Reactions of the Trimethylsilyl Ion with 1,2-Cyclopentanediol Isomers in the Collision Region of a Triple Quadrupole Instrument

William J. Meyerhoffer and Maurice M. Bursey

Department of Chemistry, Campus Box 3290, Venable Hall, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, USA

Ion-molecule reactions with the trimethylsilyl ion were used to distinguish between *cis*- and *trans*-1,2-cyclopentanediol isomers. The ion kinetic energy of $[Si(CH_3)_3]^+$ was varied from 0 eV to 15 eV (center of mass frame of reference). At low ion kinetic energies (<4 eV), there are significant differences in the relative stabilities and decomposition behavior of the adduct ions $[M + Si(CH_3)_3]^+$. The *cis*-1,2-cyclopentanediol isomer favors decomposition of $[M + Si(CH_3)_3]^+$ to yield the hydrated trimethylsilyl ion $[Si(CH_3)_3OH_2]^+$ at m/z 91. For the *trans* isomer, the formation of the hydrated trimethylsilyl ion is an endothermic process with a definite threshold ion kinetic energy.

INTRODUCTION

Tetramethylsilane has been previously used as a reagent gas in the chemical ionization (CI) spectra of alcohols, ethers and several aliphatic diols.¹⁻⁵ The trimethylsilyl ion, which is the predominant ion in tetramethylsilane CI, has a high sensitivity for a variety of polar oxygencontaining compounds and exhibits little reactivity with hydrocarbons.⁶ There have also been numerous ion cyclotron resonance (ICR) studies examining ionmolecule reactions of the trimethylsilyl ion with compounds of varying trimethylsilyl affinities.⁷⁻¹⁰ These investigations have shown that the trimethylsilyl ion has the ability to form abundant $[M + Si(CH_3)_3]^+$ adduct ions for many polar compounds. The decomposition reactions of these adduct ions may provide information which permits isomer differentiation.

In contrast to the limits of ICR and chemical ionization, the ion kinetic energy of a reactant ion can be controlled using a triple quadrupole mass spectrometer.^{11,12} Ion-molecule reactions with the trimethylsilyl ion may be explored in a new and uniquely different way: the yields of ion-molecule reaction products can be monitored as a function of the ion kinetic energy of the precursor ion.

Under high pressure CI conditions, ions such as $[Si_2(CH_3)_5]^+$ (m/z 131), $[Si_2(CH_3)_7]^+$ (m/z 161) and $[Si_2(CH_3)_5CH_2]^+$ (m/z 145) formed in the source may react with the sample and interfere with the analysis.^{1,2} Additionally, protonated trimethylsilanol $[Si(CH_3)_3OH_2]^+$ (m/z 91) can result from reactions with background water in the ionization source.³ In the triple quadrupole instrument, the particular ion of interest $[Si(CH_3)_3]^+$ (m/z 73) can be mass-selected by the first quadrupole and transmitted into the collision region. Reactions that might result from interfering ions in the source are thus eliminated.

0030-493X/89/040246-07 \$05.00 © 1989 by John Wiley & Sons, Ltd. The purpose of this study was to determine whether ion-molecule reactions with the trimethylsilyl ion could be used to differentiate between the two configurational isomers *cis*- and *trans*-1,2-cyclopentanediol. In an earlier study,¹³ the 1,2-cyclopentanediol isomers were successfully distinguished by the reactivity of their [MH]⁺ ions with both N₂ and NH₃ collision gases; the [MH]⁺ ions were formed in the ionization source by 100 eV isobutane CI. In comparison, in this set of experiments the 1,2-cyclopentanediol isomers are used as the reactive collision gases and function as targets for the [Si(CH₃)₃]⁺ ions which are created in the source by 20 eV EI (electron ionization) of tetramethylsilane and are subsequently accelerated into the collision region.

EXPERIMENTAL

Chemicals

The cis-1,2-cyclopentanediol isomer was synthesized using a low temperature permanganate oxidation of cyclopentene¹⁴ and purified by vacuum distillation, b.p. 124–125 °C (28 mm Hg), lit. b.p. 88–92 °C (2 mm Hg).¹⁴ The trans-1,2-cyclopentanediol isomer, obtained by oxidation of cyclopentene with performic acid,¹⁵ solidified at 54 °C, b.p. 138 °C (10 mm Hg), lit. m.p. 52 °C; b.p. 103–104 °C (2 mm Hg).¹⁶ NMR spectra were taken (Bruker 250 MHz) to confirm the identity of the cis- and trans-1,2-cyclopentanediols.

Both tetramethylsilane (Aldrich, 99.9%) and perdeuterated tetramethylsilane (Merck, 99 atom.% D) were used without further purification; their mass spectra confirmed adequate purity. The 1,2-cyclopentanediol-O, $O-d_2$ isomers were prepared by repeated exchange of the diols with deuterium oxide (Aldrich, 100 atom.% D).

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Instrument

Ion-molecule reactions were studied with an ExtrEL triple quadrupole mass spectrometer.¹⁷ Precursor $[Si(CH_3)_3]^+$ ions were generated by 20 eV EI of tetramethylsilane at an ion source temperature of 80 °C and a sample pressure of 4×10^{-6} Torr; under these conditions, $[Si(CH_3)_3]^+$ was the base peak in the spectrum. The second quadrupole (Q2) collision region was at an ambient temperature of 24 °C. Ions were detected with a Channeltron electron multiplier/conversion dynode (Galileo Electro-Optics).

For initial experiments, the source potential and collision cell (Q2) potential were held constant at 23 V and 15 V, respectively, giving an ion translational energy in Q2 of 8.0 eV (lab frame of reference). Both the transmission efficiency and resolution of ions leaving the source were optimized by applying a potential of 13 V to the first quadrupole Q1. Precursor $[Si(CH_3)_3]^+$ ions formed in the source were mass-selected in Q1 and subsequently transmitted to the collision region. Low mass discrimination was minimized by adjusting the potential of the third quadrupole Q3 to -2 V relative to that of Q2.

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).^{18,19} For both isomers, it was necessary to heat the collision gas inlet system to achieve sufficient volatility. Daughter ion spectra were then obtained by scanning Q3 over the selected mass range.

The ion kinetic energy of $[Si(CH_3)_3]^+$ precursor ions was varied to examine its effect on the relative intensity of any ion-molecule reaction products. Only in these specific ion kinetic energy studies were the *cis*- and *trans*-1,2-cyclopentanediols admitted to Q2 at previously demonstrated single collision conditions^{17,19} (analyzer pressure: 5×10^{-6} Torr). For all of the remaining experiments, multiple collision conditions were used. Translational energies were imparted to the selected parent ions by holding the source potential constant at 23 V while changing the Q2 potential from 23 V to -2 V. Thus the trimethylsilyl ion could be accelerated into the collision region with a range of kinetic energies from 0 to 25 eV (laboratory frame of reference).

In investigations with Si(CD₃)₄ and the 1,2cyclopentanediol- $O,O-d_2$ isomers, the daughter ion spectra quoted were obtained with the ion kinetic energies of [Si(CD₃)₃]⁺ and [Si(CH₃)₃]⁺ at 2.2 eV and 2.0 eV (laboratory frame of reference) respectively. The 1,2cyclopentanediol- $O,O-d_2$ isomers were admitted into the collision region at an analyzer pressure of 5×10^{-5} Torr. Prior to these last experiments, labile hydrogens from molecules adsorbed on instrument surfaces in the Q2 collision region had been exchanged by repeated exposure to D₂O introduced through the collision gas inlet.

RESULTS AND DISCUSSION

The main difference in the daughter ion spectra of the two 1,2-cyclopentanediol isomers results from the relative stability of their $[M + Si(CH_3)_3]^+$ adduct ions. Ion-molecule reaction products that are observed from the decomposition of $[M + Si(CH_3)_3]^+$ are highly indicative of isomer configuration and thus can serve as a sensitive stereochemical probe. The more pronounced stereochemical effects are seen at lower precursor ion kinetic energies.

The trimethylsilyl ion can react rapidly with most compounds possessing a nucleophilic center.9 Consequently, reactions between $[Si(CH_3)_3]^+$ and some polar compounds may be so exothermic that the $[M + Si(CH_3)_3]^+$ adduct ion decomposes before it can be collisionally stabilized. The formation of a bond between the electrophilic trimethylsilyl ion and the 1,2cyclopentanediol is clearly exothermic (eqn. (1)); but for low precursor ion kinetic energies, the ٢M + Si(CH₃)₃]⁺ adduct ion at m/z 175 is the base peak in the trans-1,2-cyclopentanediol daughter ion spectrum and one of the major ions in the cis isomer spectrum (Fig. 1). The adduct is thus sufficiently large to have a lifetime greater than that required for detection.

$$[\operatorname{Si}(\operatorname{CH}_3)_3]^+ + \operatorname{M} \to [\operatorname{M} + \operatorname{Si}(\operatorname{CH}_3)_3]^+ \tag{1}$$

The extent of adduct ion formation may depend on the temperature of the Q2 collision region where the reactions of the diols with the trimethylsilyl ion occur. In all of the experiments conducted, the second quadrupole remained at ambient temperature. At these relatively low temperatures, significant adduct ion formation is generally observed when the adduct ion has enough degrees of freedom.⁶ In particular, ICR studies with the trimethylsilyl ion have indicated abundant adduct ions $[M + Si(CH_3)_3]^+$ for many oxygenated compounds at temperatures near 25 °C.⁷ There is a question however, concerning the actual mechanism of adduct ion formation.

One possible mechanism involves the rapid displacement of water from the initially formed hydrated trimethylsilyl ion via a series of bimolecular reactions (eqns (2) and (3).⁶

$$[Si(CH_{3})_{3}]^{+} + C_{5}H_{8}(OH)_{2} \rightarrow$$
$$[Si(CH_{3})_{3}OH_{2}]^{+} + C_{5}H_{7}OH \quad (2)$$

$$[Si(CH_{3})_{3}OH_{2}]^{+} + C_{5}H_{8}(OH)_{2} \rightarrow$$
$$[Si(CH_{3})_{3}C_{5}H_{8}(OH)_{2}]^{+} + H_{2}O \quad (3)$$

However, at low precursor ion kinetic energies in the *trans*-isomer spectrum, $[Si(CH_3)_3OH_2]^+$ is not created to any significant extent. Therefore a more reasonable explanation would be adduct ion formation by a simple bimolecular addition reaction between the trimethylsilyl ion and the diol isomers. At analyzer pressures of 5×10^{-5} Torr collisional stabilization of the relatively long-lived intermediate complex may occur.

Differences in daughter ion spectra at low precursor ion kinetic energies

Daughter ion spectra were taken for both 1,2-cyclopentanediol isomers at a $[Si(CH_3)_3]^+$ precursor ion kinetic energy of 1.2 eV (COM) and a collision gas pres-



Figure 1. Daughter ion spectra at $[Si(CH_3)_3]^+$ ion kinetic energy of 1.2 eV (COM); analyzer pressure (ion gauge) of 5×10^{-5} Torr; (a) *cis*-1,2-cyclopentanediol, and (b) *trans*-1,2-cyclopentanediol.

sure of 5×10^{-5} Torr (Fig. 1) (low range of multiple collision conditions).^{18,19} At this low ion kinetic energy, significant differences in the relative intensities of several ion-molecule reaction products are observed. The presence of a peak at m/z 103 indicates that the [MH]⁺ ion is generated by a proton transfer reaction involving either the trimethylsilyl ion or one of the fragment ions present in the daughter ion spectrum. The cis-diol has a higher proton affinity than the trans-diol because of its intramolecular hydrogen bonding.²¹ As a result, the relative abundance of [MH]⁺ is greater in the cis-diol spectrum. A proton transfer reaction involving $[Si(CH_3)_3]^+$ is not possible. The proton affinity (PA) of $Si(CH_3)_2CH_2$ is 947 kJ mol⁻¹,²² which is greater than the proton affinities of cis- and trans-1,2-cyclopentanediol, 886 kJ mol⁻¹ and 823 kJ mol⁻¹, respectively.13 Therefore another species formed in the collision region must contribute to the protonation of the neutral diols. It is interesting to note that $[Si(CH_3)_3OH_2]^+$, m/z 91, is an abundant ion in the cisisomer spectrum and may be responsible for protonation of the diol as shown in eqn (4).² There exist two values given in the literature for the proton affinity of Si(CH₃)₃OH, (824 \pm 8 kJ mol⁻¹ and 769 kJ mol⁻¹).^{4,23}

The proton affinity of cis-1,2-cyclopentanediol is greater than both of these values. Therefore under the multiple collision conditions used, protonation of the cis-diol can occur by subsequent collisions with the hydrated trimethylsilyl ion. However the $[Si(CH_3)_3OH_2]^+$ ion, m/z91, producing a peak in the spectrum of the transisomer probably is irrelevant to other major protonation pathways because it is of such low abundance. The small amount of $[Si(CH_3)_3OH_2]^+$ ion in the spectrum of the trans-isomer presumably arises from reaction with background water (eqn (5)). The graph of $I/I_{\text{max}}[Si(CH_3)_3OH_2]^+$ vs. ion kinetic energy $[Si(CH_3)_3]^+$ (Fig. 4) confirms this conclusion since the precursor ion kinetic energy used (1.2 eV (COM) is below the indicated threshold ion kinetic energy of 1.42 eV (see below)). For eqn (5), the ΔH_r is -179 kJ mol^{-1} (see Appendix), and so any background water present in the collision region will easily react with $[Si(CH_3)_3]^+$ to form the hydrated trimethylsilyl ion.

$$[Si(CH_3)_3OH_2]^+ + M \to [MH]^+ + Si(CH_3)_3OH (4)$$

$$[Si(CH_3)_3]^+ + H_2O \to [Si(CH_3)_3OH_2]^+ (5)$$

Ions derived from dissociative reactions with the diols

such as $[M - OH]^+$ at m/z 85, $[M - OH - H_2O]^+$ at m/z 67 and m/z 61, presumably $[HOCHCH_2OH]^+$, are seen in both daughter ion spectra. The relative intensities of these ion-molecule reaction products are similar to those obtained from collision activated decomposition (CAD) studies using N₂ as an inert collision gas.¹³ The $[M - OH]^+$ ion may be generated either by hydroxide abstraction from the diol or by collisional dissociation of the $[M + Si(CH_3)_3]^+$ adduct ions. Decomposition of small amounts of $[MH]^+$ to form $[MH - H_2O]^+$, m/z 85, is negligible. The $[H_2SiCH_3]^+$ ion at m/z 45 is created by a low-energy loss of C₂H₄ from the trimethylsilyl ion.²⁴

At the low ion kinetic energy of 1.2 eV (COM), one of the reactions of the trimethylsilyl ion with the *cis*-1,2cyclopentanediol isomer is highly selective: the formation of the hydrated trimethylsilyl ion at m/z 91. In contrast, the generation of $[Si(CH_3)_3OH_2]^+$ for the *trans* isomer requires additional energy input, although we offer no thermodynamic calculations since the structure of the neutral product is not obvious. At an ion kinetic energy of 4.7 eV (COM), the ion at m/z 91 is the base peak in the daughter ion spectrum of the *trans*-diol. When ion-molecule reactions were examined at these higher ion kinetic energies, the spectra obtained for the diols were virtually indistinguishable.

Additional ions seen at m/z 157 and m/z 173 are due to decomposition of the m/z 175 adduct ion (Scheme 1). The $[C_8H_{17}OSi]^+$ ion at m/z 157 results from loss of a molecule of water from $[M + Si(CH_3)_3]^+$ and is found in the daughter ion spectra for both isomers. It is not certain whether this ion exists as a linear or a cyclic structure. The proposed structures for the ion at m/z157 and the neutral mass 84 are achievable by a reasonable mechanism of m/z 175 adduct ion decomposition but are not proven.

Experiments with the perdeuterated trimethylsilyl precursor ion and the 1,2-cyclopentanediol- $O,O-d_2$ isomers were used to confirm the structures of the m/z 175 adduct ion decomposition products. In the first set of experiments, $[Si(CD_3)_3]^+$ was the precursor ion and



Scheme 1. Decomposition of m/z 175 adduct ion for *cis*-1,2-cyclopentanediol collision gas.



Scheme 2. Decomposition of m/z 184 perdeuterated TMS adduct ion for *cis*-1,2-cyclopentanediol collision gas.

the diol isomers served as collision gases. The perdeuterated trimethylsilyl adduct ion $[M + Si(CD_3)_3]^+$ at m/z 184 decomposes into the following major products: $[Si(CD_3)_3OH_2]^+$, m/z 100; $[M + Si(CD_3)_3 - H_2O]^+$, m/z 166; and $[M + Si(CD_3)_3 - D_2]^+$ m/z 180 (Scheme 2). The shifts expected for the proposed reactions occur to an extent greater than 95% and the relative abundances of the ion-molecule reaction products for both the cis- and trans-1,2-cyclopentanediol isomers are similar to those obtained using the $[Si(CH_3)_3]^+$ precursor ion. An additional product $[D_2SiCD_3]^+$ at m/z 50 is generated by loss of C₂D₄ from the perdeuterated trimethylsilyl ion. The formation of the $[M + Si(CD_3)_3]$ $-D_2$]⁺ ion at m/z 180 indicates that the loss of a hydrogen molecule occurs from the trimethylsilyl groups and not from the ring or hydroxyl hydrogens. Additionally, the existence of the $[M + Si(CD_3)_3]$ $-H_2O$ ⁺ ion in the spectra of both isomers provides evidence for the loss of H₂O from hydrogens of the diol, possibly those located on adjacent hydroxyl groups.

Further investigations with the 1,2-cyclopentanediol- $0, 0 - d_2$ isomers as collision gases, and $[Si(CH_3)_3]^+$ as precursor ion, revealed somewhat less conclusive evidence concerning the structures of the trimethylsilyl adduct ion decomposition products (Scheme 3). The hydroxy deuterated adduct ion at m/z 177 dissociates for both diol isomers to give a mixture of products at m/z 93 [Si(CH₃)₃OD₂]⁺, m/z 92 [Si(CH₃)₃OHD]⁺ and m/z 91 [Si(CH₃)₃OH₂]⁺. From the predominant product at m/z 93, one can conclude that both hydroxyl hydrogens are involved in the primary decomposition reaction to yield the hydrated trimethylsilyl ion. The ions at m/z 92 and m/z 91 are significantly less abundant; less than 10% relative intensity of the predominant m/z 93 ion. However, the presence of these by-products suggests that the proposed reactions for



Scheme 3. Decomposition of m/z 177 adduct ion formed by collisions with the hydroxy deuterated *trans*-1,2-cyclopentanediol collision gas.

this system are not occurring to greater than 95%. The 1,2-cyclopentanediol- $O,O-d_2$ collision gases may not have been completely deuterated. Nevertheless, the formation of $[M + Si(CH_3)_3 - D_2O]^+$ at m/z 157 in conjunction with the information from the previous $[Si(CD_3)_3]^+$ experiment clearly establishes the loss of water from adjacent hydroxyl groups. The ion at m/z 175 provides additional proof for loss of H₂ from the $[M + Si(CH_3)_3]^+$ adduct ion occurring at the trimethylsilyl groups.

Effects of varying $[Si(CH_3)_3]^+$ precursor ion kinetic energy

Relative intensities (defined within each daughter ion spectrum) of m/z 175 peaks due to adduct ions



Figure 2. I/I_{max} (*m*/*z* 175 adduct ion intensity) vs. ion kinetic energy of $[Si(CH_3)_3]^+$ precursor ion; (a) $\Box = cis$ -1,2-cyclopentanediol, and (b) $\bigcirc = trans$ -1,2-cyclopentanediol.



Figure 3. I/I_{max} (m/z 91 hydrated trimethylsilyl ion intensity) vs. ion kinetic energy of $[Si(CH_3)_3]^+$ precursor ion; *cis*-1,2-cyclopentanediol collision gas, analyzer pressure of 5 × 10⁻⁶ Torr.

 $[M + Si(CH_3)_3]^+$ were monitored for both diol compounds as a function of [Si(CH₃)₃]⁺ precursor ion kinetic energy (Fig. 2). At very low ion kinetic energies, the relative intensities of the m/z 175 peaks in the daughter ion spectra of the cis- and trans- diols are quite similar. The m/z 175 ion at these low ion kinetic energies $\{ < 0.7 \text{ eV} (COM) \}$ is the base peak in both diol isomer spectra. However, for ion kinetic energies ranging from 0.7 eV to 4.0 eV, there are significant differences in the relative stabilities of the trimethylsilyl adduct ion. When the $[Si(CH_3)_3]^+$ ion kinetic energy is greater than 1.0 eV (COM), the adduct ion is no longer the base peak in the cis- diol spectrum (Fig. 1), and other products appear. In cis-1,2-cyclopentanediol, the lower stability of the m/z 175 adduct ion is in part caused by steric crowding between the Si(CH₃)₃O⁺H and the adjacent cis OH groups. In the trans-1,2-cyclopentanediol configuration, the absence of this steric hindrance then results in a more highly stabilized adduct ion that is less likely to decompose before analysis. For the cis- isomer, unlike the trans- diol, presumably there is a new major exothermic decomposition channel, which is likely to be the one yielding the hydrated trimethylsilyl ion. The dependence of the decomposition reaction of the m/z 175 adduct ion on energy can be clearly seen from the graph of I/I_{max} vs. ion kinetic energy (Fig. 2). At ion kinetic energies greater than 5.0 eV (COM), relative intensities of the adduct ions are very similar. As the ion kinetic energy is increased, decomposition processes within the cyclopentane ring become more important. Ions such as $[M - OH]^+$, m/z85; $[M - OH - H_2O]^+$, m/z 67; $[C_4H_7]^+$, m/z 55; $[C_3H_5O]^+$, m/z 57; and $[HOCHCH_2OH]^+$, m/z 61 are seen in increased abundance in both of the 1,2-cyclopentanediol isomer spectra.

Differences in the relative stabilities of the m/z 175 adduct ion suggest that monitoring the formation of the hydrated trimethylsilyl ion at varying ion kinetic energies might serve as a useful probe of this decomposition process. The intensity of $[Si(CH_3)_3OH_2]^+$ was recorded as a function of $[Si(CH_3)_3]^+$ ion kinetic energy (Figs 3 and 4). Both *cis*- and *trans*-1,2-cyclopentanediol were



Figure 4. I/I_{max} (m/z 91 hydrated trimethylsilyl ion intensity) vs. ion kinetic energy of $[Si(CH_3)_3]^+$ precursor ion; *trans*-1,2-cyclopentanediol collision gas, analyzer pressure of 5 × 10⁻⁶ Torr.

admitted into the collision region at an analyzer pressure of 5×10^{-6} Torr (single collision conditions).^{19,20} For the *cis*- diol isomer, the formation of $[Si(CH_3)_3OH_2]^+$ is an exothermic process with the maximum product ion intensity at ion kinetic energies approaching 0 eV; that is, it does not require any additional energy input from the accelerated $[Si(CH_3)_3]^+$. In contrast, for the trans- diol the m/z 175 adduct ion is apparently more stable at the lower ion kinetic energies, with a threshold ion kinetic energy at which the trimethylsilyl ion transfers enough internal energy to the m/z 175 collision complex to produce the hydrated trimethylsilyl ion (m/z 91). From Fig. 4, this threshold ion kinetic energy was determined to be 1.42 eV (COM); suggesting that the reaction is endothermic by 137 kJ mol^{-1} . We interpret this onset as a thermodynamic value rather than a reaction barrier on the basis of consistent prior experience with group transfers and rearrangement reactions. Experimental data obtained for both the cis- and trans- isomers are consistent with previously demonstrated behavior of endothermic and exothermic reactions in a triple quadrupole instrument.17,20

An additional ion-molecule reaction product of interest is the $[M + Si(CH_3)_3 - H_2O]^+$ ion at m/z 157. This decomposition product of the m/z 175 adduct ion was also examined as a function of trimethylsilyl ion kinetic energy (Fig. 5). For the *cis*-1,2-cyclopentanediol isomer the maximum abundance of m/z 157 is seen at predominantly low ion kinetic energies (<2.0 eV) and decreases nearly to zero at energies greater than 2.0 eV. With the *trans*- diol, there is little formation of m/z 157 at low ion kinetic energies; the maximum product ion intensity



Figure 5. I/I_{max} (m/z 157 ion intensity; $[M + Si(CH_3)_3 - H_2O]^+$ vs. ion kinetic energy of $[Si(CH_3)_3]^+$ precursor ion; (a) $\Box = cis-1,2$ -cyclopentanediol, and (b) $\bigcirc = trans-1,2$ -cyclopentanediol.

occurs at approximately 2.1 eV (COM). Presumably as a consequence of the *trans*- diol configuration, the m/z175 adduct ion is more stable at low energy and decomposes to m/z 91 and m/z 157 only at higher ion kinetic energies. Since formation of the m/z 157 ion is dependent on diol isomer configuration, its structure must maintain the integrity of the orientation of the hydroxy groups to one another.

CONCLUSIONS

Ion-molecule reactions with the trimethylsilyl ion in a triple quadrupole mass spectrometer can distinguish between 1,2-cyclopentanediol isomers. When the ion kinetic energy of [Si(CH₃)₃]⁺ was varied, substantial differences were seen in the relative abundances of the trimethylsilyl adduct ion for each isomer, especially at low ion kinetic energies. There the formation of the hydrated trimethylsilyl ion $[Si(CH_3)_3OH_2]^+$ is selective for the cis-diol. For the trans- diol compound, the formation of $[Si(CH_3)_3OH_2]^+$ is an endothermic process with a translational energy onset. Decomposition behavior of the $[M + Si(CH_3)_3]^+$ ion is highly indicative of isomer configuration. These studies reveal the general utility of the trimethylsilyl ion as a stereochemical probe. The relative ease of formation, low internal energy content and high reactivity of $[Si(CH_3)_3]^+$ with many polar compounds make it an ideal choice as a precursor ion for collision experiments in a triple quadrupole instrument.

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APPENDIX

For the reaction

$$[Si(CH_3)_3]^+ + H_2O \rightarrow [Si(CH_3)_3OH_2]^+$$

 $\Delta H_{\rm r}$ was determined to be -179 kJ mol⁻¹ from the following:

$$\Delta H_{\rm f}[{\rm Si}({\rm CH}_3)_3]^+ = 630 \text{ kJ mol}^{-1}.^{25}$$
$$\Delta H_{\rm f}[{\rm H}_2{\rm O}] = -242 \text{ kJ mol}^{-1}.^{26}$$

 $\Delta H_{\rm f}[{\rm Si}({\rm CH}_3)_3{\rm OH}_2]^+ = 209 \text{ kJ mol}^{-1}.^4$