Resonant dissociative electron capture by simple tripeptides

M. V. Muftakhov and P. V. Shchukin*

Institute of Molecule and Crystal Physics, Ufa Research Center of the Russian Academy of Sciences, 51 prospekt Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347) 235 9522. E-mail: LMSNI@anrb.ru

The processes of resonant electron capture by tripeptide molecules of diglycylalanine and trialanine were studied in the electron energy range 0—14 eV. The experimentally observed H-shift rearrangement reactions, metastable dissociations of fragmentation ions, and electron autodetachment processes by the fragmentation ions indicate that short-lived molecular negative ions are formed in vibrationally excited states in the whole energy range and their subsequent fragmentation occurs predominantly *via* nonradiative transitions. The characteristic reactions in negative ions of peptides were identified and considered to be model reactions in protein decomposition processes through electron-molecular interactions.

Key words: mass spectrometry, resonant electron capture, negative ions, diglycylalanine, trialanine.

Considerable interest in studying negative ions (NIs) of biologically significant compounds (nitrogenous bases of nucleic acids, sugars, and amino acids representing elementary units of DNA, RNA, and protein macromolecules) appeared after the processes of nucleic acid decomposition due to the interaction with low-energy (up to "zero") electrons were found.[1] This discovery turned over the traditional concept that biomolecules can decompose only upon the interaction with electrons with an energy higher than the ionization potential of the molecules. As experimentally shown, the efficiency of the decomposition of nucleic acids on collisions with low-energy electrons has a resonant character and attains a maximum in two energy regions of 0—4 and 6—15 eV: one thread is cleaved in the first region, and one- and two-thread cleavages of the DNA chain are observed in the second region. This fact suggested that the degradation of DNA molecules occurs due to the resonant capture of electrons resulting in the formation of a short-lived molecular negative ion (MNI), which further decomposes in dissociative reactions. It is most likely that similar processes can also occur in protein molecules upon collisions with low-energy electrons, but the study of reactions of NIs of amino acids[2—9] provides no exhaustive information on this problem.

To elucidate this problem, we started the cycle of studies of oligopeptides consisting of amino acid residues glycine (Gly) and alanine (Ala). When choosing objects of the study it was assumed that an insignificant difference in the side substituent at the C_α atom in amino acids (H atom in Gly and Me group in Ala) does not drastically affect the total pattern of ion formation in peptides but will help to identify the elemental composition and structure of formed NIs. The NIs from dipeptides diglycine (Gly-Gly), dialanine (Ala-Ala), and glycylalanine (Gly-Ala) were studied in the previous works.[10—12]

This work is devoted to the study of processes of resonant capture of energy-controlled electrons by tripeptide molecules of diglycylalanine (Gly-Gly-Ala) and trialanine (Ala-Ala-Ala).

Experimental

Experiment was carried out on a MI—1201V magnetic mass spectrometer (Sumy, Ukraine) modified for the work with negative ions.[13] Electrons emitted by the cathode interacted in the ionization chamber with vapors of the samples to form negative ions. The latter were taken out of the chamber, formed into a beam, accelerated by masses in a magnetic analyzer, and detected with a secondary electron multiplier. The electron beam energy was controlled with a computer in which the detected ionic signal was synchronously injected. An additional electrode was mounted in the area of an ion receiver for the deviation of the charged component of the ion beam in the transverse electrical field and detection of neutrals formed by electron autodetachment for the flight of ions through the second fieldless region.[13] The electron energy scale was calibrated by the resonance peak maxima SF_6^-/SF_6 (~0 eV) and $[M - H]^-$/MeCOOH (~1.55 eV).[14] The mass resolution of the instrument was ~2000 at the closed slit of the ion receiver, which makes it possible to separate the curves of the effective yield of isobaric ions. Since the intensity of the ionic signal was lowered, the main work was carried out with an open slit of the receiver, which made it possible to detect low-intensity ions.

Samples of the compounds were purchased at Sigma/Aldrich Chemical Co. The studied sample was placed on the bottom

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of the ionization chamber from where it was vaporized due to heating. An experiment with the Ala-Ala-Ala samples was carried out at the temperature of the chamber ~190 °C, and that with Gly-Gly-Ala was carried out at ~220 °C. Unlike using the tube for direct injection of solid samples, this procedure provides a necessary vapor pressure in the chamber at fairly low heating temperatures, which is very important for the work with peptides. The fact that the color of the sample remained unchanged after the experiment confirms the absence of thermodestructive processes.

Results and Discussion

An analysis of the experimental data suggested that the processes of NIs of tripeptides are similar to those for the earlier studied dipeptides, whereas the observed insignificant differences are caused by sizes of the molecules only. Based on the results[10] for Gly, Ala, Gly-Gly, Gly-Ala, and Ala-Ala, we reconstructed some reactions for NIs from tripeptides, which are presented below without detailed substantiation. These reactions do not exhaust the whole variety of processes of dissociative capture of electrons by tripeptide molecules but are characteristic because represent the main directions of fragmentation of MNIs from any peptides. Thus, they can be considered as model reactions in the processes of protein decomposition upon the interaction with low-energy electrons for the determination of the role of each reaction in the processes. At the same time, these reactions contain information about the mechanisms of fragmentation of MNIs of peptides in the excited state and, hence, they are of general interest for the theory of resonant electron scattering on molecules in respect of the adaptation of its statements applied to processes in polyatomic NIs.

Reaction schemes. The resonant capture of electrons by Gly-Gly-Ala and Ala-Ala-Ala molecules occurs in the energy range 0—12 eV and results in the formation of various fragmentation NIs, whose dependences of the effective yield on the electron energy (E) are shown in Figs 1 and 2. The whole energy range in which the resonance peaks of NIs were detected was conventionally divided into three regions: low-energy (<4 eV), medium-energy (4—7 eV), and high-energy (>7 eV). In the low-energy region, MNIs decompose *via* less number of channels than in other energy regions but with a much higher efficiency. This reaction is characteristic by intense H-shift processes in MNIs, and the rearrangement ions contribute mainly to the full ionic current. In the energy region higher than 4 eV, molecular ions undergo fragmentation through the simple bond cleavage, whereas the low-intensity isomerization processes occur in fragmentation ions.

Selected reactions of MNI decomposition from molecules M = $NH_2CH(R)CONHCH(R)CONHCH(CH_3)$-COOH (R = H (Gly-Gly-Ala), Me (Ala-Ala-Ala)) are grouped according to energy regions and the type of cleaved bonds.

Low-energy region. In the low-energy energy, ions $[M - H]^-$ are formed with high intensity by the attachment of the H atom of the carboxy group

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CONHCH(Me)COO^- + H^\cdot \quad (1)$$

m/z 202 (R = H), *m/z* 230 (R = Me).

This decomposition channel is characteristic of the earlier studied amino acids[4—10] and dipeptides[10] in which ions $[M - H]^-$ are formed by the pre-dissociation of MNIs generated by vibrationally excited resonance (dipole-bound state) and the shape resonance (valent state with one electron on the lowest unoccupied molecular orbital).

Other examples for reactions of simple bond cleavage (cleavage of the central N—C_α bonds) are presented below

$$M + e \longrightarrow NH_2CH(R)CONH^- + CH(R)CONHCH(Me)COOH^\cdot \quad (2)$$

m/z 73 (R = H), *m/z* 87 (R = Me),

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CONH^- + CH(Me)COOH^\cdot \quad (3)$$

m/z 130 (R = H), *m/z* 158 (R = Me).

Ions with the structure $XCOO^-$ were identified, which is similar to the structure of ions $[M - H]^-$, are caused by the migration of the H atom of the COOH group to the N atoms followed by the central bond cleavage. For example, the radical ions are formed by the dissociation of the N—C_α bonds

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CONH_2 + CH(Me)COO^{\cdot -} \quad (4)$$

m/z 72 (R = H, Me),

$$M + e \longrightarrow NH_2CH(R)CONH_2 + CH(R)CONHCH(Me)COO^{\cdot -} \quad (5)$$

m/z 129 (R = H), *m/z* 143 (R = Me),

$$M + e \longrightarrow NH_3 + CH(R)CONHCH(R)CONHCH(Me)COO^{\cdot -} \quad (6)$$

m/z 186 (R = H), *m/z* 214 (R = Me),

and the cleavage of the peptide bonds results in the formation of fragmentation ions with the filled electron shell

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CO^\cdot + NH_2CH(Me)COO^- \quad (7)$$

m/z 88 (R = H, Me),

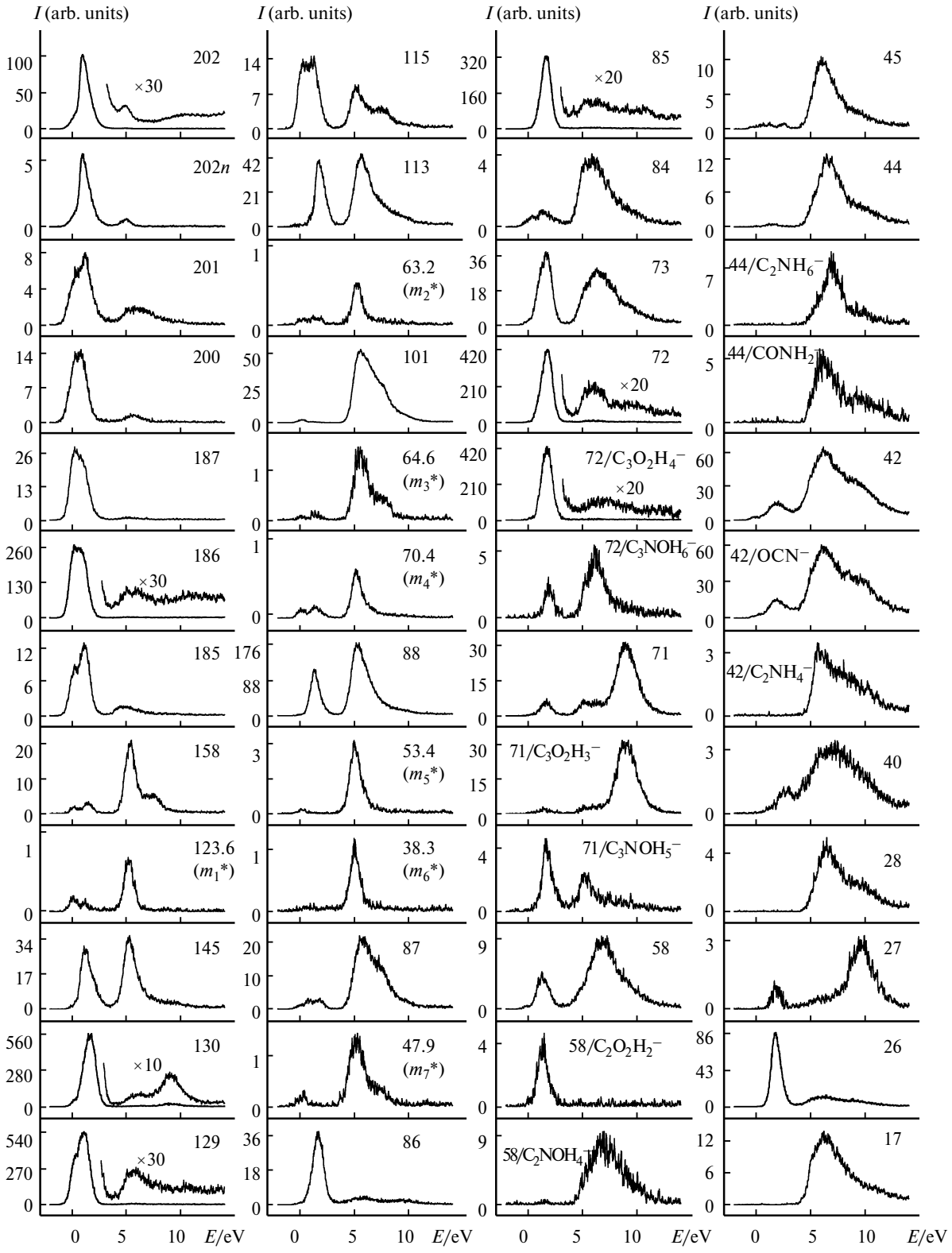

Fig. 1. Curves of the effective yield of NIs from Gly-Gly-Ala (ion source without an electronic monochromator, $\Delta E_{1/2} = 0.56$ eV). The mass number (m/z) of ions is shown in the upper right corner. The overall curves of the effective yield and individual curves recorded with the broad and narrow slits of the ions receiver, respectively, are presented for isobaric ions with m/z 72, 71, 58, 44, and 42.

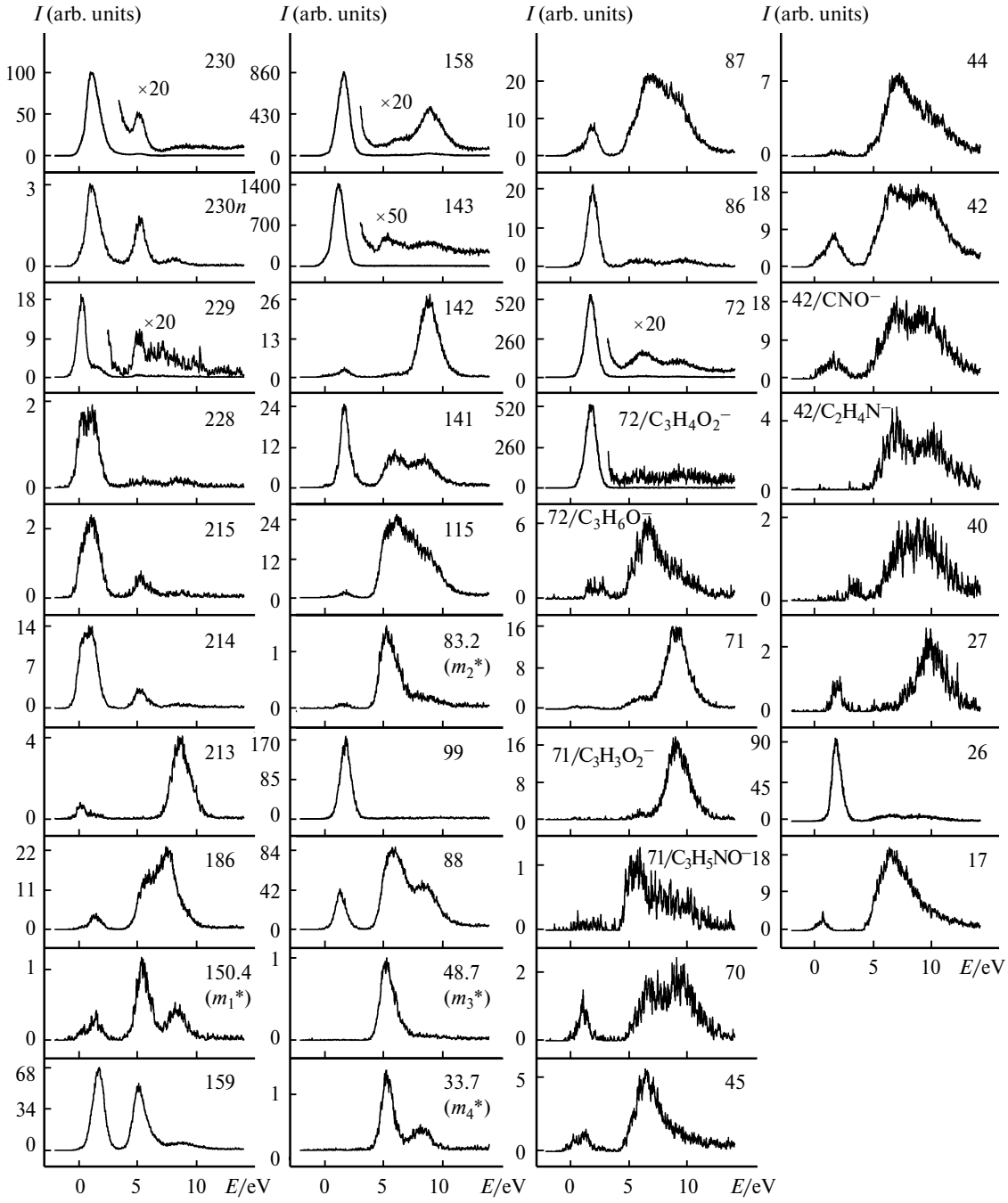

Fig. 2. Curves of the effective yield of NIs from Ala-Ala-Ala (ion source without an electronic monochromator, $\Delta E_{1/2} = 0.54$ eV). The mass number (m/z) of ions is shown in the upper right corner. The overall curves of the effective yield and individual curves recorded with the broad and narrow slits of the ions receiver, respectively, are presented for isobaric ions with m/z 72, 71, and 42.

$$M + e \longrightarrow NH_2CH(R)CO^{\cdot} + NH_2CH(R)CONHCH(Me)COO^- \quad (8)$$

m/z 145 (R = H), m/z 159 (R = Me).

The mechanism of these reactions in MNIs of dipeptides was discussed earlier,[10] and it was concluded that they can occur in conformers with an intramolecular hydrogen bonds between the H atom of the carboxy group and the nitrogen atom of the amine or amide groups. The metastable peaks with imaginary m/z 56.0 and 68.5 in the mass spectra of Gly-Gly-Ala and Ala-Ala-Ala, respectively, indicate that ions $[M—NH_2CH(R)CONH_2]^{\cdot}$ (product of reaction (5)) undergo intensive fragmentation

with the rejection of the CO_2 molecule. No similar process was observed in NIs of dipeptides.

Another example for the rearrangement process in MNIs of tripeptides is the concerted reaction leading to the low-intensity fragmentation ion of the cyclic structure

$$M + e \longrightarrow cyclo(\text{—}CH(R)C(O)NCH(R)C(O)NH\text{—})^- + \\ + H^{\cdot} + NH_2CH(Me)COOH \quad (9)$$

m/z 113 (R = H), *m/z* 141 (R = Me).

It follows from the published results[10] that this reaction occurs in the conformer with the intramolecular hydrogen bond between the H atom of the amine group and the nitrogen atom of the amide group.

Medium-energy region. The following reactions of simple cleavage of the central bonds in MNIs of tripeptides were identified in the medium-energy region:

(a) dissociation of peptide bonds

$$M + e \longrightarrow NH_2CH(R)CO^{\cdot} + \\ + NHCH(R)CONHCH(Me)COOH^- \quad (10)$$

m/z 145 (R = H), *m/z* 159 (R = Me),

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CO^{\cdot} + \\ + NHCH(Me)COOH^- \quad (11)$$

m/z 88 (R = H, Me),

$$M + e \longrightarrow NH_2CH(R)CO^- + \\ + NHCH(R)CONHCH(Me)COOH^{\cdot} \quad (12)$$

m/z 58 (R = H), *m/z* 72 (R = Me),

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CO^- + \\ + NHCH(Me)COOH^{\cdot} \quad (13)$$

m/z 115 (R = H), *m/z* 143 (R = Me);

(b) dissociation of $N\text{—}C_\alpha$ bonds

$$M + e \longrightarrow NH_2CH(R)CONH^- + \\ + CH(R)CONHCH(Me)COOH^{\cdot},$$

m/z 73(R = H), *m/z* 87(R = Me), (14)

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CONH^- + \\ + CH(Me)COOH^{\cdot} \quad (15)$$

m/z 130 (R = H), *m/z* 158 (R = Me);

(c) dissociation of $C_\alpha\text{—}C$ bonds

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)^- + \\ + CONHCH(Me)COOH^{\cdot} \quad (16)$$

m/z 87 (R = H), *m/z* 115 (R = Me),

$$M + e \longrightarrow NH_2CH(R)CONHCH(R)CONHCH(Me)^- + \\ + COOH^{\cdot} \quad (17)$$

m/z 158 (R = H), *m/z* 186 (R = Me).

The metastable peaks detected in the mass spectra of tripeptides indicate the consecutive decompositions of MNIs (Fig. 3) (the curves of the yield of metastable ions *m** are shown in Figs 1 and 2). In some reactions, ions $[M - H]^-$ with the carboxy structure acts as intermediate ions

$$M + e \longrightarrow NH_2CH(R)C(O)NHCH(R)C(O)NHCH(Me)COO^- + \\ + H^{\cdot} \longrightarrow NH_2CH(R)C(O)NHCH(R)C(O)NHCH(Me)^- + \\ + CO_2 \quad (18)$$

m/z 123.6 / $202^- \rightarrow 158^-$ (R = H),

m/z 150.4 / $230^- \rightarrow 186^-$ (R = Me)

or $[M - H]^-$ with the oxide-ionic structure

$$M + e \longrightarrow H^{\cdot} + \\ + NH_2CH(R)C(O)NHC(R)=C(O)NHCH(Me)COOH^- \longrightarrow \\ \longrightarrow NH_2CH(R)C(O)NHC(R)=C=O + \\ + NHCH(Me)COOH^- \quad (19)$$

In other reactions, ions formed by the simple cleavage of one of peptide bonds are intermediate

$$M + e \longrightarrow NH_2CH(R)C(O)^{\cdot} + \\ + NHCH(R)C(O)NHCH(Me)COOH^- \longrightarrow \\ \longrightarrow NH_2C(R)=C=O + NHCH(Me)COOH^- \quad (20)$$

m/z 53.4 / $145^- \rightarrow 88^-$ (R = H),

m/z 48.7 / $159^- \rightarrow 88^-$ (R = Me)

$$M + e \rightarrow NH_2CH(R)C(O)^{\cdot} + \\ + NHCH(R)C(O)NHCH(Me)COOH^- \longrightarrow \\ \longrightarrow NH_2CH(R)C(O)NHCH(Me)^- + CO_2 \quad (21)$$

m/z 70.4 / $145^- \rightarrow 101^-$ (R = H),

m/z 83.2 / $159^- \rightarrow 115^-$ (R = Me).

In reaction (21), ions *m/z* 101 and *m/z* 115 represent internal ions. Another example of internal ion formation is demonstrated by reaction (22) in Gly-Gly-Ala

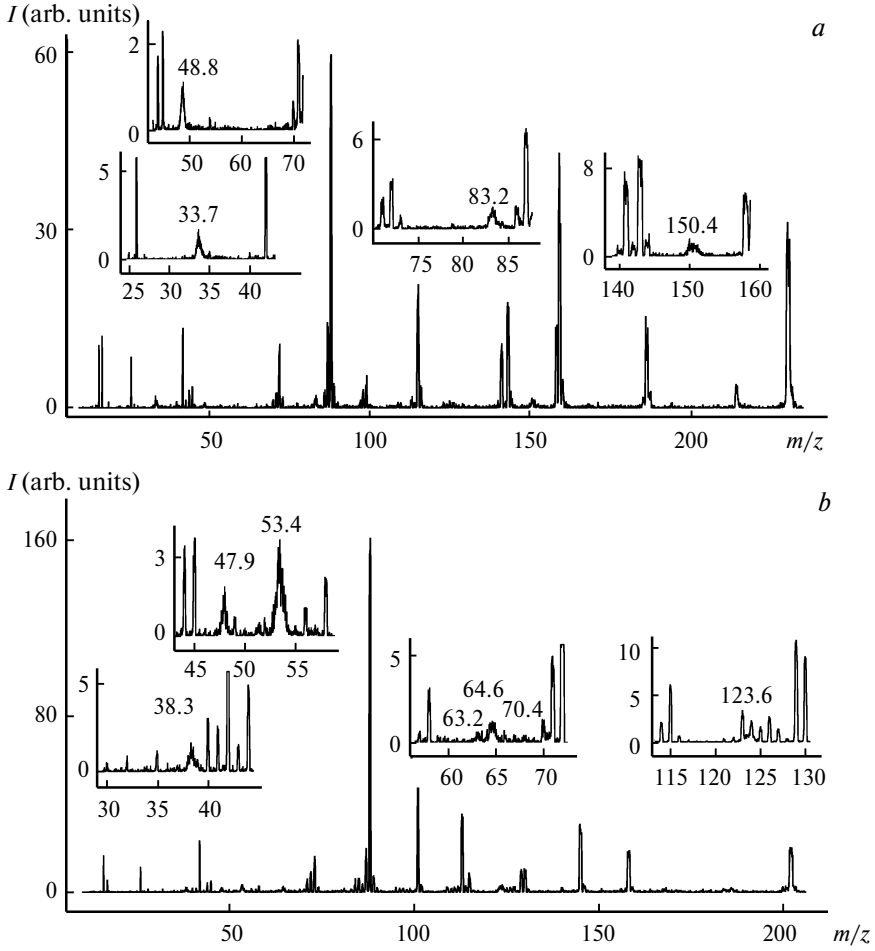

Fig. 3. Mass spectra of negative ions Ala-Ala-Ala (*a*) and Gly-Gly-Ala (*b*) recorded at an electron energy of 5.0 eV. Insets: the regions of abundance of metastable peaks in the amplified scale.

$$M + e \longrightarrow NH_2CH_2C(O)NHCH_2C(O)NHCH(Me)^- + \\ + COOH^{\cdot} \longrightarrow NH_2CH{=}C{=}O + \\ + NH_2CH_2C(O)NHCH(Me)^- \qquad (22)$$

m/z 64.6 / $158^- \rightarrow 101^-$.

Perhaps, a similar reaction occurs in Ala-Ala-Ala but is not identified because of the low intensity of the metastable peak. The following reactions were also detected in Gly-Gly-Ala only

$$M + e \longrightarrow NH_2CH_2C(O)NHCH_2C(O)NHCH(Me)^- + \\ + COOH^{\cdot} \longrightarrow NH_2CH_2C(O)NHCH_2^- + \\ + O{=}C{=}NCH_2Me \qquad (23)$$

m/z 47.9 / $158^- \rightarrow 87^-$,

$$M + e \longrightarrow H^{\cdot} + \\ + NH_2CH{=}C(O)NHCH_2C(O)NHCH(Me)COOH^- \longrightarrow \\ \longrightarrow NH{=}CHC(O)NHCH_2C(O)^- + \\ + NH_2CH(Me)COOH \qquad (24)$$

m/z 63.2 / $202^- \rightarrow 113^-$.

We do not exclude the possibility of formation of isomeric ions in reactions (18)—(24) caused by the H-shift processes (or double H-shift) in intermediate ions, but the study of the kinetics of similar metastable decompositions of NIs from dipeptides using the RRKM statistical theory shows[12] that the presented structures of the ions are most probable.

Slow fragmentation of MNIs of peptides. The fundamentals of the theory of formation and decomposition of NIs were founded at the middle of the XX century. The

theory is based on the Born—Oppenheimer approximation, according to which a molecular system can be divided into two subsystems: fast electronic and slow nuclear subsystems. According to this concept, electron capture by the shape resonance or electron-excited resonance involves no motion of nuclei, *i.e.*, almost instantly, unlike the vibrationally excited resonance, and the MNIs formed also rapidly reject the captured electron. Under these conditions, their fragmentation can occur only in the fast process of direct bond cleavage along the repulsive potential surface. Thus, according to the Born—Oppenheimer concept, the fast decomposition of NIs is a process without excitation of nuclear vibrations and, correspondingly, the motion of the nuclear framework of the molecular system is involved in the slow decomposition. According to this formulation, the slow decomposition include predissociation and rearrangement fragmentation: the processes that proceed *via* the nonradiative transitions in NIs. The theory was confirmed in early experiments with two- and three-atomic objects. A classical example of the fast decomposition is the formation of H^- ions from molecular hydrogen for which the high isotopic effect was detected in the cross section of dissociative electron capture.[15] Therefore, several questions arise: are slow decompositions of polyatomic MNIs are possible in the shape resonances and electron-excited resonances, under which conditions do they occur, and what is their role in the total pattern of ion formation?

The most intensive channels of decomposition of MNIs of tripeptides in the low-energy region are processes of rejection and migration of the carboxyl H atom: reactions (1) (pre-dissociation) and (4)—(6) (isomerization) in which $XCOO^-$ ions are formed. The total contribution of the intensity of these channels (taking into account the further decomposition of products of reaction (5) and with allowance for rearrangement reactions (7)—(9)) to the full ionic current is 78—81%. Thus, the shape resonance in the low-energy region decomposes predominantly due to slow fragmentations of MNIs. This conclusion is also valid for processes in NIs from dipeptides and amino acids.

One of the indications to the slow decomposition of MNIs is the formation of fragmentation ions in the autodetachment (unstable with respect to electron rejection) state. There is an opinion (Yu. V. Vasil´ev, private communication) that there is no enough time for the excitation of other vibrational degrees of freedom of MNIs in the fast direct bond cleavage along the purely repulsive potential surface, except for the bond extension along the reaction coordinate, and the excessive energy of the process is liberated to the kinetic energy of fragments. However, if the molecular ion is initially formed in the bound state and can survive for a longer time than the period of characteristic vibrations, then there is a chance for other vibrational modes that are not related to the reaction coordinate to excite. This excitation is also retained in the fragmentation ion, which is further naturally eliminated due to electron rejection or further fragmentation when any of these processes becomes energetically possible. It follows from this that the metastable decomposition of fragmentation ions also an indication to the formation of the latter by the slow fragmentation of molecular ions.

The curves of the effective yield of neutrals $[M - H]^0$ are caused by the loss of electrons by the $[M - H]^-$ ions in the second fieldless region of the mass spectrometer (in Figs 1 and 2 marked as 202n and 230n, respectively). In the low-energy region, they exactly repeat the curves of the yield of ions but with the intensity two orders of magnitude lower. Here ions are formed near the threshold and, therefore, the electron loss is possible only as a result of the collision of ions with molecules of the intrinsic or residual atmospheric gas. In the medium-energy region, the ratio of peak intensities of ions and their neutrals differs from that in the low-energy region and indicates that the process of spontaneous electron rejection by ions formed after the loss of different types of H atoms occurs along with the "collision" process. Therefore, in the energy of electron excitation of peptide molecules,[16] MNIs are formed in the vibrationally excited state, which is the necessary conditions for nonradiative transitions to occur. The autodetachment of an electron by $[M - H]^-$ ions in the medium-energy region was detected for dipeptides and amino acids.[10,17]

The spontaneous rejection of an electron by $[M - H]^-$ ions occurs due to the fact that their internal excitation energy exceeds the energy of electron affinity of radicals $[M - H]^{\cdot}$. This is caused by the fact that the uncharged fragment of MNI decomposition represents a monoatomic particle and the whole excessive energy of the process (except for its insignificant fraction as a kinetic energy of fragments) is consumed to an increase in the internal energy of the fragmentation ion. A reason for the absence of electron autodetachment for other fragmentation ions is, most likely, such a redistribution of the excessive energy over fragments that the vibrational excitation of the ion is insufficient for electron rejection. Another reason can be related to the fact that some detected ions are represented by consecutive fragmentation products and the final stage of the process occurs with the evolution of an insignificant excessive energy. The direct proof of the consecutive fragmentation is the metastable decomposition in which the $[M - H]^-$ ions more frequently than others act as intermediate ions, for example, reactions (18), (19), and (24).

The metastable peaks in the mass spectra of tripeptides indicate the consecutive fragmentations of MNIs in which intermediate ions are not only $[M - H]^-$ but also other ions, products of reactions (20)—(23). Therefore, the first stage of these processes (reactions (10) (simple cleavage of the peptide bond) and (17) (simple cleavage of the C_α—C bond)) is the slow decomposition of MNIs. The overall intensity of these two channels of MNI fragmentation is

low, being 11% (ions with m/z 145 and 158 in Gly-Gly-Ala) and 21% (ions with m/z 159 in Ala-Ala-Ala) of the full ionic current in the medium-energy region. For other ions, no direct confirmation of their formation in the slow decompositions of MNIs was found, but the comparison of the relative intensities of ion peaks in the mass spectra does not allow one to conclude that they are formed in fast reactions.

Single examples of low-intensity metastable decompositions of fragmentation ions were obtained in the high-energy region, and the $[M - H]^-$ ions from Ala-Ala-Ala were detected in the autodetachment state (see Figs 1 and 2).

Simulation of protein decomposition through the formation of negative ions in peptides. As mentioned above, the most intense channels of the decomposition of MNIs of simplest peptides in the low-energy region are processes of rejection or migration of the carboxyl H atom, namely, reactions (1) and (4)—(6), in which ions $XCOO^-$ are formed. However, the polycondensation of amino acids to peptides is accompanied by the formation of water molecules consisting of the OH group of the carboxyl fragment and the H atom of the amino group. Due to this, polypeptides contain few functional COOH groups, whose number of determined only by the number of fragments of aspartic and glutamic acids in the chain. Therefore, reactions (1) and (4)—(6) (as well as reactions (7) and (8)) cannot make a large contribution to the decomposition of polypeptides. A similar conclusion is valid for reaction (9) mainly due to its low intensity and a unique structure of the fragmentation ion. Therefore, the decomposition of the primary structure of proteins upon low-energy electron capture can be simulated by processes in simplest peptides that do not involve the hydroxy group of the carboxyl fragment of the molecules and the amino group. Among them are reactions (2) and (3) in which the fragmentation ions are formed by the simple cleavage of the central $N—C_\alpha$ bonds. In the medium-energy region, the number of reactions of simple central bond cleavage in the MNIs of peptides is much higher, and the proved reactions (10)—(17) represent only an insignificant part of them. The latter make the main contribution to the total ionic current in this energy region: 55% (Gly-Gly-Ala) and 72% (Ala-Ala-Ala). Among them the processes proceeding *via* the dissociation of peptide bonds with the retention of an additional charge on the nitrogen atoms are most significant: reactions (10) and (11); the contribution of reactions (12)—(17) is less considerable. It should be mentioned that the reactions of consecutive decomposition of MNIs involving no OH groups are ignored, but these reactions can also occur in polypeptides, for example, reaction (24) and others.

The secondary protein structure is the organization of the polypeptide chain stabilized by hydrogen bonds between the oxygen atom of the carbonyl group and the hydrogen atom of the amide group entering into the composition of different peptide fragments, which are separated by three amino acid residues in the case of the α-helix and belong to different polypeptide chains in the case of the folded β-structure. The damage of these bonds induces the decomposition of the secondary structure, but it is very difficult to observe these processes in the mass spectrometric experiment, because they do not result in fragmentation without accompanying reactions of chemical bond cleavage.

Thus, the mechanisms of formation and decomposition of molecular negative ions in an electron energy range of 0—12 eV were revealed from the analysis of processes of resonance capture of electrons by molecules of tripeptides and earlier studied dipeptides. In the energy region below 4 eV, the short-lived MNIs are formed due to the vibrationally excited resonance and shape resonance; their decomposition occurs mainly due to hydrogen rearrangements, since many reactions of simple bond cleavage are hindered for energy reasons. In the energy region of electron excitation of molecules (higher than 4 eV), the rearrangement processes in the MNIs are suppressed by reactions of simple bond cleavage. The experimentally observed properties of slow NI decomposition indicate that in the whole studied range of captured electron energy molecular ions are formed in the vibrationally excited state and their fragmentation occurs predominantly due to nonradiative transitions. The characteristic reactions in NIs of peptides were identified: they are model reactions in processes of protein decompositions in electron-molecular interactions. It was assumed that the decomposition of the polypeptide chain in the ionized form of proteins can occur as a result of the simple cleavage of central bonds, predominantly of the $N—C_\alpha$ and peptide bonds.

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