

Mass Spectrometric Study of Some Organotellurium(IV) Compounds

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A series of tetracoordinated organotellurium(IV) compounds with potential immunomodulating properties were studied mass spectrometrically using high-resolution positive ion desorption chemical ionization and constant B/E and B^2/E linked-scanning techniques. The nature of the organic ligand bonded to the Te(IV) has a major influence on the mass spectral behavior of these compounds. When only monodentate ligands —OR are bonded to the Te(IV), no molecular or protonated molecular ion appears in the spectrum, although polynuclear species are present. When the compounds contain bis-bidentate ligands of the type —ORO—, the protonated molecular ion becomes the base peak and the polynuclear species are not present. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The tellurium atom has two electrons short of the configuration of the next noble gas and this is reflected in its essentially non-metallic covalent chemistry. Tellurium may complete the noble gas configuration by forming Te^{2-} compounds (which exist only in the salts of the most electropositive elements) or by two electron-pair bonds in which the tellurium is in the form Te^{2+} . In addition to such divalent species, the tellurium forms compounds in formal oxidation states IV and VI with four, five or six bonds. Owing to this behavior, the chemistry of tellurium compounds is diverse and very interesting. Despite their chemical and biological interest,^{1–10} only a few of them have been studied mass spectrometrically.^{11–19} Recently, organotellurium compounds containing alkoxy groups, e.g. trichloro(dioxoethylene-*O,O'*)-tellurate were found to have immunomodulation effects.²⁰

The tellurium(IV) alkoxy derivatives which have potential immunomodulation effects investigated in this work (Table 1) have not been studied previously by mass spectrometry (MS), the majority of them being new compounds. We tested these materials using different MS ionization modes [electron impact (EI), chemical ionization (CI)] with ammonia, isobutane and methane as reagent gas and fast atom bombardment (FAB). Only desorption chemical ionization (DCI) gave satisfactory spectra for all the compounds.

During the MS investigations, we observed a tendency for these materials to polymerize under the MS

conditions, thus extending the MS analysis to metastable ion measurements by B/E or B^2/E linked-scanning techniques.

EXPERIMENTAL

Mass spectrometry

DCI- CH_4 (high- and low-resolution) mass spectra were measured on an AutoSpec E double-focusing instrument (VG-Fisons, Manchester, UK). The EI spectra were obtained with a low-resolution Finnigan 4000 quadrupole instrument.

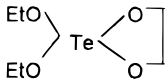
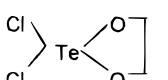
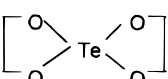
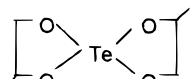
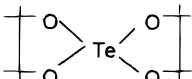
The magnetic sector instrument was operated under the following conditions: accelerating voltage, 8 kV; ion source temperature, 180 °C; and reagent gas: methane (ultra-high purity) at a pressure of 0.3 Torr (1 Torr = 133.3 Pa). For high-resolution measurements the instrument was set to a resolution of 8000, calibrated with perfluorokerosene. The scan speed was 2 s per decade. Metastable ion data were obtained with constant B/E or B^2/E linked scanning following collisions in the first field-free region. Argon was used as the collision gas at a pressure that attenuated the main beam intensity by 50%. The scan speed was 5 s per decade.

Materials

All alcohols and solvents were dried prior to use. TeCl_4 (Merck, Darmstadt, Germany) was used as received.

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Table 1. Names and structures of compounds 1–9

$(R_1)_nTe(OR)_{4-n}$ Monodentate ligands				
1	$n = 0$	$R = CH_2CH_3$	Tetraethoxytellurane	$Te(OEt)_4$
2	$n = 0$	$R = CH(CH_3)_2$	Tetraisopropoxytellurane	$Te(OiPr)_4$
3	$n = 2$	$R_1 = Ph$	Diethoxydiphenyltellurane	$Ph_2Te(OEt)_2$
4	$n = 3$	$R = CH_2CH_3$ $R_1 = Ph$ $R = CH_2CH_3$	Ethoxytriphenyltellurane	$Ph_3Te(OEt)$
$(R_1R_1)_nTe(R_2)_2$ Mono- and bidentate ligands				
5	$n = 1$	$(R_1R_1) = C_2H_4O_2$	1,3-Dioxa-2-telluracyclopentane-2,2-diethoxide	
6	$n = 1$	$R_2 = OCH_2CH_3$ $(R_1R_1) = C_2H_4O_2$	1,3-Dioxa-2-telluracyclopentane-2,2-dichloride	
$Te(R_1R_1)_2$ Bis-bidentate ligands				
7		$(R_1R_1) = C_2H_4O_2$	1,4,6,9-Tetraoxa-5-telluraspiro[4.4]nonane	
8		$(R_1R_1) = C_3H_6O_2$	2,7-Dimethyl-1,4,6,9-tetraoxa-5-telluraspiro[4.4]nonane	
9		$(R_1R_1) = C_6H_{12}O_2$	2,2,3,4,7,7,8,8-Octamethyl-1,4,6,9-tetraoxa-5-telluraspiro[4.4]nonane	

Compound 1 was prepared by the procedure of Denney *et al.*^{21,22} MH^+ : EtOH, found 264.998 (22.1%); calculated 265.008.

Compound 2 was prepared by the method of Menothra and Mathur.^{22,23} MH^+ : iPrOH, found 307.038 (100%); calculated 307.055.

Compound 3 was prepared according to Wieber and Kanzinger's method.¹⁸ MH^+ : EtOH, found 329.013 (10%); calculated 329.018.

Compound 4 was prepared as follows: 1.59 mmol of Ph_3TeCl in ethanol was allowed to react with 1.59 mmol of $AgNO_3$ for 2 h with continuous stirring. The $AgCl$ that precipitated was filtered and 1.67 mmol of $NaHCO_3$ in ethanol was added. After filtration, the ethanol was removed by distillation and the residue was dried under vacuum. The yield of the white solid product was 83%; m.p. 162 °C (decomp.). MH^+ : EtOH, found 361.013 (7.98%); calculated 361.023.

Compound 5 was prepared as follows: to 1.82 mmol of $Te(OEt)_4$ was added with stirring 1.82 mmol of ethylene glycol and a white precipitate formed immediately. The dried product was a white solid, yield 89%; m.p. 200 °C (decomp.). MH^+ : found 281.0038 (3.63%); calculated 281.0032.

Compound 6 was prepared as follows: 0.01 mol of $TeCl_4$ was dissolved in 60 ml of benzene followed by the addition of 0.005 mol of ethylene glycol and refluxing for 4 h. The white precipitate that formed was filtered and dried in vacuum: yield 95%; m.p. 195 °C (decomp.). MH^+ : found 260.861 (0.18%); calculated 260.872.

Compounds 7 and 9 were prepared according to Ref.

(22). For 7, MH^+ : found 250.963 (100%); calculated 250.956. For 9 MH^+ : found 363.073 (100%); calculated 363.081.

Compound 8 was prepared as follows: 0.17 g (2.26 mmol) of propane-1,2-diol was added to a stirred solution of 0.41 g (1.13 mmol) $Te(OiPr)_4$ in propan-2-ol. The reaction was exothermic and a white precipitate formed immediately. The propan-2-ol was distilled off under reduced pressure. The residue was dried under vacuum [0.005 Torr (1 Torr = 133.3 Pa)] to give 0.31 g of product, yield 99%; m.p. 89 °C (decomp.). MH^+ : found 278.962 (4.82%) calculated 278.987.

RESULTS AND DISCUSSION

The DCI- CH_4 mass spectra of compounds 1–9 are reported in Table 2.

For the telluranes containing tetracoordinated monodentate ligands (1–4) no molecular ion was found in the spectra under CI and DCI conditions (reagent gases CH_4 , NH_3 and iC_4H_{10}) (Fig. 1). Compounds 5 and 6, which have one bidentate ligand, gave a small protonated quasi-molecular ion under DCI conditions, while 7, 8 and 9, containing bis-bidentate ligands, gave a strong molecular ion even in the EI spectra (Fig. 2). The large number of polynuclear ions present in the DCI spectra of 1–4 arise from the ionization/fragmentation of associated neutral species formed by thermal decomposition of the mononuclear neutral compounds. The abundance of such polymers decreases in the more ther-

Table 2. DCI-CH₄ mass spectra of compounds 1–9: *m/z* values with relative ion current (%) in parentheses^a

	1	2	3	4	Compound 5	6	7	8	9
MH ⁺	311 (0)	367 (0)	375 (0)	407 (0)	281 (3.63)	261 (0.14)	251 (100)	279 (4.82)	363 (100)
MH ⁺ – ROH	265 (22.13)	307 (100)	329 (10)	361 (7.98)	235 (100)		—	—	—
MH ⁺ – R ₁ H						225 (100)			
[(OR) ₂ Te=O]H ⁺	237 (0.78)	265 (56.88)			—	—	—	—	—
[R ₁) ₂ Te=O]H ⁺			301 (53.95)	301 (21.09)					
(R ₁ R ₁)Te=OH ⁺	—	—	—	—	207 (24.63)	207 (15.64)	207 (16.04)	221 (0.1)	263 (90.17)
[Te(O ₂ R ₂)] ⁺⁺	220 (0.31)	248 (7)			—	—	—	—	—
Te(R ₁) ₂ ⁺⁺			284 (97.34)	284 (100)					
Te(R ₁ R ₁) ⁺⁺	—	—	—	—	190 (27.39)	190 (11.76)	190 (5)	204 (0.20)	246 (31)
TeR ₁ ⁺	—	—	207 (100)	207 (35)			—	—	—
TeR ₂ ⁺					175 (5.4)	165 (3.5)			
(OH) ₂ Te=OH ⁺	181 (0.05)	181 (5.42)	181 (0)	181 (0)	181 (1.66)	181 (0.08)	181 (0)	181 (0.08)	181 (8.27)

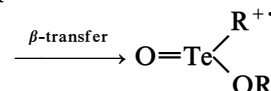
^a All the masses were accounted for with the ¹³⁰Te, ³⁵Cl isotopes.

mally stable compounds 5 and 6 and they disappear completely in the bis-bidentate telluranes 7–9.

The fragmentation pathway of these compounds is characterized by the loss of neutral species. Ions commonly formed by ion–molecule reactions such as DCI protonation generally prefer the formation of an even-electron (EE⁺) ion plus an even-electron (EE) neutral molecule. Scheme 1 shows the fragmentation pathway of Te(OEt)₄ as representative for all the alkoxytelluranes. The most favored primary fragmentation involves the cleavage of a protonated alkoxy group ROH yielding the (OR)₂Te=OR⁺ (compounds 1 and 2), Ph₂Te=OR⁺ (3), Ph₃Te⁺ (4) and (R₁R₁)Te=OR⁺ (5) ions (Scheme 1).

However, thermal decomposition prior to the ionization cannot be excluded, taking into consideration the low thermal stability of these compounds. The EE⁺ cation F₁ yields the EE⁺ ions F₂, F₄ and F₅ together with the neutral molecule C₂H₄. This fragmentation pathway is preferred for EE⁺ ions.²⁴ The ion F₁ also undergoes one-bond cleavage fragmentation yielding an RO[•] radical and an OE⁺⁺ radical cation F₃. This behavior, which is an exception to the 'even-electron rule',²⁵ was confirmed by constant *B/E* and *B²/E* linked-scanning measurements (Fig. 3). Figure 3 clearly shows that the fragment F₃ (*m/z* 220) is the daughter peak of F₁ (*m/z* 265) and also that the F₁ fragment is the parent peak of F₃. For compounds 1 and 2 this fragmentation has to be followed by β-transfer of the R group to the tellurium in order to keep the formal oxidation state of Te(IV) unchanged. The oxidation state of the tellurium in all the starting materials used in this

work was IV and this formal oxidation state is assumed to be maintained during the mass measurements. The β-transfer of alkyl groups in coordination compounds of tellurium is well established in the literature.¹¹



When two or three —OR— groups are replaced by a phenyl group, the Ph₂Te⁺⁺ cation radical becomes the base peak.

The high abundance and large number of polynuclear species observed in the DCI spectra of 1 and 2 arise from ion–molecule reactions between fragment ions and neutral molecules (including the original molecule) present in the gas phase.

The Te(OR)₃⁺ ion (the main fragment ion) recombines with one or more neutral molecules to yield bi- or polynuclear species. The polymeric species of compounds 1 and 2 are formed by the reactions shown in Scheme 2.

The path presented in Scheme 2 was confirmed by metastable peak analysis, as can be seen in Fig. 4. The spectra of 3 and 4 are dominated by the fragment ions of *m/z* 301, 284 and 207, corresponding to the species

Ph₂Te=OH⁺, Ph₂Te⁺⁺ and PhTe⁺, respectively. The recombination of these species with neutral molecules is described in Scheme 3.

Daughter peaks and neutral loss analysis confirm these reactions steps in polynuclear species formation (Fig. 5).

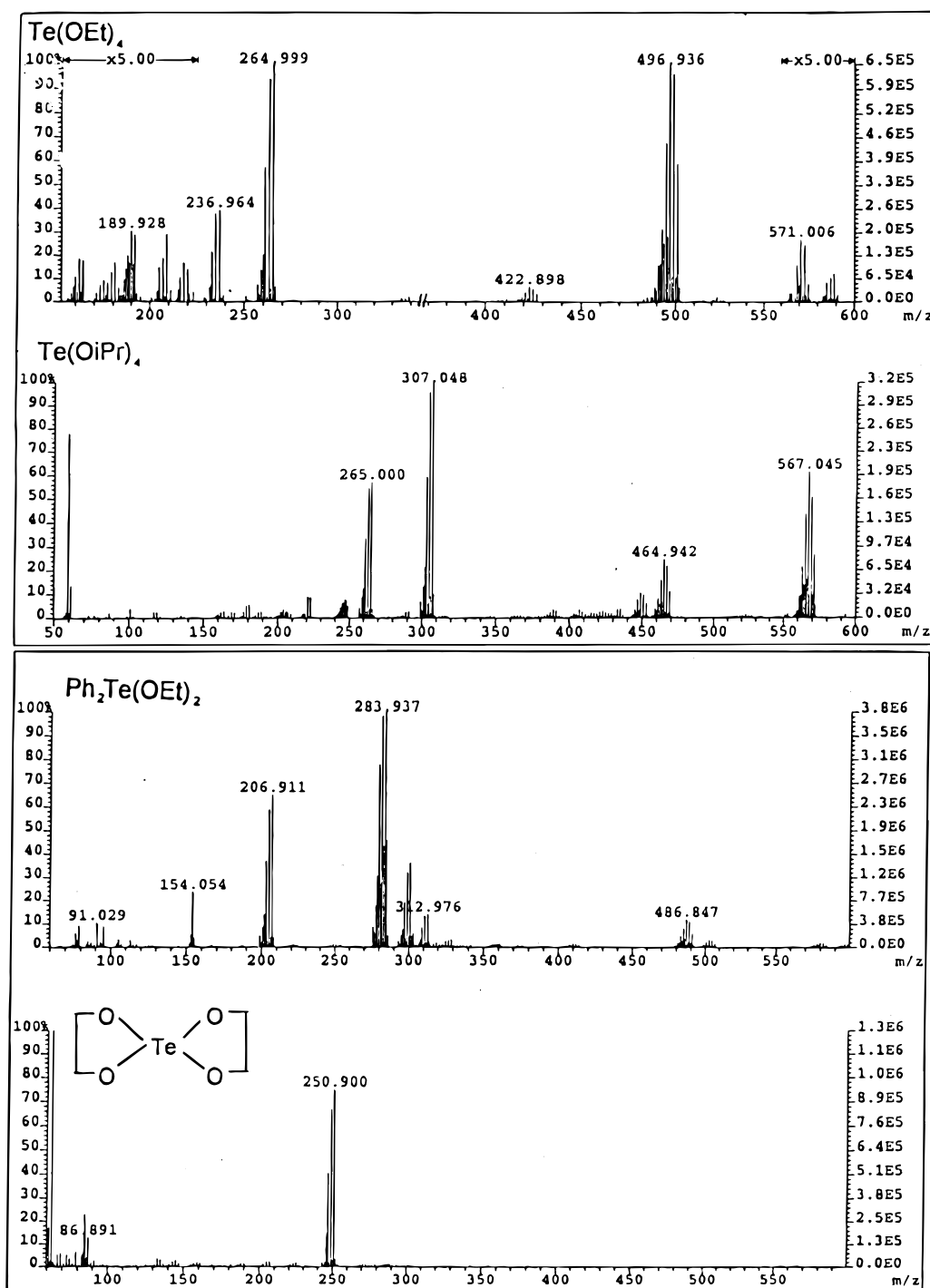


Figure 1. DCI-CH₂ mass spectra of compounds 1, 2, 3 and 7.

In the polymerization reactions depicted by Eqns (1.1), (2.1a) and (2.1b), the original neutral molecules $\text{Te}(\text{OEt})_4$, $\text{Ph}_2\text{Te}(\text{OEt})_2$ and Ph_3TeOEt are involved. This indicates the existence of the original molecules in the gas phase. These molecules give rapid ion-molecule reactions yielding thermally stabilized dimeric ions. The process occurs only in the gas phase during MS analysis. The monomeric character of these materials in the solid state is demonstrated by their NMR spectra, melting points and solubility in organic solvents (in which the polymeric forms do not dissolve).

On replacing two of the monodentate ligands by a bidentate ligand (compounds 5 and 6), the mass spectra obtained present a detectable, protonated molecular ion, followed by a more intense $\text{Te}(\text{R}_1\text{R}_1)^+$ ion. The bis-bidentate telluranes gave a very stable protonated molecular ion (Fig. 1). Fragmentation under DCI conditions was undetectable.

Constant B/E and B^2/E linked-scanning measurements combined with collision-induced dissociation (CID) showed that the loss of a neutral oxirane molecule is the main fragmentation under DCI conditions (Scheme 4).

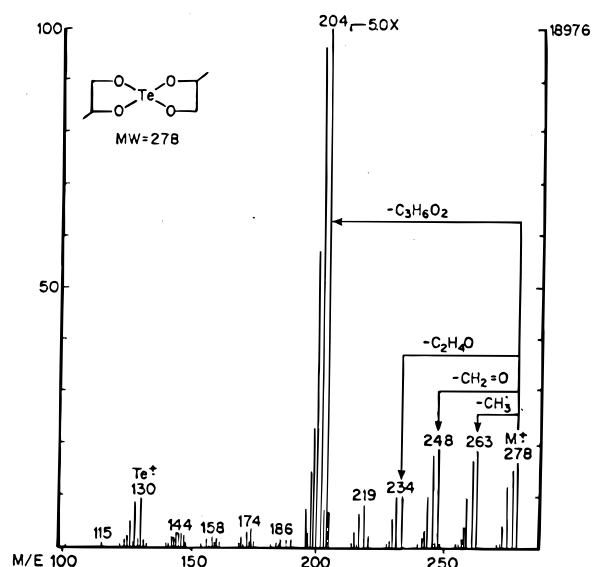


Figure 2. EI mass spectrum of compound 8.

However, the EI spectra showed a large number of fragment ions. The unimolecular decompositions of

these compounds occur in the common way, yielding an even-electron neutral molecule and an odd-electron radical cation:²⁶



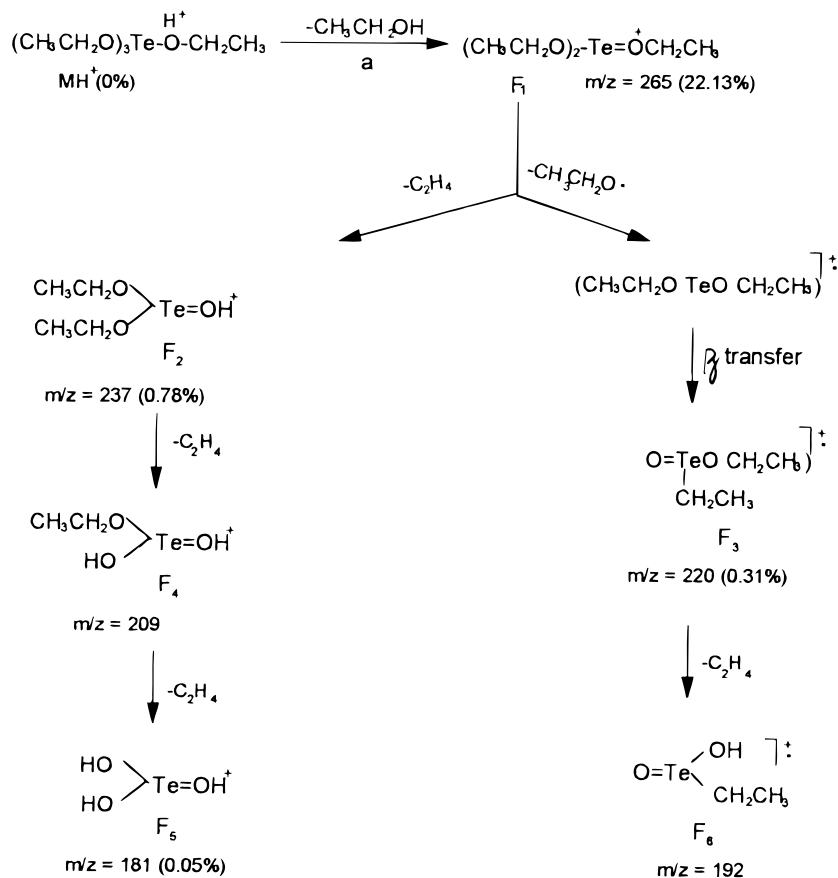
CONCLUSION

Compounds 1–9 can be classified according to their tendency to polymerize under MS conditions as follows: Te(IV) monodentate ligands > Te(IV) mono- and bidentate ligands > Te(IV) bis-bidentate ligands.

The tendency to give polymeric species decreases with increasing thermal stability of these compounds.

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Scheme 1

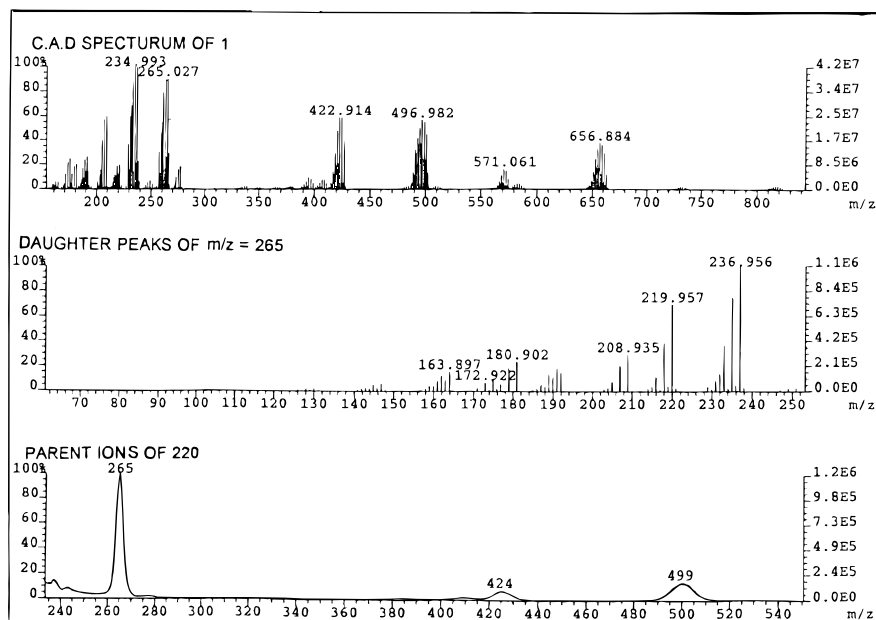
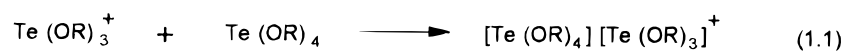


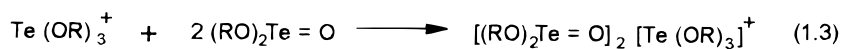
Figure 3. Constant B/E and B^2/E linked-scan measurements for compound 1.



- 1 $M^+ = 575$ amu
- 2 $M^+ = 673$ amu



- 1 $M^+ = 501$ amu
- 2 $M^+ = 571$ amu



- 1 $M^+ = 737$ amu
- 2 $M^+ = 803$ amu

Scheme 2

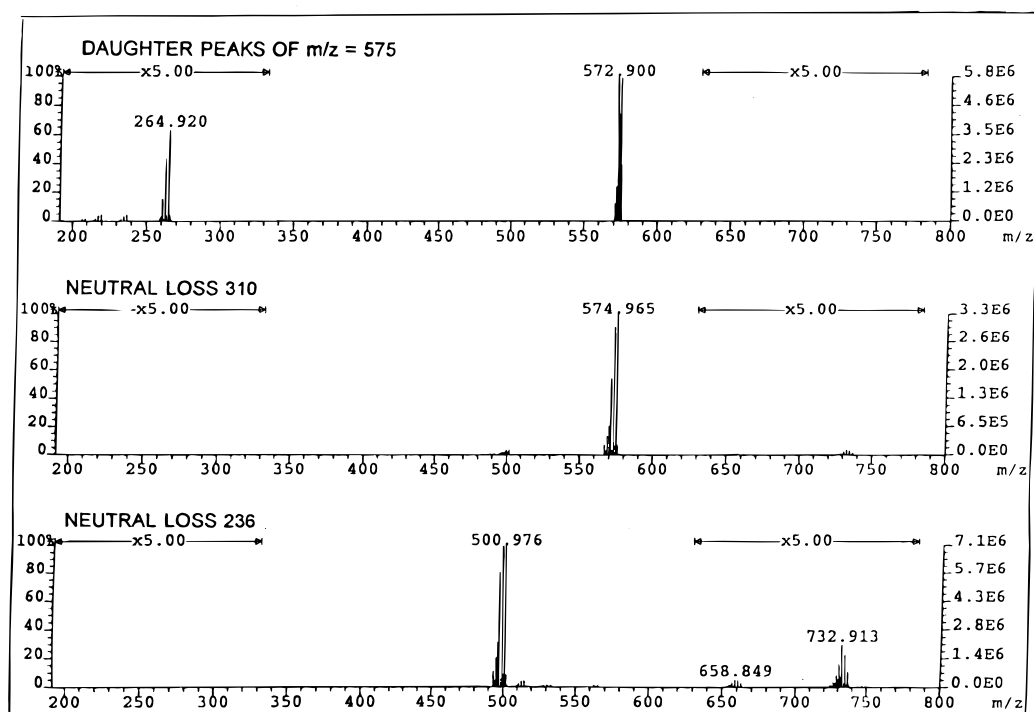
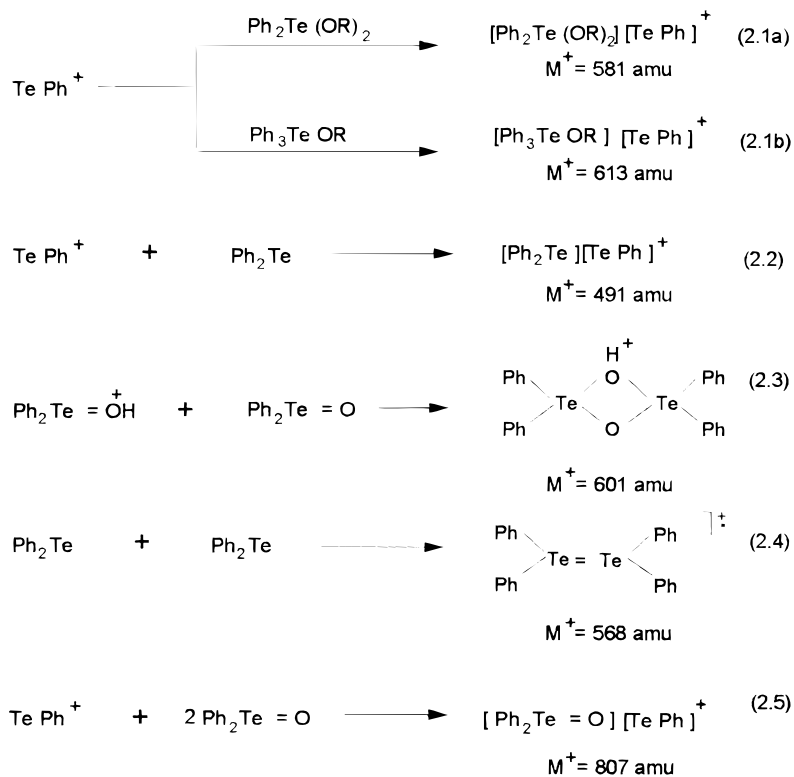


Figure 4. Constant B/E and B^2/E linked-scan measurements for the polynuclear species generated by compound 1.



Scheme 3

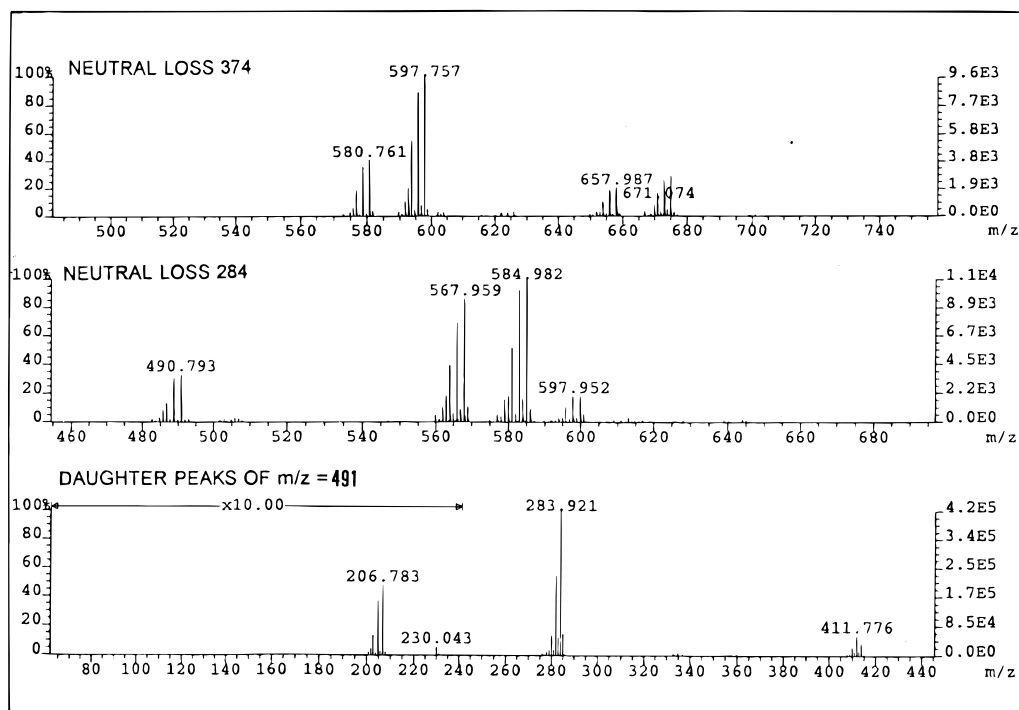
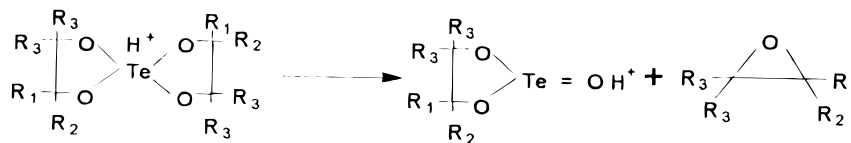


Figure 5. Constant B/E and B^2/E linked-scan measurements for the polynuclear species generated by compound 3.



$$m/z = 207 \quad (7)$$

$$m/z = 221 \quad (8)$$

$$m/z = 263 \quad (9)$$

Scheme 4

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