REARRANGEMENT PROCESSES AND STABILITY OF MOLECULAR IONS IN THE MASS SPECTRA OF 3-ARYL-5-METHYLISOXAZOLE-4-CARBOXYLIC ACIDS

K. K. Zhigulev, R. A. Khmel'nitskii,
M. A. Panina, I. I. Grandberg,
and B. M. Zolotarev

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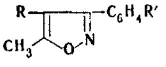
The effect of steric and electronic factors on the stability of the molecular ion and the probability of its isomerization in the mass spectra of 3-aryl-5-methylisoxazole-4-carboxylic acids were examined. The relationship between the resistance of the molecules to electron impact and the intensity of disintegration of the isoxazole ring was demonstrated. The formation of the primary rearrangement ions is discussed on the basis of the mass spectra of labeled compounds and the substituent effect.

Intramolecular interaction of directly unbonded atoms or groups is often the reason for both the high and anomalously low resistance of molecules to electron impact. Interesting relationships between the stability of the molecular ion and the molecular structure can be observed in the case of 3-aryl-5-methylisoxazole-4-carboxylic acid.



I–V

I R=COOH, R'=*m*-NO_2; I a R=COOD, R'=*m*-NO_2; II R=COOH, R'=H; III R=COOH, R'=*m*-NH_2; III a R=COOD, R'=*m*-ND_2; IV R=COOH, R'=*p*-(–N=CHC_6H_4OH-*o*); V R=COOH, R'=*o*-Cl

Some characteristics of the dissociative ionization of I–V are presented in Table 1.

The resistance of structures I–V to electron impact (W_M) varies over a very wide interval of values from 0.45 for V to 29.3 for IV. A comparison of the most important directions of dissociative ionization of I–V reveals the importance of two fundamental factors that determine the stability of the molecular ion (M^+): the electronic structure of substituent R' and its spatial orientation relative to the carboxyl group.

The first factor determines the distribution of the charge and energy of electron excitation in M^+ and consequently, the probability of disintegration of the isoxazole ring, which is the most labile element of the structure. The importance of the second factor is associated with the appearance of an effective channel for disintegration of M^+, which is due to interaction of the R' and COOH groups when the R' substituent is

TABLE 1. Some Characteristics of the Dissociative Ionization of I–V

J_i	Compound				
	I	II	III	IV	V
W_M	9;8	13,3	20,4	29,3	0,4
$J_{CH_3CO^+}$	24,9	13,3	6,5	4,6	9,7
$J_{(m-CO_2)^+}$	5,7	6,7	1,1	0,3	—
$J_{(M-59)^+}$	4,5	13,3	9,6	2,0	6,0
$J_{(M-59)^+}/J_{(m-CO_2)^+}$	0,8	2,0	8,7	6,7	—

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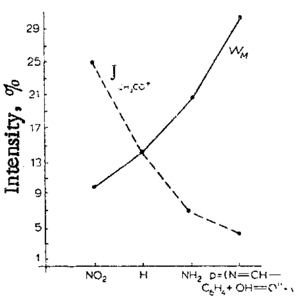
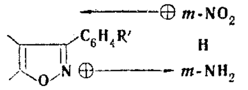
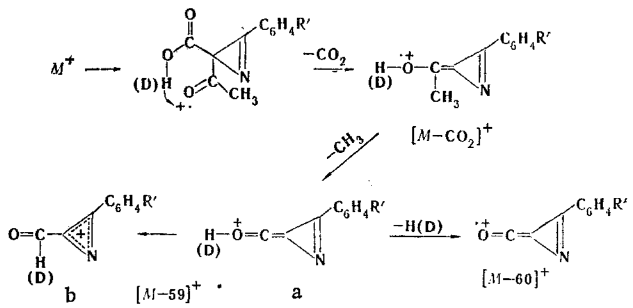


Fig. 1. Effect of substituent R' on the resistance of the molecule to electron impact and intensity of formation of CH_3CO^+ ions.

in the o-position relative to the isoxazole ring. The first factor is the determining one for structures I-IV, in which this sort of interaction is absent. As seen from the data in Table 1, the stability of the molecular ion decreases in the order IV > III > II > I. The charge distribution in the molecular ion is apparently associated with the direction of migration of charge in the Het$-C_6H_4-$R' structure and is determined by the character of substituent R'. This direction can be judged from the intensity of the peaks of the CH_3CO^+ ions – the most typical for the mass spectra of 5-methylisoxazoles [1,2]. It follows from Fig. 1 that an inverse dependence between the stability of M^+ and the intensity of the peaks of the CH_3CO^+ ions formed as a result of disintegration of the isoxazole ring is observed. Thus replacement of a hydrogen atom by NO_2 or NH_2 groups leads to opposite effects. In the first case (R' = m-NO_2), the charge migrates toward the isoxazole ring, increasing the fraction of ions associated with its disintegration and lowering as a whole the resistance of the molecule to electron impact. On the other hand, when the substituent is an amino group (R' = m-NH_2), the charge migrates in the opposite direction, and one observes an increase in the stability of the molecular ion as compared with the case when R' = H:



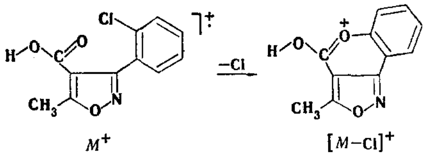
The character and position of substituent R' also have an appreciable effect on the distribution of the intensities of the peaks of the major rearrangement ions $(M-CO_2)^+$ and $(M-59)^+$.



An investigation of the mass spectra of labeled compounds IIa and IIIa demonstrated that the M$-$59)$^+$ ions retain deuterium almost completely. The formation of $(M-59)^+$ ions should therefore, at least in the case of I-IV, occur primarily via the reaction $(M-CO_2)^+ \rightarrow (M-CO_2-CH_3)^+$ [an alternative possibility for the formation of $(M-59)^+$ ions consists in the reaction $M^+ \rightarrow (M-CH_2CO-OH)^+$]. An examination of the $J_{(M-59)^+}/J_{(M-CO_2)^+}$ ratio demonstrates that the probability of the reaction $(M-CO_2)^+ \rightarrow (M-CO_2-CH_3)^+$ decreases markedly in the order (R')NH_2 > H > NO_2. In addition, the intensity of the detachment of a hydrogen from the $(M-59)^+$ ion increases in the same order, and the $J_{(M-60)^+}/J_{(M-59)^+}$ ratio for I-III is NH_2 (0.15) < H (0.3) < NO_2 (0.7). These data indicate the importance of substituents R' for the stabilization of the charge in the structure of the $(M-59)^+$ ion, which is probably associated with rearrangement of ion a to ion b [3].

It follows from the data in Table 1 that the resistance to electron impact of V is very small and is more than one order of magnitude lower than the stability of the remaining compounds. The reason for this is interaction of the chlorine atom with the carboxyl group, which leads to intensive elimination of the chlorine atom and the formation of an aromatic structure – the pyrylium ion.

It is important to note that the formation of $(M-Cl)^+$ ions (the corresponding peak is a maximum in the mass spectrum) is possible only from those M^+ ions that have retained the aromatic structure of the isoxazole ring, and the intensity of the peak of the $(M-Cl)^+$ ion may serve as an estimate of the resistance of the isoxazole ring to isomerization during electron impact for this type of compound. The molecular ions that have retained the isoxazole ring $(M_0{}^+)$ apparently correspond to the low-energy states in the

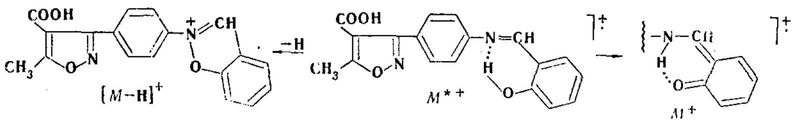


$\{M_i{}^+\}$ spectral set. That is, the disintegration of these ions via the reaction $M_0{}^+ \rightarrow (M_0-Cl)^+$ causes a sharp decrease in the intensity of the M^+ peak on passing from I-IV to V.

The following position is valid in the general case. The appearance of a new channel for disintegration of the molecular ion should lead to a decrease in the resistance of the molecule to electron impact (W_M) if this direction is associated with dissociation of those states in set $\{M_i{}^+\}$ that are relatively stable to disintegration reactions over all of the remaining channels.

If the character of the intramolecular interaction for structure V causes low stability of the molecular ion, a different pattern is observed for IV, which has an unusually high W_M value. Except for the molecular ion peak, which is a maximum in the mass spectrum (100%), relatively high-intensity CH_3CO^+ (18.8%) and $(M-H)^+$ (16.9%) peaks correspond to only two ions.

The phenomenon of photochromism, which is a consequence of transfer of a proton to form a quinoid structure, is well known for this type of structure (aromatic o-hydroxyazomethines). This sort of isomerization to a more energy-rich structure is associated with dissipation of the energy of electronic excitation and usually leads to a decrease in the quantum luminescence yield or photochemical reactions [3]. The reason for the increased stability of M^+ of V is apparently similar. The fact that the hydrogen atom of the hydroxyl group participates substantially in the formation of the behavior of the molecule under the influence of electronic impact is displayed in the presence of the corresponding $(M-H)^+$ ions.



The mass spectra of I-V were obtained with an SN-6 spectrometer with a system for direct inlet of the sample into the ion source at an ionizing voltage of 70 eV and an ionizing-chamber temperature of 180°. Ion peaks with intensities greater than 5% of the maximum are presented.

Mass Spectrum of the Investigated Compounds

I: 43 (100), 50 (11,9), 63 (6,7), 75 (9,6), 76 (14,0), 77 (6,2), 143 (8,9), 188 (12,3), 189 (18,3), 204 (24,7), 230 (8,7), 231 (7,4), 248 (34,6).

Ia: 43 (100), 50 (12,0), 63 (6,8), 75 (9,2), 76 (15,1), 77 (6,3), 144 (9,1), 188 (19,2), 190 (12,3), 205 (32,0), 230 (11,3), 249 (35,0).

II: 39 (12,3), 43 (100), 50 (17,5), 51 (56,6), 52 (5,4), 63 (13,2), 69 (7,1), 74 (6,6), 75 (8,0), 76 (11,8), 77 (87,0), 78 (9,9), 89 (9,9), 93 (52,2), 94 (5,7), 104 (7,1), 105 (7,5), 116 (17,0), 117 (12,8), 143 (30,4), 144 (100), 145 (12,3); 159 (56,2), 160 (8,5), 161 (8,5), 188 (15,6), 203 (100), 204 (11,8).

III: 31 (6,0), 39 (14,5), 43 (36,8), 52 (5,9), 64 (5,8), 65 (57,8), 66 (5,9), 91 (5,3), 92 (48,2), 104 (5,9), 108 (8,6), 120 (11,2), 131 (7,6), 132 (9,3), 134 (7,2), 158 (8,3), 159 (54,3), 160 (6,0), 174 (6,2), 218 (100), 219 (15,1).

IIIa: 31 (5,2), 39 (11,0), 40 (13,3), 43 (52,7), 52 (6,9), 53 (7,5), 55 (6,4), 64 (8,7), 65 (18,0), 67 (25,4), 92 (11,0), 93 (36,0), 94 (52,6), 95 (13,3), 105 (6,9), 106 (6,4), 109 (6,9), 110 (11,0), 111 (9,9), 120 (6,4), 121 (11,6), 122 (16,7), 123 (7,0), 133 (8,1), 134 (12,1), 135 (13,9), 136 (11,0), 159 (8,7), 160 (26,0), 161 (41,0), 162 (40,0), 163 (8,1), 176 (8,1), 177 (9,2), 219 (36,0), 220 (89,5), 221 (100), 222 (21,0).

IV: 43 (18,8), 51 (7,5), 76 (6,1), 77 (9,7), 102 (5,8), 114 (5,1), 120 (6,6), 167 (5,8), 195 (10,5), 196 (6,9), 221 (5,5), 261 (5,8), 263 (8,5), 321 (16,9), 222 (100), 323 (21,9).

V: 43 (41,3), 50 (8,2), 75 (16,0), 111 (7,8), 113 (7,8), 123 (5,5), 127 (12,8), 129 (5,0), 150 (10,1), 160 (13,2), 177 (5,5), 178 (19,2), 180 (6,2), 202 (100), 203 (14,6), 237 (1,4).

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