

Can mono- or di-butyltin chlorides produce tributyltin chloride at elevated temperatures? Implications for applications in chemical vapour deposition

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Abstract

The thermolysis of the butyltin chlorides at 200–300 °C in the liquid phase has been investigated by ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy. The stabilities follow the order: Bu₂SnCl₂ > Bu₃SnCl > BuSnCl₃. Only tributyltin chloride showed any evidence of redistribution, giving dibutyltin dichloride, together with metallic tin, butane, and but-1-ene, which would be formed by decomposition of tetrabutyltin. Dibutyltin dichloride decomposed to give mainly butane with no other apparent liquid organotin compound. Butyltin trichloride gave butane, some butene, and metallic tin, and showed no evidence of forming tributyltin chloride by the redistribution reaction, which would have environmental implications for its use in the CVD coating of glass.

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Keywords: Butyltin chlorides; Thermolysis; Redistribution; CVD

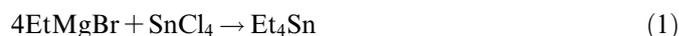
1. Introduction

Organotin halides and their derivatives find a number of important applications in industry and agriculture [1,2], and some of these applications involve high temperatures. In particular, to strengthen it, glass is coated with SnO₂ by treating it with BuSnCl₃ at about 600 °C in the presence of air (atmospheric pressure chemical vapour deposition, APCVD) [3]. This raises a question over the use of organotin chlorides, particularly butyltin trichloride, in the CVD process, where the spent gases are exhausted to air.

In the press one often sees the statement made that tributyltin chloride and its derivatives are “highly toxic”. Although this is true for molluscs, the risks have been often overstated for mammals [2,4–6]. It has been suggested that the spontaneous formation of even 0.1% tributyltin chloride (and tetrabutyltin) may be responsible for the apparent

toxicity of dibutyltin dichloride in environmental studies [7]. If, therefore, tributyltin chloride could be formed under CVD conditions by the redistribution of alkyl and chloride groups of the precursor, the deposition process might present a significant environmental hazard. In view of this, some regulatory authorities have questioned whether the process should be permitted.

Examples of the redistribution of alkyl and halogen groups bonded to tin have been known since the early days of organotin chemistry [8–10], but the reaction is usually named after Kocheshkov who, from 1926 onwards, exploited it as a route to organotin halides that could not be prepared directly by the Grignard reaction (e.g. Eqs. (1) and (2)) [11–15].

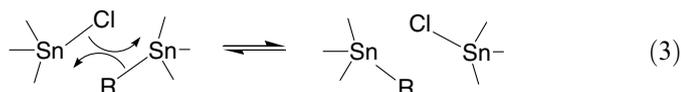


The reaction is general in organometallic chemistry, and is not confined to organic and halogeno groups. A review

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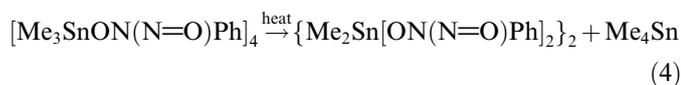
by Moedritzer in 1971 on redistribution reactions listed more than 1000 examples, 62 of which involved the exchange of organic and halogen substituents on tin [16].

The redistribution reactions are, as a rule, reversible, the equilibria usually favouring the compound with the highest degree of shuffling of the ligands (comproportionation), rather than the compounds with a lower degree of shuffling (disproportionation). The rates of the redistribution reactions increase in the sequence $I < Br < Cl$, and higher alkyl < ethyl < methyl < vinyl < benzyl < phenyl. The mechanism of the reactions probably involves a 4-centre transition state, with the nucleophilic power of the halogen being dominant (Eq. (3)), consistent with the reported rate trends.



The reactions involving organotin compounds are often carried out in the absence of solvents, and Lewis acids, such as $AlCl_3$, can act as catalysts. However, in some cases the presence of a Lewis acid may also lead to the formation of alkyl chloride and tin(II) chloride, particularly from the alkyltin trichlorides (when the alkyltin trichloride itself may act as its own Lewis acid). Platinum(II) and palladium(II) phosphine complexes catalyse the reaction of dibutyltin dichloride with tin tetrachloride at 110 °C during 10 h, to give butyltin trichloride in good yield [17]. At the higher temperatures that may be needed in the absence of a catalyst, the alkene and HCl, rather than the alkyl chloride, may be formed [18,19].

High temperatures are not always needed, however. There are a number of reports of observations of adventitious disproportionation when organotin compounds were being handled. For example, when triallyl tin chloride was treated with a sodium alkoxide, tetraallyl tin and the diallyl tin dialkoxide were obtained [20]. There is also a very interesting recent report of a disproportionation reaction in the solid state. Cupferonatotrimethyltin, $Me_3SnON(N=O)Ph$, is a cyclic tetramer in the crystal. It is stable at room temperature, but at 100 °C in open vials it disproportionates into crystalline $Me_2Sn[ON(N=O)Ph]_2$, which is a dimer, and Me_4Sn . At 100 °C in the melt, the reaction is second order in monomer with a rate constant of $1.6 \times 10^{-4} \pm 6.9 \times 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$ [21].



Grant and Van Wazer showed that, in a few days at 175 °C, 35% of $MeSnCl_3$ partially disproportionated into Me_2SnCl_2 and $SnCl_4$ ($K_{448K} = 7 \times 10^{-2}$) [22]. The reaction is faster in polar solvents such as isopropyl alcohol or water (where the reaction has been shown to be second order in stannane), and in 4 days at 50 °C, 26% of $MeSnCl_3$ undergoes disproportionation ($K_{323K} = 1 \times 10^{-2}$), and is catalysed by stannophilic ligands such as Cl^- or ClO_4^- (Eq. (2))

[23]. Although Grant and Van Wazer also reported equilibrium constants for the disproportionation of Me_2SnCl_2 into Me_3SnCl and $MeSnCl_3$ ($K_{448K} = 1 \times 10^{-4}$), and for Me_3SnCl into Me_4Sn and $SnCl_4$ ($K_{448K} = 3 \times 10^{-3}$), the precise values are questionable since they are based on imperfectly balanced equations. Nevertheless, these values provide us with reasonable order of magnitude estimates. The equilibria for the ethyltin halides lay almost entirely on the left-hand side (Eq. (5), $R = Et$).



Phenyltin trichloride reacts with tributylphosphine at room temperature to give Ph_2SnCl_2 and $SnCl_4$ as their complexes with Bu_3P [24,25].

In view of the commercial importance of the butyltin chlorides, it is surprising that there appears to be no report of a study of their thermal decomposition and disproportionation. However, Razuvaev et al. [26] reported that, at 400 °C for 4 h in a sealed tube, tetrabutyltin gave metallic tin, butane, mixed butenes, some octane, ethene, ethane, and hydrogen. In a later FT-IR study, Harrison [27] showed that, at 300 °C for 22 min in the gas phase, it underwent substantial decomposition to give a mixture of but-1-ene and *cis*- and *trans*-but-2-ene, together with a small amount of butane.

We report here a preliminary study of the effect of heat on butyltin chlorides, Bu_nSnCl_{4-n} , and on tetrabutyltin. The principal techniques that we have used are ^{119}Sn , ^{13}C , and 1H NMR spectroscopy.

2. Experimental

NMR spectra were run at room temperature (20 °C) on a Bruker AMX400 spectrometer, operating at 149.21 MHz for ^{119}Sn , 100.63 MHz for ^{13}C , and 400.14 MHz for 1H . The ^{13}C spectra were all run in the 1H -decoupled, gated decoupled, or DEPT mode.

Bulk metallic tin was identified by X-ray diffraction with a Bruker AXS D8 diffractometer using unfiltered $Cu K\alpha$ radiation, with a collimated X-ray beam (0.5 mm collimator) and a general area detector. Data were collected in reflection geometry with a fixed 5° angle of incidence angle. Bruker GADDS software was used for acquisition and Bruker EVA software for data manipulation.

The butyltin chlorides, without solvent, were sealed under vacuum in 5 mm NMR tubes. The samples were then heated in an oven at ca. 200 °C, or in a tube furnace at ca. 300 °C; in the latter case, the tubes were enclosed in a copper tube in case of explosion, which sometimes did occur. The samples were then cooled, and the ^{119}Sn , ^{13}C , and 1H NMR spectra were recorded.

3. Results

The NMR data for the neat liquids for Bu_nSnCl_{4-n} , $n = 1$ and 3, and for the solution in decalin when $n = 2$ (as dibutyltin dichloride is a solid, m.p. 39–41 °C), are

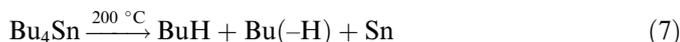
given in Table 1. They are in accord with previous results in the literature, which have usually been obtained on solutions in CDCl₃; they confirm the absence of any impurities containing tin or organic groups, and, further, they indicate that there is no significant difference in the structures of the chlorides, $n = 1$ or 3, in solution or as the neat liquids.

Tributyltin chloride was heated at 200 °C for 48 h. The ¹¹⁹Sn NMR spectrum (Table 2) then showed signals for Bu₃SnCl at δ 144.1, and a second signal for Bu₂SnCl₂ at δ 114.7, the identity of which was confirmed by the ¹³C spectrum; the relative intensity of the two signals was 3.6:1. There was no signal for Bu₄Sn ($\delta^{119}\text{Sn} -12$), or for any other tin species, but a black granular solid was deposited in the tube, and, in some experiments, a mirror-like film and a small amount of an off-white solid collected on the upper parts of the tube.

The NMR spectra showed the presence of but-1-ene [$\delta^{13}\text{C}$ 139.5 (=CH–), 112.6 (=CH₂), 25.4 (CH₂), and 12.6 (CH₃); $\delta^1\text{H}$ 5.34 (=CH–), 4.42 (=CH₂) and 1.58 (CH₂)] and of butane [$\delta^{13}\text{C}$ 24.4 (CH₂) and 12.4 (CH₃)] in approximately equal amounts.

On further heating, the intensity of the spectra which we ascribed to butane and butene increased, but, if anything, that of the ¹¹⁹Sn signal for Bu₂SnCl₂ diminished.

The formation of dibutyltin dichloride suggests that disproportionation does occur, but that the tetrabutyltin does not survive the conditions of the thermolysis (Eqs. (6) and (7)).



A sample of tetrabutyltin was therefore heated under the same conditions; again a granular black solid was deposited, and this was identified, by powder X-ray diffraction, to be metallic tin.

When dibutyltin dichloride was heated at 200 °C for two days no significant change in the ¹³C or ¹¹⁹Sn NMR spectrum was observed, though a small amount of an off-white solid was apparent, and the contents resolidified on cooling. The tube was therefore heated at 300 °C for two days, when the sample remained liquid after cooling. The only ¹¹⁹Sn signal was still that for Bu₂SnCl₂ at δ 119.3, but the ¹³C spectrum was now dominated by peaks at δ 24.3 and 12.7 corresponding to the CH₂ and CH₃ groups of butane. The ¹³C spectra in Fig. 1 illustrate the presence of the butane, and the surprising absence of butene, though there is a small unidentified peak for a CH or CH₃ group at $\delta^{13}\text{C}$ 23.0.

Butyltin trichloride (δSn 0.31) was kept at 200 °C for two days. A large amount of black crystalline solid sepa-

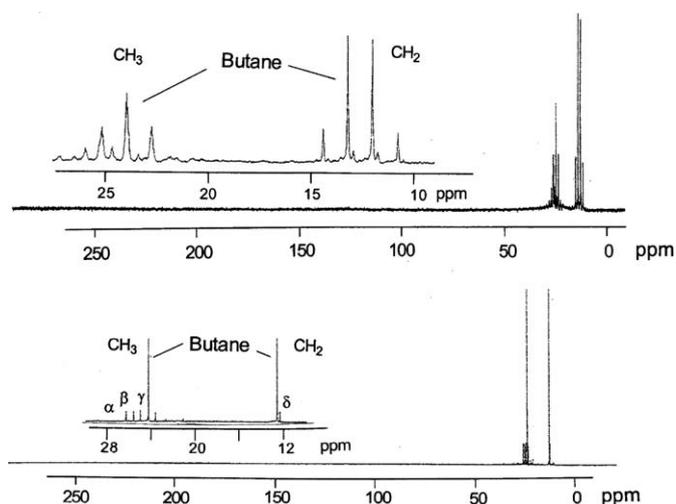


Fig. 1. ¹³C NMR spectra of the products of thermolysis of dibutyltin dichloride, showing the formation of butane. Bottom: ¹H decoupled; the signals for the α , β , γ , and δ carbon atoms of the butyl groups in the reactant are marked. Top: with gated decoupling.

Table 1
Reference NMR spectra of the butyltin chlorides^a

	$\delta^{119}\text{Sn}$	$\delta^{13}\text{C}\alpha$	$\delta^{13}\text{C}\beta$	$\delta^{13}\text{C}\gamma$	$\delta^{13}\text{C}\delta$
Bu ₃ SnCl	144.1	17.5 (329.8/345.0)	27.8 (24.1)	26.7 (63.1)	13.4
Bu ₂ SnCl ₂	119.4	26.7 (427)	26.3 (34)	25.4 (104)	12.77
BuSnCl ₃	0.3	33.7 (613.7/642.0)	26.4 (61.7)	25.2 (115)	13.0

^a Values of $^nJ(^{13}\text{C}^{117/119}\text{Sn})$ (Hz) (or an average if the pair of satellites in the ¹³C spectrum were not resolved) are given in parentheses.

Table 2
NMR spectra of the butyltin chlorides after heating^a

	$\delta^{119}\text{Sn}$	$\delta^{13}\text{C}\alpha$	$\delta^{13}\text{C}\beta$	$\delta^{13}\text{C}\gamma$	$\delta^{13}\text{C}\delta$
Bu ₃ SnCl	144.1 114.7	17.0	27.2	26.3	12.9
Bu ₂ SnCl ₂	119.3	26.3	25.7	25.0	12.4
BuSnCl ₃	3.2 –174.2	33.1 (632.0)	26.3 (59.9)	25.0	12.8

^a The average values of $^nJ(^{13}\text{C}^{117}\text{Sn})$ and $^nJ(^{13}\text{C}^{119}\text{Sn})$ (Hz) are given in parentheses.

rated, and a metallic mirror formed on the tube. The only ^{119}Sn NMR signal was a strong peak at $\delta -145.1$, which we assign to SnCl_4 ; no signal for BuSnCl_3 remained, and none for Bu_2SnCl_2 appeared. The ^{13}C and ^1H spectra were complex, but the ^{13}C spectrum was dominated by strong peaks at $\delta 24.0$ and 13.1 , corresponding to butane, and the ^1H spectrum indicated the presence of some alkene. When the tube was opened, acrid acid fumes (HCl) were evolved.

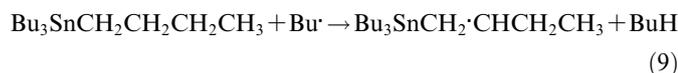
To avoid such extensive decomposition, a sample of BuSnCl_3 was kept at 200°C for one day. Again, a black crystalline solid was formed. The Sn NMR spectrum showed a strong peak for the starting material at $\delta 3.2$, and a smaller signal (relative amplitudes 10.5:1) at $\delta -174$. This latter signal probably corresponds to SnCl_4 carrying a fifth ligand, probably $\text{H}^+\text{SnCl}_5^-$; unfortunately, the ^{119}Sn chemical shift of this compound appears not to have been determined, but the upfield shift by 29 ppm from that of SnCl_4 would be characteristic of an increase in coordination from 4 to 5. Apart from the major peaks of the BuSnCl_3 , the ^{13}C NMR spectrum showed new small peaks at $\delta 60.0, 44.4, 34.0, 32.7, 24.3, 24.2, 22.6, 22.1, 21.7, 19.4, 13.3,$ and 10.5 . Eight of these peaks might reasonably be ascribed to 1-chloro- and 2-chloro-butane, but the groups of peaks at $\delta 24.2, 22.7, 22.1,$ and 21.7 (which the DEPT spectrum showed to be CH or CH_3), are not accounted for. The absence of peaks at $\delta 113.5$ and 140.5 rule out the presence of butene.

4. Discussion

The differences in the thermal stability and the thermolysis patterns of the three butyltin chlorides are striking and do not follow the order of substitution. The general thermal stability is in the sequence $\text{Bu}_2\text{SnCl}_2 > \text{Bu}_3\text{SnCl} > \text{BuSnCl}_3$.

Our results indicate that Bu_3SnCl undergoes redistribution to give Bu_2SnCl_2 and Bu_4Sn (Eq. (6)); the former of these is relatively stable at the temperature of the reaction, but the latter decomposes into metallic tin, butene and butane (Eq. (7)).

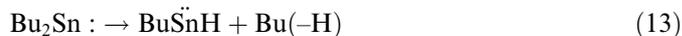
Two reasonable mechanisms can be suggested for the decomposition of Bu_4Sn . First, homolysis of the $\text{Sn}-\text{C}$ bond would give a butyl radical (Eq. (8)), which would react with Bu_4Sn to give butane and a β -stannylalkyl radical, and this in turn would eliminate butene. Repetition of this process could give the observed products.



This first step would be similar to Paneth and Hofeditz's classic generation of alkyl radicals in the gas phase by the thermolysis of R_4Pb with an $\text{R}-\text{PbR}_3$ bond dissociation energy of about 205 kJ mol^{-1} [28], but it seems unlikely

that it could account for the decomposition of Bu_4Sn under our conditions. If the $\text{Bu}-\text{SnBu}_3$ bond dissociation energy is taken to be 257 kJ mol^{-1} , and the pre-exponential factor is of the order of 10^{15} , the half life of the unimolecular homolysis at 200°C would be expected to be of the order of 10^{13} s. A more rapid reaction of course might occur on the surface of the glass.

An alternative mechanism would involve alternating β -elimination and reductive elimination (Eqs. (11) and (12)); repetition would give BuSnH and thence metallic tin (Eqs. (13) and (14)). Although there are no precise precedents for these reactions, they appear to be reasonable in view of related organotin chemistry [25].



A referee has suggested that deuterium labelling experiments might be used to probe these alternatives. However, starting from $(\text{CH}_3\text{CH}_2\text{CD}_2\text{CH}_2)_4\text{Sn}$, both mechanisms would give $\text{CH}_3\text{CH}_2\text{CD}=\text{CH}_2$ and $\text{CH}_3\text{CH}_2\text{CD}_2\text{CH}_2\text{D}$ making it impossible to distinguish between them.

Whatever the correct mechanism, it is noteworthy that Bu_2SnCl_2 does not undergo this type of reaction, even at 300°C . The formation of butane, without butene, from Bu_2SnCl_2 was surprising, but is unambiguous (Fig. 1). It could be brought about by adventitious water in the Bu_2SnCl_2 , when the initial reactions would be those shown in Eqs. (15) and (16), but the presence of enough water to bring about such extensive dealkylation of the tin is most unlikely, and the absence of an ^{119}Sn NMR signal for any other soluble tin compound [such as BuSnCl_3 or $(\text{ClBu}_2\text{Sn})_2\text{O}$], and the absence of any substantial amount of an insoluble oxygen-containing tin compound [such as Bu_2SnO , $\text{BuSnO}(\text{OH})$], or metallic tin, leaves unanswered questions.



The decomposition of BuSnCl_3 appears best to be accounted for by reductive elimination of BuCl leaving SnCl_2 which may decompose in part to give SnCl_4 and metallic tin; *t*- BuSnCl_3 has been reported to decompose at room temperature to give SnCl_2 and *t*- BuCl [36]. In the higher range of temperature, the butyl chloride eliminates HCl , which can react with the initial BuSnCl_3 to give butane and SnCl_4 . Alternatively, one can envisage retrodehydrostannation giving butane and HSnCl_3 , which decomposes into HCl and SnCl_2 . The SnCl_4 does not appear to arise from a disproportionation reaction, as the other product would be Bu_2SnCl_2 , which is not detected, and would not be expected to decompose at the temperature of the experiment.

With all three compounds of course, the NMR spectra would not have detected the elements in the solids that were observed. The black solid was identified as metallic tin, and the white solid appears to be largely SnCl_2 (as reported by Neumann for the decomposition of EtSnCl_3) [18].

5. Thermochemical aspects of the exchange

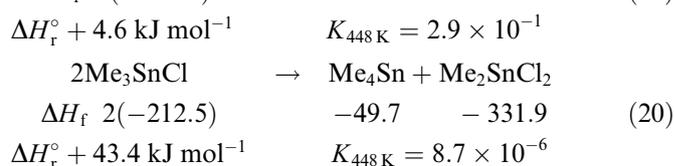
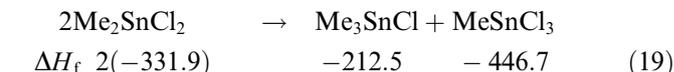
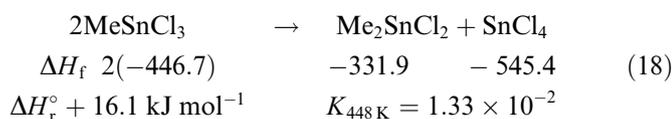
It is informative to attempt to rationalise why these redistribution reactions, at equilibrium, usually maximise the degree of mixing of the alkyl and halogen groups.

The number of bonds of any one type does not change during the redistribution reaction; for example, in reaction (5), there are 2 SnMe bonds and 6 SnCl bonds on both sides of the equation. If bond strengths were additive within the molecules, a statistical distribution of the possible combinations of ligands should be reached at equilibrium, yet reaction (1) proceeds to give methyltin trichloride in 90% yield. Why should the additivity principle break down to favour the mixed-ligand combination MeSnCl_3 ?

If the equilibrium lies in favour of comproportionation, the free energy of formation of the comproportionated products (such as MeSnCl_3) must be greater than the free energies of formation of the disproportionated pair of reactants (such as Me_2SnCl_2 and SnCl_4). Entropy contributions to the reaction are likely to be very small, hence, to a good approximation, Eq. (17) should hold.

$$\Delta G^\circ \approx \Delta H^\circ = -RT \ln K \quad (17)$$

Unfortunately, only a few relevant enthalpies of formation of organotin compounds are known, and none for the butyltin chlorides. Selected values for the methyltin halides [29–31], based largely on Skinner's determination of the heats of mixing of tetramethyltin with tin tetrachloride in the liquid phase [32] are given in Eqs. (18)–(20), which lead to the reaction enthalpies shown, and thence, by Eq. (17), to the equilibrium constants, K , at 448 K, the temperature of Grant and Van Wazer's [23] equilibrium studies. These derivations should be treated with caution, however, as the enthalpies of formation are uncertain to the extent of about $\pm 7 \text{ kJ mol}^{-1}$.

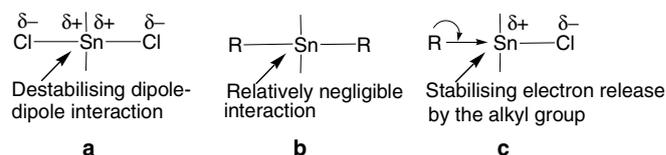


The breakdown of the additivity principle, and the resulting equilibration in favour of a maximum degree of mixing of the ligands can be rationalised as follows. The $\text{Sn}^{\delta+}-\text{Cl}^{\delta-}$ bond is strongly polar in the sense that is shown in Scheme 1, whereas the $\text{Sn}-\text{R}$ bond is relatively non-polar ($\text{R} = \text{alkyl}$). If two or more Cl ligands are bound to one tin atom, there will be a destabilising interaction between the positive ends of the two dipoles. With two alkyl groups on tin, any such destabilisation will be trivial. With one alkyl and one chloro ligand, the alkyl group can inductively, and perhaps hyperconjugatively, release electrons to accommodate the demand of the positive centre at tin, to produce a more stable system [33].

If an appropriate mechanism for the reaction is available, redistribution will therefore take place to minimise the number of electronegative ligands on the tin.

This qualitative model is supported by the results of Del Re calculations, which are designed to take account of the interaction between sigma bonds.

Table 3 shows the partial charges, q , on the atoms H, C, Sn, and Cl in the tetramethyltin, the methyltin halides, and tin tetrachloride, as calculated by Gupta and Hughes by the Del Re method [34], and the corresponding ^1H and ^{13}C NMR chemical shifts. In accord with the model in Scheme 1, the negative charge on Cl is greatest in Me_3SnCl where three alkyl groups release electrons into one SnCl bond, and conversely the negative charge on C is lowest, and the positive charge on H is greatest in MeSnCl_3 where three SnCl dipoles combine to attract electrons from one alkyl group.



Scheme 1.

Table 3
Local partial charges, and NMR chemical shifts of $\text{Me}_n\text{SnCl}_{4-n}$, $n = 0-4$

Compound	q_{H}	δ_{H}	q_{C}	δ_{C}	q_{Sn}	q_{Cl}
Me_4Sn	+0.030	0.05	-0.2500	-9.3	+0.6400	-
Me_3SnCl	+0.0330	0.59	-0.2053	-0.8	+0.7066	-0.3868
Me_2SnCl_2	+0.0364	1.19	-0.1537	7.5	+0.7654	-0.3379
MeSnCl_3	+0.0405	1.66	-0.0935	10.8	+0.8142	-0.2807
SnCl_4	-	-	-	-	+0.848	-0.212

The NMR chemical shifts of carbon and hydrogen (though not of tin) reflect the electron densities on the atoms [35], and, as shown in the table, the values of q_H and q_C do correlate with those of δ_H and δ_C respectively.

6. Conclusion

Our results show that, as the neat liquids at 300 °C, the principal reaction of the $BuSnCl_3$ and Bu_2SnCl_2 is that of decomposition rather than of redistribution. Evidence for disproportionation was found only for Bu_3SnCl , giving Bu_2SnCl_2 and Bu_4Sn , which decomposed. In particular, no detectable Bu_3SnCl was formed from $BuSnCl_3$. As such disproportionation reactions would be second order, they are even less likely to occur under the gas phase conditions that are used in the CVD treatment of glass.

Acknowledgements

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