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ELECTRON IMPACT FRAGMENTATION OF SOME ORGANOTIN COMPOUNDS

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Apart from the mass spectrum of tetramethyltin reported in general studies of the fragmentation of Group IVB tetramethyls (1,2) there appears to be no data available on the electron impact fragmentation of organotin compounds. Such information is useful not only for structure determination but more generally in classifying the fragmentation modes attributable to the presence of heteroatoms.

The principal ion species observed in the mass spectra of the compounds studied are listed in Table 1, and the appearance potentials and heats of formation of some fragment ions in Table 2. Ionization efficiency curves were similar to that of krypton used in calibration except for the Sn ion in $SnMe_4$ and the SnPh ion in $SnPh_4$. For these a correction was applied for the low intensity tails following Warren's method (3). Heats of formation were obtained using the experimental value of $\Delta H_f SnMe_4$ (4) and values of 112 Kcal/mole for $\Delta H_f SnPh_4$ and -56 Kcal/mole for $\Delta H_f SnPr_4$ calculated by Franklin's method (5). The value of $\Delta H_f Sn^+$

TABLE 1.

Relative Intensity of Principal Peaks in the Mass Spectra of Organotin Compounds.

Compound SnR_4		M.	SnR_3	SnR_2H	SnR_2	$SnRH_2$	SnR	$SnCH_3$	SnH_3	SnH	Sn	R
I	R = Me	0.6	100	x	21	x	27	27	x	6	12	2
II	R = Et	3	100	91	2	56	46	1	2	40	15	1
III	R = Pr	0.1	66	100	x	93	26	8	13	56	16	7
IV	R = Bu	0.1	58	80	1	100	21	3	14	43	9	4
V	R = Vi	0.1	100	58	27	10	66	x	x	29	92	1
VI	R = Ph	0.2	100	2	42	x	57	x	x	x	71	7

VII	$SnBu_2Vi_2$	M	$SnBu_2Vi$	$SnBuVi_2$	SnBuViH	$SnVi_2H$	$SnViH_2$	SnVi	SnH_3	SnH	Sn	Bu
		0.1	2	90	7	100	24	32	1	21	12	2

VIII	$SnEt_3F$	M	$SnEt_3$	$SnEt_2F$	$SnEt_2H$	$SnEt_2$	SnEtFH	SnEtF	$SnEtH_2$	SnEt	SnF	SnH	Sn	Et
		11	4	100	5	2	8	11	4	55	74	14	8	28

x less than 1%

Me = CH_3 Et = C_2H_5 Pr = n-C_3H_7 Bu = n-C_4H_9 Vi = CH_2=CH Ph= C_6H_5

from the fragmentation of $SnPh_4$ is in good agreement with the value (243 Kcal/mole) quoted by Hobrock & Kiser (1).

TABLE 2

Appearance Potentials and Heats of Formation of Organotin Fragment Ions

Compound	Ion	Appearance Potential (eV)	ΔH_f (Kcal/mole)	Neutral Products
$SnMe_4$	$SnMe_3$	9.7 ± 0.2 ‡ (9.9 ± 0.15)	179	$CH_3^{\cdot}$
	$SnMe_2$	13.0 ± 0.2 ‡ (13.1 ± 0.2)	224	$2CH_3^{\cdot}$
	† Sn	17.5 ± 0.5 ‡ (18.1 ± 0.3)	266	$4CH_3^{\cdot}$
$SnPr_4$	$SnPr_3$	8.8 ± 0.2	125	$C_3H_7^{\cdot}$
	$SnPr_2H$	10.6 ± 0.2	161	$C_3H_6 + C_3H_7^{\cdot}$
$SnPh_4$	$SnPh_3$	10.1 ± 0.2	279	$Ph^{\cdot}$
	$SnPh_2$	9.1 ± 0.2	278	Ph_2
	† SnPh	16.1 ± 0.5	288	$3Ph^{\cdot}$
	Sn	9.4 ± 0.2	241	$2Ph_2$

† Low intensity Type 1 tail (3). ‡ Data of Hobrock & Kiser (1).

The data presented in Tables 1 and 2 together with observed metastable transitions lead to the recognition of three major modes of fission. Fragmentation of the molecular ion by elimination of a ligand radical is common to all compounds; the elimination of either ligand occurs in compounds having mixed ligands. Further elimination of ligand radicals occurs only in the spectra of $SnMe_4$ and $SnPh_4$

$$\overset{+}{\mathrm{Sn}}\mathrm{Me}_3 \xrightarrow[*]{} .\overset{+}{\mathrm{Sn}}\mathrm{Me}_2 \xrightarrow[*]{} :\overset{+}{\mathrm{Sn}}\mathrm{Me}$$

$$\overset{+}{\mathrm{Sn}}\mathrm{Ph}_3 \xrightarrow[*]{} .\overset{+}{\mathrm{Sn}}\mathrm{Ph}_2 \quad \text{and} \quad :\overset{+}{\mathrm{Sn}}\mathrm{Ph} \xrightarrow[*]{} :\overset{+}{\mathrm{Sn}}$$

(reactions confirmed by the appropriate metastable ions are indicated by a star) whilst appearance potential measurements support the occurrence of

$$(\mathrm{SnMe}_4)^{+\cdot} \longrightarrow :\overset{+}{\mathrm{Sn}} + 4\mathrm{Me}^{\cdot} \quad \text{and} \quad (\mathrm{SnPh}_4)^{+\cdot} \longrightarrow :\overset{+}{\mathrm{Sn}}\mathrm{Ph} + 3\mathrm{Ph}^{\cdot}$$

Ligand loss by elimination of an unsaturated hydrocarbon with hydrogen rearrangement gives rise to many of the intense peaks observed in the spectra of compounds II, III, IV, V, and VII. This process is a minor one in fragmentation of the molecular ion but a major one in the fragmentation of (M-R) ions. The reactions

$$\overset{+}{\mathrm{Sn}}\mathrm{R}_3 \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{R}_2\mathrm{H} \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{RH}_2$$

occur in the mass spectra of compounds II, III, IV and V. Dibutyldivinyltin (VIII) fragments by the elimination of butene according to the scheme

$$\overset{+}{\mathrm{Sn}}\mathrm{Bu}_2\mathrm{Vi} \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{BuViH} \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{ViH}_2$$

and $\overset{+}{\mathrm{Sn}}\mathrm{BuVi}_2 \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{Vi}_2\mathrm{H}$

The analogous elimination

$$\overset{+}{\mathrm{Sn}}\mathrm{Et}_2\mathrm{F} \xrightarrow[*]{} \overset{+}{\mathrm{Sn}}\mathrm{EtFH}$$

is observed in the spectrum of triethyltinfluoride (VIII). In keeping with recent results (6,7) on hydrogen transfer in the fragmentation of even-electron ions, no specificity of hydrogen transfer is assumed in these reactions. Reactions involving the elimination of a neutral molecule from an even-electron ion are frequently observed (8) in the spectra of organic compounds and may be attributed to the relative stability of the new even-electron ion formed. (The further process $\overset{+}{\mathrm{Sn}}\mathrm{RH}_2 \xrightarrow[*]{} :\overset{+}{\mathrm{Sn}}\mathrm{R}$ was observed in the spectra of II and III.)

The elimination of neutral ligand pairs by the reactions

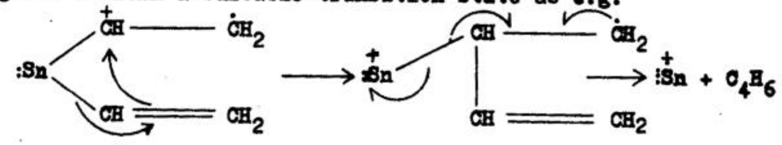
$$\overset{+}{\mathrm{Sn}}\mathrm{Me}_3 \xrightarrow[*]{} :\overset{+}{\mathrm{Sn}}\mathrm{Me}$$

$$\overset{+}{\mathrm{Sn}}\mathrm{Vi}_3 \xrightarrow[*]{} :\overset{+}{\mathrm{Sn}}\mathrm{Vi} \qquad .\overset{+}{\mathrm{Sn}}\mathrm{Vi}_2 \xrightarrow[*]{} \vdots\overset{+}{\mathrm{Sn}}$$

$$(\mathrm{SnPh}_4)^{+\cdot} \xrightarrow[*]{} .\overset{+}{\mathrm{Sn}}\mathrm{Ph}_2 \xrightarrow[*]{} \vdots\overset{+}{\mathrm{Sn}}$$

$$\begin{tikzcd} & :\overset{+}{\mathrm{Sn}}\mathrm{F} \\ \overset{+}{\mathrm{Sn}}\mathrm{Et}_2\mathrm{F} \arrow[ur, "*"'] \arrow[dr, "*"] & \\ & :\overset{+}{\mathrm{Sn}}\mathrm{Et} \end{tikzcd}$$

were observed in the spectra of compounds I,V,VI and VIII respectively. Expulsion reactions (9) in which two moieties not directly bonded in a molecule are found combined in a fragment ion have been observed in the fragmentation of aromatic (10) and aliphatic (11) sulphides, esters of arylphosphonic acids (12), aromatic epoxides (13), and compounds of the type Ar-X-Y-Z-Ar (14). The ligand pair eliminations occurring in the mass spectra of the organotin compounds may be regarded as an expulsion reaction in which the positive charge is retained on the central moiety. The driving force for these reactions may be derived from the ability of the ligands to form a suitable transition state as e.g.



It may also arise from the ability of tin to form stable fragment ions having one or more unpaired electrons, and from lower energy required to eliminate a radical pair as a molecule.

In contrast to the corresponding lead alkyls (15), the spectra of tin alkyls show a low abundance of ions from which part of a ligand has been lost. However the reaction

$$:\overset{+}{Sn}R \xrightarrow[*]{} :\overset{+}{Sn}CH_3$$

was observed in the spectra of III and IV.

The effect of multiple metal valence on the fragmentation of metal co-ordination compounds has been noted (16). The extension of these principles to covalent tin compounds predicts the radical-pair eliminations observed but not the radical eliminations. Although there is no *a priori* reason why the elimination of a ligand radical from the molecular ion giving an even-electron ion should not occur in both classes of compounds, the fragmentation process giving a new radical-ion with a lower metal valence appears to occur preferentially in co-ordination compounds. In covalent tin compounds, the species ${}^{IV}\overset{+}{Sn}R_3$, $({}^{II}SnR_2)^{+\cdot}$, ${}^{II}\overset{+}{Sn}R$ all occur abundantly.

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After this work was concluded the mass spectra of compounds II and VI appeared in the literature (17). The fragmentations described are in agreement with those presented here.

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