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CHEMICAL IONIZATION MASS SPECTROMETRY OF ORGANOTIN COMPOUNDS

Richard H. Fish*, Roy L. Holmstead and John E. Casida
Toxicology Laboratory, Division of Entomology and Parasitology
University of California, Berkeley, California 94720

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Chemical ionization (CI) mass spectrometry (MS) is a relatively new aspect of conventional mass spectrometry[1]. In this technique sample molecules are ionized via ion--molecule reactions in the gas phase, as opposed to the more common electron impact process. Thus, reagent gas ions, which are generated (eg. CH_5^+ and $C_2H_5^+$ from CH_4) by reactions of high energy electrons with the reagent gas, react with the sample causing the sample molecules to ionize in the ion source.

The only reported use of CI MS with organometallic compounds has been the recent work by Hunt _et al._[2], which showed great promise for CI MS in studying electrophilic reactions of these compounds in the gas phase. In this regard, we wish to communicate our results on the CI MS of a variety of organotin compounds[3] using methane as the reagent gas. We wish to point out that all the organotin compounds examined showed no M+1, M+29 or M-1 ions, which is in contrast somewhat to Hunt's findings on transition metal complexes[2].

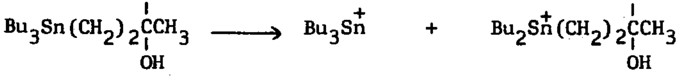
The fragmentation ions formed with methane as the reagent gas for the general formulas R_4Sn, R_3SnR', $R_2SnR'_2$, R_3SnX, R_2SnX_2 and $R_2SnR'(X)$ are presented with respect to the normalized relative abundances (%) of the ^{120}Sn isotope[4].

$\underline{R_4Sn}$

$Bu_4Sn \longrightarrow Bu_3\overset{+}{Sn}$

1 100%, _m/e_ 291

$\underline{R_3SnR'}$

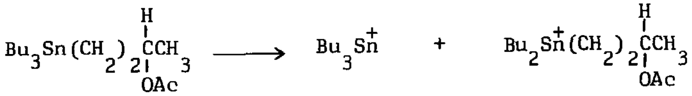


$Bu_3Sn(CH_2)_2\underset{OH}{\overset{H}{C}}CH_3 \longrightarrow Bu_3\overset{+}{Sn} + Bu_2\overset{+}{Sn}(CH_2)_2\underset{OH}{\overset{H}{C}}CH_3$

2 59%, _m/e_ 291 41%, _m/e_ 307

$$\mathrm{Bu_3Sn(CH_2)_4OH} \longrightarrow \mathrm{Bu_3\overset{+}{Sn}} + \mathrm{Bu_2\overset{+}{Sn}(CH_2)_4OH}$$

3 49%, *m/e* 291 51%, *m/e* 307



$$\mathrm{Bu_3Sn(CH_2)_2\overset{H}{\underset{OAc}{C}}CH_3} \longrightarrow \mathrm{Bu_3\overset{+}{Sn}} + \mathrm{Bu_2\overset{+}{Sn}(CH_2)_2\overset{H}{\underset{OAc}{C}}CH_3}$$

4 76%, *m/e* 291 24%, *m/e* 349

$$\mathrm{Bu_3Sn(CH_2)_4OAc} \longrightarrow \mathrm{Bu_3\overset{+}{Sn}} + \mathrm{Bu_2\overset{+}{Sn}(CH_2)_4OAc}$$

5 59%, *m/e* 291 41%, *m/e* 349

$\underline{\mathrm{R_2SnR'_2}}$

$$\mathrm{Bu_2Sn(C_6H_5)_2} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}C_6H_5} + \mathrm{Bu\overset{+}{Sn}(C_6H_5)_2}$$

6 66%, *m/e* 311 34%, *m/e* 331

$\underline{\mathrm{R_3SnX}}$

$$\mathrm{Bu_3SnOAc} \longrightarrow \mathrm{Bu_3\overset{+}{Sn}}$$

7 100%, *m/e* 291

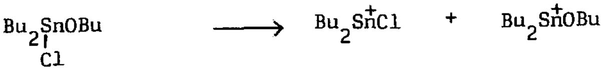
$$\mathrm{Bu_3SnCl} \longrightarrow \mathrm{Bu_3\overset{+}{Sn}} + \mathrm{Bu_2\overset{+}{Sn}Cl}$$

8 72%, *m/e* 291 28%, *m/e* 269

$\underline{\mathrm{R_2SnX_2}}$

$$\mathrm{Bu_2SnCl_2} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}Cl} + \mathrm{Bu\overset{+}{Sn}Cl_2}$$

9 95%, *m/e* 269 5%, *m/e* 241



$$\mathrm{Bu_2\underset{Cl}{Sn}OBu} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}Cl} + \mathrm{Bu_2\overset{+}{Sn}OBu}$$

10 87%, *m/e* 269 13%, *m/e* 307

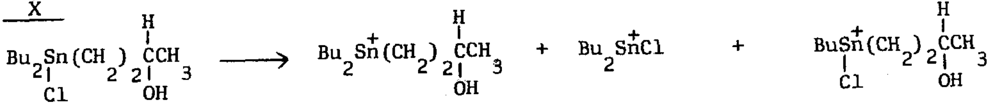
$$\mathrm{Bu_2Sn(OAc)_2} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}OAc}$$

11 100%, *m/e* 293

$$\mathrm{Bu_2\underset{Cl}{Sn}O\underset{Cl}{Sn}Bu_2} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}Cl}$$

12 100%, *m/e* 269

$\underline{\mathrm{R_2\underset{X}{Sn}R'}}$

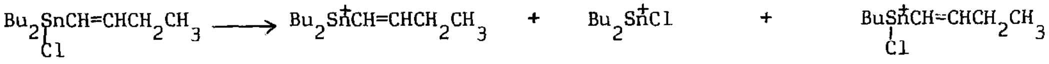


$$\mathrm{Bu_2\underset{Cl}{Sn}(CH_2)_2\overset{H}{\underset{OH}{C}}CH_3} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}(CH_2)_2\overset{H}{\underset{OH}{C}}CH_3} + \mathrm{Bu_2\overset{+}{Sn}Cl} + \mathrm{Bu\underset{Cl}{\overset{+}{Sn}}(CH_2)_2\overset{H}{\underset{OH}{C}}CH_3}$$

13 74%, *m/e* 307 21%, *m/e* 269 5%, *m/e* 285

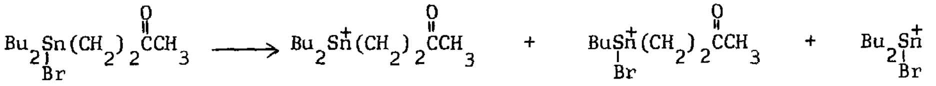
$$\mathrm{Bu_2\underset{Cl}{Sn}(CH_2)_4OH} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}(CH_2)_4OH} + \mathrm{Bu_2\overset{+}{Sn}Cl} + \mathrm{Bu\underset{Cl}{\overset{+}{Sn}}(CH_2)_4OH}$$

14 — 69%, *m/e* 307 — 18%, *m/e* 269 — 13%, *m/e* 285



$$\mathrm{Bu_2\underset{Cl}{Sn}CH{=}CHCH_2CH_3} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}CH{=}CHCH_2CH_3} + \mathrm{Bu_2\overset{+}{Sn}Cl} + \mathrm{Bu\underset{Cl}{\overset{+}{Sn}}CH{=}CHCH_2CH_3}$$

15 — 72%, *m/e* 289 — 18%, *m/e* 269 — 10%, *m/e* 267

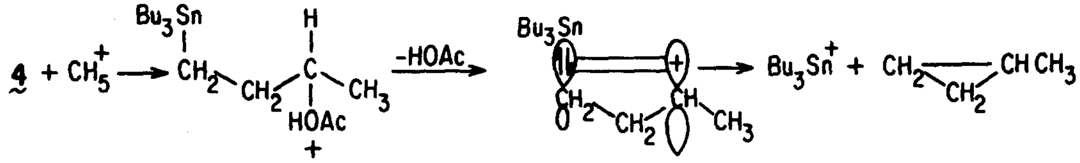


$$\mathrm{Bu_2\underset{Br}{Sn}(CH_2)_2\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow \mathrm{Bu_2\overset{+}{Sn}(CH_2)_2\overset{O}{\overset{\|}{C}}CH_3} + \mathrm{Bu\underset{Br}{\overset{+}{Sn}}(CH_2)_2\overset{O}{\overset{\|}{C}}CH_3} + \mathrm{Bu_2\underset{Br}{\overset{+}{Sn}}}$$

16 — 85%, *m/e* 305 — 11%, *m/e* 327 — 4%, *m/e* 313

The results parallel to some extent the electrophilic cleavage reactions of organotin compounds occurring in solution using a proton as the electrophile[5]. For example, the CI MS of compound 6 shows a predominance in the loss of the phenyl group (66%) over the butyl group (34%) and is consistent, qualitatively, with what occurs in acid solution[5]. Also the protonation[1], presumably by CH_5^+, on substituents attached to the tin is in the order Sn-O > Sn-Cl > Sn-C. This trend is borne out with compounds 10 and 12. Of particular interest are compounds 2-5, 13 and 14, since they can be related to the discovery by Kuivila and Scarpa[6] pertaining to the increased reactivity of gamma (γ)-substituted organotin derivatives particularly in solvolysis reactions. Thus we compared in compounds 2 and 3 the loss of the butyl group containing a hydroxyl group γ to the tin atom and delta (δ) to the tin atom relative to the unsubstituted butyl groups in each compound. In this comparison the loss of the γ-BuOH/Bu in 2 is ~1.5 times greater than the loss of the δ-BuOH/Bu in 3. Furthermore replacement of the hydroxyl with an acetate group (4 and 5) in each case results in an increase in that ratio to ~2.2. Obviously the γ alcohol and acetate show a preponderance for the generation of the $\mathrm{Bu_3\overset{+}{Sn}}$ ion over the corresponding δ isomer and this is probably related to carbon-tin sigma (σ) electron stabilization of the γ carbonium ion causing an increase in their ability to destannylate[6]. Interestingly enough, in comparing compounds 13 and 14 the loss of γ-BuOH/Bu is on the average[7] ~3.0 times greater for 13 than it is for 14, but in both compounds loss of HCl is the predominant fragmentation after protonation of the chloride by CH_5^+. These latter results point out the valuable nature of CI MS in studying the interaction of carbon-tin σ electrons with carbonium ion centers, free of solvent effects, in the gas phase.

An example of this type of carbon-tin σ stabilization via neighboring group participation[8], in the gas phase, is illustrated with compound 4.



We are continuing our studies on the CI MS of organotin compounds to further elucidate electrophilic reactions in the gas phase for comparison with those occurring in solution.[†]

References

1. F. H. Field, Accounts Chem. Res., 1, 42 (1968), and references therein.
2. D. F. Hunt, J. W. Russell and R. L. Torian, J. Organometal. Chem., 43, 175 (1972).
3. All new compounds gave appropriate elemental analyses and spectroscopic data.
4. The CI mass spectra were obtained on a Finnigan 1015D instrument (methane~1 Torr) coupled with a System Industries Model 150 computer with plotter. The source temperature was 100° and the probe temperature was varied from 50-175° depending on compound volatility.
5. M. Gielen and J. Nasielski, "Organotin Compounds", Ed. A. K. Sawyer, Vol. 3 p. 625, Dekker, New York (1972).
6. H. G. Kuivila and N. Scarpa, J. Amer. Chem. Soc., 92, 6990 (1970).
7. Compound 13 was found to be extremely temperature sensitive when introduced by the solid probe technique. Caution is therefore needed in interpreting the results with this type of compound.
8. T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton and R. S. Brown, J. Amer. Chem. Soc., 93, 5715 (1971).

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