Mass Spectrometric Studies of Sulfur Compounds: The Alpha and Beta Substituted Naphthylthiaalkanes

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The mass spectra of fifteen members of the alpha and beta substituted naphthylthiaalkanes with a molecular weight range of 202 to 300 are reported. The data are used to illustrate the process of correlation and delineation of fragmentation routes in a class of compounds to benefit mass spectroscopists. Spectra from low, medium, and high resolution instruments are employed, showing the necessity and usefulness of multiple approaches in obtaining a complete understanding of the pathways involved. Application of low ionization voltage, metastable ion data, doubly charged ions, and high resolution mass spectrometry is described to arrive at an outline of the major fragmentation routes in a given class of compounds. For unknown compounds in their class, the analyst can readily make an identification from the predicted mass spectrum by utilizing this information.

Introduction

This report covers a portion of an extensive program to determine the reference mass spectra of a number of classes of organosulfur compounds. The presence of large quantities of sulfur containing compounds in much of the world's fossil fuel supplies leads to problems for both the processing and refining of such materials. Undesirable products from the incomplete

combustion of sulfur containing fuels are also a problem. Identification of these classes of compounds requires reference spectra, whether mass, nuclear magnetic resonance, or infrared. In lieu of the availability of a plethora of such spectra, the mass spectroscopist can utilize the class approach to study fragmentation mechanisms for previously unreported compounds. From this information, predictions of the behavior of the entire class can be made.

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Fifteen members of the alpha and beta-naphthylthiaalkanes are studied and discussed in this work. Mass spectra of some thienylthiaalkanes have been reported^{1,2)}, as have the alkylthiaalkanes^{3,4,5,6)}. A number of other classes of sulfur compounds have been studied and most of these can be found in the listing of spectra in Hamming and Foster's text⁷⁾.

The mass spectroscopist prefers to have a number of isomers of the class to be studied, extending to alkyl chain lengths of at least 8 carbon atoms and including some branched chain compounds for each species of compounds to be studied. In the case of multisubstitutions upon ring system compounds, this might require many individual isomers, beyond the possibility of synthesis. This further justifies correlation studies to expound fragmentation mechanisms which can be applied in similar systems. The studies of Meyerson and his coworkers^{8,9,10)} on the alkylbenzenes are examples of how fragmentation principles have been applied to other aromatic systems at a later time.

Kinney and Cook¹¹⁾ and Cook and Foster²⁾ showed similar correlations for the alkylthiophenes and indicated important differences in fragmentation behavior due to the presence of the sulfur atom in the ion moieties. Frequently the tertiary butyl, isopropyl, and sometimes the methyl derivatives of such compounds give spectra not in accord with the mechanisms proposed for the class. The differences were usually typical of that type of alkyl group and are observed wherever the general structural conditions permitted. Budzikiewicz, Djerassi and Williams¹²⁾ have summarized several

skeletal rearrangements that have been observed for aromatic thioethers. In mass spectra of alkyl ethers of thiophenols, α -fission accounts for the intense peaks at m/z 123. This fragmentation can be compared to the formation of the m/z 173 ion from the naphthylthiaalkanes discussed here. With this background available, the mass spectroscopist has an advantage in utilizing the class approach to fragmentation mechanisms. Any spurious production of a given ion can be detected early, and if the purity of the substance becomes a question, this too can be resolved by considering the "fit" of that particular compound into the general fragmentation scheme. As an instructive case, the mass spectra of the alpha and beta-naphthylthiaalkanes are presented.

Experimental

The compounds studied were prepared by Dr. Higgins and his students by standard methods of organic syntheses. The compounds were vacuum distilled at low pressures immediately following their synthesis and stored under nitrogen in brown bottles. These compounds were examined without further purification because of their high molecular weight and thermal sensitivity to high temperature chromatography.

The positional substitution of the thiaalkyl groups on the naphthalene ring was verified from an infrared spectrum obtained on a Perkin-Elmer Model 225 infrared spectrophotometer. Three mass spectrometers were employed: a Consolidated Electrodynamics Corporation (CEC) Model 103 was used to examine the materials in a low resolution situation. A CEC-104

Mass Spectrometric Studies of Sulfur Compounds :

Table 1. Partial mass spectra of alpha and beta-naphthylthiaalkanes, % of total ion intensity (CEC-103 data).

The alpha substituted compounds

Alkyl Group	Purity Mole %	Molecular Ion m/z	Ion Int.	$\beta+H$ 160	β 159	$\beta+2H$ 161*	$\alpha+H$ 128	α 127	$\alpha+2H$ 129	γ 173	Other Ions 115 45			Sum** Alkyls
nC ₄	99.8	216	12.4	19.9	2.8	0.16	2.7	1.7	1.1	2.1	9.0	4.5		11.2
nC ₅	98.8	230	11.5	18.0	2.7	0.14	1.9	1.3	0.8	1.8	6.5	2.5		14.4
nC ₆	96.9	244	12.4	18.9	2.9	0.18	2.2	1.5	1.0	2.0	7.4	2.0		15.5
nC ₇	99.8	258	13.6	18.2	2.9	0.19	2.1	1.5	1.0	2.1	6.8	1.9		15.0
nC ₈	97.0	272	14.2	16.7	2.5	0.37	2.1	1.4	1.3	2.0	6.1	2.5		14.1
nC ₁₀	99.9	300	15.6	14.3	2.8	0.25	1.6	1.1	0.8	2.0	4.8	1.6		16.0
iC ₄	99.2	216	9.6	20.8	2.3	0.10	2.3	1.8	1.4	2.8	7.8	3.0		13.0
iC ₅	98.4	230	10.6	21.5	2.6	0.16	2.5	1.8	1.3	3.0	7.5	2.8		12.4

The beta substituted compounds

nC ₃	98.2	202	12.3	16.1	2.4	0.10	3.1	2.2	1.7	4.4	9.5	3.5		7.6
nC ₄	98.9	216	12.8	17.1	2.5	0.26	2.8	1.9	1.4	3.3	8.6	3.1		11.4
nC ₆	95.4	244	12.0	19.8	3.4	0.0	2.5	1.7	1.5	2.6	7.4	2.9		12.8
nC ₈	97.9	272	14.8	17.1	2.1	0.22	2.0	1.3	1.0	2.8	6.5	1.8		15.2
nC ₁₀	99.4	300	13.4	16.9	2.0	0.39	1.7	1.0	1.0	2.7	4.2	1.9		13.6
iC ₅	98.5	230	10.9	22.2	3.3	0.0	2.3	1.5	1.0	1.8	8.8	2.0		13.0
cyclo C ₆	99.7	242	7.9	28.3	2.4	0.03	2.1	1.1	0.3	0.2	8.4	0.8		5.3

*Excess above isotopic contributions from m/z 159 and 160 peaks.

**Sum Alkyls= m/z 41, 43, 55, 57, 69, 71, 83, 85, 97, and 99, etc.

instrument was used to determine the Low Voltage Mass Spectrometry (LVMS) purities, for examination at low ionization voltages, and for intermediate resolution work. A CEC-110 instrument was used to obtain high resolution data and, in some instances, metastable ion information. These instruments were operated at nominal standard conditions for each type of spectrum desired. Table 1 contains a listing of these compounds, their approximate purities, and partial mass spectral data. Complete low resolution mass spectral data is to be found in the American Petroleum Institute Research Project 44 (API-RP-44) files as Serial Numbers: 433-m to 447-m⁽¹³⁾.

Results and Discussion

The Alpha Naphthylthiaalkanes

A strong molecular ion intensity is noted for all the compounds, with a slight decrease in intensity for the two isoalkyl derivatives examined. The ion of largest intensity in each spectrum is a rearrangement ion at m/z 160 coming from cleavage beta from the naphthyl ring and alpha to the sulfur atom. A hydrogen atom is rearranged from somewhere on the alkyl chain. Earlier work with deuterated alkylthiophenes shows a similar rearrangement which is partially a McLafferty-type rearrangement and partially a random process⁽¹⁴⁾. Evidence from thienyl sulfides^(1,2) and the benzo (b) thienyl sulfides⁽¹⁴⁾ also supports

this type of behavior with only a part of the hydrogen transfer coming through a McLafferty-type rearrangement. Consideration of the double McLafferty rearrangement in which two hydrogens move indicates less than 2 percent excess above the expected isotopic contribution on the m/z 161 ion. Therefore, this is insignificant and unimportant in the case of these types of sulfur compounds. The ion at m/z 159, formed either by direct beta cleavage or possibly by the loss of a neutral hydrogen atom from the rearrangement peak at 160, is only from 10-15 percent of the intensity of the 160 ion. Direct cleavage at the position will produce the m/z 173 ion and of less intensity than the 159 ion in all cases for the n-alkyl compounds. The isoalkyl compounds have an m/z 173 greater than 159, apparently due to the chain branching.

Additional peaks at m/z 127, 128, and 129 are shown. These may be formed by direct alpha cleavage to the ring, alpha with one hydrogen rearrangement, and alpha with two hydrogens rearranging. The m/z 128 ion is of somewhat greater intensity than the other two ions in each case. This is unlike the naphthalenes, or alkylbenzenes, but does resemble alpha cleavage in the alkylthiophenes. As in naphthalene spectra, an m/z 115 ion is detected which is $C_9H_7^+$, and which is possibly a daughter of the above ions. It is surprisingly large and may originate directly from the m/z 160 rearrangement ion. If so, the ion at m/z 45 would represent the same process except for charge competition among the sulfur containing moiety and the 115 ion. In this case, the neutral ejected would be the mass 115, whereas the pro-

duction of the 115 ion would require a neutral mass 45 ejected. The amount of 115 ion decreases with increasing chain length, and the 45, while also decreasing, appears to be increasing in relation to the 115.

The Beta-Naphthylthiaalkanes

The strong parent ion intensity is expected, as is the rearrangement ion at m/z 160. The intensity of the molecular ion plus the rearrangement ion accounts for about 30 percent of the total ionization for each compound, regardless of whether alpha or beta. An important exception is the cyclohexyl substituted compound with a smaller molecular ion and considerably larger intensity rearrangement ion. This should be expected in light of the chain branching adjacent to the sulfur atom. A comparison of the apparently direct beta and gamma cleavages at m/z 159 and 173 lead one to the observation that m/z 159 is less than 173 in intensity for the n-alkyl derivatives, whereas the reverse was true for the alpha substituted compounds. By the same token, for the isoalkyl compounds, the ratio is reversed, leading to a very unusual situation for setting up correlations. It also raises interesting questions of mechanisms and spatial conformation problems which can not be answered from these data alone.

Similar intensities for the m/z 127—129 ions are observed for the beta substituted compounds as in the case of the alpha compounds. This suggests that these ions are formed by the same mechanism regardless of the positional substitution on the naphthalene ring. For the ions at m/z

115 and 45, the only apparent difference is a slight increase in the intensity of both ions at a given carbon number. The cyclohexyl compound is again an exception giving an m/z 45 intensity far less than might be expected. The implication is that for the n-alkyl compounds, the m/z 45 ion may have its origin from a fragment containing the sulfur atom and the adjacent *primary* carbon atom of the alkyl chain. The presence of the branching requires considerably different fragmentation, which obviously does not lead to the 45 ion. That several mechanisms may be participating is shown by an increase of the 115 ion due to the charge competition in alpha cleavage to produce a 115 ion due to the presence of S-R where R is cyclohexyl- (or $83 + 32 = 115$). This will be considered further at a later point in this work.

The last column in Table 1 presents a sum of the alkyl ions appearing in these spectra. It is to be noted that shorter chain substitution produces fewer alkyl fragments, but once the chain length gets to 8 — 10 carbon atoms, a leveling off in intensities occurs. The n-propyl beta substituted compound shows the fewest alkyl fragments and at the same time the largest ion at m/z 115. The lowest alkyl intensity occurs for the cyclohexyl isomer, once again indicating a preferred loss of a neutral cyclohexene moiety with the transfer of a hydrogen atom to the charged species. The alkyl ion intensities do not dominate the spectra as they do in the thienyl-3- and 4-thiaalkanes¹⁾. The alkyl ions are of little diagnostic value except as to indicate the chain length, chain branching, and

when used with low ionizing voltage data.

Low ionization voltage data

Low ionization voltage information can often assist the mass spectroscopist, not only in determining possible fragmentation mechanisms, but also may be diagnostic for the analysis of specific isomers, differentiation of substitution, etc. In Figure 1, data are presented for four selected compounds which illustrate much of the behavior for this series of compounds. For the beta-n-propyl compound, the m/z 43 ion appears to come as a first fragment from the molecular ion, but then levels off in intensity rapidly as the ionizing voltage is increased. Not shown is the m/z 41 ion which appears as a daughter ion from it. The m/z 45 ion appears at the same time as the m/z 128 and 76 ions. Neither the 45 or 76 are shown because they are only important ions in the short chain molecules. However, 76 (SC_3H_6) always appears concurrently with the 128, suggesting that a hydrogen atom can move from either side of the sulfur atom to form a charged moiety. The intensity of the 128 ion is much larger in all compounds examined. One must conclude that the alpha cleavage with a hydrogen transfer is an energetically favored process, but which at higher energies gives way to the production of the m/z 160, or base peak ion. Also not shown is the fact that the 116 ion appears just ahead of the 115 ion moiety, and well after the 45 ion, thus, at least as a low voltage process, destroying the concept of the mechanisms proposed earlier for the 45 and 115 ions. These events are carried forth in all of the other compounds examined. The gamma

Fig. 1. Low ionization voltage data of some α and β -Naphthylthiaalkanes.

cleavage, or m/z 173 ions, appears after the 160 rearrangement and parallels it in growth throughout.

The beta n-butyl compound is similar except that m/z 57 is the first alkyl ion to appear, 43 is negligible, and m/z 41 becomes more prominent. The 173 ion (not shown) is less intense and does not increase as rapidly at low voltages as the same ion did in the propyl compound.

The beta-3-methylbutyl isomer (not shown) is much the same as the n-butyl compound except that m/z 71 is the principal alkyl ion, closely followed by the m/z 43 formed at the point of branching on the chain. In all three of these compounds, the alkyl ion appearing is first accompanied by the even ions at m/z 42, 56, and 70, respectively. This should assist the analyst.

For the beta-cyclohexyl compound (not shown), the m/z 83 ion is the first alkyl ion to appear, but practically at the same time, very minor peaks of m/z 67, 43, 42, and a modest intensity 41 ion appear. These could be expected from the breakup of the cyclohexyl fragment. The M^+ ion and the 160 ion appear just about the same as the other beta compounds.

The alpha n-butyl compound is presented as a comparison with the beta compound. Although most of the behavior is identical, one important difference exists. The m/z 41 ion is produced in much greater intensity than the 57 ion from the full alkyl chain. This suggests that the alpha compounds tend to fragment off parts of the chain easier than the beta compounds. Certainly the distribution of energy to the butyl fragment is different for the two

isomers. Also showing this same behavior is the alpha-3-methylbutyl compound which produces considerably more m/z 43 ion than 71. Also examined were the alpha-isobutyl and alpha-n-pentyl compounds. For the n-pentyl compound, the curve for the 71 ion was only slightly above that of the 43 ion. This confirms a different energy distribution within the alkyl chains in the case of the alpha substituted compounds. Other ions in the alpha spectra, i. e., 128, 76, etc, were much the same as in the beta spectra.

Metastable ion data

Metastable ion data was obtained from the high resolution instrument (CEC-110). Only seven of the compounds were examined using the CEC-110 with high resolution. A listing of the metastable ions observed is given in Table 2. A calculated value for the process is also included. It was possible to observe a metastable ion for the process producing the m/z 160 ion from the molecular ion for each compound. It must be remembered that some of the metastables observed could be for one or more processes. For example, a metastable ion shows from m/z 114.1 to 114.3 in 7 spectra. This could be from the process of m/z 174 losing a neutral HS fragment and producing the m/z 141 ion as well as for the loss of a hydrogen from 116 to give the 115 ion. The latter process appears more likely and hence is listed. Two things are evident from the data: (1) Generalized pathways of fragmentation can be verified, and (2) most of the fragments leaving are either small pieces, typical of aromatic fragmentation processes, or the loss of a

Table 2. Selected metastable peaks observed in some naphthylthiaalkanes.

m* Peak	Number of Compounds Observed in	Most Probable Transition
111.3-.4	2	M (230 ⁺) $\longrightarrow$ 160 ⁺ + R-CH=CH ₂ [°]
105.8	1	M (242 ⁺) $\longrightarrow$ 160 ⁺ + R-CH=CH ₂ [°]
105.2	1	M (244 ⁺) $\longrightarrow$ 160 ⁺ + R-CH=CH ₂ [°]
93.8-94.2	2	M (272 ⁺) $\longrightarrow$ 160 ⁺ + R-CH=CH ₂ [°]
85.3	1	M (300 ⁺) $\longrightarrow$ 160 ⁺ + R-CH=CH ₂ [°]
81.1-.2	1	M (202 ⁺) $\longrightarrow$ 128 ⁺ + R-CH=CH-SH [°]
70.9-71.3	2	M (230 ⁺) $\longrightarrow$ 128 ⁺ + R-CH=CH-SH [°]
183.2-.3	5	187 ⁺ $\longrightarrow$ 185 ⁺ + H ₂ [°]
158.1	2	160 ⁺ $\longrightarrow$ 159 ⁺ + H [°]
125.2	6	173 ⁺ $\longrightarrow$ 147 ⁺ + C ₂ H ₂ [°]
114.9	5	173 ⁺ $\longrightarrow$ 141 ⁺ + S [°]
114.1-.2	6	116 ⁺ $\longrightarrow$ 115 ⁺ + H [°]
112.4	1	160 ⁺ $\longrightarrow$ 134 ⁺ + C ₂ H ₂ [°]
102.3-.5	5	160 ⁺ $\longrightarrow$ 128 ⁺ + S [°]
96.2-3	4	173 ⁺ $\longrightarrow$ 129 ⁺ + CS [°]
93.8	NONE	141 ⁺ $\longrightarrow$ 115 ⁺ + C ₂ H ₂ [°]
84.1-.2	3	160 ⁺ $\longrightarrow$ 116 ⁺ + CS [°]
83.2-.4	4	159 ⁺ $\longrightarrow$ 115 ⁺ + CS [°]

long alkyl chain, either as a radical or as a neutral olefin in the case of the m/z 160 rearrangement ion. It is also noteworthy that the process for the direct production of the m/z 128 ion from the molecular species was only observed in the lower molecular weight compounds. This may account for the shape of the m/z 128 ion production curves in Figure 1 for the low

ionization data. Since the 128 ion appears before the 160 ion in every case, one can conclude that both processes are taking place albeit with different appearance potentials.

Doubly charged ions

Table 3 contains a listing of doubly charged ions observed in all of the spectra.

Table 3. Doubly charged ions observed.

m/z	2+-ion	Comment
57.5	115 ²⁺	Typical in naphthalenes
63.5	127	Atypical in naphthalenes
64.5	129	Atypical in naphthalenes
73.5	147	(benzothiapyrillrum)
79.5	159	159 disappears rapidly below 15 eV.
85.5	171	
86.5	173	Possibly from M ²⁺ $\longrightarrow$ 173 ²⁺ then $\longrightarrow$ 171 ²⁺
87.5	175	Possibly isotope from 173 ²⁺ ion
92.5	185	Probably from 187 ²⁺ $\longrightarrow$ 185 ²⁺ + H ₂ [°]
93.5	187	(M-15) ²⁺ , a high energy process
101.5	203 ²⁺	In β -nC ₃ =(M+1) ²⁺ isotope peak

It is generally recognized that the processes associated with doubly charged ion fragmentation may differ appreciably from those associated with singly charged ions from the same compound. Also, as is usually the case, the amount of doubly charged ions in alkyl substituted molecules decreases as the chain lengthens. In this case, the doubly charged ions are observed in greater quantity in lower molecular weight compounds and intensities are down markedly by the time nC_6 is reached. This is anticipated because of the extra number of oscillators able to "soak" up excess energy. There are no metastable peaks observed to support these processes, but the interconnection of the doubly charged ion given seems reasonable. In a 15 eV (nominal) spectrum, all of the doubly charged ions disappear. With them, peaks disappear that occur at even mass numbers but are nevertheless due, at least in part, to doubly charged ions. The m/z 64 and 63 peaks suffer this fate, proving that they arise from the m/z 128 and 126 species.

Additional high resolution data

While medium resolution provides some indication of the detailed mechanisms involved, particularly since in this case the sulfur-hydrogen doublets are often resolved, the verification of many ions must be left to the high resolution instrument. Table 4 contains data for selected mass fragments obtained on the CEC-110. Most of these ions were observed on all of the high resolution data taken and do confirm the makeup of the ions indicated. The m/z 114 and 113 ions were from the alpha-n-octyl compound and demonstrate that the alkyl

Table 4 High resolution data for selected mass fragments.

m/z	Experimental	Calculated	Empirical Formula
115	115.0544	115.0548	C_9H_7
115		115.0581	$C_6H_{11}S$
114	114.0450	114.0466	C_9H_6
(larger of doublet)			
114		114.1408	C_8H_{18}
(smaller of doublet)			
113	113.0426	113.0388	C_9H_5
(larger of doublet)			
113		113.1330	C_8H_{17}
(smaller of doublet)			
77	77.0392	77.0391	C_6H_5
76	76.0314	76.0313	C_6H_4
71	71.0865	71.0861	C_5H_{11}
69	69.0712	69.0702	C_5H_9
45	44.9790	44.9799	CHS

ion was not being formed for that compound. Even the high resolution instrument can fail at times. It is possible that cyclohexyl compound could produce an ion at nominal m/z 115, comprising the R-S group. The ion would be superimposed upon the 115 peak coming from the C_9H_7 ion. The accurate mass of $C_6H_{11}S$ is 115.0581 as compared to 115.0548 for the C_9H_7 ion. This is probably beyond the resolution of the CEC-110.

Summary of fragmentation pathways

Some fragmentation pathways of the alpha and beta substituted naphthylthia-alkanes are presented in Figure 2. The data obtained from the low resolution instrument permitted a fast survey, the obtaining of major features of the spectra and allowed a purity check. The medium resolution instrument provided low ionization voltage data that aided in establishing fragmentation paths and allowed some dif-

Fig. 2. Some fragmentation pathways of alpha and beta substituted Naphthylthiaalkanes.

ferentiation of ions as to sulfur or hydrocarbon in type. Both of the above instruments allowed tentative mechanisms to be developed from the spectra obtained. Metastable ions, if observed, confirm some of the path-ways and are shown by * with the number of compounds observed in, in Figure 2. The high resolution instrument firms up mechanisms and yet may fail as was presented for the doublet at m/z 115 in the cyclohexyl substituted compound. When this problem occurs, labeling with natural isotopes is indicated if one wishes to delineate the mechanism. The low ionization data, if accurately taken, can assist markedly in mechanistic studies since the energetics of some of the processes may be outside of feasible ranges when compared to the observed data. Occasionally, two pathways can be suggested as in the case of the production of the m/z 128 ion.

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