MASS-SPECTROMETRIC STUDY OF THE CYCLIZATION OF DIAZO COMPOUNDS.

10.* 2-DIAZOMALONIC ACID AMIDES. MASS SPECTRA OF THE NEGATIVE IONS

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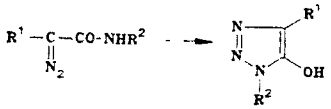
The mass spectra of the negative ions of the dissociative resonance capture of electrons of diazo amides and the isomeric triazoles were studied. The molecular negative ions of these compounds are unstable and do not undergo interisomerization. The principal fragmentation process involves the elimination of a molecule of nitrogen and transformation of the resulting $[M - N_2]^-$ ions to the heterocyclic form, which is the same for the two isomers.

It has been shown [1] that 2-diazo-2-cyanoacetamides and the isomeric 4-cyano-5-hydroxy-1,2,3-triazoles in the gas phase under electron impact form molecular ions M^+, which do not undergo interisomerization. The cyclization of the M^+ ions of a large number of diazo ketones with the elimination of a molecule of nitrogen and the formation of pseudomolecuar ions of heterocyclic compounds has been studied [2-4]; the cyclization occurs in those cases in which a similar reaction in solution, which is catalyzed by acidic agents, where the primary act is protonation of the carbon atom of the diazo group with the formation of a positively charged ion, is possible. Since the bombardment of diazo compounds with electrons leads to the formation of positively charged ions in which the charge is generally localized on the carbon atom of the diazo group, one observed analogies in the behavior of this class of compounds in the gas phase under electron impact and in solution under the influence of acidic agents [2-4]. A fundamentally different cyclization mechanism is characteristic for diazomalonic acid derivatives I. These compounds are resistant to the action of acids (with the exception of hydrohalic acids), while bases can split out a proton from the amide group with subsequent 1,5-electrocyclization of the resulting anion to 1,2,3-triazolate anions, treatment of which with acid leads to triazoles II [6].



I a-c II a-c

I, II a R^1=CN, R^2=H; b R^1=CN, R^2=CH_3; c R^1=$CONH_2$, R^2=H

An attempt to carry out a similar reaction in the chamber of a mass spectrometer by bombardment of molecules of diazo compounds I with electrons was therefore unsuccessful [1], but since an anion radical is formed in the dissociative resonance capture of an electron, one might have expected that it would behave like the anion formed in solution by the action of bases.

The dissociative resonance capture of electrons by molecules of the investigated compounds occurs in four resonance regions of the energies of the electrons. The peaks of the ions of the first resonance region at electron energies of ~0.1-0.2 eV have the greatest intensities. In the other three regions at electron energies of 1.5, 5.0, and 7.5 eV the cross sections of the formation of ions are two to three orders of magnitude lower.

The relative intensities of the peaks of the negative ions of the first resonance region are presented in Table 1. The molecular negative ions M^- themselves are unstable and were not recorded in any of the gas spectra. The principal process in the fragmentation of M^- is

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*See [1] for communication 9.

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TABLE 1. Relative Intensities of the Peaks of the Fragment Ions in the Mass Spectra of I and II (in percent relative to the maximum peak in the spectrum)

Compound	$[M-H]^-$	$[M-N_2]^-$	$[M-N_2, -NH_2]^-$	$[M-N_2, -H_2O]^-$	$[M-N_2, -NHCH_2]^-$	$[M-N_2, -HNO]^-$	NCO^-	$HC_2N^{-\cdot}$	$CN^{-\cdot}$
Ia	0,015	52,6	100,0				18,4	5,5	1,0
IIa	9,2	53,0	100,0				22,4	23,6	2,7
Ib	0,01	9,0	3,2		100,0		0,03	1,3	0,025
IIb	530,0*	10,0	3.2		100,0		0,06	1,5	0,10
Ic		100,0	4,3	2.2		0,17	0,52	0,32	
IIc		100.0	5,6	2,3		0.25	0,35	0,52	

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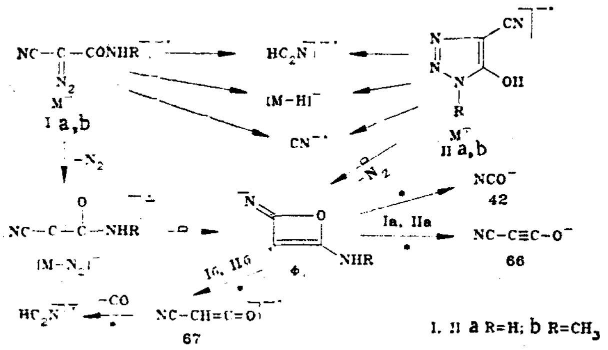
*The intensities are the values relative to the $[M-N_2, -NHCH_2]^-$ ion for greater clarity.

the ejection of a molecule of nitrogen. The $[M-N_2]^-$ ions exist in a vibrationally excited state with average lifetimes τ = 250-350 μsec relative to the ejection of an electron. The multipath fragmentation of the molecular ions [5] of Ia, b and IIa, b can be represented by general Scheme 1, which is confirmed by the peaks of metastable ions.

Scheme 1



The principal processes involved in the fragmentation of the $[M-N_2]^-$ ions in the mass spectra of Ia and IIa lead to the formation of NCO^- and NC_3O^- fragments. To make such processes possible, the primary $[M-N_2]^-$ ions formed in the fragmentation of both the linear (I) and cyclic (II) isomers should be transformed. The four-membered heterocyclic form of the fragment (F_1) presented in Scheme 1 is the most likely form.

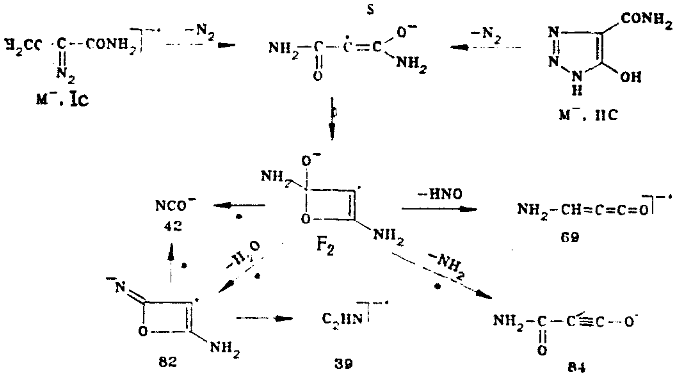
The presence of methyl substituents in Ib and IIb leads to the development of a new pathway for the fragmentation of the $[M-N_2]^-$ ion, which involves migration of a hydrogen atom with the simultaneous splitting out of a molecule of CH_2NH. The advantageousness of this process leads to suppression of other fragmentation pathways, particularly any involving the formation of an NCO^- ion (see Table 1).

The pair-by-pair comparison of the intensities of the peaks of the common fragment ions in the mass spectra of isomeric Ia and IIa and Ib and IIb makes it possible to note close values of the relative intensities of the fragments formed from the $[M-N_2]^-$ ions and differences — occasionally extremely substantial — in the intensities of the ions formed directly from the M^- ions. Consequently, one may draw a conclusion regarding the different structures of the M^- ions of the linear and cyclic isomers and the single structure of the $[M-N_2]^-$ ions of these compounds.

The mass spectra of Ic and IIc are virtually identical (see Table 1). The principal fragmentation pathways are due to the initial formation of an $[M-N_2]^-$ ion and are presented in Scheme 2. A second amide group opens up a new pathway for fragmentation of the $[M-N_2]^-$ ions, viz., ejection of a molecule of water. The $[M-N_2, -NH_2]^-$ ions in this case are formed in the ground state and do not undergo subsequent fragmentation. The formation of a common four-membered heterocyclic structure for both isomers probably also occurs in this case. This is attested to by both the common fragmentation pathways and the identical relative intensities of the peaks of the resulting secondary fragment ions (see Table 1). Precisely this structure may explain the parallel splitting out of H_2O, $NH_2\bullet$, and $HNO\bullet$ particles, as well as the formation of an NCO^- ion.

In this case one cannot speak unequivocally of the identical character of the structure of the M^- ions for isomers Ic and IIc: with the exception of splitting out of a molecule of N_2 from M^-, other fragmentation processes that could determine the structures of these ions do not occur. Starting from the completely identical character of the mass spectra of Ic and IIc one might have concluded that the M^- ions of the isomers have a common structure; however, there is no reliable evidence for this. If the isomerization of M^- does not occur, the ejection of a molecule of nitrogen in the fragmentation of both isomers with subsequent transformation of the $[M - N_2]^-$ ion leads to a fragment with the same structure (F_2).

Scheme 2



On the whole, it should be noted that, although evidence for the interisomerization of the M^- ions of I and II was not obtained in an analysis of the mass spectra of the negative ions of these compounds, the question of modeling of cyclization in solution under the influence of alkalis by means of mass spectra of this type remains open. One should evidently turn to compounds whose M^- ions will be more stable. In this case cyclization of the linear M^- ions will be considerably more likely.

EXPERIMENTAL

The investigated compounds were synthesized by the methods of [6]. The mass spectra of the negative ions were recorded with an MI-1201 spectrometer remodeled for recording negative ions [7] at sample temperatures of 20-120°C, depending on the volatility of the compound.

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