Chapter 12

Charge Transfer Processes in Key Biological Systems

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12.1 Introduction

The interaction of high-energy ionising radiation (e.g. X-rays, γ -rays, ions, protons and electrons) with biological systems generates a large amount of secondary species along the radiation track. Briefly, the primary high-energy ionising radiation interaction with living organisms occurs on a time scale triggers within the early stages of irradiation ($\sim 10^{-16}$ to 10^{-15} s), multiple sequences of physical and chemical reactions, resulting mainly in electronic excitation and ionisation of the molecular constituents, with subsequent bond breaks creating large amounts of secondary electrons and radicals. The damage in DNA macromolecule created by these secondary species are characterized by single strand breaks (SSB), double strand breaks (DSB), clustered damage, base damage and loss of the supercoiled helix integrity. The consequences of these injuries in a long-term time scale can lead to severe consequences, namely mutations, chromosome aberrations, cell inactivation and other effects that compromise the genome integrity which may even result in cancer (Goodhead et al. 1993; Goodhead 1994; Nikjoo et al. 1997; Little 2000). Given this complexity, a complete understanding of these processes represents a challenging task.

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It is now well-established that low-energy electrons (LEE) can act as primary damage agent in biological medium or induce indirect reactions through the interaction with other molecules, e.g. water or oxygen molecules, producing large quantities of highly reactive species (radicals, cations and anions). Typically, 5×10^4 secondary electrons (<20 eV) are produced per MeV of primary radiation (Cobut et al. 1998; Uehara et al. 1999; Swiderek 2006; Alizadeh et al. 2015). Along the track and due to successive inelastic interactions with the medium, these secondary electrons transfer their kinetic energy until they reach a near-zero energy (thermalisation) prior to undergoing solvation (Alizadeh and Sanche 2012; Neustetter et al. 2015). At this energy range, different electron induced processes can occur yielding different levels of molecular alterations, either producing ionisations (energies typically above 7 eV), bond rupture or resonant attachment, among several others.

In order to understand the mechanisms induced by radiation in biosystems it is necessary to describe the atomic and molecular processes involved in such interactions, through the knowledge of number of dissociative events, type of interactions, neutral and ionic species created, energy deposition, angular distribution functions and cross-section values. This comprehensive information is highly relevant to the use of radiation in medicine, namely for the development of new radiation treatments and production of new molecular compounds (Limão-Vieira et al. 2012). A pioneering study, performed by Boudaïffa et al. (2000) (updated by Huels et al. 2003), has demonstrated that electrons with energies up to 20 eV are capable to induce SSB and DSB in plasmid DNA. This study has also established that DNA damage is highly dependent on the initial kinetic energy of the incident electron, particularly below 15 eV, and even that SSB and DSB yields in the region of 7–10 eV incident electrons are one to two orders of magnitude larger than those for 10–25 eV photons. Since the quantum yields for DSBs and SSBs show a resonant-like behaviour with electron energy, electron attachment to DNA subunits was proposed to be the initial degradation step (Martin et al. 2004). Another relevant aspect of the recent experimental DEA studies to DNA pyrimidine bases (Ptasińska et al. 2005b) is that the process is both bond (C–H vs. C–N) and site selective (N1–H vs. N3–H) as to the abstraction of an hydrogen atom. Thus, a new mechanism for DNA damage has been established where dissociative electron attachment is the prevalent mechanism in the electronic interaction with biomolecules after irradiation.

Electron attachment is set as a direct electron capture by a target molecule leading to formation of a transient negative ion (TNI) with a lifetime of $\sim 10^{-16}$ s (Denifl et al. 2012). The process is considered as a resonant scattering, which means that the energy of the incident electron must be exactly the energy necessary to reach a *quasibound* state of the molecular target (resonance) (Illenberger and Momigny 1992). The formation of a TNI represents a transition in the Franck-Condon region from the electronic ground state of the neutral molecule (ABC) to the potential energy surface of the molecular anion (ABC^-). The TNI has a very short lifetime which depends on the size of the molecule as well as the width of the resonance according to the Heisenberg's uncertainty principle. As the TNI is unstable it can decay through three different channels: radiative stabilization, auto-detachment and dissociation (Eq. 12.1). DEA occurs when the TNI decay results in bond-breaking

yielding anions and one (or more) neutral species, such process typically occurring on a timescale of 10^{-14} to 10^{-12} s (Illenberger and Momigny 1992). In other words, the TNI dissociates through the instability created by the extra electron, adding an excess of internal energy to the neutral molecule, which is initially captured into an unoccupied molecular orbital (anti-bonding) and has the capability to change the intramolecular potential and. It is a competitive process with auto-detachment.

where, ABC stems for the polyatomic target molecule and $(ABC)^{-\#}$ for the TNI with an excess of internal energy.

However, many elementary collisional processes are not direct electron impact but rather depend upon electron transfer, the latter certainly more prevalent under biological conditions. In this context, the studies on molecular damage by free electron attachment processes must be complemented with studies on electronic capture of “bound” electrons (as in atom-molecule collisions).

Studies on electron transfer experiments using several complex molecular targets were previously performed showing the influence of a third body (cationic projectile post-collision) as stabiliser agent leading to different reaction channels as in contrast to DEA. Such observations were verified by Antunes et al. (2010) in a former study on nitromethane as a molecular target, where formation of a parent anion ($\text{CH}_3\text{NO}_2^{-}$) was detected in contrast to DEA studies. Other relevant studies dealt with tuning the collision energy of the hyperthermal neutral potassium beam in collisions with methylated and deuterated pyrimidine molecules. In these studies, Almeida et al. (2013a) have shown that H^{-} loss proceeds not only through the breaking of the (C–H) against (N–H) bonds but also through N1 against N3 sites. These results have shown that electron transfer to pyrimidines is also site and bond-selective (Almeida et al. 2013a). Furthermore, these authors have also studied D-Ribose (Almeida et al. 2013b) and THF (Almeida et al. 2014) where major enhancements in the formation of OH^{-} and O^{-} were observed compared to DEA experiments. Investigation on gas-phase thymine and uracil molecules by Almeida et al. (2011) also provide information about the dissociation channels and the fragmentation pattern by electron transfer as well as CNO^{-} formation as the major ring breaking anionic product for both molecules. These findings lead to novel methods in controlling chemical reactions with respect to the atomic and molecular mechanisms involved in biological damage caused by secondary electrons (Almeida et al. 2013a).

As previously mentioned, LEE are capable of inducing chemical and physical alterations in the main molecular components of cells. Within these set of molecular constituents, we find the proteins. Proteins are important structural and functional biomolecules that are a major part of every cell consisting of long chains of building block molecules termed amino acids. The amino acids can combine with each other forming chains assembled in a specific way producing a three-dimensional protein with a specific cellular function. The amino acids and subsequently proteins are close related with DNA and RNA molecular structures in a protein synthesis (Frauenfelder

2010) process. Thus, it appears essential to investigate the role of LEE interactions on proteins and their constituents to fully understand the direct and indirect mechanism of radiation induced damage processes in proteins and, consequently, in DNA.

The alterations induced by LEE (<40 eV) in aliphatic amino acids (glycine, alanine and cysteine) adsorbed on a Pt substrate were investigated through mass spectrometry experiments (Abdoul-Carime and Sanche 2004). For energies below 15 eV the anions produced were due to DEA processes while above 15 eV, the anion desorption was mainly assigned to non-resonant dipolar dissociation. Negative anions formation from thin condensed films of aromatic amino acids, such as tryptophan, histidine and proline, were also studied by electron impact (Abdoul-Carime and Sanche 2003), showing the dominance of DEA processes at low energy. These studies have revealed that the fragmentation yield of amino acids was found to be as intense as that of the nucleic acid bases. Studies in gas-phase amino acids were also performed by different research groups, where decomposition of tryptophan by LEE attachment (<10 eV) was investigated by means of a crossed electron/molecular beam experiment demonstrating that the most predominant dissociation processes occur at sub-excitation energies (Abdoul-Carime et al. 2005). Many other gas-phase amino acids were also investigated by dissociative electron attachment (Gohlke et al. 2002; Ptasińska et al. 2003, 2005a; Papp et al. 2006; Mauracher et al. 2007; Scheer et al. 2007; Ferreira da Silva et al. 2010; Muftakhov and Shchukin 2010) and electron impact ionisation (Papp et al. 2012). Electron transmission spectroscopy measurements were carried out on several amino acids in order to investigate the vertical attachment energies for the formation of low-lying temporary anion states, where attachment to the empty π^* orbital of the $-\text{COOH}$ group was assigned in all the molecular targets probed (Aflatooni et al. 2001). Other studies include electron impact ionisation of gas-phase and hydrated valine (Denifl et al. 2009), theoretical calculations were also performed to calculate the cross-section for elastic scattering by glycine (dos Santos et al. 2012) and alanine (Loupas and Gorfinkiel 2019) as well as a comprehensive analysis of the decarboxylation mechanism of amino acids with and without water (Li and Brill 2003).

Concerning electron transfer processes in gas-phase amino acids, studies were performed in atom-molecule collisions showing several differences as to the fragmentation pattern compared with free electron attachment measurements (Ferreira da Silva et al. 2010, 2014, 2016). Such experimental studies will be comprehensively discussed in this chapter.

In the next section we will discuss the main aspects about electron transfer processes in atom-molecule collisions. Further, we will briefly introduce and describe the experimental setup used in collisions with neutral potassium atoms and several molecular targets. Finally, we provide measurements of potassium collisions on different amino acids (e.g. tryptophan, tyrosine, glycine, alanine and uridine) as well as on acetic acid. We will finish with concluding remarks.

12.2 Fundamental Aspects of Electron Transfer Processes

In atom-molecule collisions the electron is not free but weakly bounded to a neutral atom, which acts as an electron donor. In such collisions, the electron is transferred from the neutral atom (e.g. alkali) to a neutral molecular target, and a negative ion is formed as part of an intermediate step or as a final product. Alkali atoms have very low ionisation energies and are therefore excellent electron donors. The alkali atom in the present case is a potassium atom (K), which has a low ionisation energy ($IE(K) = 4.34$ eV). After the electron transfer process in the interaction of the alkali atom with the molecule, several reaction channels can be accessed, such as non-dissociative ionisation (Eq. 12.2), dissociative ionisation (Eq. 12.3), associative chemionisation (Eq. 12.4) and polar dissociation (Eq. 12.5).

The electron transfer process may also be described in two separate stages. First, it is necessary for the alkali atom to undergo ionisation in the vicinity of the target molecule. The ejected electron must then be captured by the molecular target leading to formation of a transient negative ion. The electron transfer processes happens when, at small atom-molecule distances the stationary non-perturbed states, the covalent and ionic diabatic states have the same potential energy surface value (termed crossing point). In first approximation the rotational and vibrational periods are considered *zero*, which means that the molecular target is “frozen” (the molecule is rigid during the collision). This assumption is valid if the atom-molecule potential is isotropic and the electronic properties of the molecule, especially its electron affinity, are independent of its internal degrees of freedom. This is true in the case that the vibrational time is much larger than the collision time. When the collision time is approximately identical to the vibrational time, the second crossing radius is different from the first and the probability of a diabatic transition at the second crossing increases as well as ion-pair formation (Kleyn et al. 1982). For large atom-molecule distances the ionic potential energy lies above the covalent potential and the endoergicity (ΔE) of the system is given by:

$$\Delta E = IE(K) - EA(ABC) \quad (12.6)$$

where $IE(K)$ is the potassium ionisation energy and $EA(ABC)$ is the electron affinity of the target molecule. The crossing radius (R_c) in Å can be determined through the following equation:

$$R_c = \frac{e^2}{\Delta E} = \frac{14.42}{\Delta E} \quad (12.7)$$

Consequently, in a reaction where a cation and an anion (ion-pair formation) are formed, only the lowest ionic state will be involved. On the other hand, it should be noted that in these processes the electron transfer is only possible between configurations of the same symmetry and multiplicity (Hubers et al. 1976; Kleyn and Moutinho 2001; Limão-Vieira et al. 2012). Indeed, the presence of a third body (cationic projectile post-collision) in the collisional mechanism acts as a “stabiliser” in the vicinity of the system (TNI) which leads to differences in the reactions pathways that are accessible when compared with free electron attachment processes.

12.3 Experimental Section

The negative ion time-of-flight (TOF) mass spectra were obtained in collisions of potassium atoms with glycine molecules in a crossed beam set-up configuration described elsewhere (Antunes et al. 2010). Briefly, an effusive molecular beam crosses a primary beam of fast neutral potassium (K) atoms. K^+ ions produced in a potassium ion source are accelerated to 20–100 eV in the lab frame. The K^+ beam passes through an oven where it resonantly charge exchanges with neutral potassium to produce a beam of fast (hyperthermal, K^0) atoms. Residual ions from the primary beam are removed by electrostatic deflecting plates outside the oven. The intensity of the neutral potassium beam is monitored using a Langmuir-Taylor ionisation detector, before and after the collection of each TOF mass spectra. The glycine effusive beam was introduced into the collision chamber through a 1 mm diameter aperture, where it was crossed with the neutral hyperthermal potassium beam between two parallel plates at 1.2 cm mutual separation. The anions produced were extracted by a 250 V cm^{-1} pulsed electrostatic field. The typical base pressure in the collision chamber was $4 \times 10^{-5} \text{ Pa}$ and the working pressure was $2 \times 10^{-4} \text{ Pa}$ upon heating the powder sample. Mass spectra (resolution $m/\Delta m \approx 125$) were obtained by subtracting the background signal (without the heated sample) from the sample measurements. Mass calibration was carried out on the basis of the well-known anionic species formed after potassium collisions with the nitromethane molecule (Antunes et al. 2010).

Glycine samples used were purchased from Sigma-Aldrich with a minimum purity of 99% and used as delivered. The samples were heated to 428 K and the temperature was controlled using a PID unit. In order to test for thermal decomposition products in the target beam, mass spectra were recorded at different temperatures. No differences were observed in the relative peak intensities as a function of temperature. The extraction region and the TOF system were heated to approximately 393 K throughout measurements in order to prevent any sample condensation and thence charge accumulation on the electrodes.

12.4 Results

Here we describe a set of experimental results on electron transfer upon potassium collisions to gas phase biomolecules. Proteins, that are polymeric structures of amino acids, are present in every biological processes. The sequence of the amino acids in the protein determines their shape. The protein function is determined by the three-dimensional structure or conformation. To understand the function mechanism of proteins, it is essential to explore the structure and chemical properties of isolated amino acids and related molecules such as simple carboxylic acids.

The proteins of all organisms use the same 20 amino acids, as building blocks. Although the limited number of amino acids, its constitution confers different properties, and the order in which those are connected confers a limitless variety of proteins. The common 20 amino acids are α -amino acids since they have an amino and carboxylic group attached to the α -carbon. In Fig. 12.1 a representation of a general structure of an amino acid, where R is the side chain, is shown. Within the 20 amino acids present in the proteins, 19 are chiral molecules. Chiral molecules are asymmetric molecules, since they have four different groups bound to the α -carbon. The simplest amino acid, glycine, is the only among the 20 amino acids that exhibits two identical groups bounded to the α -carbon (glycine has two hydrogen atoms bounded to the α -carbon). The different R groups or side chains confer different properties to the amino acids. The 20 amino acids are organized according to their side chain group yielding therefore different properties. The side chains fall into the chemical classes of aliphatic, aromatic, sulphur containing, alcohols, basis, acids and amines (Horton et al. 1996). The mammals have a limited capability for amino acids' biosynthesis. They can produce only about half of the amino acids that they require; the others must be obtained from the in-take diet. As so, the essential amino acids are those that must be obtained from the diet and no-essential amino acids are those that mammals can synthesize in sufficient quantity for their survival.

Electron transfer studies upon potassium collisions with biological relevant molecules, have been performed comprehensively investigated over the last decade (Almeida et al. 2011, 2013b; Ferreira da Silva et al. 2013). In this chapter we describe the fragmentation patterns upon potassium collisions with acetic acid, aliphatic amino acids, such as glycine, alanine and valine, aromatic amino acid such as tyrosine

Fig. 12.1 General structure of an amino acid where R represents the side chain; depending on the type of side chain, the chiral form is represented by R or S; in brackets is the chiral form when R is heavier than acid group

and tryptophan. Acetic acid, although is an intermediate product in the synthesis of acetyl-CoA, in its ionic form yields acetate, which is also a product in the amino acid cysteine biosynthesis from serine that occurs in bacteria and plants.

12.5 Acetic Acid

Acetic acid, ($\text{CH}_3\text{CO}_2\text{H}$, HAc) is one of the simplest molecules that can act as biological prototype and a possible building block of biomolecules, namely amino acids and proteins. Within organic molecules, such as formic acid, it is considered to be an important trace species in the Earth's atmosphere (Khare et al. 1999) and has been found in the interstellar medium (Wootten et al. 1992). Simple organic molecules play an important role in atmospheric pollution (Gallego et al. 2014; Welz et al. 2014), food (Theron and Lues 2007) and solvent chemical industry (Krupadam et al. 2011). Low-energy electron (LEE) interactions with simple molecules have been widely studied in recent decades (Flosadóttir et al. 2007; Tanzer et al. 2014). LEE can efficiently induce remarkably selective reactions followed by distinctive fragmentation not only via dissociative electron attachment (DEA) (Ptasińska et al. 2005c) but by electron transfer (ET) (Almeida et al. 2013a). HAc can also be used as a prototype system for comprehensive studies on the role of the carboxylic group in the fragmentation mechanisms of biological compounds, and its interactions with LEE provide an ideal system to study the fragmentation of more complex molecules, such as amino acids. Several experimental DEA studies of simple molecules as HCOOH and HAc (Sailer et al. 2003; Prabhudesai et al. 2005; Janečková et al. 2013), as well as several ET studies of simple amino acids, have been performed in order to explore how LEE can induce fragmentation (Ferreira da Silva et al. 2012, 2014). In these studies, the role of the incoming electron yielding molecular fragmentation has been thoroughly discussed, with particular attention to the dehydrogenated formic acid anion formation and neutral hydrogen atoms. Rescigno et al. (2006) theoretical studies have shown that DEA to formic acid proceeds through a π^* resonance on the $\text{C}=\text{O}$ bond leading to excision of the OH bond. Such mechanism was proposed to involve a σ^* (OH) orbital coupling with a π^* ($\text{C}=\text{O}$) in the transient negative ion with considerable geometry change from the neutral. However, Gallup et al. (2009) calculations on the DEA cross-sections for formic acid and glycine, have shown that the mechanism of H loss involves electron capture into a σ^* (OH) orbital with no need of a π^*/σ^* coupling. Recently, Allan and co-workers (Janečková et al. 2013) DEA experimental data lent support to the mechanism proposed by Gallup et al. (2009). As far as other fragmentation patterns in HCOOC and/or HAc yielding anion formation are concerned, we note the experimental studies of Sailer et al. (2003) and Prabhudesai et al. (2008). Both sets of experimental data describe OH^- formation with no explanation for the underlying molecular mechanism yielding such anion.

Time-of-flight (TOF) mass spectra upon potassium collisions with the three different acetic acid analogues were recorded at 100 eV and a combined data is shown in Fig. 12.2 with an inset of OH/OD formation mass range, i.e. 16–18 m/z.

Fig. 12.2 Time-of-flight mass spectra of acetic acid upon potassium collisions at 100 eV lab-frame

Electron transfer in collisions of neutral K atoms with HAc molecules, leads to formation of a temporary negative ion with an excess of internal energy resulting in dissociation of anionic and neutral species. From this comprehensive study as a function of the collision energy, we focus our attention on the OH anion yield only, in order to explore the underlying mechanism that result in either direct cleavage of the OH bond from the carboxylic group or any other competitive (and even concerted) process.

Meneses et al. (2017) have explored three fragmentation pathways after electron transfer to acetic acid leading to OH anion formation and have proposed: (a) H transfer from CH_3 to form the diol structure followed by OH^- cleavage; (b) H release from COOH and subsequent intramolecular H transfer from CH_3 yielding OH^- ; (c) direct OH radical fragmentation. Although theoretical calculations support pathway (b) as the most favourable decay mechanism, experimental results suggest a competition between pathways (a) and (b). The presence of OH^- formation upon electron transfer in the case of CD_3COOH (Fig. 12.2) is supported by pathway (b), namely H release from COOH and subsequent rearrangement to eliminate OH^- , while in CH_3COOD it is formed according to pathway (a). In both cases, the diol structure is a transient species. Although, the most evident pathway for OH^- formation would result from direct cleavage of the C–OH bond pathway (c), however this pathway leads to OH radical formation.

12.6 Aliphatic Amino Acids

12.6.1 Glycine, Alanine and Valine

Amino acids in general have caught the attention of many scientists of different research fields across the globe. Special attention has been devoted to gas phase experimental studies on dissociative electron attachment to isolated aliphatic amino acids molecules (Abdoul-Carime and Sanche 2004; Ptasińska et al. 2005a; Papp et al. 2006; Denifl et al. 2009; Shchukin et al. 2010) electron impact ionisation (Denifl et al. 2009; Papp et al. 2012) and electron transmission spectroscopy (Aflatooni et al. 2001) as well as to amino acids clusters embedded in helium nanodroplets (Ferreira da Silva et al. 2010). Theoretical studies have been performed using density functional theory (DFT) calculations (Ban et al. 2000; Li and Brill 2003), the binary-encounter-Bethe (BEB) model procedure (Scheer et al. 2007) and the Schwinger multichannel method (dos Santos et al. 2012). Glycine, alanine and valine are aliphatic amino acids, differing on the aliphatic side chain. In this section the fragmentation pattern of the three simplest aliphatic amino acids, glycine ($\text{C}_2\text{H}_5\text{NO}_2$), alanine ($\text{C}_3\text{H}_7\text{NO}_2$) and valine ($\text{C}_5\text{H}_{11}\text{NO}_2$) (Fig. 12.3) is discussed.

Table 12.1 summarises the fragment anions formed at 100 eV collision energy and for the three amino acids, we can identify several common fragments as is the case of the dehydrogenated parent anion. In the case of glycine and alanine, for lower collision energies (i.e. 20 eV and 15 eV, respectively), the dehydrogenated parent anion yield is well pronounced, in contrast with valine, that for lower and higher energies the evidence is residual. In the case of formic acid, Rescigno et al. (2006) have proposed that hydrogen abstraction is due to the σ^*/π^* coupling with further O–H excision, leading to H^- formation.

Indeed, increasing the collision energy results in fewer heavier fragments produced in favour to lighter anion species. This can be rationalised in terms of the number of degrees of freedom in these molecular targets and the consequent energy distribution. Valine has an isobutyl side chain in contrast with alanine and glycine which have a methyl and hydrogen atom, respectively. The energy distribution in the case of valine will be likely redistributed leading to more prominent fragmentation for lighter masses.

Fig. 12.3 Aliphatic amino acids molecular structure, from left to the right: glycine, alanine and valine

Table 12.1 Fragment anions assigned at 100 eV potassium collisions with glycine (G), alanine (A) and valine (V) amino acids

m/z	Assignment	Glycine	Alanine	Valine
1	H ⁻	✓	✓	✓
12	C ⁻	✓	✓	✓
13	CH ⁻	✓	✓	✓
15	CH ₃ ⁻ /NH ⁻	✓	×	×
16	O ⁻ /NH ₂ ⁻	✓	✓	✓
17	OH ⁻	✓	✓	✓
24	C ₂ ⁻	✓	✓	✓
25	C ₂ H ⁻	✓	✓	✓
26	CN ⁻ /C ₂ H ₂ ⁻	✓	✓	✓
41	CHCO ⁻	✓	✓	✓
45	HCO ₂ ⁻	×	✓	×
71	C ₃ H ₃ O ₂ ⁻ /C ₄ H ₉ N ⁻	×	×	✓
74	G-H ⁻	✓	×	×
88	A-H ⁻	×	✓	×
116	V-H ⁻	×	×	✓

The fragment anion 71 m/z is only barely visible in the case of valine at 100 eV collision energy, while in alanine, at low collision energy, the fragment anion can be assigned to C₃H₃O₂⁻ due to its (neutral) high electron affinity (3.57 ± 0.18 eV (Graul et al. 1990)) and results from the loss of 18 m/z from the parent anion. However, in the case of valine such fragment anion is only observed at 100 eV and its most plausible assignment is C₄H₉N⁻ together with a neutral formic acid from the decomposition of the TNI.

HCOO/COOH anion formation occurs only in alanine at 100 eV collision energy. This negative ion was also reported in DEA studies to alanine (Ptasińska et al. 2005a) and glycine (Gohlke et al. 2002; Ptasińska et al. 2003; Muftakhov and Shchukin 2010; Shchukin et al. 2010), and formed upon electron capture into the carboxylic π^* orbital.

Another interesting aspect of negative ion formation in small amino acids is formation of isobaric species which, however are difficult to assign due to the low-mass resolution of the linear TOF setup used in these measurements. The fragments NH₂⁻/O⁻ (16 m/z) and CN⁻/C₂H₂⁻ (26 m/z) are present for the three amino acids in contrast with CH₃⁻/NH⁻ (15 m/z) that is only visible in the case of glycine. High-mass resolution DEA to glycine (Mauracher et al. 2007) reported two structures due to resonant electron capture, for each isobaric species, one in the low energy region, the other at higher energies. The fragment anion 15 m/z in glycine is formed through two distinct resonances in the electron capture process. The electron energy profile shows resonance structures peaking at 6 and 11.5 eV. The CH₃ anion formation was attributed to the lower energy resonance while the NH anion to the higher energy res-

onance. Fragment anion 16 m/z, yields NH_2^- formed via a resonance placed between 4 and 8 eV whereas O^- via a high energy resonance located between 7 and 15 eV. The 26 m/z fragment anion shows a similar behaviour, the low energy resonance, located between 4 and 8.5 eV and peaking at 6.5 eV, leads to CN^- formation while a high energy resonance, placed between 8.5 and 14 eV and peaking at 11 eV leads to C_2H_2^- formation. Electron transfer processes in potassium-amino acids collisions, yield anions formed through low-energy resonances at low-energy collisions, i.e., 20 eV in the lab-frame, i.e. 7.8, 8.2 and 9.2 eV in the centre-of-mass frame for glycine, alanine and valine, respectively. However, increasing the collision energy to 100 eV, 56.5, 58.2 and 63.2 eV in the centre-of-mass frame for glycine, alanine and valine, respectively, formation of both isobaric molecular anions is possible.

The high dipole moment for the most stable conformer for these amino acids, 5.6 D, 5.49 D for glycine and alanine respectively, can promote a strong coupling between DBS and valence state providing a doorway for the decay of valence anions via vibrationally excited dipole bound states. Similar process has been put forward for thymine and uracil (Burrow et al. 2006) and we believe that this process may also hold for the probed amino acids.

In summary, the high impact potassium energy is inducing a rich fragmentation pattern leading to lighter fragments in contrast with lower impact potassium energy, which leads to heavier fragment anions. The dehydrogenated parent anion is observed in all three amino acids, which yield decreases with increasing the number of atoms of the side chain, due to the increase of degrees of freedom. The loss of a hydrogen radical can be explained by initial electron capture into a π^* orbital that couples with an σ^* orbital leading to O–H dissociation. Three distinct fragment anions have been attributed to six isobaric fragments, i.e. 15, 16 and 26 m/z and their formation discussed on the light of the main resonances involved.

12.7 Aromatic Amino Acids

12.7.1 Tyrosine and Tryptophan

Aromatic amino acids are characterized by the aromatic side chain. There are four aromatic amino acids within the twenty existing from bacteria to humans, histidine, phenylalanine, tyrosine and tryptophan. Tyrosine ($\text{C}_9\text{H}_9\text{NO}_3/\text{Tyr}$) and tryptophan ($\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}_2/\text{Trp}$) (Fig. 12.4), are two amino acids that will be discussed within this section. Tyrosine has a phenol moiety as side chain whereas tryptophan an indole side chain. In both cases, the side chain moiety is aromatic ring characterised by a delocalized π system.

In Table 12.2 we list the fragment anions formed upon potassium interactions with tyrosine and tryptophan for the energy range between 20 and 75 eV in the lab frame.

Fig. 12.4 Aromatic amino acids molecular structure, left tyrosine and right tryptophan

Table 12.2 Fragment anions in potassium collisions with tyrosine and tryptophan, for energy range 20–75 eV in the lab frame

m/z	Assignment	Tyrosine	Tryptophan
16	O^-/NH_2^-	✓	✓
17	OH^-	✓	✓
24	C_2^-	✓	✓
25	C_2H^-	✓	✓
26	$\text{CN}^-/\text{C}_2\text{H}_2^-$	✓	✓
33	OOH^-	×	✓
92	$\text{C}_6\text{H}_4\text{O}^-$	✓	×
105	$\text{C}_7\text{H}_5\text{O}^-$	✓	×
118	$\text{C}_8\text{H}_7\text{NH}^-$	×	✓
133	$\text{C}_8\text{H}_7\text{NO}^-$	✓	×
180	Tyr-H^-	✓	×
203	Trp-H^-	×	×

Figure 12.5 shows the negative ion mass spectra of tyrosine (upper panel) and tryptophan (lower panel) at 75 eV collision energy, respectively.

Formation of the dehydrogenated parent anion is only visible in the case of tyrosine, which yield decreases with increasing collision energy; at 75 eV collision energy, such anion becomes almost indistinguishable from the background noise level. The hydrogen loss proceeds either from the carboxylic group or from the phenolic hydroxyl group. The dehydrogenation site must depend on the *pKa* of each site, although in gas-phase these values are also related to the preceding negative ion state. The most prominent dissociation channel at low-energy collision, 35 eV, is 92 m/z negative ion assigned to $\text{C}_6\text{H}_4\text{O}^-$. The branching ratio trending of this anion is similar to the dehydrogenated parent anion (Ferreira da Silva et al. 2016). The pathway leading to this fragment involves a cleavage of β -C and phenol ring *para*-C. DEA experimental results do not exhibit this anionic fragment (Vasil'ev et al. 2006). In order to fragmentation proceed yielding such anion, a coupling between low-lying π^* states with σ^* states should occur. In such π^*/σ^* coupling the nuclear wave packet needs to survive long enough allowing for diabatic crossing of both states. Furthermore, this process may also compete with autodetachment and disso-

Fig. 12.5 Time-of-flight mass spectra of tyrosine (upper panel) and tryptophan (lower panel) at 75 eV collision energy

ciation will be suppressed. In the present case, the presence of K^+ in the collision complex system may delay autodetachment long enough allowing for an intramolecular electron transfer along the π^*/σ^* states. The cleavage of α -C- β -C bond leads to C_7H_5O , 105 m/z anion formation with loss of two additional hydrogen atoms that may presumably stem from one hydroxyl side-chain group and another from the β -C. Additionally, the remaining hydrogen atom at β -C position may be transferred to the α -C remaining counterpart with neutral glycine formation. The formation of this fragment shows an independent energy collision behaviour. The branching ratio is approximately 5% over all energy range investigated. The loss of a carboxylic group and two additional hydrogen atoms leads to formation of 133 m/z $C_8H_7NO^-$ ion, which was not observed in DEA studies. Furthermore, the energy dependency shows similar behaviour as in the case of 105 m/z anion (see Fig. 12.3 in Ref. Ferreira da Silva et al. 2016). The branching ratio of low m/z increases with the increasing collision energy, following the opposite dehydrogenated trend that decreases with increasing collision energy. This trend can be explained in terms of the available energy in the system that will be channelled to further fragmentation pathways. On the other hand, if the dehydrogenated anion is formed with excess of internal energy, as in the case of the high collision energy regime, fragmentation may be the favourable channel to accommodate the excess energy. As it was observed for the aliphatic amino acids (Ferreira da Silva et al. 2012, 2014), apart from OH^- , formation of isobaric fragments NH_2^-/O^- and $CN^-/C_2H_2^-$ is also possible. In the case of OH^- , such anion formation should proceed from direct cleavage of OH in the carboxylic group, or as in acetic acid (Meneses et al. 2017), through internal rearrangement via diol formation.

Figure 12.5 lower panel shows the negative ion mass spectrum from collisions of potassium atoms with tryptophan, and in Table 12.2 we list the negative ions

together with their assignments. Apart from lighter anions (<26 m/z), the reaction leading to the side chain moiety fragmentation is the dominant channel. Neither the parent anion nor the dehydrogenated parent anion are detected. The heavier fragment detected at 188 m/z was assigned to the dehydrogenated indoline (C_8H_9N), and as far as the authors are aware this was not reported in previously gas-phase studies. The mechanism leading to dehydrogenated indoline is a complex process evolving several intramolecular rearrangements. The indole moiety is linked to the backbone chain between γ -C3 and β -C, as schematically depicted in Fig. 12.4. In the dissociation process this bond must be broken, where the electron may remain in the aromatic moiety, and the transfer of two hydrogen atoms from the amino acid backbone chain to the indole ring should take place. The intensity of this fragment anion diminishes rapidly with increasing collision energy, with no signal above 75 eV collision energy. Figure 12.6 shows the branching ratios as a function of the collision energy for indoline, HO_2^-/NH_2OH^- , OH^- , O^-/NH_2^- and CN^- .

Formation of indoline anion is favoured for low collision energies while OH^- and O^-/NH_2^- are favoured for higher energies. This fact can be rationalised in terms of available collision time: formation of indoline requires transfer of two hydrogen atoms from the amino acid backbone to the indole moiety while OH^- and O^-/NH_2^- may be formed via a direct process (simple bond breaking) since no new bonds are required to yield such fragment anions. The branching ratios for these anions are energy dependent, since they increase with increasing collision energy, meaning that they are more pronounced in shorter collision times. The branching ratio for HO_2^-/NH_2OH^- formation describes a maximum in the energy range 30–75 eV

Fig. 12.6 The collision energy dependency of the branching ratios for the fragments formed upon potassium-tryptophan collisions at 20, 30, 75 and 100 eV lab-frame

(30–19 fs), while CN^- slightly decreases with increasing collision energy, showing a similar trend to that observed for the dehydrogenated indoline anion.

12.8 Conclusions

Electron transfer mechanisms in biological relevant molecules have been proven to play an important role at molecular level. Such modifications where not only fundamental processes such as electron transport in the cellular membrane, but indirect processes triggered when high energy radiation interact with biological tissue are relevant to the nature of the chemical environment where they occur. The relevance of gas-phase electron transfer processes in potassium-molecule collisions is to better understand the fragmentation processes of biologic and biological related molecules, after electron attachment. As the outermost electron in potassium is weakly bound, the proposed experiments may provide an analogy for electron transfer from electronically excited secondary neutrals in the biological environmental.

Electron transfer mechanism yielding ion-pair formation in gas-phase acetic acid, aliphatic amino acids, such as glycine, alanine and valine, and aromatic amino acids, such as tyrosine and tryptophan through collisions with a hyperthermal neutral potassium beam, have been investigated using a crossed molecular-beam technique. The negative ions formed upon electron transfer in potassium-molecule collision were TOF mass analysed. The fragmentation pathway can be strongly influenced by the presence of the potassium cation in the vicinity of the TNI.

In the case of acetic acid, special attention has been dedicated to OH^- formation, showing the competition between two possible fragmentation pathways, with intermediate diol formation. Regarding the investigation on aliphatic amino acids, we have observed a decrease of the dehydrogenated parent anion yield with increasing the complexity of the side chain. This fact can be attributed to the increase of degrees of freedom favouring energy redistribution and consequently formation of lighter fragment anions. Additionally, electron transfer to aromatic amino acids shows the influence of delocalized π system leading to prominent formation of anionic fragments from the aromatic side chain. It has been shown in the case of tryptophan that keeping the extra electron in the aromatic side chain, yields proton transfer leading to the dehydrogenated indoline formation and in the case of tyrosine to fragment anions at 133, 105 and 92 m/z assigned to derivatives from the benzophenolic side chain. For the studied amino acids, isobaric fragments are formed and have been assigned to O^-/NH_2^- and $\text{CN}^-/\text{C}_2\text{H}_2^-$. The increase of energy transferred at higher collision energies favours direct fragmentation channels, increasing the branching ratios of those fragments, as well as OH^- formation.

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