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Thermolysis of the phenyltin chlorides, Ph_xSnCl_{4-x}, (x=1–3): products and pathways

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The thermal degradation of triphenyltin chloride, diphenyltin dichloride and phenyltin trichloride has been studied by pyrolysis at 375 °C in sealed tubes for various time periods. In all cases, biphenyl and tin(II) chloride are produced. For both phenyltin trichloride and diphenyltin dichloride, ter- and poly-phenyls are also obtained. In some cases tin(IV) chloride or elemental tin are obtained. Pathways that account for all observed products are presented.

Keywords: Thermolysis, triphenyltyin chloride, diphenyltin dichloride, phenyltin trichloride, biphenyl, terphenyl, polyphenyl

INTRODUCTION

A substantial number of organometallic compounds are observed to decompose at elevated temperatures. In general, the study of the thermal degradation of such compounds can provide useful information both on the degradation pathways and on synthetic routes to other useful compounds. The interest in this laboratory lies in the utility of various compounds as putative flame retardants for polymers. A knowledge of the species that are actually present under thermal conditions is clearly important in the investigation of the interactions between additives and polymers.

In this paper, we report on the thermal degradation of the three phenyltin chlorides, $PhSnCl_3$, Ph_2SnCl_2, and Ph_3SnCl, identify all the products that are produced upon thermolysis and propose a pathway for the degradation.

EXPERIMENTAL

Materials

Most of the chemicals used in this study ($PhSnCl_3$, Ph_2SnCl_2, Ph_3SnCl, Ph_4Sn, $SnCl_2$, biphenyl, *o*-, *m*- and *p*-terphenyl) were purchased from Aldrich Chemical. All HPLC-grade solvents were acquired from Baxter Diagnostics Inc. and Mallinckrodt Specialty Chemical Company. Fourier transform infrared (FTIR) spectra were recorded on a Mattson-4020 Galaxy Series spectrophotometer and products were identified by comparison with spectra of authentic samples or tabulated gas-phase spectra.[1] NMR spectra were obtained on a GE 300 Omega instrument. A Hewlett–Packard 5890 gas chromatograph with a Hewlett–Packard 5970 mass selective detector was used for GCMS analysis. These spectra were determined at 70 eV on a 0.25 mm × 30 m DB-1 capillary column, programmed at 70 °C for 4 min followed by a 10 °C min^{-1} gradient to 280 °C. Differential scanning calorimetry (DSC) data were obtained on a Perkin–Elmer DSC-2C differential scanning calorimeter with a heating rate of 20 °C min^{-1} and heating range of 20 mcal s^{-1} (84 mJ s^{-1}).

Thermolysis of phenyltin chlorides in sealed tubes

All reactions were carried out in break seal equipped sealed tubes with an approximate volume of 180 cm^3. A 4.00 g sample of the appropriate phenyltin chloride was placed in the tube and then evacuated on a high-vacuum line for 30 min. The tube was then sealed off from the vacuum line and heated in a muffle furnace for 2 or 25 h at 375 °C. At the end of the heating period, the tube was carefully removed from the oven and placed in liquid nitrogen. **Caution: vessels have been known to explode upon removal from the oven; care must be exercised.** The tubes were then re-attached to the vacuum line via the break seal and thoroughly evacuated. When the break seal had been opened, the volatiles were separated and identified by IR and GCMS spectra. The quantitative analysis of tin tetrachloride ($SnCl_4$) was performed by the stannic acid–hot water precipitation method.[2] The separation of $SnCl_4$, benzene, and chlorobenzene was effected by adding diethyl ether to the mixture followed by a vacuum distillation through traps at −23 °C

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(CCl_4 slush), −45 °C (chlorobenzene slush), and −63 °C (chloroform slush) to a liquid-nitrogen cooled trap.[3] The ether adduct of $SnCl_4$ was retained in the −23 °C trap, chlorobenzene was stopped at −45 °C, benzene was retained in the −63 °C trap, and excess diethyl ether was recovered in the liquid nitrogen trap. Chlorobenzene and benzene were quantified and identified by IR spectroscopy. The qualitative analysis of chlorine gas was carried out by collecting gaseous products (condensables at −196 °C) in 0.1 M sodium iodide solution and then titrating with 0.5 M $Na_2S_2O_3$ solution, using 5 cm^3 starch as an indicator. The analysis of HCl was performed by collecting condensable gases in 25.00 cm^3 of 0.9 M KOH solution and titrating unreacted KOH with 1 M HCl solution.

The tube was then removed from the vacuum line and products were extracted with chloroform. This permitted the separation of the nonvolatiles into two fractions. The chloroform-soluble fraction was analyzed by IR, GC MS and NMR. The chloroform-insoluble fraction was treated with water (or methanol or acetone) to separate soluble tin(II) chloride ($SnCl_2$) from insolubles and/or elemental tin. $SnCl_2$ and tin were identified by DSC. Infrared analysis of the insoluble material indicates that it contains only aromatic material, assumed to be polyphenyls.

Thermolysis of phenyltin trichloride

The thermolysis of 4.00 g (13.2 mmol) of phenyltin trichloride ($PhSnCl_3$) produced 1.34 g (5.15 mmol) of $SnCl_4$, 1.52 g (8.02 mmol) of $SnCl_2$, 0.32 g (2.1 mmol) of biphenyl (containing also *o*-, *m*- and *p*-terphenyls, 2-chlorobiphenyl and 4-chlorobiphenyl), 0.27 g of polyphenyls (containing 3.5 mmol phenyl groups), 0.13 g (1.2 mmol) of chlorobenzene, 0.38 g (4.8 mmol) of benzene, 0.04 g (0.6 mmol) of elemental chlorine, and a trace of HCl.

When this reaction was performed for two hours, the products were identified as 0.39 g (1.5 mmol) of $SnCl_4$, 0.53 g (2.8 mmol) of $SnCl_2$, 0.56 mg (0.008 mmol) of elemental chlorine, 0.08 g (1.0 mmol) of benzene, 2.84 g of chloroform-solubles (including biphenyl, *o*-, *m*- and *p*-terphenyls, Ph_2SnCl_2 and starting material, $PhSnCl_3$) and 0.05 g of polyphenyls.

Thermolysis of diphenyltin dichloride

When a 4.00 g sample (11.6 mmol) of Ph_2SnCl_2 is thermolyzed, the products are 0.02 g (0.08 mmol) of $SnCl_4$, 2.19 g (11.6 mmol) of $SnCl_2$, 1.02 g (6.62 mmol) of biphenyl (containing also terphenyls), 0.11 g of polyphenyls (containing 1.4 mmol of phenyl groups), 0.64 g (8.2 mmol) of benzene and 0.002 g (0.03 mmol) of elemental chlorine.

The following products were obtained from the thermolysis of Ph_2SnCl_2 samples for 2 h: 0.054 g (0.21 mmol) of $SnCl_4$, 1.92 g (10.1 mmol) of $SnCl_2$, 0.44 g (5.6 mmol) of benzene and 1.58 g of chloroform-solubles (including biphenyl, *o*-, *m*- and *p*-terphenyls, $PhSnCl_3$ and starting material, Ph_2SnCl_2).

Thermolysis of triphenyltin chloride

A 4.00 g (10.4 mmol) sample of triphenyltin chloride (Ph_3SnCl) gave 0.935 g (4.93 mmol) of $SnCl_2$, 0.685 g (5.78 mmol) of elemental tin, 1.61 g (10.5 mmol) of biphenyl containing a trace of terphenyls, and 0.831 g (10.5 mmol) of benzene.

The same reaction carried out for 2 h afforded 0.39 g (2.1 mmol) of $SnCl_2$, 0.13 g (1.1 mmol) of elemental tin, 0.07 g (0.9 mmol) of benzene and 3.31 g of chloroform-soluble material containing mainly starting material (Ph_3SnCl), tetraphenyltin (Ph_4Sn), biphenyl, a small amount of Ph_2SnCl_2, and a trace of terphenyls.

Thermolysis of tetraphenyltin

The thermolysis of a 4.00 g (8.64 mmol) sample of tetraphenyltin (Ph_4Sn) for 25 h produced 0.18 g (2.3 mmol) benzene, 0.06 g (0.5 mmol) of elemental tin, and 3.66 g (7.91 mmol) of starting material, containing also a trace of biphenyl.

When a 0.20 g sample was thermolyzed for 25 h, the results were similar. The recovered products included 0.18 g of starting material and 0.04 g (0.5 mmol) of benzene.

Thermolysis of a 1:1 mixture of tetraphenyltin/triphenyltin chloride

When a mixture of 2.00 g Ph_4Sn and 2.00 g Ph_3SnCl was thermolyzed for 25 h at 375 °C, the observed products were 0.88 g (11 mmol) benzene, 0.51 g (2.7 mmol) $SnCl_2$, 0.70 g (5.9 mmol) elemental tin and 1.81 g of chloroform-solubles. This chloroform-soluble fraction did not contain any Ph_4Sn, which had all been consumed in the presence of Ph_3SnCl during the 25 h reaction.

The same reaction carried out for 2 h afforded 0.09 g (1 mmol) benzene, 0.015 g (0.079 mmol) $SnCl_2$, 0.035 g (0.29 mmol) elemental tin, and 3.60 g of chloroform-soluble material which still contained some Ph_4Sn.

In all cases, the reported recovery for the thermolysis of the phenyltin chlorides, which is an average of several trials, indicated that all of the starting material had been accounted for in the observed products. The pyrolysis of $PhSnCl_3$ for 25 h produces 4.00 g of products whilst a 2 h pyrolysis yields 3.89 g of products. For Ph_2SnCl_2, when 4.00 g are pyrolyzed, 3.98 g of products are recovered after 25 h, while 3.99 g are recovered after 2 h. The pyrolysis of 4.00 g Ph_3SnCl yields 4.06 g of products after 25 h and 3.90 g after 2 h.

RESULTS AND DISCUSSION

Bond dissociation energies

Any discussion of the thermolysis of phenyltin chlorides must begin with the appropriate bond dissociation energies. The bond dissociation energy for Ph_4Sn has been calculated from mass spectroscopic data by Chambers and Glockling,[4] and from thermodynamic cycles by Keiser and Kana'an[5] and Pope and Skinner.[6] The respective values that have been obtained are 349 ± 42, 234 ± 7, and 258 ± 9 kJ mol^{-1}. Huggins[7] reported an average Sn–C bond dissociation energy of 252 kJ mol^{-1} from electronegativity arguments. His calculated value for the average Sn–Cl bond dissociation energy in $SnCl_4$ is 344 kJ mol^{-1}, compared with the experimental value of 323 kJ mol^{-1}. Samuel[8] derived a value of the average Sn–Cl bond dissociation energy in $SnCl_2$ as 395 kJ mol^{-1} by measurement of dissociation spectra of this compound. Finally, Syrkin and Dyatkina[9] reported an average value for Sn–Cl of 323 kJ mol^{-1}. The values in the compounds of interest here will, no doubt, be somewhat different from these average values but these may be used as guidelines and indicate that the Sn–Ph bond is most easily broken. A mass-spectroscopic investigation by Chambers *et al.*[10] indicated that Ph_3SnCl initially gives Ph_2SnCl^+ and a phenyl radical in the mass spectrometer.

Thermal degradation of $PhSnCl_3$

The thermolysis of a 13.2 mmol sample of $PhSnCl_3$ for 25 h at 375 °C produces 5.15 mmol of $SnCl_4$, 8.02 mmol of $SnCl_2$, 2.1 mmol of biphenyl (containing also terphenyls and chlorobiphenyls), 3.5 mmol of phenyl groups in polyphenyls, 4.8 mmol of benzene, 0.6 mmol of Cl_2, and a trace of HCl. No trace of starting material can be observed. When the thermolysis is performed for 2 h, not all of the starting material is consumed and Ph_2SnCl_2 is also obtained. The amount of elemental chlorine (Cl_2) is greatly diminished and organochlorine compounds are not observed.

The 4.00 g sample of $PhSnCl_3$ contains 13.2 mmol of phenyl, 13.2 mmol of tin, and 39.6 mmol of chlorine. The reaction products contain 4.8 mmol of phenyl as benzene, 1.2 mmol as chlorobenzene, approximately 4.2 mmol as biphenyl and approximately 3.5 mmol as polyphenyls. This accounts for 13.7 mmol of phenyl amongst the products. For chlorine, there is 20.6 mmol from $SnCl_4$, 16.0 mmol from $SnCl_2$, 1.2 mmol from chlorobenzene and 1.2 mmol from Cl_2. This accounts for 39.0 mmol of chlorine. For tin, 5.15 mmol from $SnCl_4$ and 8.04 mmol from $SnCl_2$ total 13.2 mmol of tin. The small discrepancies for phenyl and chlorine are due to the presence of chlorine in the biphenyl fraction. This increases the apparent molecular weight of these fractions and reduces the amount of phenyl and increases the amount of chlorine.

The thermal degradation of $PhSnCl_3$ is presented below as Scheme 1. The initial step is homolytic cleavage of either the tin–phenyl bond, giving a phenyl radical and an $SnCl_3$ radical (Eqn [1]), or cleavage of an Sn–Cl bond to give a chlorine atom and a $PhSnCl_2$ radical (Eqn [2]). The $SnCl_3$ radical produced in Eqn [1] can disproportionate to give $SnCl_2$ and $SnCl_4$ (Eqn [3]). Since equal amounts of these are not obtained

$\mathrm{PhSnCl_3 \rightarrow {}^{\bullet}Ph + \dot{S}nCl_3}$ [1]

$\mathrm{PhSnCl_3 \rightarrow Ph\dot{S}nCl_2 + {}^{\bullet}Cl}$ [2]

$\mathrm{2\,\dot{S}nCl_3 \rightarrow SnCl_2 + SnCl_4}$ [3]

$\mathrm{{}^{\bullet}Ph + {}^{\bullet}Ph \rightarrow Ph_2}$ [4]

$\mathrm{{}^{\bullet}Ph + PhSnCl_3 \rightarrow Ph_2 + \dot{S}nCl_3}$ [5]

$\mathrm{{}^{\bullet}Ph + {}^{\bullet}Cl \rightarrow PhCl}$ [6]

$\mathrm{{}^{\bullet}Ph + PhSnCl_3 \rightarrow PhCl + Ph\dot{S}nCl_2}$ [7]

$\mathrm{Ph\dot{S}nCl_2 \rightarrow {}^{\bullet}Ph + SnCl_2}$ [8]

$\mathrm{{}^{\bullet}Ph + glass \rightarrow PhH}$ [9]

$\mathrm{{}^{\bullet}Ph + Ph_2 \rightarrow PhH + {}^{\bullet}Ph{-}Ph}$ [10]

$\mathrm{{}^{\bullet}Ph{-}Ph + {}^{\bullet}Cl \rightarrow Ph{-}Ph{-}Cl}$ [11]

$\mathrm{{}^{\bullet}Ph{-}Ph + PhSnCl_3 \rightarrow Ph{-}PhCl + Ph\dot{S}nCl_2}$ [12]

$\mathrm{{}^{\bullet}Ph{-}Ph + {}^{\bullet}Ph \rightarrow Ph{-}Ph{-}Ph}$ [13]

$\mathrm{{}^{\bullet}Cl + {}^{\bullet}Cl \rightarrow Cl_2}$ [14]

$\mathrm{{}^{\bullet}Cl + PhSnCl_3 \rightarrow Cl_2 + Ph\dot{S}nCl_2}$ [15]

$\mathrm{Ph\dot{S}nCl_2 + \dot{P}h \rightarrow Ph_2SnCl_2}$ [16]

Scheme 1

($SnCl_4$, 5.15 mol; $SnCl_2$, 8.02 mmol), an additional source for $SnCl_2$ must be discovered. Biphenyl may be produced by the combination of two phenyl radicals (Eqn [4]) or by attack of a phenyl radical on starting material, producing biphenyl and another $SnCl_3$ radical (Eqn [5]). The production of chlorobenzene may arise either from the combination of a phenyl radical and a chlorine atom (Eqn [6]) or via the reaction of a phenyl radical and $PhSnCl_3$, giving chlorobenzene and a $PhSnCl_2$ radical (Eqn [7]). The $PhSnCl_2$ radical, produced in one or other of Eqns [2], [7], [12] or [15], will undergo further degradation to produce phenyl radicals and $SnCl_2$ (Eqn [8]). This accounts for the additional $SnCl_2$ mentioned above. Benzene arises both from the interaction of a phenyl radical with the glass surface of the reaction vessel (Eqn [9]) and by reaction of a phenyl radical with biphenyl, producing benzene and a biphenyl radical (Eqn [10]). The two chlorobiphenyls may result from the radical combination of a biphenyl radical and a chlorine atom (Eqn [11]) or from attack of a biphenyl radical on $PhSnCl_3$ to give chlorobiphenyls and a $PhSnCl_2$ radical (Eqn [12]). Terphenyls are produced from the radical combination of a biphenyl radical and a phenyl radical (Eqn [13]). Elemental chlorine is obtained by the combination of two chlorine atoms (Eqn [14]) or by attack of a chlorine atom on starting material to give Cl_2 and a $PhSnCl_2$ radical (Eqn [15]). The source of chlorine atoms for all of the above reactions is Eqn [2], cleavage of starting material to give a chlorine atom and a $PhSnCl_2$ radical. Quaterphenyls and higher polyphenyls, are formed by a reaction analogous to Eqns [10] and [13] for the formation of terphenyls. Ph_2SnCl_2 is observed in a 2 h reaction but not a 25 h reaction; this is probably produced by the combination of a phenyl radical and a $PhSnCl_2$ radical (Eqn [16]). The thermal degradation of Ph_2SnCl_2 will be elucidated in the next section.

When the reaction is performed for 2 h, the amount of Cl_2 is greatly diminished. This seems to indicate that Eqn [2] only operates when the reaction is permitted to proceed over long time periods. From the bond dissociation energies reported above, one would expect the Sn–Ph bond to be preferentially cleaved relative to the Sn–Cl bond.

It would seem that the production of Cl_2 can only arise through the intermediacy of a chlorine atom, since if 0.60 mmol of Cl_2 is observed, then at least 0.60 mmol of starting material must degrade through reaction [2]. If the combination of chlorine atoms is an important source of Cl_2, then this amount is increased. Further, if Eqns [6] and [11] are important, then the extent to which Eqn [2] operates will be even larger.

Since the production of $SnCl_4$ can only arise from the disproportionation of $SnCl_3$ radicals, and 5.15 mmol of $SnCl_4$ is obtained, then a minimum of 10.3 mmol of $PhSnCl_3$ must degrade according to Eqns [1] and [3]. An alternative production route for $SnCl_4$ would be attack of the $SnCl_3$ radical on starting material to produce $SnCl_4$ and a $PhSnCl_2$ radical, or a radical combination of a chlorine atom with an $SnCl_3$ radical. Either of these processes generates the $PhSnCl_2$ radical which would then produce the phenyl radical and $SnCl_2$, so this leads to the same result as disproportionation.

A minimum of 0.60 mmol of $PhSnCl_3$ must degrade by Eqn [2] in order to obtain elemental chlorine; the degradation of the remaining 2.3 mmol of starting material may commence by either Eqn [1] or [2]. One can place minimum and maximum values on the amount of the degradation that begins via cleavage of an Sn–Ph and an Sn–Cl bond. A minimum of 0.6 mmol and a maximum of 2.90 mol of $PhSnCl_3$ degrades via cleavage of an Sn–Cl bond; this corresponds to a minimum of 4.5% to a maximum of 22% of degradation by this route. The corresponding values for the cleavage of the Sn–Ph bond are a minimum of 78% and a maximum of 94.5%.

Thermal degradation of Ph_2SnCl_2

The thermolysis of a 11.6 mmol sample of Ph_2SnCl_2 for 25 h at 375 °C produces 0.08 mmol of $SnCl_4$, 11.6 mmol of $SnCl_2$, 6.62 mmol of biphenyl (containing also terphenyls), 1.4 mmol of phenyl groups in polyphenyls, 8.2 mmol of benzene, and 0.03 mmol of Cl_2. All of the starting material is consumed in the course of a 25 h reaction. When the reaction is performed for 2 h, no elemental chlorine is observed and $PhSnCl_3$, in addition to starting material, may be recovered.

The starting material, Ph_2SnCl_2 (4.00 g), contains 1.38 g of tin and 0.83 g of chlorine. The mass balance for both tin and chlorine is excellent. The two tin compounds, $SnCl_4$ and $SnCl_2$, contain exactly 1.38 g of Sn, whilst the chlorine-containing products $SnCl_4$, $SnCl_2$, and Cl_2, account for 0.83 g of chlorine. For the phenyl groups, 8.17 mmol are present as benzene, 6.62 mmol of biphenyl indicate approximately 13.2 mmol of phenyl radicals, and 0.11 g of polyphenyls indicate 1.43 mmol of phenyl radicals. The total quantity of phenyl radicals, 22.84 mmol, is in good agreement with the phenyl radicals present in the starting material, 23.20 mmol.

The degradation of Ph_2SnCl_2 takes place via Scheme 2. Cleavage of both the Sn–Ph bond (Eqn [17]) and the Sn–Cl bond (Eqn [18]) may be considered for this compound. The $PhSnCl_2$ radical, formed by cleavage of the Sn–Ph bond, can undergo further degradation by the formation of phenyl radicals and $SnCl_2$ (Eqn [19]); it can also react with starting material to give $PhSnCl_3$ and the Ph_2SnCl radical (Eqn [20]), or it can recombine with a chlorine atom and form the intermediate product $PhSnCl_3$ (Eqn [21]). As noted above, this species degrades by the loss of phenyl radical and the formation of an $SnCl_3$ radical (Eqn [22]) and this $SnCl_3$ radical disproportionates to $SnCl_2$ and $SnCl_4$ (Eqn [23]). It should be noted that $PhSnCl_3$ is an observed product in a 2 h reaction. The chlorine atom produced in Eqn [18] can attack Ph_2SnCl_2 to give Cl_2 and a Ph_2SnCl radical (Eqn [24]). The Ph_2SnCl radical, produced in Eqn [18], [20] or [24], can be consumed by reaction with $PhSnCl_3$, regenerating starting material and the $PhSnCl_2$ radical [Eqn [25]). These various processes continue until all Ph_2SnCl_2, $PhSnCl_3$ and Ph_2SnCl radicals are consumed. Ph_2SnCl radicals may also react wih Ph_2SnCl_2, producing Ph_3SnCl and the $PhSnCl_2$ radical by cleavage of the Sn–Ph bond in Ph_2SnCl_2 (Eqn [26]), or Ph_2SnCl_2 and the Ph_2SnCl radical by cleavage of an Sn–Cl bond (Eqn [27]). Equation [27] cannot be important because no overall change occurs in this reaction. Since Ph_3SnCl is not observed as a reaction product, regardless of the duration of reaction, Eqn [26] is also unimportant.

$$Ph_2SnCl_2 \rightarrow Ph\dot{S}nCl_2 + \dot{P}h \qquad [17]$$

$$Ph_2SnCl_2 \rightarrow Ph_2\dot{S}nCl + \dot{C}l \qquad [18]$$

$$Ph\dot{S}nCl_2 \rightarrow SnCl_2 + \dot{P}h \qquad [19]$$

$$Ph\dot{S}nCl_2 + Ph_2SnCl_2 \rightarrow PhSnCl_3 + Ph_2\dot{S}nCl \qquad [20]$$

$$Ph\dot{S}nCl_2 + Cl^{\bullet} \rightarrow PhSnCl_3 \qquad [21]$$

$$PhSnCl_3 \rightarrow Ph^{\bullet} + \dot{S}nCl_3 \qquad [22]$$

$$2\dot{S}nCl_3 \rightarrow SnCl_2 + SnCl_4 \qquad [23]$$

$$Cl^{\bullet} + Ph_2SnCl_2 \rightarrow Cl_2 + Ph_2\dot{S}nCl \qquad [24]$$

$$Ph_2\dot{S}nCl + PhSnCl_3 \rightarrow Ph_2SnCl_2 + Ph\dot{S}nCl_2 \qquad [25]$$

$$Ph_2\dot{S}nCl + Ph_2SnCl_2 \rightarrow Ph_3SnCl + Ph\dot{S}nCl_2 \qquad [26]$$

$$Ph_2\dot{S}nCl + Ph_2SnCl_2 \rightarrow Ph_2SnCl_2 + Ph_2\dot{S}nCl \qquad [27]$$

$$Ph^{\bullet} + Ph^{\bullet} \rightarrow Ph\text{—}Ph \qquad [28]$$

$$Ph^{\bullet} + \text{glass} \rightarrow PhH \qquad [29]$$

$$Ph^{\bullet} + Ph\text{—}Ph \rightarrow PhH + Ph\text{—}Ph^{\bullet} \qquad [30]$$

$$^{\bullet}Ph\text{—}Ph + Ph^{\bullet} \rightarrow Ph\text{—}Ph\text{—}Ph \qquad [31]$$

$$2\,Cl^{\bullet} \rightarrow Cl_2 \qquad [32]$$

Scheme 2

These first nine reactions (Eqns [17] to [25]) generate all of the materials that are now consumed in subsequent reactions. Biphenyl is formed by the combination of two phenyl radicals (Eqn [28]) or by the attack of phenyl radicals on starting material. As suggested above, benzene arises both from the reaction of phenyl radicals with the glass surface and by reaction of phenyl radicals with biphenyl (Eqns [29] and [30]). The three terphenyls (*o*, *m* and *p*) are produced from the radical combination of a biphenyl radical and a phenyl radical (eqn [31]) or by attack of a biphenyl radical on starting material. In addition to its production by Eqn [24], Cl_2 may also arise from the combination of two chlorine atoms (Eqn [32]). Finally, polyphenyls are produced as noted above for $PhSnCl_3$.

Since the amount of $SnCl_4$ is quite small compared with that of $SnCl_2$, one may conclude that Eqns [21], [22] and [23] are less important than reaction [19] but still proceed to a limited extent. Also, since the amount of Cl_2 is quite small, the concentration of chlorine atoms cannot be large and Eqn [18] is not important. Thus the major process is cleavage of both Sn–Ph bonds to give two phenyl radicals and $SnCl_2$ (Eqns [17] and [19]) and subsequent reactions of these phenyl radicals.

Since the amount of Cl_2 is 0.03 mmol, a minimum of 0.03 mmol (0.3%) of Ph_2SnCl_2 degrades via cleavage of an Sn–Cl bond if Eqn [24] adequately describes the formation of Cl_2. If some Cl_2 is formed by the combination of chlorine atoms, this may increase to a maximum of 0.06 mmol (0.6%) if this is the only route for the formation of Cl_2. Thus more than 99% of the reaction proceeds by the cleavage of an Sn–Ph bond.

Thermal degradation of Ph_3SnCl

When a 10.4 mmol sample of Ph_3SnCl is thermolyzed at 375 °C for 25 h, the products observed are 4.93 mmol of $SnCl_2$, 5.78 mmol of elemental tin, 10.5 mmol of biphenyl, and 10.5 mmol of benzene. All the starting material is consumed in a 25 h reaction. When the reaction is performed for 2 h, not all of the starting material is consumed

$$\mathrm{Ph_3SnCl \rightarrow Ph_3\dot{S}n + Cl^{\bullet}} \qquad [33]$$

$$\mathrm{Ph_3SnCl \rightarrow Ph_2\dot{S}nCl + Ph^{\bullet}} \qquad [34]$$

$$\mathrm{Ph_2\dot{S}nCl + Ph_3SnCl \rightarrow Ph_2SnCl_2 + Ph_3\dot{S}n} \qquad [35]$$

$$\mathrm{Ph_3\dot{S}n + Ph_3SnCl \rightarrow Ph_4Sn + Ph_2\dot{S}nCl} \qquad [36]$$

$$\mathrm{Ph_3\dot{S}n + Ph^{\bullet} \rightarrow Ph_4Sn} \qquad [37]$$

$$\mathrm{Ph_4Sn + Cl^{\bullet} \rightarrow Ph_3SnCl + \dot{P}h} \qquad [38]$$

$$\mathrm{Ph_4Sn + Ph_2\dot{S}nCl \rightarrow Ph_3SnCl + Ph_3\dot{S}n} \qquad [39]$$

$$\mathrm{Ph_3Sn^{\bullet} \rightarrow Ph_2Sn + Ph^{\bullet}} \qquad [40]$$

$$\mathrm{Ph_2Sn \rightarrow Ph\dot{S}n + Ph^{\bullet}} \qquad [41]$$

$$\mathrm{Ph\dot{S}n \rightarrow Sn + Ph^{\bullet}} \qquad [42]$$

$$\mathrm{Ph_2\dot{S}nCl \rightarrow PhSnCl + Ph^{\bullet}} \qquad [43]$$

$$\mathrm{PhSnCl \rightarrow ClSn^{\bullet} + Ph^{\bullet}} \qquad [44]$$

$$\mathrm{2ClSn^{\bullet} \rightarrow Sn + SnCl_2} \qquad [45]$$

$$\mathrm{Ph^{\bullet} + glass \rightarrow PhH} \qquad [46]$$

$$\mathrm{Ph^{\bullet} + Ph^{\bullet} \rightarrow Ph{-}Ph} \qquad [47]$$

Scheme 3

and Ph_4Sn and Ph_2SnCl_2 are also observed amongst the products.

A 4.00 g portion of starting material contains 31.1 mmol of phenyl, 10.4 mmol of tin, and 10.4 mmol of chlorine. Phenyl radicals found in this system amount to 31.5 mmol, 10.6 mmol from benzene and 20.9 mmol from biphenyl; the amount of tin found is 10.7 mmol (4.93 mmol from $SnCl_2$ and 5.78 mmol from elemental tin) 9.86 mmol of chlorine are obtained, all from $SnCl_2$. All of these are in reasonable accord with the starting material.

Scheme 3 presents an interpretation for all of the products obtained in the thermolysis of Ph_3SnCl. Either the Sn–Cl bond (Eqn [33]) or the Sn–Ph bond (Eqn [34]) is initially cleaved. The Ph_2SnCl radical from Eqn [34] may interact with starting material to give a Ph_3Sn radical and Ph_2SnCl_2 (Eqn [35]), also observed in a 2 h reaction but not in a 25 h reaction. The Ph_3Sn radical, formed in either reaction [33] or [35], can now interact with starting material to produce Ph_4Sn and a Ph_2SnCl radical (Eqn [36]). Ph_4Sn can also be produced by the radical combination of a Ph_3Sn radical and a phenyl radical (Eqn [37]).

Since Ph_4Sn is only observed as a product in reactions of short duration, it must be consumed in reactions over longer periods. When Ph_4Sn alone is thermolyzed under identical reaction conditions, more than 90% is recovered as unreacted starting material along with a small amount of elemental tin and benzene. Since no Ph_4Sn is recovered when the reaction is performed over a long time, something else in the system must interact with the Ph_4Sn.

When a 1:1 mixture of Ph_3SnCl and Ph_4Sn is thermolyzed, no Ph_4Sn is found. This indicates that some radical in the reaction mixture combines with Ph_4Sn to effect its degradation. One possibility is that chlorine atoms from Eqn [33] may interact to regenerate starting material and phenyl radicals (Eqn [38]). It is more likely that Ph_4Sn interacts with the dominant radical in the system, Ph_2SnCl, to produce the Ph_3Sn radical and starting material (Eqn [39]). The Ph_3Sn radical degrades in a stepwise fashion by the loss of phenyl radicals with the formation of elemental tin (Eqns [40]–[42]).

In addition to the Ph_3Sn radical, the major species responsible for the observed products is the Ph_2SnCl radical. In two steps both phenyls are lost as radicals and the SnCl radical is formed (Eqns [43] and [44]). The SnCl radical disproportionates to give elemental tin and $SnCl_2$ (Eqn [45]). Phenyl radicals from either step may interact with glass to give benzene (Eqn [46]) and combine to form biphenyl (Eqn [47]).

The fact that Cl_2 is not observed indicates that Eqn [33] cannot be an important route for degradation of Ph_3SnCl and that the reaction proceeds by cleavage of an Sn–Ph bond, similarly to what is observed in the other systems. This further implies that reaction [38] cannot be important. The major reaction is successive loss of phenyl radicals from starting material with eventual formation of elemental tin, $SnCl_2$, and reaction products of the phenyl radicals. A minor reaction route involves the formation of Ph_4Sn, probably by reaction [36], followed by reaction of Ph_4Sn with the Ph_2SnCl radical to give the Ph_3Sn radical and the degradation of the Ph_3Sn radical to phenyl radicals and elemental tin. If this last series of reactions did not occur, one would expect equimolar amounts of $SnCl_2$ and Sn. The excess of elemental tin over $SnCl_2$ indicates that the latter reaction does proceed to some extent; the observation of Ph_4Sn in 2 h reactions confirms the presence of a route similar to this.

CONCLUSION

In all cases the Sn–Ph bond is most easily broken. For both $PhSnCl_3$ and Ph_2SnCl_2, the production of Cl_2 indicates that the Sn–Cl bond is also cleaved to a lesser extent. Since Cl_2 is not observed in the thermolysis of Ph_3SnCl, the initial cleavage of a Sn–Cl bond is unlikely to occur. This is likely to be a simple consequence of the relative number of Sn–Cl bonds in these molecules. For all three compounds, the important degradation pathway is successive loss of phenyl radicals with the concomitant formation of $SnCl_3$ radicals, $SnCl_2$, and SnCl radicals respectively. The first and last of these disproportionate, as might be expected.

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