MASS SPECTRA OF SOME ALKYL- AND PHENYL-SUBSTITUTED THIAZOLES

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The mass spectra of a number of alkyl- and methyl-phenyl-substituted thiazoles at various ionizing electron energies were studied. The predominant disintegration reactions are processes involving contraction of the starting ring to form charged sulfur-containing fragments and nitrogen-containing neutral particles. It was noted that the peaks of the $(M-H)^+$ and $(M-CH_3)^+$ ions are of low intensity, that the probability of rearrangement processes with ring expansion is low, and that the position of the methyl groups has a pronounced effect on the disintegration of the molecules during electron impact.

A limited number of studies [1-3] have been devoted to the investigation of the mass spectra of thiazole systems, although their disintegration on electron impact is of undoubted interest in the light of the examination of the effect of two heteroatoms situated in a single ring on the dissociative ionization. This paper is devoted to an investigation of the mass spectra of 2,4-dimethylthiazole (I), 4,5-dimethylthiazole (II), 2,4,5-trimethylthiazole (III), 5-ethyl-4-n-propylthiazole (IV), 4-methyl-2-phenylthiazole (V), 4,5-dimethyl-2-phenylthiazole (VI), and 2,4-diphenylthiazole (VII). The mass spectra of II-VI were studied for the first time.

The mass spectra were recorded with a modified MKh-1303 mass spectrometer at an ionizing chamber and inlet system temperature of 250° and ionizing electron energies of 50, 30, 20, and 15 eV. The mass spectra of I-IV and V-VII, respectively, obtained at ionizing electron energies of 50 eV, are presented in Tables 1 and 2 (peaks with intensities >3% of the maximum are given). The resistances to electron impact (W_M), which are the fractions of polyisotropic molecular ions in the total ion current (in percent), and the selectivities, which are the numbers of most intense peaks whose sum is half the total ion current, were also determined.

The resistance to electron impact of I-III and the selectivities of their disintegration are quite high (W_M 22.2-26.3, $S_{1/2} \sim 3$), which attests to the stability of the thiazole aromatic system. The maximum peak in the mass spectra of I-III at all of the examined ionizing electron energies corresponds to the molecular ion.

The extremely low intensity of the $(M-H)^+$ and $(M-CH_3)^+$ ions is a characteristic peculiarity of the disintegration of methylthiazoles. Their intensities with respect to the total ion current at 50 eV, respectively, are 0.24 and 0.0 for I, 3.1 and 2.3 for II, and 1.8 and 0.1 for III. A low intensity was noted for the $(M-H)^+$ peaks in the mass spectra of alkylisoxazoles [4], which have an extremely labile N−O bond, and in the mass spectra of oxazoles [5]. In the case of the quite stable aromatic ring under consideration, it can be assumed that this fact indicates the absence of rearrangement processes that lead to ring expansion. In particular, the ring expansion to form thiazines proposed for methylisothiazoles [6] hardly occurs here.

The disintegration of II during electron impact differs somewhat from the dissociative ionization of I described in [1]. The presence of two adjacent methyl groups activates the detachment of H and CH_3, which, although the probability that such processes occur is low as compared with other methyl-substituted hetero-

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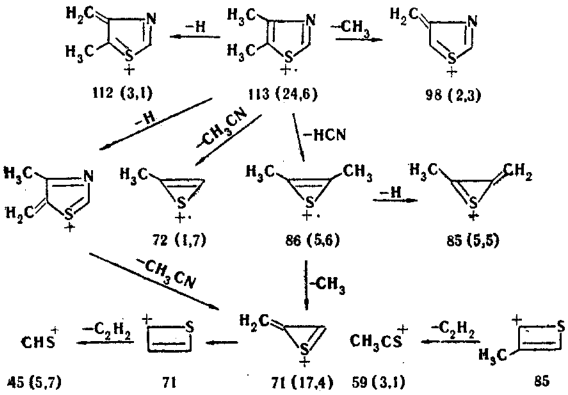
TABLE 1. Mass Spectra of Alkylthiazoles

m/e	I	II	III	IV
26	4,0	3,8	—	4,3
27	8,7	10,0	10,9	29,8
29	7,7	—	—	10,9
38	4,4	—	—	3,3
39	20,2	8,3	9,7	30,6
40	17,7	—	3,3	5,2
41	3,0	6,1	8,5	39,5
42	10,3	4,0	11,5	7,3
43	—	3,3	9,2	47,1
45	32,2	23,2	20,6	32,2
46	3,5	—	—	—
47	—	—	—	3,9
50	3,6	3,9	3,6	—
51	—	5,5	5,7	6,7
52	—	3,3	3,3	4,0
53	—	8,8	10,2	9,7
54	—	3,2	—	—
55	—	—	—	13,0
57	3,5	—	—	—
58	3,6	8,0	11,0	8,0
59	5,0	12,5	24,4	15,6
65	—	—	—	15,4
66	—	—	—	3,1
67	—	—	—	4,6
68	3,6	—	3,5	—
69	10,9	6,2	5,9	12,5
70	3,9	—	—	6,1
71	91,1	70,9	95,1	50,0
72	88,9	7,1	5,2	4,3
73	10,2	3,7	5,2	5,5
74	5,1	—	—	—
77	—	—	—	9,2
79	—	—	—	5,5
84	—	—	—	5,3
85	—	23,4	32,1	9,0
86	—	23,8	71,0	—
87	—	—	5,7	—
88	—	—	3,6	—
97	—	—	—	7,6
98	—	9,3	—	22,5
99	—	—	—	20,9
111	—	—	—	3,8
112	—	12,5	3,7	20,9
113	100,0	100,0	—	4,4
114	8,3	7,3	—	—
115	6,2	4,4	—	—
124	—	—	—	3,6
125	—	—	—	5,2
126	—	—	9,3	80,0
127	—	—	100,0	100,0
128	—	—	8,5	10,5
129	—	—	5,3	4,9
140	—	—	—	28,2
141	—	—	—	3,7
154	—	—	—	12,5
155	—	—	—	29,8
156	—	—	—	4,05
W_M	22,9	26,3	22,2	3,8
$S_{1/2}$	<3	3	>3	9



cyclic compounds, still occur to a much greater extent than in the mass spectrum of I.* It should be noted that the intensity of the $(M-H)^+$ ion peak in the mass spectrum of II, obtained at an ionizing electron energy of 15 eV, is relatively higher than at 50 eV (4.2 and 3.1% of the total current, respectively).

The absence of a methyl substituent in the 2 position results in the fact that the detachment of CH_3CN, which corresponds to the maximum fragment peak in the spectrum in the case of I, is suppressed by the formation of the $(M-HCN)^+$ ion. The relative intensity of the peak of this ion increases from 5.6 to 12.1% with respect to the total current as the ionizing electron energy is decreased from 50 to 15 eV.

An examination of the mass spectra of II and III indicates that the proposed path for the formation of the ion of mass 71 from the ion of mass 72 [1] occurs only in the case of I. Thus the intensity of the peak of ions of mass 72 in the mass spectrum of II, obtained at an electron energy of 50 eV, is 1.7% of the total current, while the intensity of the peak of ions of mass 71 is 17.4% at an ionizing electron energy of 50 eV and 7.9% at an electron energy of 15 eV. The intensity of the peak of ions of mass 71 in the mass spectrum of III at an ionizing electron energy of 15 eV is 8.6% of the total current (the third largest peak in the spectrum), while the peak of ions of mass 72 is generally absent at the indicated electron energy and constitutes only 1.0% of the total current at 50 eV; the peak of ions of mass 71 is 18.5%. Thus the ion of mass 71 is not genetically associated with the ion of mass 72. The sharp decrease (by almost half) of the relative intensity of the peak of ion of mass 71 as the ionizing electron energy decreases provides a basis for assuming that it is not formed in the first stage of the disintegration of the molecular ion. From all appearances, its origin is associated with subsequent disintegration of the fragment $(M-HCN)^+$ ions and, to a lesser degree, of the $(M-H)^+$ ions. The subsequent disintegration of the ion of mass 71 leads to a fragment of mass 45; a homologous "weighted" ion of mass 59 is probably formed by an analogous path from the ion of mass 85.

The dissociative ionization of III is, in general, similar to the disintegration of II. However, it should be noted that the presence of a methyl group in the 2 position naturally leads to a sharp (as compared with II) increase in the probability of the detachment of CH_3CN, and the $(M-CH_3CN)^+$ ion becomes the maximum fragment peak in the spectrum. Its intensity is somewhat less than the intensity of the peak of the fragment

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*Here and elsewhere, the numbers under the formulas in the schemes correspond to the mass number of the ion, while the numbers in parentheses correspond to the peak intensities in percent of the total current.

TABLE 2. Mass Spectra of Phenylthiazoles

m/e	V	VI	VII
26	—	5,1	—
27	3,7	13,1	—
29	4,2	9,2	4,5
38	—	3,5	—
39	10,5	13,7	4,1
40	9,4	13,3	—
41	—	11,1	—
42	—	5,1	—
43	6,8	10,9	—
45	15,5	25,6	3,8
50	4,3	15,6	—
51	7,8	18,5	5,8
52	—	7,5	—
53	—	10,0	—
55	—	5,3	—
58	—	7,0	—
59	—	13,1	—
63	—	5,5	6,2
69	3,8	5,3	6,0
71	53,7	67,6	—
72	100,0	5,3	—
73	7,2	5,9	—
74	6,1	4,5	—
75	—	8,4	—
76	6,3	30,0	4,2
77	11,6	21,8	6,2
78	—	3,9	—
85	—	26,1	—
86	—	94,6	—
87	—	7,6	—
87,5	3,7	—	—
88	—	5,7	—
89	—	—	20,7
90	—	—	20,4
94,5	—	3,3	—
100	—	3,7	—
102	—	—	5,9
103	5,8	56,8	4,3
104	17,3	15,4	—
105	—	6,3	—
121	—	9,4	—
133	—	—	5,2
134	—	—	100,0
135	—	—	12,4
136	—	—	6,2
174	—	5,5	—
175	88,0	—	—
176	10,8	—	—
177	4,8	—	—
188	—	19,6	—
189	—	100,0	—
190	—	14,7	—
191	—	5,7	—
237	—	—	77,2
238	—	—	17,0
239	—	—	5,7
W_M	23,8	15,7	25,5
$S_{1/2}$	3	6	2

TABLE 3. Peak Intensities of Several Ions in the Mass Spectra of Methylphenylthiazoles at Various Ionizing Electron Energies*

Ionizing electron energy, eV	Ion	Compound		
		V	VI	VII
50	$(M{-}H)^+$	0,23	2,7	0,60
15		—	4,3	0,95
50	$(M{-}C_6H_5CN)^+$	22,9	13,0	22,5
15		22,2	22,2	21,7
50	$C_6H_5CN^+$	1,3	7,8	1,1
15		1,2	9,8	0,7
50	$C_6H_5CNH^+$	4,0	2,1	0,24
15		3,3	—	—
50	$C_6H_5CS^+$	0,4	1,3	0,2
15		—	—	—
50	$C_6H_5CH^+$ or	0,4	—	5,2
15	$C_6H_4N^+$	—	—	5,1
50	$C_6H_5C^+$	0,4	—	5,3
15		—	—	5,8
50	$C_6H_5^+$	2,7	3,0	1,6
15		1,8	—	0,9

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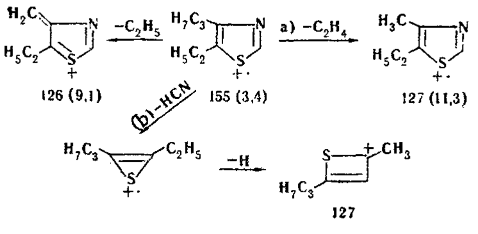
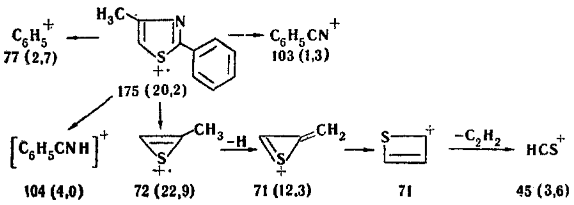
*In percent of the total ion current.

ion in the mass spectrum of I at an ionizing electron energy of 50 eV (17.7 and 13.8% with respect to the total current) and is approximately equal to it at 15 eV (22.4 and 20.0%, respectively).

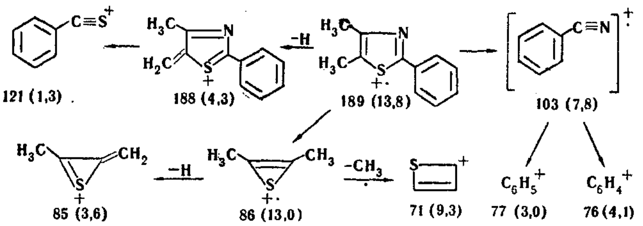
An increase in the length of the alkyl groups in the 4 and 5 positions (IV) sharply reduces the stability of the molecule (W_M = 3.8) and the selectivity of the disintegration ($S_{1/2}$ = 9). The absence of high-resolution mass-spectral data makes it impossible to unambiguously judge the structure of the $(M-28)^+$ fragment ion, which corresponds to the maximum peak in the spectrum. It may be formed either as a result of the detachment of a neutral ethylene particle from the molecular ion (a) or detachment of HCN and H from the molecular ion (b), or, finally, both processes may occur. The intensity of the peak of the $(M-28)^+$ and $(M-28-1)^+$ ions increases as the ionizing electron energy is reduced to 15 eV: from 11.3 to 28.5% and from 9.0 to 10.7%, respectively, of the total current. This emphasizes the important role played in the overall disintegration picture by the indicated ions, which are formed in the first stages of the dissociative ionization.



The introduction of one or several phenyl groups (Tables 2 and 3) has virtually no effect on W_M owing to two dissimilarly acting factors – the increase in the size of the molecule and the stabilizing effect of phenyl groups. As before, the extremely low probability of the formation of $(M-H)^+$ and $(M-CH_3)^+$ ions remains the characteristic feature of the disintegration, while the maximum peaks of the fragment ions develop during detachment of a cyano-containing neutral particle (C_6H_4CN in this case). The probability of the detachment of this particle, especially at low ionizing electron energies, is approximately the same for V-VII (Table 3). Even at an ionizing electron energy of 50 eV, the mass spectrum of V contains only seven peaks with intensities of about 10% of the maximum, and the scheme of its disintegration is extremely simple:



As in the case of methylthiazoles, the presence of adjacent methyl groups in the ring of 4,5-dimethyl-2-phenylthiazole (VI) changes the mass spectrum to a considerable extent. Thus the probability of detachment of H increases by a factor of about 10, and the intensity of the $(M-C_6H_5CN)^+$ peak decreases somewhat due to an increase in the probability of the formation of a charged $C_6H_5CN^+$ particle. The series of ion peaks of masses 75, 76, and 77 that is characteristic for benzonitrile quite reliably indicates that this process occurs. A certain fraction of the $C_6H_5^+$ ions probably also arises during the direct formation of a phenyl fragment from the molecular ion. Ions of mass 121 in the mass spectrum of VI are of rather appreciable intensity. The absence of a metastable peak makes it possible to express only an assumption regarding the formation of it from the extremely stable $(M-H)^+$ ion:



The mass spectrum of VII is more like the mass spectrum of V with respect to the direction of disintegration than that of VI and differs from them by the presence of rather intense peaks of ions of masses 89 and 90. The development of the first of them is readily interpreted, but it is difficult to conceive of a mechanism for the formation of the ion of mass 90; it requires either migration of hydrogen to the positively charged particle from the second phenyl ring or migration of a phenyl group to the nitrogen in the excited molecular ion.

An examination of the spectra of alkyl- and methylphenylthiazoles makes it possible to conclude that rearrangement processes are either absent or are unlikely. The presence of two different heteroatoms in the ring leads to predominance of disintegration reactions and contraction of the starting ring to form sulfur-containing, charged fragment and neutral, nitrogen-containing particles. Doubly charged ions play a very small role.

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