Journal of Organometallic Chemistry, 373 (1989) 143–152
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20019

Distinguishing 1,2-cyclopentanediol isomers via gas-phase reactions with trimethyl-group 14 cations

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(Received February 6th, 1989; in revised form April 7th, 1989)

Abstract

Reactions with trimethyl-group 14 $(CH_3)_3X^+$ ions (X = C, Si, Ge, Sn) are used to distinguish between *cis*- and *trans*-1,2-cyclopentanediol isomers in a triple quadrupole mass spectrometer. At a kinetic energy of 1.2 eV (center of mass), there are substantial differences in the decomposition behavior of the $[M + (CH_3)_3X]^+$ adducts, particularly for trimethylsilyl and trimethylgermyl ions. The *cis*-1,2-cyclopentanediol isomer favors decomposition of $[M + (CH_3)_3X]^+$ to produce a hydrated trimethyl-group 14 ion $[(CH_3)_3XOH_2]^+$. For the *trans*-diol, formation of $[(CH_3)_3XOH_2]^+$ apparently is an endothermic process requiring additional energy input. At the ion kinetic energy employed, *trans*-1,2-cyclopentanediol exhibits greater adduct ion stabilities. The trimethylgermyl reactant was found to be more sensitive and stereochemically selective than the other group 14 cations. The t-butyl ion in contrast provided the least effective stereochemical probe.

Introduction

There have been numerous studies involving reactions of the trimethylsilyl ion with alcohols, ethers and several aliphatic diols [1–5]. A majority of the studies have utilized tetramethylsilane chemical ionization (CI) in a single analyzer instrument. These investigations and additional ion cyclotron resonance (ICR) experiments [6,7] have revealed the ability of the trimethylsilyl ion to generate abundant $[M + Si(CH_3)_3]^+$ adduct ions for many polar oxygenated compounds. The decomposition behavior of these adduct ions can provide information which permits isomer differentiation.

Recently, we have successfully distinguished between the *cis* and *trans* isomers of 1,2-cyclopentanediol by reactions with $[Si(CH_3)_3]^+$ precursor ions in a triple quadrupole mass spectrometer [8]. The trimethylsilyl ion is mass-selected in the first quadrupole (Q1) and subsequently transmitted into the second quadrupole (Q2)

0022-328X/89/$03.50

collision region. Yields of ion-molecule reaction products are monitored in the third quadrupole (Q3) as a function of precursor ion kinetic energy [9,10]. Therefore it is feasible to optimize stereochemical differences by controlling the reactant ion kinetic energy.

The purpose of this investigation is to examine other trimethyl-group 14 ions as possible alternative stereochemical probes. Tandem mass spectrometry with a triple quadrupole instrument allows mass selection of a single monoisotopic $[(CH_3)_3X]^+$ ion prior to analysis. Reactions of this specific ion with an appropriate collision gas may be observed. Isotopic and fragment ion interferences are thus effectively eliminated. Triple quadrupole mass spectrometry thus provides a highly sensitive and selective method for examining the gas-phase behavior of organometallic ions and their possible role in stereoisomer differentiation. Product ion mass spectra are compared at a single kinetic energy (1.2 eV, center of mass (COM)). The ion-molecule reactions for the trimethyl cations can distinguish *cis/trans* isomers of cyclic diols.

Experimental

(a) Chemicals

The *cis*-1,2-cyclopentanediol isomer was synthesized using a low temperature permanganate oxidation of cyclopentene [11] and purified by vacuum distillation, b.p. 124–125 °C (28 mmHg), lit. b.p. 88–92 °C (2 mmHg) [11]. The *trans*-1,2-cyclopentanediol isomer, obtained by oxidation of cyclopentene with performic acid [12], solidified at 54 °C, b.p. 138 °C (10 mmHg), lit. m.p. 52 °C; b.p. 103–104 °C (2 mmHg) [13]. NMR spectra were acquired (Bruker 250 MHz) to confirm the identity of the *cis*- and *trans*-1,2-cyclopentanediols. Mass spectra (70 eV) and chromatographic analysis indicated adequate purity.

The trimethyl group 14 ions were derived from the following sources: t-butyl ion from t-butyl chloride (Aldrich 99%), $Si(CH_3)_3^+$ from tetramethylsilane (Aldrich 99.9%), $Ge(CH_3)_3^+$ from bromotrimethylgermane (Alfa Products 98.6%) and $Sn(CH_3)_3^+$ from tetramethyltin (Aldrich 99%). In each case the ion chosen as the primary ion (which was mass-selected for reaction with the diols) for analysis was that of the most abundant isotope of the group 14 element, (^{28}Si, ^{74}Ge, and ^{120}Sn). In all the MS/MS spectra acquired the precursor ion is the base peak, but is deleted for the sake of clarity.

(b) Instrument

Ion-molecule reactions were studied with an ExtrEl triple quadrupole mass spectrometer. Precursor $[(CH_3)_3X]^+$ ions were generated by 70 eV electron ionization (EI) of t-butyl chloride, tetramethylsilane, bromotrimethylgermane and tetramethyltin. Ionization source temperature was 80 °C with typical sample pressures of 4×10^{-6} torr. The Q2 collision region remained near ambient temperature. Ions were detected with a Channeltron electron multiplier (Galileo Electro-Optics).

The source potential was held constant at 20 V and collision cell potential adjusted for each precursor ion giving an ion translational energy of 1.2 eV (center of mass (COM) frame of reference). Transmission efficiency and ion resolution were optimized by applying a potential of 10 V to the first quadrupole Q1. The $[(CH_3)_3X]^+$ ions formed in the source were mass-selected in Q1 and accelerated into

the collision region with a kinetic energy determined by the difference between the source and Q2 potentials. Low mass discrimination was effectively mitigated by setting the potential of the third quadrupole (Q3) to −2 V negative with respect to that of Q2 [9].

The *cis*- and *trans*-1,2-cyclopentanediol isomers were introduced into the collision region at an analyzer pressure (ion gauge) of 5×10^{-5} torr (multiple collision conditions) [14–16]. Under these conditions there was a greater than 60% attenuation of the main beam intensity. The relative abundances of the product ions in these experiments may be sensitive to the exact pressures of the two diols in the Q2 collision region as indicated by the high pressure CI and ICR studies on alcohols [4,6]. Therefore careful control of the analyzer pressure was maintained for each sample within ±3% resulting in fairly reproducible spectra. For both isomers, the inlet system was heated to achieve sufficient volatility. Product ion spectra were acquired by scanning Q3 over the mass range of interest. The kinetic energy of $[(CH_3)_3X]^+$ precursor ions can be varied to examine the effect on the relative intensities of ion-molecule reaction and decomposition products. However in this particular investigation, results are presented for a fixed COM energy of 1.2 eV for each $(CH_3)_3X^+$ ion.

Results and discussion

Ion-molecule reactions with $C(CH_3)_3^+$

The spectrum of product ions obtained by colliding the t-butyl ion with both isomers is dominated by unimolecular decomposition reactions which include elimination of CH_4 and a loss of ethylene to produce the $C_2H_5^+$ ion at *m/z* 29 (Fig. 1) [17]. Ions at $[M - OH]^+$ *m/z* 85, and $[M - OH - H_2O]^+$ *m/z* 67 are found in all trimethyl cation spectra. The $[M - OH]^+$ ion may be generated either by hydroxide abstraction from the diol or by collisional dissociation of the $[M + Si(CH_3)_3]^+$ adducts.

There is a slight difference between the isomers in the abundance of the *m/z* 159 $[M + C(CH_3)_3]^+$ adduct ion. The *trans*-1,2-cyclopentanediol isomer apparently favors adduct ion formation while the *cis*-diol preferentially decomposes to the hydrated t-butyl ion *m/z* 75 $[(CH_3)_3COH_2]^+$. The $[M + C(CH_3)_3 - H_2O]^+$ ion at *m/z* 141 is an additional ion-molecule reaction product in the *cis*-isomer spectrum. Although the mass spectra for the diol compounds are somewhat different, the relatively low abundance of any ion-molecule reaction products compared to those of the ions at *m/z* 41 and *m/z* 29 (the major unimolecular decomposition products of $[C(CH_3)_3]^+$) makes it difficult to distinguish the diol isomers. Comparison of the ratio of t-butyl ions (*m/z* 29, 41) to that of diol-related ions (*m/z* > 55) indicates that the total reaction cross section of the t-butyl ion with the two diol isomers is not significantly different. The slight difference in the abundance of $[M + C(CH_3)_3]^+$ may result from small fluctuations of sample pressure in the collision region.

Adduct ion generation for the electrophilic trimethyl group 14 cations and the 1,2-cyclopentanediol isomers is necessarily an exothermic process. The oxygen atom of the diol hydroxyl group serves as a nucleophilic site in bond formation [7]. The degree of adduct ion production can best be compared by considering the relative binding of each cation with a particular base. Stone has measured the following dissociation energies for group 14 trimethyl cations with water: $D[(CH_3)_3C^+ - OH_2]$

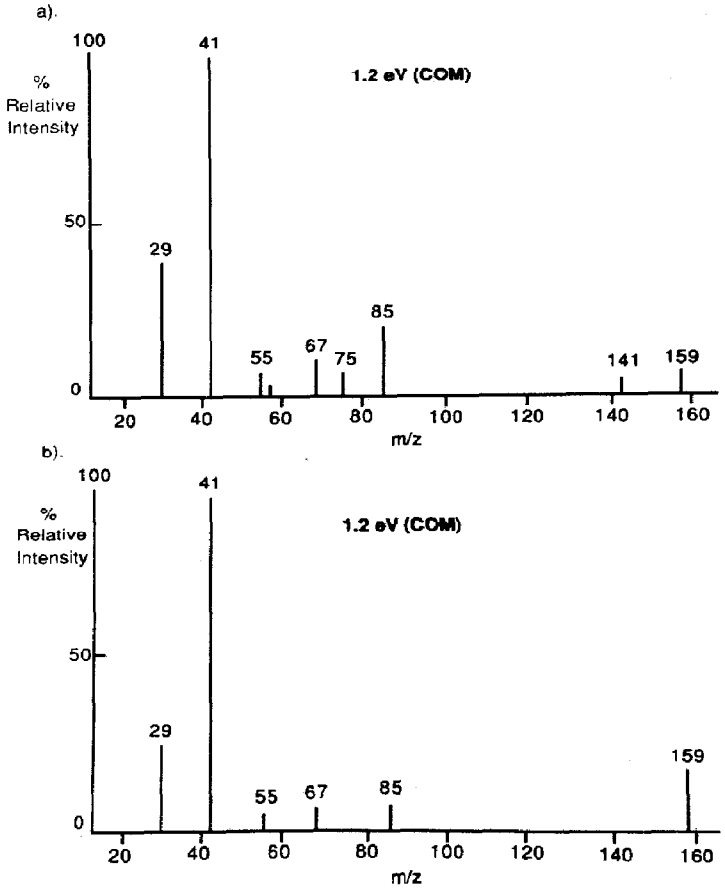


Fig. 1. Daughter ion mass spectra of t-butyl precursor ion; collision gas pressure is 5×10^{-5} torr (ion gauge); (a) *cis*-1,2-cyclopentanediol; (b) *trans*-1,2-cyclopentanediol.

11 kcal mol^{-1} [18] $D[(CH_3)_3Si^+ - OH_2]$ 30 kcal mol^{-1} [18], and $D[(CH_3)_3Sn^+ - OH_2]$ 25.7 kcal mol^{-1} [9].

The very low enthalpy of dissociation of $(CH_3)_3COH_2^+$ to $(CH_3)_3C^+$ and H_2O is indicative of the inherent stability of $(CH_3)_3C^+$. Solvation by a single H_2O molecule does not significantly stabilize the t-butyl cation. In contrast further stabilization of $(CH_3)_3Si^+$, $(CH_3)_3Ge^+$ and $(CH_3)_3Sn^+$ is possible. The higher binding energies of the trimethylsilyl, trimethylgermyl and trimethylstannyl cations are reflected in the greater adduct ion abundances found in their product ion spectra compared to the relatively small adduct seen for the t-butyl cation (Fig. 2–4).

Additional parameters such as the integral energy content of the precursor ion, collision cell pressure, collision cell temperature and steric hindrance effects may influence adduct ion formation. In the experiments conducted, the collision cell pressure and temperature remained constant (within experimental error). Although the initial internal energy content of the t-butyl precursor ion is decreased by thermalization from source collisions at high pressure, excess internal energy still results in the predominantly unimolecular decompositions involving losses of methane and ethylene.

Reactions with $Si(CH_3)_3^+$ cations

For low precursor ion kinetic energies (1.2 eV COM), there are significant differences in the product ion spectra of the two 1,2-cyclopentanediol isomers (Fig. 2). The major distinction results from the relative stabilities of the $[M + Si(CH_3)_3]^+$ adduct ions. The *m/z* 175 adduct ion is represented by the base peak in the *trans*-1,2-cyclopentanediol spectrum and a predominant peak in the *cis*-isomer spectrum. In the *trans*-diol, the absence of steric hindrance between vicinal hydroxyl groups results in a more highly stabilized adduct ion. [16]. However, even though it is of lower abundance, the *cis*-adduct may actually be more stable than the *trans*-adduct but have a lower barrier to fragmentation (as in the case of *cis*-NH_4^+ adducts) [20].

The extent of adduct ion formation depends on both the temperature and pressure of the Q2 collision region where the reactions with the diol compounds occur. Prior investigations have determined that adduct ion production is generally observed at relatively low temperatures provided the adduct ion has sufficient degrees of freedom [6,21]. Since the collision region remained at ambient tempera-

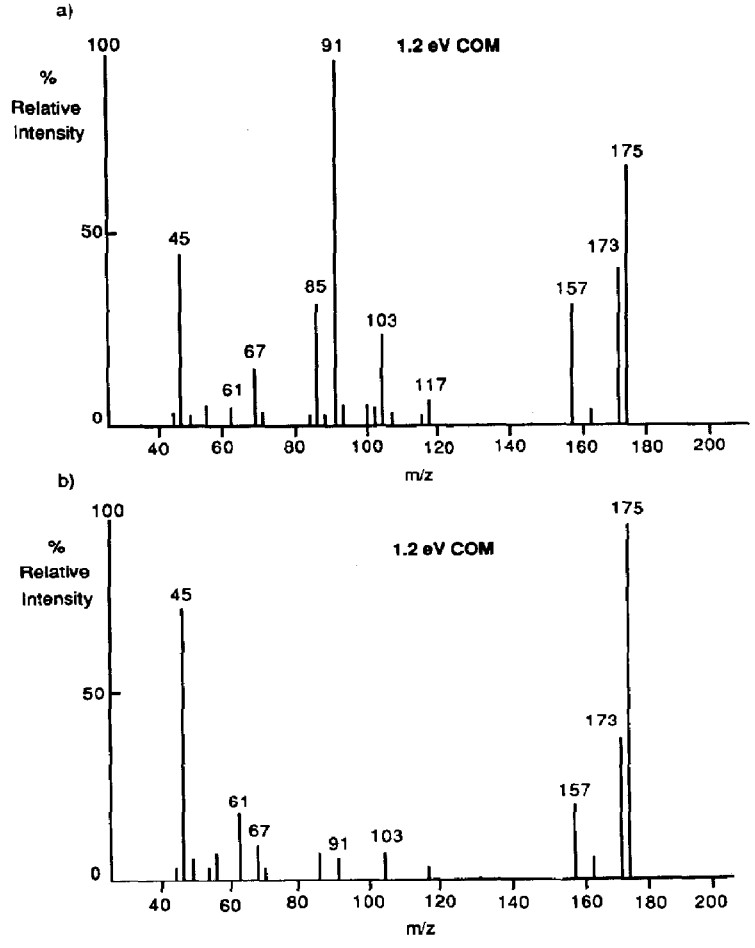


Fig. 2. Daughter ion mass spectra of trimethylsilyl precursor ion; collision gas pressure is 5×10^{-5} torr (ion gauge): (a) *cis*-1,2-cyclopentanediol; (b) *trans*-1,2-cyclopentanediol.

ture for all the experiments conducted, significant adduct ion abundances can be expected. Concerning the actual mechanism of adduct ion formation, a simple bimolecular addition reaction resulting in Si–O bond formation between the trimethylsilyl ion and one oxygen atom of the diol has been postulated [8]. This mechanism would require some additional interaction with the second vicinal hydroxyl group in the molecule.

At the low precursor ion kinetic energy of 1.2 eV (COM), one of the reactions of the trimethylsilyl ion with the *cis*-1,2-cyclopentanediol isomer is highly stereoselective. There is a major exothermic decomposition channel which yields the hydrated trimethylsilyl ion at *m/z* 91. In contrast, for the *trans*-diol, the *m/z* 175 adduct ion is more stable at the lower ion kinetic energies and decomposes to *m/z* 91 only at higher energies. Previous experiments for the *trans*-isomer have indicated a definite threshold ion kinetic energy, above which the trimethylsilyl ion transfers enough internal energy to the *m/z* 175 collision complex to create the hydrated trimethylsilyl ion [8]. At precursor ion kinetic energies significantly greater than this threshold value, $[Si(CH_3)_3OH_2]^+$ is represented by the base peak in the product ion spectrum.

In the unimolecular decomposition of the trimethylsilyl ion, the loss of ethylene predominates to yield $H_2SiCH_3^+$ at *m/z* 45 [17]. Past multiple collision studies have suggested that protonation of the *cis*-diol forming $[MH]^+$ at *m/z* 103 can occur by subsequent collisions with $Si(CH_3)_3OH_2^+$ [1,8]. The hydrated trimethylsilyl ion can also react with the diols by ligand exchange to give $[M + Si(CH_3)_3]^+$ [2–4]. The amount of $Si(CH_3)_3OH_2^+$ present in the *trans*-diol spectrum is so small that it could arise from reactions with background water present in the collision region of the instrument. Additional ions seen at *m/z* 157 $[M + Si(CH_3)_3 - H_2O]^+$ and *m/z* 173 $[M + Si(CH_3)_3 - H_2]^+$ are created by further decomposition of the *m/z* 175 adduct ion. Labeling experiments confirming their structures are described in detail in a previous paper [8].

Reactions with $Ge(CH_3)_3^+$ cations

The trimethylgermyl cation reacts with both 1,2-cyclopentanediol isomers to produce an abundance of $[M + Ge(CH_3)_3]^+$ adducts ions at *m/z* 221 (Fig. 3). As was the case with the trimethylsilyl ion, at a given precursor ion kinetic energy, the *trans*-diol also has the greater adduct ion stability. The *cis*-1,2-cyclopentanediol isomer participates in a stereoselective decomposition to the *m/z* 137 hydrated trimethylgermyl ion $[Ge(CH_3)_3OH_2]^+$. Water loss from the adduct (primarily the *cis*-diol adduct) yields the $[M + Ge(CH_3)_3 - H_2O]^+$ ion at *m/z* 203 (Scheme 1).

In the mass spectra of both isomers, the formation of ion-molecule reaction products such as $[M + Ge(CH_3)_3]^+$ is favored over unimolecular decompositions. The *m/z* 221 adducts are observed in greater relative abundance compared to either the trimethylsilyl or trimethylstannyl cation spectra. Although there are no values reported in the literature pertaining to the binding energies of the trimethylgermyl cation, the greater adduct ion abundances obtained in this investigation suggest that $Ge(CH_3)_3^+$ may well have a higher binding energy than the trimethylsilyl ion. ICR experiments have also revealed more abundant adduct ions with $Ge(CH_3)_3^+$ than for its corresponding silicon analog [22].

Furthermore, germanium has an anomalously higher electronegativity than either silicon or tin. Based upon the Allred and Rochow scale, the group 14 elements are

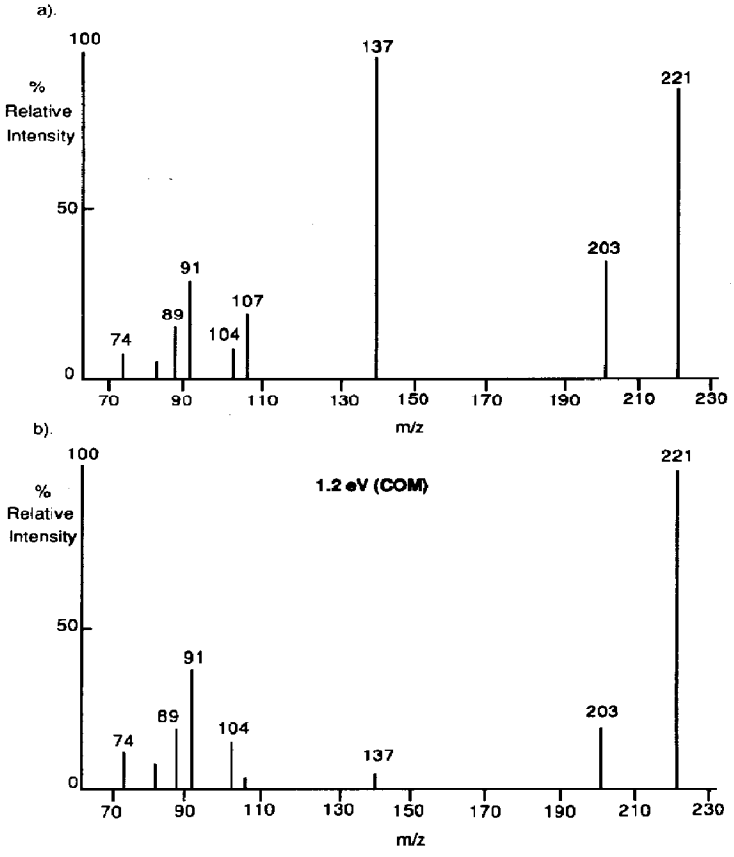
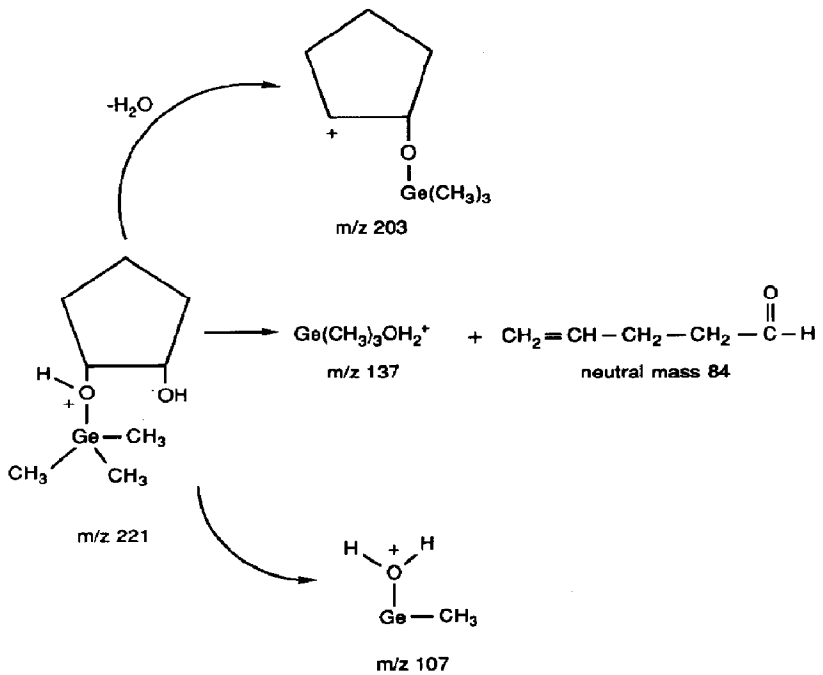


Fig. 3. Daughter ion mass spectra of trimethylgermyl precursor ion; collision gas pressure is 5×10^{-5} torr (ion gauge): (a) *cis*-1,2-cyclopentanediol; (b) *trans*-1,2-cyclopentanediol.



Scheme 1. Decomposition of the m/z 221 $[M + Ge(CH_3)_3]^+$ adduct ion for trimethylgermyl precursor ion.

assigned the following relative electronegative values: (Si = 1.90; Ge = 2.01; Sn = 1.94) [23]. Germanium and silicon have approximately the same size atomic radius. Thus any steric hindrance effects are negligible.

The trimethylgermyl cation undergoes a low-energy elimination of ethylene by a process similar to that of the trimethylsilyl ion to produce the *m/z* 91 ion $[H_2GeCH_3]^+$ [17]. Further unimolecular decomposition products of $[Ge(CH_3)_3]^+$ involving losses of methyl and C_2H_6 are discussed in an earlier paper [17]. The observation of *m/z* 89 $[Ge(CH_3)]^+$ and *m/z* 107 $[Ge(CH_3)OH_2]^+$ in the mass spectra of both isomers emphasizes the elevated importance of the germanium +2 oxidation state in comparison to ions where germanium has a +4 charge. However CAD products such as $Ge(CH_3)_2^+$ (*m/z* 104) and $Sn(CH_3)_2^+$ (*m/z* 150) with a +3 formal oxidation state are found in similar abundance in both the trimethylgermyl and trimethylstannyl spectra. This suggests that ions with metals/metalloids in the +2 oxidation state have no special stability.

Reactions with $Sn(CH_3)_3^+$ cations

The trimethylstannyl cation is equally effective as a stereochemical probe compared to its silicon and germanium analogs especially in regard to stereoselective

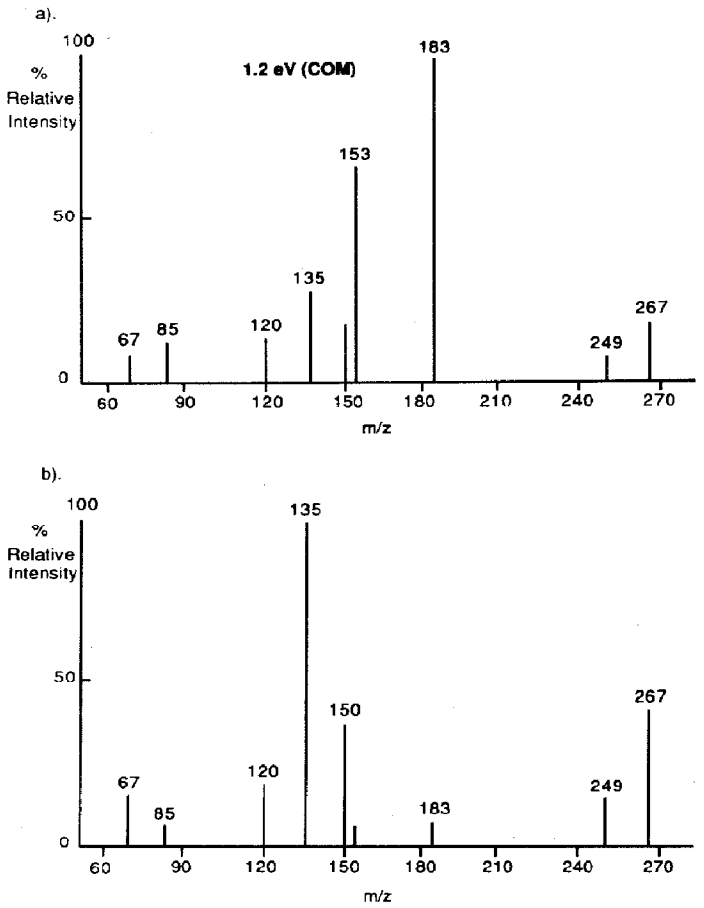


Fig. 4. Daughter ion mass spectra of trimethylstannyl precursor ion; collision gas pressure is 5×10^{-5} torr (ion gauge): (a) *cis*-1,2-cyclopentanediol; (b) *trans*-1,2-cyclopentanediol.

$[Sn(CH_3)_3OH_2]^+$ formation. At the relatively low precursor ion kinetic energy of 1.2 eV, the hydrated trimethylstannyl ion $[Sn(CH_3)_3OH_2]^+$, m/z 183, is signified by the base peak in the *cis*-diol spectrum but is only about 10% relative abundance in the spectrum of the *trans*-diol. The $[M + Sn(CH_3)_3]^+$ adduct ion (m/z 267), although no longer the base peak in the spectrum, is of greater relative abundance for *trans*-1,2-cyclopentanediol (Fig. 4). Interestingly, an abundant tin(II) hydrated ion $[Sn(CH_3)OH_2]^+$ m/z 153 is observed for the *cis*-isomer in accordance with the tendency for the higher atomic number group 14 elements to accommodate both +2 and +4 oxidation states [24].

The decreased adduct ion abundances in the trimethylstannyl spectra are reflective of the larger atomic radius of the tin atom. A larger atomic radius results in a less stabilized adduct ion because of increased steric hindrance. As the size increases, the metal becomes more polarizable and rearrangement reactions are less competitive with simple metal-carbon bond cleavages [25]. The mass spectra observed for the trimethylstannyl ion support this hypothesis. Unimolecular decompositions involving successive losses of methyl groups become more important relative to the formation of stereoselective ion-molecule reaction products (Fig. 4). In this respect, the $Sn(CH_3)_3^+$ ion is perhaps less sensitive than its silicon or germanium analogs.

For the trimethylstannyl precursor ion, the major decomposition pathway involves the loss of C_2H_6 [17]. The predominant ion in the *trans*-isomer spectrum is $[Sn(CH_3)]^+$ at m/z 135. The relative abundances of unimolecular decomposition products are consistent with previously obtained helium CID (collision induced decomposition) spectra of gas-phase $[Sn(CH_3)_3]^+$ ions [17]. The ions at m/z 150 $[Sn(CH_3)_2]^+$ and m/z 120 Sn^+ are of significant intensity and provide additional proof of the importance of the unimolecular decomposition process for the larger group 14 trimethyl cations. Furthermore, these experiments suggest that the trimethylplumbyl cation would probably be a less sensitive stereochemical probe than $[Sn(CH_3)_3]^+$. Precursors to $[(CH_3)_3Pb]^+$ were not available to us to test this hypothesis.

Conclusions

Both the trimethylgermyl and trimethylstannyl precursor ions provide useful alternative stereochemical probes for the differentiation of 1,2-cyclopentanediol isomers. In particular, the trimethylgermyl ion is more sensitive than its silicon analog, producing a greater relative abundance of analytically useful ion-molecule reaction products. The t-butyl ion is the least effective; its mass spectra are dominated by the presence of unimolecular decomposition products. Adduct ion formation depends on several factors including precursor ion internal energy, steric hindrance, electrophilicity of the group 14 element and trimethyl cation binding energy. Generally, detection of adduct ions is favored for precursor ions having low internal energy and containing a central atom of high electronegativity and small atomic radius. For $[Sn(CH_3)_3]^+$ and to a lesser extent $[Ge(CH_3)_3]^+$, ions observed are representative of both the +4 and +2 oxidation states.

The general applicability of this technique is limited by the requirement for a volatile analyte. However, the method can be employed for less volatile compounds of biological interest such as sugars. Previous studies in our laboratory have focused

on the differentiation of permethylated derivatives of D(−)-ribose and D(−)-arabinose isomers [26]. Biologically significant isomers of increased structural complexity may be distinguished by tandem mass spectrometry if a suitable method of sample ionization such as fast atom bombardment (FAB) is incorporated into the system and combined with a stereoselective collision gas.

These experiments reveal the general utility of several group 14 trimethyl cations as possible stereochemical probes in mass spectrometric analysis. It would however be interesting to extend this investigation to other types of organometallic ions. Freiser has demonstrated selective ion-molecule reactions of transition metal cluster ions such as $MgFe^+$ and $CoFe^+$ with alcohols [27,28]. Consequently, future stereochemical studies exploring gas-phase reactions of these transition metal ions with 1,2-cyclopentanediol isomers should be quite promising.

References

1 T.J. Odiorne, D.J. Harvey and P. Vouros, J. Org. Chem., 38 (1973) 4274.
2 D. Clemens and B. Munson, Org. Mass Spectrom., 20 (1985) 368.
3 D. Clemens and B. Munson, Anal. Chem., 57 (1985) 2022.
4 R. Orlando, D.P. Ridge and B. Munson, Org. Mass Spectrom., 23 (1988) 527.
5 V.C. Trenerry, I.A. Blair and J.H. Bowie, Aust. J. Chem., 33 (1980) 1143.
6 I.A. Blair, G. Phillipou and J.H. Bowie, Aust. J. Chem., 32 (1979) 59.
7 V.C. Trenerry, I.A. Blair and J.H. Bowie, J. Chem. Soc. Perkin Trans. 22, (1979) 1640.
8 W.J. Meyerhoffer and M.M. Bursey, Org. Mass Spectrom., 24 (1989) 246.
9 P.H. Dawson, J.B. French, J.A. Buckley, D.J. Douglas and D. Simmons, Org. Mass Spectrom., 17 (1982) 212.
10 S.A. McLuckey and R.G. Cooks, in F.W. McLafferty (Ed.) Tandem Mass Spectrometry, Wiley–Interscience, New York, 1983, p. 303.
11 L.N. Owen and P.N. Smith, J. Chem. Soc., (1952) 4026.
12 A. Roebuck and H. Adkins, Org. Syn. Coll. Vol. 3, (1955) 217.
13 E.L. Eliel and C. Pillar, J. Am. Chem. Soc., 77 (1955) 3600.
14 E.L. White, J.C. Tabet and M.M. Bursey, Org. Mass Spectrom., 22 (1987) 132.
15 P.J. Todd and F.W. McLafferty, Int. J. Mass Spectrom. Ion Phys., 38 (1981) 371.
16 W.J. Meyerhoffer and M.M. Bursey, Org. Mass Spectrom., 24 (1989) 169.
17 G.S. Groenewold, M.L. Gross, M.M. Bursey and P.R. Jones, J. Organomet. Chem., 235 (1982) 165.
18 J.A. Stone, A.M. Wojtyniak and W. Wytenburg, Can. J. Chem., 64 (1986) 575.
19 J.A. Stone and D.E. Splinter, Int. J. Mass Spectrom. & Ion Process., 59 (1984) 169.
20 F.J. Winkler and D. Stahl, J. Am. Chem. Soc., 101 (1979) 3685.
21 R. Orlando, F. Strobel, D.P. Ridge and B. Munson, Org. Mass Spectrom., 22 (1987) 1359.
22 V.C. Trenerry and J.H. Bowie, Org. Mass Spectrom., 16 (1981) 344.
23 J. Huheey, Inorganic Chemistry, 2nd, edit., Harper and Row, New York, p. 726.
24 J.J. de Ridder and G. Dijkstra, Rec. Trav. Chim., 86 (1967) 737.
25 M.R. Litzow and T.R. Spaulding, Mass Spectrometry of Inorganic and Organometallic Compounds, Elsevier, Amsterdam, p. 34.
26 W.J. Meyerhoffer and M.M. Bursey, Biomed. and Environ. Mass Spectrom., in press.
27 D.B. Jacobson and B.S. Freiser, J. Am. Chem. Soc., 107 (1985) 1581.
28 L. Setlak and B.S. Freiser; presented at the 1989 Pittsburgh Conference in Analytical Chemistry; Atlanta, Georgia, March 6-10, 1989.