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MASS-SPECTROMETRIC BEHAVIOR OF ISATIN OXIMES

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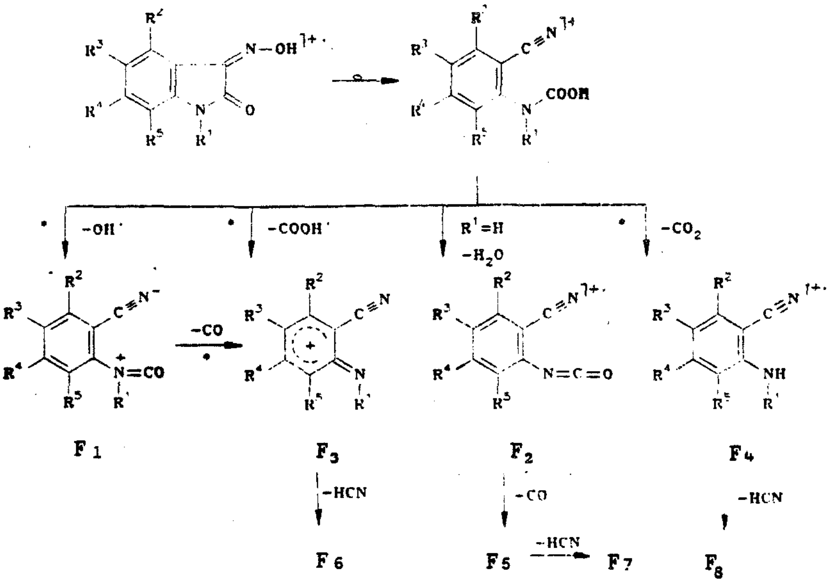
On the basis of an analysis of the mass spectra of a large series of benzo-substituted isatin oximes it is shown that their molecular ions undergo type II Beckmann rearrangment to the corresponding o-N-carboxyaminobenzonitriles.

It is known that, like many benzolactams [1], oxindole under electron impact loses a molecule of CO with the formation of an ion that has a structure similar to that of a 2-methyl nitrene, since its subsequent fragmentation coincides with the fragmentation of the $[M - N_2]^+$ ion of a 2-methyl azide [2]. The fragmentation of the molecular ion (M^+) of isatin is also determined by primary elimination of a molecule of CO, chiefly from the 2 position [3-5]. The same primary fragmentation process (the loss of CO) is also characteristic for the M^+ ions of 3-aryl-iminoisatins [5] and isatin 3-thiosemicarbazones [6]. Up until now, the mass-spectrometric behavior of isatin-3-oximes has not been investigated, even though it is known that such 3-hydroxyiminolactams may exist in several tautomeric forms [7], and thermal type II Beckmann rearrangement, which takes place at temperatures above 200°C [8-11] in vacuo [10] and leads to o-aminobenzonitriles, has been observed for isatin oximes. Since transformations of M^+ ions that are similar to certain reactions of the same compounds in the condensed phase are frequently observed under the conditions of mass-spectrometric experiments [12-15], we studied the behavior of a series of isatin 3-oximes I-XII under electron impact.



An M^+ peak, the intensity of which (Table 2) depends to a considerable degree on the character of the substituent and its position in the benzene ring, is observed in the mass

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TABLE 1. Mass Spectra of I-XIII

Compound	mp, °C	Mass spectra,* m/z (relative intensity, %)
I	224	162 (31), 145 (12), 144 (20), 132 (12), 118 (100), 117 (14), 116 (7), 91 (40), 90 (13), 64 (14), 63 (13)
II	191—193	176 (87), 159 (29), 158 (28), 132 (36), 131 (100), 130 (20), 129 (17), 104 (16), 103 (37), 77 (16), 63 (10)
II-D_3	189—190	179 (100), 162 (40), 160 (64), 135 (34), 134 (62), 133 (34), 118 (24), 107 (30), 106 (28), 91 (20), 78 (26)
III	220	176 (59), 169 (30), 158 (100), 131 (36), 130 (28), 116 (26), 115 (43), 105 (36), 104 (69), 89 (26), 78 (39)
IV	243,5	176 (43), 159 (11), 158 (12), 132 (55), 131 (100), 130 (5), 105 (3), 104 (8), 103 (2), 77 (7), 51 (4)
V	229	176 (9), 159 (4), 158 (3), 132 (100), 131 (75), 130 (4), 105 (3), 104 (9), 103 (2), 78 (4), 77 (9)
VI	242—243	176 (100), 159 (31), 158 (15), 132 (11), 131 (52), 129 (11), 104 (10), 103 (18), 89 (15), 78 (15), 77 (10)
VII	>260	240† (7), 222† (15), 196† (21), 146 (19), 115 (17), 105 (26), 104 (100), 91 (18), 90 (24), 77 (27), 63 (17)
VIII	185	212 (2), 194 (10), 169 (10), 168 (100), 141 (7), 140 (17), 132 (2), 131 (3), 114 (6), 113 (3), 91 (2)
IX	202—204	216 (55), 200 (43), 119 (91), 198 (100), 197 (35), 171 (36), 139 (11), 114 (6), 97 (5), 83 (5), 63 (5)
X	225—227	212 (0,5), 194 (64), 168 (100), 166 (7), 141 (4), 140 (14), 139 (11), 114 (6), 97 (5), 83 (5), 63 (5)
XI	>300	216 (47), 199 (21), 198 (55), 172 (39), 171 (28), 170 (100), 169 (55), 155 (25), 144 (25), 115 (24), 91 (22)
XII	245—247	216 (100), 199 (36), 198 (50), 188 (50), 172 (27), 171 (40), 170 (60), 156 (24), 144 (38), 116 (22), 115 (22)
XIII	175—175,5	176 (100), 145 (29), 144 (10), 118 (29), 117 (49), 116 (6), 102 (11), 90 (22), 76 (6), 64 (6), 63 (8)

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*The molecular-ion peak and the 10 most intense peaks are presented.

†Ions that contain the ^{79}Br isotope.

spectra of all of the investigated compounds. The most stable M^+ ions were those of 1-methyl-, 5-methyl-, and 7-methylisatin-3-oximes (II, IV, VI) and 5,6-tetramethyleneisatin-3-oxime (XII), i.e., compounds in which a substituent with a + I effect is located in the ortho or para position relative to the heteroring nitrogen atom. The introduction of a methyl group in the 4 position (III) or 6 position (V) of the benzene part of the molecule and of a bromine atom in the 5 position (VII) or benzo-annelation in the 4,5 (VII) or 6,7 (X) positions leads to a sharp decrease in W_M; in contrast to the data in [16], aromatization of IX and XI (conversion to benzo derivatives VIII and X) makes the molecules less resistant to electron impact. All of these facts suggested that, as a result of ionization, the heterocyclic ring of isatin is destroyed, and the M^+ ion undergoes isomerization (rearrangement) to the acyclic form of the corresponding o-N-hydroxycarbonylaminobenzonitrile.

Isomerization takes place precisely in the M^+ ion and is not the result of thermal action prior to ionization, since the temperatures at which the mass spectra were recorded did not exceed 100-120°C. The occurrence in the M^+ ions of a type II Beckmann rearrangement is also indicated by the character of their fragmentation. Thus the peaks of $[M - CO]^+$ ions, which are characteristic for isatins and their 3-oximes [2-5], as well as peaks of $[M - NO]^+$ or $[M - NHOH]^+$ ions, which are typical for the mass spectra of oximes, particularly the oximes of tetralone and other cyclic ketones [16-18], are absent in all of the mass spectra. At the same time, the M^+ ions of I-XII readily eliminate OH (F_1), H_2O (F_2), and, successively, OH and CO particles (F_3), as well as CO_2 (F_4) (see the scheme); the formation of F_1, F_3, F_4, and F_6 ions is generally confirmed by metastable transitions. In addition, the elementary compositions of the F_1-F_7 ions in the mass spectra of III and VI were established by the accurate determination of the masses of these ions (Table 3).

Shifts of the mass numbers of the F_1, F_3, and F_4 ions (3 amu) and of the F_2 ion (2 amu) were observed in the mass spectrum of 3-hydroxyimino-1-trideuteromethyloxindole (II-D_3); this demonstrates the participation of the 1-methyl hydrogen atoms in the loss of water by the molecular ion, i.e., it also confirms the noncyclic form of the M^+ ion. In complete conformity with the fragmentation scheme, shifts of the masses of the F_1, F_3, and F_8 ions (1 amu) and the F_4 ion (2 amu) were observed in the mass spectrum of I-D_2, which contains deuterium atoms in the hydroxy group and attached to the nitrogen atom; the mass numbers of the F_2, F_5, F_6, and F_7 ions did not change.

TABLE 2. Intensities of the Principal Characteristic Ions in the Mass Spectra of Oximes I-XII (% Σ_{39})

Compound*	R^2	R^3	R^4	R^5	W_M	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8
I	H	H	H	H	10,3	3,9	6,4	4,3	31,2	2,2	1,2	4,1	12,5
II	H	H	H	H	22,2	6,9	6,7	24,1	6,2	4,8	8,8	3,8	1,7
III	CH_3	H	H	H	7,7	2,1	11,4	4,0	2,3	3,2	1,3	7,9	4,0
IV	H	CH_3	H	H	18,8	4,5	4,8	41,6	22,8	1,8	1,1	3,2	1,2
V	H	H	CH_3	H	4,2	1,6	1,1	33,0	43,9	1,9	0,8	4,0	1,3
VI	H	H	H	CH_3	27,0	7,2	3,3	12,0	2,6	1,8	4,1	2,3	1,0
VII	H	Br	H	H	3,6	0,5	8,1	—	10,8	—	—	—	6,9†
VIII	$-(CH)_4-$		H	H	1,4	—	6,0	—	62,1	—	—	—	4,1
IX	$-(CH_2)_4-$		H	H	6,9	9,6	10,5	3,8	2,3	10,5	3,8	2,1	—
X	H	H	$-(CH)_4-$		0,4	—	28,6	—	43,0	3,0	—	4,5	1,9
XI	H	H	$-(CH_2)_4-$		9,6	2,6	10,1	5,0	7,0	18,0	4,5	—	—
XII	H	$-(CH_2)_4-$		H	16,5	4,9‡	6,8	5,4	3,7	8,1	5,2	1,9	—

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*For I and III-XII, $R^1 = H$; for II, $R^1 = CH_3$.

†The F_4 ion initially loses a Br atom [m/z 117 (3.0%)] and then a molecule of HCN.

‡In addition, an $[M - C_2H_4]^+$ ion (6.8%) is observed.

TABLE 3. High-Resolution Mass Spectra of III and VI

Compound	Found	Ion	Elementary composition	Calc.
VI	159,0542	F_1	$C_9H_7N_2O$	159,0558
III	158,0455	F_2	$C_9H_8N_2O$	158,0480
VI	158,0456	F_2	$C_9H_8N_2O$	158,0480
III	132,0668	F_4	$C_8H_8N_2$	132,0687
VI	132,0676	F_4	$C_8H_8N_2$	132,0687
III	131,0595	F_3	$C_8H_7N_2$	131,0578
VI	131,0591	F_3	$C_8H_7N_2$	131,0578
III	129,0454	$[F_2 - CHO]^+$	$C_8H_5N_2$	129,0458
III	105,0523	F_5	C_7H_7N	105,0578
III	104,0502	F_6	C_7H_6N	104,0500
VI	104,0504	F_6	C_7H_6N	104,0500
VI	103,0429	F_7	C_7H_5N	103,0426

The mass spectrum of the thermally stable 3-methoxy-iminooxindole (XIII), which we synthesized, showed that, in addition to a maximum M^+ peak and an intense $[M - OCH_3]^+$ ion peak (145),* peaks of $[M - HNCO]^+$ (133)* and $[M - OCH_3 - HCN]^+$ (118)* ions are observed in it (see Table 1), the 145 → 118 + 27 transition is confirmed by the metastable ion with an apparent mass of 96.0 (calculated value 96.0), which can be possible only in the case of a cyclic lactam form of the M^+ ion of XIII.

Thus an analysis of the mass-spectrometric behavior of isatin oximes makes it possible to establish a similarity in their mass-spectrometric and thermal behavior.

As we were putting this paper into its final form, we became aware of a communication [19] in which the mass spectrum of isatin-3-oxime (I) was briefly described. However, the presented hypothetical fragmentation scheme was not confirmed by more thorough investigations (high-resolution spectra and metastable ions) and therefore evidently cannot lay claim to serious validity. At the same time, an analysis of the ions presented in this paper does not contradict our proposed rearrangement of the molecular ion.

EXPERIMENTAL

The mass spectra were recorded with MKh-1303 and MAT-112 spectrometers with direct introduction of the substances into the ion source at ionization energies of 50 and 70 eV. The high-resolution mass spectra were obtained with an MAT-311 spectrometer by the peak-coincidence method.

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*These are the m/z values.

The synthesis of the isatin oximes was accomplished by the methods in [9-11]; the constants of the compounds obtained are presented in Table 1. Compound II-D_3 was synthesized in analogy with the method in [10, 18], and XIII was synthesized in analogy with the method in [20]. Deuterium derivative I-D_2 was obtained by threefold dissolving of I in CH_3OD with successive evaporation of the solutions in vacuo. According to the mass spectrum, the product contained 89% and 11%, respectively, of the di- and monodeuterated analogs.

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