EFFECT OF STRUCTURAL FACTORS ON THE DISINTEGRATION OF THE MOLECULAR IONS OF NITROPHENYLISOXAZOLES DURING ELECTRON IMPACT

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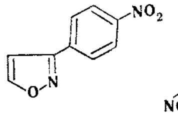
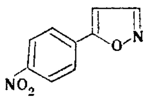
The dissociative ionization of some nitrophenylisoxazoles was investigated. The effect of the energy of the ionizing electrons and the temperature of the inlet system on the elimination of NO by the molecular ion is examined. On the basis of a comparison of the intensities of the peaks of the $(M-NO)^+$ ions, the presence of a correlation between the probability of detachment of NO from the molecular ion and the stability of the cyclic conjugated structures with localization of the charge on the oxygen atom is demonstrated.

Aromatic nitro compounds have quite frequently been considered as subjects for an investigation of the effect of electronic and steric factors on the isomerization of the molecular ion and its behavior in the first steps of dissociative ionization [1-6]. The presence of a nitro group in the molecule leads to the appearance of a number of specific ions $-(M-NO_2)^+$, $(M-NO)^+$, $(M-O)^+$, $(M-NO_2H)^+$, $(M-OH)^+$, and $(M-H_2O)^+-$ among which the $(M-NO)^+$ fragments associated with the formation of a rearranged molecular ion [2] are of particular interest.

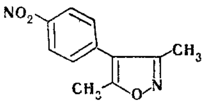
In the present research we continued our investigation of the effect of structural factors on the dissociative ionization of isoxazoles [7-11]. The mass spectra of p-nitrophenylisoxazoles I-III were studied.



I



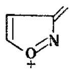
II



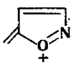
III

The mass spectra of these compounds were obtained with a modified MKh-1303 spectrometer at ionizing-electron energies of 50 (Table 1), 30, 20, 15, and 12 eV, an emission current of 1.5 mA, and accelerating voltage of 2 kV, and an inlet-system and ion-source temperature of 250°C.

In the elimination of NO from the molecular ions of I-III, one may expect the formation of cyclic conjugated structures, A, B, and C with localization of the charge on the oxygen atom.



A



B

C

$$E_A^{\pi} = 6\alpha^{\circ} + 11{,}3218\beta^{\circ},\quad E_B^{\pi} = 6\alpha^{\circ} + 11{,}4022\beta^{\circ},\quad E_C^{\pi} = 6\alpha^{\circ} + 12{,}8584\beta^{\circ}$$

Structures A, B, and C are nonequivalent with respect to their energies. The probability of their formation and, consequently, the intensity of the peaks of the $(M-NO)^+$ ions should therefore differ for I-III. An idea regarding the relative stabilities of structures A, B, and C can be obtained by comparing the intensities of the peaks of the $(M-NO)^+$ ions that arise at low ionizing-electron energies, where the

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TABLE 1. Mass Spectra of Nitrophenylisoxazoles I-III Obtained at Electron Energies of 50 eV

I	39 (13,2), 42 (6,1), 50 (34,2), 51 (14,8), 62 (14,0), 63 (27,7), 64 (6,1), 74 (11,6), 75 (30,3), 76 (29,5), 77 (11,6), 87 (5,4), 88 (10,1), 89 (68,0), 90 (13,2), 102 (15,5), 115 (7,1), 116 (16,0), 132 (10,1), 143 (31,0), 144 (9,5), 148 (5,9), 162 (11,6), 174 (5,4), 189 (96,7), 190 (100,0), 191 (11,8)
II	39 (18,7), 40 (9,3), 41 (5,5), 43 (8,8), 45 (9,5), 50 (43,7), 51 (20,2), 52 (11,8), 62 (14,0), 63 (34,4), 64 (9,7), 65 (8,9), 68 (11,2), 74 (15,6), 75 (28,0), 76 (48,3), 77 (25,0), 73 (5,3), 88 (6,7), 89 (84,5), 90 (9,5), 90 (9,5), 92 (23,2), 102 (5,7), 104 (35,8), 116 (10,3), 117 (7,4), 120 (22,0), 132 (26,6), 144 (7,6), 150 (41,0), 160 (38,1), 189 (13,3), 190 (100,0), 191 (11,2)
III	39 (26,4), 40 (19,5), 41 (19,5), 42 (11,7), 43 (100,0), 50 (14,7), 51 (25,4), 52 (11,7), 53 (7,8), 55 (10,7), 62 (19,5), 63 (27,4), 64 (13,7), 65 (14,6), 74 (7,8), 75 (16,6), 77 (58,5), 78 (15,6), 87 (11,7), 88 (22,4), 89 (21,5), 90 (7,8), 91 (42,0), 92 (7,8), 101 (9,8), 102 (23,4), 103 (53,7), 104 (26,4), 105 (10,7), 114 (9,8), 115 (9,8), 117 (11,7), 118 (29,3), 119 (75,5), 120 (9,8), 128 (7,8), 129 (17,5), 130 (25,4), 131 (11,7), 134 (9,8), 144 (7,8), 145 (14,6), 146 (14,6), 157 (9,8), 172 (14,6), 175 (17,6), 188 (58,5), 189 (10,7), 203 (18,0), 218 (100,0), 219 (14,6)

TABLE 2. Intensities of the Ion Peaks in the Mass Spectra of p-Nitrophenylisoxazoles

	Energy, eV	Compound		
		I	II	III
$I(M-NO)^+/I_{M^{+\cdot}}\cdot 100\%$	50	4,4	38,1	43,0
	12	5,5	22,1	117,2
$\Sigma' I_i/\Sigma I_i\cdot 100\%$	50	11,4	15,7	19,5
Mass numbers of the ions whose intensities enter into $\Sigma' I_i$		160 132 89	160 132 89	188, 146 119, 118 104, 103 102

role of secondary disintegration processes is small. In the comparison of the mass spectra obtained at relatively low electron energies one must take into account the intensities of the peaks of the fragments formed in the ensuing steps of the disintegration of the $(M-NO)^+$ ions. The intensities of the peaks of the $(M-NO)^+$ ions at ionizing electron energies of 50 and 12 eV, the sums of the intensities of the $(M-NO)^+$ ion peaks, and the most important fragments formed during their disintegration are presented in Table 2. The mass numbers of the ions whose peak intensities are summarized are presented in the last line of Table 2.

It follows from the results obtained that the probability of the disintegration $M^+ \rightarrow (M-NO)^+$ increases in the order I < II < III. When there is a correlation between the stability of the $(M-NO)^+$ ions and the probability of their formation, the above signifies that $E_A < E_B < E_C$, where E is the electron energy of the structure.

The higher stability of structure C as compared with A and B also follows from an examination of the effect of the ionizing-electron energy on the $I(M-NO)^+/IM^+$ ratio.

A very pronounced increase in this ratio as the ionizing-electron energy is reduced from 50 to 12 eV is observed only in the case of III. It therefore follows that the energy of activation of the process under consideration is low in the case of III as compared with that for I and II.

We investigated the effect of the ionizing electron energy and the inlet-system temperature on the probability of elimination of NO by the molecular ion of III over a relatively wide range of values of the indicated parameters (Figs. 1 and 2). It can be seen that the $I(M-NO)^+/IM^+$ ratio remains virtually unchanged up to ionizing-electron energies of 30-25 eV. The effect of temperature in this interval is also only slight. A very pronounced increase in the $I(M-NO)^+/IM^+$ ratio is observed at 15-9 eV. Moreover, the effect of temperature on the yield of $(M-NO)^+$ ions also increases sharply.

On the basis of the data obtained, it can be assumed that the disintegration of the molecular ion $M^+ \rightarrow (M-NO)^+$ in the case of III apparently proceeds in the ground electron state, during which retention of the isoxazole ring is an important factor that determines the effectiveness of the elimination of NO. The pronounced dependence of the probability of the realization of this path of disintegration on the temperature indicates the importance of the vibrational excitation of the molecule for the formation of $(M-NO)^+$ ions.

It seemed of interest to compare the intensities of the $(M-NO)^+$ ion peaks with the π-electron energies (E^π) of structures A, B, and C. For this, we calculated the $E_A{}^\pi$, $E_B{}^\pi$, and $E_C{}^\pi$ values by means of the MO LCAO method within the Hückel approximation [12-14].

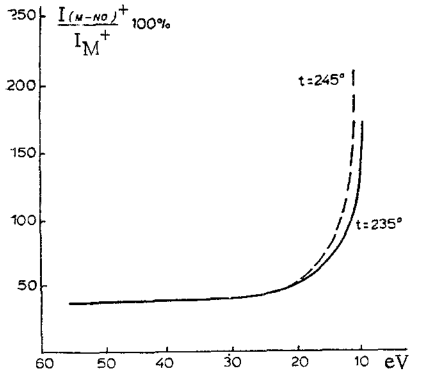


Fig. 1

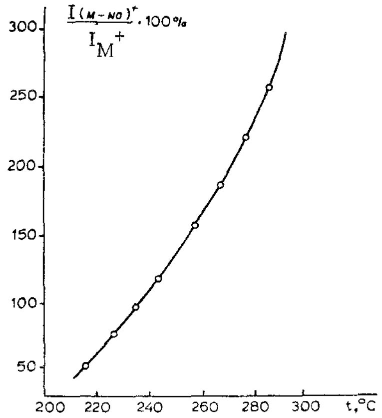


Fig. 2

Fig. 1. Dependence of the ratio of the intensities of the $(M-NO)^+$ and M^+ ion peaks on the ionizing electron energy for two inlet-system temperatures.

Fig. 2. Dependence of the ratio of the intensities of the $(M-NO)^+$ and M^+ ion peaks on the inlet-system temperature of the mass spectrometer at an ionizing-electron energy of 12 eV.

The results of the calculation show that the stability of the examined structures increases in the order $A < B \ll C$. Thus, a correlation between the intensity of the peaks and the π-electron energy of the fragments of the structures of the $(M-NO)^+$ ions is observed.

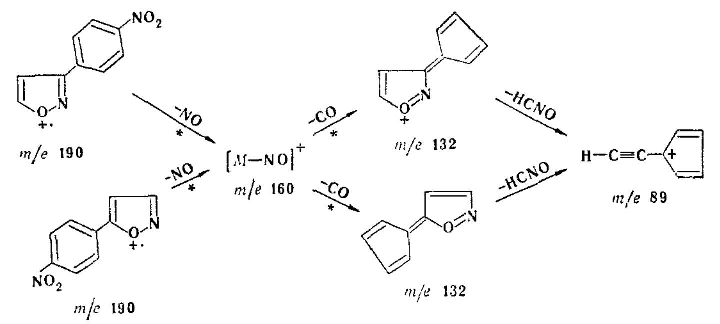
This result makes it possible to explain the interesting fact that the formation of $(M-H)^+$ ions in the mass spectra of methylisoxazoles (in the absence of interaction of the adjacent groups) is observed only when the methyl group is attached to the C^4 atom [15], in which case the formation of structures of the C type is possible.

The disintegration of the molecular ions of I and II includes the most important features of the dissociative ionization of unsubstituted 3- and 5-phenylisoxazoles [15]. Thus, intense $(M-H)^+$ ion peaks are present in the mass spectra of 3-phenylisoxazole and its nitro derivative (I). The formation of acyl $PhCO^+$ or $p\text{-}NO_2C_6H_4CO^+$ ions is characteristic for the dissociative ionization of 5-phenylisoxazole and 5-(p-nitrophenyl)isoxazole. Moreover, the introduction of a nitro group into the benzene ring leads to considerable complication of the mass spectra. Thus, the formation of $(M-O)^+$, $(M-NO)^+$, and $(M-NO_2)^+$ ions is observed in the dissociative ionization of I-III.

Despite the considerable difference in the structures of isomers I and II a series of peaks that correspond to the same mass numbers (160, 132, and 89) is present in their mass spectra. In all likelihood, these ions are formed as a result of the successive disintegration of the molecular ion:

$$M^{+} \rightarrow (M-NO)^{+} \rightarrow (M-NO-CO)^{+} \rightarrow (M-NO-CO-HCNO)^{+}.$$

Ions with mass 89, the peaks of which are distinguished by particularly high intensities, are of considerable interest. It is reasonable to assume that the conditions for the realization of the reaction $M^+ \rightarrow (M-NO-CO-HCNO)^+$ should ensure the effective formation of ions with mass 89 in the case of both isomers



II and III. It is seen from the disintegration schemes presented above that the probable structures of ions with mass 132 are favorable from the point of view of the possibility of their disintegration and the formation of ions with mass 89.

Taking into account the high intensities of the peaks of these ions, one should note the possibility of their additional stabilization due to rearrangement to the dehydrotropylium structure.

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