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Selenium and Sulfur Trichalcogenides from the Chalcogenide Exchange Reaction

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Various selenium- and sulfur-containing volatiles have been detected and characterized as products of chalcogen exchange reactions. The formation of all possible selenium- and sulfur-containing trichalcogenide isomers (–SeSS–, –SSeS–, –SeSeS–, –SeSSe– and –SeSeSe–) was observed at room temperature in the solutions containing diselenide and trisulfide. Because of the low activation barrier of the selenium exchange reaction, these species are expected also to form in biological systems in the presence of diselenides and higher sulfides. Methyl and ethyl derivatives of these species were characterized using gas chromatography coupled to time-of-flight mass spectrometry with electron impact, chemical, and field ionization. Rearrangements of triselenides lead also to the formation of isomeric branched-structure triselenides, selanadiselenides. Because of the very similar structural properties, the behavior of these novel species was studied under various ionization modes (EI+, CI+, EI–, and CI–).

Introduction

Recent developments in selenium speciation in systems of biological importance have increased the interest in exploring the chemistry of selenium-containing metabolites.[1,2] Not surprisingly, the synergy of various analytical methods can be very advantageous for speciation studies. Atomic mass spectrometry with its capability to selectively show the presence of particular element-containing metabolites when used along with other mass spectrometry techniques for structural information can provide good characterization of previously unidentified species.

Despite the growing interest in Se biospecies, the availability of selenium-containing volatile standards is limited to a small number due to their instability and infrequent use in environmental analysis.[3] Selenides and diselenides are the major Se-volatiles found in the environment; however, only diselenides possess significant chemical reactivity due to the redox-sensitive Se–Se bond.[1,4]

Inductively coupled plasma mass spectrometry, ICP-MS, is an attractive technique for sensitive and selective screening of the interactions of selenium-containing volatiles.[3,5] Equilibrium constants and kinetics of the diselenide exchange reaction can be easily measured by element-specific detection. For example, a mixture of dimethyldiselenide and diethyldiselenide after equilibration (within a few hours at room temperature) shows a typical pattern with peak areas of 1:2:1, which corresponds to the statistical equilibrium constant of $K = 4$. Also, due to the element specific detection, Se- or S-only-containing species do not have to be chromatographically well resolved, as they are recorded in different mass domains.

Gas chromatography/time-of-flight, GC/TOF, mass spectrometry has the benefit of detection capabilities comparable to those of ICP-MS, which makes it a very promising complementary technique for trace-level elemental speciation. The ability to do precise exact mass measurements (up to 0.0001 u) is very beneficial for studying the mass spectral fragmentation pathways of the selenium compounds.[6] The benefits of exact mass measurements become more important for accurate assignment of the polyselenide molecular ions because of skewed isotopic distribution patterns.

Diselenide/trisulfide interactions are of importance in biological systems, and, in this regard, it is useful to examine the possible interaction pathways of these species. In this

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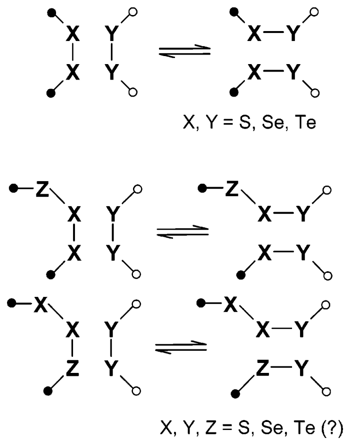
10.1021/ic0494206 CCC: $27.50

Scheme 1. General View of the Chalcogenide Exchange Reaction[a]



[a] White and black dots represent non-hydrogen substitution.

study, we report the formation of all selenium- and sulfur-containing trichalcogenides and several higher polychalcogenides from the Se/S exchange reaction at room temperature. Rearrangements of these volatiles may lead to the formation of isomeric branched structures. Because of very similar structural properties, the behavior of these novel species was studied under various ionization modes (EI+, CI+, EI−, and CI−).

Results and Discussion

The dichalcogenide exchange reaction[7] (Scheme 1), whose mechanism has not yet been fully elucidated, is probably one of the most intriguing riddles in Se chemistry. This reaction occurs through the rupture of the X−X bond as the RX moiety is conserved. For linear alkyl chains containing dichalcogenides, the enthalpy change is zero within experimental error, and, therefore, this is an entropy-driven reaction and the equilibrium constant does not vary with temperature.[7,8] Such exchange reactions are also reported to occur with biologically active bis(alkylthio)selenides.[8,9]

In the case of linear chain alkyl groups, the equilibrium constant of dichalcogenide exchange is governed solely by the statistical factors and is close to the $K = 4$.[7] Low activation energy barriers and an equilibrium constant close to unity result in the accumulation of the exchange reaction products. Thus, pure asymmetric species, such as MeSeSeEt or MeSeSMe, will be in equilibrium with its exchange products (MeSeSeMe + EtSeSeEt and MeSSMe + MeSeSeMe). This implies that asymmetric dichalcogenides cannot be isolated in a pure form unless the chalcogenide exchange is suppressed. On the other hand, products of the exchange reaction can serve as important biomarkers of diselenides and selenosulfenates.

Formation of Polychalcogenides. Analogous to the dichalcogenide exchange (Scheme 1), trisulfides interact with diselenides through steps of several consecutive exchange reactions as shown in Scheme 2.

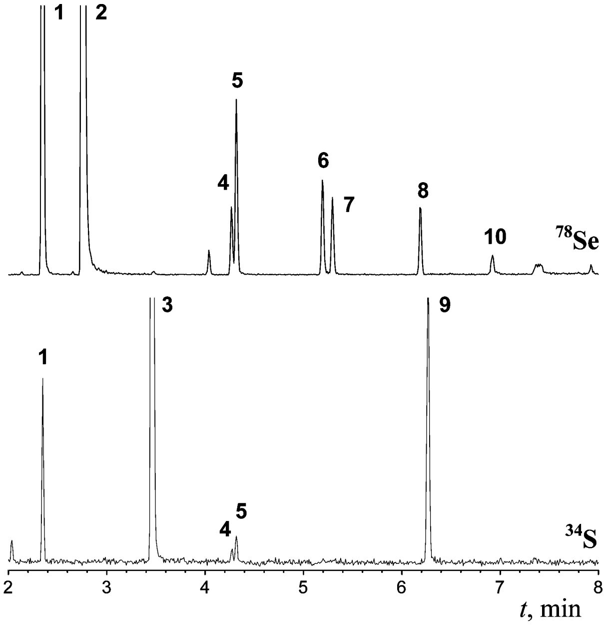
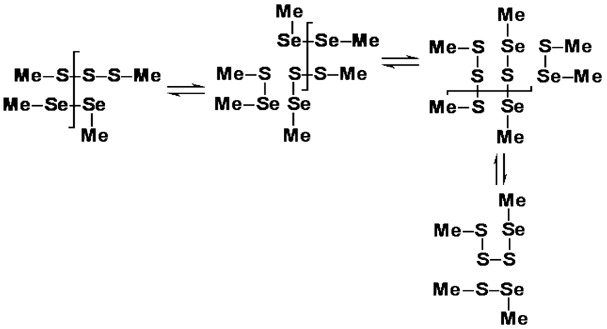


Figure 1. ^{34}S and ^{78}Se GC/ICP-MS chromatograms of the S/Se exchange reaction products identified from MeSeSeMe and MeSSSMe. (**1**) MeSeSMe, (**2**) MeSeSeMe, (**3**) MeSSSMe, (**4**) MeSSeSMe, (**5**) MeSSSeMe, (**6**) MeSeSeSMe, (**7**) MeSeSSeMe, (**8**) MeSeSeSeMe, (**9**) MeSSSSMe impurity from MeSSSMe, (**10**) MeSeSSSMe.

Scheme 2. Consecutive Se/S Exchange Reactions between Dimethyldiselenide and Dimethyltrisulfide



As the change in enthalpy is zero, this reaction can be considered from a statistical point of view. With respect to this, trichalcogenides can interact with dichalcogenides in two different routes as shown in Scheme 1. The products of such interaction processes can be easily detected with GC/ICP-MS (Figure 1). The abundance of the species diminishes in each of the consecutive steps, and the decreasing volatility also inhibits the detection of reaction products with more than four chalcogen atoms per molecule. Under constant temperature ramp conditions (ΔT = const), linear chain dimethyl polychalcogenides possess systematic incremental retention time behavior on a nonpolar polysiloxane DB-1 capillary column. Elution of these species can be summarized in a two-dimensional retention time grid as shown in Figure 2. The existence of multidimensional retention time grids for selenium-substituted dimethyl chalcogenides was first recognized by Hillen and Werner in 1973. However, the detection and characterization of the various

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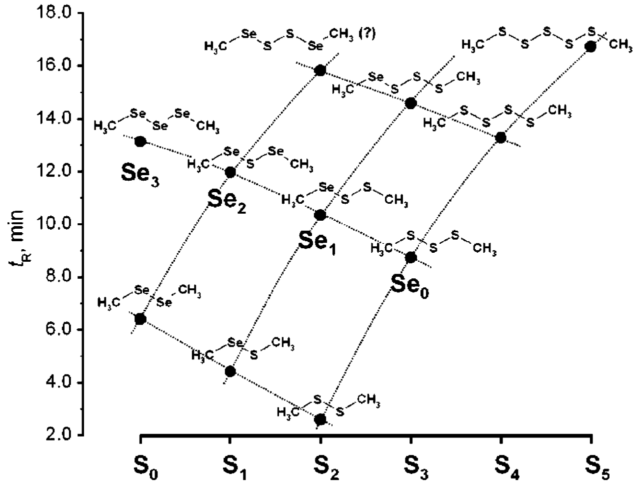
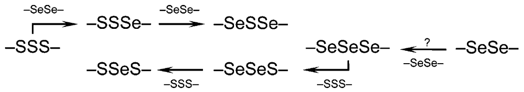


Figure 2. Two-dimensional GC retention time grid of the linear chain dimethyl polychalcogenides, $CH_3S_nSe_mCH_3$ ($0 \leq n \leq 5$ and $0 \leq m \leq 3$).

Scheme 3. Formation of All of the Se/S Trichalcogenides in the MeSeSeMe/MeSSSMe System



isomeric species was out of the question due to the technical limitations at the time.[10]

Increments in retention times due to sulfur replacement with selenium also suggest that the −SeS− moiety can be considered as an average between the corresponding diselenides and disulfides. In other words, the behavior of MeSeSMe can be considered as an average between the MeSSMe and MeSeSeMe. This is also true not only for the boiling points or molecular weights of these species, but also for ionization energies, bond lengths, and bond dissociation energies. An initial estimate of various properties of Se−S species can be generated by averaging those of the corresponding Se−Se and S−S species.

Because of the very low abundance, $MeSe_2S_2Me$ shown in Figure 2 was only identified from the molecular ion and retention time. The actual structure, however, was not elucidated.

For higher sulfur- and selenium-containing chalcogenides, several structural isomers are possible as shown in Scheme 3. Both $MeSeS_2Me$ isomers, MeSeSSMe and MeSSeSMe, were detected from the mixture of MeSeSeMe and MeSSSMe. MeSeSSMe is always present at the highest levels as it is formed directly from the interaction of the main diselenide and trisulfide, while the formation of MeSSeSMe requires triselenide, which is a minor component (see Scheme 3).

Thus, the chalcogen exchange reaction between dimethyl diselenide and dimethyl trisulfide leads to the formation of all of the six Se/S trichalcogenides plus several higher polychalcogenides providing an attractive way to obtain an all-in-one standard mixture of these otherwise commercially unavailable species. Se/S exchange between trisulfides and diselenides can also be used as an alternative approach to bis(thio)selenides over the Painter reaction[8,11] or selenium transfer reagents.[12] To date, the Se/S exchange reaction has been successfully used for the preparation of otherwise commercially unavailable dichalcogenides;[3,13] however, it can be easily extended also to higher chalcogenides.

Biogenic bis(thio)selenides are of special importance as they are formed in vivo from selenite (SeO_3^{2-}) with thiols (Painter reaction).[8] Volatile bis(methylthio)selenide (**4**) has been also found in natural elephant garlic and onion oil, and its EI+ mass spectrum is in agreement with our results.[13]

Isomeric polychalcogenides **4**, **5** and **6**, **7** have very similar retention behaviors on a nonpolar GC column as expected due to their structural similarities. The formation of selenosulfenates (−SeS−) and more complex species, such as selanyl disulfides (−SeSS−) or selanediylsulfides (−SeSSe−), can be easily detected by simultaneous monitoring of the S and Se isotopes in GC/ICP-MS. Also, the elemental ratios in the eluting species are accessible by recording the isotope ratio chromatogram with respect to the reference compound for which the S:Se ratio is known (data not shown).

Reductive cleavage of the Se−Se bond in diselenides or selenosulfenates occurs easily in the presence of 1,4-dithio-2,3-butanediol (DTT), and the addition of DTT is widely used to elucidate whether the species of interest contains the Se−Se or Se−S bond (in such a case, the chromatographic peak will disappear after the addition of DTT).[14] Triselenides, on the other hand, are not highly susceptible to Se−Se bond cleavage in the presence of DTT. Similarly, symmetrical trichalcogenides such as MeSSeSMe and MeSeSSeMe are not reduced in the presence of DTT, in contrast to their asymmetric isomers (data not shown). This finding, however, requires more research regarding the structural effects on reduction of higher selenium-containing chalcogenides.

Mass Spectra of Trichalcogenides. The mass spectral behavior of heteroatom-containing trichalcogenides in fact is a challenge due to the variety of rearrangements under EI+ ionization conditions. Selenium-containing trichalcogenides very easily undergo the Se/S exchange reaction; thus asymmetric species always will be contaminated with the exchange reaction products, which can also appear at masses higher than that of the molecular ion. As a consequence of this, in the EI+ ionization spectra of all of the CH_3Se-containing trichalcogenides (MeSeSeSeMe, MeSeSSeMe, MeSeSeSMe, and MeSeSSMe), one can easily see abundant signals at $m/z = 190$, corresponding to the dimethyl diselenide formed during the self-exchange reaction of these species (Figure 3). CH_3S- and CH_3Se-containing trichalcogenides (MeSeSSMe and MeSeSeSMe) show the presence of dimethyl selenosulfenate (at $m/z = 142$) in their

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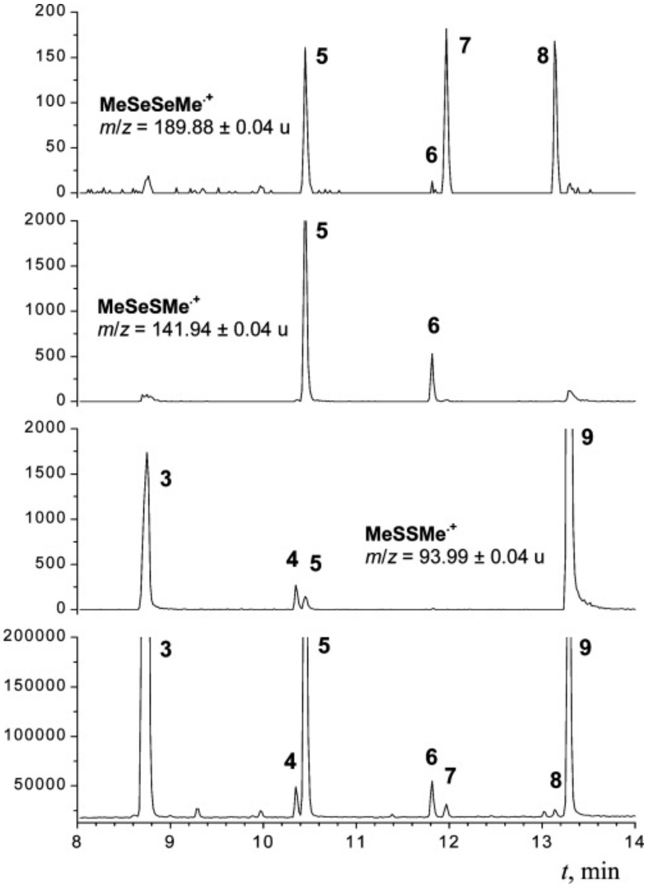
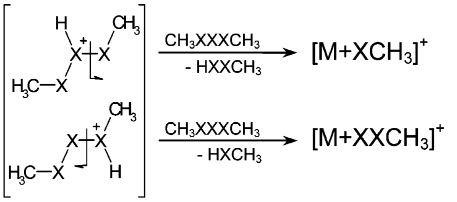


Figure 3. Selected ion monitoring in EI+ ionization GC/TOF-MS detection showing the structure-specific signals in the chromatogram of the S/Se exchange reaction products identified from MeSeSeMe and MeSSSMe.

Scheme 4. Adduct Formation in CI+ Mass Spectra of Se/S Chalcogenides



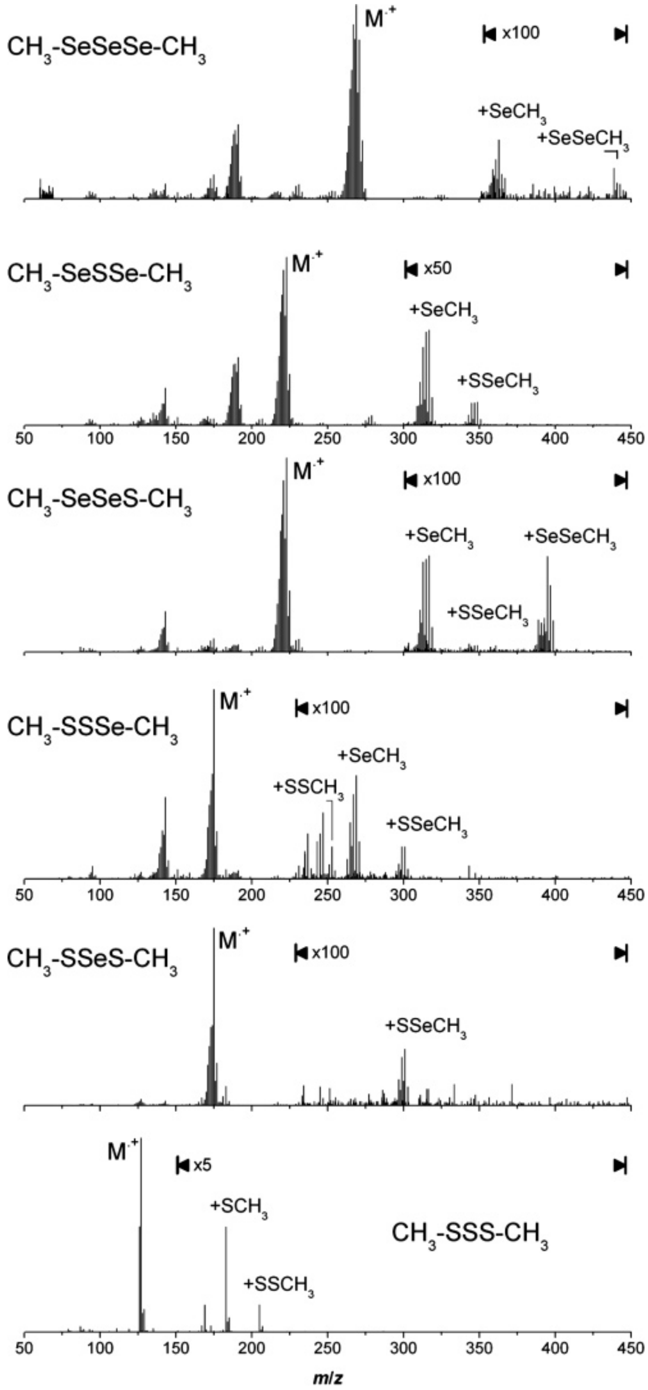


Figure 4. Positive chemical ionization mass spectra of S/Se dimethyl trichalcogenides showing the adduct formation.

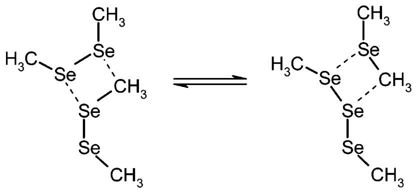
EI+ mass spectra. CH_3S-containing species show a dimethyl disulfide signal.

The phenomena of Se-containing chalcogenide self-exchange should also be considered when analyzing asymmetric isotopically labeled species. In other words, pure $^{13}CH_3-SeSe-CH_3$, for example, is expected to equilibrate in a 1:2:1 mixture of $CH_3-SeSe-CH_3$, $^{13}CH_3-SeSe-CH_3$, and $^{13}CH_3-SeSe-^{13}CH_3$.

Besides the self-exchange reaction, evidenced in EI+ spectra, trichalcogenides also show structure-specific adduct formation in CI+ as summarized in Scheme 4. Similar adduct formation is also recently reported for diselenides.[6] This is valuable in structural elucidation. For example, both isomers of $MeSe_2SMe$ could be easily identified solely from the adduct information in addition to the molecular mass information provided from CI+ mass spectra. While MeSeSSeMe shows only $[M + SeCH_3]^+$ and $[M + SSeCH_3]^+$, its isomer MeSeSeSMe shows abundant adducts $[M + SeCH_3]^+$, $[M + SeSeCH_3]^+$, and $[M+SeSCH_3]^+$ (Figure 4). Adduct formation in the CI+ mass spectra of di-, tri-, and higher selenium-containing chalcogenides is an attractive way of species identification at trace levels. With regard to this, CI+ offers lower detection levels as compared to EI+ (due to the ionization chamber geometry and no fragmentation-based loss of the signal), also providing structural information.

Symmetrical MeSSeSMe can be distinguished from its asymmetric isomer MeSSSeMe also via their negative chemical ionization mass spectra. Similar to dichalcogenides,[6] the presence of the negative charge (in CI− or EI−

Scheme 5. Suggested Mechanism of Triselenide Formation from Diselenides[a]



[a] Adapted from Milne et al.[15]

ionization) greatly reduces the energy of the dichalcogen bond, thus making the molecular ion extremely fragile. In CI− ionization, symmetrical MeSSeSMe leads only to the MeSSe$^-$ fragment, whereas MeSSSeMe gives MeSe$^-$, MeSeS$^-$, and MeSS$^-$ fragments and almost no molecular ion, in contrast to MeSSeSMe.

Formation of Triselenides. Several studies have shown that diselenides take part in disproportionation equilibria.

$$2\mathrm{RSeSeR} = \mathrm{RSeR} + \mathrm{RSeSeSeR} \qquad (1)$$

Such a reaction is reported for R = −Cl,[15] −Br,[15] and −C≡N[16] with an equilibrium constant of $K \approx 1 \times 10^{-4}$. Similar to these studies, dimethyl (**8**), diethyl (**12**), and ethylmethyl triselenides (**11**) were detected in the mixtures of diselenides after prolonged equilibrating time (several months). The relative amounts of these three triselenides were in agreement with the $K \approx 1 \times 10^{-4}$. These species can be formed similar to dichloro and dibromo diselenides[15] as shown in Scheme 5.

Asymmetrical ethylmethyl triselenide is presumably formed from dimethyl and diethyl diselenides according to this scheme or in an exchange reaction between dimethyl and diethyl triselenides. All three triselenides **8**, **11**, and **12** were characterized by electron impact and chemical ionization in both positive and negative modes.

Statistically, the most abundant ion in the triselenide ion cluster is ^{78}Se^{80}Se^{80}Se and not ^{80}Se^{80}Se^{80}Se as might be expected, analogous to diselenides or selenides (see Figure 5). Ignoring this issue may erroneously lead to incorrect molecular formula assignment. Dimethyl triselenide ($C_2H_6Se_3$) mass spectrum, for example, has been interpreted erroneously as cyclic 1,2,4-triselenolane ($C_2H_4Se_3$).[17] It is interesting to note that Figure 5 also explains the appearance of the ^{78}Se−^{80}Se−^{82}Se isotope pattern if the most abundant m/z = 160 ion (or its equivalent) would be subjected to tandem MSMS.

Branched Trichalcogenides. When analyzing the chromatograms of triselenides using post-acquisition selected accurate mass monitoring, minor triselenide satellite peaks were found corresponding to the molecular formula of $C_3H_8Se_3$ and $C_4H_{10}Se_3$ (see Figure 6). The validity of this molecular formula was also confirmed by the correct isotope pattern distribution in the eluting satellite species (as calculated by the polynomial expansion method[18]).

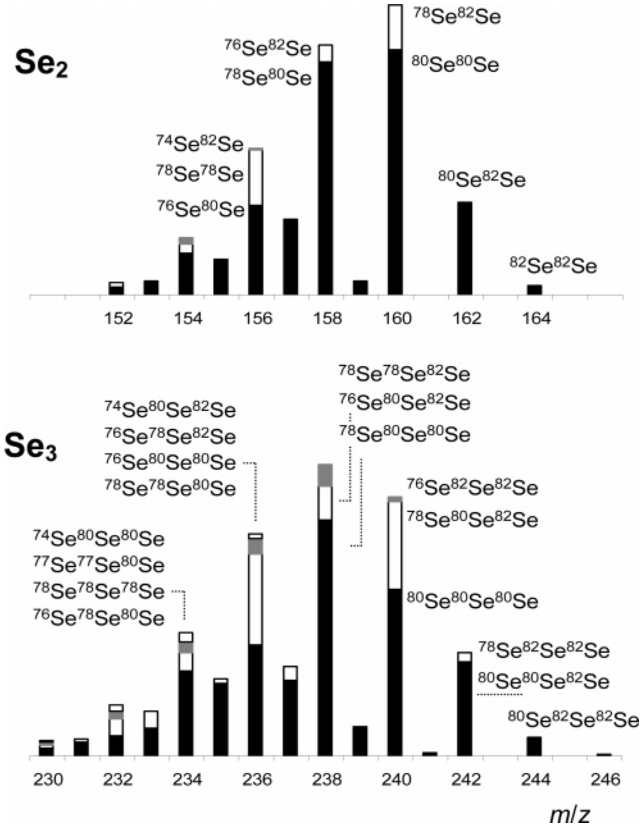


Figure 5. Formation of polyselenide isotope patterns: ^{80}Se^{80}Se^{80}Se is not the most abundant ion in triselenide clusters.

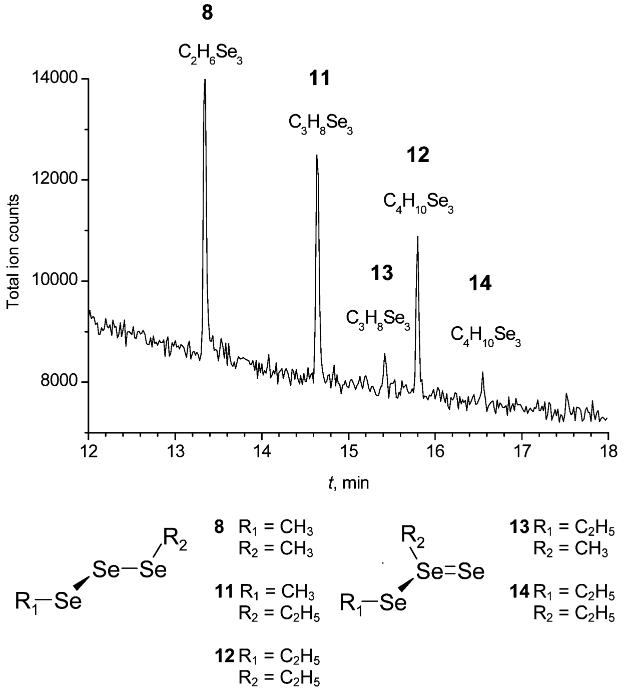


Figure 6. GC/TOF-MS CI+ total ion mass chromatogram showing the presence of isomeric triselenides **13** and **14**.

The mass spectra of these isomeric species (**13**, **14**) show several differences between their corresponding linear chain triselenides (**11**, **12**). The presence of the Se═Se$^{\bullet+}$ ion (center

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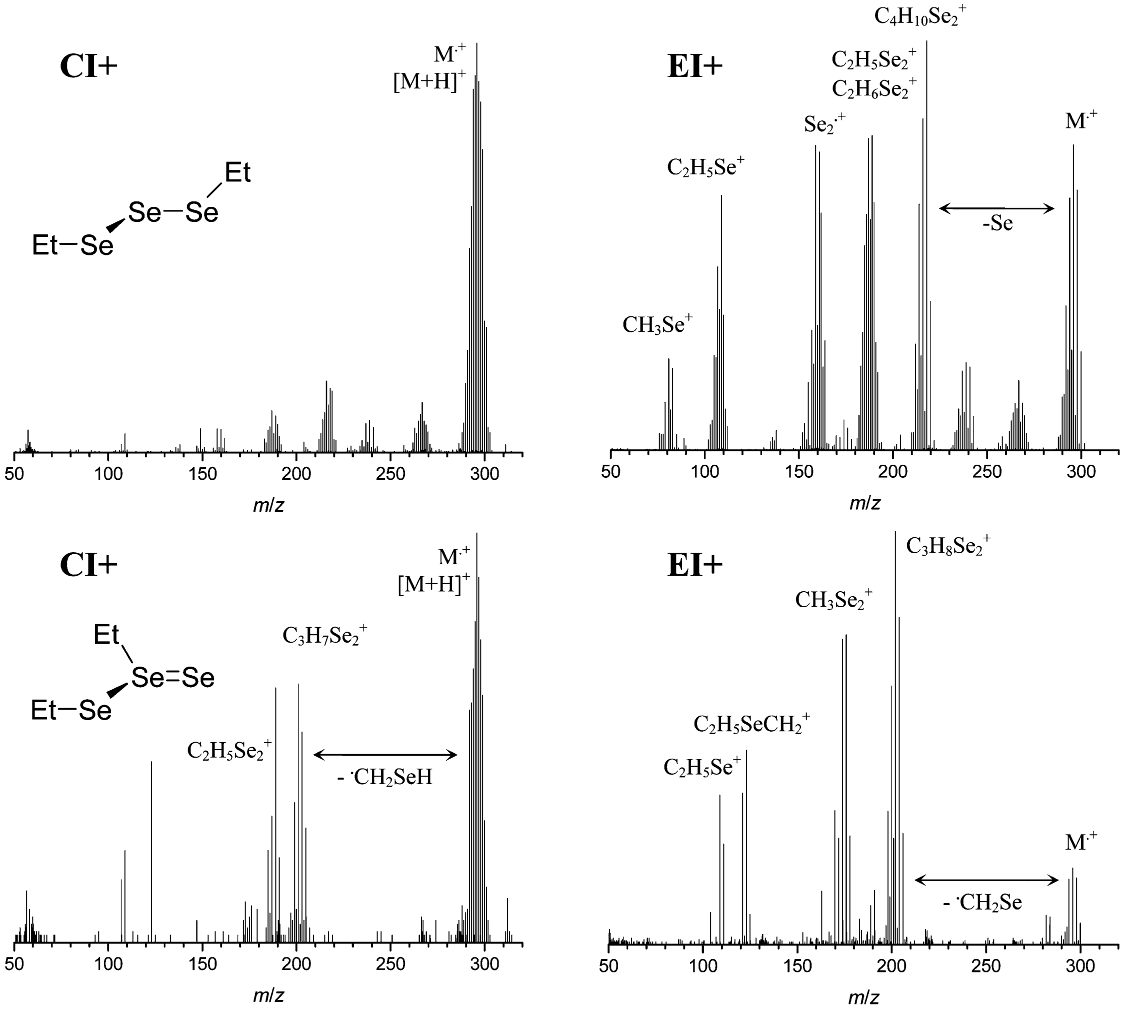
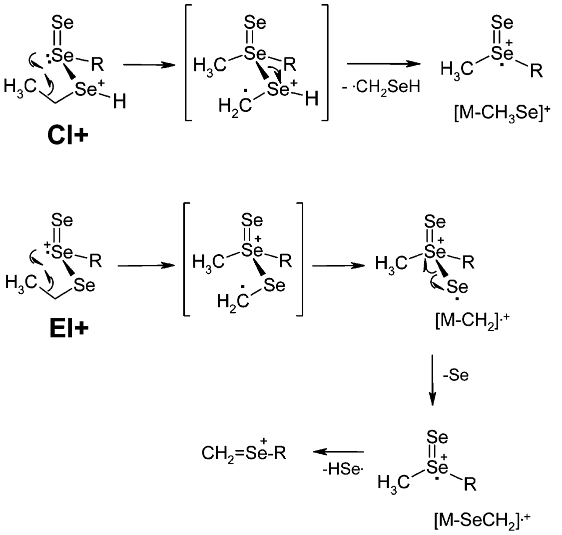


Figure 7. CI+ and EI+ mass spectra of diethylselanadiselenide (**14**) and diethyltriselenide (**12**).

at *m*/*z* = 159.8332 u) in EI+ conditions is not characteristic for the satellite species, while the Se═Se•+ cluster is one of the most abundant in the EI+ spectra of triselenides (Figure 7). The extrusion of the selenium atom is apparent in the mass spectra of triselenides via the formation of the corresponding diselenide, while this feature is not observed for the isomeric species. While the major clusters in EI+ mass spectra of linear triselenides are characterized by the consecutive loses of $H_2C{=}CH_2$ and extrusion of the central selenium, ethylated selanadiselenides also show major rearrangement leading to the loss of $^{\bullet}CH_2$ and $^{\bullet}CH_2Se$ (in EI+) and $^{\bullet}CH_2SeH$ (in CI+) as shown in Figure 7. Although the loss of $^{\bullet}CH_2$ from ethyl group as observed in EI+ ionization is rare in mass spectrometry,[19] such a behavior is consistent with the four-member ring rearrangement in selanadiselenides as shown in Scheme 6. In EI+ conditions, this terminal CH_3- group rearrangement leads to the loss of CH_2 and Se which is reflected in two clusters $[M - CH_2]^+$ and $[M - CH_2Se]^+$. $CH_2{=}SeR^+$ species are also formed (*m*/*z* = 122.97 u for R = Et and *m*/*z* = 108.96 u for R = Me), and they are not observed for linear chain species. In CI+ conditions, however, the loss of the protonated [CH_2Se] moiety is evident, leading to the abundant cluster $[M - CH_2SeH]^+$ (Scheme 6 and Figure 7).

Scheme 6. Proposed Four-Member Ring Rearrangement of Ethylmethyl- (**13**, R = CH_3) and Diethylselanadiselenide (**14**, R = C_2H_5) in CI+ and EI+ Ionization



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[19] McLafferty, F. W., personal communication, 2004. An example of low abundance methylene elimination from the ethyl group is the mass spectra of Et_4Sn, Et_4Ge, Et_4Pb: $Et_3X^+ \rightarrow Et_2XCH_3^+ + CH_2$. Chambers, D. B.; Glocking, F.; Weston, M. *J. Chem. Soc. A* **1967**, *11*, 1759−1769. Glocking, F.; Light, J. R. C. *J. Chem. Soc. A* **1968**, *3*, 717−734.

The apparent instability of the positively charged molecular ion of selenadiselenides is also supported by EI+ mass spectra where its abundance is less than 20% (for linear chain triselenides, $M^{\bullet+}$ is one of the most abundant ions).

On the basis of all of these properties, it was concluded that the isomeric species represent a new class of branched-structure triselenides, selenadiselenides (Figure 6, compounds **13** and **14**). The formation mechanism of these species was not investigated; however, due to their low abundance, it may be that linear chain triselenides are their precursors. The search for neutral and ionic branched chalcogenides has been widely discussed in the past.[20,21] Branched structure isomers (thiosulfoxides, $R_2S{=}S$) are known in sulfur chemistry;[22] however, analogous selenides are rare in the literature and require further research. To our knowledge, only dichlorodiselenide[23] and di(β-naphthyl)diselenide[24] are reported as possibly having a branched structure.

In conclusion, it has been shown that diselenides and triselenides easily participate in intermolecular chalcogen exchange reactions, leading to the formation of all of the Se/S trichalcogenides. This feature can be used in the identification of polychalcogenides mass spectra and also to obtain the standards of all of the trichalcogenides simultaneously. The high reactivity of Se−Se and Se−S bonds in trichalcogenides is also reflected in the mass spectral behavior of these species.

Experimental Section

Reagents and Standards. All reagents were of analytical grade and were used without any further purification. Dimethyl selenide, dimethyl sulfide, and dimethyl disulfide were purchased from Fluka (Milwaukee, WI). Dimethyl diselenide, dimethyl trisulfide, diethyl disulfide, and dithiothreitol were purchased from Sigma-Aldrich (Milwaukee, WI). Diethyl diselenide was purchased from Strem Chemicals (Newburyport, MA). Stock solutions of 1000 ppm were prepared by dilution of 2.5 μL of compound with 2500 μL of HPLC grade methanol (Fisher Scientific; Fair Lawn, NJ).

Instrumentation. An Agilent 6890 (Agilent Technologies; Palo Alto, CA) gas chromatograph was utilized in this work and coupled to a Micromass GCT orthogonal time-of-flight mass spectrometer (Micromass, Manchester, UK) and Agilent Technologies 7500c inductively coupled plasma mass spectrometer (Agilent Technologies, Tokyo, Japan).

In TOF-MS, a single fragment of the reference compound is used as an internal reference signal (lock mass). Accurate mass measurements were performed using heptacosafluorotributylamine as a mass calibration compound in EI+, EI−, CI+, and CI− ionization modes (with no reagent gas during the calibration in CI+ mode). Heptacosafluorotributylamine was used as a lock mass compound in EI+ ionization mode (218.9856 u), 2,4,6-tris-(trifluoromethyl)-1,3,5-triazine was used in CI+ mode (286.0027 u), and chloro- and bromopentafluorobenzene were used in CI− mode (201.9609 and 245.9104 u, respectively). Instrumental grade isobutane was used as a reagent gas. If the average mass accuracy exceeded 0.001−0.002 u, the instrument was recalibrated. The estimated resolution of the instrument $m/\Delta m = 3700$.

ICP-MS was used with a hydrogen octapole reaction system, and the instrument was operated at standard operating conditions described elsewhere.[3]

GC Conditions. A splitless injection mode was used, and the temperature of the injector was programmed at 220 °C. The column oven was initiated at a temperature of 75 °C and immediately ramped at 10 °C min^{-1} to a temperature of 220 °C. Helium was used as the carrier gas, and the column flow was set at a constant flow of 1.5 mL min^{-1}. An HP-5 (5% phenyl, 95% methylpolysiloxane) capillary column (30 m, 0.25 mm i.d., 0.25 μm film thickness) was used for separation.

Procedures. All of the oligochalcogenides were obtained in solution by mixing equal volumes of methanol solutions of dimethyl trisulfide (1000 ppm) and dimethyl or diethyl diselenide (1000 ppm) in a closed vial. The resulting solution was allowed to equilibrate at room temperature for a few hours, and, after dilution with pentane, the obtained mixture was subjected to chromatographic separation. The formation of triselenides and selanadiselenides appears to be a much slower process, and these species were detected only a few months after the mixing of the dimethyl trisulfide and methyl or ethyl diselenide. No cross-interaction products were obtained if the mixture was subjected to GC analysis immediately after the mixing of the reagents. The effect of temperature and acid- or base-catalysis was not studied.

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Supporting Information Available: High-resolution GC/TOF-MS electron impact (positive and negative ionization) and chemical ionization (positive and negative) mass spectra of the characterized species. This material is available free of charge via the Internet at http://pubs.acs.org.

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