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Resonance Electron Capture by Serine

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Formation of negative ions via dissociative electron attachment (DEA) to the amino acid serine in the gas phase was studied using two different crossed electron/molecular beam techniques and quantum chemical calculations. Resonance electron capture mass spectrum and effective ion yield curves of 16 negative ions were measured over the electron energy range from close to 0 to 11 eV. The negative ions from serine were detected from resonance states in the vicinity of 0, 1.3, 5, and 8 eV. The dominant reaction channel at low electron energies was $(M - H)^-$. The relative cross section for this ion exceeds more than 20 times that of any other fragment negative ions. A high-resolution experiment was applied to study fine structures in $(M - H)^-$ cross section. We have found that the second OH group influences some dissociative channels. Quantum chemical calculations were applied to interpret products of the DEA reaction channels.

Introduction

Direct interaction of ionizing radiation with living cells is not the exclusive source of a cell's damage. Secondary particles, such as free radicals, ions, and electrons, that are very efficiently formed due to the exposure of the cells to radiation can also participate in a cell's death. Electrons, as the most abundant secondary species, are generated with an estimated quantity of $\approx 5 \times 10^4$ electrons by a 1 MeV particle.¹ The electrons, possessing initial kinetic energies up to 20 eV, can be thermalized in the course of successive inelastic collisions with the medium within 10^{-12} s before they reach some stage of solvation and become chemically rather inactive species.²

The ability of free secondary electrons (3–20 eV) to induce single- and double-strand breaks in DNA has been shown by Sanche and co-workers.³ It was demonstrated that the DNA strand breaks can be initiated by the formation and decay of transient negative ions. This work gave impulse for intensive examination of low-energy interactions between electrons and molecules directly related to the DNA building blocks⁴ and other model biologically relevant molecules.⁵ These investigations stimulated similar studies of resonance electron capture (REC) by amino acids.⁶ The importance of reactions of solvated electrons with amino acids has been earlier recognized by time-resolved pulse radiolysis experiments.⁷ Recently, several studies on REC by aliphatic amino acids have been reported.^{8,9} As far as we know, gas phase REC by serine has not so far been studied in the literature, except for the low-pressure plasma formation of negative ions from serine and other amino acids at fixed electron energies by Voigt and Schmidt.¹⁰

Serine is an aliphatic amino acid and contains a COOH group in the side chain (Figure 1). Additionally, to other aliphatic

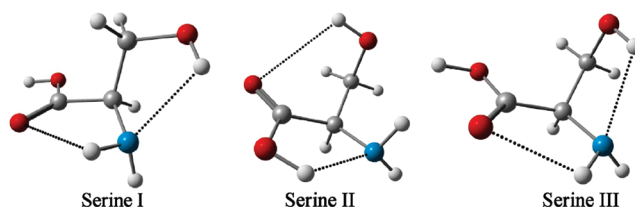


Figure 1. The structures of the three most stable conformers of serine based on G3MP2 calculations. The nomenclature is by Gronert and O'Hair.¹⁴

amino acids (glycine, alanine, and valine), serine exhibits an additional OH group which could change the dissociation behavior of the serine to the above-mentioned amino acids. As has been shown in the case of other aliphatic amino acids,^{8,9} the presence of the carboxylic group in amino acids (and specifically, the OH group) plays an important role in dissociative electron attachment, resulting in the most abundant fragmentation channel associated with the carboxylic H atom loss and generation of the $(M - H)^-$ closed-shell negative ions. The presence of the second OH group in serine may thus lead to a possible interference between competing fragmentation channels that produce $(M - H)^-$ negative ions with different structures.

Experimental Section

REC by serine was studied by means of an orthogonal time-of-flight mass spectrometer, oTOF-MS, at Oregon State University (OSU; Corvallis, OR) and a quadrupole MS at Comenius University in Bratislava, both equipped with monochromators for production of quasimonochromatic electron beams. The energy and mass scales in both instruments were calibrated using, respectively, maxima yield versus electron energy and mass peaks of negative ions from SF_6 and CCl_4 that were present in the ion chambers during the experiments. Serine sample was introduced into the instruments via a custom-made

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direct insertion probe (Corvallis experiments) or a metal oven with a 0.5 mm capillary outlet (Bratislava experiments). The TOF-MS apparatus affords the opportunity to measure three-dimensional (3D) electron energy m/z ion yield spectra in one process. On other hand, the Bratislava apparatus has better electron beam resolution and allows measurement of mass-selected ion yields. Using this apparatus, we were able to resolve the vibrational structures in the $(M - H)^-$ signal.

To have enough serine pressure in the ion chambers, the direct insertion probe and the metal oven were resistively heated to ~ 420 K. This temperature was far below conditions for the sample thermal degradation.¹¹ A serine sample of a stated 99% purity was purchased from Sigma/Aldrich Chemical Co. (St. Louis, MO) and was used without further purification.

TOF-MS. REC-oTOF-MS at OSU was built¹² on the platform of a JEOL JMS-DX300 instrument with the custom-made Ionwerks oTOF mass analyzer. The instrument is capable of producing unique four-dimensional REC spectra of a particular compound in real time that includes gas chromatography (GC) retention time, electron energy, and the ion's m/z and intensity. A commercial JEOL trochoidal electron monochromator, TEM, operating with permanent magnets was modified to improve the electron energy resolving power. The REC-oTOF-MS has several inlet systems for the sample introduction (GC, a custom-made direct insertion probe with a vacuum lock and gas/liquid ports). In the present experiments, the energy ramping rate over 0–10 eV was 10 Hz, and the ion extraction frequency was 80 kHz, which at energy step 2.4 meV and acceleration voltage 2 kV allowed recording 2 ion acquisitions per energy step within an m/z range of ~ 300 . Despite such fast scanning of the oTOF analyzer, accumulation of the three-dimensional REC spectrum of serine required from 40 to 70 min because experimental time was determined by the quality (reasonable signal/noise ratio) of the effective yield curves of the fragment negative ions with the lowest cross sections. The energy spread of the electron beam in these experiments (fwhm) was set to 200 meV to securely record negative ions from serine with large and small formation cross sections.

Quadrupole MS Apparatus. The experimental setup at Comenius University in Bratislava has been described in details elsewhere.¹³ In brief, it consists of a quadrupole mass analyzer Pfeiffer Vacuum QMS400 (mass range 4–2000 amu) and TEM for the generation of the electron beam. The metal oven for the production of the serine molecular beam allowed precise control of the beam during all experimental time. REC mass spectra of serine were recorded at several fixed electron energies, whereas the effective yield curves of the negative ions of interest as functions of electron energy over the range from 0 to 15 eV were recorded after selection of them by the quadrupole mass filter. The energy resolution of the electron beam in these experiments was around 100 meV, which was just enough to find a fine vibrational structure in the yield curve of $(M - H)^-$ negative ions from serine.

Theory. Quantum chemical calculations of the geometrical and electronic structures of neutral serine molecule, its negative ions, and that of fragment negative ions, neutral fragments and radicals formed via REC reactions were carried out. Gronert and O'Hair¹⁴ reported on calculations of 51 structures for L-serine. In the present work, six of the most stable structures of serine determined by Gronert and O'Hair¹⁴ were considered using DFT B3LYP method with the 6-311++G(2df,2pd) basis set. Three of the most stable conformers of them were then studied on the basis of the G3MP2 level of theory.¹⁵ The DFT calculations showed that serine I (the nomenclature by Gronert

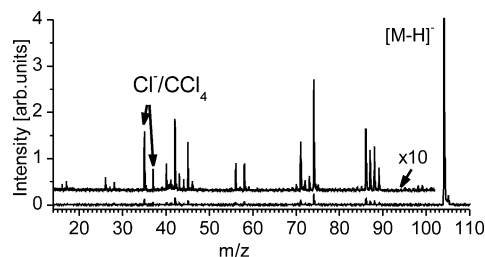


Figure 2. DEA mass spectrum of serine summarized over the 0–11 eV electron energy range; obtained with TOF-MS. CCl_4 was used for the calibration of the mass and energy scales (see the Experimental section).

and O'Hair¹⁴ was used throughout the text) was more stable than serine II (the enthalpy of formation difference was ~ 0.85 meV). The G3MP2 method reversed the order of the conformers, showing that serine II is 6 meV more stable than serine I. The predicted difference in the enthalpies of formation is small, however, and presumes that serine in the gas phase at elevated temperatures should present a mixture of these conformers. The last hypothesis has been confirmed by the data of Fourier transform microwave, FTMW, spectroscopy by Blanco and co-workers.¹⁶ Serine II was predicted to be the most stable canonic form in solution¹⁷ that was in line with the results of NMR studies.¹⁸

Dipole moments of three of the most stable conformers of serine were determined using DFT calculations, and the following values were predicted: 1.96 D for serine I, 4.14 D for serine II, and 2.88 D for serine III. All conformers possess dipole moments exceeding the critical value of 1.625 D that is required to bind an electron to a dipole.¹⁹ The heats of formation of a number of fragment negative ions, neutral even-electron fragments, and radicals relevant to the DEA reactions in serine have been calculated at the G3MP2 level of theory. The results of these calculations then were used for prediction of the reaction enthalpies for different DEA channels in serine.

Vibrational overtones of the OH stretch mode were calculated. The O–H bond potential curve was estimated on the B3LYP/6-311+G(2df,2pd) level of theory using quasi diatomic approximation and analyzed using the approach of Dunham.²⁰

Results and Discussion

The mass spectrum of serine, integrated over the entire electron energy scale (0–11 eV), was obtained with TOF-MS (Figure 2, Table 1) and consists of 24 negative ion peaks of different intensities. The assignment of some of the negative ions and the possible mechanism of their formation will be discussed below. It is quite clear that the mass spectrum exhibits patterns that are similar to those of other aliphatic amino acids studied so far. The loss of a hydrogen atom resulting in the production of the $(M - H)^-$ ions (m/z 104) is the dominant fragmentation process in serine. Although negative ions with m/z 74 are the second most abundant species in the mass spectrum, their relative intensity is only 5.2%. The last ions are most probably formed via cleavage of the CH_2OH group. The relative intensities of other fragment negative ions from serine were found to be significantly lower than that of these two negative ions (Table 1).

As mentioned above, the dominant DEA channel in serine is the following reaction:

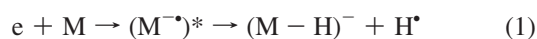


TABLE 1: Relative Intensity (RI) of the Negative Ions, Formed via Resonance Electron Capture to Serine, at the Maximum of the Particular Resonance (E_m) as Obtained from the MS-TOF Experiment

m/z	negative ions	RI, % (E_m , eV)
104	$(M - H)^- = C_3H_6NO_3^-$	100 (1.1)
89	$(M - NH_2)^- = C_3H_5O_3^-$	1.23 (1.3)
88	$C_3H_6NO_2^-/C_3H_4O_3^-$	0.86 (0)
87	$C_3H_5NO_2^-/C_3H_3O_3^-$	0.3 (0)
86	$C_3H_4NO_2^-/C_3H_2O_3^-$	0.4 (0)
74	$C_2H_4NO_2^-$	1.46 (1.3)
73	$C_2H_3NO_2^-/C_3H_5O_2^-$	1.45 (1.3)
71	$C_3H_3O_2^-/C_2H_5NO^-$	1.47 (1.2)
58	$C_2H_2O_2^-/C_3H_4O^-$	1.34 (5.4)
56	$C_3H_6N^-/C_2H_2NO^-$	5.16 (5.7)
45	$COOH^-$	2.05 (1.4)
42	$NCO^-, C_2H_4N^-$	0.53 (5.6)
28	CO^-	1.42 (5.2)
26	$CN^-/C_2H_2^-$	0.8 (6.3)
17	OH^-	0.64 (8.3)
16	O^-, NH_2^-	2.55(5.7)
		1.66 (5.6)
		1.06 (7.4)
		0.5 (5.5 – 7)
		0.36 (5.5)

Formation of $(M - H)^-$ negative ions from amino acids near 1 eV has been widely discussed in the literature, and several scenarios have been reported that included electron attachment to a $\pi^*(COO)$ orbital, resulting in carboxylate anion structure^{6,21} and hydrogen atom loss from different sites of amino acids.²² Simple thermochemical calculations predicted that at these low energies, only carboxylate negative ions can be formed,^{22,23} whereas analysis of the resonance energy producing these ions excluded electron capture into a $\pi^*(COO)$ orbital at energies lower than ~ 1.5 eV.^{22,24} High-energy resolution experiment²⁶ indicated vibrational Feshbach resonances producing $(M - H)^-$ negative ions at these low energies. The effective yield curve of $(M - H)^-$ ions from serine (Figure 3) was recorded using oTOF-MS (Corvallis experiments, fwhm is 200 meV) and Q-MS (Bratislava experiments, fwhm is 100 meV). Higher electron energy resolution used in the Bratislava experiments revealed a vibrational structure in the $(M - H)^-$ effective yield curve (Figure 3B) that is similar to that observed earlier for glycine and alanine.^{25,26} The structure in the serine DEA cross section is presumably caused by vibrational Feshbach resonances, whereas the question of electron capture to serine either directly via a $\sigma^*(OH)$ shape resonance^{31,23} or dipole-bound state²⁵ still remains unclear because of insufficient energy resolution applied in these experiments. Gallup and co-workers²⁷ using their

TABLE 2: Energy Positions of Vibrational Feshbach Resonances (VFR) in the $(M - H)^-$ Ion Yield Curve, Calculated $\nu(O-H)$ Stretch Overtones of the $COOH$ Group, Reaction Enthalpies $\Delta H(OH)$ for the OH Bond Cleavage at the Carboxylic Group for the Three Most Stable Conformers of Serine According to the G3MP2 and DFT B3LYP (in parentheses) Methods

VFR (eV), experiment	$\nu(O-H)$ stretch overtones, (eV) calculated	$\Delta H(OH)$ (eV)
0.8	$\nu_2 = 0.85$	serine II 0.85 (0.79)
1.1	$\nu_3 = 1.24$	serine I 0.91 (0.86)
1.4	$\nu_4 = 1.62$ $\nu_5 = 1.97$	serine III 1.007 (0.916)

R-matrix calculations showed that $\sigma^*(OH)$ shape resonance, initially suggested by Allan,²⁸ can be a doorway state for dissociation into $(M - H)^-$ negative ions with down-step structures in a DEA cross section.

Table 2 shows a comparison between experimentally observed features in a DEA cross-section and calculated vibrational progression for the $\nu(O-H)$ stretch as well as theoretical thresholds for the $(M - H)^-$ production from three of the most stable conformers of serine. The vibrational progression for the $\nu(OH)$ stretch mode of the serine I conformer was calculated using quasi diatomic approximation (see Theory section). It is important to mention that the initial vibrational quantum in the discussed case was $E_{v1-v0} = \sim 0.434$ eV. In the case of the serine II conformer, the internal hydrogen bond between the amino group and the carboxylic hydrogen reduces the vibrational quantum of around 30 meV (on the basis of DFT calculations). The agreement between experimental and theoretical data is reasonable (see Table 2). One of the most important findings from the present experiments is that the presence of another OH group in the serine's side chain does not cause additional features in the $(M - H)^-$ yield curve. Serine shows structures similar to glycine or alanine DEA cross section at low energies.^{25,26} At least possible additional structures are not apparent at the experimental conditions used in the present work, and therefore, one can conclude that the carboxylic hydrogen plays the main role in the production of the $(M - H)^-$ negative ions from serine at energies near 1.2 eV. Theoretical calculations of a hydrogen atom loss from different places of the serine molecule also support this conclusion (Table 3) because the threshold for H cleavage from the OH group is above 1.7 eV for all conformers.

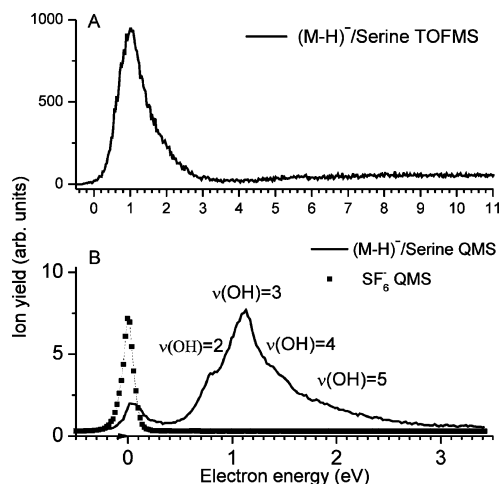


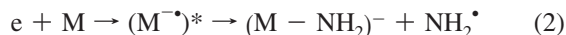
Figure 3. Effective yield curves of the $(M - H)^-$ negative ions from serine as functions of the electron energy obtained with TOF-MS (A) and Q-MS (B). The effective yield curve of SF_6^- was used for the calibration of the energy scale (see the Experimental section).

TABLE 3: The Reaction Enthalpies for Some Fragmentation Channels, Predicted on the Basis of DFT and G3MP2 Calculations

<i>m/z</i>	conf	anionic fragments	neutral fragments [ΔH_r B3LYP/ ΔH_r G3MP2, eV] ^a		
104	I	NH ₂ CH(CH ₂ OH)COO ⁻	H [0.86/0.92]		
	I	NH ₂ C(CH ₂ OH)COOH ⁻	H [1.98/2.14]		
	I	NH ₂ CH(CH ₂ O)COOH ⁻	H [1.99/2.16]		
	II	NH ₂ CH(CH ₂ OH)COO ⁻	H [0.79/0.85]		
	II	NH ₂ C(CH ₂ OH)COOH ⁻	H [1.91/2.13]		
	II	NH ₂ CH(CH ₂ O)COOH ⁻	H [1.71/1.87]		
	III	NH ₂ CH(CH ₂ OH)COO ⁻	H [0.92/1.01]		
	III	NH ₂ CH(CH ₂ O)COOH ⁻	H [1.96/2.15]		
	III	NH ₂ C(CH ₂ OH)COOH ⁻	H [1.95/2.13]		
89	I	OHCH ₂ CHCOOH ⁻	NH ₂ [1.09/1.45]		
	II	OHCH ₂ CHCOOH ⁻	NH ₂ [1.22/1.59]		
88	I	NH ₂ CH(CH ₂)COOH ⁻	OH [3.05/3.29]		
	I	NH ₂ CH(CH ₂ OH)CO ⁻	OH [3.64/3.82]		
	I	OCH ₂ CHCOOH ⁻	NH ₃ [0.44/1.48]	NH ₂ + H [5/6.1]	
	I	OCHCH ₂ COOH ⁻	NH ₃ [-0.2/0.69]	NH ₂ + H [4.54/5.32]	
	II	OHCH ₂ CHCOO ⁻	NH ₃ [-0.54/-0.09]	NH ₂ + H [4.02/4.54]	
87	I	NH ₂ C(CH ₂ OH)CO ⁻	H ₂ O [1.08/1.46]	OH + H [6.11/6.57]	
	I	NH ₂ C(CH ₂)COOH ⁻	H ₂ O [-0.05/0.35]	OH + H [4.98/5.46]	
	I	NH ₂ CH(CH ₂)COO ⁻	H ₂ O [-0.16/0.14]	OH + H [4.86/5.25]	
	I	OCHCHCOOH ⁻	NH ₃ + H [0.51/1.15]	NH ₂ + H ₂ [0.53/1.21]	NH ₂ + H + H [5.068/5.77]
	I	(OCH ₂ CH)COO ⁻	NH ₃ + H [2.05/2.30]	NH ₂ + H ₂ [2.06/2.36]	NH ₂ + H + H [6.6/6.92]
	I	OCHCH ₂ COO ⁻	NH ₃ + H [0.7/1.06]	NH ₂ + H ₂ [0.72/1.12]	NH ₂ + H + H [5.26/5.68]
	II	NH ₂ C(CH ₂ OH)CO ⁻	H ₂ O [1.18/1.57]	OH + H [6.2/6.68]	
	II	NH ₂ C(CH ₂)COOH ⁻	H ₂ O [0.03/TS]	OH + H [5.06/TS]	
	II	OCHCHCOOH ⁻	NH ₃ + H [0.39/0.8]		
	II	OCHCH ₂ COO ⁻	NH ₃ + H [0.7/1.07]		
	II	OCHCHCOO ⁻	NH ₃ + H ₂ [0.44/0.52]	NH ₃ + H + H [4.98/5.09]	NH ₂ + H ₂ + H [5/5.15]
	I	NH ₂ C(CH ₂)COO ⁻	H ₂ O + H [1.03/1.27]	OH + H ₂ [1.51/1.81]	OH + H + H [6.05/6.38]
	74	NH ₂ CHCOOH ⁻	H ₂ COH [1.47/1.95]	H ₂ CO [1.74/2.33]	H ₂ CO + H [2.85/3.21]
	I	NH ₃ CCOOH ⁻	H ₂ COH [4.25/4.67]	H ₂ CO [4.52/5.05]	H ₂ CO + H [5.64/5.94]
	I	NH ₂ CH ₂ COO ⁻	H ₂ COH [0.32/0.76]	H ₂ CO [0.6/1.14]	H ₂ CO + H [1.71/2.02]
	II	NH ₂ CHCOOH ⁻	H ₂ COH [1.54/2.05]	H ₂ CO [1.81/2.43]	H ₂ CO + H [2.92/3.31]
71	I	NH ₂ C(CH ₂)CHO ⁻	H ₂ O ₂ [3.26/3.83]	OH + OH [5.27/5.89]	
	I	NH ₂ CH(CH ₂)CO ⁻	H ₂ O ₂ [frag./5.7]	OH + OH [frag./7.76]	
	I	OCH ₂ CHCO ⁻	NH ₃ + OH [3.09/frag.]		
	II	CH ₂ CHCOO ⁻	NH ₃ + OH [1.21/1.61]		

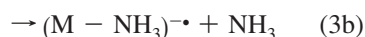
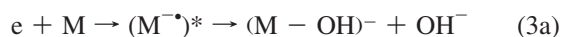
^a Frag. = resulting anionic structure is not stable and dissociates, TS=transitional state, stable anionic structure not found.

Negative ions with *m/z* 89 were observed at a resonance with a maximum at an electron energy of ~1.3 eV (Table 1, Figure 4A) and supposedly formed by loss of a neutral fragment with a mass of 16 u. The neutral particle is either a NH₂[•] group or O[•]. The elimination of the atomic oxygen is energetically less favorable³⁰ than the following reaction.



This interpretation is supported by calculations carried out by B3LYP and G3MP2 levels of theory, yielding for the reaction enthalpies $\Delta H = 1.09$ or 1.45 eV, respectively, for serine I and $\Delta H = 1.22$ eV or 1.592 eV, respectively, for serine II.

Negative ions with *m/z* 88 with maxima of the resonances near 0 and 1.3 eV (Table 1, Figure 4B) can be produced via two different fragmentation pathways:



According to the present calculations (Table 3), channel 3a is endothermic by ~3 eV, whereas channel 3b is predicted to be exothermic by ~0.5 eV. Therefore, we believe that these ions are exclusively formed via channel 3b. The ~0 eV peak arises from electron capture to vibrationally excited molecules where

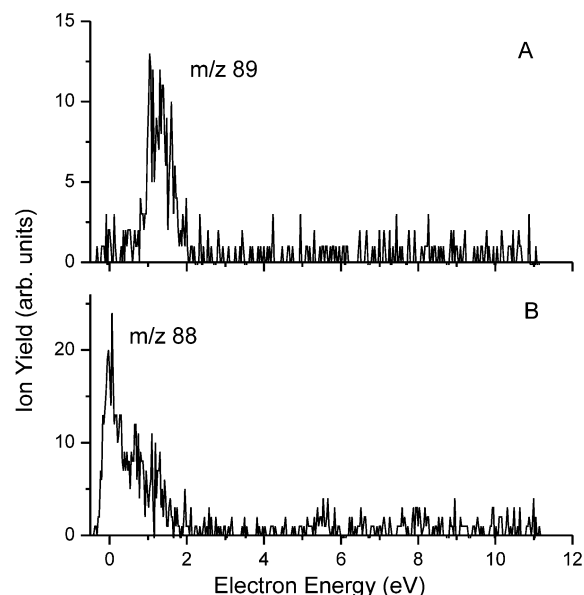


Figure 4. Effective yield curves of negative ions with *m/z* 89 (A) and 88 (B) from serine as functions of electron energy.

the low population of the excited states is compensated by the high s-wave electron capture cross section.

The negative ions with *m/z* 87 are formed at resonances peaking at around 0, 1.3, and 8.2 eV (Table 1, Figure 5A). Loss

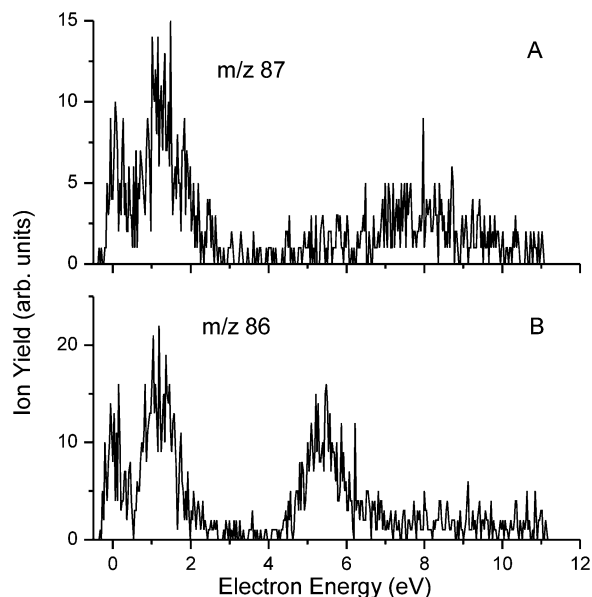
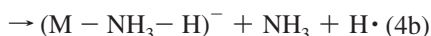
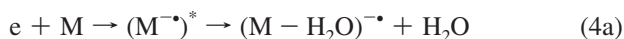
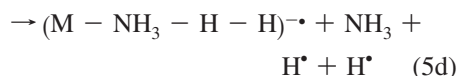
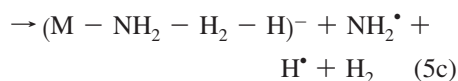
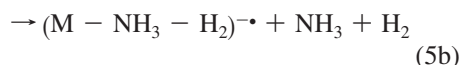
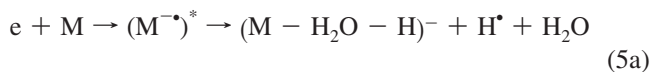


Figure 5. Effective yield curves of negative ions with m/z 87 (A) and 86 (B) from serine as functions of electron energy.

of a neutral fragment with mass 18 u from serine molecular negative ions can be explained via two possible reaction pathways:



The enthalpies of these reactions were calculated (Table 3) for two serine conformers, and the calculations predicted that both pathways can occur from resonances at 1.3 and 8.3 eV. Production of these ions at near 0 eV is unclear and perhaps associated with electron attachment to vibrationally excited molecules. To distinguish between these two decay channels, high-resolution mass spectrometry or isotopic labeling would be of help. Negative ions with m/z 86 were observed from resonances at energies near 0, 1.3, and 5.5 eV (Table 2, Figure 5B). The most probable reactions producing these negative ions are



Some of these reactions were calculated (Table 3). According to the calculations, the first two reactions (5a and 5b) were predicted to occur from a resonance state near 1.3 eV, whereas only high-energy resonance at 5.5 eV is open for the last two reactions (5c

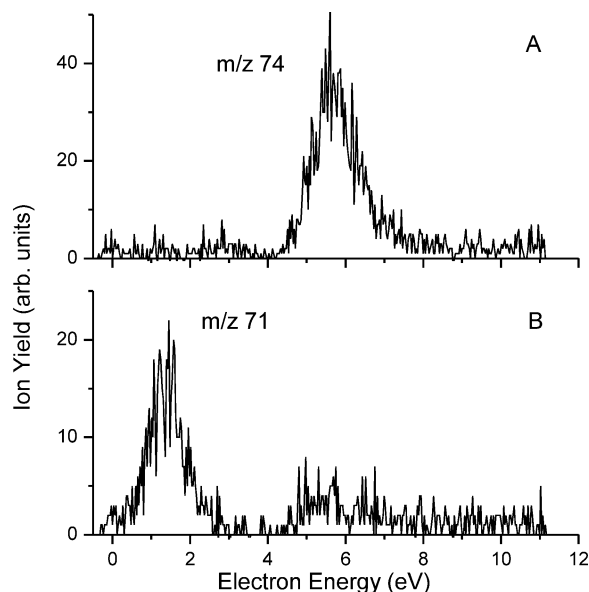


Figure 6. Effective yield curves of negative ions with m/z 74 (A) and 71 (B) from serine as functions of electron energy.

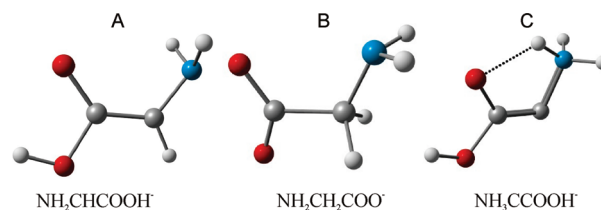


Figure 7. Possible structures for fragment negative ion with m/z 74 according to DFT and G3MP2 methods.

and 5d). It is interesting that amino acids studied by Vasil'ev et al.²⁹ fragmented into negative ions with loss of a water molecule and a hydrogen atom only at higher energies. The present calculations predict a decrease in the enthalpy for this reaction due to an additional OH group in serine, and therefore, this fragmentation process is allowed to occur at lower energies.

Negative ions with m/z 74 were detected with a maximum yield at 5.7 eV (Figure 6A, Table 1), and they can be formed via the following reactions:



Three ionic structures (Figure 7) corresponding to these reactions were considered. The enthalpies of reactions 6 were calculated using the DFT B3LYP and G3MP2 theories (Table 3). The calculations predict that reaction 6b, producing ions with the glycine carboxylate anion structure B, has the lowest enthalpy. The simple bond cleavage reaction 6a is more endothermic than 6b; however, it is kinetically more favorable because it is realized during one vibration. Similar ions associated with loss of the side chain of amino acids were clearly observed in the case of aromatic amino acids and suppressed in the case of alanine but not for its methyl ester.²⁹ The situation with glycine was rather difficult, since these ions in glycine

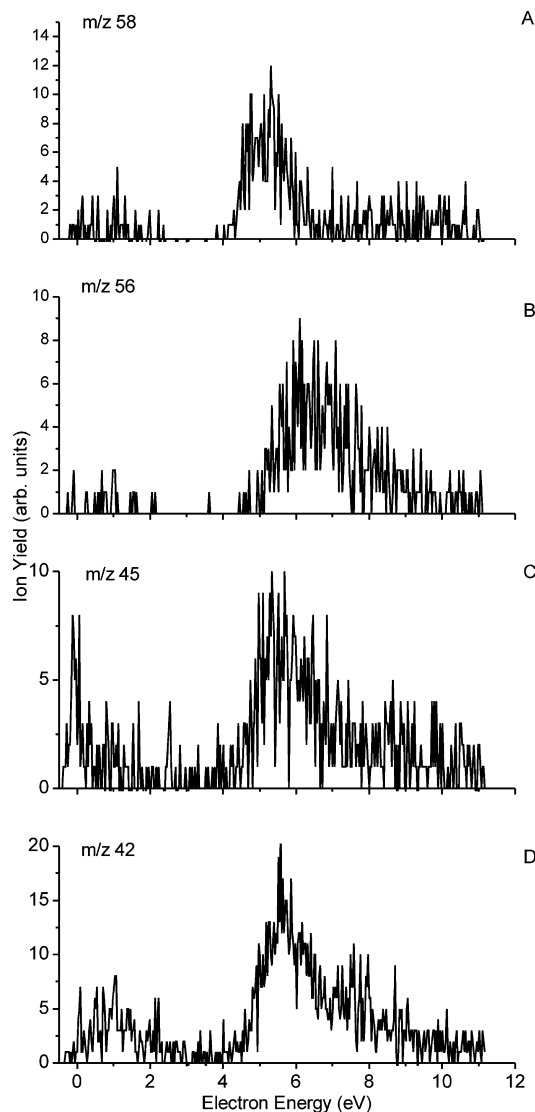


Figure 8. Effective yield curves of negative ions with m/z 58 (A), 56 (B), 45 (C), and 42 (D) from serine as functions of electron energy.

could be easily confused with any other $(M - H)^-$ ions; however, C_α -deuterated glycine confirmed production of the $(M - D)^-$ ions at higher energies, thus proving loss of the “side chain” to occur in the case of glycine. The enthalpy of reaction 6c was also found to be lower than the resonance energy, and although generation of negative ions with m/z 74 via this reaction should presumably involve some rearrangement processes, in principle, it should not be ignored. Since all of these ions have exactly the same masses, application of high-resolution mass spectrometry and metastable decay analysis may help to answer the fragmentation pathways of the negative ions with m/z 74.

Negative ions with m/z 71 were observed (Figure 6B, Table 1) at low (1.4 eV) and high (5.4 eV; perhaps they are also formed at ca. 7 eV, however S/N ratio was too low to determine it most certainly) energies and can be generated via the following fragmentation processes:



Quantum chemical calculations predict (Table 3) that the low-energy resonance can decay only via channel 7b, whereas both

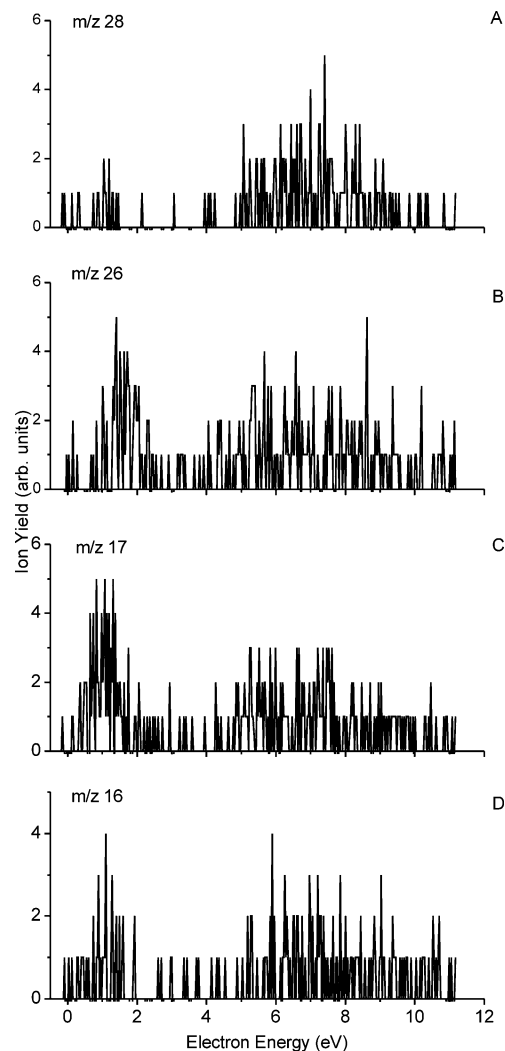


Figure 9. Effective yield curves of negative ions with m/z 28 (A), 26 (B), 17 (C), and 16 (D) from serine as functions of electron energy.

fragmentation pathways 7a and 7b can occur from a higher resonance state. Two more fragment negative ions with structures $\text{NH}_2\text{CH}(\text{CH}_2)\text{CO}^-$ and $\text{OCH}_2\text{CHCO}^-$ also having m/z 71 have been considered (Table 3). However, both were found to be unstable and probably fragment to $\text{CO}^- + \text{CH}_2\text{CHNH}_2$ and $\text{CH}_2\text{O} + \text{CHCO}^-$, respectively (charge delocalization based on relative electron affinities of fragments).

Negative ions with m/z 58 and 56 were observed at higher energies (Figure 8, Table 1) and can have two different structures: $\text{C}_2\text{H}_2\text{O}_2^-$ or $\text{C}_3\text{H}_6\text{O}^-$ and $\text{C}_3\text{H}_6\text{N}^-$ or $\text{C}_2\text{H}_2\text{NO}^-$, respectively. All of these ions were earlier reported in DEA studies of other amino acids.^{4,29} In the case of m/z 58, cleavage of the CN bond is required for production of the proposed ions, whereas disruption of a CO bond is necessary to form negative ions of any proposed structures with m/z 56. Since the CO bond dissociation enthalpy is generally higher,³⁰ it is expected to observe negative ions with m/z 58 at lower energies. Comparison of the maximum yields for these ions (Table 1; Figure 8A, B) confirms this suggestion derived from general consideration.

Formation of negative ions of low masses from aliphatic and aromatic amino acids was described earlier in great detail by Vasil'ev et al.²⁹ Ptasinska et al.⁴ and Papp et al.²² discussed production of CHOO^- (m/z 45) via direct bond cleavage. Ptasinska et al.²¹ reported on detection of negative ions with m/z 42 (CON^- or $\text{C}_2\text{H}_4\text{N}^-$) from alanine. Both of these ions

were observed from serine (Figure 8C, D; Table 1). Negative ions with a lower m/z ratio, such as 28, 26, 17, 16, produced from amino acids were also discussed earlier.^{8,29} Mauracher et al.²³ and Sulzer et al.³¹ using a double focusing instrument with high mass resolving power reported on accurate mass measurements of some of the ions. Bearing in mind these accurate mass measurements, negative ions with m/z 26 from serine (Table 1; Figure 9) can be interpreted as $C_2H_2^-$ (high energies) and CN^- (low energies), whereas negative ions with m/z 17 and m/z 16 can be attributed, respectively, to OH^- and O^- or NH_2^- . The ion signal at m/z 28 we are not able to assign unequivocally. The negative ions H_2CN (EA = 0.511 eV³²), and CH_2C (EA = 0.4466 eV³³) are known to have positive electron affinity. Unfortunately, the intensities of the ion signal at m/z 28 and 26 ($CN^-/C_2H_2^-$) were rather weak for precise determination of their maximum yields and to give more precise picture of the reactions.

Conclusions

The REC to serine was studied experimentally using two different crossed electron/molecular beam techniques with mass spectroscopic analysis of the products and high-resolution electron beam. The measured mass-selected ion yields were interpreted on the basis of quantum chemical calculations. The dominant product of DEA to serine was the $(M - H)^-$ ion. The high-resolution electron beam study of this resonance shows vibrational structures that were assigned to the OH group of COOH. The mechanism of $(M - H)^-$ formation was discussed. We have found that the second OH group does not contribute to the $(M - H)^-$ formation at the main resonance. The calculations show that the presence of the additional OH group in serine reduces the reaction enthalpies for H_2O and $H_2O + H$ formation so that these reaction channels are already accessible at low energy resonance, ~ 1.3 eV. We have assigned ionic structures to fragment anions present in the mass spectra on the basis of calculated reaction enthalpy limits. The $m/z = 74$ ion was assigned to the H_2COH moiety loss via direct dissociation of the R group or via a more complex process. The origin of low m/z ions was discussed on the basis of comparison with previous DEA studies to aliphatic amino acids.

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