

The Mass Spectra of Some Aliphatic and Aromatic Selenium Dihalides

ERIK REBANE

Chemical Institute, University of Uppsala, P.O.B. 531, S-751 21 Uppsala 1, Sweden

The mass spectra of some representative organic selenium dibromides, R_2SeBr_2 , and partial mass spectra of the corresponding selenium dichlorides, R_2SeCl_2 , are given. Generally, peaks due to molecular ions are absent. The characteristic fragment is instead $[M-X]^+$. Two main fragmentation routes of the $[M-X]^+$ ions are observed. Elimination of the remaining halogen with formation of $[R_2Se]^+$ is an important process, being the only fragmentation mode of the $[M-X]^+$ ions in diarylselenium dihalides. In the spectra of dialkyl and alkyl aryl selenium dihalides, fission of one carbon-selenium bond with elimination of an alkyl group is observed, a process which may also be associated with hydrogen transfer to the charged selenious fragment. Further fragmentations of the resulting $[RSeX]^+$ ions involve selenium-halogen, selenium-carbon, and C_1-C_2 bond fissions.

Organic selenium dihalides, R_2SeX_2 , particularly the dibromides, have long been utilized for the isolation and purification of selenides from other components in a reaction mixture.¹ Furthermore, they have been used as intermediates in syntheses of selenoxides, being of particular advantage for the preparation of pure aliphatic selenoxides.² During a mass spectrometric investigation of selenium-oxygen compounds, a number of selenium dibromides and selenium dichlorides were needed as precursors for selenoxides. Interest was also focused on the mass spectrometric behaviour of this type of compound during work on the preparation of aliphatic selenones by ozonization of the corresponding selenoxides in trichloromethane or tetrachloromethane solution. The products thus obtained were frequently contaminated by components, the mass spectra of which indicated the presence of both selenium and chlorine in the molecule. No descriptions, however, could be found in the literature on the fragmentation modes of organic selenium dihalides on electron impact. The mass spectra of some selenium dibromides, I-V, and partial spectra, Table 1, (including only ions containing Se-Cl bonds and some fragments obtained from their further degradation) of the corresponding selenium dichlorides, V-IX, of different types, Table 2, are given. In the following

discussion the ions containing selenium, bromine, or chlorine are represented by fragments containing the main natural isotopes ^{80}Se , ^{79}Br , and ^{35}Cl .

Compounds of the type, R_2SeX_2 , $\text{X} = \text{Br}, \text{Cl}$, are slightly thermally unstable³ and the question arises if the mass spectra of I–IX (Table 2) may be appreciably contaminated by fragments originating from thermal decomposition of the substances in the inlet system prior to ionization. Apparently there have been no exhaustive studies of the thermal properties of aliphatic selenium dihalides.³ However, there are reports indicating that dialkylselenium dihalides may decompose into selenium and the corresponding alkylhalides upon heating.³ Methyl phenylselenium dihalides are reported to give methyl halide and phenylselenium halide ($\text{C}_6\text{H}_5\text{SeX}$),³ while in the case of diphenyl selenium dihalides the decomposition products are diphenyl selenide, diphenyl selenide, halogenated in one or both phenyl groups, and hydrogen halide.³ Furthermore, in tetrachloromethane solution, the diphenylselenium dihalides have been shown to partly dissociate into the selenide and free halogen.⁴

The mass spectra of the freshly prepared pure selenium dihalides, I–IX, were recorded at rather low to moderate temperatures of the inlet system ($25 - 65^\circ$). The mass spectra of the aliphatic compounds I–III and VI–VII do not exhibit fragments (Figs. 1–3) derivable from products which would be formed by the reported mode of their thermal decomposition.³ The same is true for fragments which may originate from ring-halogenated diphenyl selenide in the case of V and IX. However, particularly in the spectra of IV and V, ions are found at m/e 158 $[\text{Br}_2]^+$ and abundant $[\text{R}_2\text{Se}]^+$ fragments at m/e 172 and m/e 234, respectively. Also, III exhibits a minor peak at m/e 158 due to $[\text{Br}_2]^+$. All the selenium dichlorides investigated, VI–IX, are also characterized by abundant $[\text{R}_2\text{Se}]^+$ fragments (Table 1). Small amounts of $[\text{Cl}_2]^+$ ions, however, are found only in the case of VIII (0.2 %) and IX (4.8 %). No metastable peaks for an electron-impact induced formation of

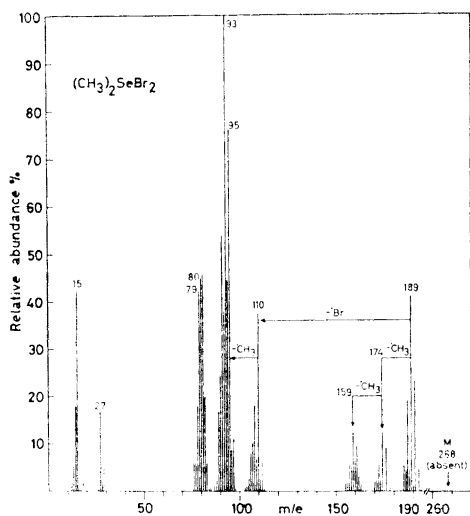


Fig. 1.

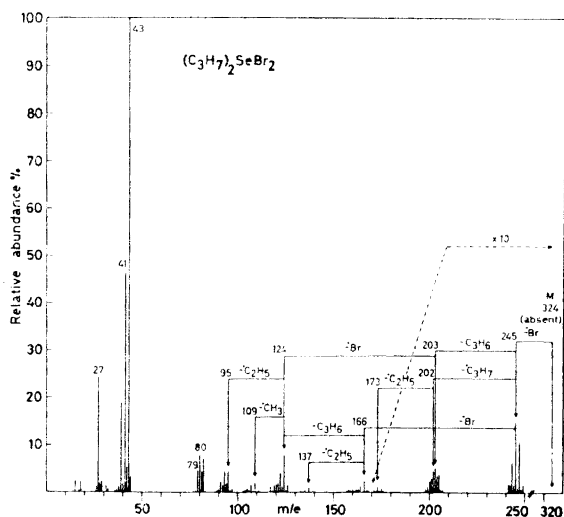
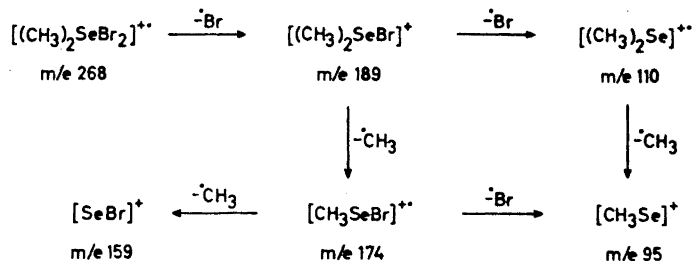


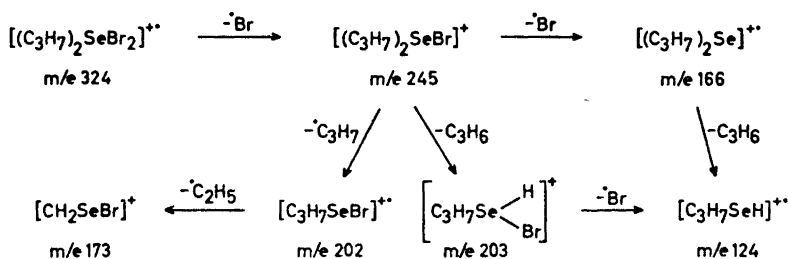
Fig. 2.

the $[M - X_2]^+$ ions are observed. Some dissociation of the selenium dihalides, particularly those containing aryl-selenium bonds, into the corresponding selenide and halogen before ionization thus cannot be excluded. However, the mode of the electron-impact induced degradations around the selenium dihalide function, as indicated by the recorded spectra, can in its essential parts be distinguished from the fragmentations of the decomposition products mentioned thus revealing a number of fragments which are characteristic for compounds of the type R_2SeX_2 , $X = Br, Cl$.

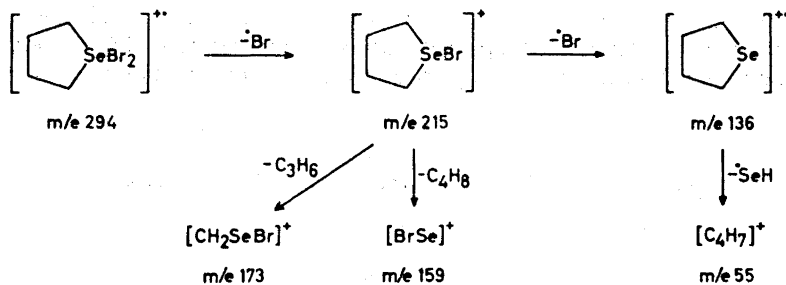


Scheme 1.

A general feature of the mass spectra of the selenium dihalides, I–IX, is absence of peaks due to molecular ions (Figs. 1–5). The only exception is VI, which exhibits a weak molecular ion, 0.1 %. Instead, these compounds are characterized by $[M - X]^+$ ions, $X = Br, Cl$. In the spectrum of I (Fig. 1) the abundant $[M - Br]^+$ fragment at m/e 189 is degraded by two alternative routes (Scheme 1). One fragmentation mode implies the preservation of the selenium-bromine bond and involves the elimination of methyl groups giving the ions $[CH_3SeBr]^+$ at m/e 174 and $[SeBr]^+$ at m/e 159. The alternative route implies cleavage of the selenium-bromine bond with charge retention on the selenide fragment at m/e 110. The subsequent degradation of this fragment is analogous to that already described for dimethyl selenide.⁵ In addition, however, the group of peaks around m/e 80 contains the fragment $[Br]^+$ at m/e 79. In the spectrum of VI, fragments are observed in accordance with those mentioned for I which provides further support for the fragmentation pattern proposed in Scheme 1.



Scheme 2.



Scheme 3.

In the spectra of the other aliphatic selenium dihalides investigated, II (Fig. 2), III (Fig. 3), and VII (Table 1), fragments containing selenium-halogen bonds are of lower abundance. As in the case of I, simple Se-Br bond

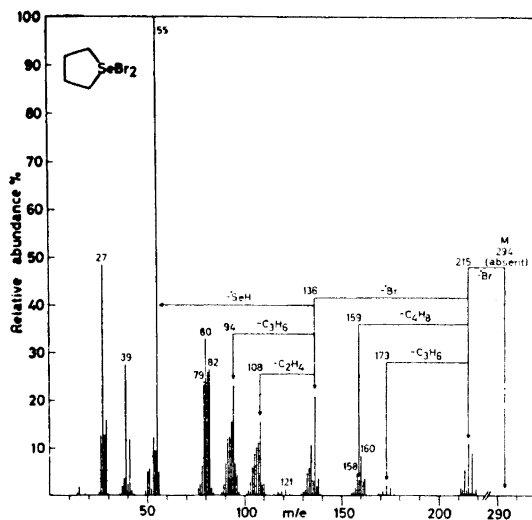
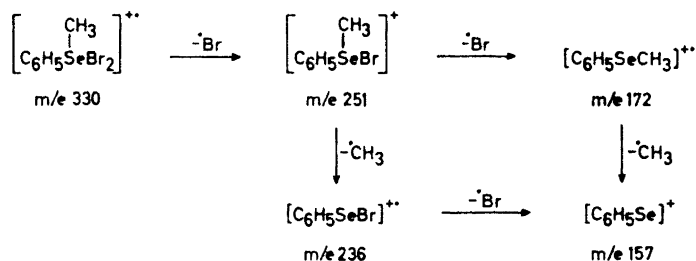


Fig. 3.

Table 1. Relative intensities (I) of ions containing Se-Cl bonds and their degradation fragments in the mass spectra of $R_2\text{SeCl}_2$.

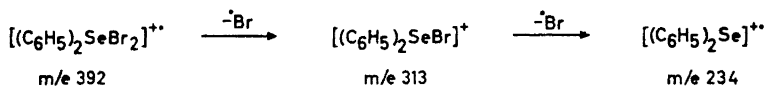
m/e	VI % I	m/e	VII % I	m/e	VIII % I	m/e	IX % I
180	0.1	206	—	242	—	304	—
145	14.0	171	2.5	207	1.8	269	0.2
130	3.4	136	42.5	192	0.5	234	53.8
115	0.9	129	1.1	172	100	192	0.1
110	100	115	0.4	157	84.4	157	6.8
95	91.1						

rupture in the $[M - Br]^+$ ions at m/e 245 and m/e 215 in II and III, respectively, is observed generating the fragments at m/e 166 and m/e 136 (Schemes 2 and 3). In addition, fragments arising from carbon-selenium bond cleavage of the



Scheme 4.

$[M - Br]^+$ ions are found. In the case of II (Fig. 2) elimination of a propyl radical leads to $[\text{C}_3\text{H}_7\text{SeBr}]^+$ at m/e 202 (Scheme 2). The transition is followed by a $\text{C}_1 - \text{C}_2$ bond cleavage, forming $[\text{CH}_2\text{SeBr}]^+$ at m/e 173. Similar processes involving $\text{C}_1 - \text{C}_2$ bond fissions are frequently observed in the spectra of, for example, selenides, sulphides, and ethers.⁵⁻⁷ An analogous process is also proposed as the origin of the fragment at m/e 173 in the spectrum of III (Scheme 3). Furthermore, the carbon-selenium bond rupture in the $[M - Br]^+$ ion in II is also associated with hydrogen migration to the charged fragment forming $[\text{C}_3\text{H}_8\text{SeBr}]^+$ at m/e 203. This transition is similar to $M \rightarrow m/e$ 124 in the spectrum of dipropyl selenide.⁵ In the spectrum of III, fission of both selenium-carbon bonds gives $[\text{BrSe}]^+$ at m/e 159 (Scheme 3), a fragment which is present to a minor extent in the case of II. The spectrum of VII (Table 2), reveals a fragmentation pattern in agreement with that given for III, although the relative abundance of ions containing Se-Cl bonds is, however, considerably lower. Finally, the spectra of II, III, and VII contain peaks at lower masses which, with the exception of peaks corresponding to $[\text{X}]^+$ and $[\text{XH}]^+$ ions, may also be recognized in the corresponding selenides.^{5,8}



Scheme 5.

The spectra of IV (Fig. 4) and VIII (Table 1) are completely dominated by fragments which are also present in the spectrum of the corresponding selenide.⁵ A detailed appraisal of these spectra gives evidence for fragmentation processes around the selenium dihalide function, as visualized for IV in Scheme 4, and which are very similar to the degradation pattern of I. Thus the $[M - X]^+$ ions at m/e 251 in IV and at m/e 207 in VIII are the origin of part of the abundant ions at m/e 172 $[\text{C}_6\text{H}_5\text{SeCH}_3]^+$, and by expulsion of a methyl radical

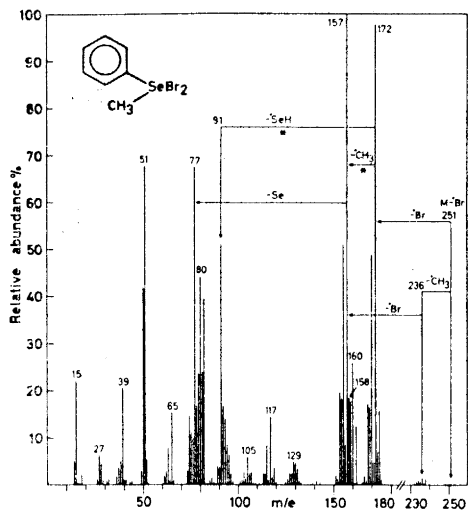


Fig. 4.

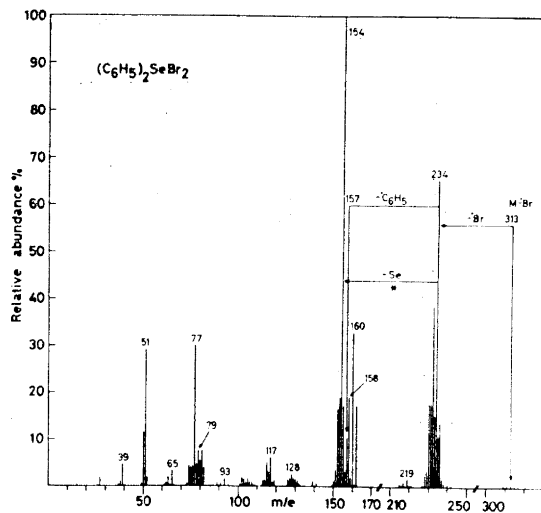


Fig. 5.

also of the $[\text{C}_6\text{H}_5\text{SeX}]^+$ fragments at m/e 236 and 192, respectively. Ions derived from the less favourable selenium-aryl bond cleavage in the $[\text{M}-\text{X}]^+$ fragment are not observed.

The mass spectra of the diarylselenium dihalides, V (Fig. 5) and IX (Table 1) are also dominated by fragments, which, with the exception of the $[\text{X}_2]^+$, $[\text{X}]^+$, and $[\text{XH}]^+$ ions are also present in the spectrum of the corresponding selenide.⁹ The weak peaks present at m/e 313 (Fig. 5) and m/e 269 (Table 1), deriving from fragments containing both selenium and halogen, indicate that the electron-impact induced processes around the selenium dihalide function in these compounds mainly involve the stepwise elimination of the halogens (Scheme 5) from the molecular ion leading to m/e 234 $[(\text{C}_6\text{H}_5)_2\text{Se}]^+$. A weak peak at m/e 192 in the spectrum of IX is ascribed to $[\text{C}_6\text{H}_5\text{SeCl}]^+$.

EXPERIMENTAL

The mass spectra were recorded on an LKB 9000A gas chromatograph-mass spectrometer, operating at 70 eV. The spectra were recorded using the direct inlet technique. The purity of the selenium dihalides was checked by microanalysis for selenium. The melting points are uncorrected.

The selenium dibromides, I–V, were prepared by addition of bromine to the corresponding pure selenides⁵ in tetrachloromethane solution.¹ The selenium dichlorides, VI–VIII, were prepared analogously by addition of chlorine to the selenides, while IX was obtained by oxidation of the selenide with nitric acid followed by addition of hydrochloric acid.¹⁴ The selenium dihalides were purified by repeated recrystallizations from methanol or tetrachloromethane. The melting points are given in Table 2.

Table 2. Selenium dihalides, R_2SeX_2 .

R	Selenium dibromides M.p. °C	Ref.	Selenium dichlorides M.p. °C	Ref.
CH ₃	I 83.5–84 d	2	VI 60–61	15
C ₃ H ₇	II 49–50	2	—	—
—(CH ₂) ₄ —	III 96–98	10	VII 91–92	10
C ₆ H ₅	IV 115–116 d	11	VIII 133–134 d	13
CH ₃	V 150–151 d	12	IX 185–187	14
C ₆ H ₅				

Acknowledgements. I express my sincere gratitude to Professor Göran Bergson for the facilities put at my disposal. Thanks are also due to Mr. O. Eriksson for skilled technical assistance with the figures. The mass spectra were recorded by Mr. K. Janné and Mr. L. Grehn.

REFERENCES

1. Rheinboldt, H. In Houben–Weyl, *Die Methoden der organischen Chemie*, G. Thieme, Stuttgart 1955, Vol. 9, p. 1005.
2. Paetzold, R. and Bochmann, G. *Z. anorg. allg. Chem.* **360** (1968) 293.
3. Rheinboldt, H. In Houben–Weyl, *Die Methoden der organischen Chemie*, G. Thieme, Stuttgart 1955, Vol. 9, p. 1015.
4. McCullough, J. D. *J. Am. Chem. Soc.* **64** (1942) 2672.
5. Rebane, E. *To be published.*
6. Levy, E. J. and Stahl, W. A. *Anal. Chem.* **33** (1961) 707.
7. McLafferty, F. W. *Anal. Chem.* **29** (1957) 1782.
8. Duffield, A. M., Budzikiewicz, H. and Djerassi, C. *J. Am. Chem. Soc.* **87** (1965) 2920.
9. Bergman, J. *Acta Chem. Scand.* **22** (1968) 1883.
10. Morgan, G. T. and Burstall, F. H. *J. Chem. Soc.* **1929** 1096.
11. Edwards, O. K., Gay-Thwaite, W. R., Kenyon, J. and Phillips, H. *J. Chem. Soc.* **1928** 2293.
12. Lyons, R. E. and Bush, G. C. *J. Am. Chem. Soc.* **30** (1930) 831.
13. Foster, D. G. and Brown, S. F. *J. Am. Chem. Soc.* **50** (1928) 1182.
14. Leicester, H. M. *Org. Syn. Coll. Vol.* **2** (1943) 240.
15. Jackson, C. L. *Ber.* **8** (1875) 109.

Received April 18, 1973.