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Interaction of He^{2+} ions with heterocyclic cyclodialanine molecules

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Mass spectrometric analysis of alpha-particle-induced fragmentation of heterocyclic molecules of the dipeptide cyclo(Ala-ala) ($C_6H_{10}N_2O_2$, 3,6-Dimethylpiperazine-2,5-dione) has been performed. Relative cross sections of various elementary processes occurring during single collisions of cyclo(Ala-ala) with ions have been measured for the first time. The geometry of molecules and singly charged ions, as well as reaction pathways of various experimentally observed fragmentation channels of these ions, have been calculated using the multiconfigurational self-consistent field method in the complete active space (CASSCF). The optimized geometry of molecules and singly charged ions, as well as their total energy, have been calculated using the density functional theory (DFT).

Keywords: electron capture, dipeptides, molecular ion fragmentation, mass spectrometry, DFT, CASSCF metho.

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Introduction

The chains of amino-acid residues connected with a peptide bond form peptides. Dipeptides, which consist of two amino-acid residues, are simple peptides represented both by a linear and a cycle form; two peptide bonds are typical for the latter. Cyclo-dialanine (3,6-Dimethylpiperazine-2,5-dione) — is one of the simplest cyclopeptides. It consists of a six-membered ring structure of the 2,5-diketopiperasine (DKP), wherein the side radicals (H) are replaced by two methyl groups (CH_3).

In order to study the radiation stability of the peptides, it is possible to use a mass spectrometric analysis of fragmentation of molecular ions, which are formed during single collisions of the molecules in the gas phase with an ionizing particle, thereby excluding a role of radiation-chemistry processes that occur when the ionising radiation interact with solutions or a solid body [1].

There is little research of the processes accompanying ionization of the dipeptide molecules. For some of them, the databases, for example, [2], contain mass spectra of fragments formed during electron ionization. The work [3]has studied the mass spectra of the fragment ions which are formed during electron ionization of the cyclic dipeptides cyclo(Gly-Gly) or DKP and cyclo(Ala-Ala). The work [4] has investigated a mechanism of radiation damage of molecules of the dipeptides Gly-Gly, Gly-Leu and cyclo(Gly-Gly) in the gas phase when interacting with the He^{2+} ions.

The photoelectron spectroscopy method was used to carry out the experimental studies of the electron structure of the cyclic dipeptides in the gas phase for DKP, cyclo(Leu-Pro) and cyclo(Phe-Pro) [5] as well as for more complex cyclic dipeptides containing six-membered DKP ring [6]. The measured electron spectra were interpreted by means of the *ab initio* calculations. The works [[7–9] have studied interactions of the isolated molecules of cyclo(Ala-Ala) with vacuum ultraviolet radiation with the energy of 60 eV using the photoelectron photoion coincidence spectroscopy (PEPICO). The authors used the Gaussian16 software for analysis of the experimental data. The dynamic and energetic information about the processes of fragmentation of the molecular ions was obtained as a result of the *ab initio* calculations of the molecular dynamics and potential energy surfaces using the density functional theory (DFT) method. The calculations included the use of the B3LYP functional in combination with the atomic basic set 6−311G(d,p). For analysis of the photoelectron spectra and calculation of the ionization potential, the ab initio quasi-particles methods OVGF and P3+ were used [8].

The purpose of the present work was to study a mechanism of radiation damage of isolated molecules of cyclo(Ala-Ala) by measuring relative cross-sections of various elementary processes which occur when a charge state of collision partners changes

$$\mathrm{He}^{2+} + \mathrm{C_6H_{10}N_2O_2} \rightarrow \mathrm{He}^{(2-s)+} + \{\mathrm{C_6H_{10}N_2O_2}\}^{n+}$$

$$+(n-s)e^- \rightarrow \mathrm{He}^{(2-s)+} + \Sigma_n \mathrm{Fr}_n^+ + \Sigma_i \mathrm{Fr}_i^0 + (n-s)e^-,$$

where $\{C_6H_{10}N_2O_2\}^{n+}$ — the intermediate state of the molecular ion formed during capturing by the ion He^{2+} s-electrons ($s = 1, 2$), $(n-s)$ — the number of free electrons occurring during capture, Fr_n^+ — the fragment ions that are usually singly-charged, Fr_i^0 — the neutral fragments. The charge states of the interacting particles are described by the three numbers $\{2(2-s)n\}$. Relative cross-sections of the respective processes are designated as $\sigma_n^{2(2-s)}$.

The mechanism of fragmentation of the singly-charged molecular ions $C_6H_{10}N_2O_2^{\bullet+}$ was studied by applying the quantum chemical calculations. The fragmentation channels of the singly-charged molecular ions were chosen for analysis according to the experimental mass spectra of the fragment ions Fr_n^+ which are formed during capturing of one electron $\{211\}$ by the ions He^{2+}.

1. Experimental procedure

The present work was carried out using the experimental procedure earlier applied to study interaction of the ions with various biologically significant molecules, including the dipeptides [4,10–13]. The interaction region of the He^{2+} ion beam with the energy of 4 keV/u (the velocity $V_p = 0.41$ a. u.) with an effusion jet of the target molecules was in the homogeneous 150 V/cm-strength electrical field, which pulled out the formed target ions into an ion-optical system of the linear time-of-flight mass spectrometer. After the optical system of the mass-spectrometer, the ions were additionally accelerated by the 14 kV to enable their recording with high and almost the same efficiency irrespective of a mass, in a computation mode.

The charge state of charges after the interaction was defined by an electrostatic analyzer. The arrival time of the He^+ ions or the He atoms, formed after capturing one or two electrons, to the detector served as a start signal of the recording system. The time-of-flight mass spectrometer detector signals were recorded in the „multistop“ mode. The ion-optical system of the mass-spectrometer ensured full collection of the fragment ions with initial values up to 9 eV.

The effusion molecule jet that is isolated by a mechanical valve when measuring a background component, was obtained by furnace heating of the crystalline (Ala-Ala). A capillary forming the molecular jet and a container containing the studied substance were made of PTFE which allowed to avoid the impact of catalytic action of the furnace material on the sublimation of the studied substance. The studied substance was procured from the „Vekton“ company[14]. The absolute furnace temperature was measured with accuracy ±0.12 %, and its temperature drift during the spectra measurement did no exceed 0.4 °C. Within the temperatures 150−203 °C the intensity ratio of the base peak was not changed in the mass spectra. During a series of measurements of relative cross-sections the beam intensity He^{2+} and the sample heating temperatures (195−197 °C) were selected for guaranteed operation in the single-collision mode where the effusion jet interacts with the charges.

The relative cross-sections of the charge state changes of the collision partners were determined based on mass spectra analysis without the background component. The mass spectra obtained after background subtraction were rated for an amount of the substance transmitted through the interaction region and a bombarding ion beam current integral. The measurement results processing included formation of the mass spectra for the processes with simultaneous formation of one, two, three or four charged molecular fragments. In this way, it has separated the processes of single-electron capture$\{211\}$, electron capture with ionization $\{212\}$ and electron capture with double ionization $\{213\}$. It also included separation of the processes that occur due to capture of two electrons. Two-electron capture $\{202\}$, capture of two electrons with ionization $\{203\}$ and capture of two electrons with double ionization $\{204\}$ [4].

2. Quantum chemical calculations

The experimentally observed process were analyzed in a set of the quantum chemical calculations.

First of all, the optimized geometry of molecules and singly-charged ions as well as their full energy were calculated in accordance with the DFT method using the software module DMol^3 of the Materials Studio package. The calculations included the use of the B3LYP functional and the DNP all-electron atom basis (version 3.5) with unlimited spin polarization [15,16]. The selected procedure ensured the energy convergence below $10^{-5}\,E_h$ and the geometry one — 5×10^{-3} Å.

The calculated full energies of the molecules and ions allow to calculate reaction energies for the fragmentation channels of the ions being formed

$$\Delta E_{re} = \sum E_{prod} - \sum E_{react},$$

where ΔE_{re} — the reaction energy, $\sum E_{prod}$ — the sum of the full energies of the reaction products, $\sum E_{react}$ — the full energy of the initial molecular ion, $\Delta E_{re} < 0$ — the exothermic reaction; $\Delta E_{re} > 0$ — the endothermic reaction.

Secondly, the reaction paths of various experimentally observed channels of fragmentation of the molecular ions and optimized geometry of the molecules and the singly-charged ions were calculated using the software GAMESS-US(2023) [17] by the self-consistent field method in the complete active space CASSCF(n, m), where n — the number of the active electrons, the m — the number of the active orbitals. The neutral molecule of cyclodialanine was described using the active space which includes 12 active electrons distributed by 12 active orbitals of CASSCF (12, 12). One electron was deleted from the active space for a cation, thereby providing the method CASSCF(11,12). The calculations were carried out in the atom basis 6-311G(d, p).

Table 1 shows the results of calculation of the vertical potential of ionization of the molecule cyclo(Ala-Ala). As it is clear from the provided data, all the calculated potentials of ionization are below the measured one, but the best compliance with the experimental data is in our calculation by the CASSCF method.

Table 1. Vertical potentials of ionization of the molecule cyclo(Ala-Ala)

Program	GAMESS	DMol3	Gaussian16			Experiment [8]
Method	CASSCF	DFT-B3LYP	DFT-B3LYP[7]	OVGF[8]	P3+[8]	
IP_v, eV	9.35	7.269	9.14	8.985	9.287	9.53 ± 0.05

Table 2. Relative cross-sections of elementary processes $\{2(2-s)n\}$. The relative number of protons $\mathrm{N}_{s,n}(\mathrm{H}^+)$ and molecular ions of hydrogen $\mathrm{N}_{s,n}(\mathrm{H}_2^{\bullet+})$, formed in the processes $\{2(2-s)n\}$, of the total number of the recorded protons $\Sigma_{s,n}\mathrm{N}_{s,n}(\mathrm{H}^+)$ and the molecular hydrogen ions $\Sigma_{s,n}\mathrm{N}_{s,n}(\mathrm{H}_2^{\bullet+})$

Process	σ rel. u.	$\mathrm{N}_{s,n}(\mathrm{H}^+)/\Sigma_{s,n}\mathrm{N}_{s,n}(\mathrm{H}^+)$ %	$\mathrm{N}_{s,n}(\mathrm{H}_2^{\bullet+})/\Sigma_{s,n}\mathrm{N}_{s,n}(\mathrm{H}_2^{\bullet+})$ %
$\Sigma_n\{21n\}$	56.9 ± 4.5	12.5 ± 0.7	22.5 ± 3
$\{211\}$	42.0 ± 4.5	3.0 ± 0.6	0.5 ± 0.2
$\{212\}$	12.0 ± 1.5	6.1 ± 0.6	12.9 ± 2
$\{213\}$	2.9 ± 0.5	3.4 ± 0.5	9.0 ± 2
$\Sigma_n\{20n\}$	43.1 ± 4.4	87.5 ± 5.7	77.5 ± 5
$\{202\}$	24.6 ± 4.3	44.9 ± 4	29.5 ± 3
$\{203\}$	15.1 ± 1.7	34.6 ± 4	26.3 ± 3
$\{204\}$	3.4 ± 0.5	8.0 ± 1	11.8 ± 2

3. Experimental results and discussion

3.1. Relative cross-sections of processes 2(2-s)n

The relative cross-sections of the charge state changes of the collision partners are given in Table 2. As it is clear from the listed data, when the He^{2+} ion collides with the molecules of cyclo(Ala-Ala), the main cross-section process is the single-electron capture process $\{211\}$, which, as it is well known, is effectively taking place at high impact parameters. Nevertheless, 58 % of the complete cross-section of the charge state changes of the collision partners falls on multi-electron processes, whereof the total cross-section of the processes accompanied by formation of the free electrons is 33.4 %. As follows from Table 2, when the molecules of cyclo(Ala-Ala) interact with the ions, the free protons are formed mainly due to multi-electron processes, i.e. fragmentation of the intermediate molecular ions $\{\text{cyclo(Ala-Ala)}\}^{n+}$ $n \geq 2$.

It is clear from analysis of the obtained mass spectra that a process of fragmentation of formed molecular ions of $\{\text{cyclo(Ala-Ala)}\}^{n+}$ can be accompanied by formation of the H_2^+, wherein this process happens, as in the case of formation of the free protons, during fragmentation of the intermediate multicharged molecular ions of the $\{\text{cyclo(Ala-Ala)}\}^{n+}$ $n \geq 2$ (Table 2).

The multi-electron processes are efficiently carried out at lower impact parameters (for example, [18]) than those typical for the process of single-electron capturing $\{211\}$. It is obvious that during interaction of the ions with condensed media there are no process with the impact parameters exceeding the typical internuclear distance in the medium. Therefore, analysis of interaction of the ions with such objects shall take into account influence of such fragments as H^+ and H_2^+ on the processes of radiation damage.

3.2. Fragmentation of singly-charged ions cyclo(Ala-Ala)$^{\bullet+}$

Table 3 shows the relative cross-sections of formation of the basic fragment ions during single-electron capture $\sigma_1^{21}(\mathrm{He}^{2+})$ in interaction of the He^{2+} ions with the molecules of cyclo(Ala-Ala). The fragments of the table are 85 % of the complete cross-section of the single-electron capture. For comparison, Table 3 shows the relative cross-sections of fragmentation when cyclo(Ala-Ala) is ionized by the electrons $\sigma_{ion}(\mathrm{el})$ [2] and vacuum ultraviolet radiation (VUV radiation) $\sigma_{ion}(\mathrm{VUV})$ [7–9]. The mass spectra of the fragments formed during ionization of the molecules by VUV radiation are represented in the works [7–9] by a sum of photoelectron photoion coincidence spectra measured within the bond energies of electrons in the molecule $\mathrm{BE} = 8 - 25$ eV, which corresponds to the excitation energies of the formed molecular ions within $E_{ex} = \mathrm{BE} - \mathrm{IP}_v \approx 0 - 17$ eV, where IP_v — the vertical potential of ionization.

The fragment ions were identified using the structural formula of the molecule (Fig. 1) based on the assumption that the ions with the mass m are formed as a result of rupture of a minimum number of chemical bonds and

Table 3. Relative cross-sections of formation of the fragment ions when capturing one electron by the He^{2+} ions for the molecules of cyclo(Ala-Ala), when ionizing these molecules by the electrons [2] and VUV radiation [7-9]

Fragment ion	m, u	$\sigma_1^{21}(He^{2+})$, rel. u.	σ_{ion}(el), rel. u.	σ_{ion}(VUV), rel.u.
H^+	1	45		
$H_2^{\bullet+}$	2	1		
N^+, $CH_2^{\bullet+}$	14	7	16	
$NH^{\bullet+}$, CH_3^+	15	22	39	
CN+, $C_2H_2^{\bullet+}$	26	14	20	
$CHN^{\bullet+}$, $C_2H_3^+$	27	32	75	33
$CO^{\bullet+}$, CH_2N^+, $C_2H_4^{\bullet+}$	28	98	201	502
HCO^+, $CH_3N^{\bullet+}$, $C_2H_5^+$	29	16	25	33
$C_3H_3^+$	39	5	9	
$C_2O^{\bullet+}$, $C_3H_4^{\bullet+}$	40	10	32	
$C_2H_3N^{\bullet+}$, C_2HO^+	41	15	51	6
CNO^+, $C_2H_4N^+$, $C_2H_2O^{\bullet+}$	42	59	189	147
$CHNO^{\bullet+}$, $C_2H_5N^{\bullet+}$	43	71	125	120
CH_2NO^+, $C_2H_6N^+$	44	999	999	999
$CH_3NO^{\bullet+}$, $C_2H_7N^{\bullet+}$	45	49	25	33
$C_2HNO^{\bullet+}$, $C_3H_3O^+$	55	9	36	21
$C_2H_2NO^+$, $C_3H_4O^{\bullet+}$	56	70	139	99
$C_2H_3NO^{\bullet+}$, $C_3H_5O^+$	57	10	13	11
$C_2H_2N_2O^{\bullet+}$, $C_3H_4NO^+$	70	20	39	44
$C_2H_3N_2O^+$, $C_3H_5NO^{\bullet+}$	71	76	125	55
$C_2H_4N_2O^{\bullet+}$, $C_3H_6NO^+$	72	25	15	
$C_3H_3N_2O_2^+$, $C_4H_5NO_2^{\bullet+}$, $C_5H_9NO^{\bullet+}$	99	254	598	181
$C_3H_4N_2O_2^{\bullet+}$, $C_4H_6NO_2^+$, $C_5H_{10}NO^+$	100	76	39	
$C_4H_6N_2O_2^{\bullet+}$, $C_5H_{10}N_2O^{\bullet+}$	114	18	31	18
$C_6H_{10}N_2O_2^{\bullet+}$	142	123	133	148
$^{13}CC_5H_{10}N_2O_2^{\bullet+}$	143	12	13	

Note: The data is rated to peak intensity with mass 44 u. The italicized fragments are the most probable ones.

taking into account migration of the hydrogen atoms only. Due to the cycle structure of cyclo(Ala-Ala), almost all the channels of the fragmentation processes are realized in rupture of at least two bonds. Rupture of one bond may result in a process of tear-off of a side chain (CH_3) during rupture of the bond C3–C9 or C6–C7 with formation of an experimentally unobserved ion with the mass $m = 127$ u. The DFT calculation shows that the endothermic effect of the reaction of formation of the ion $C_5H_7N_2O_2^+$ is $\Delta E_{re} = 1.618$ eV. The tear-off of the cation CH_3^+ ($m = 15$ u) is of low probability (Table 3) and most likely related to more complicated processes than rupture of the single bond. The endothermic effect of the reaction of formation of the ion CH_3^+ is $\Delta E_{re} = 4.554$ eV. The process of tear-off of the hydrogen atom resulting in formation of the ion of the mass $m = 141$ u is also of low probability. The proton tear-off is mainly related to multi-electron processes (Table 2).

Thus, unambiguous identification of the majority of the peaks observed in the mass spectra requires additional information, in particular, it is possible to consider changing of lengths of the chemical bonds during ionization. Table. 4 shows the bond lengths (calculated by us in the CASSCF and the DFT methods) for the molecule R_{mol} and the ion R_{ion}, and it also includes data of calculation for the

Table 4. Lengths of bonds between the non-hydrogen atoms in cyclo(Ala-Ala)

Bond	R_{mol}, Å				R_{ion}, Å		$R_{ion} - R_{mol}$, Å	
	X-ray [19]	Gaussian [19]	CASSCF	DMol^3	CASSCF	DMol^3	CASSCF	DMol^3
N1−C6	1.454	1.4606	1.482	1.459	1.523	1.456	0.041	−0.003
N4−C3		1.4606	1.482	1.458	1.470	1.455	−0.012	−0.003
N1−C2	1.331	1.3623	1.362	1.365	1.278	1.357	−0.084	−0.008
N4−C5		1.3623	1.362	1.364	1.378	1.357	0.016	−0.007
C2−C3		1.5336	1.516	1.519	1.506	1.524	−0.010	0.006
C5−C6	1.518	1.5336	1.516	1.516	1.522	1.525	0.006	0.008
C6−C7	1.514	1.5294	1.529	1.535	1.524	1.539	−0.005	0.004
C3−C9		1.5294	1.528	1.535	1.536	1.537	0.008	0.003
C5−O10	1.239	1.2226	1.198	1.236	1.182	1.227	−0.016	−0.009
C2−O8		1.2226	1.198	1.236	1.294	1.227	0.096	−0.009

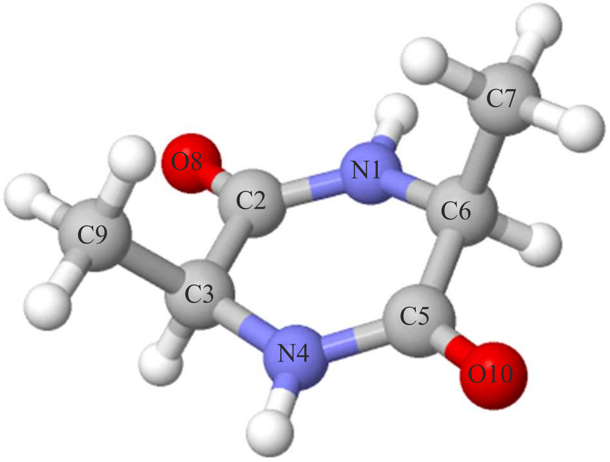

Figure 1. Structure formula of cyclo-dialanine molecule (3,6-Dimethylpiperazine-2,5-dione).

molecule by the DFT method using the software package Gaussian 98 [19]. All the calculated bond lengths for the molecule satisfactorily agree with each other and with the X-ray diffraction analysis data for cyclo-dialanin in the crystallite state [19]. The CASSCF calculation of geometrical parameters of the ions cyclo(Ala-Ala)$^{\bullet+}$ predicts that the ionization process disrupts initial symmetry of the molecule C_2 due to the fact that the singly-occupied natural orbital of the CASSCF method is localized mainly on the oxygen atom, for example, O10, i.e. during ionization the electron leaves an unshared pair of the oxygen atom. It resulted in significant difference in the lengths of the bond C5−O10 and C2−O8. This leads to the fact that the chemical bonds C5−C6 and C2−C3 become nonequivalent, which may mean the different activation energy required for disclosing the six-membered cycle along one of these bonds.

As it is clear from the provided data (Table 3), with single ionization of cyclo(Ala-Ala) there is significant probability of no fragmentation of the initial molecular ion $C_6H_{10}N_2O_2^{\bullet+}$ of the mass $m = 142$ u. It is explained by the fact that during capture of one electron by the He^{2+} ions, ionization by the electrons and photoionization studied in the works [7–9], there is no significant excitation of the molecular ions being formed. However, the probability of formation of undissociated molecular cyclo(Ala-Ala)$^{\bullet+}$ is substantially lower that formation of the ion DKP$^{\bullet+}$ during ionization of the DKP molecules [9,13], which is obviously related to various side chains in these molecules. The peak formed by the ions of the mass $m = 143$ u is caused by an isotope component and has intensity of 12 rel. u., which well agrees with the calculated data of 10 rel. u. [20].

In the mass spectra of the ions formed during {211} and during ionization by the electrons or VUV radiation, the peak that is main in terms of intensity has the mass $m = 44$ u. The DFT calculation shows that the endothermic effect of the reaction of formation of the ion CH_2NO^+ as a result of rupture of the two bonds, for example, C3−N4 and C5−C6, with simultaneous migration of the hydrogen atom from the neutral fragment to the ion being formed, is $\Delta E_{re} = 2.723$ and 5.156 eV, depending on the type of isomers being formed. The alternative channel of formation of the fragment $C_2H_6N^+$ of the mass $m = 44$ u in rupture of two bonds, for example, C2−N1 and C5−C6, with simultaneous migration of the hydrogen atoms from the neutral fragment to the ion being formed is $\Delta E_{re} = 2.167$ eV. Thus, the ions with the mass $m = 44$ u in the mass spectra are, most likely, identified as $C_2H_6N^+$. It is obvious that more exact identification requires consideration of the reaction paths rather than their energy effects only.

Fig. 2 show results of CASSCF calculation of the path of the reaction resulting in formation of the ion $C_2H_6N^+$

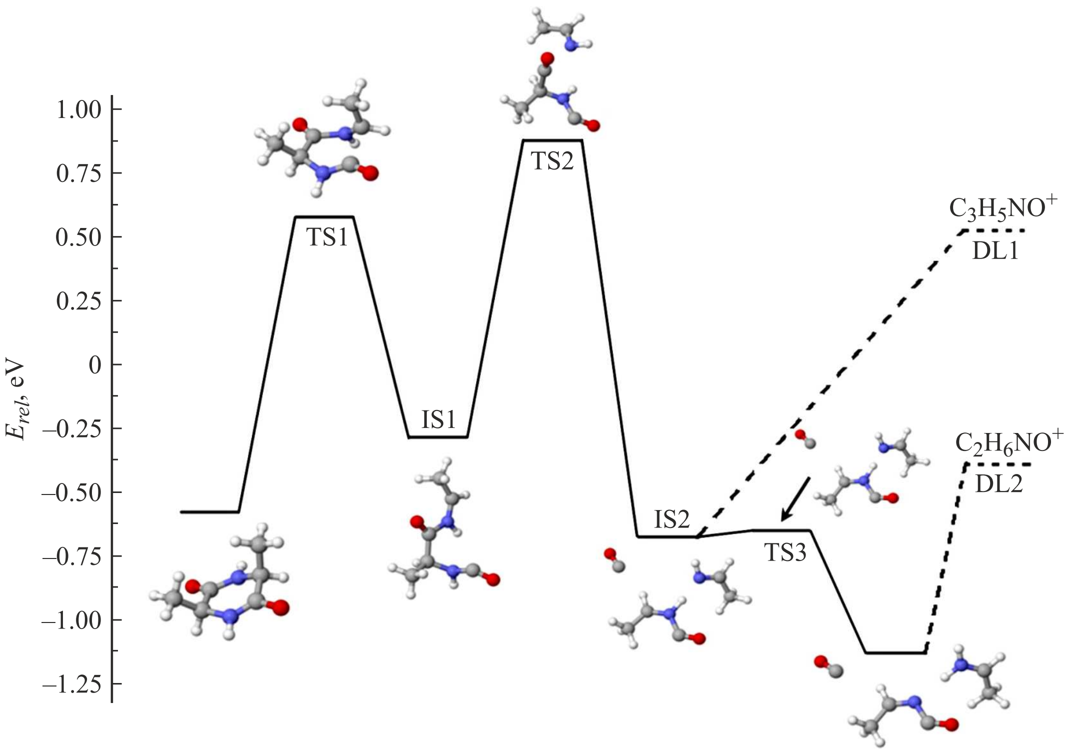

Figure 2. Stationarity points along the path of the reaction of fragmentation of the ion cyclo(Ala-Ala)$^{\bullet+}$, resulting in formation of the fragmentation ions with the masses 44 or 71 u. TSn — the transition state *n*, ISn — the intermediate minimum *n*, DLn — the reaction dissociation limit.

($CH_3CHNH_2^+$) or the ion of the mass $m = 71$ u $C_3H_5NO^{\bullet+}$. The complete energy of the ion cyclo(Ala-Ala)$^{\bullet+}$ in the optimal geometry of the neutral molecule is taken as a starting point. The process turns out to be more complicated that just rupture of two bonds C2−N1 and C5−C6 accompanied by migration of the hydrogen atom from the neutral fragment to the ion and begins with rupture of the shorter bond C5−C6. The arrival of the system to the first transition state TS1 requires the activation energy of 0.583 eV in relation to the energy of the ion cyclo(Ala-Ala)$^{\bullet+}$ in the optimal geometry of the neutral molecule. In the second intermediate minimum IS2, there is release of the CO molecules and formation of the system bound with the hydrogen bond $C_3H_5NO^{\bullet+} \cdots C_2H_5N$. The point of this intermediate minimum can have formation of the ion $C_3H_5NO^{\bullet+}$, but the system can further develop to result in the TS3 point having transfer of the proton from the fragment $C_3H_5NO^{\bullet+}$ to the neutral fragment, thereby resulting in formation of the ion of the fragment $C_2H_6N^+$. It follows from the given reaction path that the energy of appearance of the fragments $C_3H_5NO^{\bullet+}$ ($m = 71$ u) and $C_2H_6N^+$ ($m = 44$ u) is defined by the energy of the second transition state (TS2). Taking into account the vertical potential of ionization (Table 1), the energy of appearance of these ions AE = 10.23 eV. The endothermic effect of the reactions defined by the dissociation limits (DL), for the reaction of formation of the ion $C_2H_6N^+$ and the neutral fragments $C_3H_4NO^\bullet$ and CO is $\Delta E_{re} = 0.19$ eV, so is for the ion $C_3H_5NO^{\bullet+}$ and the neutral fragments C_2H_5N and CO — $\Delta E_{re} = 1.10$ eV. The DFT calculation of the energy effect of the reaction of formation of the $C_3H_5NO^{\bullet+}$ as a result of simple rupture of two bonds, for example, N1−C6 and N4−C3 (Fig. 1), which lead to formation of two fragments with the same gross formulae provides$\Delta E_{re} = 4.87$ eV, which is significantly higher than for the above-considered reaction with formation of the three fragments.

The alternative paths of the fragmentation reaction are shown on Fig. 3. Until the first intermediate minimum IS1, these processes develop similar to that of Fig. 2. With further development of the system, there is rotation of the fragments around the bond C2−C3 and the geometrical configuration of TS2 is a point of intramolecular electron transfer, wherein the electron vacancy of the atom C5 migrates basically to the carbon atom C6. The point TS2 is matched by the barrier height of 0.864 eV, i.e. it is lower than the barrier height for the stationarity point TS2 for the case of Fig. 2 (0.882 eV). In the point of the second intermediate minimum IS2, there is a chemical bond being formed between the atoms O8−C5. In terms of energy, the structure containing a five-membered cycle (IS2) is the most advantageous intermediate structure of the ion $C_6H_{10}N_2O_2^{\bullet+}$. The further development of the system can be in two ways.

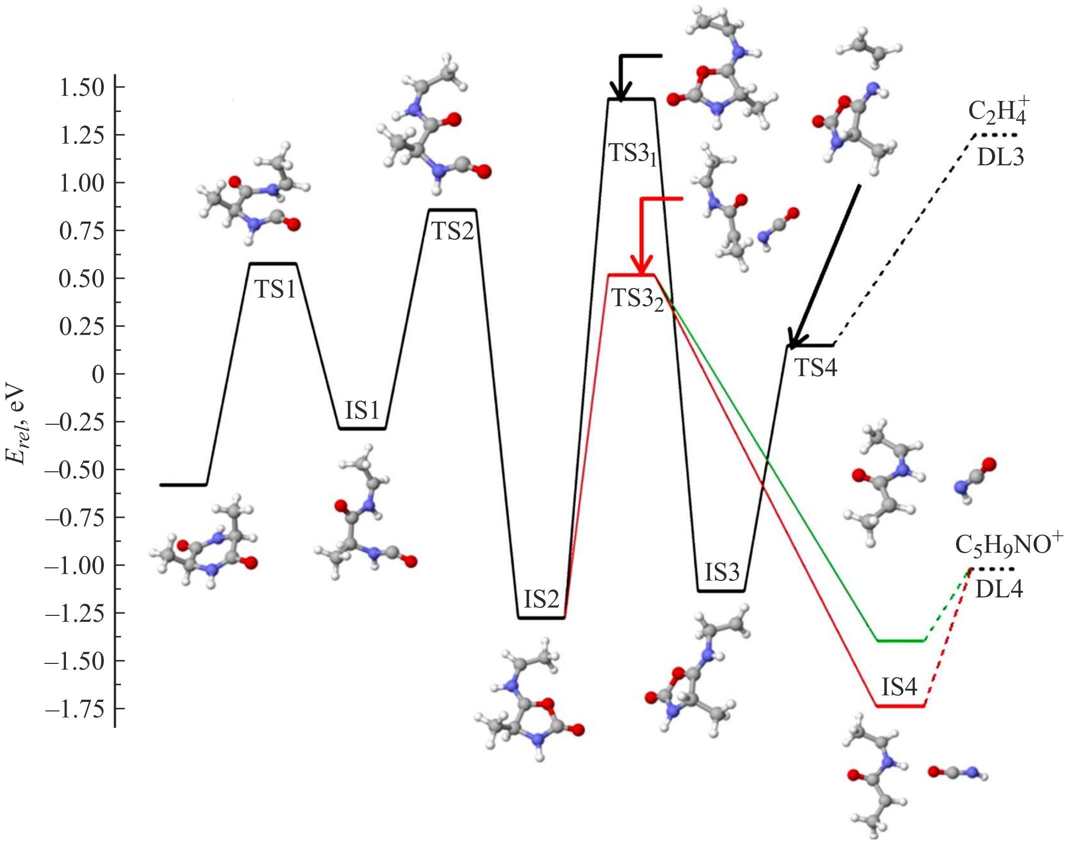

Figure 3. Stationarity points along the path of the reaction of fragmentation of the ion cyclo(Ala-Ala)$^{\bullet+}$, resulting in formation of the fragmentation ions with the masses 99 or 28 u. TSn — the transition state *n*, ISn — the intermediate minimum *n*, DL — the reaction dissociation limit.

First of all, via the intermediate state $TS3_1$, due to migration of the proton from the atom C7 to the atom C6, there is formation of the intermediate minimum IS3. Rupture of the bond C6−N1 results in formation of the fragment $C_2H4^{\bullet+}$. It follows from the considered reaction path that the energy of appearance of the fragment $C_2H4^{\bullet+}$ ($m = 28$ u) is defined by the energy of the third transition state ($TS3_1$). Taking into account the vertical potential of ionization (Table 1), the energy of appearance of these ions $AE = 10.80$ eV. Taking into account the dissociation limit DL3, the endothermic effect of the reaction of formation of the ion $C_2H_4^{\bullet+}$ is $\Delta E_{re} = 1.84$ eV.

Secondly, when the system develops through the intermediate state $TS3_2$ with releasing the neutral fragments NHCO with almost simultaneous rupture of the two chemical bonds O8−C5 and C3−N4 and formation of the charged fragment $C_5H_9NO^{\bullet+}$ ($m = 99$ u). Formation of the intermediate minimum IS4 may include formation of two structures either with the hydrogen bond $O8 \cdots H$ (the hydrogen atom is bound with the atom N4), or $N1 \cdots H$ (the hydrogen atom is bound with the atom C7), which still have the same dissociation limit DL4 (Fig. 3). The energy of appearance of the ion $C_5H_9NO^{\bullet+}$ is defined by the energy of the second transition state TS2 and is $AE = 10.21$ eV. The exothermic effect of the reaction is $\Delta E_{re} = -0.47$ eV.

The reaction path of Fig. 4 starts from the excited state of the cyclo-dialanine ion, which, unlike the ground state ion, has the electron vacancy localized basically on the nitrogen atom N1. The process of fragmentation starts with rupture of the bond C6−N1 in the point of the first transition state TS1. During optimization of the geometry, the point of the first intermediate minimum IS1 is formed. After the system passes the point of the second intermediate state TS2, the second minimum IS2 is formed, in which there is rupture of the bond C2−C3, resulting in formation of the ion $C_5H_9NO^{\bullet+}$ ($m = 99$ u) and the neutral fragment NHCO. The energy of appearance of the ion $C_5H_9NO^{\bullet+}$ is defined by the energy of the second transition state TS2 and is $AE = 11.47$ eV. The endothermic effect of the reaction of formation of the ion $C_5H_9NO^{\bullet+}$, which is defined by the dissociation limit DL4, is $\Delta E_{re} = 0.97$ eV.

There is possibility of further fragmentation of the ion $C_5H_9NO^{\bullet+}$, wherein the system passes the transition state TS3, in which there is transfer of the proton from the atom C9 to the atom C3 with transition into the state of the intermediate minimum IS3. Ethylene molecule tear-off and formation of the ion $C_3H_5NO^{\bullet+}$ ($m = 71$ u) occur when the system passes the transition state TS4. The endothermic effect of the reaction of formation of the ion $C_3H_5NO^{\bullet+}$, which is defined by the dissociation limit

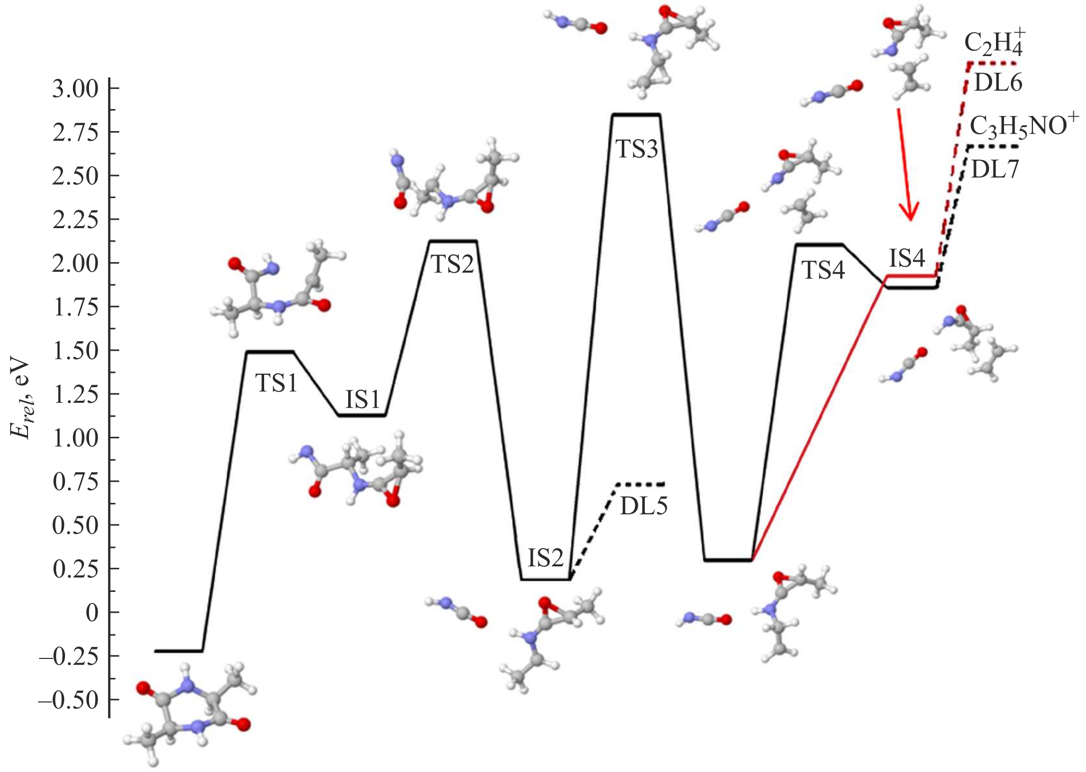

Figure 4. Stationarity points along the path of the reactions of fragmentation of the excited ion cyclo(Ala-Ala)$^{\bullet+}$, resulting in formation of the fragment ions with the masses 99, 71 and 28 u. TSn — the transition state *n*, ISn — the intermediate minimum *n*, DL — the reaction dissociation limit.

DL7, is $\Delta E_{re} = 2.90$ eV. The calculation show that from the intermediate minimum IS3 the system can pass into a final state, in which there is tear-off of the charged fragment $C_2H4^{\bullet+}$ ($m = 28$ u) rather than the neutral one. The endothermic effect of this reaction is $\Delta E_{re} = 3.48$ eV. At the same time, the energy of appearance o the ions $m = 28$ and 71 u is defined by the energy of the transition state TS3 and is AE $= 12.20$ eV. As it is clear from the listed data, the energies of appearance of the ions of the masses 99, 71 and 28 u during fragmentation of the ion in the considered excited state exceed the respective energies of appearance during fragmentation of the ion in the ground state.

Conclusion

The measurements of the relative cross-sections of the charge state changes of the collision partners have shown that during interaction of the hetero-cyclic molecule of cyclo-dialanine with the ion He^{2+}, the main cross-section process is the single-electron capture process{211}. However, the total cross-section of all the multi-electron processes exceeds the cross-section of the process {211} and is 58 % of the complete cross-section of processes of the charge state change of the collision partners. At the same time, the total cross-section of the processes accompanied by formation of the free electrons is 33.4 % of the complete cross-section. Formation of the light fragments H^+ and H_2^+, which can cause secondary radiation effects, is mainly related to the multi-electron processes and the intramolecular charge transfer. The molecular ions that are formed during single-electron capture basically fragment, although there is still quite high probability of formation of the undissociated ions, which seems to distinguish the hetero-cyclic molecules from the majority of the biologically significant molecules. The quantum chemical analysis of the fragmentation processes of the singly-charged molecular ions has shown that processes of fragmentation, in which two neutral fragments, are the most likely ones.

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Conflict of interest

The authors declare that they have no conflict of interest.

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