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UNIMOLECULAR AND COLLISION INDUCED DECOMPOSITIONS OF GAS-PHASE GROUP IVA ENIUM IONS $(CH_3)_3M^+$

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Summary

The fragmentation characteristics of the trimethyl-Group IV cations have been studied using mass analyzed ion kinetic energy (MIKE), $V^{1/2}/E$ (linked) metastable and consecutive reaction monitoring techniques. Both unimolecular (low energy) and collision induced (high energy) decompositions were studied. These methods give information on the ion of interest without interfering contributions from the precursor ion of the trimethyl cation. The results have been interpreted in terms of the decreasing metal—carbon bond strength and the increasing preference for the +2 oxidation state going down Group IV from carbon to lead.

Introduction

We report here a mass spectral investigation of isolated trimethyl-Group IV (C, Si, Ge, Sn, and Pb) cations employing both unimolecular and collision induced dissociation metastable analyses. The purpose of the reported experiments was to gain insight into the structures and fragmentations of the isolated trimethyl cations, with the hope of forming accurate generalizations concerning fragmentation within the Group. The applicability of mass analyzed ion kinetic energy (MIKE) and $V^{1/2}/E$ collision induced decomposition (CID) spectroscopy to the study of organometallic ion chemistry is of additional interest.

This work is related to the work on the tetramethyl-Group IV compounds by

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De Ridder and Dijkstra [1]. They determined fragmentation mechanisms primarily by studying the intensities of source formed ions and also by investigating metastable transitions. These are techniques which are complementary to the methods used in the present work. Group IV organometallic compounds have also been the subject of several other mass spectrometry studies [2—8], and Levsen has previously investigated the t-butyl cation using collisional activation spectroscopy [9]. These studies provide benchmark experiments which allow comparison with the chemistry presently observed and evaluation of the experimental techniques used.

Results and discussion

Mass analyzed ion kinetic energy (MIKE) scans of both unimolecular and collision induced dissociation (CID) processes are one of two scans employed in this work (see Fig. 1 for a typical MIKE scan). This scan benefits from mass selection of the $(CH_3)_3M^+$ ion prior to analysis, which precludes observation of decompositions of the parent $(CH_3)_3MX$ radical cation. A second advantage is that only one isotope containing species is mass selected, and, as a result, decompositions appear as single peaks instead of as isotopic clusters. The existence of several isotopes often makes the quantitative interpretation of the mass spectra of organometallic compounds confusing. The MIKE scan suffers from poor resolution, a problem which becomes more severe as the mass of the parent ion increases.

The second type of analysis used was the $V^{1/2}/E$ (linked) scan (see Fig. 2 for a typical $V^{1/2}/E$ scan). For this scan the daughter ions from the $(CH_3)_3M^+$ are sequentially focussed at a higher resolution than is attainable using a MIKE scan. The drawbacks of the $V^{1/2}/E$ scan include poor ion statistics and artifact peaks which appear at adjacent masses as a result of refocussing of broad metastable transitions [10]. In addition, only ions whose masses are greater than one-half the mass of the $(CH_3)_3M^+$ parent ion are sampled.

The data for the five trimethyl cations are given in Tables 1—5. The MIKE spectra are expressed as a relative abundance (R.A.) percentage of the total fragment ion current which can be converted to millivolts of signal per volt of signal of the $(CH_3)_3M^+$ ion (i.e., the main beam). For example, the 22% R.A.

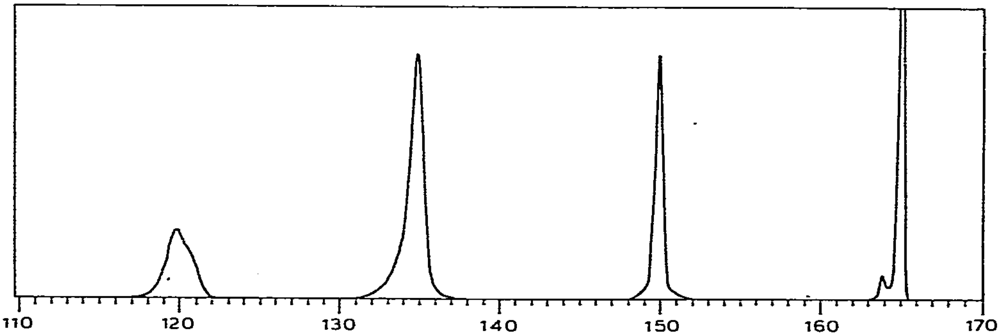


Fig. 1. Typical MIKE scan. Collision induced decomposition (CID) of trimethylstannyl cation. $(CH_3)_3Sn^+$ parent ion occurs at *m/e* 165.

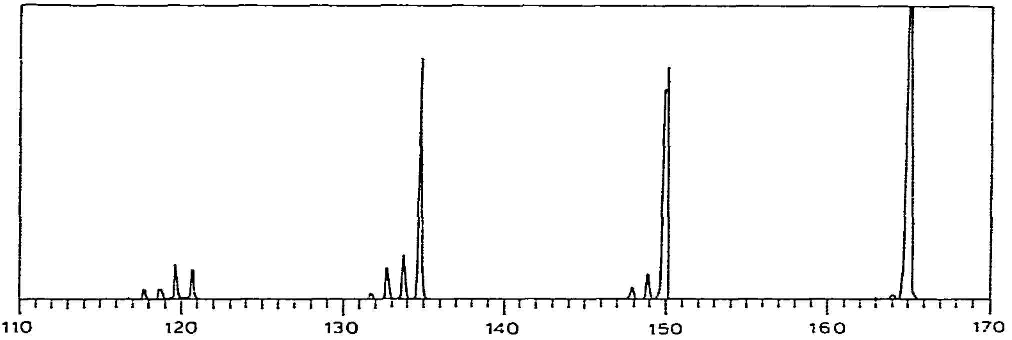
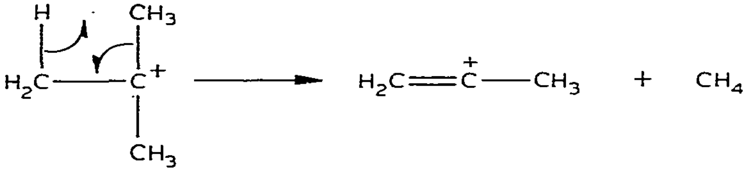


Fig. 2. Typical $V^{1/2}/E$ (linked) scan. Collision induced decomposition (CID) of trimethylstannyl cation. $(CH_3)_3Sn^+$ parent ion occurs at m/e 165.

CH_4 elimination seen in the MIKE CA spectrum of the t-butyl cation corresponds to 25 mV per volt main beam. The $V^{1/2}/E$ data are expressed as a relative abundance percentage of the intensity of the base peak. The CID data have not been corrected for metastable contributions because these account for no more than 6% of the absolute intensity of any given peak. Unimolecular $V^{1/2}/E$ scans suffered from poor reproducibility as a result of low signal intensities and, accordingly, were not performed.

$C(CH_3)_3^+$

The dominant unimolecular process for the t-butyl cation is loss of CH_4 (eq. 1), and this process is accompanied by a small loss of H_2 as well (see Table 1). There is also an important loss of ethylene, which will increase in significance in the context of the other $M(CH_3)_3^+$ ions (see below). These processes and a loss of H account for most of the low-energy fragmentations detected as unimolecular processes.



(1)

The same processes are also dominant in the collision induced spectrum. New high energy paths, now opened because of collision, account for no more than 20% of ion current, and the two most prominent of these are methyl cleavage from t-butyl and from its $(M - CH_4)^+$ ion formed in eq. 1. These processes are the most obvious high energy processes to be anticipated among collision-induced reactions because they correspond to simple cleavages, however energetically unfavorable [11].

The $V^{1/2}/E$ data do not include significant H losses; instrumental reasons prevented our acquiring the C(2) and C(3) envelope. The agreement of $V^{1/2}/E$ and MIKE spectra of the C(1) envelope is qualitative.

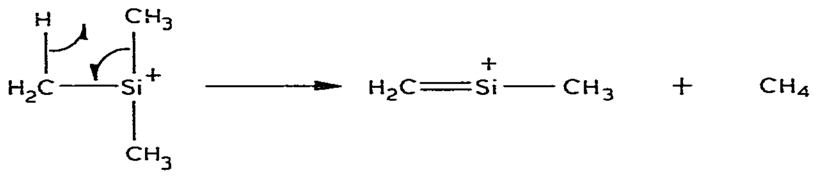
TABLE 1

t-BUTYL CATION

Loss	MIKE unimolecular R.A.	MIKE CA R.A.	$V^{1/2}/E$ CA R.A.
H	9.4	14.4	
H_2		2.6	0.1
H_3		0.4	
H_4		2.3	
H_5		0.5	
H_6		2.2	0.1
H_7		2.2	
H_8		0.4	
CH_2		0.1	
CH_3		3.9	5.8
CH_4	81.3	22.0	100.0
CH_5		2.5	7.2
CH_6	4.2	18.9	58.1
CH_7		3.9	11.0
CH_8		2.1	6.3
CH_9		0.4	1.1
C_2H_4	3.1	9.5	
C_2H_5		1.6	
C_2H_6	2.1	7.7	
C_2H_7		1.4	
C_2H_8		0.3	
C_3H_6		0.7	
C_3H_7		0.2	

$Si(CH_3)_3^+$

The low-energy decompositions of the trimethyl silyl ion are no longer dominated by CH_4 loss, which would require the formation of a double bond to silicon (eq. 2). Instead the C_2H_4 loss is seven times more intense than in the t-butyl cation (see Table 2). This process is obviously a rearrangement. Little analogy exists for the postulation of a carbon—silicon scrambling which may be intercepted by the fragmentation (eq. 3).



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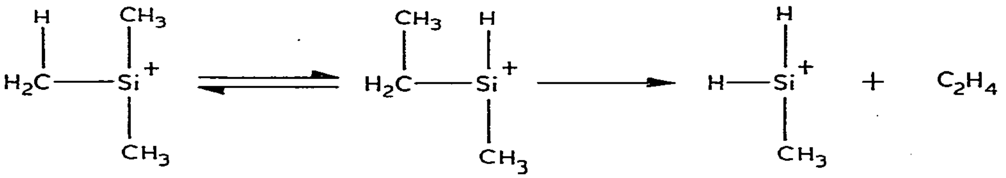

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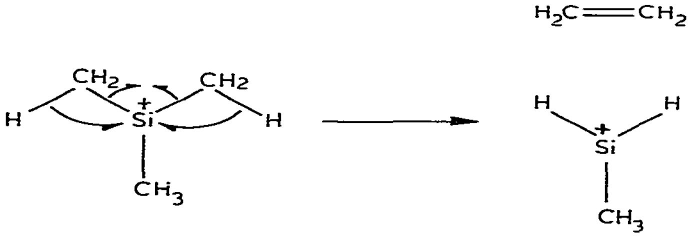
TABLE 2

TRIMETHYLSILYL CATION

Loss	MIKE unimolecular		MIKE CA		$V^{1/2}/E$ CA	
	mV/V	R.A. (%)	mV/V	R.A. (%)	R.A. (%)	S.D.
H	0.16	10.3	14.75	13.9		
H_2	0.02	1.3	1.62	1.5		
H_3			0.91	0.9		
H_4			0.10	0.1		
H_6			0.18	0.2		
H_7			0.21	0.2		
H_8			0.13	0.1		
CH_2			0.51	0.5		
CH_3	0.04	2.6	8.59	8.1	8.0	1.6
CH_4	0.02	1.3	2.83	2.7	2.1	0.9
CH_5			0.51	0.5		
CH_6	0.01	0.6	3.84	3.6	2.1	0.5
CH_7			0.81	0.8		
CH_8	0.01	0.6	3.84	3.6	2.4	0.3
C_2H_4	1.17	75.0	20.61	19.5	100.0	11.2
C_2H_5	0.03	1.9	5.45	5.2	22.5	2.0
C_2H_6	0.07	1.9	23.64	22.4	82.9	12.4
C_2H_7	0.02	1.3	6.26	5.9	21.4	3.0
C_2H_8			1.82	1.7	6.9	0.9
C_3H_6			0.91	0.9		
C_3H_7			0.20	0.2		
C_3H_8	0.01	0.6	4.95	4.7		
C_3H_9	2.32	2.2				
$SiCH_6$			0.30	0.3		
$SiCH_7$			0.10	0.1		
SiC_2H_6			0.30	0.3		
SiC_2H_7			0.10	0.1		

On the other hand, the increased loss of C_2H_4 after collisional activation may be ascribed either to further decompositions of low-energy rearranged $EtMeSiH^+$ or to a contribution similar to that in eq. 4 [2]. For the mechanism depicted in eq. 4, elimination of C_2H_4 would be achieved by the extension of vibrations rather than through an activated complex bringing together distant ends of the molecule (as shown in eq. 3). The mode of decomposition shown in eq. 4 would be entropically competitive with cleavages [11]. Again, loss of CH_3 increases in relative importance, as does the loss of C_2H_6.

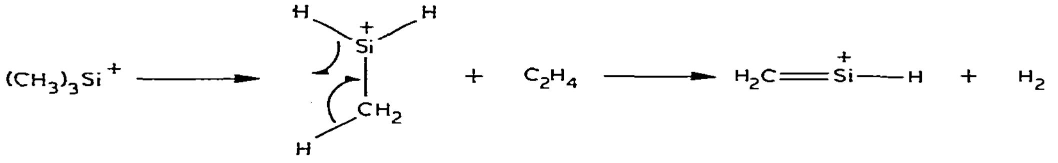


(4)

The collision induced elimination of C_2H_6 could be achieved by the cleavage of two methyl groups to give a $SiCH_3^+$ ion (see eq. 5). Alternatively, loss of C_2H_6 could arise from the loss of H_2 from the $H_2MCH_3^+$ ion (formed by loss of C_2H_4, see eq. 4), a sign that the high-energy doubly-bonded silicon is now accessible by collision (see eq. 6). These two mechanistic possibilities were further investigated by monitoring consecutive reactions using a unique feature of the triple analyzer mass spectrometer [12]. In these experiments, the mass spectrometer was focussed on the $(CH_3)_2Si^+$ and $CH_3SiH_2^+$ ions resulting from collision induced decompositions occurring in the first field free region of the mass spectrometer. The unimolecular decompositions of these ions in the third field free region were then recorded (see Fig. 3,4). The unimolecular metastable spectrum of the $(CH_3)_2Si$ (loss of CH_3) ions formed in this experiment was dominated by the loss of CH_3, which accounted for 87% of the total metastable ion current. The absolute intensity of the signal was 1.2 mV/V of first field free region metastable signal. The corresponding spectrum of the CH_3SiH_2 (loss of C_2H_4) ions showed that the loss of H_2 accounted for greater than 93% of the total metastable ion current. The absolute intensity of this transition was 0.5 mV/V of first field free region metastable signal.

These consecutive reaction experiments suggest that both of the mechanisms (eq. 5 and 6) are operative. The ratio of the two collision induced C_2H_6 elimination processes, estimated using the absolute intensities (mV/V) and the [CH_3 loss]/[C_2H_4 loss] intensities in Table 2, was 1.5/1.0.

$$(CH_3)_3Si^+ \longrightarrow (CH_3)_2Si^{+\bullet} + \bullet CH_3 \longrightarrow H_3C\text{—}Si^+ + \bullet CH_3 \qquad (5)$$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A third mechanistic alternative for the C_2H_6 elimination is the loss of H_2 from $(CH_3)_3Si^+$ followed by the loss of C_2H_4. This possibility was not investi-

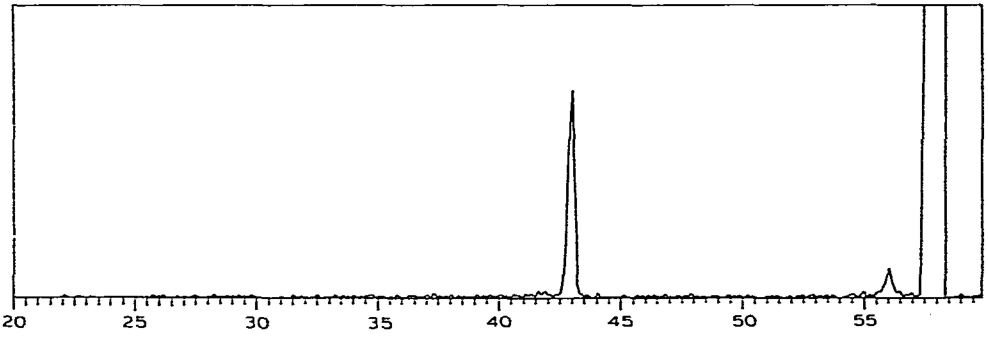


Fig. 3. Unimolecular MIKE scan of *m/e* 58 ($(CH_3)_2Si^+$) formed from a collision induced decomposition of $(CH_3)_3Si^+$ in the first field free region of the mass spectrometer (see eq. 5).

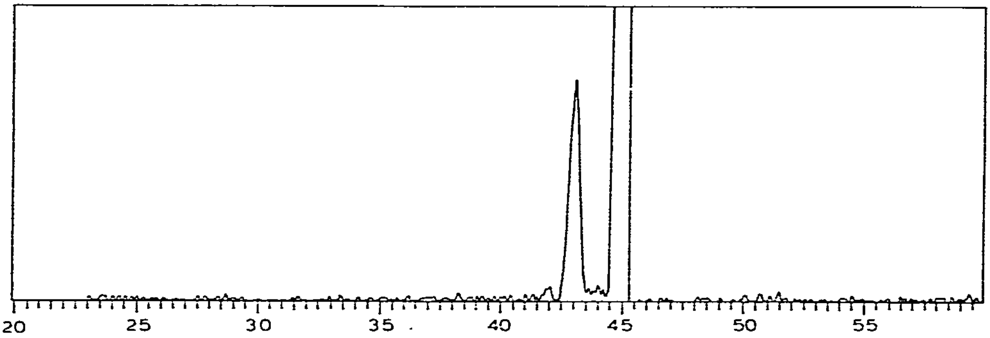


Fig. 4. Unimolecular MIKE scan of *m/e* 45 ($CH_3SiH_2^+$) formed from a collision induced decomposition of $(CH_3)_3Si^+$ in the first field free region of the mass spectrometer (see eq. 6).

gated via the consecutive reaction technique because the intensity of the H_2 loss was too low (see Table 2).

The only peak of >4% intensity not related to these or other simple cleavage products by the shedding of H or H_2 is the SiH^+ ion (loss of C_3H_8). Its intensity serves as a guide to the importance of high-energy silicon(II) forms.

Ge(CH₃)₃⁺

The trimethylgermyl cation likewise undergoes a low-energy loss of ethylene, probably by a process similar to eq. 4, and there are low-energy losses of methyl and C_2H_6. Since a double bond to Ge is not as likely as one to Si, the substantial signal for the loss of C_2H_6 is not likely to be the high-energy $HGe{=}CH_2^+$ and is assigned to the formation of the germanium(II) species CH_3Ge^+ by loss of two methyl groups. Methyl losses also dominate the high-energy fragmentations. The other germanium(II) species, HGe^+, also accounts for a greater share of the high-energy spectrum, and an atomic ion Ge^+ is substantial.

TABLE 3

TRIMETHYLGERMYL CATION

Loss	MIKE unimolecular		MIKE CA		$V^{1/2}/E$ CA	
	mV/V	R.A. (%)	mV/V	R.A. (%)	R.A. (%)	S.D.
H	0.02	4.8	13.03	9.8		
CH_3	0.05	11.9	34.55	26.1	49.8	7.1
CH_4			3.64	2.8	4.3	0.3
CH_6			1.02	0.8	1.3	0.1
CH_8			0.76	0.6		
C_2H_4	0.31	73.8	10.91	8.2	82.8	18.1
C_2H_6	0.04	9.5	49.17	37.1	100.0	10.9
C_3H_8	0.01		10.39	7.9	27.6	7.5
C_3H_9	0.01		8.94	6.8	18.3	2.5

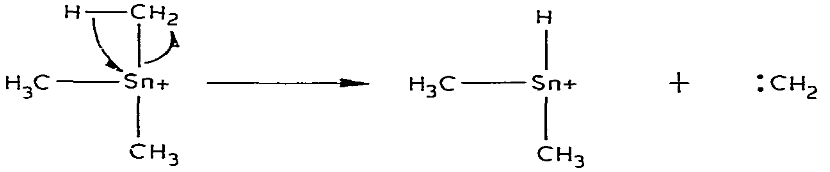
TABLE 4

TRIMETHYLSTANNYL CATION

Loss	MIKE unimolecular R.A. (%)	MIKE CA R.A. (%)	$V^{1/2}/E$ CA R.A. (%)
H	2.3	3.6	
CH_2	6.0		
CH_3	74.9	39.1	100.0
C_2H_6	13.1	39.1	99.2
C_3H_8	1.7	7.6	11.7
C_3H_9	2.0	10.7	14.2

$Sn(CH_3)_3^+$

In the trimethylstannyl spectra, the unimolecular processes are dominated by losses of one, two, and three methyl groups. The loss of ethylene is completely bypassed, suggesting that alternative reaction pathways remove ions which cannot conjoin CH_2 groups at low energy, possibly because of the size of the central atom. Curiously, a loss of CH_2 appears, a rare process in unimolecular mass spectra. This loss may signal that a process like eq. 7 is favorable, and it is probably reflective of the stability of the +4 oxidation state. Since the loss of CH_2 is not enhanced by collision, the process may require a stepwise rearrangement. In the high-energy spectra, the loss of two methyl groups to give the tin(II) species CH_3Sn^{II} is about as important as in the Ge compound. Most other peaks are related to the successive loss of methyl groups or H. The HSn^+ ion also appears in unimolecular processes.



(7)

$Pb(CH_3)_3^+$

The trimethylplumbyl ion shows only losses of methyl groups and of CH_2; here lead(II) is so important that loss of C_2H_6 dominates both the low-energy and the high-energy processes. Equally, the atomic species (Pb^+) accounts for more of the ion current than in any other spectrum. The PbH^+ ion (loss of C_3H_8) is detected only in the $V^{1/2}/E$ scan. It cannot be detected in the MIKE scan because of less than unit resolution for the higher mass parent. The behavior of the Pb containing ions completes the trends detected in the Si, Ge, and Sn ions.

Several generalizations can be made about the data in Tables 1—5. As the size of the central metal in the trimethyl cation becomes larger, the collision induced decomposition spectra become less complicated, consisting only of the

TABLE 5

TRIMETHYLPLUMBYL CATION

Loss	MIKE unimolecular R.A. (%)	MIKE CA R.A. (%)	$V^{1/2}/E$ CA R.A. (%)
H		2.3	
CH_2	4.0		
CH_3	27.0	33.6	38.1
C_2H_6	58.6	47.1	100.0
C_3H_8			2.4
C_3H_9	10.3	17.0	15.8

successive removal of methyl radicals. This behavior is similar to that observed by Weber, Visel and Levsen in the CID spectrum of $(n\text{-}C_4H_9)_4Sn$ [13]. The relationship between spectral simplicity and the size of the metal is probably reflective of the decreasing carbon—metal bond strength as we go down the Group, as had been suggested by De Ridder and Dijkstra in their study of the tetramethyl-Group IV compounds [1]. This would mean that rearrangements are no longer competitive with simple metal—carbon bond cleavages [2].

Another trend present in the collision induced decomposition data is the increasing relative intensity of the $M(CH_3)^+$ (loss of C_2H_6) ion as the central atom goes from carbon to lead. This is further evidence of the increasing importance of the +2 oxidation state, a trend which has been observed in the electron impact mass spectra of several organometallic Group IV compounds, including the tetramethyl derivatives [1].

Two other ions in the CID data serve to illustrate competition between the two trends discussed above: increasing importance of the +2 oxidation state and decreasing carbon—metal bond strength. These are the losses of C_3H_8 and C_3H_9, respectively. The ratio of C_3H_8 elimination to C_3H_9 elimination steadily decreases, suggesting that the weakness of the carbon—metal bond is the salient factor influencing the fragmentation of the trimethyl-tin and -lead cations.

Conclusions

The data presented here illustrate the utility of combining analysis of low-energy and high-energy decomposition spectra of ions to assess qualitatively the energetics of formation of multiply bonded and low-valent species in organometallics. Elimination of CH_4 in the CID spectrum of the trimethyl-silyl and -germyl cations is evidence for multiply bonded species of these elements. The intensity of the $M—C_2H_6$ ion in the various spectra demonstrates the preference of the Group IV cations for the +2 oxidation state. The consecutive reaction experiments used to investigate the elimination of C_2H_6 from the $(CH_3)_3Si$ ion provide a direct approach to the study of multiple and competing mechanisms.

The MIKE and $V^{1/2}/E$ CID spectra are significantly different for several of the ions studied. This occurs because ions of shorter lifetime are sampled in the $V^{1/2}/E$ scan. Furthermore, poorer ion statistics pertain to the $V^{1/2}/E$ method because the peaks are more narrow and the source detunes as the spectrum is acquired [10,14]. As a result, the standard deviation (s.d.) for peak height measurements was as large as 14%. In addition, $V^{1/2}/E$ scans are known to suffer from interfering metastable decompositions originating from ions one and two amu removed from the ion of interest (main beam) [14]. These interferences also contribute to the discrepancy between the $V^{1/2}/E$ and MIKE data. Since the source is not defocussed in the case of the MIKE scans, the ion transmission is greater and the uncertainty in these scans is on the order of 1 to 2%.

For the above reasons, the MIKES experiments are considered to be a better source of reliable quantitative information. Nevertheless, the $V^{1/2}/E$ scans produce valuable qualitative information, which is free from isotopic interferences. This is important for organometallic ions. The $V^{1/2}/E$ technique also does not require a reverse geometry mass spectrometer, as does the MIKE experiment. Therefore, it is a more generally applicable technique.

Experimental

The t-butyl ion was prepared from t-butyl chloride; $(CH_3)_3Si^+$ from tetramethylsilane; $(CH_3)_3Ge^+$ from bromotrimethylgermane; $(CH_3)_3Sn^+$ from tetramethyltin; $(CH_3)_3Pb^+$ from trimethyllead acetate.

Several Group IV elements are characterized by an abundance of isotopes. Ions chosen for analysis contained abundant isotopes and no substantial interference from isobaric ions of other compositions: m/e 57 for $C_4H_9^+$, m/e 73 for $SiC_3H_9^+$, m/e 119 for $GeC_3H_9^+$, m/e 165 for $SnC_3H_9^+$, and m/e 253 for $PbC_3H_9^+$.

The instrument employed was a Kratos MS-50 triple analyzer (EBE) mass spectrometer which is equipped with collision cells in the first and third field free regions. Ions were made in the source at 250° C using 70 eV electrons. In the case of the MIKE scan, the ions were accelerated from the source at 8 kV. The trimethyl cation of interest was mass selected using the first electrostatic sector and the magnet. Decompositions occurring in the third field free region were sequentially detected at the collector by scanning the second electrostatic sector. The $V^{1/2}/E$ scans sample decompositions occurring in the first free region and are produced by scanning the accelerating voltage and the two electrostatic sector voltages upward such that $V^{1/2}/E$ is a constant. The parent ion is observed at 2 kV, followed by the lower mass daughter ions which are focussed as the voltages are increased. Collisional activation spectra were acquired by bleeding He into the appropriate collision cell until the intensity of the parent ion was suppressed by 30%. A few of the peaks in the MIKE spectra of the Ge, Sn and Pb ions were not resolved and their intensities are approximate. A typical experiment (MIKE and $V^{1/2}/E$) consisted of summing approximately 20 scans using a Data General Nova 4 computer and software written in the Nebraska laboratory.

The consecutive reaction experiments (see Figs. 3 and 4) were performed by setting the first electrostatic sector to pass the appropriate first field free region collision induced decomposition. The magnet was then set to focus at m_2^2/m_1, where m_2 was either m/e 58 (loss of CH_3) or m/e 45 (loss of C_2H_4) and m_1 was m/e 73 ($(CH_3)_3Si^+$) in both cases. The second electrostatic sector was then scanned to record unimolecular decompositions occurring in the third field free region.

Acknowledgement

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