Appendix E

Characterization of 2-Methylglyceric Acid Oligomers in Secondary Organic Aerosol Formed from the Photooxidation of Isoprene Using Trimethylsilylation and Gas Chromatography/Ion Trap Mass Spectrometry[*]

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Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry

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In the present work, we have characterized in detail the chemical structures of secondary organic aerosol (SOA) components that were generated in a smog chamber and result from the photooxidation of isoprene under high-NO_x conditions typical for a polluted atmosphere. Isoprene high-NO_x SOA contains 2-methylglyceric acid (2-MG) and oligoester derivatives thereof. Trimethylsilylation, in combination with capillary gas chromatography (GC)/ion trap mass spectrometry (MS) and detailed interpretation of the MS data, allowed structural characterization the polar oxygenated compounds present in isoprene SOA up to 2-MG trimers. GC separation was achieved between 2-MG linear and branched dimers or trimers, as well as between the 2-MG linear dimer and isomeric mono-acetate derivatives thereof. The electron ionization (EI) spectra of the trimethylsilyl derivatives contain a wealth of structural information, including information about the molecular weight (MW), oligoester linkages, terminal carboxylic and hydroxymethyl groups, and esterification sites. Only part of this information can be achieved with a soft ionization technique such as electrospray (ESI) in combination with collision-induced dissociation (CID). The methane chemical ionization (CI) data were used to obtain supporting MW information. Interesting EI spectral differences were observed between the trimethylsilyl derivatives of 2-MG linear and branched dimers or trimers and between 2-MG linear dimer mono-acetate isomers. Copyright © 2006 John Wiley & Sons, Ltd.

INTRODUCTION

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is a volatile organic compound (VOC) that is emitted in large amounts by terrestrial vegetation, estimated at about 500 Tg/year worldwide.[1] In the past, isoprene was assumed not to contribute significantly to secondary organic aerosol (SOA) formation because of the high volatility of its first-generation oxidation products (i.e. methacrolein, methyl vinyl ketone and formaldehyde).[2] However, during the past 3 years evidence from both field[3–7] and laboratory[4,8–13] studies has been obtained that isoprene is photooxidized to polar oxygenated products which are present in the aerosol phase. The aerosol yields from photooxidation of isoprene are rather

low (maximum about 3%);[11,12] a recent modeling study, however, shows that this aerosol source is quite significant on a global scale.[14] Knowledge of the detailed chemical structures of isoprene oxidation products is required in order to gain insights into the underlying photochemical oxidation mechanisms of isoprene, which so far are only partially understood.

In a recent work,[10] we characterized the chemical structures of SOA components that were produced in a smog chamber from photooxidation of isoprene under both high- and low-NO_x conditions. A combination of several mass spectrometric techniques was used, including electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI), aerosol mass spectrometry (MS), and derivatization gas chromatography (GC). It was shown in that study that isoprene high-NO_x SOA contains 2-methylglyceric acid (2-MG), formed by further photooxidation of methacrolein, a

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first-generation oxidation product of isoprene, and oligoester derivatives of 2-MG.

Soft ionization techniques such as ESI and MALDI are widely used currently in the analysis of oligomers and polymers, including oligomeric substances formed by photooxidation of biogenic and anthropogenic hydrocarbons such as isoprene,[13] α-pinene,[15–18] cycloalkenes[16] and trimethylbenzene.[19] Combination of these techniques with collision-induced dissociation (CID) and tandem MS techniques generally only partially provide the structural information that is needed for elucidation of unknown multifunctional compounds. In the case of the oligomeric isoprene SOA compounds studied here, partial structural information was obtained by (−/+)ESI-ion trap MS and by upfront CID mode of analysis on a LC/ESI-MS instrument.[10] The major fragmentation observed for 2-MG oligomers was loss of 102 Da 2-MG residue(s), likely corresponding to 2-hydroxy-2-methylpropiolactone and formed through a nucleophilic reaction directed by the negative charge on the terminal ionized carboxylic acid function. In the present study, we demonstrate that additional structural information can be achieved on oligomeric isoprene SOA compounds by trimethylsilylation in combination with GC/ion trap MS and detailed interpretation of the electron ionization (EI) spectra.

A derivatization protocol based on methylation of carboxylic acid functions prior to trimethylsilylation of neutral hydroxyl groups has been successfully applied in a previous work[20] to the analysis of polar oxygenated compounds present in organic aerosol. In the present work, preference was given to a one-step trimethylsilylation procedure that converts neutral and acidic hydroxyl functions to trimethylsilyl (TMS) ether or ester functions and allows the analysis of polar multifunctional compounds in the EI and/or chemical ionization (CI) mode. The EI mass spectra of trimethylsilylated compounds generally contain a wealth of structural information but often provide insufficient molecular weight (MW) information.[6,20,21] The latter shortcoming can however be overcome by recording spectra in the CI mode. In the EI mode, information can be obtained on functional groups and their locations owing to the fragmentation-directing effect of ionized trimethylsilylated hydroxyl groups. Rearrangement reactions of the trimethylsilyl group may occur, rendering EI mass spectra quite complex and difficult to interpret, but have the merit that they can yield structurally characteristic ions.

The isoprene high-NO$_x$ SOA examined in the present study contains 2-MG, 2-MG dimers, 2-MG dimer mono-acetate derivatives, and 2-MG trimers. We will first discuss the EI fragmentation behaviors of the 2-MG monomer and its oligomeric derivatives. In addition, we will examine the fragmentation behaviors of the ethyl ester derivatives that are formed by subjecting isoprene high-NO$_x$ SOA to acidic hydrolysis in ethanol. Part of this work has been briefly presented in our previous study dealing with the overall chemical composition and mechanism of SOA formed from the photooxidation of isoprene under low- and high-NO$_x$ conditions.[10]

EXPERIMENTAL

Aerosol samples and workup

SOA was generated from isoprene (500 ppb) in Caltech's indoor 28 m^3 Teflon chambers using hydrogen peroxide as the OH radical precursor and 800 ppb NO; the oxidation reaction was initiated by UV irradiation,[11,12] and the SOA was collected on Teflon filters. Full details about SOA generation from isoprene are given in our previous study.[10] The SOA sample used in the present study was from a high-NO$_x$ isoprene nucleation (seed-free) experiment (Experiment 5). 2-MG and a branched and linear dimer thereof were prepared by reacting methacrylic acid (250 µl; purity, 99%; Sigma, St. Louis, MI, USA) with hydrogen peroxide (250 µl; 50% aqueous solution) in the presence of formic acid (125 µl) for ten days at room temperature, following a procedure adapted from a previously reported one.[4] The yield of 2-MG, as determined by trimethylsilylation GC with flame ionization detection and using glyceric acid (Sigma) as an internal recovery standard, was 222 mg; the 2-MG linear and branched dimer were produced in small yield (combined yield estimated at about 3.3 mg assuming a similar EI response as 2-MG), and the ratio branched/linear 2-MG dimer was 1 : 10.

The sample workup of the isoprene SOA sample consisted of extraction of the filter with methanol under ultrasonic agitation and derivatization. The extract was divided into two parts; one part was trimethylsilylated, while the other part was subjected to a hydrolysis/ethylation procedure. For analysis of the methacrylic acid reaction products, 2 µl of the 30 times diluted reaction mixture (with methanol) was dried and trimethylsilylated. Trimethylsilylation was performed by reacting the extract residue with 40 µl of a mixture containing 1 ml *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (+1% trimethylchlorosilane) (Pierce, Rockford, IL, USA) and 500 µl of dry pyridine (Merck) for an hour at 70 °C. The reagent employed for deuterium labeling of the TMS methyl groups, *N*,*O*-bis(trimethyl-^{2}H$_9$-silyl)acetamide, was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). The hydrolysis/ethylation procedure involved reaction of the extract residue with 40 µl of analytical-grade ethanol and 8 µl of trimethylchlorosilane (Supelco, Bellafonte, PA, USA) for 1 h at 60 °C. Aliquots of 1 µl were used for GC/MS analysis and were injected in the splitless mode.

GC/ion trap MS

GC/MS analyses were performed with a system comprising a TRACE GC2000 gas chromatograph, which was coupled to a Polaris Q ion trap mass spectrometer equipped with an external ionization source (ThermoElectron, San Jose, CA, USA). A Heliflex AT-5MS fused-silica capillary column (5% phenyl, 95% methylpolysiloxane, 0.25 µm film thickness, 30 m × 0.25 mm i.d.) preceded by a deactivated fused-silica precolumn (2 m × 0.25 mm i.d.) (Alltech, Deerfield, IL, USA) was used to separate the derivatized extracts. Helium was used as the carrier gas at a flow rate of 1.2 ml/min. The temperature program was as follows: isothermal hold at 50 °C for 5 min, temperature ramp of 3 °C/min up to 200 °C, isothermal hold at 200 °C for 2 min, temperature ramp of

30 °C/min up to 310 °C; and isothermal hold at 310 °C for 2 min. The analyses were performed in the full-scan mode (mass range: m/z 50–800), and were first carried out in the EI mode and subsequently in the CI mode. The ion source was operated at an electron energy of 70 eV and temperatures of 200 °C and 140 °C in the EI and CI modes, respectively. The temperatures of the GC injector and the GC/MS transfer line were 250 °C and 280 °C, respectively. For CI, methane was introduced as the reagent gas at a flow rate of 1.8 ml/min. We present here mainly data collected in the EI mode; data collected in the CI mode was used to obtain supporting MW information.

For CID experiments, the ions of interest were activated by applying a percentage of a 5-V supplementary a.c. potential to the end-caps of the ion trap at the resonance frequency of the selected ion [referred to as *collision energy level* (CEL)]. The CEL was 16%, while the excitation time was 15 ms. Helium was introduced as damping and collision gas at a flow rate of 1.1 ml/min. In some cases, MS/MS experiments were performed on several mass-selected precursor ions sequentially during the same chromatographic run. For this purpose, the width of the isolation waveform at which the ion trap separation of the precursor ions turned out to be the best was determined; the optimized value ranged between 3.5 and 5 a.m.u. For each precursor ion, the excitation time was 12 ms.

RESULTS AND DISCUSSION

Figure 1 shows a GC/MS total ion current chromatogram (TIC) obtained for SOA produced from the photooxidation of isoprene under high-NO$_x$ conditions. Compound **1** was identified as the dihydroxymonocarboxylic acid, 2-MG (where 2-methylglyceric acid is its common name), which has retained part of the isoprene skeleton. This compound was reported for the first time in rural PM$_{2.5}$ aerosol collected at K-puszta, Hungary, during a 2003 summer field campaign,[4]

and has since been reported in several field studies.[5,7,8] In addition, it was shown in smog chamber studies that 2-MG is formed by photooxidation of isoprene[8] and, more specifically, by further oxidation of methacrolein, which is a first-generation photooxidation product of isoprene.[10] Compound **2a** was characterized in our previous laboratory study as a linear oligoester dimer of 2-MG (denoted as 2-MG linear dimer), using a combination of several MS techniques, including ESI-MS, MALDI-MS, aerosol-MS, and trimethylsilylation GC/MS.[10] In the present work, we discuss the EI behavior of the TMS derivative of the 2-MG linear dimer in more detail and compare it with that of the branched dimer (**2b**), which is not formed during photooxidation of isoprene under high-NO$_x$ conditions (and therefore is not shown in Fig. 1) but which together with the 2-MG linear dimer is produced as a minor reaction product during the acid-catalyzed oxidation of methacrylic acid with hydrogen peroxide. The 2-MG branched dimer was found to elute at an earlier retention time (RT = 50.37 min) compared to the linear dimer (RT = 51.59 min) (GC/MS TIC not shown). No conclusions can be drawn about the relative amounts of 2-MG and its oligoester derivatives in the samples since it is possible that 2-MG oligoester derivatives are partially degraded owing to hydrolysis during the trimethylsilylation procedure which uses an acidic catalyst (i.e. trimethylchlorosilane). Figure 2 shows the m/z 219 mass chromatogram obtained after subjecting the isoprene high-NO$_x$ SOA extract to acidic hydrolysis in ethanol, an experiment that was performed to obtain evidence for ester linkages in the 2-MG oligomers. Compounds identified are the ethyl ester derivatives of 2-MG (**1-Et**), a branched (**2b-Et**) and linear 2-MG dimer (**2a-Et**), and a branched (**3b-Et**) and linear 2-MG trimer (**3a-Et**). In a following section, we will first discuss in detail the rather complex fragmentation behavior of the TMS derivatives of 2-MG (**1**) and its ethyl derivative (**1-Et**) and will limit the discussion to diagnostic ions with m/z values >140. In subsequent sections, we will then use this information to derive
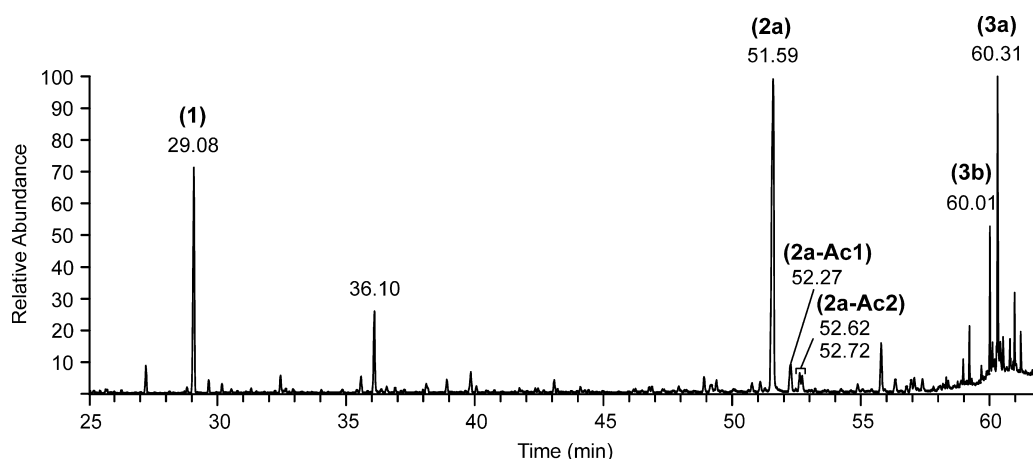

Figure 1. GC/MS TIC obtained for a trimethylsilylated extract of isoprene high-NO$_x$ SOA. Peak identifications: **1**, 2-MG; **2a**, 2-MG linear dimer; **2a-Ac1** and **2a-Ac2**, 2-MG linear dimer mono-acetates; **3a**, 2-MG linear trimer; **3b**, 2-MG branched trimer. The peak eluting at 36.10 min is not discussed in the present work; it was found to correspond to an oxidation product of isoprene but not to be related to 2-MG, and was tentatively identified as 2-hydroxymethyl-3-ketopropanoic acid. Other peaks not marked were also found in a control filter and were identified as fatty acids and monoglycerides thereof. Reprinted from *J. Phys. Chem. A*, **110**, Surratt JD *et al*., Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, 9665, Copyright (2006), with permission from American Chemical Society.
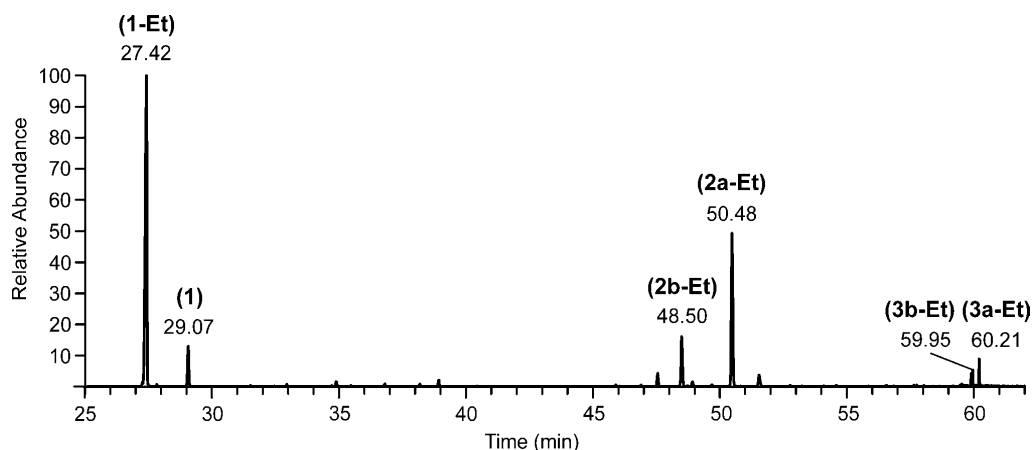
Figure 2. GC/MS extracted ion chromatogram (m/z 219) obtained for an extract of isoprene high-NO$_x$ SOA subjected to a hydrolysis/ethylation procedure prior to trimethylsilylation. Reprinted from *J. Phys. Chem. A*, **110**, Surratt JD *et al*., Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, 9665, Copyright (2006), with permission from American Chemical Society.
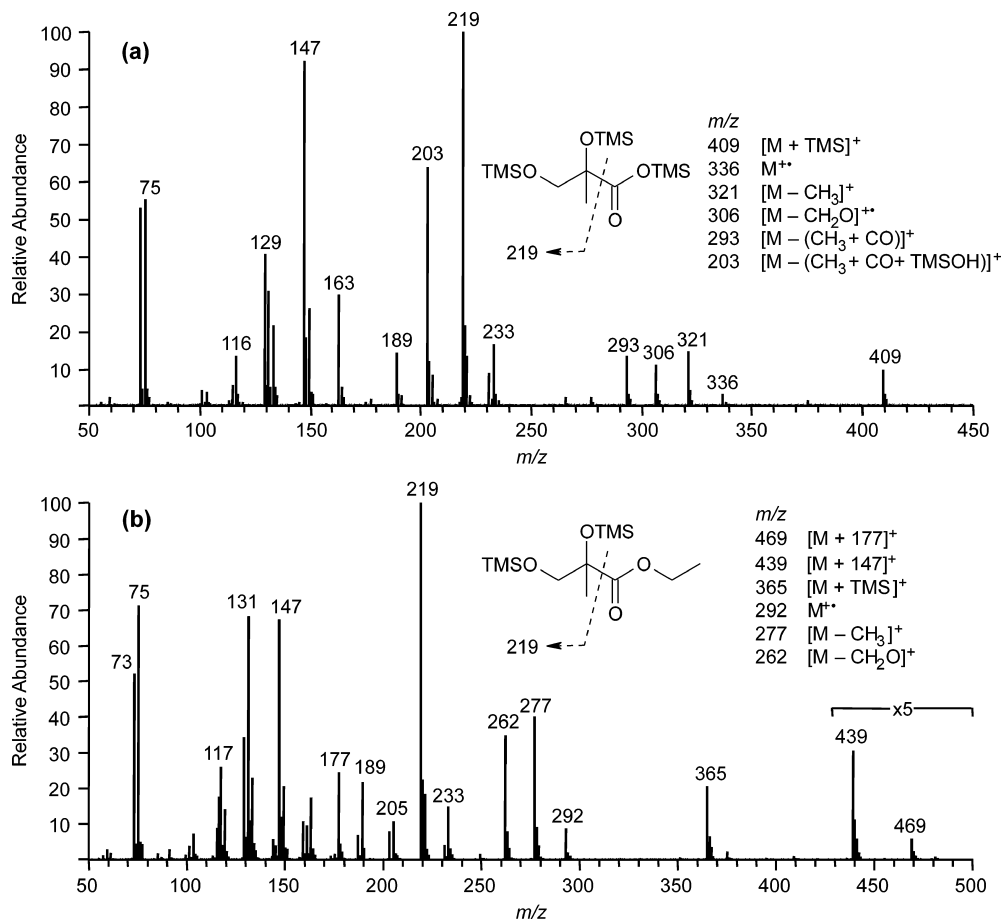
Figure 3. EI mass spectra for the TMS derivatives of (a) 2-MG (**1**) and (b) its ethyl ester derivative (**1-Et**). Part (a) reprinted from *J. Phys. Chem. A*, **110**, Surratt JD *et al*., Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, 9665, Copyright (2006), with permission from American Chemical Society.

structural information for 2-MG dimers (**2a,b**), 2-MG trimers (**3a,b**), the ethyl derivatives of 2-MG dimers (**2a,b-Et**), as well as mono-acetate derivatives of the 2-MG linear dimer (**2a-Ac1,2**). In order to support fragmentation pathways, ion trap MS/MS experiments were used; only in the case of the 2-MG monomer was deuterium labeling of the TMS groups carried out.

Fragmentation behavior of 2-methylglyceric acid and its ethyl ester derivative

Figure 3 shows the EI mass spectra of the TMS derivatives of (a) 2-MG (**1**) and (b) its ethyl ester derivative (**1-Et**). The fragmentation pathways of the TMS derivative of 2-MG are summarized in Schemes 1 and 2; all pathways supported by an MS^2 ion trap experiment are indicated
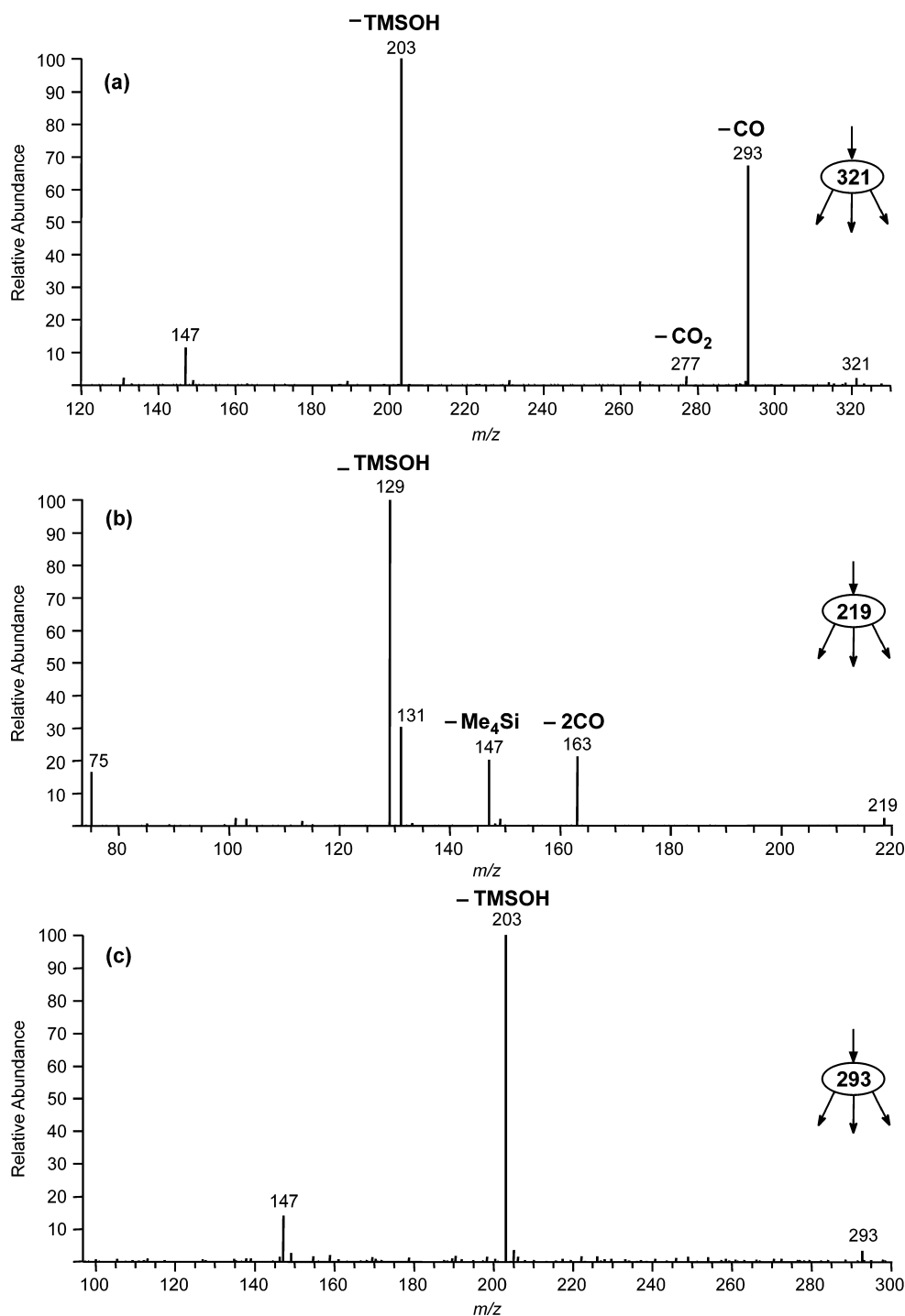
Figure 4. MS^2 ion trap spectra for selected ions of the TMS derivative of 2-MG: (a) m/z 321, (b) m/z 219 and (c) m/z 293.

with an asterisk, while mass shifts obtained by introducing a deuterium labeled TMS group are given in parentheses. The molecular ion (M$^{+\bullet}$; m/z 336) of the TMS derivative of 2-MG is very weak, as is generally the case for TMS derivatives of compounds containing multiple hydroxyl groups.[6,21] The molecular ion region has a signature that is characteristic of a trimethylsilylated carboxylic acid, i.e. the [M − CH$_3$]$^+$ ion (m/z 321) and the [M − (CH$_3$ + CO)]$^+$ ion (m/z 293). Proof that m/z 321 is the precursor of m/z 293 was obtained through an MS^2 ion trap experiment on m/z 321 (Fig. 4(a)). Besides the M$^{+\bullet}$ ion, other useful ions for inferring the MW

(336) are the [M − CH$_3$]$^+$ ion (m/z 321) and the [M + TMS]$^+$ ion (m/z 409). In addition, the molecular ion region contains a [M − CH$_2$O]$^{+\bullet}$ ion (m/z 306), which is indicative of a terminal trimethylsilylated hydroxymethyl function and can be explained via a rearrangement reaction of a TMS group to the ionized ester function as outlined in Scheme 3.

The ion at m/z 219 is the base peak in the mass spectrum and can be explained by a homolytic α-cleavage (Scheme 2). Fragmentation of m/z 219 (Fig. 4(b)) yields the specific signature that was previously reported for the m/z 219 ion of trimethylsilylated 2-methyltetrols,[21]
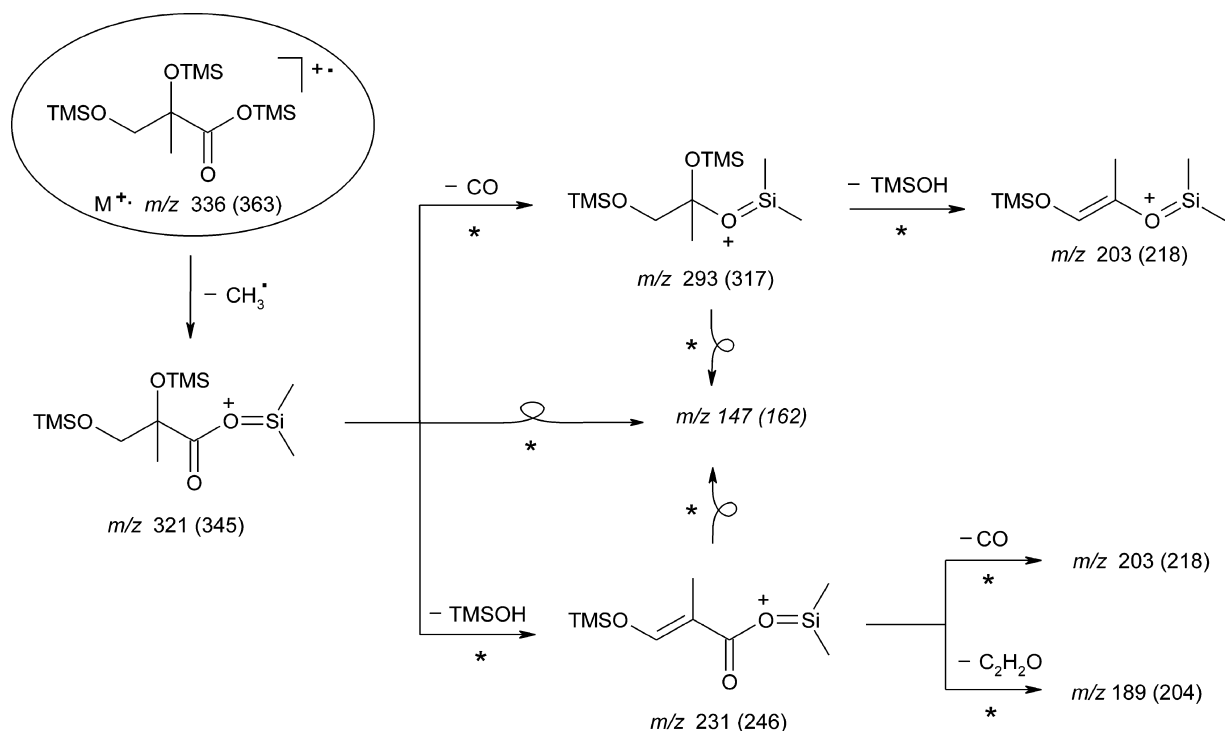
Scheme 1. Main fragmentation pathways for the TMS derivative of 2-methylglyceric acid. All pathways supported by an MS^2 ion trap experiment are indicated with an asterisk.
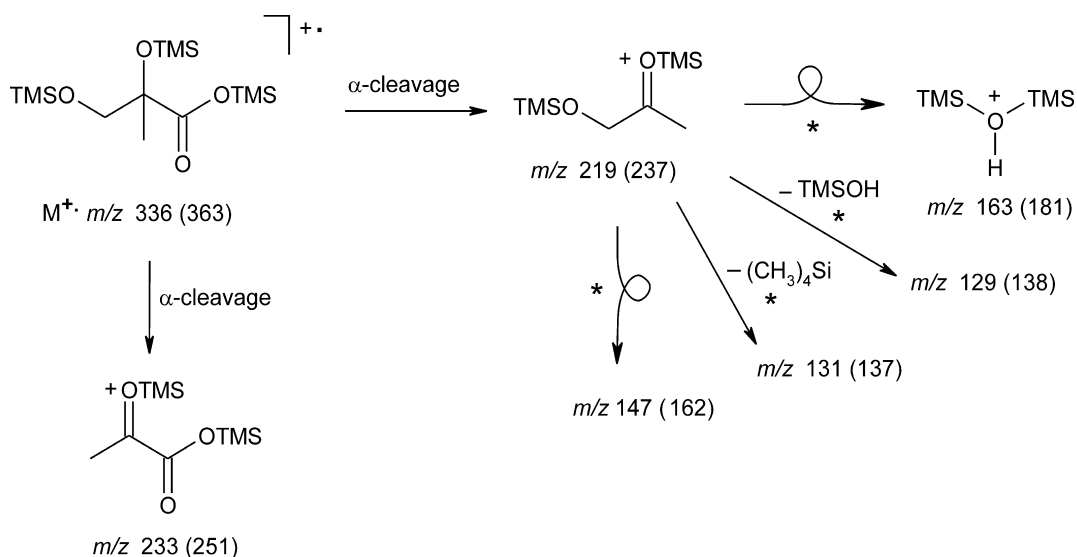
Scheme 2. Proposed pathways for m/z 233 and 219 formed from the TMS derivative of 2-MG and pathways for formation of m/z 219.
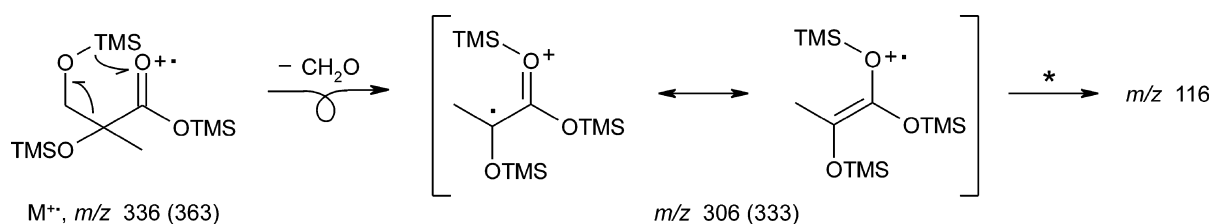
Scheme 3. Postulated gas-phase rearrangement process for the TMS derivative of 2-MG resulting in a resonance-stabilized m/z 306 ion.
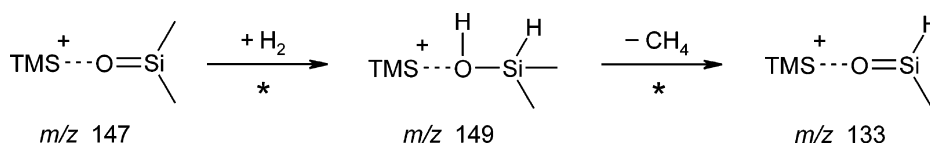
Scheme 4. Hydrogenation reaction of m/z 147 occurring in the ion trap resulting in m/z 149 and 133.
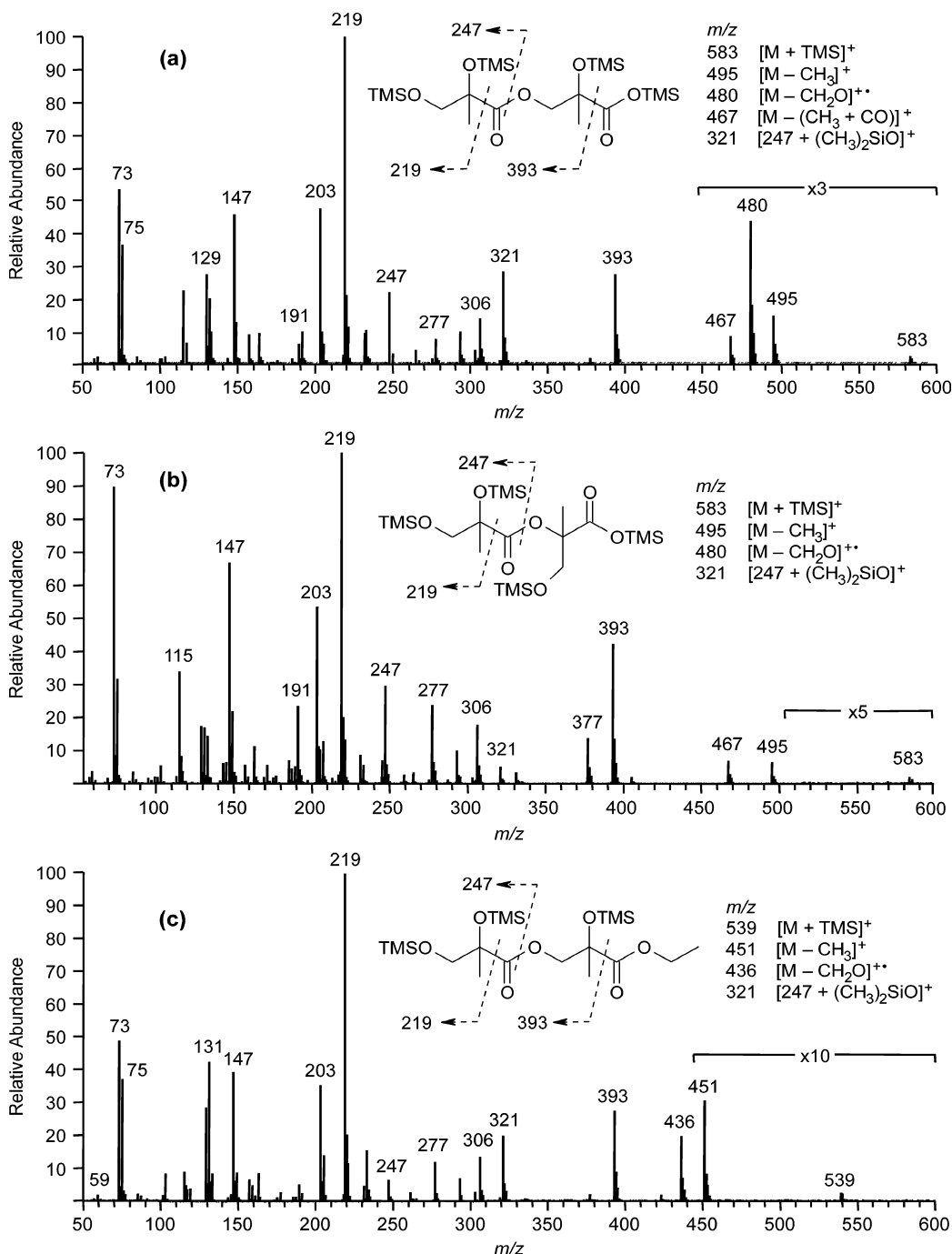

Figure 5. EI mass spectra of the TMS derivatives (a) 2-MG linear dimer (**2a**), (b) 2-MG branched dimer (**2b**), and (c) 2-MG linear dimer ethyl ester (**2a-Et**). Part (a) reprinted from *J. Phys. Chem. A*, **110**, Surratt JD *et al*., Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene, 9665, Copyright (2006), with permission from American Chemical Society.

and is therefore consistent with a trimethylsilylated 1,2-dihydroxy-2-methylethyl group in the molecule. The m/z 203 ion can be explained by loss of TMSOH from m/z 293 (Scheme 1; Fig. 4(c)), while the m/z 147 ion corresponding to $(CH_3)_2Si = O^+ - TMS$ is due to interaction between two TMSO groups[22] and indicates that the molecule contains at least two TMSO groups. The m/z 147 ion is accompanied by a m/z 149 ion which was shown to be formed from the m/z 147 ion, and is explained by addition of hydrogen in the ion trap, and fragments to m/z 133 through loss of methane (Scheme 4).

Comparison of the spectra of the TMS derivatives of 2-MG (Fig. 3(a)) and its ethyl ester (Fig. 3(b)) shows that ethylation results in the expected mass shifts but has little effect on the fragmentation pathways. MW information is provided by the $M^{+\bullet}$ ion (m/z 292), the $[M − CH_3]^+$ ion (m/z 277), and the $[M + TMS]^+$ ion (m/z 365). It is worth noting that the higher m/z region contains additional adduct ions at m/z 439 $[M + 147]^+$ and m/z 469 $[M + 177]^+$. Of these ions, m/z 439 can be explained by adduct formation of the 2-MG ethyl ester molecule with m/z 147, which is an abundant ion in the spectrum. The formation of m/z 177 likely involves the further addition of formaldehyde (30 Da), which is generated in the formation of m/z 262 $[M − CH_2O]^+$. The latter ion supports a terminal trimethylsilylated hydroxymethyl function, while the base peak at m/z 219 is consistent with a trimethylsilylated 1,2-dihydroxy-2-methylethyl group.[21]
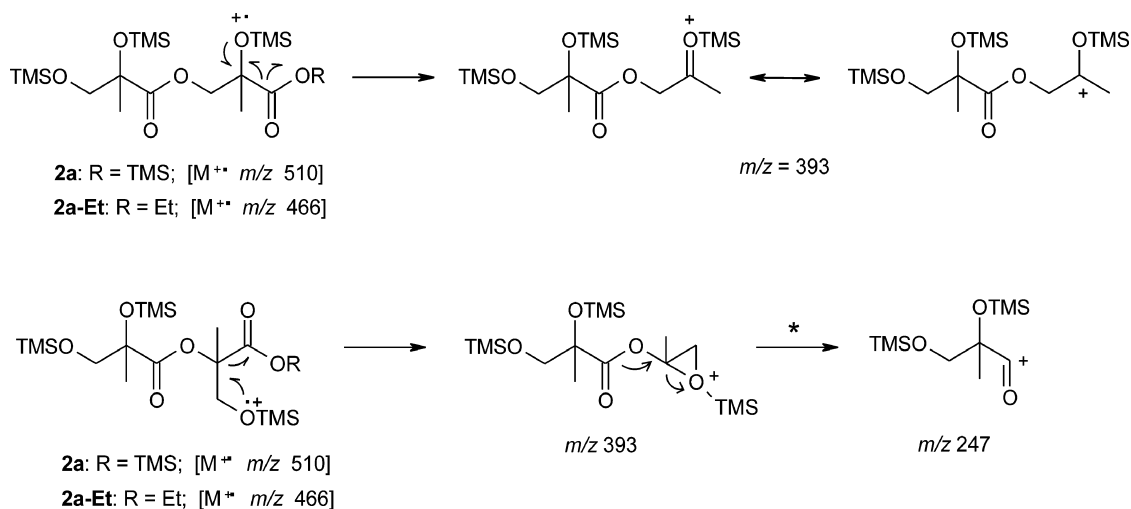
Fragmentation behavior of 2-MG dimers and their ethyl ester derivatives

Figure 5 shows the EI mass spectra of the TMS derivatives of (a) the linear (**2a**) and (b) branched dimer of 2-MG (**2b**) and (c) the ethyl ester derivative of the 2-MG linear dimer (**2a-Et**). Examination of the m/z range 450–600 provides information about the MW. In the case of the 2-MG linear dimer (Fig. 5(a); MW 510), these ions include m/z 583 $[M + TMS]^+$, m/z 495 $[M − CH_3]^+$, and m/z 467 $[M − (CH_3 + CO)]^+$. The latter ion supports the presence of a terminal COOTMS group in the molecule as has been discussed above for 2-MG (Scheme 1). In the case of the 2-MG linear dimer ethyl ester (Fig. 5(c)), the MW (466) is supported by m/z 539 $[M + TMS]^+$ and m/z 451 $[M − CH_3]^+$. The ion at m/z 393 detected for both of the 2-MG linear and branched dimers and their ethyl esters can be readily explained by a homolytic α-cleavage reaction as depicted in Scheme 5.

The mass spectra of the TMS derivatives of the 2-MG linear dimer as well as of its ethyl ester display an abundant $[M − CH_2O]^{+\bullet}$ ion (m/z 480 and m/z 436, respectively), which is consistent with a terminal trimethylsilylated hydroxymethyl function as has been discussed above for the 2-MG monomer (Scheme 2). Subsequent elimination of a neutral (130 Da) through a rearrangement of a TMS group leads to m/z 306, an ion that is also observed for the 2-MG monomer (Fig. 3(a)) and is stabilized by resonance (Scheme 6).

Comparison of the EI spectrum of the TMS derivative of the 2-MG linear dimer (Fig. 5(a)) with that of the branched dimer (Fig. 5(b)) reveals some interesting differences. It can be seen that the $[M − CH_2O]^{+\bullet}$ ion (m/z 480) is absent in the case of the 2-MG branched dimer. However, it is noted that a m/z 306 ion is also present in the 2-MG branched dimer, suggesting that the internal TMS group rearrangement (shown for **2a** in Scheme 6) occurs prior to

2a: R = TMS; $[M^{+\bullet}$ m/z 510]
2a-Et: R = Et; $[M^{+\bullet}$ m/z 466]

$m/z = 393$

2a: R = TMS; $[M^{+\bullet}$ m/z 510]
2a-Et: R = Et; $[M^{+\bullet}$ m/z 466]

m/z 393 m/z 247

Scheme 5. Formation of the m/z 393 characteristic of the 2-MG linear and branched dimers and their ethyl esters via a homolytic α-cleavage reaction.

$M^{+\bullet}$, m/z 466 m/z 436 m/z 306
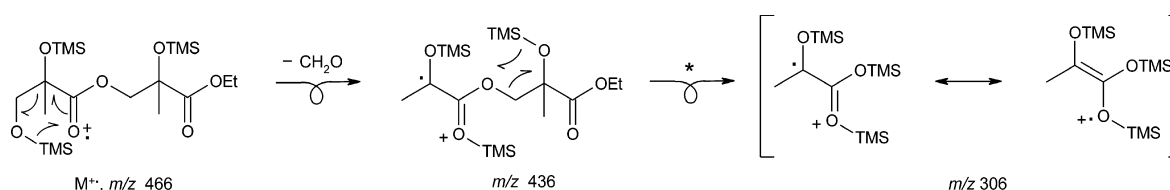
Scheme 6. Plausible mechanisms for the formation of m/z 436 and 306 from the TMS derivative of 2-MG linear dimer ethyl ester.

CH$_2$O loss. Furthermore, it can be seen that there is an additional ion at m/z 377 in the latter case, which corresponds to [M − (CH$_3$ + CO + TMSOH)]$^+$. An MS/MS experiment confirmed that m/z 467 is the precursor for m/z 377; a possible explanation is a favorable 1,3-elimination of TMSOH in the branched carboxylic acid-containing 2-MG residue.

Figure 6 shows the m/z 393 product ion spectra for the two isomeric 2-MG dimers. Interesting differences can be noted, with m/z 247 being most abundant in the branched case; this information will be used in the following section to establish an esterification site in the 2-MG branched

trimer. In the case of the 2-MG branched dimer, m/z 247 can be readily formulated through a charge-directed loss of trimethylsilylated hydroxyacetone (Scheme 5).

Other structurally informative ions in the EI spectra of the TMS derivatives of the 2-MG linear and branched dimers worth discussing are m/z 247 and 321. The m/z 247 ion is explained by an α-cleavage relative to the ester C = O bond (Scheme 7) but can also be formed by other pathways (e.g. from m/z 393; Scheme 5) and is characteristic for the presence of an ester linkage in the molecule. The ion at m/z 247 fragments further to m/z 231, 219, 203, and 157, as confirmed
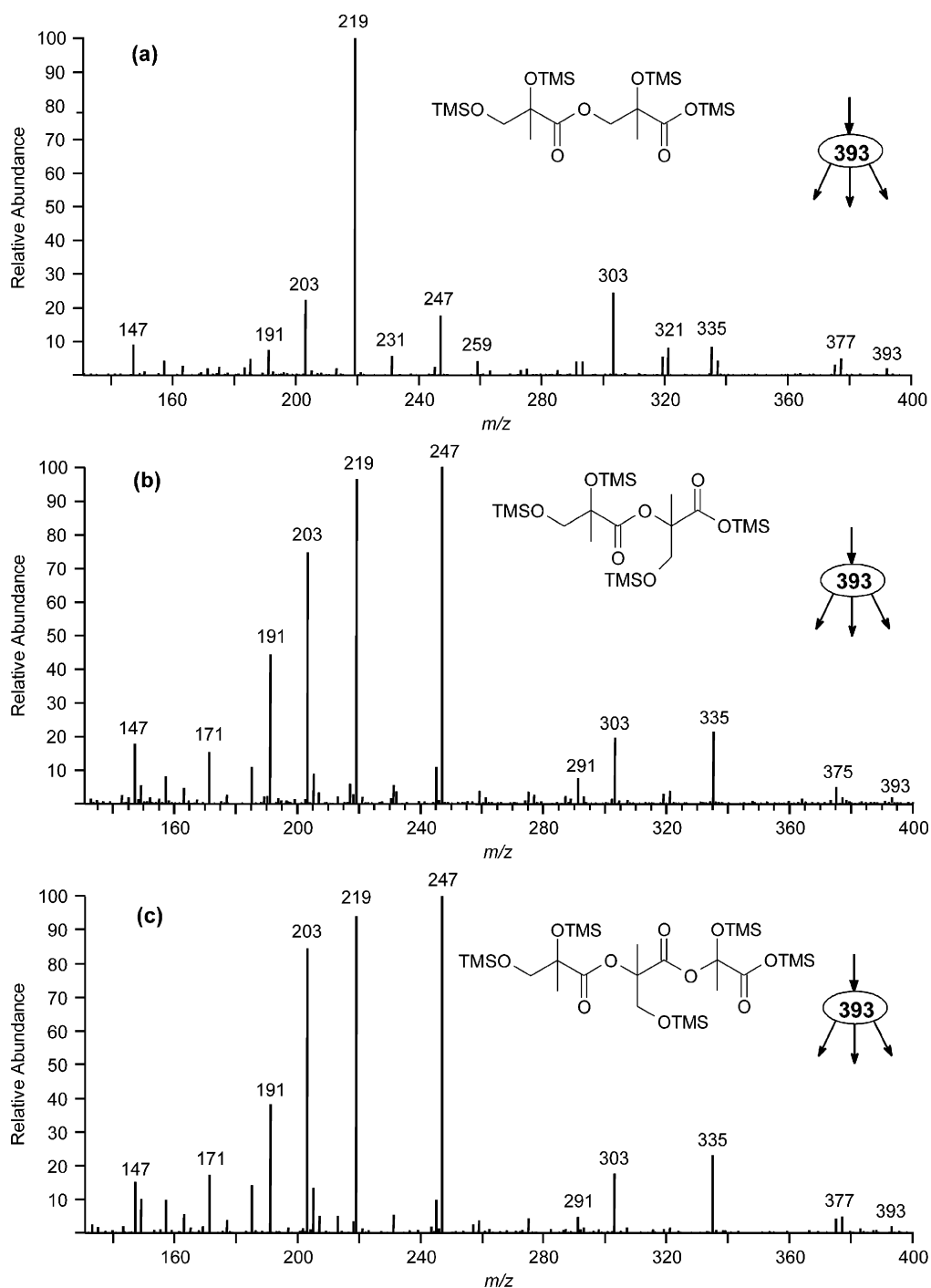

Figure 6. MS^2 ion trap spectra for m/z 393 of the TMS derivative of (a) the 2-MG linear dimer, (b) the 2-MG branched dimer and (c) the 2-MG branched trimer.
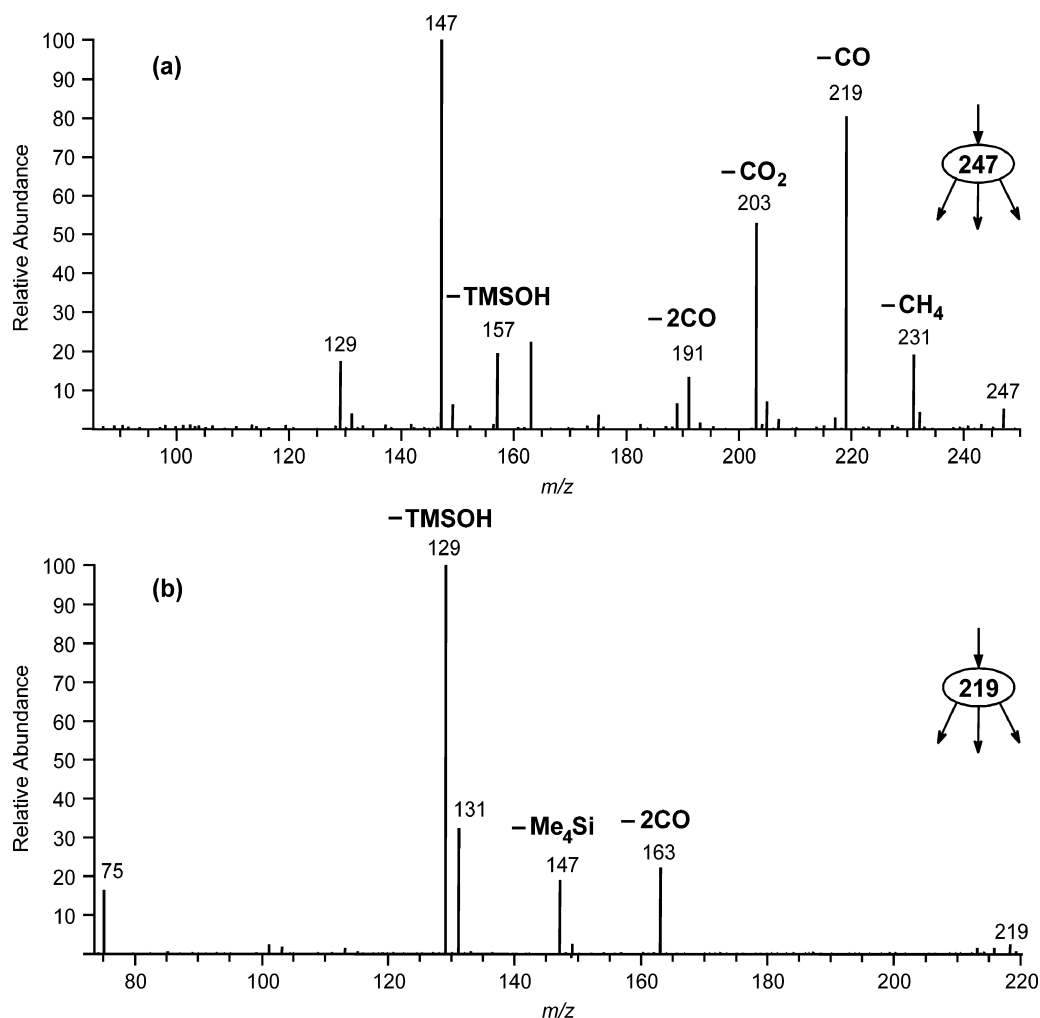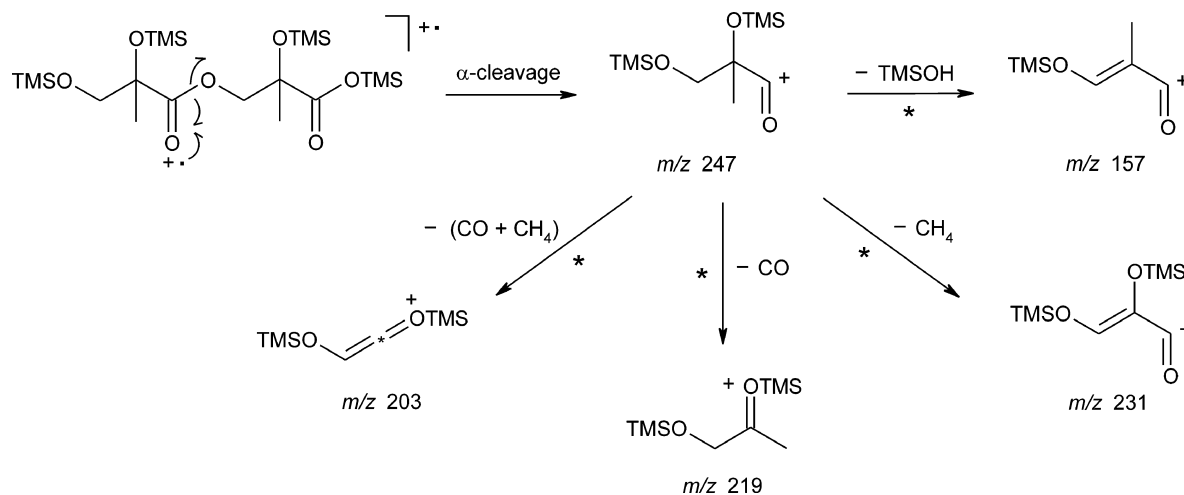
Figure 7. MS^2 ion trap spectra for selected ions of the TMS derivative of the 2-MG linear dimer: (a) *m/z* 247 and (b) *m/z* 219.

Scheme 7. A plausible formation mechanism for *m/z* 247 and its further fragmentation as confirmed by MS^2 ion trap experiments.

by MS^2 experiments (Fig. 7(a); Scheme 7). The MS^2 ion trap spectrum of *m/z* 219 (Fig. 7(b)) unambiguously proves that its structure is consistent with a trimethylsilylated 1,2-dihydroxy-2-methylethyl group,[21] which has already been discussed above in the case of 2-MG and its ethyl ester derivative.

Fragmentation behavior of 2-MG trimers and their ethyl esters

Figure 8(a) and (b) shows the EI mass spectra of the TMS derivatives of the two isomeric trimers of 2-MG that were detected in the GC/MS TIC of high-NO$_x$ isoprene SOA (Fig. 1). Since both spectra display the same set of ions
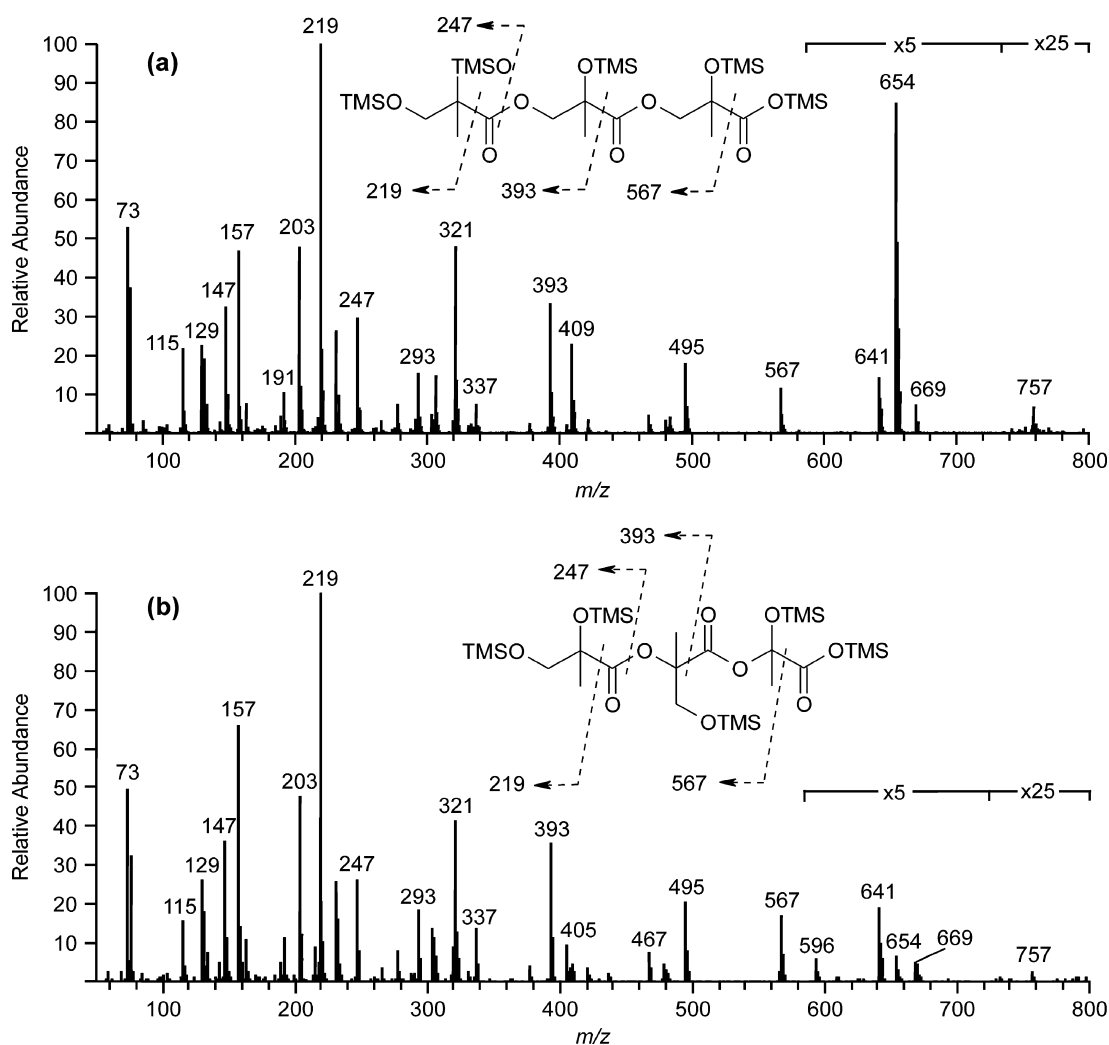
Figure 8. EI mass spectra of the TMS derivatives of 2-MG (a) linear (**3a**) and (b) branched trimer (**3b**).

differing only in terms of their relative abundances, one can conclude that they represent isomeric compounds. The most abundant compound which elutes at the latest retention time (RT = 60.31 min) is attributed to the linear trimer (**3a**), while the other one (RT = 60.01 min) is attributed to a branched trimer (**3b**), given that under the GC conditions employing a nonpolar stationary phase, branched isomers, which have a more compact structure than their linear forms, elute at an earlier retention time. As will be discussed below, evidence for a branched internal 2-MG residue was obtained. However, we have no evidence for the esterification site in the terminal carboxylic acid-containing 2-MG residue and assume that after dimer formation, esterification proceeds by reaction with a terminal hydroxymethyl group of a 2-MG molecule, thus resulting in a linear form, since the formation of linear forms is sterically less hindered.

As in the case of the 2-MG dimers, examination of the high m/z range enables us to infer the MW (684). Both isomers reveal a very weak $[M + TMS]^+$ adduct ion (m/z 757) as well as $[M - CH_3]^+$ ion (m/z 669) and $[M - (CH_3 + CO)]^+$ ions (m/z 641). The latter ion also supports a terminal carboxyl group in the underivatized molecules. It can be seen that the abundance of the $[M - CH_2O]^{+\bullet}$ ion (m/z 654) is strikingly different and is more abundant for the linear

system compared to the branched one. The same observation was made for the $[M - CH_2O]^{+\bullet}$ ion (m/z 610) in the mass spectra of the 2-MG dimers and the ethyl derivatives of 2-MG trimers (results not shown). A possible explanation for this phenomenon is given in Scheme 8. A TMS group transfer may not only proceed from the terminal TMSOCH$_2$ group but also from an internal TMSOCH$_2$ group, involve different geometries of the transition state, and take place at a different rate. The interaction between the terminal TMSOCH$_2$ group and a neighboring ester function involves a 6-centered transition state, while that between the internal TMSOCH$_2$ group of the branched isomer and a neighboring ester function involves a 7-centered state which is less favorable but may be formed faster.

The m/z 393 ion can be explained by an α-cleavage directed by the ionized internal TMSO group of the inner 2-MG residue. Figure 6(c) shows that the m/z 393 product ion profile of the branched trimer is very similar to that of the branched dimer (Fig. 6(b)), suggesting that the branched 2-MG trimer contains an inner branched 2-MG residue. In the following discussion, attention will be given to structurally informative ions, which were not present in the case of the 2-MG dimers. Both the linear and branched 2-MG trimer reveal an ion at m/z 495 which can be explained
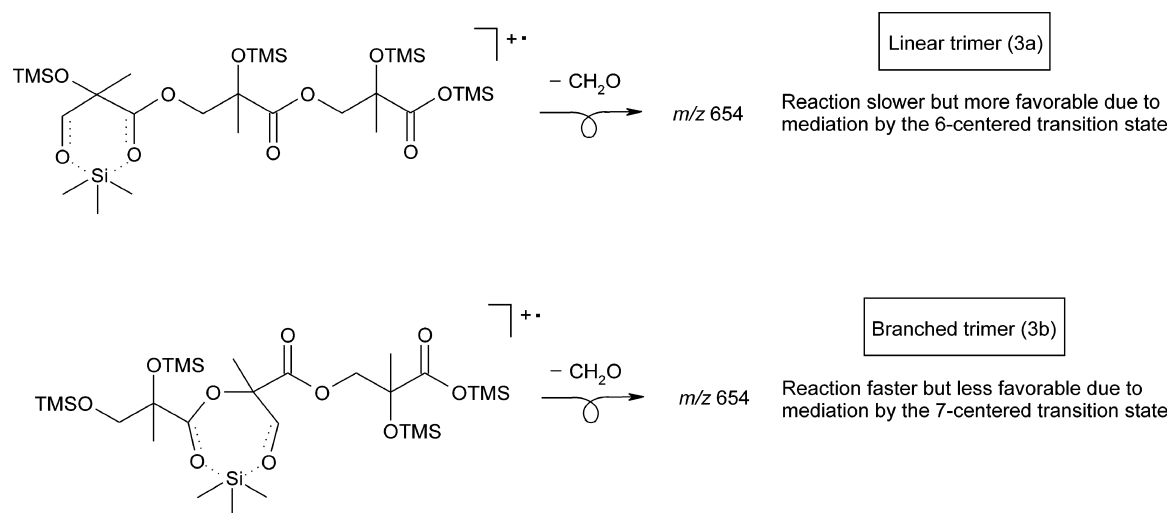
Scheme 8. Differences in the geometry of the transition state providing a rational explanation for the more favorable loss of formaldehyde from the $M^{+\bullet}$ ion of the TMS derivative of the 2-MG linear trimer compared to that of the branched form.
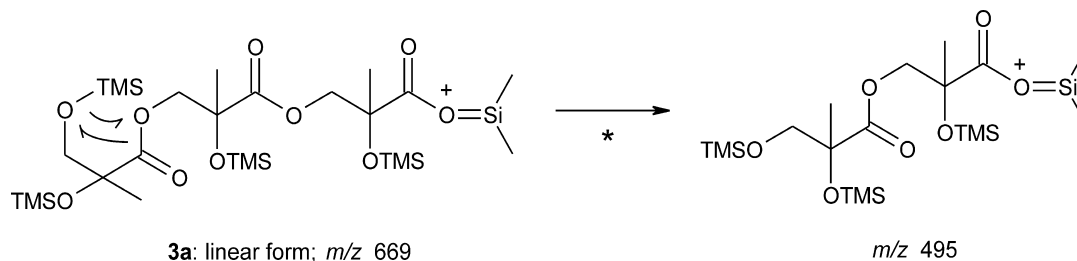
Scheme 9. Formation of m/z 495 in the case of the TMS derivative of the 2-MG linear trimer. The same mechanism can be proposed for the 2-MG branched trimer.
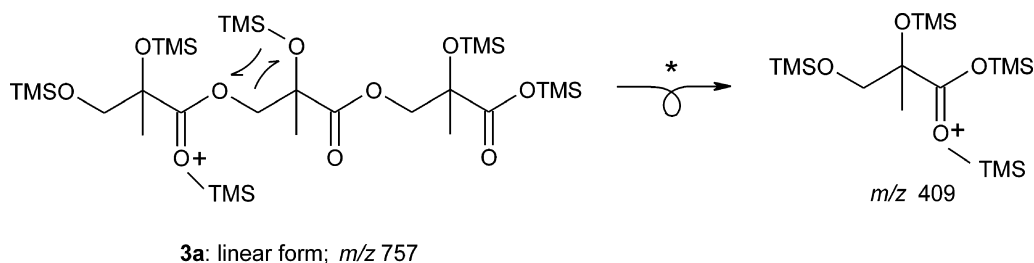
Scheme 10. Pathway leading to m/z 409 in the TMS derivative of the 2-MG linear trimer.

from the $[M - CH_3]^+$ ion by loss of a neutral (174 Da) from the terminal 2-MG residue through a rearrangement of a TMS group (Scheme 9). In addition, ions are present, which are isomer-specific. In the case of the 2-MG linear trimer, an ion can be seen at m/z 409, while the 2-MG branched trimer reveals an ion at m/z 596. The m/z 409 ion can be generated from the $[M + TMS]^+$ adduct ion by an internal rearrangement of a TMS group resulting in the $[2\text{-MG} + TMS]^+$ adduct ion (Scheme 10). The m/z 596 ion characteristic of the 2-MG branched trimer is believed to result from a favorable interaction in the $M^{+\bullet}$ ion between the trimethylsilylated hydroxymethyl group of the branched unit and a trimethylsilylated hydroxyl group, leading to loss of $(CH_3)_4Si$ (88 Da).

Fragmentation behavior of 2-MG linear dimer mono-acetate derivatives

The two small peaks in the GC/MS TIC of high-NO_x isoprene SOA (Fig. 1) eluting just after the 2-MG linear dimer (**2a**) were

identified as isomeric 2-MG linear dimer mono-acetates (**2a-Ac1,2**). These products were already partially characterized in our previous study using (−) ESI-MS, and are formed by esterification between the 2-MG linear dimer and acetic acid, which is also generated from isoprene in the smog chamber under high-NO_x conditions.[10] As will be discussed below, a more complete characterization of the isomeric 2-MG linear dimer mono-acetates was possible by detailed interpretation of the EI mass spectral data. The EI spectra of the TMS derivatives of the isomeric 2-MG linear dimer mono-acetates are shown in Fig. 9. The peak eluting at a RT of 52.3 min was characterized as the isomer containing an internal acetate group (**2a-Ac1**), while the peak at a RT of 52.6 min was attributed to the isomer containing a terminal acetate group (**2a-Ac2**). The partial splitting noted in the latter chromatographic peak can be explained by diastereoisomerism.

Examination of the high m/z range enables us to infer the MW (480); the EI spectra of the TMS derivatives of both
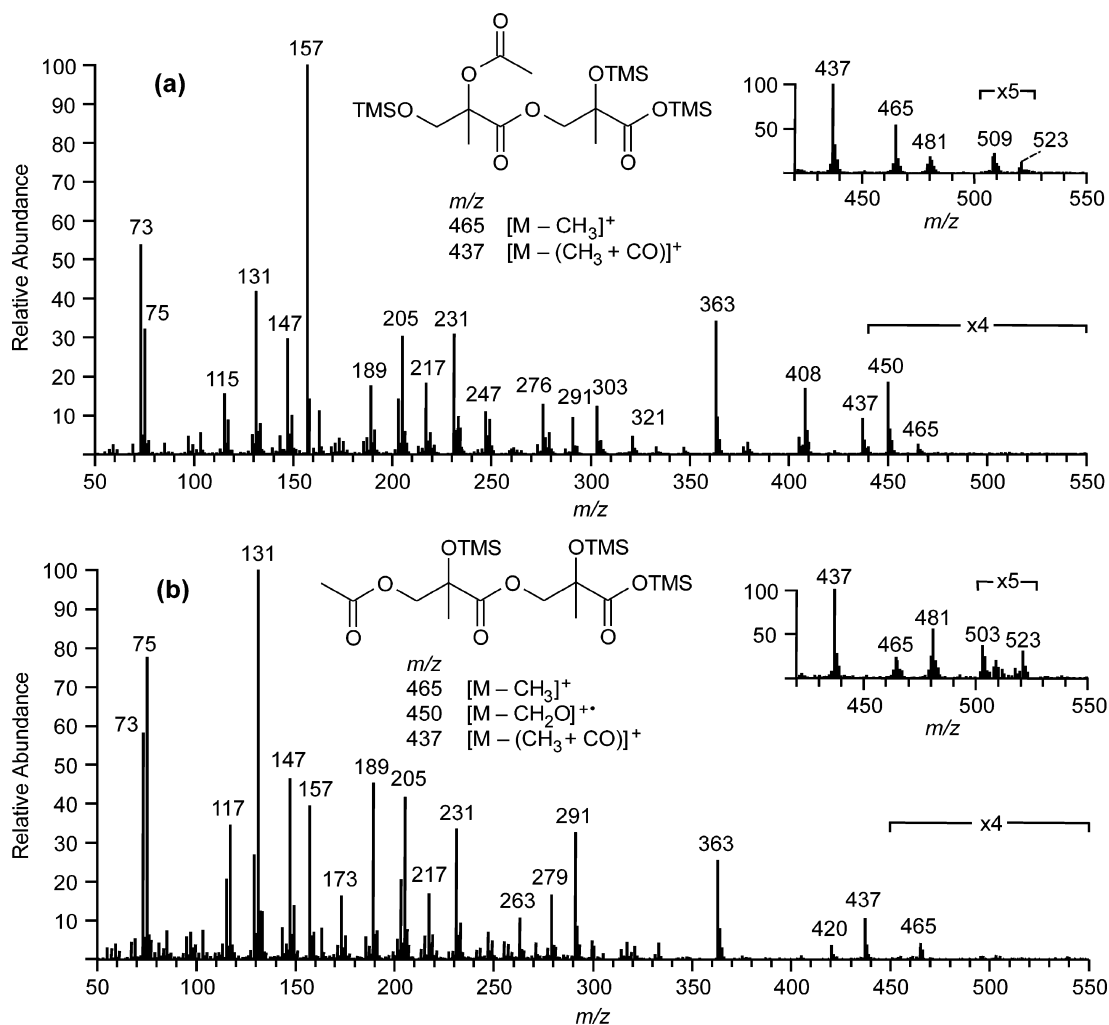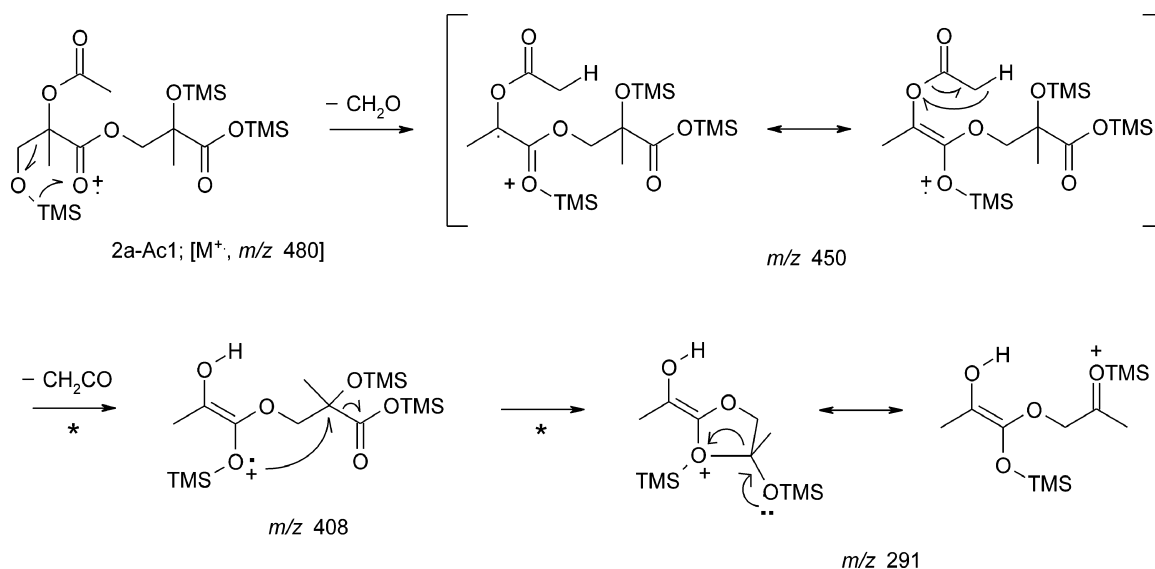
Figure 9. EI mass spectra of the TMS derivatives of 2-MG linear dimer mono-acetates bearing the acetate group at (a) the terminal hydroxymethyl group (**2a-Ac1**) and (b) an internal hydroxyl group (**2a-Ac2**). Insets: CI (methane) data.
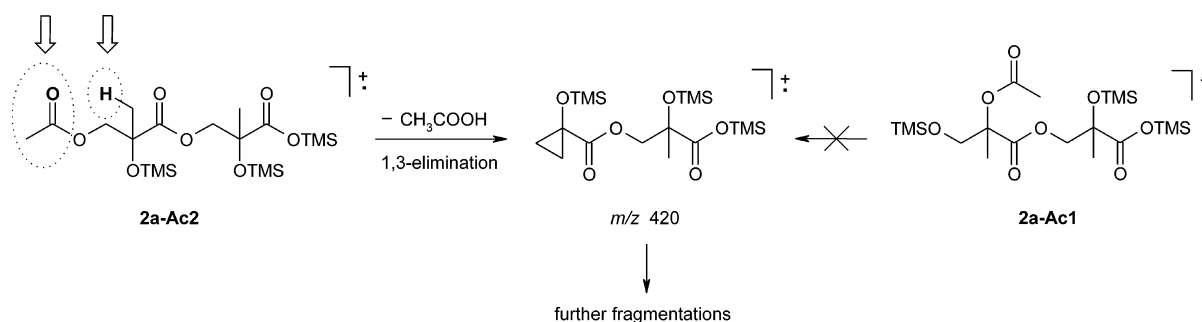

Scheme 11. Mechanisms proposed for the formation of m/z 450, 408, and 291 present in the EI spectrum of the TMS derivative of the 2-MG dimer mono-acetate isomer eluting at RT 52.3 min (**2a-Ac1**).

2-MG linear dimer mono-acetates show $[M - CH_3]^+$ (m/z 465) and $[M - (CH_3 + CO)]^+$ ions (m/z 437). Supporting MW information was derived from the CI (methane) mass spectra (insets in Fig. 9), which reveal $[M + H]^+$ (m/z 481), $[M + C_2H_5]^+$ (m/z 509), and $[M + C_3H_7]^+$ (m/z 523) ions as well as $[MH - CH_4]^+$ ions (m/z 465). It can be
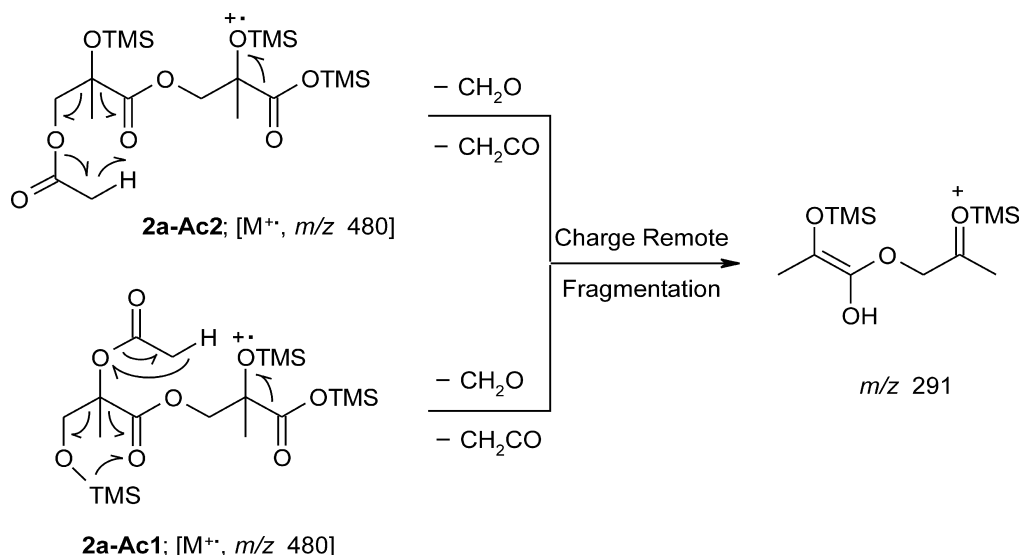
Scheme 12. Possible formation pathways for *m/z* 291 in the TMS derivatives of both 2-MG dimer mono-acetate isomers through charge-remote fragmentation reactions.

Scheme 13. Mechanism proposed for the formation of *m/z* 420, an ion characteristic of the TMS derivative of the 2-MG dimer mono-acetate bearing an acetyl group at the terminal hydroxymethyl group of the non-carboxylic acid-containing 2-MG residue (**2a-Ac2**). Parts of the molecule engaged in the elimination process are circled.
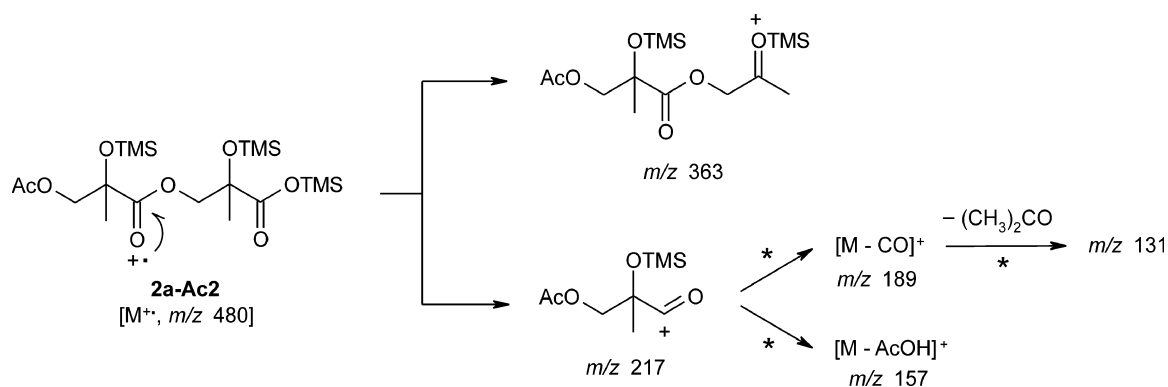
Scheme 14. Mechanisms proposed for formation of *m/z* 363, 217, 189, 157, and 131 in the TMS derivative of an 2-MG linear dimer mono-acetate (**2a-Ac2**). The same mechanisms hold for the isomer **2a-Ac1**.

seen that the spectrum of the first-eluting isomer (**2a-Ac1**) contains an ion at *m/z* 450, corresponding to the [M − CH₂O]⁺• ion formed through a rearrangement of a TMS group (Scheme 11). This ion firmly supports the presence of a terminal trimethylsilylated hydroxymethyl group in the non-carboxylic acid-containing 2-MG residue and is consistent with a nonbranched carboxylic acid-containing

2-MG residue. Following the loss of formaldehyde, *m/z* 450 fragments by loss of ketene (42 Da) from the acetate group, resulting in *m/z* 408. Further fragmentation of *m/z* 408 through loss of a TMSO(CO)• radical leads to *m/z* 291. It can be seen that *m/z* 291 is also present in the case of the 2-MG dimer mono-acetate isomer eluting at a RT of 52.6 min (**2a-Ac2**); an alternative explanation for *m/z* 291

in both 2-MG dimer mono-acetate isomers through charge-remote rearrangement reactions involving neutral loss of both ketene (42 Da) and formaldehyde (30 Da) is outlined in Scheme 12.

The EI spectrum of the compound corresponding to the 2-MG dimer mono-acetate isomer eluting at a RT of 52.6 min (**2a-Ac2**) (Fig. 9(b)) shows a unique ion at m/z 420, which is explained by loss of acetic acid from the $M^{+\bullet}$ ion (Scheme 13). This favorable elimination of acetic acid involves a hydrogen at a 3-position relative to the acetate group[23] and does not occur in the other isomer (RT 52.3 min) in which only hydrogen atoms at the 2-position are available.

Ions present in the spectra of the TMS derivatives of both isomeric 2-MG linear dimer mono-acetates worth discussing are m/z 363, 217, 189, 157, and 131. Their formation mechanisms are given in Scheme 14. The formation of m/z 217 and 189 in both isomers is consistent with the presence of an acetate group in the non-carboxylic acid-containing 2-MG residue. As expected, m/z 157 is more prominent in the case of the 2-MG dimer mono-acetate bearing an acetyl group at the terminal hydroxymethyl group because of the favorable 1,3-elimination of acetic acid. On the other hand, the formation of m/z 131 due to loss of acetone from m/z 189 seems to be a favored pathway in the case of the 2-MG dimer mono-acetate bearing an internal acetyl group.

CONCLUSIONS

Detailed interpretation of the EI mass spectral data of the TMS derivatives of 2-MG and oligoester derivatives thereof allows one to obtain key structural features of the molecules and as such to elucidate their chemical structures and differentiate isomeric compounds. The m/z 219 ion containing the trimethylsilylated 1,2-dihydroxy-2-methylethyl group is a characteristic ion of 2-MG and its oligomers. Evidence for an ester function in the 2-MG dimers and trimers is indicated by the m/z 247 ion formed by an α-cleavage in the ester group linking the non-carboxylic acid-containing 2-MG residue to the remaining part of the molecules. In addition, evidence for an inner branched 2-MG residue in the case of the 2-MG branched trimer was obtained, while the 2-MG linear and branched dimers could be readily differentiated. Characteristic ions of the terminal carboxyl group are the $[M - CH_3]^+$ and $[M - (CH_3 + CO)]^+$ ions, while the terminal hydroxymethyl group was found to give rise to a $[M - CH_2O]^{+\bullet}$ ion in linear 2-MG oligomers. Furthermore, it was possible to differentiate isomeric mono-acetates of the 2-MG linear dimer containing an acetyl group in the non-carboxylic acid-containing 2-MG residue and locate the position of the acetyl group. We can conclude that the EI spectra of the TMS derivatives contain a wealth of structural information, including information about the MW, ester linkages, terminal carboxylic and hydroxymethyl groups, and esterification sites.

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