MASS SPECTRA OF SOME PHENYL- AND CHLORO-SUBSTITUTED THIANAPHTHENES AND THEIR SULFONES

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The mass spectra of 2,3-dichlorothianaphthene, 2-phenylthianaphthene, 2,3-diphenylthianaphthene, 3-chlorothianaphthene 1,1-dioxide, 2,3-dichlorothianaphthene 1,1-dioxide, 2-phenylthianaphthene 1,1-dioxide, 3-phenylthianaphthene 1,1-dioxide, and 2,3-diphenylthianaphthene 1,1-dioxide were studied. The fundamental mechanisms of fragmentation of molecules of these compounds under the influence of electron impact are examined.

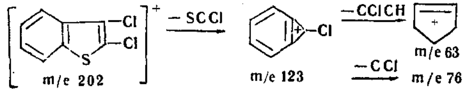
The fundamental paths for the fragmentation of molecules of thianaphthene, phenylthianaphthenes, and thianaphthene 1,1-dioxide were established during a study of the disintegration of molecules of these compounds under the influence of electron impact [1,2]. However, a further mass spectrometric investigation of thianaphthene derivatives and their sulfones is necessary both for elucidation of the effect of substituents on the fragmentation during electron impact and to obtain a more complete picture of the dissociative processes during ionization of these molecules.

We have studied the mass spectra of some compounds of this type, which were obtained with an MKh-13-03 mass spectrometer under standard conditions in an ion source. The mass spectra of all of the compounds except 2-phenylthianaphthene were obtained for the first time. A comparison of the mass spectra that we obtained for 2-phenylthianaphthene with that in [1] indicates satisfactory agreement in the distribution of the intensities of the major mass lines in the mass spectra. The only substantial difference is that our mass spectrum of 2-phenylthianaphthene lacks a mass line with m/e 145 (which corresponds to the loss of a C_5H_5 group).

The molecular ion lines have the maximum intensities in the mass spectra of the thianaphthenes [2,3-dichlorothianaphthene (I), 2-phenylthianaphthene (II), and 2,3-diphenylthianaphthene (III)].

The mass spectrum of 2,3-dichlorothianaphthene is extremely simple: the detachment of one chlorine atom is observed (peak with a mass of 167 and 25% relative intensity); the removal of two chlorine atoms gives a line with m/e 132 (15%). Elimination of a SCCl group forms ions with m/e 123, the subsequent loss of CClCH by which results in a line of mass 63.

Scheme 1



The line with a mass of 166 corresponds to splitting out of HCl from the molecular ion, while the simultaneous loss of HCl and SCCl gives ions with m/e 87.

The mass spectrum of 2-phenylthianaphthene (II) falls into the scheme for molecular ion disintegration proposed by Porter [1]. The ejection of CHS and CHC_6H_5 groups forms ions, whose disintegration (like the disintegration of the 2,3-dichlorothianaphthene ion with m/e 123) gives ion peaks with a mass of 63.

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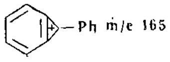
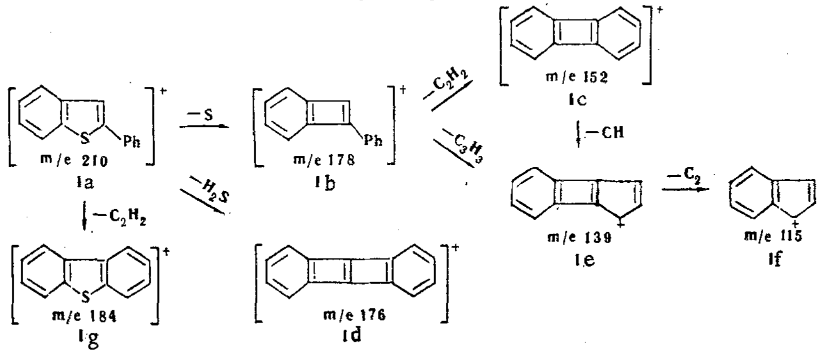
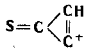
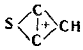


In contrast to 2,3-dichlorothianaphthene, one observes removal of a sulfur atom and H_2S to form ions with m/e 178 and 176. Ions with m/e 178 (Ib, Scheme 1) in turn lose C_2H_2 and are converted to ions with m/e 152 (the line with mass number 152 in the mass spectrum of II has an intensity of less than 1%), the assumed structure of which is given in Scheme 2.

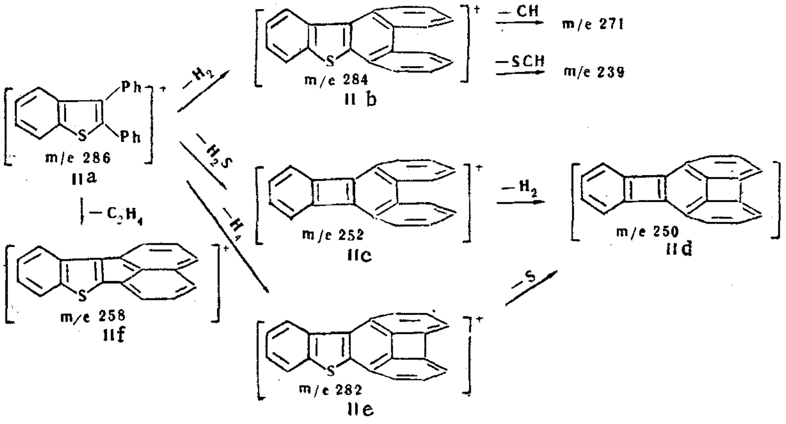
Scheme 2



The direct expulsion of C_2H_2 from the molecular ion forms dibenzothiophene ions (m/e 184, 1.4% relative intensity), while the ion peaks with masses 139 and 115 correspond to the loss of SC_3H_3 and SC_5H_3 by the molecular ion. Judging from the mass spectra of dibenzothiophenes, the disintegration of ion Ig creates peaks with masses of 152, 139, 115, and 63, so that ions Ic, Ie, and If can arise by different dissociation paths. The ion peak with m/e 69 observed in the spectrum of I is characteristic for the spectra of benzothiophene and dibenzothiophenes. It contains a sulfur atom in its structure; i.e., the formula of this SC_3H^+ ion is  or . The absence of processes involving the removal of S and SC_6H_5 is characteristic for the fragmentation of 2,3-diphenylthianaphthene. Peaks with masses of 165, 139, 115, and 63 are therefore absent in the mass spectrum.

The presence of two phenyl substituents in the molecule directs the disintegration of the molecular ion toward the formation of condensed systems (Scheme 3). Energetically favorable condensation processes prevail over all other possible fragmentation processes.

Scheme 3



The seven-membered ring ion $C_7H_7^+$, whose formation may be the result of all of the disintegration paths presented, may correspond to the line of mass 91 which is observed in the mass spectrum of II.

According to [1], the dissociation of the molecular ion of thianaphthene 1,1-dioxide is determined by its rearrangement – by expansion of the five-membered ring to a six-membered ring with the formation of a C–O bond.

A comparison of the mass spectra that we obtained for the 1,1-dioxides of chloro and phenyl derivatives of thionaphthene makes it possible to isolate several primary paths of dissociation of the starting ion –

TABLE 1. Intensity Distribution in the Mass Spectra of the Investigated Compounds

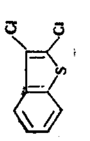
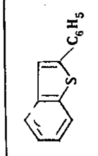
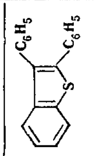
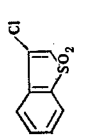
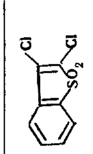
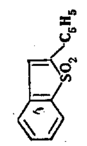
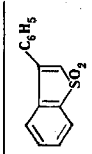
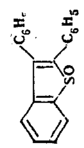
e/m	 I	 II	 III	 IV	 V	 VI	 VII	 VIII
I	2	3	4	5	6	7	8	9
63	2,0	2,8		19,2	4,65	10,4	4,7	
64		2,4		8,1	3,2	3,2	14,6	
69	4,7	6,9	3,3	8,5	4,8	4,2		
74				27,3	18,1			
75				35,8	10,5	7,8	4,06	
76	7,8			7,26	3,29	25,5	5,7	
77		4,5	3,1	6,83	5,65	30,7		10,0
84				3,85	4,85			
85				2,56	9,59			
86				2,9	5,66			
87	2,45				3,84	4,4	2,27	
88						7,64		
89		2,14		30,7		10,8	3,08	
91		5,9	2,88			3,0		
92		5,9				4,0		
97				3,85	5,0			
98				7,26	7,27			
99				7,7	23,3			
101	10,0			16,6	3			
105						100	9,43	23,7
106						6,5		2,2
108				47,4	42,6	2,2		
109				19,2	11,1	16,7		
110				3,8	4,0			
111				2,13	16,1			
113			2,44			2,3		11,4
115		2,38				3,2	2,43	
120				2,13	2,63			
121				6,98		3,0		
123	16,5			2,56	16,0			
124				3,8				
125	5,02				5,66			7,4
126			4,2			4,06		16,6
129								3,7
132	15,0							
133				2,1				
134				2,1	3,4			
135					14,5			
136				50,4	52,7	2,6		3,3
137				9,8	9,9	78,0		
138				2,5	2,5	6,34		
139		2,6				8,78	3,9	
141			4,88					5,5
142			6,0					6,6
143			3,11	32,2	21,8			3,7
145				8,1	7,9			
150						7,49	3,2	2,6
151						12,1	7,3	2,2
152				5,9		18,5	6,8	3,3
155				2,1	4,0			
158					3,43			
163		2,85				4,22	2,7	2,2
164		2,85				4,0	2,4	
165		17,8		3,8		30,7	14,1	3,7
166	2,67	3,3				6,0	2,4	
167	25,1							
168	3,86			2,6				
169	9,7							
170					12,1			
171				100	100			
172				8,1	10,0			
173				38,5	38,9			
174				2,4	3,1			
176		2,4				29,2	7,96	3,7
177						14,4	2,9	
178		10,4				20,6	4,2	2,6
179						7,3		
184		1,4				2,3	33,6	18,5
185							6,3	2,6
186					2,2			
194						15,6		

TABLE 1 (continued)

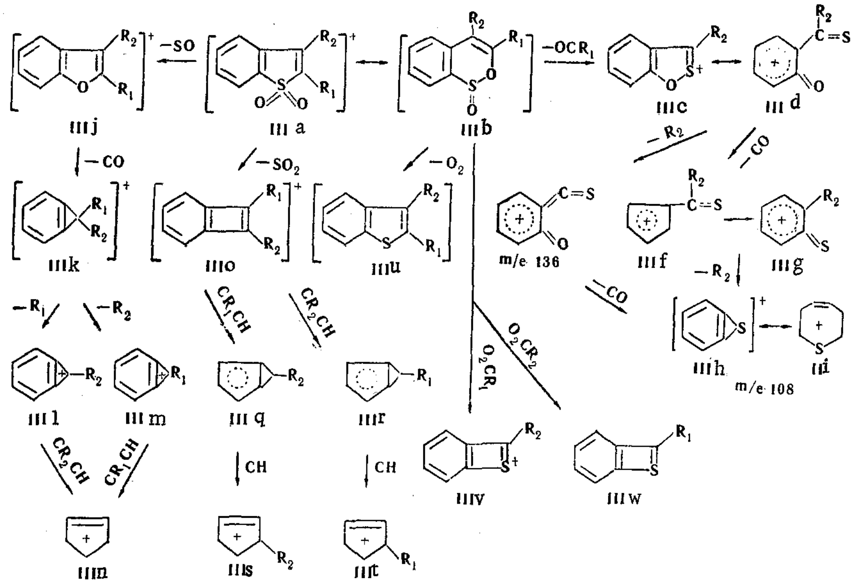
1	2	3	4	5	6	7	8	9
197						2,9	2,6	
199				3,4				
200				33,0				
201				4,3				
202	100			13,2				
203	10,0							
204	64,8							
205	6,47							
206	13,3							
208		11,4				7,15		
209		100				5,0		
210		13,0				48,2	7,3	
211						7,3		
213							100	100
214							15,7	15,7
215							5,85	6,6
224								2,6
226								4,4
234					40,8			
235					3,8			
236					31,7			
237					2,4			
239			3,55					
242						52,6	11,2	
243						7,8	2,27	
250			3,3					13,7
251								6,6
252			12,6					46,6
253			6,44					21,8
254								9,25
258			4,4					3,3
271			14,20					10,7
282			7,55					5,9
283			6,6					5,5
284			34,0					23,7
285			34,8					23,7
286			100,0					66,6
287			19,3					14,8
288			5,5					4,4
318								50,0
319								11,1
320								3,7

TABLE 2. Mass Spectrum of Dissociative Electron Capture by 2,3-Dichlorothianaphthene Molecules

Ion	eV		
	0,15	4,1	6,6
$(M-H)^-$	7,5	19,3	6,9
$(M-3)^-$	12,6	—	—
$(M-Cl)^-$	4,3	15	2,6
CCl^-	120	—	—
Cl^-	1000	30	17
Cl_2^-	8	—	—
Half-height width, eV	0,5	0,9	1,8

splitting out of OCR_1 (R_1 is a hydrogen, chlorine, or phenyl radical attached to C_2), O_2, SO_2, and SO (Scheme 4).

Scheme 4



The elimination of OCR_1 is the most probable process for all of the sulfones investigated. The peaks of maximum intensity are those of mass 171 in the spectra of the 1,1-dioxides of the chloro-substituted thianaphthenes (IV and V) and those of mass 213 in the spectra of the 1,1-dioxides of 3-phenylthianaphthene (VII) and 2,3-diphenylthianaphthene (VIII). The peak of the $OCC_6H_5^+$ ion (m/e 105) has the maximum intensity in the mass spectrum of 2-phenylthianaphthene 1,1-dioxide (VI); the line of the ions formed by removal of OCR_1 (m/e 137) has an intensity of 78% of the maximum. Both lines correspond to ions formed by the same disintegration process – removal of OCR_1 (OCC_6H_5) – but in one case the charge is concentrated on the sulfur atom or in the six-membered naphthene ring while, however, the charge is concentrated on the oxygen atom and phenyl group during the formation of $OCC_6H_5^+$ ions.

The expulsion of carbon monoxide from IIIc and IIId gives intense peaks of mass 143 in IV and V (31.2 and 21.8%) and an ion peak with m/e 109 (16.7%) in VI. Ions with m/e 185, which are formed in smaller amounts (6.3 and 2.6%) than in the other sulfones, correspond to the expulsion of CO from VII and VIII. Ions with m/e 185 (IIIf and IIIg, where R_2 is a phenyl radical) are apparently readily converted with the loss of hydrogen to dibenzothiophene ions (m/e 184) Ig. This explains the low intensity (as compared with the other thionaphthene 1,1-dioxides) of the line of the IIIf and IIIg ions and the relatively high yields of ions with m/e 184 (33.6% in VII and 18.5% in VIII, as compared with 2.3% in VI and 1.4% in II, where the dibenzothiophene ions are formed only via other disintegration channels).

Ions with m/e 108 (IIIh and IIIi) can be formed by the removal of substituent R_2 from IIIf and IIIg, and the formation of IIIh and IIIi through ions with m/e 136 by successive cleavage of R_2 and CO is also possible. In fact, the lines of mass 108 are of considerable intensity (47.4 and 42.6%) in the mass spectra of the chloro-substituted sulfones, but high intensity of the lines of mass 136 (50 and 52%) is characteristic for them.

The intensity of the peak with mass 136 in the mass spectrum of VI is 2.6%, while that of the peak with mass 108 is 2.2%; both of these peaks are absent in the spectrum of VII.

Dissociation of the molecular ion initiated by elimination of SO is reported for thianaphthene 1,1-dioxide [1]. This sort of process does not occur in the case of VII and VIII: a phenyl substituent in the 3-position closes this channel for disintegration. The spectra of VII and VIII do not contain lines corresponding to ions of structures IIIj and IIIi. Further disintegration of III also gives ions with mass numbers 123 and 89 (IV), 123 (V), and 165 and 89 (VI) and ions with m/e 63.

Ions IIIl, IIIm, and IIIn are observed in the spectra of VII and VIII; i.e., during the ionization of the sulfones, ions of these structures are formed by other paths of dissociation, both through expulsion of SO_2 and through expulsion of O_2.

The removal of O_2 leads to the formation of the molecular ion of the corresponding thianaphthene (IIIu); the disintegration of IIIu creates the mass spectrum of thianaphthene. All of the lines observed in the spectrum of 2-phenylthianaphthene and 2,3-diphenylthianaphthene are also present in the spectra of the corresponding sulfones.

Ion IIIu is not formed during the ionization of 2,3-dichlorothianaphthene 1,1-dioxide, i.e., the channel of disintegration initiated by the removal of O_2 is closed. Lines characteristic for the spectra of I (peaks with masses of 167, 166, and 132) are correspondingly absent in the mass spectrum of 2,3-dichlorothianaphthene 1,1-dioxide.

An ion peak with a mass of 123 (IIIl and IIIm) is observed in the spectrum of 2,3-dichlorothianaphthene and in the spectrum of 2,3-dichlorothianaphthene 1,1-dioxide. Direct expulsion of an SCCl group from the molecular ion occurs in the first case, while in the second case the formation proceeds via the described channel of successive splitting out of SO, CO, and Cl and also via the disintegration channel, the first step of which is the expulsion of SO_2.

The splitting out of an SO_2 group is an independent process and not a second step after the removal of SO or O_2. Lines which correspond to the structure of ion IIIo are observed in the spectra of all of the investigated sulfones and in the spectra of VII and VIII (where the channel for the elimination of SO is closed) and in the spectrum of V, where ions IIIu are not formed. The disintegration of ions of the IIIo structure via the directions indicated in scheme 4 (expulsion of CRCH and CRC_2H_2) also occurs during the ionization of 2-phenylthianaphthene molecules (ions Ib); expulsion of a sulfur atom to form ions IIIo does not occur during the ionization of 2,3-dichlorothianaphthene molecules; lines for ions with m/e 110 (IIIq) and 97 (IIIs) are absent in the spectrum of I.

The elimination of O_2CR_1 and O_2CR_2 is represented in Scheme 4 by a separate process. Ions IIIv and IIIw are not observed in the mass spectra of thianaphthenes, so that it is possible to assign them as being due to further disintegration of ions IIIu only if ions IIIu are formed during dissociative ionization of thianaphthene 1,1-dioxides with higher excitation energies than the molecular ions of thianaphthenes during the ionization of thianaphthenes.

This process of elimination of O_2CR does not occur in the case of VIII, although the line of ions IIIu amounts to 66% relative intensity. At the same time, it is observed in the spectrum of 2,3-dichlorothianaphthene 1,1-dioxide (m/e 155).

A peculiarity of the fragmentation of molecules of chloro-substituted thianaphthene 1,1-dioxides is the ease of splitting off of a chlorine atom from the molecular ion (peaks of mass 165 and 199 in the spectra of V and VI) and from the ions of structure IIIo (peaks of mass 101 and 135).

Lines of ions of condensed structures (Scheme 3), which are formed after the expulsion of O_2 and SO_2, occupy a high specific weight in the mass spectrum of 2,3-diphenylthianaphthene 1,1-dioxide. Ions which do not contain a sulfur atom in their structures (m/e 254, 250, and 239) are observed in large quantities during the ionization of 2,3-diphenylthianaphthene 1,1-dioxide. The ratio is just the opposite (m/e 284, 271, 258, and 288) for ions which do contain sulfur atoms. In the first case there are two paths for the disintegration of molecular ion VI: expulsion of SO_2 with subsequent condensation, and expulsion of O_2 with subsequent elimination of H_2S and H_4S (Scheme 3). In the second case there is one channel which coincides with the channel for the disintegration of 2,3-diphenylthianaphthene ions.

Data on the formation of negative ions by the interaction of molecules with slow electrons are presented in Table 2. Depending on the energy of the latter, one observes three peaks for the formation of the negative molecular ion, the result of the disintegration of which is the mass spectrum presented in Table 2. It is characteristic that the capture of electrons with energies close to zero leads to the formation of $SCCl^-$, Cl_2^-, and $(M-3)^-$ ions which are not observed during the fragmentation of higher energy quasisteady states $(M^-)^*$.

The formation of S^- and SH^- ions, whose lines are the most intense in the mass spectra of negative alkylthiophene ions [3], does not occur. The presence of the more electronegative chlorine atoms apparently directs the disintegration of $(M^-)^*$ via another path.

LITERATURE CITED

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