# Mass Spectrometric Fragmentation of Saturated Six Membered Heterocyclic Systems Containing Two Chalcogen Family Atoms

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The mass spectra of six-membered saturated heterocycles containing oxygen, sulphur, selenium and tellurium in the 1,4-positions have been measured. The differing fragmentation modes have been characterized using high resolution, low voltage and metastable ion scan techniques. The important decomposition reactions of the molecular ions involve elimination of  $C_2H_4$  and  $CH_2X$  (X is a chalcogen atom) and formation of  $[C_2H_4X]^+$  and  $C_2H_5^+$ . The propensities of these reactions vary systematically as a function of the ability of the chalcogen to stabilize a positive charge.

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### Introduction.

In the present work, the comparative behavior upon electron impact fragmentation of saturated six-membered heterocyclic systems and their dihalogen substituted derivatives is reported. Mechanisms for the various decompositions are postulated based on metastable studies of oxygen and sulphur compounds as models.

There are few reports (1-5) of the mass spectral fragmentations of heterocyclic systems containing the heavy atoms of group VI of the periodic table. The differing fragmentation modes observed in these heterocyclic systems have been ascribed to electronegativity difference of atoms and the strength of heteroatom-carbon bonds.

The mass spectral fragmentation of organoselenium and organotellurium compounds have often been presented without detailed analysis. The reason is that there are six natural isotopes of selenium and eight of tellurium with significant abundances of isotopes situated at one, two or three mass units apart. When, in addition, chlorine and bromine atoms are present, analysis of ion abundances arising from overlapping peaks is difficult and may require manipulation of the data by computer.

### General Fragmentation Modes.

The mass spectra of 1,4-dioxane (I), 1,4-oxathiane (II), 1,4-oxaselenane (III), 1,4-oxatellurane (IV), 1,4-dithiane (V) and 1,4-diselenane (VI) show intense molecular ions (Table 1). The heterocycles containing the heavier heteroatoms give more abundant molecular ions. This may be because these molecules have lower ionization potentials, and the heteroatoms have greater ability to stabilize positive charge. The lower ionization potential will permit more nondecomposing states of the molecular ion assuming that the appearance energies of the fragments do not change significantly in this series of compounds. No thermal decomposition is indicated. The fragmentation, in general, leads to ions which contain the heteroatom, and this is due to the ability of the chalcogens to stabilize the positive charge by electron pair donation or by their polarizibility.

Loss of hydrogen atom from the molecular ion is observed only in the spectrum of 1,4-dioxane. In this respect these six membered heterocycles resemble five membered heterocycles reported by Djerassi, et al. (1). Hydrocarbon fragment ions are not abundant, particularly among the

Table 1
Principal Fragmentations of Chalcogen Containing Heterocycles (a)

Composition of the ion	1,4-Dioxane	1,4-Oxathiane	1,4-Oxaselenane	1,4-Oxatellurane	1,4-Dithiane	1,4-Diselenane
M*·	77	100	100	100	100	100
M-C₂H₄	<1	5.0	14	36	14	48
M-CH <sub>2</sub> O	59	26	<1	<1		_
$C_2H_5X$ (a)	7	66	51	.7	53	10
$C_2H_4X$	7	14	90	44	19	15
CH <sub>2</sub> X	13	99	85	13	49	17
C <sub>2</sub> H <sub>4</sub>	100	3.0	10	15	81	10

(a) X = oxygen, sulphur, selenium or tellurium.

analogs containing the heavier chalcogens. In this respect, the mass spectrum of 1,4-oxaselenane (III) differs significantly from that of isomeric selenacyclopentane-loxide (5). In the mass spectrum of the latter compound, the base peak is due to non-selenious ion C<sub>4</sub>H<sub>7</sub><sup>+</sup> at m/e 55 (5). Mass spectrometry, therefore, can be used to characterize cyclic selenoxide from isomeric selenate.

The five dominant fragmentation modes, observed for each of the heterocycles (see equation 1), exhibit a systematic variation in terms of branching ratios as the heteroatom is changed from oxygen to tellurium. These decompositions are discussed in the following paragraphs.

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\end{array} & \begin{array}{c}
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 & -c_2H_5
\end{array} & \begin{array}{c}
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 & -c_2H_5
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 & -c_3H_6
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\end{array} & \begin{array}{c}\\\\ & -c_3H_$$

C<sub>2</sub>H<sub>4</sub> Loss.

The loss of C<sub>2</sub>H<sub>4</sub> from the various molecular ions, demonstrated by exact mass measurements and meta-

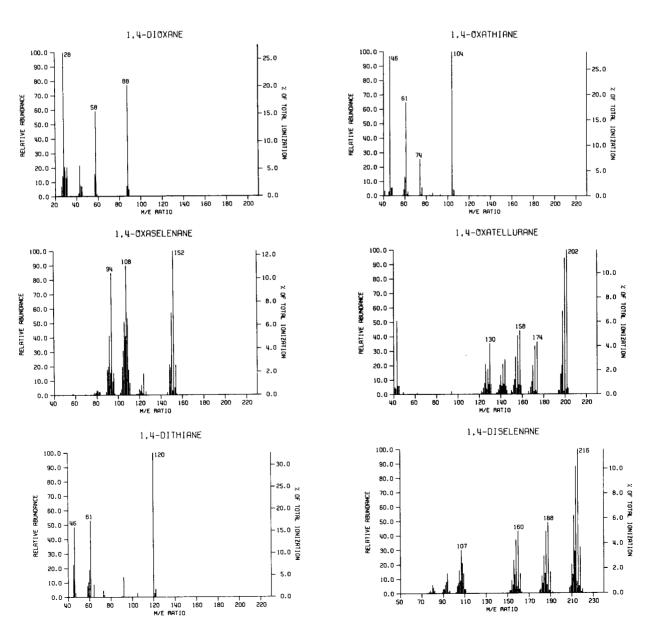


Figure 1. Mass Spectra of Chalcogen-Containing Heterocycles at 70 eV of Ionizing Energy.

Table 2

Metastable Ion Characteristics of C<sub>3</sub>H<sub>4</sub>O\* Ions

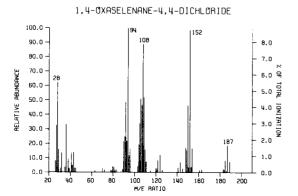
Source of C <sub>3</sub> H <sub>6</sub> O <sup>+-</sup> Ions	<b>58</b> → <b>57</b>	58 <b>→</b> 43	58 - 42	58 <b>→</b> 31	58 <b>-</b> 30	58 <b>→</b> 29	58 <b>→</b> 28	58 <b>→</b> 27
1,4-Dioxan	82 (a) (150) (b)	3 (570)	_		7 (18)	2 (27)	(6 (20)	1 (—)
Trimethylene Oxide	93 (126)	_		_	2 (10)	1 (28)	4 (36)	_
Propylene Oxide	43 (178)	33 (498)		2 (—)	13 (10)	2 (40)	5 (27)	3 (—)
Propanaldehyde	81 (130)			_	3 (24)	8 (51)	5 (52)	3 (78)
Vinyl Methyl Ether	45 (145)	35 (478)	11 (92)	1 (75)	1 (35)	1 (83)	2 (32)	2 (67)
Allyl Alcohol	100 (32)	_	_ ` `		_	_		_
Acetone		100 (27)						

(a) Percentage of total ion current. (b) Kinetic energy released in the transition in meV.

stable scans, increases in the series from 1,4-dioxane to 1,4-oxatellurane (Figure 1). From the variation of spectra with changes in the electron energy, it can be seen that  $C_2H_4$  expulsion is the most facile decomposition for X =Se and second most for X = Te. At higher energies for 1,4-dithiane and 1,4-diselenane a second C,H, is lost to give  $[X_2]^+$ . In accordance with Collin, et al. (6), we postulate that the [M-C<sub>2</sub>H<sub>4</sub>]\* must be cyclic at some point so that it may undergo a second loss of C, H,. This reaction may be termed a cycloreversion, the reverse of which would correspond to a cycloaddition of ethylene and [X<sub>2</sub>]\*. The higher tendency for the loss of C<sub>2</sub>H<sub>4</sub> from the higher molecular weight members of the series can be ascribed to the stability of heteroatom-carbon bonds (3a). Elimination of C<sub>2</sub>H<sub>4</sub> from M<sup>+</sup> requires cleavage of C-O and C-X bonds. Since C-Se bonds are weaker than C-S bonds and C-Te bonds weaker still (3a), it is not surprising that C2H4 loss is most abundant for the tellurium analogs and of lower importance for oxygen and sulphur containing compounds.

### CH<sub>2</sub>O Loss.

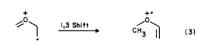
Loss of formaldehyde (CH<sub>2</sub>O) is significant only in the spectra of I and II and amounts to less than 1% for III and IV (Table 1). Collin, et al. (6), suggested that the resultant



(M-CH<sub>2</sub>O)<sup>+</sup> ion is probably cyclic. We have chosen to examine the unimolecular metastable decompositions of (M-CH<sub>2</sub>O)<sup>+</sup> in order to substantiate this suggestion (see Table 2). Comparison of relative branching ratios and kinetic energy release show that the dominant fraction of decomposing [C<sub>3</sub>H<sub>6</sub>O]<sup>+</sup> from 1,4-dioxane has a structure similar to ionized trimethylene oxide with possibly a small contribution from ionized propylene oxide. This does not prove that the structures of these ions are cyclic. In fact, the similarity can be accounted for readily in terms of ring-opened structures (see equation 2). Clearly there is

$$\begin{bmatrix} \begin{smallmatrix} 0 \\ 0 \end{smallmatrix} \end{bmatrix}^{\frac{1}{2}} \longrightarrow \begin{bmatrix} \begin{smallmatrix} 0 \\ 0 \end{smallmatrix} \end{bmatrix} \xrightarrow{-cH_2O} \begin{bmatrix} \begin{smallmatrix} 0 \\ 0 \end{smallmatrix} \end{bmatrix} \xrightarrow{-cH_2O} \begin{bmatrix} \begin{smallmatrix} 0 \\ 0 \end{smallmatrix} \end{bmatrix}$$

little isomerization to other  $[C_3H_6O]+\pm$  structures such as ionized acetone, allyl alcohol or vinyl methyl ether. The lack of propensity to isomerize to vinyl methyl ether may be another example of the high energy requirement for a 1,3-hydrogen shift for radical cation (7-8) (equation 3).



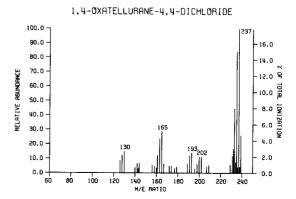


Figure 2. Mass Spectra of Dihalogen Substituted Chalcogen-Containing Heterocycles at 70 eV of Ionizing Energy.

This structural assignment is in agreement with that of McLafferty, et al. (9) who concluded that  $[C_3H_6O]^{*-}$  from 1,4-dioxane probably has the structure of ionized trimethylene oxide (both ions may have undergone ring opening, however). The structures of other  $[C_3H_6O]^{*-}$  ions have been studied by various techniques such as ICR (10), isotope labelling (11), collisional activation (9) and metastable decomposition (12). The various isomeric ions appear to have unique properties and resist interconversion, even when in the form of energized decomposing ions, as has been confirmed by the metastable ion study reported here.

The absence of formaldehyde elimination for the selenium and telluriun analogs may be ascribed to the instability of the resulting cyclic species. For example, three-membered cyclic selenirane has not been isolated and the four-membered cyclic selenetane is only stable at low temperature in the dark (13).

### C<sub>3</sub>H<sub>6</sub>O Loss

Whereas the formation of  $[C_3H_6O]^{+}$  from dioxane is important, the higher analogs show abundant loss of neutral  $C_3H_6O$  to form  $[CH_2X]^{+}$ . This is one of the most facile reactions in 1,4-oxathiane and is of considerable importance for the other heterocycles. There is little question about the structure of this ion. The trend in product ion intensities can be understood in terms of relative stabilities of  $[CH_2=X]^{+}$  which increase with the increasing electropositive nature of X.

## C<sub>2</sub>H<sub>4</sub>O Loss.

Expulsion of  $C_2H_4O$  gives the ion  $[C_2H_4X]^+$  which is of little importance for the low molecular weight members of the series (X=0,S). In fact, based on low voltage spectra, the ions are probably secondary and tertiary in nature. However, for X=Se and X=Te, this loss dominates the low voltage spectra. This latter fact is consistent with the process having a low energy requirement, presumably due again to the ability of selenium and tellurium to accommodate the positive charge.

The structure of  $[C_2H_4X]^+$  is difficult to assign because of its low intensity for simpler members and the lack of model compounds for X = Se and Te of this heterocyclic series. However, the number of reasonable structures is only three (VII, VIII, IX).

As reported by Holmes and Terlouw (14), it was found that the metastable peak shape for  $C_2H_4O^+ \rightarrow C_2H_3O^+ + H$  decomposition is a composite indicating mainly  $[CH_2=CHOH]^{+-}$  structure with smaller contribution from

the oygen analogs of VIII and IX. This is because  $C_2H_4O^+$  ions are formed by two routes; viz., by loss of hydrogen atom from  $C_2H_5O^+$  and directly from the dioxane molecular ion, by  $\beta$ -cleavage, having ethylene oxide structure. The structures of  $[C_2H_4X]^+$  can only be inferred by analogy.

### C<sub>2</sub>H<sub>3</sub>O Loss.

Direct elimination of C<sub>2</sub>H<sub>3</sub>O must involve ring opening and a hydrogen rearrangement. Although it is a minor process for 1,4-dioxane, the reaction is of major importance for other analogs. Once again the ability of the higher chalcogens to stabilize positive charge, this time for a closed shell ion, has been demonstrated.

The structure of C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> from acyclic molecules is one of the classic ion structure problems in organic mass spectrometry (15). The three most likely structures are X, XI,

XII. Unimolecular dissociation for metastable C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> allows easy distinction between protonated acetaldehyde and methylated formaldehyde. This analysis has not been applied to C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> from 1,4-dioxane. Consequently, we have obtained the relevant data.

Metastable decompositions of C<sub>2</sub>H<sub>5</sub><sup>+</sup> ions from 1,4-dioxane revealed a flat-topped metastable for the

elimination of CH<sub>4</sub> with a release of kinetic energy which is equal to that determined from  $C_2H_5O^+$  ions from 2-propanol. The ratio of metastable peak heights for the two decompositions  $m_2^*/m_1^*$  was approximately equal to 3 for both the isomers. This indicates that the decomposing  $C_2H_5O^+$  ions from 1,4-dioxane probably possess structure XII but could have been formed initially as structures X or XII. To account for this, the following scheme can be written starting with C-O bond cleavage to open the ring (equation 4).

An attempt was made to determine the structures of  $C_2H_sS^+$  ions from 1,4-oxathiane and 1,4-dithiane. The metastable scans of  $C_2H_sS^+$  ions indicated the following transitions (equation 5).

The metastable peak corresponding to elimination of C<sub>2</sub>H<sub>2</sub> was most intense, and peak shapes were gaussian indicating little kinetic energy release. Metastable peak height ratios for the transitions m\*(-C<sub>2</sub>H<sub>2</sub>)/m\*(-CH<sub>4</sub>) and m\*(-C<sub>2</sub>H<sub>2</sub>)/m\*(-H<sub>2</sub>S) were 11 and 8.5, respectively, for C<sub>2</sub>H<sub>5</sub>S<sup>+</sup> ions from different precursors. Therefore, it is concluded that C<sub>2</sub>H<sub>2</sub>S<sup>+</sup> ions from different precursor molecular ions, in spite of their initial structural differences, all isomerize to common intermediates prior to fragmentation. Similar observations on C<sub>2</sub>H<sub>5</sub>S<sup>+</sup> ion abundance ratios by metastable defocusing technique in the first field free region have been reported by Broer and Weringa (16). Consequently, only the unique characteristics of C<sub>2</sub>H<sub>5</sub>O<sup>+</sup> ions allow us to conclude anything about general mechanism of the C<sub>2</sub>H<sub>5</sub>X<sup>+</sup> formation. Reasoning by analogy, we conclude that these ions are initially formed as the sulfur analog of XII.

Mass Spectral Fragmentation of Dihalogen Heterocycles.

The dihalogen substituted compounds are relatively non-volatile and difficult to purify by gas chromatography; in fact, under gas chromatographic conditions they undergo structural change.

In their mass spectra, peaks resulting from small impurities of the starting material and from tary products (17) may overlap with fragment ion peaks of the sample and complicate the analysis. A comparison of experimentally observed ion abundances in the region of interest with that calculated by computer for species likely to interfere is necessary for proper identification.

The mass spectra of these dihalogen substituted compounds (Figure 2) do not show significant peaks corresponding to molecular ions. The halogen atoms are eliminated in one or two steps although no metastables were observed to support either mechanism. The  $[M-X_2]^+$  ion probably has the structure of molecule ion of the unsubstituted heterocycle because it shows a fragmentation pattern similar to the corresponding non-halogenated compounds.

In the mass spectrum of the dichloro compound (XIIIA), a strong peak is observed at m/e 187, which could be ascribed to the loss of one chlorine atom from the molecular ion. The relative ion abundances in the region m/e 180-190 is consistent with the composition C<sub>4</sub>H<sub>8</sub>OSeCl<sup>+</sup>, i.e. (M-Cl)<sup>+</sup>. There is no interference from the peaks of SeCl<sub>3</sub><sup>+</sup> which may arise due to impurities. The (M-Cl)<sup>+</sup> ion then eliminates Cl<sup>-</sup> and OC<sub>2</sub>H<sub>4</sub> (see equation 6 for an overall scheme).

The relative ion abundances in the region m/e 145-155 are consistent with composition C<sub>4</sub>H<sub>8</sub>OSe<sup>+</sup> and indicate the absence of the fragment SeCl<sup>+</sup><sub>2</sub> which could arise from molecular ion of XIIIA or from impurities of the starting material. In the mass spectrum of XIIIA, peaks observed in the region m/e 294-300 (C<sub>2</sub>H<sub>4</sub>Se<sub>2</sub>Cl<sub>3</sub>), m/e (259-263) C<sub>2</sub>H<sub>4</sub>Se<sub>2</sub>Cl<sub>2</sub> etc. are due to impurities from the starting material. The spectra in Figure 2 do not extend to these high m/e values.

The fragmentation of the corresponding dichloro tellurium analog XIIIB is similar to XIIIA (see equation 7). A small ion peak in the region m/e (230-240) is consistent with the composition of  $C_4H_8OTeCl^+$ , i.e. (M-Cl)+, and no interference from  $TeCl_3^+$  ion peaks which could arise from starting material. Similarly, deconvolution of peak heights in the region m/e 190-202 is consistent with the composition  $TeC_4H_8O^+$  and no contribution from  $TeCl_2^+$  ion intensities.

The mass spectrum of dibromo compound of selenium (XIVA) showed no peaks corresponding to molecular ion M<sup>+</sup> or M-Br<sup>+</sup> ion, whereas the corresponding dibromo derivative of tellurium XIVB shows a cluster of peaks at m/e 360, 362, 364 which can be ascribed to molecular ion C<sub>4</sub>H<sub>8</sub>OTeBr<sub>2</sub><sup>+</sup>. In the mass spectrum of the dibromo compound XIVB, a cluster of peaks in the region m/e 120-130 (Te<sup>+</sup>), m/e (295-310) (Te<sub>2</sub>C<sub>2</sub>H<sub>4</sub>O<sup>+</sup>) and m/e (320-334) (Te + TeC<sub>4</sub>H<sub>8</sub>O<sup>+</sup>) can be ascribed to tarry products formed in the reaction between starting materials and organic residues. Their relative abundances were dependent on the probe temperature. Again, these large m/e peaks have been omitted in Figure 2.

The mass spectrum of the 1,4-oxaselenane diiodide showed no peaks corresponding to M<sup>+</sup> or (M-I)<sup>+</sup>. Probably the compound 1,4-oxaselenane-4,4-diiodide isomerized to 1-4-oxaselenane-iodine adduct upon heating which then loses iodine under the high vacuum conditions in the mass spectrometer as shown below.

$$\begin{bmatrix}
Se \\
0
\end{bmatrix}
\xrightarrow{S}$$

$$\begin{bmatrix}
Se \\
0
\end{bmatrix}$$

$$+ 1_{2} (8)$$

The mass spectral fragmentation behavior of the compound 1,4-diselenane-1,1-diiodide was similar to XVA. No peaks corresponding to molecular ion or loss of iodine atoms from M<sup>+</sup> were observed. In both of these diiodides strong peaks at m/e 127 and m/e 254 correspond to I<sup>+</sup> and I<sub>2</sub><sup>+</sup>.

The mass spectrum of the salt 1,4-oxatellurane hydroxynitrate showed no molecular ion peak. It seems that the compound is hydrolysed and a peak at m/e 237 corresponds to protonated telluroxan dihydroxide. The base peak is at m/e 202 and further fragmentation of this ion is similar to 1,4-oxatellurane.

### Conclusion.

To summarize, this study shows that mass spectral fragmentations of heterocycles containing heavy atoms of the group VI can be rationalized on the basis of electronegativity of the heteroatoms and the strength of heteroatom-carbon bonds. Fragmentations requiring cleavage of selenium-carbon and tellurium-carbon bonds are preferred. The dihalogen derivatives of the heterocycles preferentially lose halogen atoms and the resulting species shows a fragmentation pattern similar to the corresponding non-halogenated heterocyclic species.

### **EXPERIMENTAL**

The compounds described were prepared by the published methods using commercial chemicals without further purification. Except, where noted, literature values for melting points were reproduced. However, we have made modifications in some published methods, and they are described below. All preparations were carried out under dry nitrogen. The purity of the compounds was tested by comparison of their melting points with published values.

### Chemicals.

The following chemicals were obtained from the sources indicated: aluminum (Allied Chemical and Dye Corporation); selenium and tellurium powders (Alfa Products); ethylene bromide and sodium hydroxide (Fisher Scientific Company); sodium formaldehydesulfoxylate (Eastman Kodak Company);  $\beta$ , $\beta$ '-dichlorodiethyl ether (I.C.N, K. and K. Laboratory, Inc.); potassium metabisulfite and ethylene dichloride (Matheson Coleman and Bell); bromine, iodine and carbon tetrachloride (A. R. Grade); 1,4-oxathiane and 1,4-dithiane (Aldrich Chemical Company).

Preparation of the Compounds.

1.4-Diselenane.

This compound was prepared by the method of McCullough and Tideswell (18), without any modification m.p. 114° (lit. m.p. 112.5-113.5°).

### 1.4-Diselenane Diiodide.

The procedure used was that described by McCullough and Tideswell for the tetraiodide (18), but isolation was by mixing 1,4-diselenane and iodine in the molar ratio of 1:2, m.p. 151-152°.

#### 1,4-Oxaselenane and 1,4-Oxaselenane Dibromide.

The method of McCullough and Gibson (19) was followed in part. Rather than steam distilling to isolate the plain ring, the heavy, oily part of the product was extracted at room temperature with carbon tetrachloride. The dried extract solution was treated with bromine to slowly precipitate the dibromide. Recrystallization from ethylene dichloride and slow evaporation of that solvent produced acicular crystals of excellent quality. The plain oxaselenane was made from the dibromide following the literature method.

#### 1,4-Oxatellurane 4,4-Dichloride.

Our preparation followed Farrer and Gulland (20) but somewhat variant results were obtained. The literature reports describe white plate crystals of melting point of 179.5° (with partial decomposition). In contrast, we obtained block-type parallelepipeds with melting point at 175° without decomposition. These crystals, stable for at least three months, were obtained by extracting with chloroform the oxatellurane ring compound from the reaction mixture, passing chlorine through the dried extract and recrystallization of the dichloride from acetone.

### 1,4-Oxatellurane and Oxatellurane Dibromide.

These compounds were prepared by the method of Farrer and Bulland (20).

### Mass Spectrometry.

All spectra reported in this paper were taken using a Kratos MS-50 mass spectrometer interfaced to an INCOS 2000 data system. Low voltage spectra are reported at nominal voltages applied to the filament. Metastable ion data taken only to verify fragmentation pathways were acquired in the defocused  $V^{\frac{1}{2}}/E$  mode (21) using the MS-50. High resolution spectra produced exact masses which agreed with the predicted masses to within  $\pm$  3 parts-per-million.

The more detailed metastable ion studied and kinetic energy release measurements were done using an Hitachi RMU-6D mass spectrometer modified to operate as a mass analyzed ion kinetic energy spectrometer. Kinetic energy released was calculated (22) from peak widths at half-heights using a main beam of 5500 eV. Samples were ionized at 70 eV. Metastable branching rations were calculated from peak heights.

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