Mass Spectral Studies of the Anhydrous Methyl Tin Nitrates †

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The mass spectra for the series of compounds $Me_xSn(NO_3)_{4-x}$ (x = 0—3) have been examined at 70 and 20 eV. The fragmentation patterns for the complexes are suggested with the aid of metastable-ion studies. Fragmentation paths are found to be similar to other alkyltin systems in that marked preference isshown for Sn^{IV} and Sn^{II} valence states in tin-containing fragments. Removal of the first nitrate group from the parent ion is accomplished by NO_3 elimination; however, subsequent nitrate elimination proceeds, in part, *via* stepwise fragmentation of the nitrate group involving N–O bond rupture.

THE series of compounds, $Me_xSn(NO_3)_{4-x}$ ($x = 0$—3), have been the subject of several recent structural studies. Crystallographic data for $Sn(NO_3)_4$ [1] show that the molecule contains four symmetrically bidentate nitrate groups while Mössbauer evidence indicates that eight tin orbitals are used in Sn–O bond formation.[2] Asymmetric bidentate nitrate groups are present in both $MeSn(NO_3)_3$ and $Me_2Sn(NO_3)_2$ [3,4] and the number of tin orbitals used in bonding are seven and six respectively.[2] The compound Me_3SnNO_3, however, is polymeric in the solid state, with bridging nitrates [2] and five tin orbitals are involved in bonding.[2]

Since all the compounds of this series are both volatile and relatively thermally stable, it was thought that electron-impact studies might provide an interesting insight into the fragmentation patterns for the nitrate group in bridging and bidentate co-ordination modes. While mass spectral data for a variety of alkyltin halides have been documented,[5] no such information has been reported for an organotin nitrate. Indeed, information concerning fragmentation patterns for organometallic nitrates in general is scarce.

EXPERIMENTAL

The compounds $Me_xSn(NO_3)_{4-x}$ (x = 0—3) were prepared by literature methods.[6-9] Mass spectra were obtained on an A.E.I. MS-30 double-beam mass spectrometer at 70 and 20 eV with a 4 kV accelerating voltage, resolution being set at 1000 with a 300 μA trap current. Spectra of the compounds were found to be unchanged with source temperatures of either 100 or 200 °C; however, due to the volatile nature of the complexes, source temperatures of 80—100 °C were normally used. Samples were admitted to beam 1 *via* the direct probe at room temperature, while (PFK) (low boiling) was admitted *via* a gas/liquid probe into beam 2 to serve as a chemical mass marker. Since the complexes are extremely moisture sensitive, the samples were loaded in a dry-box into concentric glass crucibles. The crucibles were kept in sealed glass vials prior to insertion into the probe. The probe and lock assembly could be surrounded by a N_2-filled dry bag when necessary.

Isotopic patterns for particular ions were calculated using the FORTRAN program BMASROS ‡ while relative abundances of overlapping isotopic multiplets for various ions were computed by a least-squares fit of the output of BMASROS to the observed spectrum using the FORTRAN program BMASBD.§ All computations were carried out on a B5500 computer. Metastable transitions were studied by the MIKES technique described previously.[10] Normal metastables were not observed in the routine spectra of the compounds but were initially detected by inserting the sample into beam 2, setting the voltage ratio of the modified beam 2 deflector plate (10) equal to m_2/m_1 for a transition $m_1 \longrightarrow m_2$. A magnetic scan resulted in only ions due to m_2 and m^* ($= m_2^2/m_1$) reaching the beam 2 detector. The resulting suppression of normal ions permitted use of maximum gain to detect the m^* peaks, while the masses of m^* could be accurately measured with respect to PFK as a mass marker in beam 1, which is unaffected by the beam 2 deflector voltage setting.[11]

RESULTS AND DISCUSSION

Spectra obtained at 70 and 20 eV were essentially identical; however, the metastable ion and mass-analysed ion kinetic-energy spectra were much more intense at 20 eV. Consequently, all results have been calculated from the 20 eV spectra. The partial mass spectra of the compounds [tabulated in Supplementary Publication No. SUP 21241 (11 pp.)||] are expressed as a percentage of total positive-ion current for tin-containing species with all isotopic contributions to a particular species summed. It should be noted, however, that the strongest *single* peaks in the spectra of $Sn(NO_3)_4$, $MeSn(NO_3)_3$, and $Me_2Sn(NO_3)_2$ are due to the ions NO^+ and NO_2^+ (Table 1). Thermal decomposition cannot be ruled out as a source of some of these ions.

All four compounds, in spite of their higher co-ordination number, exhibit fragmentation patterns similar to those found for tetravalent tin.[5] Thus, the parent molecular ion is absent from the spectra of all four compounds and the most abundant ion fragments are those containing tin in the +4 oxidation state. The

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‡ D. Rosenthal, Research Triangle Institute, North Carolina; personal communications to J. M. M.

§ Listings of this program written by J. M. M. are available from the author.

|| For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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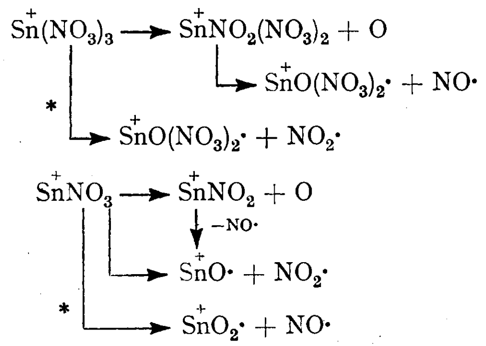
TABLE 1

Relative ion abundance of NO^+ and NO_2^+ compared to strongest ^{120}Sn peak

Ion	$Sn(NO_3)_4$	$MeSn(NO_3)_3$	$Me_2Sn(NO_3)_2$	Me_3SnNO_3
NO^+	25·0	7·8	2·2	0·11
NO_2^+	16·3	7·7	1·24	0·08
$^{120}Sn(NO_3)_3^+$	1·0			
$Me^{120}Sn(NO_3)_2^+$		1·0		
$Me_2{}^{120}SnNO_3^+$			1·0	1·0

tendency for the odd-electron parent ion to undergo radical elimination, in this case either $NO_3\cdot$ or $CH_3\cdot$, has been well documented for compounds containing sp^3 hybridized tin.[5] Only the spectrum of Me_3SnNO_3 has ion species, in low abundance, of higher molecular weight than that expected for the parent molecular ion. Ion clusters with *m/e* values of 335—323 and 305—293 have observed tin isotopic patterns consistent with those computed for Sn_2^+ species, suggesting empirical formulas of the type $Sn_2^+NO_2Me_3$ and $Sn_2^+OMe_3$ respectively. This behaviour may well be a result of the polymeric nature of the compound in the solid state.[2] Also, consistent with the similarity in fragmentation patterns between the tin nitrates and other four-co-ordinate tin systems, the next most abundant ions contain tin in the +2 oxidation state, while ions containing Sn + 5, Sn + 3, and Sn + 1 make only small contributions to the total tin-ion current.

The mass spectrum of $Sn(NO_3)_4$ allows the fragmentation pattern of tin nitrate species, free from methylated or hydrogenated ions, to be established. The first NO_3 group is eliminated from the parent molecular ion apparently by simultaneous cleavage of two Sn–O bonds. Further removal of the nitrate groups can occur by Sn–O bond rupture but also takes place by stepwise fragmentation of $SnNO_3$ species. Thus, N–O bonds are broken, yielding $NO\cdot$ or $NO_2\cdot$ as in the following:



* (metastable ion supported)

Apparently elimination of the first NO_3 radical effects a strengthening of the remaining Sn–O bonds, lessening their susceptibility to bond rupture while, at the same time, a weakening of the N–O bonds occurs.

The molecule $MeSn(NO_3)_3$ clearly fragments by paths (a) or (b):

(a) $Me\overset{+}{Sn}(NO_3)_3\cdot \longrightarrow Me\overset{+}{Sn}(NO_3)_2 + NO_3\cdot \longrightarrow$ Fragments

(b) $Me\overset{+}{Sn}(NO_3)_3\cdot \longrightarrow \overset{+}{Sn}(NO_3)_3 + CH_3\cdot \longrightarrow$ Fragments

As with $Sn(NO_3)_4$, elimination of the first nitrate group from the parent ion occurs by cleavage of two Sn–O bonds; however, competition between Sn–O and N–O bond breaking takes place for the fragmentation of both $Me\overset{+}{Sn}(NO_3)_2$ and $\overset{+}{Sn}(NO_3)_3$. Fragmentation by path (a) will result in the formation of methylated and hydrogenated ions (*e.g.* $Me\overset{+}{Sn}ONO_3\cdot$, $\overset{+}{Sn}OH$) as well as the rearrangement ion $Me_2\overset{+}{Sn}NO_3$. The remaining ions in the spectrum arise from both $Me\overset{+}{Sn}(NO_3)_2$ *via* (a) and $\overset{+}{Sn}(NO_3)_3$ *via* (b). It would be expected, by statistical arguments, that the contribution to the total positive ion current of tin-containing ions generated by (a) would be three times that of ions generated by (b). For a particular ion formed by both fragmentation schemes (*e.g.* $\overset{+}{Sn}NO_3$), the contribution due to (b) can be crudely estimated from the spectrum of $Sn(NO_3)_4$, showing that fragmentation arising from (a) occurs six times more readily than that arising from (b). $NO_3\cdot$ Elimination from the parent molecular ion is preferred to $CH_3\cdot$ elimination by a factor of 2 : 1.

The mass spectrum of $Me_2Sn(NO_3)_2$ exhibits many of the features found for $MeSn(NO_3)_3$. The parent molecular ion fragments according to schemes (c) or (d):

(c) $Me_2\overset{+}{Sn}(NO_3)_2\cdot \longrightarrow Me_2\overset{+}{Sn}NO_3 + NO_3\cdot \longrightarrow$ Fragments

(d) $Me_2\overset{+}{Sn}(NO_3)_2\cdot \longrightarrow Me\overset{+}{Sn}(NO_3)_2 + CH_3\cdot \longrightarrow$ Fragments

Further fragmentation of $Me_2\overset{+}{Sn}NO_3$ and $Me\overset{+}{Sn}(NO_3)_2$ involves N–O bond breaking in addition to Sn–O and Sn–C bond rupture. The contribution to a particular ion current by (d) can be estimated from the spectrum of $MeSn(NO_3)_3$. This shows that path (c) is favoured to path (d) by a factor of 3 : 1 and, hence, again $NO_3\cdot$ elimination from the parent molecular ion is preferred to $CH_3\cdot$ elimination. This preference is seen to be somewhat greater than that found for $MeSn(NO_3)_3$. The apparent weaker tin–nitrate interaction in $Me_2\overset{+}{Sn}(NO_3)_2\cdot$ compared to that in $Me\overset{+}{Sn}(NO_3)_3\cdot$ parallels the situation found for the neutral molecules, for which it has been shown that weaker Sn–O bonding occurs in the case of the dinitrate.[2,4,7,12]

The fragmentation pattern of Me_3SnNO_3, while similar to the other methyltin nitrate complexes, is unusual in that the parent molecular ion eliminates $CH_3\cdot$ more readily than $NO_3\cdot$. Thus, fragmentation can occur *via* routes (e) or (f)

(e) $Me_3\overset{+}{Sn}NO_3\cdot \longrightarrow Me_2\overset{+}{Sn}NO_3 + CH_3\cdot \longrightarrow$ Fragments

(f) $Me_3\overset{+}{Sn}NO_3\cdot \longrightarrow Me_3Sn^+ + NO_3\cdot \longrightarrow$ Fragments

and the contribution to a particular ion current due to (e) can be calculated using the spectrum of $Me_2Sn(NO_3)_2$. Fragmentation *via* (e) is observed to be preferred to (f)

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[12] D. Potts, Ph.D. Thesis, University of Toronto, 1970.

by a factor of 6 : 1, compared to a predicted ratio of only 3 : 1. In this respect, $\mathrm{Me_3SnNO_3}$ resembles other $\mathrm{R_3SnX}$ systems (R = alkyl, X = halogen) (5), where the base peaks arise from $\mathrm{R_2\overset{+}{Sn}X}$ ions. The apparently stronger tin–nitrate interaction in $\mathrm{Me_3\overset{+}{Sn}NO_3}$ may be a consequence of a different mode of nitrate co-ordination.

Metastable Ions.—Metastable transitions were not observed in the routine spectra of the compounds, the peaks being obscured by the polyisotopic nature of tin. Metastable ions were observed, however, by the MIKES technique[10] and magnet scans with particular m_2/m_1 ratios set in the beam 2 deflector, but such transitions were virtually absent in spectra obtained at 70 eV and were only observed at ionizing voltages of 20 eV, whereas the normal ion spectra were relatively unchanged between 70 and 20 eV. The number of observable transitions was found to increase as the degree of methylation of the tin atom increased. These transitions are presented in Table 2.

TABLE 2

Metastable ion supported transitions for the compounds $\mathrm{Me_{\mathit{x}}Sn(NO_3)_{4-\mathit{x}}}$ (x = 0—3)

$\mathrm{Sn(NO_3)_4}$	$\mathrm{MeSn(NO_3)_3}$
$\mathrm{\overset{+}{Sn}(NO_3)_3} \longrightarrow \mathrm{\overset{+}{Sn}O(NO_3)_2\cdot + NO_2\cdot}$ (a, b)	$\mathrm{Me\overset{+}{Sn}(NO_3)_2} \longrightarrow \mathrm{Me\overset{+}{Sn}NO_3\cdot + NO_3\cdot}$ [a, c]
$\mathrm{\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}O_2\cdot + NO\cdot}$ (w) (a)	$\mathrm{Me\overset{+}{Sn}(NO_3)_2} \longrightarrow \mathrm{Me\overset{+}{Sn}ONO_3\cdot + NO_2\cdot}$ [a, b]
	$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + C_2H_6}$ [a, b]
	$\mathrm{Me\overset{+}{Sn}ONO_3\cdot} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + CH_3O\cdot}$ [a, b]
$\mathrm{Me_2Sn(NO_3)_2}$	$\mathrm{Me_2SnNO_3}$
$\mathrm{Me\overset{+}{Sn}(NO_3)_2} \longrightarrow \mathrm{Me\overset{+}{Sn}NO_3\cdot + NO_3\cdot}$ (a–c)	$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me_2\overset{+}{Sn}O\cdot + NO_2\cdot}$ [a–c]
$\mathrm{Me\overset{+}{Sn}(NO_3)_2} \longrightarrow \mathrm{Me\overset{+}{Sn}ONO_3\cdot + NO_2\cdot}$ (a–c)	$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me_2\overset{+}{Sn}\cdot + NO_3\cdot}$ (w) [a, c]
$\mathrm{Me\overset{+}{Sn}(NO_3)_2} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + MeNO_3}$ (a–c)	$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me\overset{+}{Sn} + MeNO_3}$ [a, c]
$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + C_2H_6}$ (a–c)	$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + C_2H_6}$ [a–c]
$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me_2\overset{+}{Sn}O\cdot + NO_2\cdot}$ (a–c)	$\mathrm{Me_3\overset{+}{Sn}} \longrightarrow \mathrm{Me\overset{+}{Sn} + C_2H_6}$ [a–c]
$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me_2\overset{+}{Sn}\cdot + NO_3\cdot}$ (w) (a, c)	$\mathrm{Me_3\overset{+}{Sn}} \longrightarrow \mathrm{Me_2\overset{+}{Sn}\cdot + CH_3\cdot}$ [a–c]
$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}Me + MeNO_3}$ (a–c)	$\mathrm{Me_2\overset{+}{Sn}O\cdot} \longrightarrow \mathrm{\overset{+}{Sn}O\cdot + C_2H_6}$ [a–c]
$\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{EtNO_3 + \overset{+}{Sn}H}$ (w) (a, b)	$\mathrm{Me_2\overset{+}{Sn}O\cdot} \longrightarrow \mathrm{Me\overset{+}{Sn}O + CH_3\cdot\ (Me_2\overset{+}{Sn}\cdot + 0)}$ (w) [a–c]

w = weak.

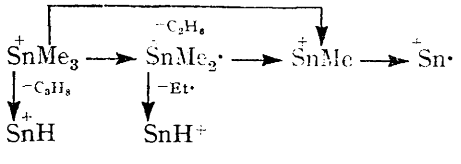
[a] m_2 Detected by magnetic scan with beam 2 deflector voltage = m_2/m_1. [b] m^* Detected by magnetic scan with beam 2 deflector voltage = m_2/m_1. [c] Transition observed in MIKE spectrum.

Metastable peaks arising from the fragmentations

$$\mathrm{Me_3\overset{+}{Sn}} \longrightarrow \mathrm{Me\overset{+}{Sn} + C_2H_6}$$

$$\mathrm{Me_3\overset{+}{Sn}} \longrightarrow \mathrm{Me_3\overset{+}{Sn}\cdot + CH_3\cdot}$$

are among those reported by Fishwick and Wallbridge[13] for the fragmentation of $\mathrm{Me_3\overset{+}{Sn}}$ ions observed in the mass spectrum of $\mathrm{Me_4Sn}$. Their complete fragmentation pattern for this ion is shown in the following scheme:



We were not able to detect metastable peaks corresponding to the remaining fragmentations. This is probably due to the relatively low abundance of $\mathrm{Me_3\overset{+}{Sn}}$ found in the spectrum of $\mathrm{Me_3SnNO_3}$.

The metastable transition, $\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{Me_2\overset{+}{Sn}O\cdot + NO_2\cdot}$, is observed in the spectra of both $\mathrm{Me_3SnNO_3}$ and $\mathrm{Me_2Sn(NO_3)_2}$. This transition could also conceivably correspond to the fragmentation, $\mathrm{Me_2\overset{+}{Sn}NO_3} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + Me_2O}$, as both daughter ions have $m/e = 166$ (based on ^{120}Sn). The former scheme is thought to be of greater importance since a weak peak at $m/e = 167$ is observed in the spectrum of $\mathrm{Me_2Sn(NO_3)_2}$ presumably due to $\mathrm{Me^{13}CH_3SnO}$. This peak is, as expected, absent in the spectra of $\mathrm{MeSn(NO_3)_3}$ and $\mathrm{Sn(NO_3)_4}$, but cannot be resolved from peaks associated with $\mathrm{Me_3\overset{+}{Sn}}$ in the spectrum of $\mathrm{Me_3SnNO_3}$.

The metastable transition, $\mathrm{Me\overset{+}{Sn}ONO_3\cdot} \longrightarrow \mathrm{\overset{+}{Sn}NO_3 + CH_3O\cdot}$, observed in the spectrum of $\mathrm{MeSn(NO_3)_3}$, is unusual in that it arises from one of the few metastable ions found using ionization voltages of 70 eV; it is absent when voltages of 20 eV are used.

Thus, although the complete fragmentation schemes could not be verified by metastable ion studies, an interesting series of fragmentations are observed. Despite structural evidence in the solid and solution phases for bidentate or bridging nitrate groups, the mass spectra surprisingly show no major deviations from those of the alkyltin halides.

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[13] M. Fishwick and M. G. H. Wallbridge, *J. Chem. Soc.* (*A*), 1971, 57.