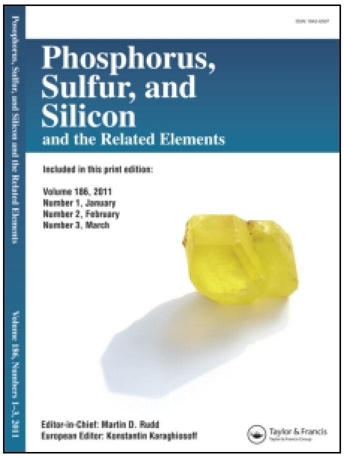

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STUDIES OF HETEROCYCLIC COMPOUNDS: VI[1] THE MASS SPECTRA OF SOME 2-THIOPHENEMERCURIC DERIVATIVES

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STUDIES OF HETEROCYCLIC COMPOUNDS: VI[1] THE MASS SPECTRA OF SOME 2-THIOPHENEMERCURIC DERIVATIVES

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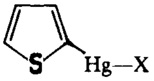
The mass spectra of some 2-thiophenemercuric derivatives are determined and the fragmentation interpretations are based on mechanistic analogy and supported in some cases by metastable peaks and low energy mass spectra. They all fragment ultimately to the 2-thienyl cation formed either through a two-step process, by cleavage of Hg—X bond to give the 2-thienylmercuric cation, followed by extrusion of mercury, or by a one-step process through cleavage of carbon–mercury bond. Their base peaks being the $C_3H_3^+$ ion (*m/e* 39).

INTRODUCTION

Alkyl- and arylmercury compounds has been used for years on agricultural land as seed dressings, turf fungicides and for other fungicidal uses.[2] However, in recent years, there has been great concern about occurrence of these compounds in the environment and their possible toxicological effects.[3] Many of these organomercury derivatives are now either obsolete in Canada and U.S.A. or approved for specific uses only. Mass spectrometry is now one of the techniques routinely used to characterise these compounds and this technique offers the advantages of identifying small samples directly.

A number of papers on the mass spectra of various mercury compounds have been published.[4–9] These papers concern the fragmentation of diaryl- and dialkyl mercurials, aryl- and alkylmercuric halides and organomercuric halides containing the trimethylsilmethyl or trimethylgermyl methyl groups. Since the beginning of organic mass spectrometry, correlations have often been sought[10] between the mass spectral fragmentations and the thermal or photochemical fragmentations of compounds. Accordingly, a series of 2-thiophenemercuric derivatives (I–VI, Figure 1), whose thermal decomposition reactions have been studied and reported,[11] are subjected to fragmentation studies.



(I): $X = Cl$
(II): $X = N_3$
(III): $X = SCN$
(IV): $X = Th$
(V): $X = OCOCH_3$
(VI): $X = OSO_2CF_3$

FIGURE 1 Compounds studied.

RESULTS AND DISCUSSION

The six 2-thiophenemercuric compounds were prepared as given in Part III of this series.[11] The 70 eV spectra of these compounds are given in Table I.

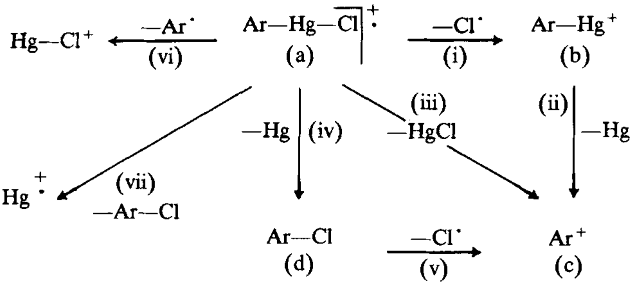
The fragmentation interpretations of the 2-thiophenemercuric compounds are based on mechanistic analogy and supported in some cases by metastable peaks and low energy mass spectra. The compounds give parent ions varying in intensity from 1.1% in the trifluoromethanesulfonate (VI) to 50.2% in the chloride (I); their base peaks all occurring at *m/e* 39. It is noteworthy to state here that the spectra of compounds (II, III, V and VI) resemble those of dithienyl mercury (IV) when the compounds were run at inlet temperatures of about 150°, hence, they were introduced at low temperatures ($\leqslant$ 25°).

The spectrum of 2-thiophenemercuric chloride (I) shows that it fragments in a manner similar to those reported for other arylmercuric chlorides,[6,9] (Scheme 1).

TABLE I[a]

m/e	X = Cl 11 eV	X = Cl 70 eV	X = SCN	X = OCOCH$_3$	X = N$_3$	X = Th	X = OSO$_2$CF$_3$
39		100	100	100	100	100	100
43					98.2	12.3	
45		23.4	24.4	98.0	25.0	18.4	22.0
51						5.6	
57		40.0	40.8	40.9	37.5	23.8	
58		5.1	5.2				45.0
60				43.6			
64							2.8
69		7.8					3.0
77						5.8	
83	70.8	61.5	32.0	59.1	45.8	42.6	67.2
108						5.7	
118	37.5	25.5					
120							
121						8.2	
134						3.3	
166						4.1	
202	54.2	1.8	15.0	36.4	20.8	15.1	3.2
237		2.6					
244					2.1		
285	16.7	5.0	4.2	18.2	7.9	6.2	9.3
311			3.9				
320	100 (M)$^{+\cdot}$	50.2 (M)$^{+\cdot}$					
327					4.2 (M)$^{+\cdot}$		
329				4.2			
343			6.9 (M)$^{+\cdot}$				
344				3.1 (M)$^{+\cdot}$			
351							0.2
368						11.5 (M)$^{+\cdot}$	3.8
434							1.1 (M)$^{+\cdot}$

[a] Only peaks due to chlorine-35 and mercury-202 are used in tabulating these mass spectra. Parent peaks denoted by (M)$^{+\cdot}$.



SCHEME 1 General fragmentation pathway upon electron impact of aromatic-mercuric chloride.

The ion corresponding to (b), (Th—Hg$^+$, m/e 285) in the spectra of I has a relative intensity of 5.0% at 70 eV and the ion corresponding to (d) (Th—Cl$^+$, m/e 118) has a relative intensity of 25.5% at 70 eV and 37.5% at 11 eV.

With thiophenemercuric chloride, it is evident that all the fragmentation pathways (i), (iii) and (iv) are in operation. Process (iii) is favoured over process (vi), i.e., cleavage of the C—Hg bond occurs with charge retention on carbon rather than mercury.

In the azide (II), thiocyanate (III), acetate (V) and trifluoromethanesulfonate (VI), their spectra are similar to that of the chloride (I) with the fragmentation dominated by the mercury-substituent (Hg—X) cleavage (pathway (i), Scheme 1) and carbon-mercury (Th—Hg—X) cleavage (pathway (iii), Scheme 1) with charge retention on carbon. However, the following exceptions and comments are worth noting. Pathway (iv), i.e., the extrusion of mercury from the molecular ion is not observed in any of these compounds. The same is true for pathway (vi) except for the azide (II) where the $\overset{+}{H}gN_3$ ion, at m/e 244, occurs with a relative intensity of 2.1%. In addition, in the azide (II), there was no peak corresponding to the loss of nitrogen molecule to give the thiophenemercuric nitrene (Th—Hg—N). This agrees with what was observed in its thermal decomposition where, upon heating in cyclohexene at about 160° for 3 days, only2,2′-dithienylmercury and no other product was obtained.[11]

The spectrum of the thiocyanate (III) also shows a M-32 ion, at m/e 311, corresponding to the loss of sulfur atom from the molecular ion to give 2-thiophenemercuric cyanide ion, $ThHg—\overset{+}{C}N^{\cdot}$ with a relative intensity of about 4%.

In the mass spectrum of compound (V), a peak is observed at m/e 329 with relative intensity of 4.2%, corresponding to a loss of a CH_3 group from the molecular ion. In addition, an ion corresponding to CH_3COOH is observed at m/e 60 with a relative intensity of 43.6%. The formation of CH_3COOH was also observed (in about 20% yield) during the thermal decomposition of the acetate (V).[11]

The spectrum of the 2-thiophenemercuric trifluoromethanesulfonate (VI) exhibits peaks which suggest that it undergoes two main fragmentations—loss of CF_3SO_3 radical (mercury-oxygen bond cleavage) from the molecular ion to give the thiophenemercury ion at m/e 285 (rel. int., 9.3%) and loss of $HgOSO_2CF_3$ (carbon-mercury bond cleavage) to give the thienyl cation (m/e 83, rel. int., 67.2%

with preferential charge retention on carbon. The $\overset{+}{H}gOSO_2CF_3$ ion is also observed at *m/e* 351 but with only 0.2% relative intensity. It is worth noting that none of the ions one would expect from characteristic fragmentations of the trifluoromethane-sulfonate (triflate) group ($—OSO_2CF_3$), as in aryl triflates,[12] is observed. For example, no simple S—O bond cleavage occurs which would have led to an ion peak at *m/e* 301 (for Th—Hg—O^+). Further, there was no loss of the CF_3 group as a radical, neither was there any SO_2 expulsion to give $(ThHg—OCF_3)^+$, (no $(M\text{-}64)^{\overset{+}{\cdot}}$ ion), followed by the loss of CF_3 group to give the $ThHgO^+$ ion. However, the appearance of ions at *m/e* 69 and *m/e* 64 in the mass spectrum probably indicates the presence of the CF_3SO_2 group.

The spectrum of compound (VI) also shows the presence of an ion at *m/e* 368 (rel. int., 3.8%), even when the sample was introduced at low temperatures, corresponding to the 2,2′-dithienylmercury, probably formed by thermal decomposition prior to ionization. From this single study, one cannot generalise yet on how aryl-mercuric triflates fragment upon electron-impact especially their dimethyl sulfoxide complexes which are more stable to handle.

The mass spectrum of 2-thiophenemercuric chloride (I) is shown in Figure 2, as an example and the total fragmentation route of 2-thiophenemercuric chloride (I), azide (II), thiocyanate (III), acetate (V) and the trifluoromethanesulfonate (VI), is shown in Scheme 2. In the mass spectrum of the dithienylmercury (IV), the molecular ion has a relative intensity of 11.5% and the thiophene–mercury ion (*m/e* 285), with a relative intensity 6.2% is formed through a metastable process (metastable peak lying

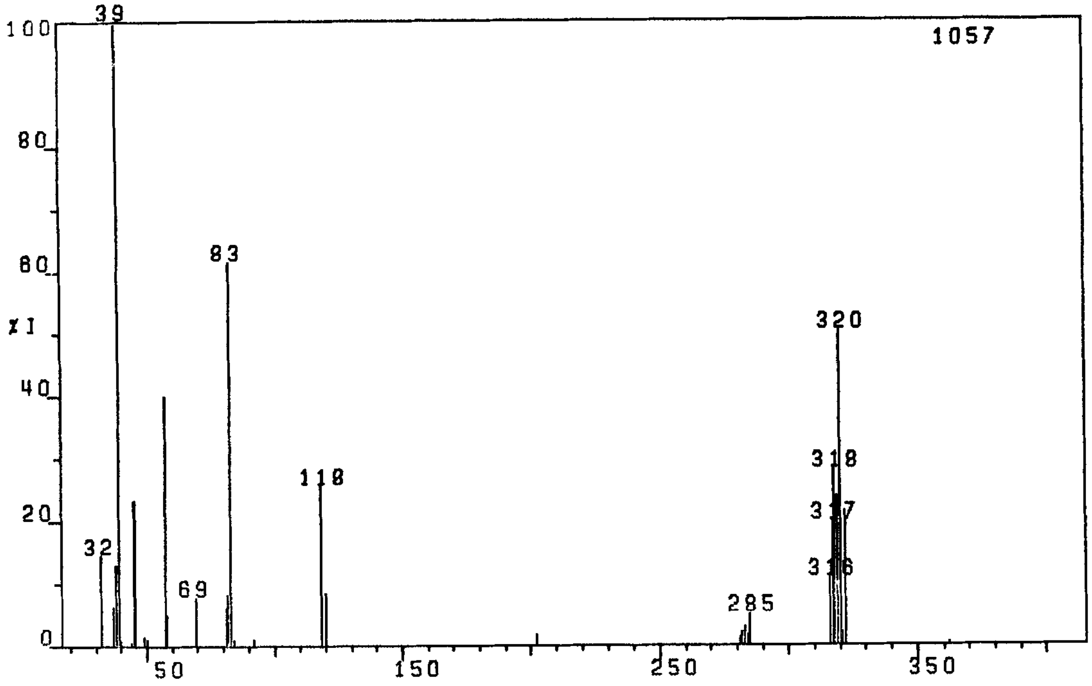
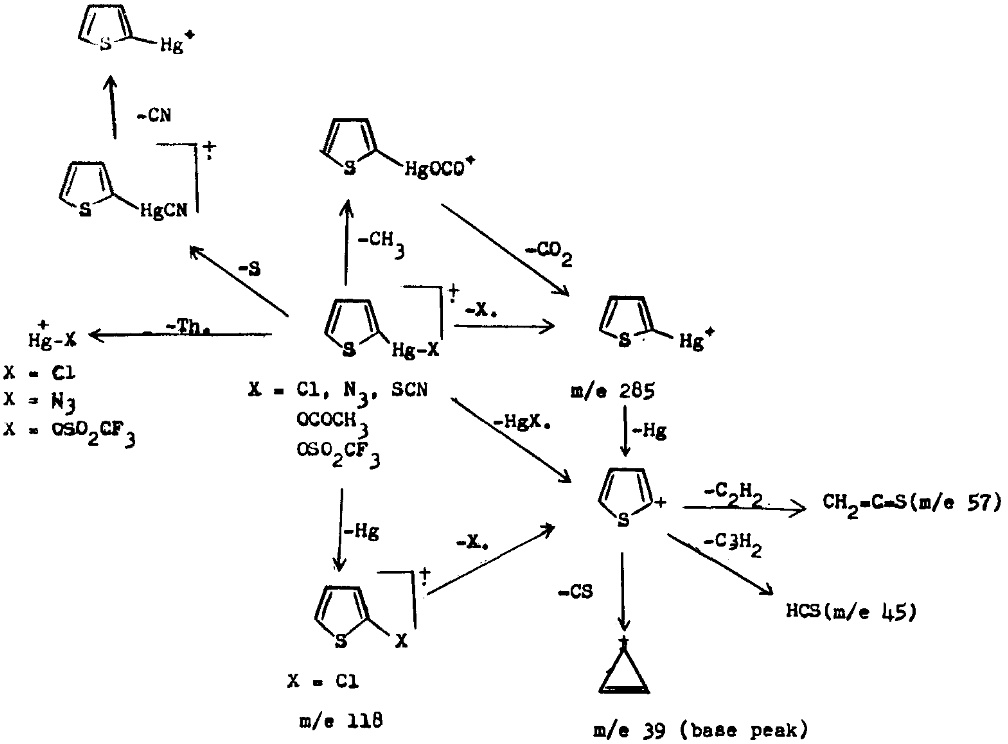


FIGURE 2 The mass spectrum of 2-thiophenemercuric chloride.



SCHEME 2 Fragmentation route of 2-thiophenemercuric chloride (I), azide (II), thiocyanate (III), acetate (V) and the trifluoromethanesulfonate (VI).

between *m/e* 220 and 221). Another fragmentation pathway observed in the spectrum is the expulsion of a mercury atom to give the 2,2′-dithiophene ion ($\overset{+}{\text{Th—Th}}{}^{\cdot}$) at *m/e* 166 with a relative intensity of 4.1%. This 2,2′-dithiophene ion fragments further in a manner similar to that of 3,3′-thienylthiophene[13] and authentic 2,2′-dithiophene[14] with the same metastable peaks.

From these fragmentation processes (for compounds I–VI), one can conclude that they all fragment ultimately to the 2-thienyl cation (*m/e* 83) which fragments further in the usual manner.[15] The 2-thienyl cation arises generally either through a two-step process, by cleavage of Hg—X bond to give the 2-thienymercuric cation (*m/e* 285) followed by extrusion of mercury, or a one-step process by cleavage of carbon–mercury bond to give the 2-thienyl cation directly. This result is similar to what was found in the thermal decomposition (Paper III) of these compounds where the decomposition first leads to the thiophene, followed by a further degradation to a black insoluble residue.

EXPERIMENTAL

All compounds were prepared as described in part III[11] and mass spectra were run on an AEL-MS-12 and Micromass 707OF spectrometers at 70 eV. Samples were introduced at low temperature to avoid decomposition.

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