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Regular Article - Atomic and Molecular Collisions

Fragmentation of tyrosine by low-energy electron impact

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Abstract. New experimental data on the fragmentation of the tyrosine amino acid molecule ($C_9H_{11}NO_3$) are presented being related to the formation of the ionized products due to the low-energy electron impact. The resulting fragments have been identified and analyzed using an extensive DFT theory approach. The results allowed the main pathways of the electron-impact tyrosine molecule fragmentation to be suggested. The absolute appearance energies for several fragments have been measured experimentally and calculated theoretically, compared and analyzed.

1 Introduction

Tyrosine is one of the 20 standard amino acids that are used by cells to synthesize proteins [1]. It is necessary to mention that this amino acid is sensitive even to light; thus, proteins, consisting of tyrosine, can be converted into various degradation products via several distinct mechanisms including low-energy electron impact and photoionization [2]. Tyrosine degradation products can change the physical and chemical properties of proteins [3,4] and, as consequence, cause various diseases. On the other hand, tyrosine plays an essential role in the charge transfer processes in biological systems [5–7]. These processes could also be disturbed due to degradation of this amino acid. Regulation of cellular functions in many diseases, including cancer, could be deranged due to the degradation of tyrosine because the receptor protein–tyrosine kinases are involved in this regulating [8,9]. It was suggested that tyrosine cleavage reaction may be relevant to light-induced inactivation, aggregation, fragmentation or immunogenicity of protein therapeutics [2]. However, the potential role of tyrosine damage as a causative factor in human disease remains largely unknown.

Currently, experimental studies exhibited a role of low-energy electrons in radiation-induced damage to biologically relevant molecules and functionality of the biological-redox system (see [10,11] and references therein). To identify proteins, the subsequent fragmentation with collision-induced dissociation should be studied using mass analysis instruments with high mass accuracy and sensitivity. However, the methods applied are not effective for all proteins. It has been estimated that up to 30% of collision-induced dissociation reactions do not lead to unambiguous peptide and protein assignment [12]. Taking into account that product-ion-spectra features are generally richer and more complex fragmentation patterns, it was proposed that the usage of peptide radical cation can supply some complementary sequence information [12]. Peptide radical cations were investigated using low-energy gas-phase methods [10,11]. It is obvious that the prevalence of radical-driven or charge-directed cleavages is determined by the types of amino acids in the sequence. Hence, the data on the cleavage of amino acids are urgent to determine protein and peptide chemical composition and their sequence.

Here, we report on the recent results of studying tyrosine fragmentation by low-energy electrons aiming to shed some light on the above process mechanisms. We have measured the appearance energies for several fragments with low peak intensities in the mass spectrum. Nevertheless, this allowed us to obtain not only the chemical composition of the cations produced, but also to suggest the pathways of their formation and explain the specificity of the mass spectrum of this amino acid.

2 Experimental

The experimental apparatus used in our investigation is a typical crossed-beam setup based on an MI1201 magnetic mass spectrometer. Its main characteristics are analyzed in our previous papers (see, e.g., [13]). The MI1201 operating mass range is m/z = 1–600 (m/z being the mass-to-charge ratio of the ions under study), and it provides high ion detection sensitivity ($\sim 10^{-16}$ A) and mass resolution (±0.25 a.m.u.; however, it is lower in the region of $m/z > 100$) allowing the fragmentation products to be effectively detected

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and identified. The tyrosine molecule beam having a $\sim 10^{10}$ molecule/cm^3 density was produced by an effusion source operating within the temperature range not exceeding 150 °C, excluding, thus, possible thermal degradation of the molecule under study.

A three-electrode electron gun was applied to produce an electron beam with a current of 30–50 μA. When determining the ion fragment appearance energies, the incident electron energy was varied from 7 to 30 eV allowing the energy dependence of the different ion fragment yields to be measured. The electron energy scale was calibrated against the Ar and N_2 ionization thresholds providing accuracy not worse than ±0.2 eV. The tyrosine molecule mass spectrum was recorded in an automatic PC-controlled mode at fixed electron energy (70 eV, typical for mass spectrometric measurements). The accuracy of measuring the appearance energies for the most intense ion fragments was not worse than ±0.2 eV as well.

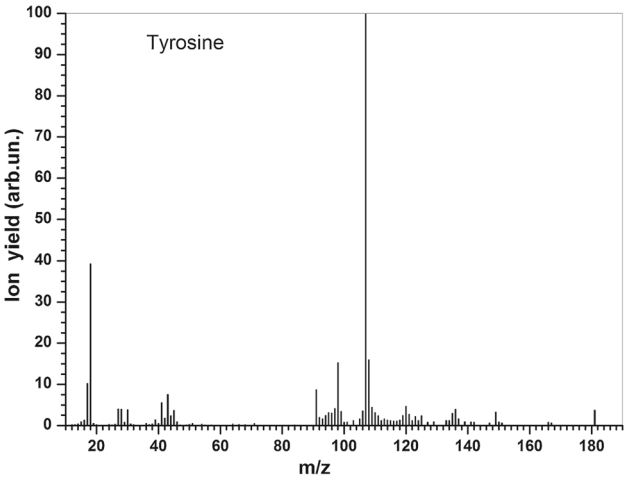

Fig. 1 The tyrosine molecule mass spectrum measured at the 70 eV incident electron energy

3 Theoretical

Both theoretical approach and method were described in detail in our recent papers [14–16]. The most stable conformers described in [17] were used to create new shapes of tyrosine molecule and obtain its most stable conformers. We 'rotated' the COOH group with respect to a core part of this molecule together with the NH_2 group and changed the positions of the H atom of carboxyl acid and OH groups. The new structure of the conformers of the neutral tyrosine molecule was optimized without any symmetry constraints (all bonds length, angles and dihedral angles are changed) by using Becke's three-parameter hybrid functional approach with non-local correlation provided by Lee, Yang and Parr (B3LYP) [18] and the cc-pVTZ basis set implemented in a Gaussian package [19]. The vibrational analysis was performed to be sure that the equilibrium point was found. The comparison of total energies allowed us to select the most stable conformers. The structure of the conformers selected was used to obtain the tyrosine ion structure within repeating the above procedures.

The fragments with the $n(n = -1, 0, 1)$ charge were predicted by using the geometric and electronic structure of the most stable conformer selected. The total energy of the fragments at the equilibrium point was also found to evaluate the fragment appearance energies. This energy was calculated as the difference between the total energy of the conformer chosen and the sum of that of the fragments predicted. The calculated and the measured appearance energy values were compared to suggest the most probable fragmentation (dissociation) reaction. The coincidence of these values indicated the final products of the more probable reactions of the fragment production.

The adiabatic ionization potentials were calculated to predict the fragmentation threshold energy, i.e., the activation energy. We also predicted that fragmentation of the Ph (phenyl) ring is rather possible because the decomposition of conjugated bonds required much more energy than that of a single bond.

4 Results and discussion

First, we have measured the initial tyrosine molecule mass spectrum (see Fig. 1).

It shows a fairly good correlation with that known from the NIST database [20] demonstrating rather poor fragmentation pattern. One may see that the most prominent ion fragment peaks are located in the areas of $m/z < 20$, $m/z = 27$–45, $m/z = 91$–99, $m/z = 106$–125 and $m/z = 131$–142 with a bright dominating peak at $m/z = 107$. Another interesting fact is that the spectrum measured demonstrates a peak at $m/z = 181$ corresponding to the yield of the parent molecular ion $C_9H_{11}NO_3^+$. Such pattern is not typical for most of amino acids, where the initial molecule decays immediately in the electron–molecule collision act, and is due to electron resonance stabilization of aromatic ring.

We have also measured the near-threshold areas of the yield curves for some of the fragment ions, i.e., those having $m/z = 18, 28, 39$, 44, 64, 91 and 107. Some of them are shown in Fig. 2. The experimental appearance energies were determined by means of a fitting technique based on the least-square method approximation using the Marquardt–Levenberg algorithm (see, e.g., [12]).

We have obtained no most stable conformers differing from those presented earlier [17,21] despite their variety (10 new conformers designed from the two most stable ones mentioned in [21]). The view of the most stable conformers obtained by us is depicted in Fig. 3.

The above figure demonstrates the suitability of the approach used. Fragmentation of only one conformer was investigated because the position of the H atom of OH joined to the phenyl (Ph) ring is not crucial for

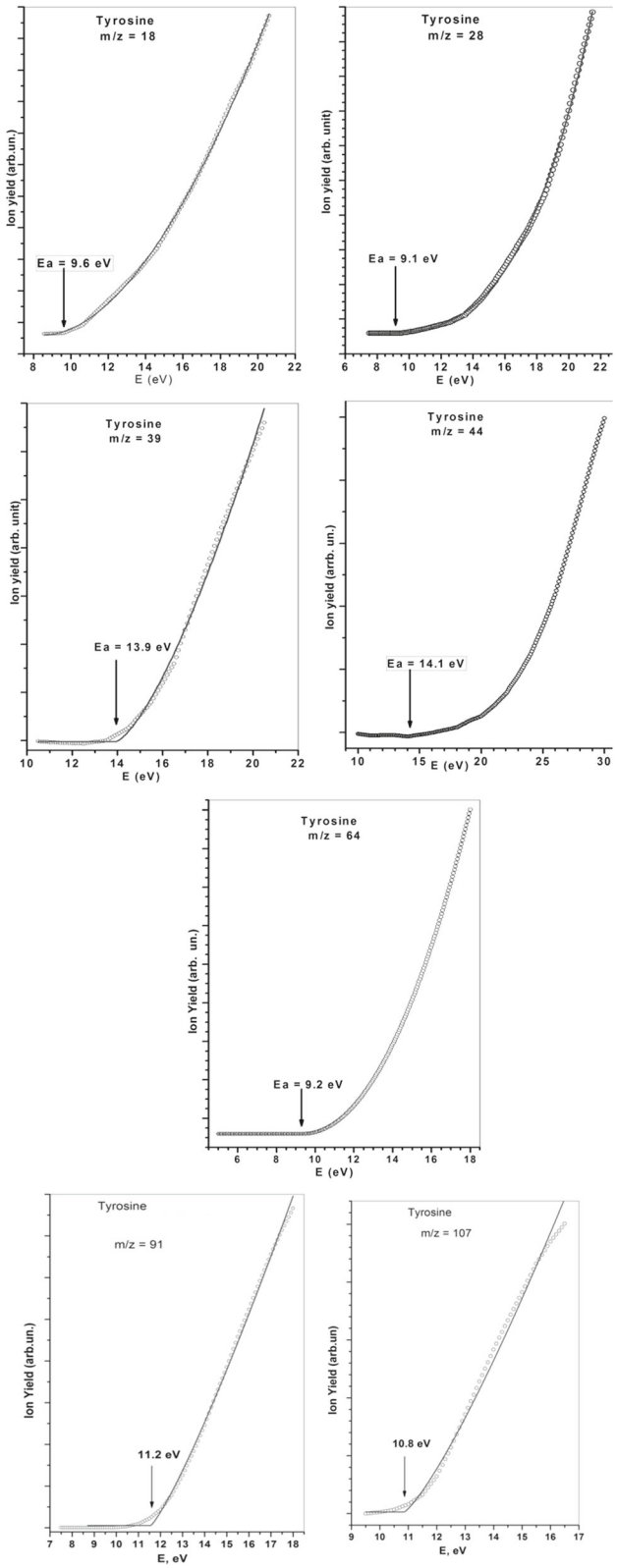

Fig. 2 The initial areas of the yield functions for the $m/z = 18, 28, 39, 44, 64, 91$ and 107 fragment ions. Open circles—experimental data; solid lines—result of fitting using a standard Marquardt–Levenberg least-square technique

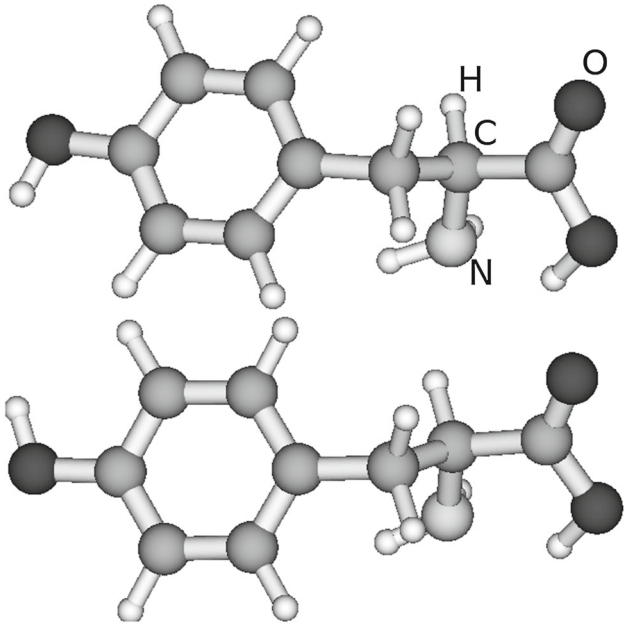

Fig. 3 The most stable conformers of tyrosine obtained by B3LYP/cc-pVTZ approach

the appearance energy of the fragment since there is no significant (less than 0.02 eV) difference in the total energies of these conformers, and the structure of the fragmentation products is different only in the case of the COOH loss, when the structure of the complementary fragment is different.

As mentioned above, the mass spectrum of tyrosine cations is different from those of other amino acids investigated by us [22]. It has few weak series of fragments, and, for example, no intense mass spectrum peaks are observed in the $m/z = 27$–30 mass region, although the fragments of these masses are often present in the mass spectra of such amino acids as glutamine, alanine and tryptophan. To explain this difference, we paid attention to the ionization energy of the molecule and compared it with the appearance energy of the fragment produced under low electron impact.

It is worth mentioning that amino acids with aromatic radicals as a side chain have lower ionization energies than other amino acids [20,23]. Indeed, the tyrosine ionization potential calculated by us is equal to 7.94 eV, while that of, say, tryptophan is 8.3 eV, i.e., the activation energy of tyrosine for the fragmentation by low-energy electrons is lower even than that of tryptophan [24].

Table 1 shows both experimental and calculated appearance energies for the main tyrosine molecule fragments produced due to low-energy electron impact. The results presented in Table 1 indicate that the appearance energy of the vast majority of cations is higher than the tyrosine ionization energy. The exception is the $m/z = 164, 107, 92, 28$ fragments, whose appearance energies are less than 2 eV higher than the ionization potential.

Formation of the $m/z = 92$ fragment is rather complicated because it requires decomposition of both C–C

Table 1 Appearance energies for the main tyrosine molecule fragments formed due to low-energy electron impact

m/z	Positively charged fragment	Complementary fragment	Appearance energy, eV	
			Calculated	Experimental
164	$C_9H_{10}NO_2$	OH	11.22	
153	$C_8H_9O_3$	CH_2N^-	10.32	
152	$C_8H_8O_3$	CH_3N	10.44	
152	$C_8H_{10}NO_2$	CHO	14.06	
136	$C_8H_{10}NO$	CHOO	7.93	
108	C_7H_8O*	$C_2H_3NO_2^-$	10.77	
107	C_7H_7O	$C_2H_4NO_2^-$	8.04	10.8
		$C_2H_4NO_2$	9.06	
106	C_7H_6O	$C_2H_5NO_2$	10.31	
93	C_6H_5O	$C_3H_6NO_2^-$	11.86	
92	C_6H_4O	$C_3H_6NO_2^- + H$	7.70	
91	C_6H_3O	$C_3H_6NO_2^- + 2H$	13.09	11.2
88	$C_3H_6NO_2$	$C_6H_5O^-$	9.24	
74	$C_2H_4NO_2$	$C_7H_7O^-$	9.30	
64	C_5H_4**	C_2H_3O	8.32	9.2
64	C_5H_4	$C_4H_7NO_3$	13.50	
45	CHOO	$C_8H_{10}NO$	11.61	
44	CO_2	$C_8H_{11}NO^-$	14.63	14.1
39	C_3H_3	$C_6H_8NO_3^-$	13.60	13.9
29	CHO	$C_8H_{10}NO_2^-$	12.65	
29	CH_3N	$C_8H_8O_3$	10.65	
		$C_8H_8O_3^-$	11.13	
28	CH_2N	$C_8H_9O_3^-$	9.08	9.6
16	CH_4***	C_6H_3O	9.62	
18	H_2O	C_8H_9NO+CO	14.00	9.1
17	HO	$C_9H_{10}NO_2^-$	20.38	
16	NH_2	$C_9H_9O_3^-$	14.78	
15	NH	$C_9H_{10}O_3^*$	17.31	

*H bonding reaction takes place
**Formed from $m/z = 107$ ($C_7H_7O^+$)
***Formed from $m/z = 107$ ($C_7H_7O^+$) and the H bonding reaction takes place

and OH bonds:

$$C_9H_{11}NO_3 + e \rightarrow C_6H_4O^+ + (C_3H_6NO_2 + H)^- + e.$$

On the other hand, the appearance energy of this fragment according to the scheme presented is similar to the tyrosine ionization potential. This indicates that decomposition of this amino acid could start without ionization when the tyrosine molecule excited by electron splits into an ion pair. However, theoretical investigation does not prove the ionized tyrosine decomposition. This means that the appearance energy of the $m/z = 92$ fragment is indeed lower than the ionization potential (activation energy); thus, its production does not occur under the experimental conditions.

On the other hand, the experimental results prove formation of the $m/z = 91$ anion with chemical composition of C_6H_3O. So, the decomposition

$$C_9H_{11}NO_3 + e \rightarrow C_6H_3O^+ + (C_3H_6NO_2 + 2H)^- + e$$

occurs. The measured appearance energy of this fragment is equal to 11.2 eV. In fact, we did not obtain coincidence between the values of calculated and measured appearance energies despite that various final products of $C_3H_6NO_2 + 2H$ reactions were studied. In fact, this non-coincidence occurred due to the limitation of the theoretical approach because it is not possible to foresee how far fragments should be from each other under tyrosine decomposition and their possible bonding with other fragments formed. Hence, this result confirms the possibility of the formation of fragments due to H bonding (see below).

The main pathway of the tyrosine molecule fragmentation, similarly to other aromatic amino acids, proceeds through a scission of the $C_\alpha - C_\beta$ bond with the elimination of the cationic side-chain fragment [25]. This type of fragmentation is due to the HOMO that is obviously related to the π molecular orbital of the tyrosine aromatic moiety (Fig. 4). This statement is confirmed by vertical ionization energies calculated for tyrosine and phenol: the difference is about 0.2 eV [26].

The tyrosine molecule has a prominent selectivity of molecular ion dissociation over other aromatic amino acids [27]. Intensities of the fragment ions in the experimental mass spectrum do not reach even 20% of that

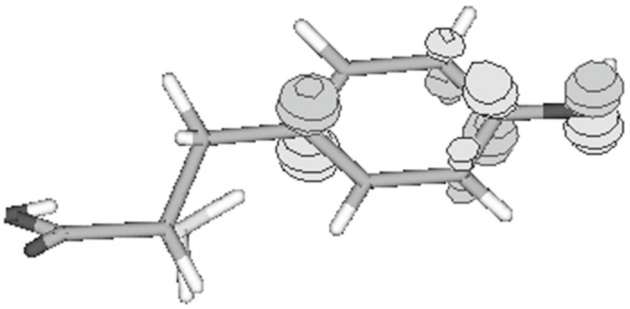

Fig. 4 View of the HOMO orbital of tyrosine

of the main one [20]. It is especially interesting if one compares it with the phenylalanine mass spectrum, since this molecule has a similar structure except of a lack of a hydroxyl in the *para*-position. This OH group presumably makes the side chain of tyrosine able to keep the positive charge more effectively due to electron-donating effect, and moreover, the intramolecular hydrogen bonding between the amino group and the carboxylic oxygen makes complementary fragment with a glycine structure more stable too.

Hence, the main dissociation channel of ionized tyrosine molecule is as follows:

$$C_9H_{11}NO_3 + e \rightarrow C_7H_7O^+ + C_2H_4NO_2^0 + 2e,$$

with the calculated appearance energy of 9.06 eV. However, formation of this fragment could be also realized through the ion pair formation with the absence of other competing fragmentation pathways. In this case, the appearance energy of this fragment (8.04 eV) is the smallest. The experimentally measured appearance energy of this fragment is 10.8±0.2 eV. It is necessary to mention that this value fits the calculated appearance energy for $m/z = 106$. It could indicate the difficulty to separate these two fragments during measurements due to fast proton transfer. On the other hand, we may predict that $m/z = 107$ is formed when C_7H_6O binds H, i.e., the main dissociation channel of the ionized tyrosine molecule could be as follows:

$$\begin{aligned} C_9H_{11}NO_3 + e &\rightarrow (C_7H_6O + H)^+ + C_2H_4NO_2^0 + 2e, \\ &\rightarrow C_7H_7O^+ + C_2H_4NO_2^0 + 2e. \end{aligned}$$

Hydrogen bonding in the tyrosine molecule was carefully described in [28], and it plays a main role in proton transfer that causes the fluorescence quenching. Authors observed a proton transfer from the carboxyl and amino groups to the carbon atoms of the phenol ring. This mechanism may be responsible, when an ion with $m/z = 108$ arises. The intensity of this peak (12.9%) is higher than that of the first isotopic peak ($C^{13}C_6H_7O$, about 8%), so the third part of the $m/z = 108$ peak is due to $C_7H_8O^+$ formed by a proton transfer.

The proton transfer is also indicated by the presence of the $m/z = 18$ fragment peak in the mass spectrum measured. This peak could be H_2O^+ formed when OH is joined with H^+. The OH fragment is complementary one for $m/z = 164$ (Table 1).

In case of tyrosine, the importance of the proton transfer is illustrated by low-intensity peaks of the $m/z = 28$ and $m/z = 29$ fragments. We identified these fragments as CH_2N^+ and CH_3N^+, respectively. Formation of the $m/z = 28$ fragment directly from tyrosine is more probable because its appearance energy is smaller than that of $m/z = 29$ (Table 1), and its stability is higher [14]. However, the low intensity of the $m/z = 28$ peak indicates that this fragment joins fast with H and forms the $m/z = 29$ fragment, and as consequence, the intensity of the above peaks is low and this makes the tyrosine mass spectrum different from those of other amino acids.

The results of our investigation confirm the formation of the $m/z = 42$ and $m/z = 39$ fragments. Their ways of formation are predicted in Table 1. Obviously, the phenyl ring could decompose under low-energy electron impact if its energy is higher than ∼ 14 eV in the case of tyrosine. We also obtained that the $m/z = 64$ fragment is formed from the $m/z = 107$ anion accompanied by the H atom bonding. It results in the assumption that amino acids decomposition under low electron impact is accomplished by accidental reactions.

5 Conclusions

This work presents the new data on the tyrosine ($C_9H_{11}NO_3$) molecule fragmentation under low-energy electron impact. We have calculated the appearance energies for most of ions found in the mass spectrum of the most stable conformers of this molecule. The results of our study show that the tyrosine mass spectrum differs essentially from those of other amino acids investigated by us earlier, e.g., glutamine, alanine and tryptophan. We have concluded that this amino acid decomposition could start directly during ionization. The main dissociation channel of ionized tyrosine molecule has been found. The proton transfer during fragmentation was confirmed experimentally.

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Author contributions

The authors contributed to this paper in the following proportions: Jelena Tamuliene (theoretical calculations, discussion of results)—40%, Liudmila Romanova (dis-

cussion of results)—20%, Vasyl Vukstich (experimental measurements)—20%, Alexander Snegursky (discussion of results)—20%.

Data Availability Statement This manuscript has no associated data or the data will not be deposited. [Authors' comment: The datasets generated during and analysed during the current study are available from the corresponding author on reasonable request.].

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