REACTIONS OF SOME METHYLTIN HALIDES WITH LIQUID BORON TRICHLORIDE AND BORON TRIBROMIDE

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Abstract—When Me_nSnX_{4-n} compounds (n = 3, 2 or 1) are dissolved in liquid BX₃ (where X = C1 or Br) at room temperature a reaction occurs which may involve either halogen exchange alone or the cleavage of a methyl group from the alkyltin compound accompanied by halogen exchange. The extent of the reaction depends upon the particular alkyl tin and boron halide present together with the reaction conditions used. We have studied these reactions and identified the products using vibrational spectroscopy.

INTRODUCTION

Alkylation of boron halides by tetraalkyltin compounds is well established and the cleavage of tin-carbon bonds has been used as the basis of a preparative route to new alkylboron halides. For example, Gerrard et al. [1] reacted R_4Sn with BCl₃ to produce R_2SnCl_2 and RBCl₂. Similar reactions occur with BBr₃ however, they noted that, in contrast to the phenyl system, not more than two of the alkyl groups attached to tin could be transferred to boron.

As part of a spectroscopic investigation into the behaviour of alkyltin halides in a variety of non-aqueous solvents we have recently carried out a detailed study of the reactions which occur when the alkyltin halides $Me_n SnX_{4-n}$ (where n = 1-3) are dissolved in liquid BCl₃ and BBr₃ as solvents. We report here our results which show that the reactions may involve either halogen exchange between BX₃ and $Me_n SnX_{4-n}$ (where n = 1) or cleavage of a methyl group from the alkyltin compound (where n = 2 or 3) accompanied by halogen exchange. The extent of the reaction depends upon the particular parent compounds present together with the reaction temperature chosen.

EXPERIMENTAL

The compounds Me_3SnX , Me_2SnX_2 (X = Cl or Br) and $MeSnCl_3$ were supplied by Lancaster Synthesis Limited, and they were used without further purification. Liquid BCl₃ and BBr₃ (BDH) were also used directly. Reactions between alkyltin halides and liquid BCl₃ were carried out on a vacuum line. Solid reaction products were separated off in a glove bag under nitrogen and the solid was then further dried on the vacuum line. The vibrational spectra of the solid, liquid and vapour phases were examined separately. The analogous reactions with BBr₃ were carried out in a nitrogen-filled glove bag.

Raman spectra were recorded on a Cary Model 81 instrument converted to 90° operation by Anaspec Limited. This incorporated a triple prism premonochromator, a Brookdeal 9511 quantum photometer and a cooled photomultiplier tube. The spectra were excited using the 488.0 nm line (\sim 800 mW at sample) from a Coherent Radiation Model CR3 argon ion laser. The samples were contained in 4 mm diameter pyrex capillary tubes fitted with Rotaflo teflon taps. The spectra were calibrated

against carbon tetrachloride and they are believed to be accurate to $\pm 2 \text{ cm}^{-1}$.

IR spectra were obtained using a Perkin-Elmer Model 457 spectrometer. The solid samples were examined as Nujol mulls between KBr plates. The gaseous samples were run in 10 cm gas cells fitted with KBr plates. Gaseous BCl₃ reacts slowly with KBr and a weak absorption band in the 1200-1400 region is observed. However, this impurity band does not hinder the interpretation of the spectrum in the other regions.

The \dot{IR} and Raman spectra were all recorded at room temperature.

RESULTS AND DISCUSSION

As a preliminary to this investigation the spectra of the methyltin compounds were first of all examined in a variety of solvents such as CCl_4 , C_6H_{12} , C_6H_6 , CS_2 and liquid SO₂. The first four solvents have been used previously and our results are in agreement with those of Edgell *et al.* [2] and Petrosyan *et al.* [3]. The vibrational spectra of the boron halides [4] and the alkyl boron halides [5] are well documented in the literature.

Reaction between Me₃SnCl and liquid BCl₃

Me₃SnCl is appreciably soluble in liquid BCl₃ at 20°C. When Me₃SnCl is reacted with an excess BCl₃ the relative intensities of the bands in Raman spectrum of the solution, especially in the 450-600 cm⁻¹ region, change with time. After standing overnight a white solid precipitates out from the solution and the vibrational spectrum of the solid is identical with the spectrum of pure crystalline Me₂SnCl₂. The Raman spectrum of the supernatent liquid exhibits bands due to BCl3 but in addition the spectrum shows a medium intense band at 277 cm⁻¹ as well as a strong band at 543 cm⁻¹; both of these features may be assigned to MeBCl₂. Bands due to small amounts of Me₂SnCl₂ are also observed in solution (see Table 1). The IR spectrum of the vapour above the solution exhibits bands which can be assigned to BCl₃ and MeBCl₂.

These results confirm the following reaction between Me₃SnCl and BCl₃:

 $Me_3SnCl(s) + excess BCl_3(1) \xrightarrow{20^{\circ}C}$

 $Me_2SnCl_2(s) + MeBCl_2(1).$

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Table 1. Raman frequencies of the liquid which remains when Me₃SnCl has reacted with liquid BCl₃ (after removal of solid Me₂SnCl₃)

| v/cm ⁻¹ | Assignment |
|--------------------|------------------------------------|
| 258 m | v ₄ ^{BCt} 3 |
| 277 s | v_3 and v_5 MeBCl ₂ |
| 362 m | vs (Sn-Cl) Me2SnCl2 |
| 472 s | V, BCI3 |
| 529 m | vs (Sn-C) Me2SnCl2 |
| 543 vs | v ₂ MeBCl ₂ |

2. Reaction between Me₃ SnCl and liquid BBr₃

Me₃SnCl dissolves in a slight excess of liquid BBr₃ at room temperature. A white solid slowly precipitates, however, and the vibrational spectrum of this solid is identical to that of pure solid Me₂SnBr₂.

The Raman spectrum of the remaining liquid phase is complex (see Table 2) but the assignment becomes straight forward once it is realised that the following reaction equilibrium may be present:

 $BCl_2Br + BClBr_2 \rightleftharpoons BCl_3 + BBr_3$.

Vibrational studies of this equilibrium have been published previously by Lindeman *et al.* [4] and this work together with the published spectra for $MeBCl_2$ and $MeBBr_2$ [5] simplifies our assignments.

The IR spectrum of the vapour phase above the remaining liquid phase also shows the presence of the above equilibrium species and in addition confirms the presence of both $MeBBr_2$ and $MeBCl_2$ in the vapour phase (see Table 3). Thus it is apparent that both halogen exchange and cleavage reactions are taking place. To account for these results we propose that the following reaction occurs when $Me_3SnCl(s)$ is dissolved in a slight excess of BBr_3 :

 $Me_3SnCl + BBr_3 \rightarrow Me_2SnBr_2 + MeBBrCl.$

A further reaction such as:

$$MeBBrCl + BBr_3 \rightarrow MeBBr_2 + BBr_2Cl$$

coupled with the above equilibrium will account for the presence of the observed species.

3. Reaction between Me₃SnBr and liquid BCl₃ Me₃SnBr is soluble in an excess of liquid BCl₃ at room

Table 2. Raman frequencies of the liquid which remains when Me₃SnCl has reacted with liquid BBr₃ (after removal of solid Me₂SnBr₂)

| v/cm ⁻¹ | Assignment |
|--------------------|---|
| 157 w | v ₄ ^{BBr} ₃ |
| 180 m | MeBBr ₂ |
| 242 s | V5 MeBBr2; V1 (Sn-Br) Me2 SnBr2 |
| 282 m | $v_1 BBr_3$; v_3 and $v_5 Me BCl_2$ |
| 350 m | BBr ₂ Ci |
| 413 w | b BBrCl 2 |
| 426 s | v2 MeBBr2 |
| 476 s | v ₁ ^{BCl} 3 |
| 527 w | v, (Sn-C) Me ₂ SnBr ₂ |
| 546 m | v ₂ MeBCl ₂ |

Table 3. IR frequencies of the vapour above a solution which remains when Me₃SnCl has reacted with liquid BBr₃

| v/cm ⁻¹ | Assignment |
|--------------------|-----------------------------------|
| 3008 w | v CH ₃ |
| 1408 m | 8 CH ₃ |
| 1310 s | SCH3 |
| 1325 s | 8 сн ₃ |
| 1080 s | v ₁ MeBCl ₂ |
| 1040 vs | v ₁ MeBBr ₂ |
| ~ 1020 vs | ν4 ^{MeBCl} 2 |
| ~ 990 vs | v ₄ ^{MeBBr} 2 |
| 960 m | V3 BC13 |
| 920 w | V1 BBr2Cl |
| 880 w | v1 BBrCl2 |
| 835 m | v ₃ ^{BBr} 3 |
| 770 m | MeBCl ₂ |
| 708 m | MeBBr ₂ |
| 545 w | v2 ^{MeBCl} 2 |
| 480 w | v2 ^{BCl} 3 |

temperature and a white solid gradually precipitates. The vibrational spectrum of the solid shows new strong bands at 317 cm^{-1} in the v Sn-Cl region (see $v \text{sym} \text{SnCl} = 312 \text{ cm}^{-1}$ for Me₂SnCl₂) and 221 cm⁻¹ in the v Sn-Br region (see $v \text{sym} \text{SnBr} = 226 \text{ cm}^{-1}$ for Me₂SnBr₂). In addition the v sym and v asym Sn-C modes at 514 and 564 cm⁻¹ correspond to Me₂SnX₂ compounds and not Me₃SnX compounds. Hence, by comparison with the Raman and IR spectra of Me₃SnBr, Me₃SnCl, Me₂SnCl₂ and Me₂SnBr₂ both in the solid state and in a variety of solvents, we conclude that the solid precipitated in this reaction is probably Me₂SnBrCl and we propose the following overall reaction scheme:

 $Me_3SnBr(s) + excess BCl_3(1) \xrightarrow{20^{\circ}C}$

$$Me_2SnBrCl(s) + MeBCl_2(1).$$

The presence of BCl₃, MeBCl₂ and Me₂SnBrCl are also apparent in the liquid phase spectrum after the solid has been separated and the first two compounds are volatile enough to appear in the vapour phase spectrum. Thus at room temperature, cleavage of an Sn-C bond takes place together with an exchange of halogen atoms.

IV. Reaction between Me₃SnBr and liquid BBr₃

Me₃SnBr dissolves in an excess liquid BBr₃ to yield solid Me₂SnBr₂. The Raman spectrum of the remaining solution shows the presence of BBr₃, MeBBr₂ and Me₂SnBr₂ while the IR spectrum of the vapour phase confirms the presence of BBr₃ and MeBBr₂. The reaction may be represented as:

 $Me_3SnBr(s) + BBr_3(1) \rightarrow Me_2SnBr_2(s) + MeBBr_2(1).$

To summarise these four reactions we observe that when either Me₃SnCl or Me₃SnBr react with excess BCl₃ at room temperature then cleavage of one methyl group takes place. Chlorine atom exchange may occur when Me₃SnCl reacts with liquid BCl₃ but this could not be detected by vibrational spectroscopy. Replacement of the bromine atoms in Me₃SnBr by chlorine atoms does not apparently occur. In contrast when excess liquid BBr₃ is used as the solvent an additional reaction is observed for Me_3SnCl . The bromine groups exchange with the chloride groups attached to Me_3SnCl . The bromine groups may also exchange with Me_3SnBr but this could not be detected by vibrational spectroscopy.

V. Reaction of Me₂SnCl₂ with liquid BCl₃

 Me_2SnCl_2 is readily soluble in liquid BCl₃. The resulting solution is colourless and the Raman spectrum of this solution is the same as for Me_2SnCl_2 dissolved in benzene. In contrast, the IR spectrum of the vapour phase shows bands due to BCl₃ only. Thus, there is no evidence from vibrational spectroscopy for cleavage or exchange reactions occurring between Me_2SnCl_2 and BCl₃ at room temperature.

VI. Reaction of Me₂SnCl₂ and liquid BBr₃

When Me_2SnCl_2 is dissolved in an excess of liquid BBr_3 , a white solid precipitates after a short time. The solid exhibits a vibrational spectrum identical to Me_2SnBr_2 . The Raman spectrum of the liquid phase (after the solid has precipitated) indicates the presence of Me_2SnBr_2 , BBr_3 and BBr_2Cl together with some weak bands assigned to BCl_3 and $BBrCl_2$. The IR spectrum of the vapour phase also indicates the presence of $BBrCl_2$, BBr_2Cl , BBr_3 and BCl_3 . In the light of these results it appears reasonable to suppose that the following reaction occurs between Me_2SnCl_2 and BBr_3 :

$$3Me_{3}SnCl_{2}(s) + 2BBr_{3}(1) \rightarrow 3Me_{2}SnBr_{2}(s) + 2BCl_{3}(1)$$
.

VII. Reaction between Me_2SnBr_2 and liquid BX_3 where X = Cl or Br

Our spectroscopic studies indicate that there is no observable reaction when solid Me_2SnBr_2 is dissolved in an excess of either BCl₃ or BBr₃ at room temperature.

We were surprised to find that no cleavage of the methyl groups takes place when Me_2SnX_2 compounds (X = Cl or Br) are dissolved in BCl_3 or BBr_3 . We decided to carry out one of the reactions above room temperature. A solution of Me_2SnBr_2 dissolved in an excess BBr_3 was left for about 6 hr in an oil bath at about 90°C. The solution was very dark at the end of this period and

it was not possible to obtain the Raman spectrum. However, the IR spectrum of the vapour phase was obtained and this showed clearly that cleavage of a methyl group can take place at higher temperatures to produce MeBBr₂. In fact the IR spectrum was identical to that obtained from the vapour phase above the Me₃SnBr/BBr₃ solution.

VIII. Reaction of MeSnCl₃ with liquid $BX_3/X = Cl$ or Br

The Raman spectra of liquid MeSnCl₃ has been reported previously by Edgell *et al.*; they reported the presence of a single Sn-Cl stretching mode at 363 cm⁻¹. This assignment assumed point group C_{3v} for the molecule and hence two v_{Sn-Cl} modes are expected. We observe $v_s(Sn-Cl)$ and $v_{as}(Sn-Cl)$ as strong and weak bands at 369 and 382 cm⁻¹ respectively in BCl₃ solvent. With the knowledge of the previous reactions, MeSnCl₃ is not expected to react with BCl₃ at room temperature and our spectroscopic results show this to be the case.

When MeSnCl₃ is dissolved in liquid BBr₃, however, a white solid is precipitated. We have characterised this solid as MeSnBr₃ using Raman spectroscopy. The following spectral features distinguish it from solid MeSnCl₃: (a) the ν Sn-Cl bands have disappeared completely, and (b) two new bands have appeared at 234 (vs) and 257 (m) cm⁻¹.

It is easy to show that the liquid phase is composed of BBr₃, BCl₂Br, BClBr₂ and MeSnBr₃ while the vapour phase contains a mixture of BBr₃, BCl₃, BBr₂Cl and BCl₂Br. Thus we propose that the following reaction takes place between MeSnCl₃ and BBr₃ at room temperature:

 $MeSnCl_3(s) + BBr_3(1) \xrightarrow{20^{\circ}C} MeSnBr_3(s) + BCl_3(1).$

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