MASS-SPECTROSCOPIC STUDY OF 2-AMINOTHIAZOLINE DERIVATIVES

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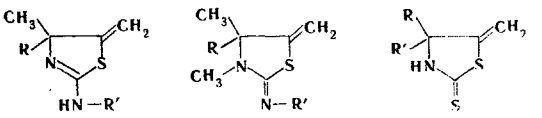
The mass spectra of 15 derivatives of 2-aminothiazoline are presented. The dependence of the intensity of the molecular ion on the substituents in the 4 and 2 positions and the intensive decomposition processes at the C_4 atom make it possible to assume primary localization of the charge on the ring nitrogen atom.

Convincing proof of the effect of charge localization on the fragmentation of molecules under electron impact is presented in the scientific literature [1, 2]. A comparison of the intensities of the peaks of the fragment ions formed from different parts of the molecule to a certain degree makes it possible to form a judgment regarding the probability of charge localization in the molecular ion in the vicinity of various functional groups and regarding their contribution to the overall picture of the fragmentation. In this sense, a study of the spectra of 2-aminothiazolines with functional substituents seems of interest.

In the present research we investigated the mass spectra of 15 compounds with the following structures:



I-VII VIII-XIII XIV, XV

The intensities of the twenty most intense peaks in each mass spectrum are presented in Table 1. An intense molecular ion peak ($M^{\dot{+}}$), the intensity of which falls as the length of the substituent in the 4 position of the ring increases (compare III and IV, VIII and IX, and X and XI), was observed in the mass spectra of most of the compounds. Replacement of C_2H_5 by C_3H_5 attached to the exocyclic nitrogen atom has almost no effect on the intensity of the molecular ion in compounds with an imino structure (compare VIII and X and IX and XI), whereas the intensity of the $M^{\dot{+}}$ ions increases in compounds with an amino structure (compare I and II). On passing from amino compounds to thiocarbonyl compounds, the intensity of the molecular ion peak increases.

The fragmentation of the investigated compounds is very specific. Detachment of the 4-alkyl substituent in the β position relative to the $N_{(3)}$ atom, the so-called α fragmentation (see scheme below), is characteristic for all of the compounds. We note that in the mass spectrum of 2-aminothiazoline [3] there is an intense $(M-1)^+$ peak, which Klayman and Milue explained by detachment of a hydrogen atom from the $C_{(5)}$ atom, i.e., of a hydrogen atom in the β position relative to the sulfur atom [3]. However, this fragmentation is not characteristic for saturated sulfur compounds [2]. At the same time, an intense $(M-1)^+$ ion is present in the mass spectra of aliphatic and cyclic amines. This convinces us that detachment of a hydrogen atom from the $C_{(4)}$ atom occurs in the case of unsubstituted 2-aminothiazoline, i.e., that there is intensive α fragmentation with respect to the ring nitrogen

*Deceased.

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TABLE 1. Mass Spectra of Thiazolines

Compound	R	R′	Mass spectra: m/e / I, %							
1	2	3	4							
I	CH_3	C_2H_5	170	156	155	100	85	83	71	
			8,9	9,1	100	19,0	27,3	12,7	5,9	
			67	60	59	58	56	55	53	45
			5,8	4,6	8,6	11,4	4,5	4,0	4,3	6,0
			44	43	42	41	39			
			4,6	10,5	12,0	17,9	11,0			
II	CH_3	C_3H_7	182	169	168	167	100	99	85	
			35,0	5,2	10,0	100	15,8	7,4	39,6	
			83	67	59	58	56	55	54	53
			18,7	11,6	12,7	17,0	11,0	7,2	4,2	8,2
			45	42	41	40	39			
			8,5	12,0	61,6	7,1	32,0			
III	CH_3	C_6H_5	218	204	203	119	118	101	100	
			28,0	14,0	100	9,0	20,0	5,5	21,0	
			91	85	77	67	65	59	58	51
			8,0	35,0	22,0	10,0	9,0	11,0	12,0	17,0
			50	45	42	41	39			
			5,0	9,0	11,0	21,0	18,0			
IV	C_3H_7	C_6H_5	246	231	203	118	100	93	91	
			10,0	6,6	100	6,2	18,9	9,5	4,5	
			85	77	65	59	58	55	53	51
			5,0	16,7	6,3	8,3	6,3	4,6	5,4	8,9
			45	43	42	41	39			
			6,4	5,3	10,6	17,9	11,2			
V	C_2H_5	$CH_2C_6H_5$	246	231	218	217	92	91	90	
			0,8	2,1	6,0	46,3	7,6	100	2,8	
			89	77	65	63	59	58	55	
			3,6	2,1	15,1	4,8	2,2	4,3	3,2	
			53	51	50	45	41	39		
			2,0	6,1	3,2	2,4	5,0	10,4		
VI	C_2H_5	COC_6H_5	260	232	231	114	113	106	105	
			1,0	8,2	56,3	8,8	5,1	7,3	100	
			100	99	85	81	78	77		
			6,5	12,0	6,5	5,0	5,0	60,3		
			58	55	53	51	50	45	41	
			4,5	4,4	5,5	21,4	6,6	8,6	8,7	
VII	†	$CH_2C_6H_5$	272	244	229	217	181	110		
			40,7	7,6	22,4	9,4	9,4	8,9		
			106	92	91	81	79	77	65	
			11,5	10,0	100	7,0	9,1	9,8	16,0	
			58	55	53	51	44	41	39	
			5,9	9,4	7,0	8,0	16,0	13,8	13,0	
VIII	CH_3	C_2H_5	184	170	169	114	100	99		
			58,0	9,9	100	57,2	8,0	7,7		
			85	83	77	69	67	59	58	
			46,0	7,5	11,8	14,1	8,8	7,5	7,0	
			57	56	55	44	42	41	39	
			14,7	22,7	7,6	9,4	12,0	14,0	8,7	
IX	C_2H_5	C_2H_5	198	183	170	169	128	114		
			14,4	11,3	10,5	100	8,3	67,3		
			113	85	77	74	69	58	57	
			5,4	9,8	5,4	5,3	9,7	11,8	9,7	
			56	55	53	42	41	39		
			29.5	12.2	10.2	19,4	16,5	10,4		
X	CH_3	C_3H_5	196	181	168	114	100	99	85	
			49,6	71,4	26,7	69,9	20.3	14,9	52,2	
			69	68	67	59	58	57	56	55
			19,0	20,3	21,9	13,9	14,6	16,7	74,7	13,8
			53	45	42	41	39			
			15,0	15,5	29,9	100	55,0			
XI	C_2H_5	C_3H_5	210	183	182	181	128	114	85	
			12,0	8,2	11,6	100	7,0	64,8	6,2	
			81	70	69	67	59	58	56	55
			6,7	6,4	8,5	9,3	6,8	9,3	36,0	9,8
			45	42	41	39				
			6,9	16,7	37,4	20,3				
XII	CH_3	C_6H_5	232	231	217	133	132	114	106	
			100	22,7	68,3	10,1	45,5	86,5	36,4	
			103	91	86	85	77	65	59	
			37,1	11,9	11,9	24,5	44,0	11,5	10,5	
			58	56	51	42	41	39		
			22,7	55,6	25,5	14,3	24,1	22,7		

TABLE 1 (continued)

1	2	3	4							
XIII	CH_3	COC_6H_5	260	246	245	183	106	105	85	
			27,3	4,0	25,0	13,7	8,0	100	8,3	
			83	78	77	76	67	59	58	56
			6,2	5,0	61,8	4,2	4,5	3,9	3,5	22,5
			51	50	42	41	39			
			25,9	6,6	5,6	10,5	8,0			
XIV	CH_3	C_2H_5	173	146	145	144	141	114	113	
			89,0	9,4	8,2	100	9,5	8,0	11,4	
			99	85	81	80	59	58	55	
			18,4	36,3	15,0	8,0	26,0	26,1	12,6	
			53	52	51	45	42	41	39	
			13,6	8,8	8,8	17,0	30,0	38,0	25,0	
XV	$-(CH_2)_5$		199	156	125	112	111	107	98	
			100	24,0	12,6	10,6	17,9	41,4	11,9	
			97	91	81	79	77	67	59	
			23,8	23,8	15,9	36,7	17,7	23,6	27,9	
			58	53	51	45	41	39		
			20,6	20,0	11,8	17,1	33,3	34,9		

*Of the 20 most intense bands [the $(M + 1)^+$ ion peaks are not presented].
†4-Pentamethylene.

atom. When substituents of different lengths are present in the β position, preferable detachment of the larger of them is observed.

Peaks of ions with m/e 59 and 60, which contain a sulfur atom and are intense in the mass spectrum of 2-aminothiazoline [3], have low intensities in the mass spectra of substituted thiazolines. When there is an N_3—CH_3 group present, one observes an intense peak with m/e 114 in the mass spectrum; a less intense peak with m/e 100 (99) is observed in the spectra of compounds that do not contain a methyl group in this position, and they are of low intensity (2-3%) in the mass spectra of benzyl and benzoyl derivatives, possibly in connection with the fact that the character of the fragmentation in these compounds differs markedly from the general pattern.

Benzyl and benzoyl substituents attached to the exocyclic nitrogen atom give rise to very intense peaks corresponding to the benzyl ion (m/e 91), which probably has the tropylium structure [2], or to a benzoyl ion (m/e 105), respectively, and also to ions of medium or moderate intensity at m/e 77, 51, and 50. A phenyl substituent attached to this same nitrogen atom has a considerably weaker effect on fragmentation.

The intense ion peaks formed by detachment of the substituent in the 4 position can be explained by charge localization near the $N_{(3)}$ atom. A comparison of the mass spectra of

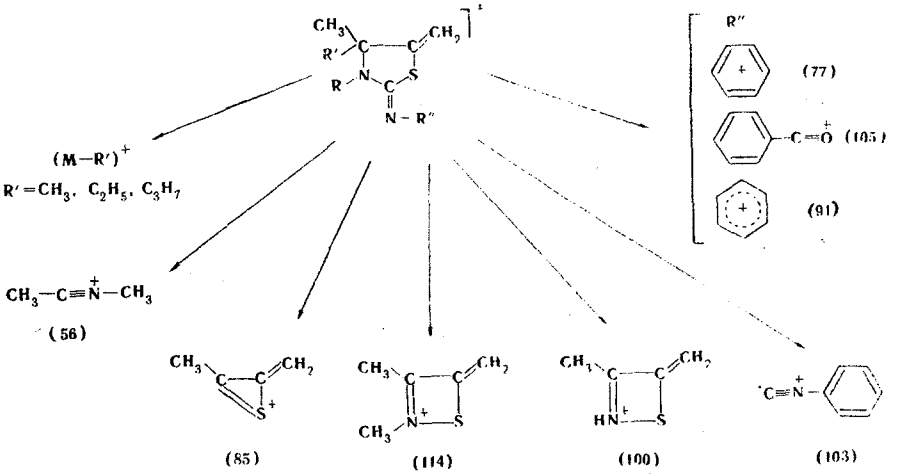

Fig. 1. Probable structures of the intense ions in the mass spectra of I-XV (the m/e values are given in parentheses).

compounds with amino and imino structures shows that the charge in both cases is apparently localized primarily on the ring nitrogen atom (peaks of ions arising during α fragmentations with close intensities). Replacement of the aliphatic substituent in the amino group by an aromatic substituent has little effect in the case of phenyl groups but has a pronounced effect in the case of benzyl, tolyl, and benzoyl substituents. In the latter three cases the charge is apparently shifted markedly to the aromatic ring, and the main peaks correspond to ions arising during fragmentation controlled from the aromatic center. Replacement of the amino group by sulfur does not appreciably affect the fragmentation (compare I and XV); the simultaneous increase in the intensity of the molecular ion is probably associated with the presence of two types of molecular ions, one of which (with charge localization on the ring nitrogen atom) was examined above, the other of which (with charge localization on the sulfur atom) is stable, disinclined to fragmentation, and makes a substantial contribution to the intensity of the M^+ ion peak.

EXPERIMENTAL

Compounds synthesized in the Laboratory of Acetylene Chemistry and described in [4-6] were used for the mass-spectrometric study. The structures and compositions of these compounds were established by chemical methods and IR and PMR spectroscopy [5]

The mass spectra were recorded with an MKh-1303 spectrometer at an inlet-cylinder heating temperature of about 100°, an ionizing voltage of 70 eV, and an accelerating voltage of 2000 V.

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