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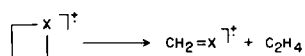
The mass spectra of thietane, trimethylene sulfoxide, and trimethylene sulfone are reported. The major competing reactions are four-center fragmentation, heteroatom group elimination and rearrangement. The oxidation state of the sulfur atom has a profound effect upon the competition among these reaction channels. As the oxidation state of the sulfur increases the molecular ion becomes increasingly less stable and consequently the amount of rearrangement decreases. Elimination of the heteroatom increases as its oxidation state increases, while the amount of four-center fragmentation decreases.

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Introduction

There have been many mass spectral investigations of sulfur heterocyclic organic compounds (1), but very few systematic studies relating the effect of ring size or oxidation state of the sulfur to the modes of fragmentation. The present study of the mass spectra of four-membered ring sulfur compounds was undertaken in conjunction with an investigation of the vacuum ultraviolet photochemistry of these compounds. Specifically, we were interested in how the oxidation state of the sulfur affects the competition among the available reaction channels.

It is well documented (2-6) that four-membered ring organic compounds of the type shown below, all undergo simple four-center cleavage in the mass spectrometer.



With the exception of azetidine (X = NH) this cleavage gives rise to the base peak of the spectrum. As indicated, most of the ion current is carried by the fragment containing the heteroatom (the only exception is oxetane). In the case of cyclobutane, oxidizing one of the carbons to form cyclobutanone does not affect the major fragmentation mode (four-center cleavage). Since sulfoxides and sulfones are known to undergo rearrangement and elimination in the mass spectrometer (7-11), it was anticipated that changing the oxidation state of the sulfur would have a significant effect on the fragmentation paths of the four-membered ring sulfur compounds.

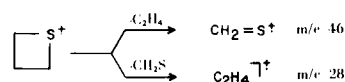
The molecules investigated were thietane (I), trimethylene sulfoxide (II), and trimethylene sulfone (III). Although the mass spectrum of thietane has been reported previously, the spectra of the sulfoxide and the sulfone are reported for the first time here.

Results and Discussion.

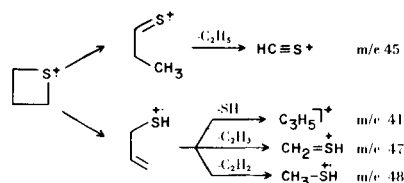
Thietane.

As we have already mentioned, the spectrum of I (Fig. 1) can be rationalized in terms of a favorable four-center cleavage.

In addition to this process there appears to be some re-



arrangement of the molecular ion involving cleavage of a carbon-sulfur linkage with hydrogen rearrangement to sulfur or carbon.



These are very common rearrangements for sulfides (12) and they usually account for a larger fraction of the ion current than they do in this case.

The only remaining ion to be accounted for is that at *m/e* 73 which is formed by loss of a hydrogen atom from the molecular ion. The relatively low intensity of this M-1 peak as compared to ethylene sulfide (13) and

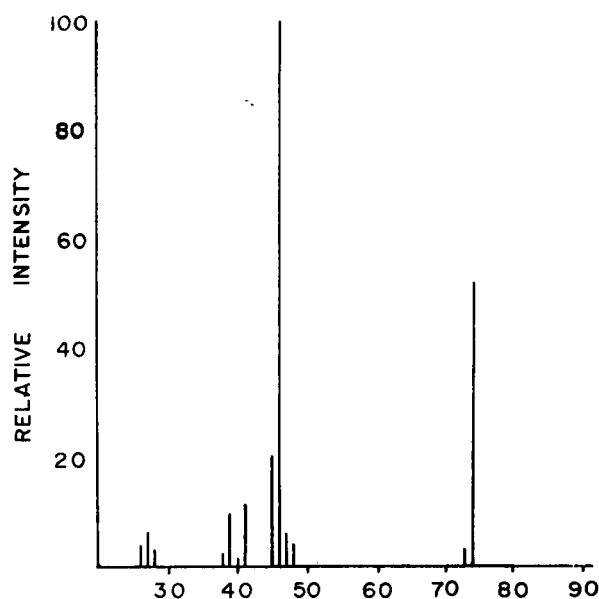


Figure 1. Mass spectrum of thietane at 70 eV.

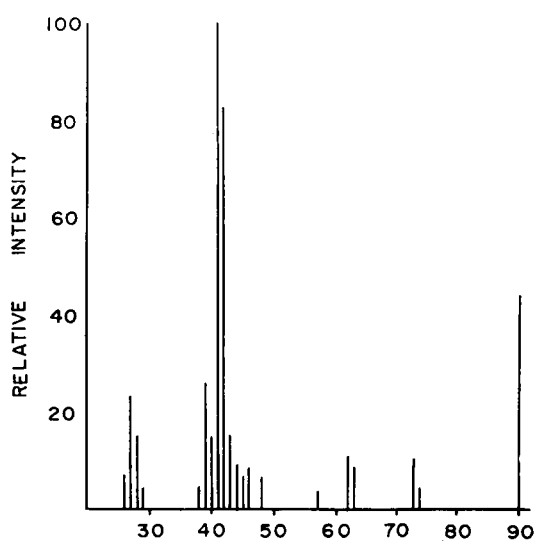


Figure 2. Mass spectrum of trimethylene sulfoxide at 70 eV.

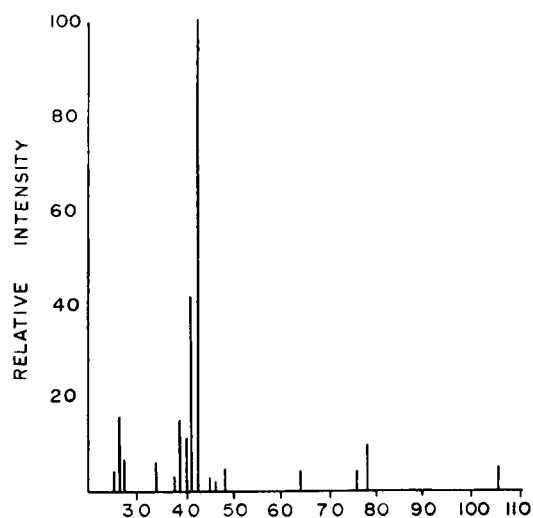
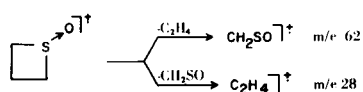


Figure 3. Mass spectrum of trimethylene sulfone at 70 eV.

tetrahydrothiophene (14), and the low contribution of fragments arising from cleavage of a carbon-sulfur bond with hydrogen rearrangement are manifestations of the ease with which the four-center cleavage takes place. These other modes cannot compete effectively with the latter process.

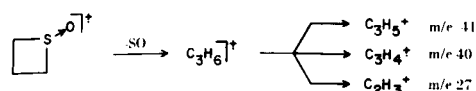
Trimethylene Sulfoxide.

The spectrum of II (Fig. 2) is more complicated than either the sulfide (Fig. 1) or the sulfone (Fig. 3). The most surprising feature is the small extent to which this compound undergoes four-center cleavage (m/e 62 and 28).



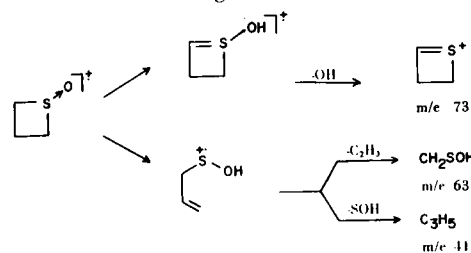
It is interesting to note that the hydrocarbon fragment (m/e 28) carries most of the ion current generated by this process. This is in sharp contrast to the sulfide (I) where most of the ion current from four-center cleavage was carried by sulfur containing fragments. The increased oxidation state of sulfur in the sulfoxide makes it a much less attractive site for localization of a positive charge.

The major fragmentation mode of II involves the loss of SO to yield C_3H_6^+ fragment ion.



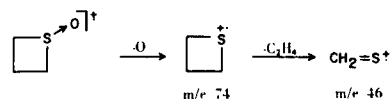
The C_3H_6^+ possesses excess energy and undergoes further decomposition as shown. We may not, however, account for all of the C_3H_5 (m/e 41) by this mechanism, since to do so would require that the C_3H_6^+ possess more energy than that produced by interaction of cyclopropane with 70 eV electrons (15).

Rearrangement of the molecular ion also takes place and accounts for the fragments shown below.



Although it is conceivable that only one sulfinic acid intermediate is involved, deuterium labeling experiments for other alicyclic sulfoxides (11) indicate that the $[\text{M}-\text{OH}]$ and the $[\text{M}-\text{SOH}]$ ions have different intermediates. The m/e 63 ion is the base peak of dimethyl sulfoxide (16) and is known to lose water by a one-step process to yield the m/e 45 ion. This latter ion could also be produced by elimination of ethylene from the m/e 73 ion.

The molecular ion may also eliminate an oxygen atom to form the thietane molecular ion which in turn undergoes facile four-center cleavage to yield, a fragment at m/e 46.



It has been suggested that loss of oxygen in sulfoxides competes with hydrogen rearrangement (11), and indeed when we compare the intensity of the $[\text{M}-\text{O}]$ peaks for the four, five, and six membered alicyclic sulfoxides, we do find that the relative intensity of this peak decreases as the amount of hydrogen rearrangement increases (as the size of the ring increases).

Table I

Comparison of the 70 eV Spectrum of Trimethylene Sulfone and the 20 eV Spectrum of Cyclopropane

	70 eV	20 eV
m/e	R.I.	R.I.
42	100	100
41	42	74
40	12	21
39	16	31
28	7	2
27	16	14

Table II

Assignment of the Fragments Ions of I, II and III to the Various Reaction Modes

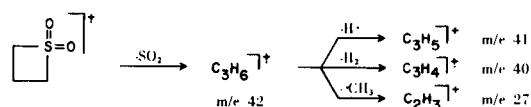
m/e	% Σ	m/e	% Σ	m/e	% Σ
74	23.6	90	11.0	106	2.1
73	1.4	74	1.1 (c)	78	4.2 (a)
48	1.8 (b)	73	2.5 (b)	76	1.7 (b)
47	2.8 (b)	63	2.0 (b)	64	1.8 (c)
46	44.9 (a)	62	2.9 (a)	48	2.3
45	9.3 (b)	57	1.0	46	0.8 (a)
41	4.9 (b)	48	1.6 (c)	45	1.2
40	0.5 (b)	46	2.0 (c)	42	41.7 (c)
39	3.0 (b)	45	1.7	41	17.5 (c)
38	0.8	44	2.2	40	5.0 (c)
28	1.4 (a)	43	3.8	39	6.7 (c)
27	2.9	42	20.3 (c) (20.3) (d)	38	1.3
26	1.6	41	24.6 (b,c) (15.0 (d))	34	2.5
		40	3.7 (c) (4.2 (d))	28	2.9 (a)
		39	6.5 (c) (6.3) (d)	27	6.7
		38	1.2	26	1.7
		29	1.0		
		28	3.7 (a)		
		27	5.7 (2.7) (d)		
		26	1.7		

(a) Ion arising from four-center cleavage. (b) Ion arising from rearrangement of the molecular ion. (c) Ion arising from an elimination reaction (other than four-center). (d) The contribution due to elimination of SO assuming that $C_3H_6^+$ reacts identical to cyclopropane ionized by 20 eV electrons.

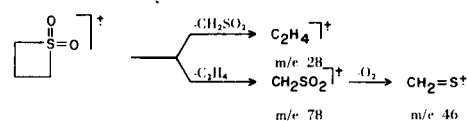
Trimethylene Sulfone.

The 70 eV mass spectrum of III is shown in Figure (3). The most striking feature is the low intensity of the molecular ion, and the overall simplicity of the fragmentation pattern. As might be expected from the high oxidation state of sulfur in this compound, almost all of the ion current is carried by hydrocarbon fragments. As suggested by Kutz and Weinger (10) the spectra of cyclic sulfones should resemble the spectra of simple olefins and/or alicyclic hydrocarbons if direct elimination of SO_2 is a major process. When we compare the 20 eV spectrum of cyclopropane with the spectrum of III (Table I), we note the amazing similarity between the two. The only real difference is that the degree of secondary decomposition is much less for the $C_3H_6^+$ produced by loss of SO_2 from the sulfone than for cyclopropane at 20 eV. This fact coupled with the low intensity of the molecular ion and that SO_2 fragmentation (m/e 64 and 48) for the sulfone is greater than that observed for SO_2 at 50 eV (17) suggests that the molecular ion is a very unstable short-lived species which does not equilibrate its excess energy. Apparently, the interaction of III and 70 eV electrons produces an ion in an electronically repulsive state whose lifetime precludes the efficient conversion of electronic energy to vibrational energy.

The mass spectrum of trimethylene sulfone can be adequately understood in terms of the following process.



Four-center cleavage also takes place in this compound, but only to a very minor extent and is responsible for the fragments at m/e 28, 78, and 46 as shown below.



It is clear that the importance of the four-center fragmentation in four-membered ring sulfur heterocycles is greatly dependent upon the oxidation state of the sulfur.

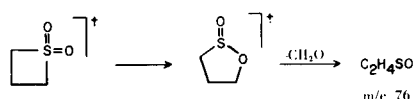
The only fragment left unaccounted for is that which

Table III

Percent of the Ion Current Due to the Various Reaction Modes of I, II and III

	Four-center	Rearrangement	Elimination	M+	Other (a)
I	46%	23%	----	24%	7%
II	7%	14%	50%	11%	18%
III	8%	2%	73%	2%	15%

(a) Ions which could not be unambiguously assigned to a particular process.



produces the ion at m/e 76. The following is a rationale for this peak.

The formation of the sulfinate ester above is an interesting rearrangement which is responsible for the major fragmentation modes of unsaturated and aromatic sulfones (7). Although there is increased p character in the bonds of III as compared to sulfolane (tetrathylene sulfone), where this rearrangement also takes place to a small extent (11), the strain on the four-membered ring does not allow this rearrangement to compete favorably with direct loss of the very stable SO_2 molecule.

The influence of the oxidation state of the sulfur atom upon the competitive processes occurring in the mass spectrometer (e.g., four-center cleavage, elimination, rearrangement) can be assessed by comparing the relative intensities of the peaks arising from these processes. In comparing the relative importance of the various reactions, the "mechanisms" for the mass spectra of I and III allow for definitive comparison, but the comparison for II is not as easily made since some ions arise by more than one mechanism. It is possible, however, to approximate the relative importance of the various fragmentation modes by making the assumption that the $C_3H_6^+$ produced in the 70 eV spectrum of II behaves in a manner similar to the molecular ion in the 20 eV spectrum of cyclopropane (Table I). There is no *a priori* justification for this assumption, and we make it only to establish a point of reference.

In Table II the various ions are assigned to the different competitive processes for the different compounds. Table III presents the percent of the ion current carried by ions originating from the important fragmentation modes for these compounds. The data in Table III indicates that as the oxidation state of the sulfur increases the molecular ion becomes increasingly less stable. Not unexpectedly, there is a direct correlation between the stability of the molecular ion and the amount of rearrangement that takes place before fragmentation. If we keep in mind that the four-center cleavage is just the elimination of ethylene, it is clear that the major mode of reaction for all of these molecules is elimination of a stable neutral particle. As the oxidation state of sulfur increases, loss of the heteroatom group increases and loss of ethylene decreases to the point where in the sulfone loss of SO_2 is the only really significant mode of reaction.

EXPERIMENTAL

All mass spectra were obtained on a DuPont Instruments 21-

491 mass spectrometer operating at 70 eV. The sulfide I was introduced through the liquid inlet system with the oven at 150° and the source at 150° . The sulfoxide and sulfone were introduced through the solid probe which was kept at ambient temperature. (It was observed that even moderate heating of the probe caused new peaks to appear in the spectra due to thermal reactions prior to ionization). The source in these instances was operated at about 50° .

The sulfide I was obtained from Aldrich and was purified by distillation on a thirty theoretical plate spinning-band column. The corresponding sulfoxide and sulfone were prepared by oxidation of the sulfide by methods reported in the literature (18), and were purified by recrystallization and sublimation.

Acknowledgment.

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