CHARGE MIGRATION IN THE MOLECULAR IONS OF ISOXAZOLE DERIVATIVES

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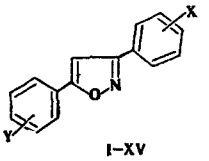
The effect of charge migration in the molecular ion on the dissociative ionization of isoxazole derivatives was examined. It is shown that charge redistribution between the substituent in the 3 position and the oxygen atom of the heteroring precedes isomerization of the molecular ion and its disintegration. The intensity of the peaks of the RCO^+ ions in the mass spectra of 5-R-3-arylisoxazoles increases as the acceptor effect of the aryl substituent becomes stronger. It is shown that the average internal energy with which the nitrobenzoyl ions are formed decreases as the probability of their formation increases, i.e., as the intensity of charge migration from the aryl substituent to the oxygen atom increases.

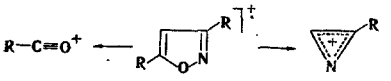
The effect of charge migration in the molecular ion on the path of disintegration of a compound upon electron impact has been noted by a number of investigators [1-4]. Continuing our research on the mass spectrometry of isoxazoles (for example, see [5-7]), we have arrived at the conclusion that, owing to the presence in molecules of these compounds of a labile N–O bond and several potential charge-localization centers, their dissociative ionization is controlled to a considerable extent by the charge distribution in the molecular ion. In addition to the systems considered previously, we have also obtained and investigated the mass spectra of a number of 3,5-diphenylisoxazole derivatives (I-XV).



I–XV

	X	Y		X	Y
I	*p*-NO_2	H	IX	*p*-Cl	*p*-NO_2
II	*m*-NO_2	H	X	*p*-Cl	*p*-Cl
III	*p*-Cl	H	XI	*p*-NO_2	*p*-Cl
IV	*p*-Br	H	XII	*p*-NO_2	*p*-NO_2
V	H	*p*-NO_2	XIII	*m*-NO_2	*m*-NO_2
VI	H	*m*-NO_2	XIV	*m*-NO_2	*p*-NO_2
VII	H	*p*-Cl	XV	*p*-NO_2	*m*-NO_2
VIII	H	*p*-Br			

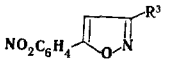
Charge migration in the molecular ion plays the decisive role under conditions of competitive disintegrations of bonds of comparable energies. Thus a shift in the intensities in favor of the formation of oxygen-containing ions is observed in the following order: isoxazole, 3,5-dimethylisoxazole, and 3,5-diphenylisoxazole [6].



43,0	R=H	95,0
72,5	R=CH_3	71,5
100.0	R=C_6H_5	6,7

K. A. Timiryazev Agricultural Academy, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 755-759, June, 1974. Original article submitted June 4, 1973.

TABLE 1. Effect of Substituents on the Probability of the Formation and Disintegration of Nitrobenzoyl Ions, $NO_2C_6H_4CO^+$, in the Mass Spectra of 5-Nitrophenylisoxazoles



Position of the NO_2 group in the $NO_2C_6H_4CO^+$ ion	R^3	Intensity ratios	
		$\frac{I_{150}+I_{120}+I_{104}}{\Sigma I}$, %	$\frac{I_{120}+I_{104}}{I_{150}}$, %
p	H	7,2	146,6
p	C_6H_5	17,7	72,3
m	C_6H_5	19,7	51,2
p	*p*-ClC_6H_4	28,5	47,1
p	*p*-$O_2NC_6H_4$	30,0	42,3
p	*m*-$O_2NC_6H_4$	30,7	33,9
m	*p*-$O_2NC_6H_4$	32,1	33,4
m	*m*-$O_2NC_6H_4$	35,6	23,0

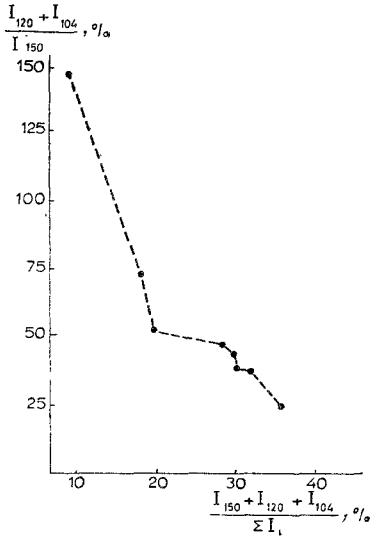
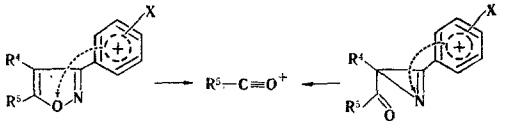


Fig. 1. Dependence between the values that characterize the probability of formation $[(I_{150}+I_{120}+I_{104})/\Sigma I_i, \%]$ and the probability of disintegration $[(I_{120}+I_{104})/I_{150}, \%]$ of nitrobenzoyl ions.

This fact is not only a consequence of an increase in the stability of the RCO^+ ions in the series R = H, CH_3, C_6H_5 but is also due to an increase in the fraction of RCO^+ ions due to charge migration from group R in the 3 position to the oxygen atom. On comparing the mass spectra of 3,5-diphenylisoxazole and 2-phenyl-3-benzoyl-1-azirine [8], one can see that the relative intensity of the peak of the benzoyl ion, $C_6H_5CO^+$, is considerably higher in the mass spectrum of the isoxazole derivative. On the other hand, the intensity of the peak with mass 116 $(M - C_6H_5CO)^+$ is higher than the mass spectrum of the azirine derivative.

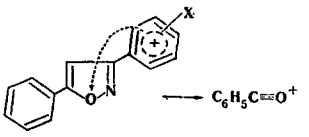
We investigated the mass spectra of the methyl ester and the amide of 3-(o-chlorophenyl)-5-methylisoxazole-4-carboxylic acid. These compounds undergo thermal isomerization to the corresponding azirine derivatives. In comparing the dissociative ionization of the isomers it was found that the intensity of the peaks of CH_3CO^+ ions is higher in the case of the isoxazole derivatives. We assumed that redistribution of the charge in the molecular ion occurs during ionization and subsequent isomerization prior to disintegration of the M^+ ion of the isoxazole derivative, during which the charge initially associated with ionization of the π-electron system of the substituent in the 3 position then migrates to the oxygen atom – the center of relative localization. Charge migration to the oxygen atom in the azirine structure is relatively hindered because of the energy barrier associated with the presence of a saturated carbon atom in the azirine ring. A result of this is the lower probability of the formation of RCO^+ ions in the case of the azirine derivative.



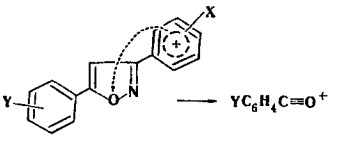
$I_{R^5CO^+}$	X	R^4	R^5	$I_{R^5CO^+}$
57,0	*o*-Cl	$CONH_2$	CH_3	44,3
42,4	*o*-Cl	$COOCH_3$	CH_3	31,8

It might be expected that the fraction of R^5CO^+ ions in the mass spectrum of the isoxazole derivative would increase as the electron-acceptor character and relative ionization cross section of the substituent in the 3 position increase. The formation of R^5CO^+ ions is one of the most important paths of dissociative ionization of isoxazole derivatives. In [4] the presence of an inverse dependence between the intensities of the peaks of the CH_3CO^+ ions and M^+ ions in the mass spectra of 3-aryl-5-methylisoxazole-4-carboxylic acids was shown. Thus the introduction of an NO_2 group into the benzene ring promotes charge migration

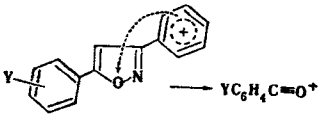
to the oxygen atom of the isoxazole ring and its disintegration to give CH_3CO^+ ions. On the other hand, the NH_2 group stabilizes the molecular ion. Thus charge distribution in M^+ may have a strong effect on its stability.



X = *p*-Br, *p*-Cl, *p*-NO_2, *m*-NO_2, H
$I_{C_6H_5CO^+}$ = 36,0; 32,8; 32,6; 29,2; 25,4

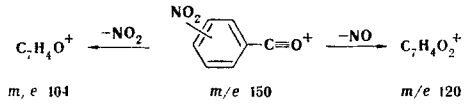


X = Y = *p*-Cl, *p*-NO_2, *m*-NO_2
$I_{YC_6H_4CO^+}$ = 38,0; 21.3; 28.9



Y = *p*-Cl, *p*-NO_2, *m*-NO_2
$I_{YC_6H_4CO^+}$ = 31,4; 10,3; 9,1

In an investigation of the dissociative ionization of 3,5-diarylisoxazoles we established that the intensity of the peak of the R^5CO^+ ions always increases when an acceptor substituent is introduced into the benzene ring attached to the C_3 atom. When Y = NO_2, substituent X has an appreciable effect not only on the probability of formation of $O_2NC_6H_4CO^+$ ions but also on the probability of their disintegration. These ions disintegrate via two competitive paths:



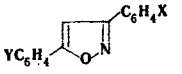
m/e 104 *m/e* 150 *m/e* 120

The sums of the intensities of the ion peaks ($I_{150}+I_{120}+I_{104}$) and the ($I_{120}+I_{104}$)/I_{150} ratios, which characterize the efficiency of the formation and disintegration of the nitrobenzoyl ions, respectively, are presented in Table 1. The introduction of substituent $R^3 = YC_6H_4$ (Y = H, p-Cl, p-NO_2, and m-NO_2) leads to an increase in I_{150} and the sum $I_{150}+I_{120}+I_{104}$. The higher the sum, the lower the $I_{120}+I_{104}/I_{150}$ ratio (Fig. 1). Consequently, the probability of the disintegration of $O_2NC_6H_4CO^+$ ions decreases as the probability of their formation increases. In other words, the average internal energy of these ions becomes lower.

EXPERIMENTAL

The mass spectra of I-XV were obtained with a Varian MAT CH-6 spectrometer (with a system for direct introduction of the sample into the ion source) at an ionizing voltage of 70 eV (50 eV in the case of I-IV). The ionization chamber temperature was 180°. Peaks of ions with intensities greater than 5% of the maximum peak are presented.

Mass spectra of arylisoxazoles I-XV



I (X = *p*-NO_2, Y = H): 51 (6,3), 77 (33,3), 95,5 (5,2), 105 (100,0), 106 (8,9), 266 (66,6), 267 (9,3)

II (X = *m*-NO_2, Y = H): 51 (5,0), 77 (31,6), 78 (9,3), 95,5 (5,9), 105 (100,0), 106 (9,3), 162 (5,5), 189 (5,3), 266 (56,3), 267 (13,2)

III (X = *p*-Cl, Y = H): 51 (6,5), 75 (5,0), 77 (34,4), 105 (100,0), 106 (9,2), 178 (6,0), 227 (6,5), 255 (39,3), 256 (6,9), 257 (14,0)

IV (X = *p*-Br, Y = H): 77 (30,4), 105 (100,0), 106 (7,7), 299 (24,0), 301 (24,6)

V (X = H, Y = *p*-NO_2): 50 (7,2), 51 (12,5), 63 (9,5), 76 (16,2), 77 (31,6), 89 (14,3), 104 (31,0), 105 (8,9), 116 (13,1), 120 (20,3), 144 (83,5), 145 (8,3), 150 (71,0), 151 (7,1), 165 (6,5), 191 (6,5), 192 (7,7), 219 (11,9), 220 (10,5), 265 (35,5), 266 (100,0), 267 (16,7)

VI (X = H, Y = *m*-NO_2): 39 (5,6), 43 (21,5), 50 (6,2), 51 (10,8), 63 (9,2), 75 (5,6), 76 (16,9), 77 (24,4), 89 (14,4), 92 (5,1), 103 (5,1), 104 (30,3), 105 (6,2), 116 (12,8), 121 (12,8), 133 (5,9), 144 (100,0), 145 (10,8), 150 (62,1), 165 (5,1), 192 (5,6), 219 (6,2), 220 (5,6), 265 (12,3), 266 (100,0), 267 (18,0)

VII (X = H, Y = *p*-Cl): 51 (7,5), 75 (6,8), 77 (9,9), 89 (7,9), 111 (26,5), 113 (10,4),

139 (100,0), 140 (7,7), 141 (34,4), 144 (17,4), 165 (5,0), 227 (6,8), 254 (14,9), 255 (59,4), 256 (15,4), 257 (19,6)

VIII (X=H, Y=*p*-Br): 39 (5,0), 43 (7,3), 50 (7,3), 51 (12,3), 57 (5,9), 63 (6,9), 75 (11,6), 76 (14,6), 77 (20,3), 89 (14,6), 94,5 (6,0), 105 (12,8), 116 (8,9), 144 (28,1), 155 (27,4), 157 (30,5), 165 (6,9), 183 (95,5), 184 (9,1), 185 (100,0), 186 (8,2), 220 (5,0), 271 (7,1), 273 (6,4), 298 (15,1), 299 (53,9), 300 (22,4), 301 (57,5), 302 (8,7)

IX (X=*p*-Cl, Y=*p*-NO_2): 63 (5,5), 79 (13,7), 76 (17,6), 89 (6,3), 92 (10,1), 111 (6,3), 120 (21,1), 123 (6,1), 137 (25,6), 150 (100,0), 151 (9,8), 153 (8,6), 178 (32,7), 180 (11,7), 219 (8,6), 300 (58,2), 301 (11,5), 302 (19,3)

X (X=Y=*p*-Cl): 75 (11,6), 111 (26,6), 113 (9,2), 139 (100,0), 140 (8,2), 141 (34,2), 219 (9,3), 289 (30,9), 290 (6,4), 291 (18,3)

XI (X=*p*-NO_2, Y=*p*-Cl): 75 (8,4), 95,5 (6,3), 111 (25,2), 113 (8,8), 139 (100,0), 140 (8,9), 141 (32,2), 300 (46,0), 301 (8,7), 302 (16,7)

XII (X=Y=*p*-NO_2): 43 (6,5), 50 (5,5), 57 (7,9), 59 (7,1), 63 (5,1), 75 (7,9), 76 (17,2), 89 (6,5), 92 (10,3), 104 (22,5), 117 (5,9), 120 (18,0), 143 (6,7), 150 (100,0), 151 (7,1), 189 (15,8), 190 (7,1), 311 (55,3), 312 (13,4)

XIII (X=Y=*m*-NO_2): 76 (15,5), 89 (6,2), 104 (21,7), 143 (6,5), 150 (100,0), 151 (9,2), 189 (17,7), 190 (8,6), 191 (5,5), 311 (57,4), 312 (12,4)

XIV (X=*m*-NO_2, Y=*p*-NO_2): 39 (6,8), 50 (16,2), 62 (9,4), 63 (10,5), 64 (6,0), 75 (13,4), 76 (26,8), 88 (6,0), 89 (11,0), 91 (7,1), 92 (18,3), 104 (24,4), 120 (9,9), 143 (7,1), 150 (100,0), 151 (10,4), 189 (15,7), 190 (8,6), 191 (6,3), 311 (66,0), 312 (13,4)

XV (X=*p*-NO_2, Y=*m*-NO_2): 39 (5,3), 50 (12,7), 63 (9,0), 76 (12,0), 76 (29,4), 89 (12,7), 92 (7,4), 104 (29,4), 120 (4,0), 143 (7,8), 150 (100,0), 151 (9,0), 189 (16,1), 190 (8,0), 191 (6,0), 311 (62,0), 312 (11,1).

LITERATURE CITED

1. F. W. McLafferty, J. Amer. Chem. Soc., 89, 5043 (1967).
2. H. Bruderer, W. Richter, and W. Vetter, Helv. Chim. Acta, 50, 1917 (1967).
3. A. Mandelbaum and K. Biemann, J. Amer. Chem. Soc., 90, 2975 (1968).
4. T. H. Kinstle and W. R. Oliver, J. Amer. Chem. Soc., 91, 1864 (1969).
5. H. Nakata, H. Sakurai, H. Yoshirumi, and A. Tatematsu, Org. Mass Spectrom., 1, 199 (1968).
6. K. K. Zhigulev, R. A. Khmel'nitskii, M. A. Panina, I. I. Grandberg, and B. M. Zolotarev, Khim. Geterotsikl. Soedin., 889 (1972).
7. K. K. Zhigulev, R. A. Khmel'nitskii, S. D. Sokolov, and N. M. Przheval'skii, Khim. Geterotsikl. Soedin., 453 (1974).
8. K. K. Zhigulev, R. A. Khmel'nitskii, and M. A. Panina, Khim. Geterotsikl. Soedin., 457 (1974).