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The mass spectra of selenophene and tellurophene have been measured and their modes of fragmentation compared with those of furan and thiophene.

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The chemistry of tellurophene has been mainly developed in this laboratory (1) and its chemical and physical properties compared with those of the other congeners furan, thiophene and selenophene.

The present paper is concerned with the mass spectra of tellurophene and selenophene. The data of furan and thiophene are taken from literature (2,3).

A mass spectrometric fragmentation study of five membered congener heteroaromatic compounds should provide experimental evidence on the ability of heteroatom (O, S, Se, Te) to stabilize the positive charge initially formed upon electron impact and thus to direct the fragmentation of the molecule. This should be of interest also in reactivity problems concerning those reactions in which an intermediate carbon ion is formed.

The fundamental fragmentation modes of furan (2,3) and thiophene (2,3) are reported in the Scheme I (X = O, S) and the % Σ_{29} are tabulated in Table I.

The two compounds qualitatively show similar ring cleavage patterns, but on quantitative grounds there are

Table I

	Fur.	Thi.	Sel.	Tel.
M ⁺	26.8	30.4	44.8	44.4
M-CHX (a, m/e 39)	43.2	8.3	3.3	0.4
M-39 (b)	6.8	17.5	5.2	1.1
M-C ₂ H ₂ (c)	3.0	19.7	16.6	4.1
M-HX (d, m/e 51)		1.1	5.7	6.6
X ⁺ (e)			4.8	21.6
M-X (f, m/e 52)			0.8	3.8

Per cent of total ionization from m/e 29 to molecular ion for the principal ions present in the mass spectra of Furan (Fur.), Thiophene (Thi.), Selenophene (Sel.) and Tellurophene (Tel.).

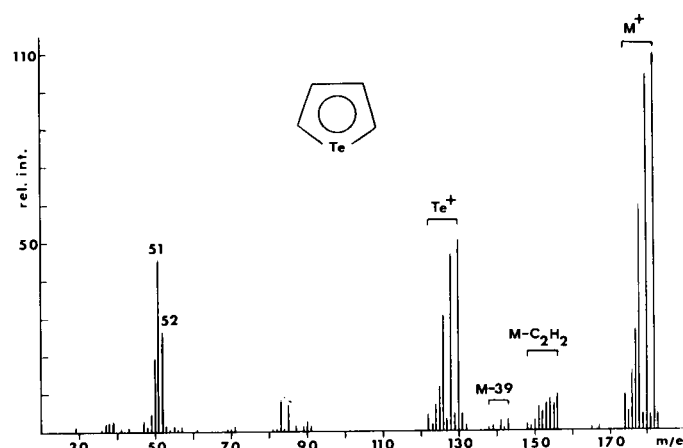
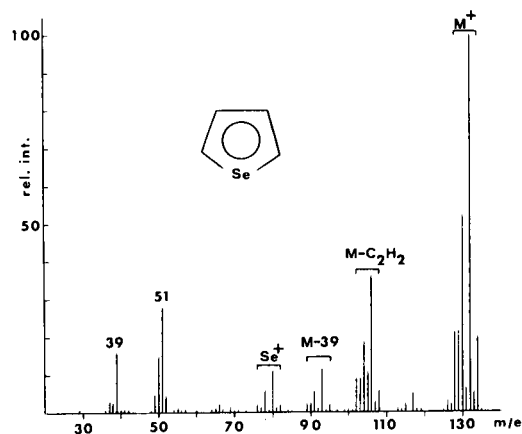
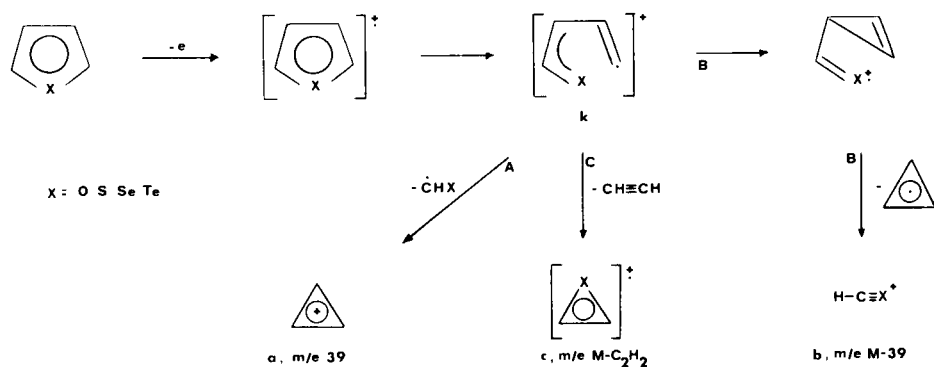


Figure I: Mass spectra of selenophene and tellurophene.

Scheme I



marked differences. The first step in each case is cleavage of carbon-heteroatom bond. The elimination of the formyl radical is the prevalent process in the fragmentation of furan (4) and the cyclopropenyl cation (m/e 39) is the base peak. Expulsion of the neutral acetylene and the cyclopropenyl radical are the main degradation reactions of thiophene and the molecular ion (m/e 84) is the base peak.

The mass spectra of selenophene and tellurophene (Figure 1) are remarkably simple. The percent of total ionization from m/e 29 to molecular ion are reported in Table I for the principal ions.

Selenium and tellurium contain many stable isotopes (5) so that heteroatom-containing ions are readily recognized by a series of peaks with characteristic ratios. In addition, previous studies on the mass-fragmentation of furan (2,3), thiophene (2,3), tetrahydroselenophene (6) and tetrahydrotellurophene (6) further facilitate the interpretation of the spectra.

The fragmentation processes of selenophene and tellurophene are similar but with important differences in the relative contribution to the percent of total ionization of various fragments.

Both compounds show the molecular ion as base peak with practically identical values of $\% \Sigma_{29}$ (Table I). The spectrum of tellurophene shows also a small amount ($\sim 2\%$) of M-1 fragment.

$M-C_2H_2$ ion is present in both spectra but is more significant in selenophene than in tellurophene. This ion is formulated as *c* (Scheme I; $X = Se, Te$) and its formation can be envisaged as proceeding from the molecular ion "via" the pathway C of Scheme I.

The ion corresponding to M-39, formulated as *b* and originating from loss of cyclopropenyl (Scheme I; $X = Se, Te$; pathway B), is clearly discernible in the spectrum of selenophene while it is poorly present in the spectrum of tellurophene.

In addition to the analogous fragments observed in the fragmentation of furan and thiophene, the spectra of selenophene and tellurophene contain X^+ , M-HX (m/e 51)

ions ($X = Se, Te$) and an important fragment of mass 52 (M-X) corresponding to the loss of heteroatom. It is interesting to note that the Te^+ ion contributes significantly to the percent to total ionization, while M-Se ion is barely visible (Table I). The genesis of m/e 51 and 52 ions can be envisaged through homolysis of carbon-heteroatom bond in the molecular ion to produce *k* which in turn yields the vinylacetylene ion (m/e 51) or the butadiene ion (m/e 52) "via" a transfer of a hydrogen atom from β -carbon to heteroatom and heterolysis of the carbon-heteroatom bond or "via" simple expulsion of heteroatom, respectively. Similarly X^+ ion can be originated directly from *k* "via" a hydrogen transfer from β to α carbon with synchronous elimination of vinylacetylene. These fragmentation modes, reported in the Scheme II, are in full agreement with analogous mechanisms reported in the fragmentation of tetrahydro-selenophene (6) and tetrahydrotellurophene (6) and with a recent study on the photochemistry of 2-phenylselenophene (7) and 2-phenyl-tellurophene (7).

On going from furan to tellurophene there is a variety of modes of fragmentation but there is also a gradual change in the pattern of fragmentation as schematized in Figure 2 in which are reported only the fragments which contribute significantly (at least 4%) to the $\% \Sigma_{29}$.

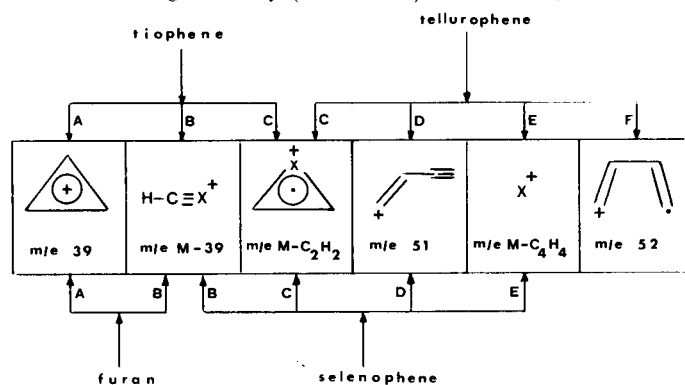
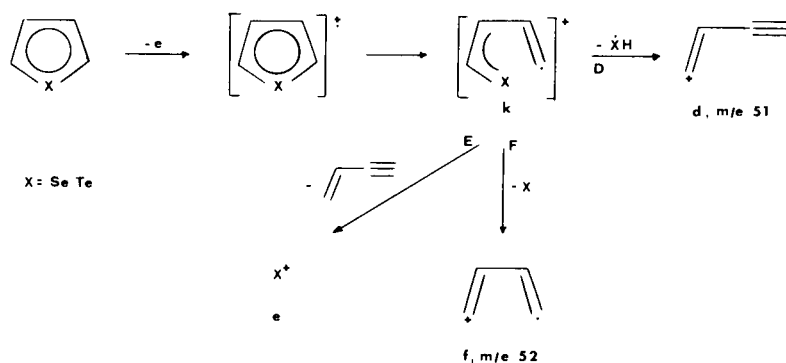


Figure II: Variety of fragments and gradual change in the pattern of fragmentation on going from furan to tellurophene.

Scheme II



The factors influencing the fragmentation are probably: (i) the stability of the molecular ion which increases on going from furan to tellurophene but which is not simply related to the electronegativity or to the +M effect of the heteroatom [compare the results of mass-fragmentation of corresponding tetrahydro derivatives (6)]; (ii) the strength of the carbon-heteroatom double bond which decreases on going from oxygen to tellurium (7); (iii) the greater difficulty for tellurium than for oxygen in giving a tricyclic cation as *b* (Scheme 1). The prevalent contribution of these opposing factors leads to the observed gradual change in the pattern of fragmentation of these heterocyclopentadienes.

EXPERIMENTAL

The mass spectra were determined on MAT-3H-A (Varian) apparatus at 70 eV. Temperature of introduction of sample was 25-30°. Mass spectra at 50 eV were also recorded but no significant differences were observed.

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