

P. S. Kulkarni, M. M. Khan, G. D. Sturgeon\* and M. L. Gross\*

Department of Chemistry, University of Nebraska, Lincoln, NE 68588, USA

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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 polarizability.

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
$M-C_2H_4$	<1	5.0	14	36	14	48
$M-CH_2O$	59	26	<1	<1	—	—
$C_2H_3X$ (a)	7	66	51	.7	53	10
$C_2H_4X$	7	14	90	44	19	15
$CH_2X$	13	99	85	13	49	17
$C_2H_4$	100	3.0	10	15	81	10

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



Table 2  
Metastable Ion Characteristics of  $C_3H_6O^+$  Ions

Source of $C_3H_6O^+$ Ions	58 → 57	58 → 43	58 → 42	58 → 31	58 → 30	58 → 29	58 → 28	58 → 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)	—	—	—	—	—	—

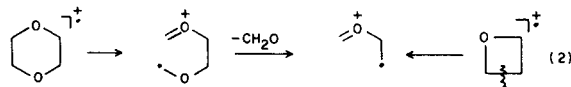
(a) Percentage of total ion current. (b) Kinetic energy released in the transition in meV.

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  $C_2H_4$  is lost to give  $[X_2]^+$ . In accordance with Collin, *et al.* (6), we postulate that the  $[M-C_2H_4]^+$  must be cyclic at some point so that it may undergo a second loss of  $C_2H_4$ . This reaction may be termed a cycloreversion, the reverse of which would correspond to a cycloaddition of ethylene and  $[X_2]^+$ . The higher tendency for the loss of  $C_2H_4$  from the higher molecular weight members of the series can be ascribed to the stability of heteroatom-carbon bonds (3a). Elimination of  $C_2H_4$  from  $M^+$  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  $C_2H_4$  loss is most abundant for the tellurium analogs and of lower importance for oxygen and sulphur containing compounds.

#### $CH_2O$ Loss.

Loss of formaldehyde ( $CH_2O$ ) 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

$(M-CH_2O)^+$  ion is probably cyclic. We have chosen to examine the unimolecular metastable decompositions of  $(M-CH_2O)^+$  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  $[C_3H_6O]^+$  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



little isomerization to other  $[C_3H_6O]^+$  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).

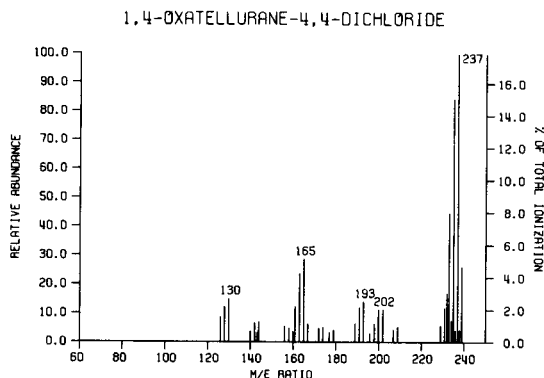
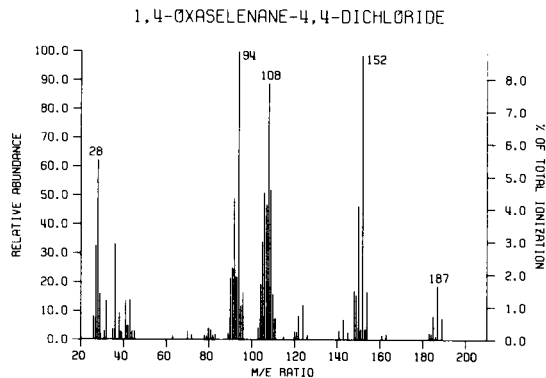
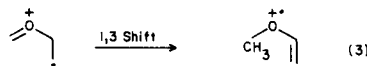
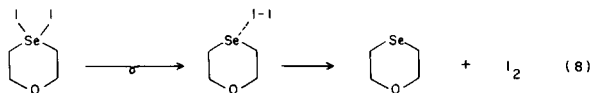


Figure 2. Mass Spectra of Dihalogen Substituted Chalcogen-Containing Heterocycles at 70 eV of Ionizing Energy.





The mass spectrum of the 1,4-oxaselenane diiodide showed no peaks corresponding to  $M^{+}$  or  $(M-I)^{+}$ . 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.



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  $M^{+}$  were observed. In both of these diiodides strong peaks at  $m/e$  127 and  $m/e$  254 correspond to  $I^{+}$  and  $I_2^{+}$ .

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.  $114^{\circ}$  (lit. m.p.  $112.5-113.5^{\circ}$ ).

##### 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.  $151-152^{\circ}$ .

##### 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  $179.5^{\circ}$  (with partial decomposition). In contrast, we obtained block-type parallelepipeds with melting point at  $175^{\circ}$  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  $V^{1/2}/E$  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 ratios were calculated from peak heights.

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