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MASS SPECTRA OF THE THIOETHERS  $C_6F_5SC_6H_4X$

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SUMMARY

The mass spectra of a number of thioethers of the type  $p-XC_6H_4SC_6F_5$  ( $X = H, Cl, NO_2, SC_6F_5, CO_2C_2H_5, C_6H_5$ ) have been examined. These spectra have been compared with those of  $(C_6H_5)_2S$  and  $(C_6F_5)_2S$ . Fragmentation patterns have been deduced from metastable peaks. The spectrum of  $p-ClC_6H_4SC_6F_5$  has been studied in more detail.

INTRODUCTION

The mass spectra of a number of derivatives of pentafluorothiophenol,  $C_6F_5SX$ , have been examined [1,2]. In all these spectra the peak at  $m/z$  199,  $C_6F_5S^+$ , was very strong, often the most abundant ion and its subsequent fragmentation pattern was the major feature of the spectra in the region with  $m/z < 199$ . It has recently been noted that the  $C_6F_5S^+$  ion was relatively weak in the primary ion mass spectra of a number of thioethers of the type  $p-XC_6H_4SC_6F_5$  [3,4].

Several of these thioethers have been prepared and their mass spectra studied in more detail,  $p-XC_6H_4SC_6F_5$  ( $X = H$ (I),  $Cl$ (II),  $NO_2$ (III),  $SC_6F_5$ (IV),  $CO_2C_2H_5$ (V),  $C_6H_5$ (VI)). Bar chart spectra of I to VI are shown in the figure. Fragmentation patterns have been deduced from a study of the metastable peaks.

The observed spectra and fragmentation patterns have been compared with those of bis(pentafluorophenyl)sulfide and diphenyl sulfide [1,5]. Initial fragmentation of the molecular ion of I is somewhat similar to both  $(C_6H_5)_2S$  and  $(C_6F_5)_2S$ , while the other initial fragmentations are markedly different. Similarly all the spectra show very weak peaks for the  $C_6F_5^+$

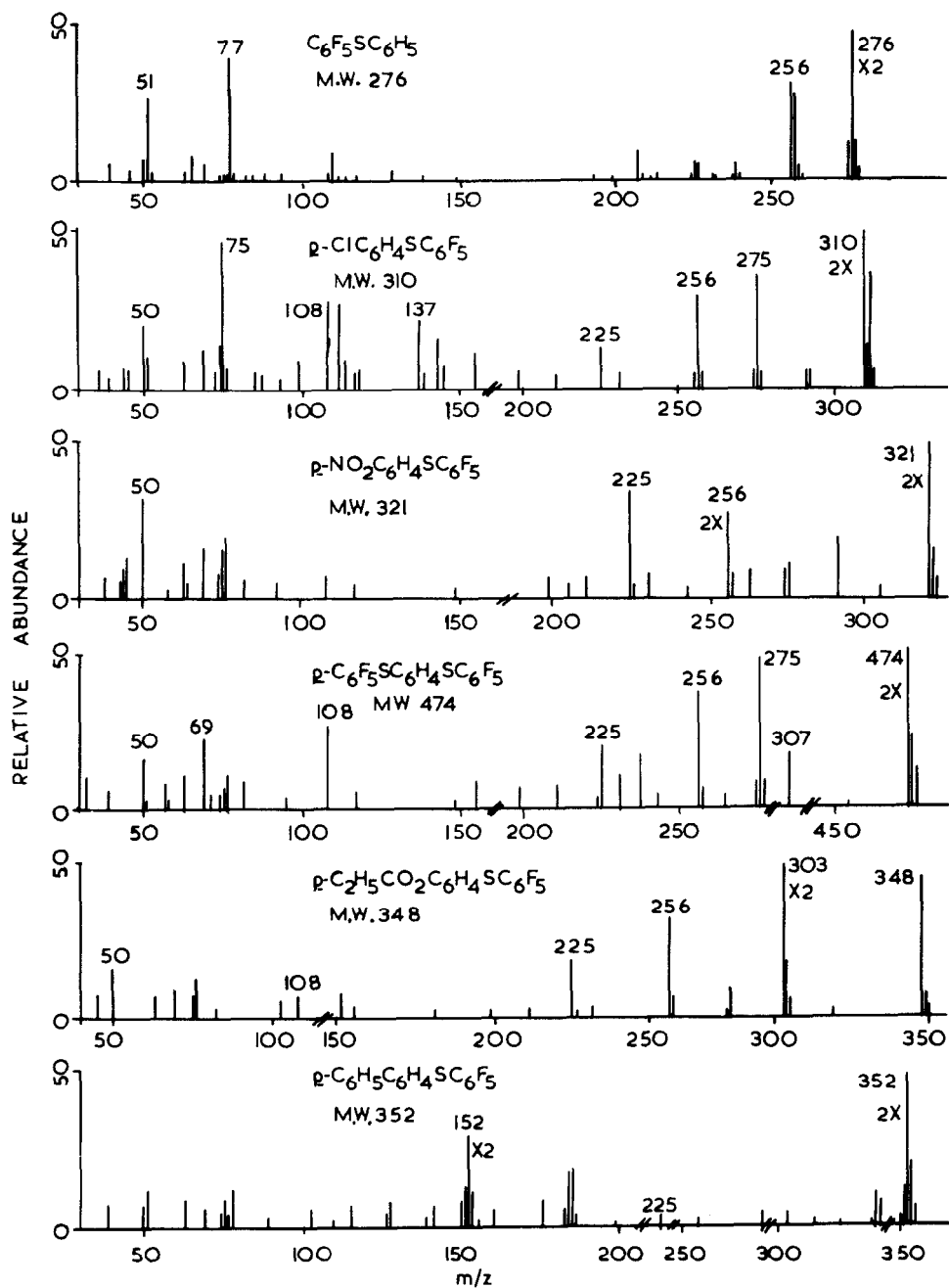
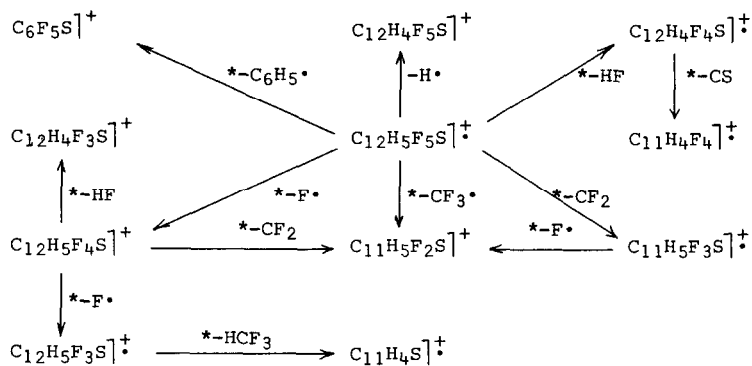


Fig. Bar chart diagrams of the mass spectra of *p*- $XC_6H_4SC_6F_5$ .

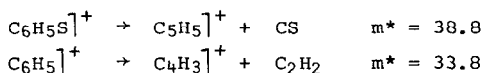
ion and even weaker ones for the  $C_6H_5S^+$  ion, and CS is only lost from the molecular ion in V; these are all characteristics of the spectra of bis(pentafluorophenyl)sulfide or diphenyl sulfide.

## RESULTS AND DISCUSSION

In the spectrum of phenyl(pentafluorophenyl)sulfide (I), metastable peaks indicate the following fragmentations.

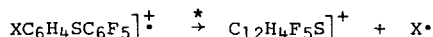


In this spectrum the molecular ion is the most abundant ion and its fragmentation is a major feature of the spectrum. The spectrum of diphenyl sulfide is somewhat similar to that of I at and below  $m/z$  109 ( $C_6H_5S^+$ ), with relatively intense ions being observed in both spectra at  $m/z$  77 ( $C_6H_5^+$ ), 69 ( $C_3SH^+$ ), 65 ( $C_5H_5^+$ ), 51 ( $C_4H_3^+$ ) and 39 ( $C_3H_3^+$ ) [5]. Similarly analogous metastable ions are observed, corresponding to the fragmentations:

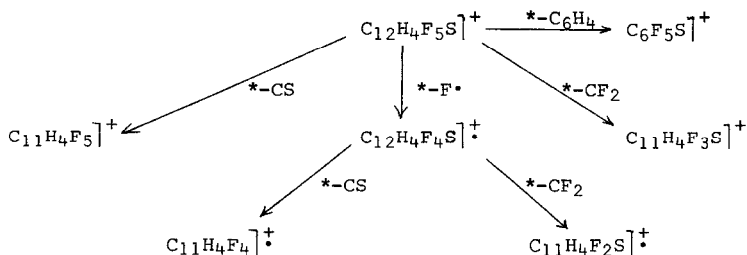


One of the main differences between the spectra of I and of both  $(C_6H_5)_2S$  and  $(C_6F_5)_2S$  is the loss of CS from the molecular ion. In both  $(C_6H_5)_2S$  and  $(C_6F_5)_2S$  this is observed and is confirmed by a metastable peak [5,1], but is absent in the spectrum of I.

In the spectra of several of the other compounds the  $C_{12}H_4F_5S^+$  ion is readily formed.

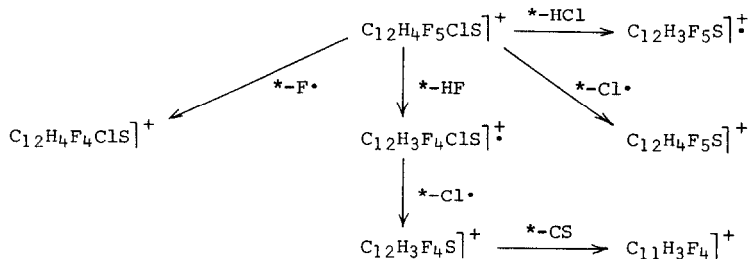


This is observed in the spectra of II, III, IV and V ( $X = Cl, NO_2, SC_6F_5,$  and  $CO_2C_2H_5$ ), but was relatively weak in VI ( $X = Ph$ ). The  $C_{12}H_4F_5S^+$  ion fragments as:

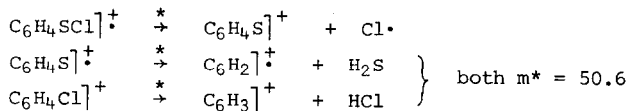


The  $\text{C}_5\text{F}_5^+$  ion is also observed in all the spectra, although the  $\text{C}_6\text{F}_5\text{S}$  ion is not observed. It has previously been shown that the  $\text{C}_5\text{F}_5^+$  ion is readily formed from  $\text{C}_6\text{F}_5\text{S}^+$  by loss of CS [1].

In the spectrum of II other fragmentations of the molecular ion involving loss of chlorine are possible. The chlorine containing ions,  $\text{CF}_2\text{Cl}^+$ ,  $\text{C}_6\text{H}_4\text{Cl}^+$ ,  $\text{ClC}_6\text{H}_4\text{S}^+$ , and  $\text{C}_{12}\text{H}_4\text{F}_4\text{SCl}^+$  can readily be identified from the isotopic distribution of Cl-35 and Cl-37. The decompositions deduced from the metastable peaks include:

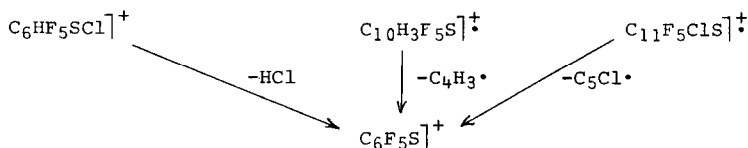


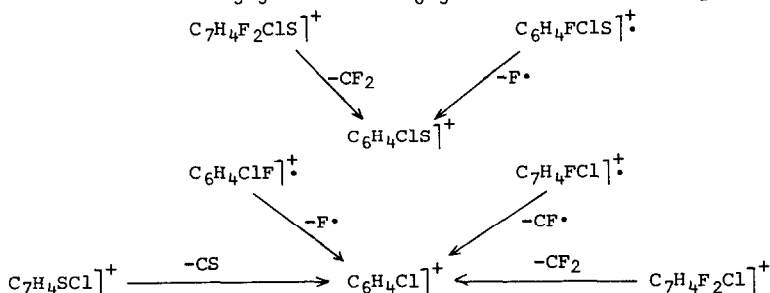
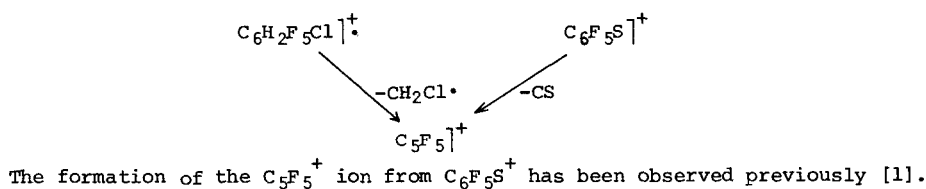
Other fragmentations observed include:



There is no loss of H from the molecular ion. The identities of the following ions were confirmed by accurate mass measurements:  $m/z$  274  $\text{C}_{12}\text{H}_3\text{F}_5\text{S}^+$ , 231  $\text{C}_{11}\text{H}_4\text{F}_5^+$ , 225  $\text{C}_{11}\text{H}_4\text{F}_3\text{S}^+$ , 211  $\text{C}_{11}\text{H}_3\text{F}_4^+$ , 199  $\text{C}_6\text{F}_5\text{S}^+$ , 117  $\text{C}_5\text{F}_3$ , 108  $\text{C}_6\text{H}_4\text{S}^+$ .

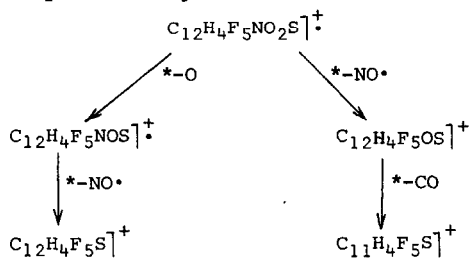
The precursor ions for  $m/z$  199 ( $\text{C}_6\text{F}_5\text{S}^+$ ), 155 ( $\text{C}_5\text{F}_5^+$ ), 143 ( $\text{C}_6\text{H}_4\text{ClS}^+$ ) and 111 ( $\text{C}_6\text{H}_4\text{Cl}^+$ ) were measured. The results show:





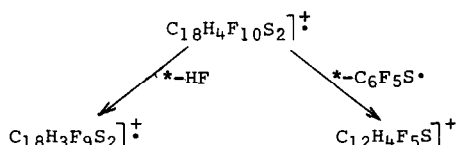
There is some ambiguity in the assignment of the ion with  $m/z$  155 as it could be either  $\text{C}_5\text{F}_5^+$  or  $\text{C}_7\text{H}_4\text{SCl}^+$ . It has previously been assigned as  $\text{C}_5\text{F}_5^+$  in the fragmentation of  $\text{C}_6\text{F}_5\text{S}^+$  [1]. The lack of an isotope peak at  $m/z$  157 mitigates against the assignment as  $\text{C}_7\text{H}_4\text{SCl}^+$ .

The spectrum of III ( $X = \text{NO}_2$ ) is somewhat similar to that of II ( $X = \text{Cl}$ ). The molecular ion is observed to fragment by loss of  $\text{NO}\cdot$  or  $\text{O}$ , but not by loss of  $\text{F}\cdot$  or  $\text{H}\cdot$ . A partial fragmentation is shown.



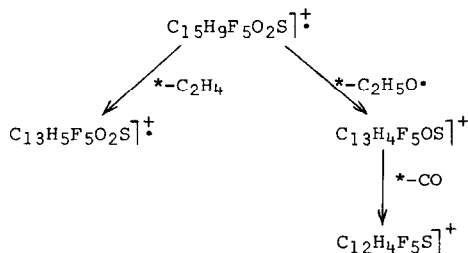
The ion at  $m/z$  263 ( $\text{C}_{11}\text{H}_4\text{F}_5\text{S}^+$ ) is not found in any of the other spectra.

The spectrum of IV ( $X = \text{SC}_6\text{F}_5$ ) also shows the formation of the  $\text{C}_{12}\text{H}_4\text{F}_5\text{S}^+$  ion ( $m/z$  275) and its subsequent fragmentation. The initial decompositions of the molecular ion detected are:

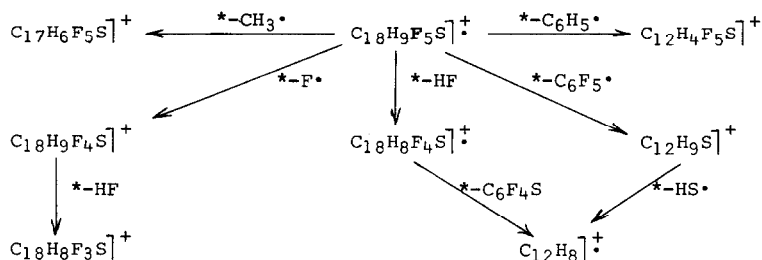


The peak at  $m/z$  307 corresponds to the ion  $\text{C}_{12}\text{H}_4\text{F}_5\text{S}_2^+$ , representing the loss of  $\text{C}_6\text{F}_5\cdot$  from the molecular ion, although this fragmentation could not be confirmed by a metastable peak.

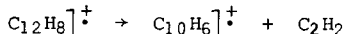
Studies on the ethyl ester V ( $X = \text{CO}_2\text{C}_2\text{H}_5$ ) show that the  $\text{CO}_2\text{C}_2\text{H}_5$  group is relatively labile. The base peak in this spectrum is the ion at  $m/z$  303 ( $\text{C}_{13}\text{H}_4\text{F}_5\text{OS}^+$ ) corresponding to the loss of  $\text{C}_2\text{H}_5\text{O}^\bullet$  from the molecular ion. Initial fragmentations detected include:



The primary ion spectrum of VII ( $X = \text{C}_6\text{H}_5$ ) is considerably different from that of the other compounds. Strong peaks at  $m/z$  185 ( $\text{C}_{12}\text{H}_9\text{S}^+$ ) and 152 ( $\text{C}_{12}\text{H}_8^+$ ) correspond to the fragmentation of the biphenyl residue. Various peaks between  $m/z$  77 and  $m/z$  185 in the spectrum which are not observed in the other spectra can be attributed to ions derived from the biphenyl rings. Metastable ions allow a primary fragmentation to be deduced.



The peak at  $m/z$  275 ( $\text{C}_{12}\text{H}_4\text{F}_5\text{S}^+$ ) is relatively weak (5% relative intensity) and its fragmentation pattern is not observed. The ion at  $m/z$  152 ( $\text{C}_{12}\text{H}_8^+$ ) is also found in the spectrum of biphenyl, benzo(c)cinnoline, dibenzothiophen phenanthrene, etc. [5]. The peak at  $m/z$  126 is formed by loss of  $\text{C}_2\text{H}_2$  [5].



## EXPERIMENTAL

The thioethers were prepared by literature methods [4,6]. The mass spectra were recorded on a DuPont/C.E.C. Model 21-491 (preliminary observations) and subsequently on a DuPont/C.E.C. Model 21-110B or a Varian MAT CH-7 mass spectrometer. Ion identifications in cases where there was ambiguity were confirmed by high resolution measurements ( $R \approx 15000$ ).

The sample temperature for the 70 eV spectra were I (25°), II (50°), III (80°), IV (120°), V (190°), VI (100°). The precursor ions were determined by the accelerating potential scan technique on a DuPont/C.E.C. Model 21-110B.

#### ACKNOWLEDGEMENTS

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