

Preliminary Note

The mass spectra of some pentafluorophenylthio derivatives *

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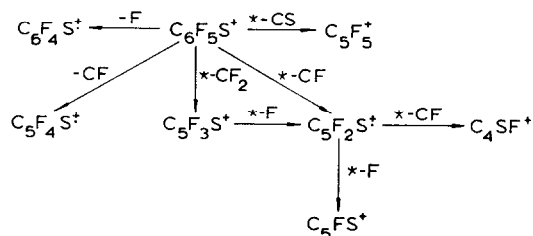
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In continuing a study of pentafluorothiophenol and its derivatives¹, the mass spectra of a number of compounds of the type C_6F_5SX ($X = H, Me, MeCO, Cl, C_6F_5$) and $(C_6F_5S)_2$, $(C_6F_5S)_2Hg$, $(C_6F_5S)_3As$ and $(C_6F_5SCH_2)_2$ have been examined. Mass spectral studies of fluoroaromatics^{2,3}, pentafluorophenyl derivatives of Groups IV and V^{4,5}, and of several sulfur-containing compounds have been reported⁶.

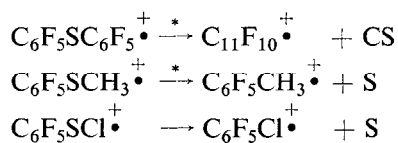
The spectra of the pentafluorophenylthio derivatives show fragmentation following electron impact differing from that for similar phenylthio derivatives and also from that for other pentafluorophenyl compounds. Many doubly charged ions are observed which indicates that relatively stable ions are formed.

One prominent feature of all the spectra is the abundance of the $C_6F_5S^+$ ion ($m/e = 199$), often as the base peak, particularly in the compounds not containing hydrogen. The spectra below $m/e = 199$ are usually very characteristic, corresponding to the fragmentation of the $C_6F_5S^+$ ion, which is partially shown below.



Another characteristic of all the spectra is that small numbers of fluorine atoms may be lost as $F\bullet$, $CF\bullet$, CF_2 and $CF_3\bullet$, and single carbon atoms as $CF\bullet$, CF_2 , $CF_3\bullet$, or CS (in the non-hydrogen-containing compounds). Loss of carbon, fluorine, or sulfur may result in skeletal rearrangements, as illustrated below in the loss of sulfur as S or CS .

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The formation of the $\text{C}_6\text{F}_5\text{Cl}^+$ ion in the spectrum of $\text{C}_6\text{F}_5\text{SCL}$ is indicated by the relatively high abundance of this ion and the C_6F_5^+ ion, one of its major fragmentation products³; the molecular ion ($m/e = 234$) is also observed, in contrast to previous observations⁷.

The appearance of ions of formulae C_5F_x^+ ($x = 5, 4, 3, 2, 1$), also observed in pentafluorophenyl compounds^{4,5}, C_3F_x^+ ($x = 5, 3, 2, 1$), $\text{C}_5\text{F}_x\text{S}^+$ ($x = 4, 3, 2, 1$) and $\text{C}_3\text{F}_x\text{S}^+$ ($x = 3, 1$) is a feature of the spectra. These ions, some of which may not be very abundant, are probably formed by successive loss of fluorine and may well be non-cyclic and acetylenic⁸.



The spectra were recorded on a DuPont/CEC Model 21-110B mass spectrometer using either direct or indirect introduction. We thank D. J. Embree for recording the spectra.

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