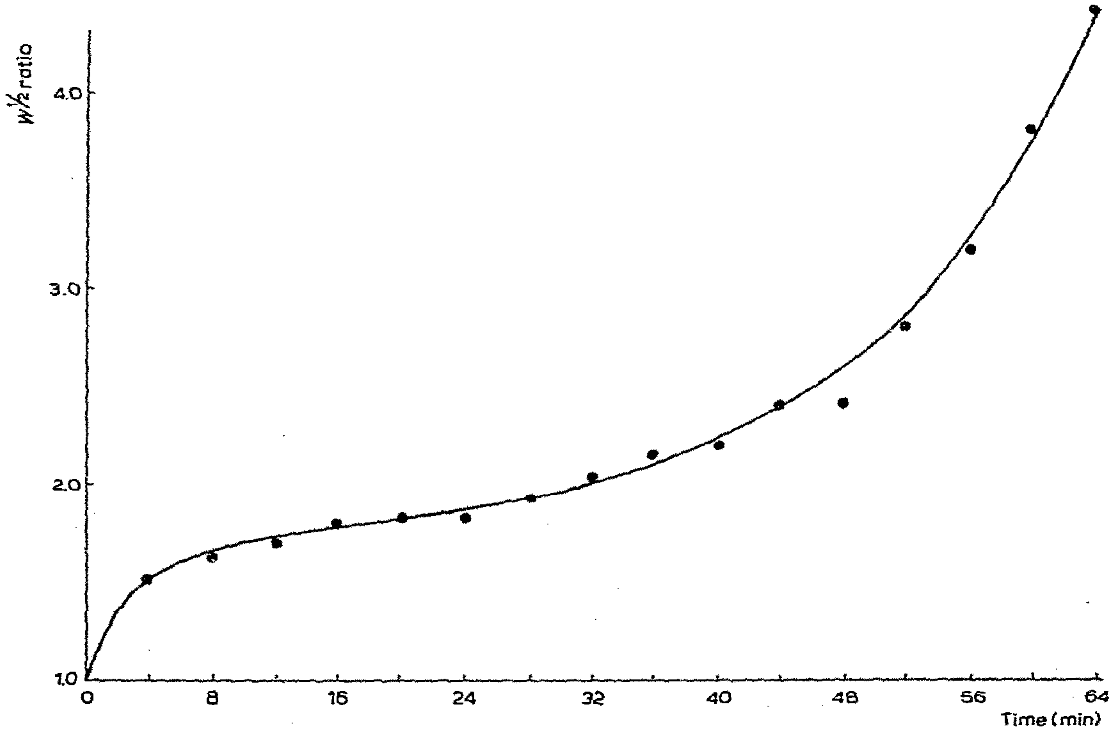


Fig. 3. Plot of $W^{1/2}_{(CH_3)_2SnCl_2}/W^{1/2}_{C_6H_{12}}$ vs. time for reaction: $(CH_3)_2SnCl_2$ (0.24 *M*) + $(CH_3)_6Sn_2$ (0.39 *M*).

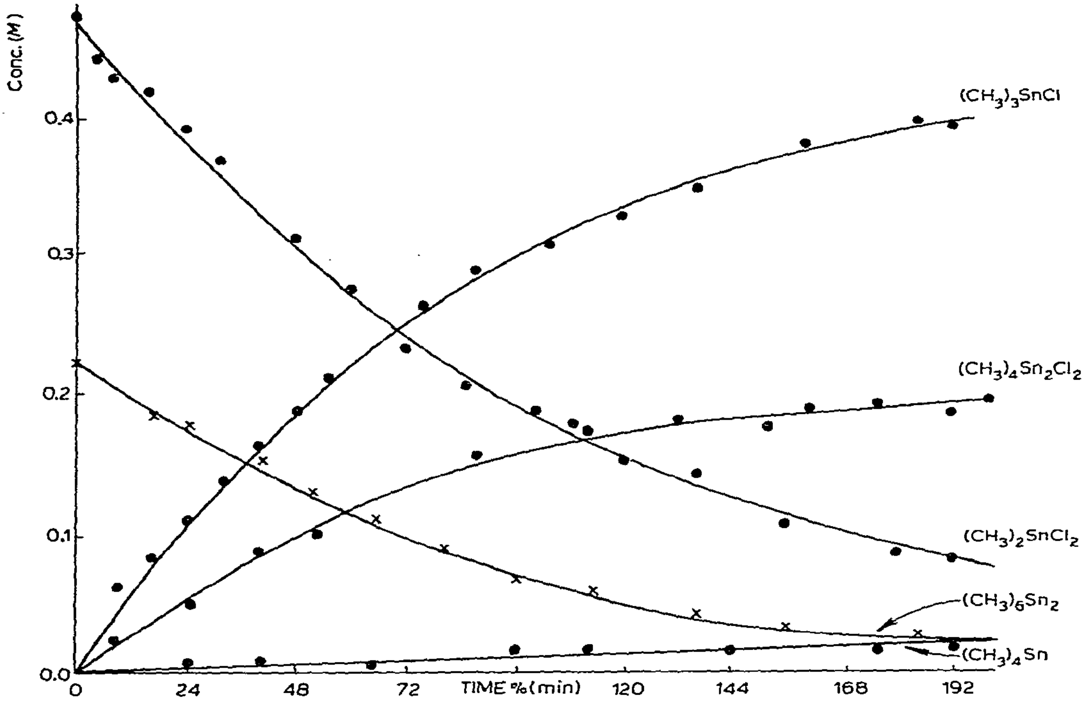


Fig. 4. Concentration-time curves for reaction: $(CH_3)_2SnCl_2$ (0.47 *M*) + $(CH_3)_6Sn_2$ (0.22 *M*).

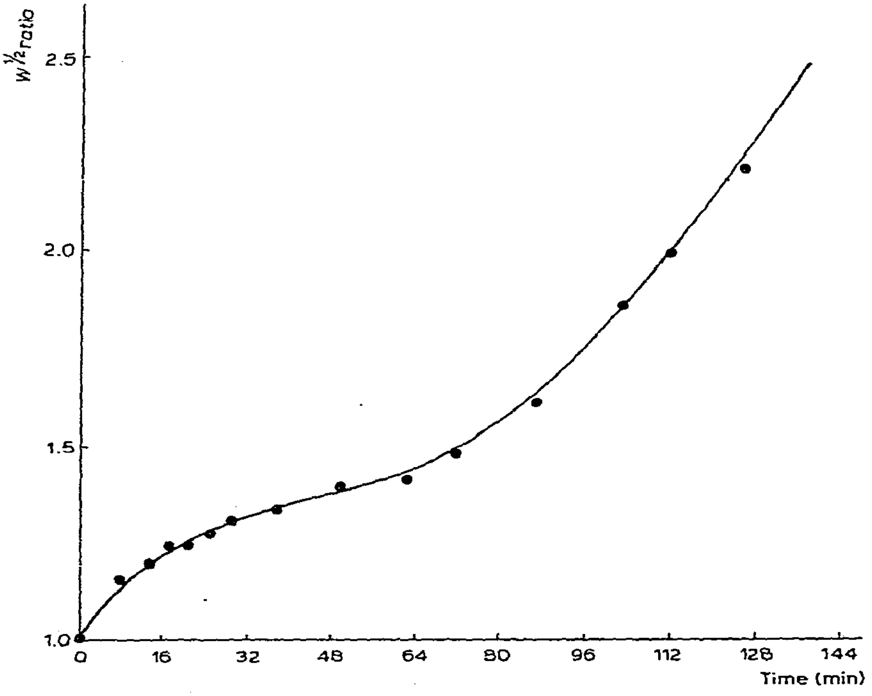


Fig. 5. Plot of $W^{1/2}_{(CH_3)_2SnCl_2}/W^{1/2}_{C_6H_{12}}$ vs. time for reaction: $(CH_3)_2SnCl_2$ (0.47 *M*) + $(CH_3)_6Sn_2$ (0.22 *M*).

A more complete expression for the rate of formation of $(CH_3)_2Sn$, assuming the mechanism of the overall reaction as detailed below, is

$$\begin{aligned}\frac{d[(CH_3)_2Sn]}{dt} &= k_{-5}Q - k_5CZ + k_{-6}D - k_6DZ \\ &+ k_{Q(-1)}Q_1 - k_{Q(1)}QZ + k_{D(-1)}D_1 - k_{D(1)}DZ \\ &+ \sum_{i=2}^{n} k_{Q(-i)}Q_i - \sum_{i=2}^{n} k_{Q(i)}Q_{i-1}Z \\ &+ \sum_{i=2}^{n} k_{D(-i)}D_i - \sum_{i=2}^{n} k_{D(i)}D_{i-1}Z\end{aligned}$$

where Q is the concentration of $(CH_3)_5Sn_2Cl$; Q_i is the concentration of $(CH_3)_{2i+5}Sn_{i+2}Cl$; and D_i is the concentration of $(CH_3)_{2i+4}Sn_{i+2}Cl_2$.

Any approach to finding a workable expression for the concentration of $(CH_3)_2Sn$ must involve some simplification of this complex rate equation. Even if the concentrations Q_i and D_i ($i = 1—n$) are always small enough to be neglectec various other quantities (e.g. k_5, k_{-5} and Q) remain. To eliminate these by consideration of a steady state in the concentration of $(CH_3)_5Sn_2Cl$ cannot be valid because it is evident that the concentrations of $(CH_3)_3SnCl$ and $(CH_3)_2Sn$ are always increasing, and hence that the concentration of $(CH_3)_5Sn_2Cl$ must also always be increasing (unless it precipitates) and a true steady state is never reached.

Although this line-broadening study has afforded the rate constant k_{-6}, it appears that the calculation of k_6 from the data available is not possible. Nonetheless a means is provided by which the build-up in solution of reactive intermediates such as $(CH_3)_2Sn$ and $(CH_3)_5Sn_2Cl$ may be assessed, and these species are present in such low concentration that it is difficult to envisage any other method by which their concentrations could be monitored more effectively.

Reaction mechanism

It is apparent that the $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ reaction system is considerably more complex than previously thought. Data presented thus far, together with conclusions drawn from investigation of the partially analogous $(CH_3)_3SnCl/(CH_3)_6Sn_2$ system [6], allow a reasonable formulation of the processes involved in the formation, early in the reaction, of methanol-soluble products and, later, in the build-up of polymeric precipitates which were accounted for in the preceeding paper [1]. All products formed via $(CH_3)_2Sn$ may be explained in terms of insertions into Sn—Cl bonds. The following sequence is indicated:

(i) Initial electrophilic attack on $(CH_3)_6Sn_2$ by $(CH_3)_2SnCl_2$ to form $(CH_3)_5Sn_2Cl$ and $(CH_3)_3SnCl$.

(ii) Subsequent dissociation of $(CH_3)_5Sn_2Cl$ to form $(CH_3)_3SnCl$ by extrusion of $(CH_3)_2Sn$.

(iii) Reversible insertion of $(CH_3)_2Sn$ into a Sn—Cl bond of $(CH_3)_2SnCl_2$ to form $(CH_3)_4Sn_2Cl_2$.

(iv) Further electrophilic attack on $(CH_3)_6Sn_2$ by both $(CH_3)_3SnCl$ (forming $(CH_3)_4Sn$ and $(CH_3)_5Sn_2Cl$) and by $(CH_3)_4Sn_2Cl_2$ (forming $(CH_3)_5Sn_2Cl$).

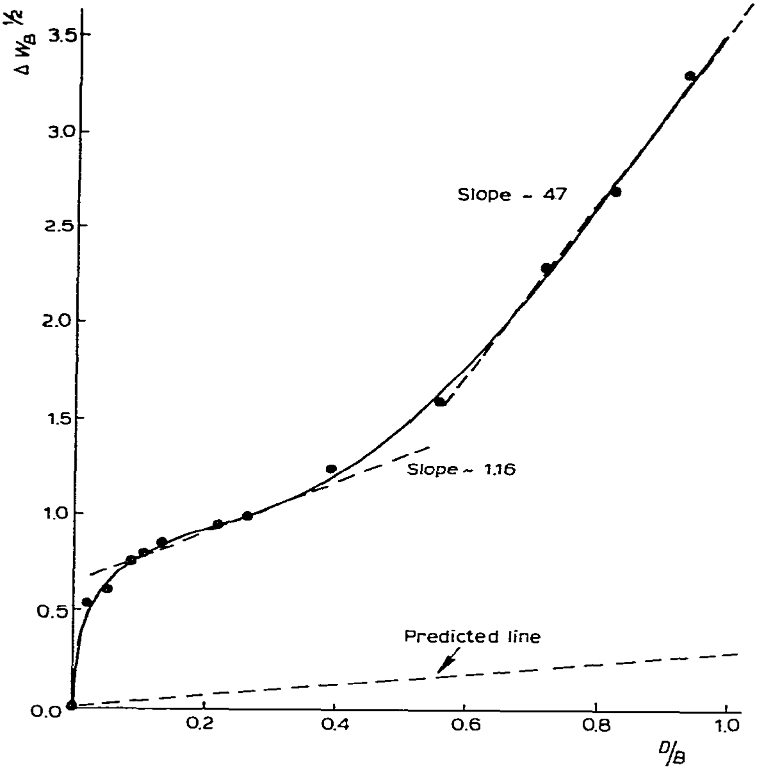


Fig. 6. Plot of $\Delta W_B^{1/2}$ vs. D/B for reaction: $(CH_3)_2SnCl_2$ (0.24 *M*) + $(CH_3)_6Sn_2$ (0.39 *M*).

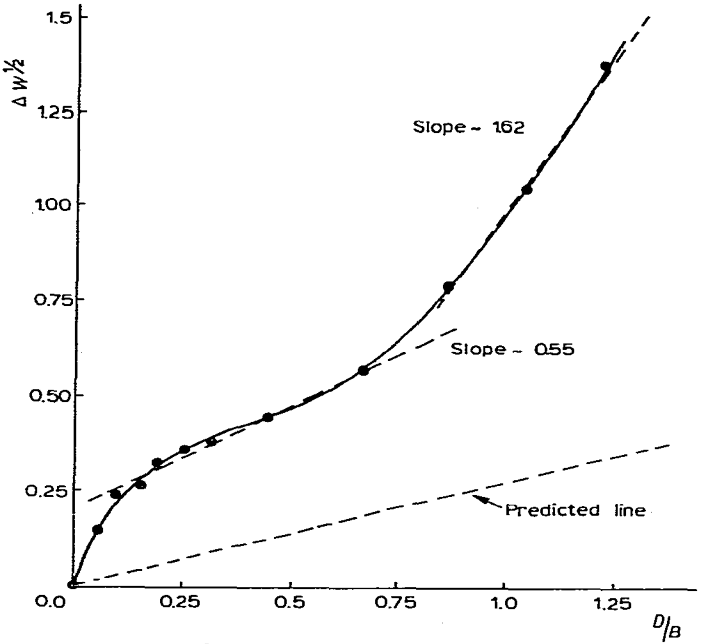


Fig. 7. Plot of $\Delta W_B^{1/2}$ vs. D/B for reaction: $(CH_3)_2SnCl_2$ (0.47 *M*) + $(CH_3)_6Sn_2$ (0.22 *M*).

(v) Build-up of long-chain dichloropolystannanes $(CH_3)_{2n}Sn_nCl_2$ by successive reversible insertions of $(CH_3)_2Sn$ into $(CH_3)_2SnCl_2$ and its homologues.

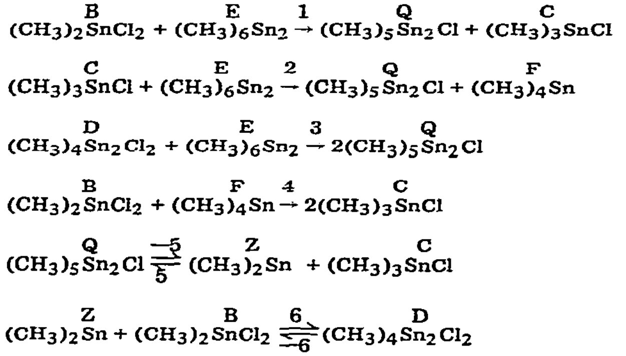
(vi) Build-up of long-chain monochloropolystannanes $(CH_3)_{2n+1}Sn_nCl$ by (a) successive insertions of $(CH_3)_2Sn$ into the homologues of $(CH_3)_5Sn_2Cl$ and (b) by reaction of dichloro compounds $(CH_3)_{2n}Sn_nCl_2$ with methyl-bearing species ($(CH_3)_4Sn$, $(CH_3)_6Sn_2$ etc.).

(vii) Formation of yellow 'dimethylstannane' polymer $(CH_3)_{2n+2}Sn_n$ (up to at least $n = 6$) by reaction of $(CH_3)_{2n+1}Sn_nCl$ with methyl-group sources $(CH_3)_4Sn$, $(CH_3)_6Sn_2$ etc.).

These processes are summarized in Scheme 1 in which all the species present are assigned labels and all the reactions numbered in accordance with the system employed throughout this and the preceeding paper [1]. Rate constants for steps 1, 2, 3, 4 and 6 have been determined and evidence has been presented for the presence of some of the intermediates P and Q. The role of $(CH_3)_2Sn$ in these systems seems clearly established and its only significant reaction appears to be Sn—Cl bond insertion. The intermediacy of this and related species in other reactions has been demonstrated [11—15]. In these cases other types of insertion reactions are observed, which implies that it is our solvent, methanol, that has a profound effect upon the reactivity of the species.

SCHEME 1

Processes occurring in $(CH_3)_2SnCl_2/(CH_3)_6Sn_2$ system



$$\overset{B}{(CH_3)_2SnCl_2} + \overset{E}{(CH_3)_6Sn_2} \xrightarrow{1} \overset{Q}{(CH_3)_5Sn_2Cl} + \overset{C}{(CH_3)_3SnCl}$$

$$\overset{C}{(CH_3)_3SnCl} + \overset{E}{(CH_3)_6Sn_2} \xrightarrow{2} \overset{Q}{(CH_3)_5Sn_2Cl} + \overset{F}{(CH_3)_4Sn}$$

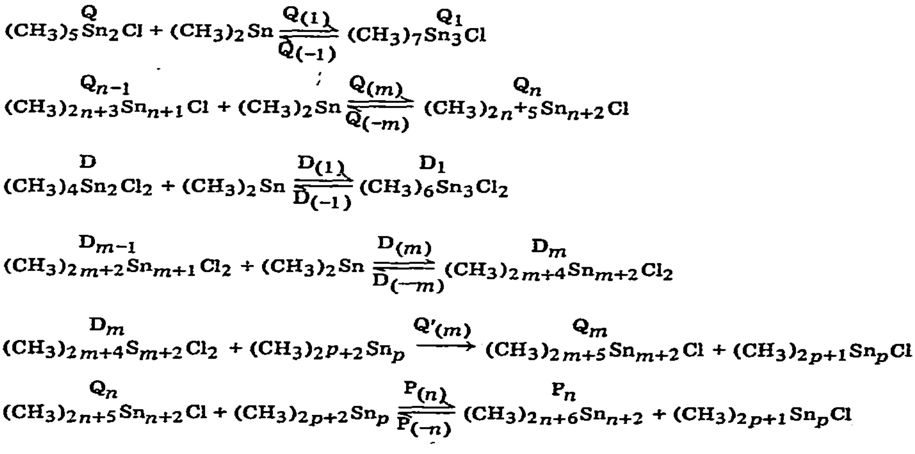
$$\overset{D}{(CH_3)_4Sn_2Cl_2} + \overset{E}{(CH_3)_6Sn_2} \xrightarrow{3} 2\overset{Q}{(CH_3)_5Sn_2Cl}$$

$$\overset{B}{(CH_3)_2SnCl_2} + \overset{F}{(CH_3)_4Sn} \xrightarrow{4} 2\overset{C}{(CH_3)_3SnCl}$$

$$\overset{Q}{(CH_3)_5Sn_2Cl} \underset{5}{\overset{-5}{\rightleftharpoons}} \overset{Z}{(CH_3)_2Sn} + \overset{C}{(CH_3)_3SnCl}$$

$$\overset{Z}{(CH_3)_2Sn} + \overset{B}{(CH_3)_2SnCl_2} \underset{-6}{\overset{6}{\rightleftharpoons}} \overset{D}{(CH_3)_4Sn_2Cl_2}$$

Processes leading to polymer formation



$$\overset{Q}{(CH_3)_5Sn_2Cl} + (CH_3)_2Sn \underset{Q(-1)}{\overset{Q(1)}{\rightleftharpoons}} \overset{Q_1}{(CH_3)_7Sn_3Cl}$$

$$\overset{Q_{n-1}}{(CH_3)_{2n+3}Sn_{n+1}Cl} + (CH_3)_2Sn \underset{Q(-m)}{\overset{Q(m)}{\rightleftharpoons}} \overset{Q_n}{(CH_3)_{2n+5}Sn_{n+2}Cl}$$

$$\overset{D}{(CH_3)_4Sn_2Cl_2} + (CH_3)_2Sn \underset{D(-1)}{\overset{D(1)}{\rightleftharpoons}} \overset{D_1}{(CH_3)_6Sn_3Cl_2}$$

$$\overset{D_{m-1}}{(CH_3)_{2m+2}Sn_{m+1}Cl_2} + (CH_3)_2Sn \underset{D(-m)}{\overset{D(m)}{\rightleftharpoons}} \overset{D_m}{(CH_3)_{2m+4}Sn_{m+2}Cl_2}$$

$$\overset{D_m}{(CH_3)_{2m+4}S_{m+2}Cl_2} + (CH_3)_{2p+2}Sn_p \xrightarrow{Q'(m)} \overset{Q_m}{(CH_3)_{2m+5}Sn_{m+2}Cl} + (CH_3)_{2p+1}Sn_pCl$$

$$\overset{Q_n}{(CH_3)_{2n+5}Sn_{n+2}Cl} + (CH_3)_{2p+2}Sn_p \underset{P(-n)}{\overset{P(n)}{\rightleftharpoons}} \overset{P_n}{(CH_3)_{2n+6}Sn_{n+2}} + (CH_3)_{2p+1}Sn_pCl$$

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References

1 M.J. Cutherbertson and P.R. Wells, J. Organometal. Chem., 216 (1981) 331.
2 C.F. Shaw and A.L. Allred, J. Organometal. Chem., 28 (1971) 53.
3 G. Plazzogna, S. Bresdola and G. Tagliavini, Inorg. Chim. Acta, 2 (1968) 333.
4 R.K. Ingam, S.D. Rosenberg and N. Gilman, Chem. Revs., 60 (1960) 495.
5 D.P. Arnold, M.J. Cuthbertson and P.R. Wells, J. Organometal. Chem., 184 (1980) 39.
6 M.J. Cuthbertson, Thesis, University of Queensland, 1980.
7 J.P. Chandler, Quantum Chemistry Program Exchange, 11 (1976) 307. This routine was adapted by Mr. R.G. Farmer for use on the PDP-11/34 minicomputer.
8 D.E. Sands, J. Chem. Educ., 54 (1977) 90.
9 D.P. Arnold and P.R. Wells, J. Organometal. Chem., 108 (1976) 345.
10 M.J. Cuthbertson and P.R. Wells, J. Org. Chem., in press.
11 K. Sisodo, S. Kozima and T. Isibasi, J. Organometal. Chem., 10 (1967) 437.
12 K. Sisodo, T. Miyanisi, K. Nabida and S. Kozima, J. Organometal. Chem., 11 (1968) 281.
13 U. Schroer and W.P. Neumann, Angew. Chem. Int. Ed., 14 (1975) 246.
14 W.P. Neumann and A. Schwarz, Angew. Chem. Int. Ed., 14 (1975) 812.
15 C. Grugel, W.P. Neumann and P. Seifert, Tetrahedron Letters, 25 (1977) 2205.