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# ORGANOMETALLIC COMPOUNDS
# VII*. ELECTRON IMPACT FRAGMENTATION OF TRIALKYLTIN HALIDES

M. GIELEN AND G. MAYENCE**
*Service de Chimie Organique, Faculté des Sciences, Université Libre de Bruxelles, 50 Avenue F. D. Roosevelt, Bruxelles 5 (Belgium)*

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## SUMMARY

The mass spectra of four different series of trialkyltin halides are described and analysed. The fragmentation rules are found to be identical to those of other alkyltin systems. The fragmentation pattern conforms to hypothesis of preferred $Sn^{IV}$ and $Sn^{II}$ valence state in the tin-containing fragments.

The ease of cleavage of a halogen–tin bond in the molecular ion parallels the bond energy in the ground state.

## INTRODUCTION

Apart from the mass spectrum of triethyltin fluoride described by Occolowitz[1], there is no publication on the electron impact fragmentation of trialkyltin halides $R_3SnX$. We now wish to report the mass spectra of different series of such organometallic compounds which were previously used in Mössbauer studies[2]; these include triethyl-, tripropyl-***, tributyl- and triisobutyltin halides.

The principal ions observed are listed in Table 1† and metastable peaks are given in Table 2.

## GENERAL DESCRIPTION OF THE SPECTRA

The results given in Table 1 show that the mass spectra of trialkyltin halides are not very different from one another and are quite similar to those obtained for mixed tetraalkyltins[3] and for aryltrialkyltins[4]. A general description of these mass spectra can then be given.

The intensity of the molecular ion $R_3SnX^+$ is generally not very large (4% of the sum of the intensities of all the tin-containing ions or less for the ethyl deriva-

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* For Part VI see ref. 3.

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*** These compounds were synthesized by Mr. Y. Gosciny.

† The following calculated isotopic distribution have been used for SnCl and SnBr (ref. 2b): SnCl: 147 (0.75%), 149 (0.76%), 150 (0.27%), 151 (11.10%), 152 (5.89%), 153 (21.74%), 154 (8.38%), 155 (30.50%), 156 (2.12%), 157 (11.62%), 159 (5.55%), 161 (1.43%).
SnBr: 191 (0.50%), 193 (0.83%), 194 (0.18%), 195 (7.67%), 196 (4.02%), 197 (19.35%), 198 (8.16%), 199 (28.40%), 200 (4.25%), 201 (18.53%), 203 (5.32%), 205 (2.87%).

TABLE 1

RELATIVE INTENSITY OF THE PRINCIPAL TIN-CONTAINING FRAGMENTS IN THE CALCULATED MONOISOTOPIC SPECTRA OF TRIALKYLTIN HALIDES AND TETRAALKYLTINS (base peak = 100)

| $R_3SnX$ | $R_3SnX^+$ | $R_2SnX^+$ | $RSnXH^+$ | $RSnX^+$ | $SnX^+$ | $R_3Sn^+$ | $R_2SnH^+$ | $R_2Sn^+$ | $RSnH_2^+$ | $RSn^+$ | $MeSn^+$ | $SnH_3^+$ | $SnH^+$ | $Sn^+$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Et_3SnF$(I) | 10 | 100 | 9 | 7 | 54 | 5 | 4 | 1 | 2 | 51 | 2 | | 8 | 2 |
| $Et_3SnCl$(II) | 8 | 100 | 14 | 11 | 51 | 13 | 9 | 5 | 1 | 36 | | | 14 | 9 |
| $Et_3SnBr$(III) | 6 | 100 | 24 | 11 | 49 | 10 | 9 | 4 | 4 | 33 | 1 | | 16 | 10 |
| $Et_3SnI$(IV) | 16 | 100 | 27 | 10 | 49 | 18 | 10 | 6 | 11 | 74 | | | 31 | 18 |
| $Et_4Sn$(V) | 5[a] | | | | | 100 | 94 | 8 | 49 | 47 | 2 | | 36 | 15 |
| $Pr_3SnF$(VI) | 5 | 100 | 12 | 5 | 27 | 4 | 4 | 3 | 4 | 57 | 5 | | 14 | 6 |
| $Pr_3SnCl$(VII) | 6 | 100 | 45 | 6 | 49 | 16 | 12 | 5 | 13 | 35 | 7 | 1 | 22 | 9 |
| $Pr_3SnBr$(VIII) | 3 | 100 | 42 | 4 | 54 | 18 | 20 | 4 | 16 | 36 | 5 | 2 | 22 | 9 |
| $Pr_3SnI$(IX) | | 0.1 | 0.3 | | 1 | 68 | 100 | 2 | 80 | 20 | 8 | 10 | 30 | 11 |
| $Pr_4Sn$(X) | 0.4[a] | | | | | 66 | 100 | 2 | 82 | 21 | 8 | 11 | 33 | 12 |
| $Bu_3SnF$[b](XI) | | 1 | 2 | | 29 | | 0.6 | | | | 15 | | 2 | 9 |
| $Bu_3SnCl$(XII) | 1 | 100 | 40 | 6 | 65 | 62 | 82 | 6 | 95 | 61 | 21 | 14 | 73 | 25 |
| $Bu_3SnBr$(XIII) | 0.5 | 100 | 29 | 4 | 29 | 4 | 2 | 1 | 4 | 20 | 1 | 1 | 10 | 3 |
| $Bu_3SnI$(XIV) | 0.6 | 100 | 39 | 4 | 36 | 14 | 4 | 1 | 6 | 16 | 1 | 1 | 10 | 4 |
| $Bu_4Sn$(XV) | 0.5[a] | | | | | 92 | 85 | 2 | 100 | 17 | 3 | 13 | 31 | 8 |
| iso-$Bu_3SnF$(XVI) | 4 | 100 | 14 | 4 | 21 | 2 | 5 | 3 | 4 | 75 | 15 | | 13 | 6 |
| iso-$Bu_3SnCl$(XVII) | 2 | 100 | 47 | 6 | 27 | 4 | 3 | 3 | 3 | 16 | 10 | 1 | 13 | 6 |
| iso-$Bu_3SnBr$(XVIII) | 2 | 100 | 61 | 8 | 58 | 9 | 8 | 3 | 7 | 25 | 23 | 3 | 31 | 15 |
| iso-$Bu_3SnI$(XIX) | 0.5 | 100 | 95 | 7 | 61 | 22 | 11 | 5 | 13 | 27 | 21 | 1 | 35 | 18 |
| iso-$Bu_4Sn$[c](XX) | | | | | | 44 | 100 | 3 | 80 | 16 | 18 | 6 | 28 | 11 |

[a] This is actually the intensity of the molecular ion $R_4Sn^+$. [b] The following peaks were also surprisingly found for tributyltin fluoride: $EtSnFH^+$ (100), $SnMeF^+$ (12) and $SnPrH_2^+$ (28). [c] The following peaks were also found for tetraisobutyltin: $SnEt^+$ (2), $SnEtH_2^+$ (10), $BuSnEtH^+$ (20) and $Bu_2SnEt^+$ (6).

TABLE 2

METASTABLE PEAKS OBSERVED FOR TRIALKYLTIN HALIDES

| Fragmentation leading to the metastable peak | Observed for compounds |
|---|---|
| $R_3SnX^+ \rightarrow R_2SnX^+$ | (II) |
| $R_2SnX^+ \rightarrow RSnHX^+$ | (II), (III), (IV), (XII), (XIV), (XV), (XVII), (XVIII), (XIX) |
| $RSnHX^+ \rightarrow RSn^+$ | (XVI) |
| $RSnHX^+ \rightarrow SnX^+$ | (XVI) |
| $R_3Sn^+ \rightarrow R_2SnH^+$ | (V), (VIII), (IX), (X), (XV), (XVII), (XX) |
| $R_2SnH^+ \rightarrow RSn^+$ | (II), (V), (XVII) |
| $R_2SnH^+ \rightarrow RSnH_2^+$ | (XV) |

tives, 2% or less for the isobutyl and the propyl compounds and less than 0.3% for the butyl series).

The base peak is a fragment which has lost an alkyl radical except for tributyltin fluoride (where it is unexpectedly $EtSnFH^+$), for tripropyltin iodide, tetrapropyl- and tetraisobutyltin ($R_2SnH^+$) and for tetrabutyltin ($BuSnH_2^+$). However, the base peak is always a tin-containing ion where the metal is tricoordinated and has thus reached a $Sn^{IV}$ oxidation state. The sum of the intensities of the different trisubstituted organotin ions reaches 80% ($Pr_3SnI$) and is always greater than 45% ($Et_3SnI$).

This state must then be very favourable, as pointed out before on other organotin systems[3,4].

On the contrary, disubstituted tin ions are not very favourable. The sum of the intensities of such ions never reaches 6% and is in some cases very small (0.4% for $Pr_3SnI$).

Monosubstituted tin fragments are more abundant. Their intensity reaches 46% (iso-$Bu_3SnI$) and is always larger than 18% for trialkyltin halides ($Pr_3SnI$)[3,4].

## DISCUSSION

### 1. *Fragmentation pattern*

On the basis of these results, a fragmentation pattern can be given, which could be a reasonable description of the fate of the molecular ion (see Fig. 1).

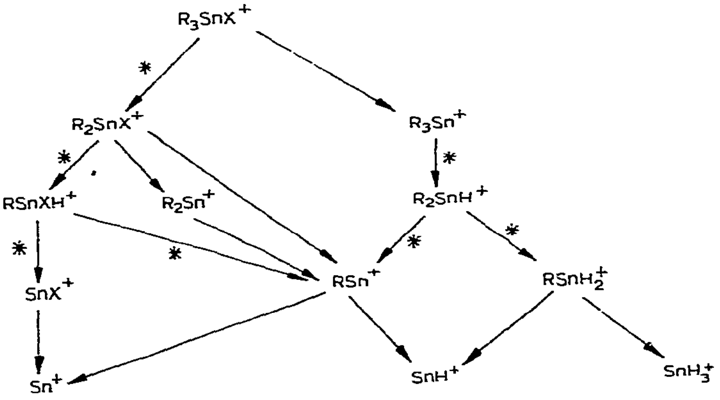

Fig. 1. Possible fragmentation pattern for $R_3SnX^+$ (* = metastable peak observed).

## 2. *Fragmentation rules*

The similarity between the fragmentation observed for trialkyltin halides and that described before for aryltrialkyltins[4] and for mixed tetraalkyltins[3] show that the general conclusions given for the $R_3SnR'$ systems must also be valid for the trialkyltin halides. The prefered $Sn^{IV}$ valence state in the tin-containing fragments is indeed reached by losing a radical ($R^\bullet$ or $X^\bullet$) from the next higher unfavourable valence state:

$$R_3SnX^{\bullet+} \rightarrow R_2SnX^+ + R^\bullet$$

or

$$R_3SnX^{\bullet+} \rightarrow R_3Sn^+ + X^\bullet$$

This valence state may also be reached by the loss of an alkene molecule from a trisubstituted tin ion, which preserves the $Sn^{IV}$ state of the metal:

$$R_2SnX^+ \rightarrow RSnHX^+ + (\text{R minus one H})$$
$$R_2SnH^+ \rightarrow RSnH_2^+ + (\text{R minus one H})$$

The $Sn^{II}$ valence state is also quite favourable and may be reached by losing a saturated molecule from a trisubstituted tin ion

$$RSnXH^+ \rightarrow RSn^+ + HX$$
$$R_2SnH^+ \rightarrow RSn^+ + RH$$

or by losing a radical from the next higher unfavourable valence state.

The same rules can thus be applied to this new system and this suggests that these rules[3,4] may indeed be considered as relatively general ones.

## 3. *Cleavage sequence*

Some of the fragmentation ions evidently come from an initial Sn–R cleavage ($R_2SnX^+$, $R_2Sn^+$, $RSnHX^+$, $SnX^+$); some other ions include $R_3Sn^+$ and its decomposition fragments ($R_3Sn^+$, $R_2SnH^+$, $RSnH_2^+$, $SnH_3^+$); finally, the remaining ions could come either from $R_2SnX^+$ or from $R_3Sn^+$ ($RSn^+$, $SnH^+$, $Sn^+$).

It is thus possible to calculate without any preconceived hypothesis two extreme values of a ratio which describes the relative ease of cleavage[3] of an alkyl group or of a halogen bound to the tin atom in the molecular ion[5]. This shows that the following cleavage sequence $I > Br$, $Cl > F$ describes the weakness of a tin–halogen bond in an excited tetrasubstituted positive organotin ion, which parallels the bond energies of the neutral ground state molecule.

## EXPERIMENTAL

## 1. *Syntheses*

*Trialkyltin bromides.* We used a new procedure for the transformation of tetraalkyltins into trialkyltin bromides which gives very pure derivatives (no traces of dialkyltin dihalides could be detected*) in very high yields (more than 90% after distillation) *by running the reaction in methanol*[6].

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* The reaction of bromine with iso-$Bu_4Sn$ *in* $CCl_4$ yields comparable quantities of the mono- and dibromides when a stoichiometric amount of bromine is used (leaving thus unreacted tetraisobutyltin). The only reaction product *in methanol* is triisobutyltin bromide. Other experiments[6b] have shown that the cleavage is really limited to a mono-bromination when methanol is used as solvent: tetrabutyltin is readily transformed into tributyltin bromide when the reaction is run in methanol. The resulting crude bromide, reacted with an excess EtMgBr gave a 95% yield of $Bu_3SnEt$; no $Bu_2SnEt_2$ could be detected[6b].

Bromine, undiluted[6] or dissolved in a minimum of $CCl_4$ is added dropwise to a saturated solution of $R_4Sn$ in methanol; the reaction is instantaneous and the first drop in excess yields a persistent colour. Although a free radical process[7] is not expected to compete with the main reaction[8], the bromination is run in dim light. Removal of the solvent (rotating evaporator under reduced pressure, the last traces being removed by a gentle flow of dry nitrogen through the residual oil heated to 100°) yields very high yields of a crude bromide which is then distilled under reduced pressure and under nitrogen.

*Trialkyl tin iodides.* Trialkyltin iodides are easily made from trialkyltin bromides. A stoïchiometric quantity of a saturated solution of sodium iodide in ethyl acetate is added to a solution of $R_3SnBr$ in the same solvent; the precipitate (NaBr)[9] is filtered and the solvent is removed (rotating evaporator under reduced pressure). The crude trialkyltin iodide is then distilled under a reduced pressure and under nitrogen. The yield is higher than 85%.

Trialkyltin chlorides and fluorides* were synthesized by the method described by Prince[10]. Distillation and sublimation were respectively used to purify these derivatives.

## 2. *Mass spectra*

The spectra were recorded on a Hitachi Perkin–Elmer RMU-6D mass spectrometer under the following conditions: electron energy: 70 eV; pressure: $1–3 \times 10^{-6}$ mm; total ionization: $10^{-10}$ amp; source temperature: 250°.

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* The NMR spectrum of trimethyltin fluoride in HMPT gives $J(H–C–Sn^{119}) = 72.6$ cps [$J(H–C–Sn^{117}) = 69.3$ cps]. This value is larger than that obtained by Drago for trimethyltin chloride[11], confirming thus the coupling constant sequence given by Van der Kelen[12] for triethyltin halides in other solvents.

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