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Electron transfer to aliphatic amino acids in neutral potassium collisions

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We dedicate this contribution to Professor Tilmann Märk, not only a distinguished scientist but also a loyal colleague and trusted friend, on the occasion of his 70th birthday.

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ABSTRACT

Electron transfer in potassium collisions with alanine ($C_3H_7NO_2$) and valine ($C_5H_{11}NO_2$) is investigated at 15 and 100 eV. The fragmentation patterns obtained in the unimolecular decomposition through time-of-flight (TOF) mass spectrometry are compared for both amino acids as a function of the collision energy. In the case of alanine, the most prominent feature in the collision regime is the relative decrease of the dehydrogenated parent anion signal with respect to the hydrogen anion as the collision energy increases. For low collision energies this can be rationalised in terms of autodetachment inhibition, whereas at higher collision energies the negative molecular ion can be formed with an excess of internal energy which might even result in fragmentation. Regarding valine, such behaviour was not observed which has been interpreted as a result of side chain effect contributing to an increase of the internal degrees of freedom in comparison to alanine.

1. Introduction

The underlying physico-chemical aspects of ionising radiation with the biological environment and their implications have been investigated intensively in the last decades in order to better understand the fundamental processes that may lead to DNA/RNA lesions [1]. Upon high energy radiation with the biological medium, several secondary species are formed along the radiation track where reactive species (neutral and ionic radicals) and a large number of secondary electrons (ballistic) with energies typically below 20 eV are known to produce more damage than the primary radiation [1]. Pioneering studies of Sanche and co-authors [2] have shown that low energy electrons (LEEs) can promote single and double strand breaks in DNA which are caused by rapid decays of transient molecular resonances on the DNA's basic components. As so, within the physiological environment such LEEs can interact with other biological material and/or cellular components as is the case of proteins [3]. DNA/RNA is directly connected to several proteins, such as histones or other cromossomic and specific proteins and thus the comprehensive knowledge of such LEEs interactions with these molecular systems and their single units, amino acids, is important for better understanding the underlying damage mechanisms at the molecular level. However, due to the lack of free electrons in the biological environment, electron transfer mechanisms may be considered as a better matching of electron attack to the target molecules. Though, potassium–molecule collisions can be used as a model to describe electron transfer processes.

In the past years, we note several gas-phase experimental studies on amino acids through dissociative electron attachment (DEA) to bare molecules [4–9], embedded in helium nanodroplets [10], electron impact ionisation [9,11] and electron transmission spectroscopy [12]. Several theoretical studies have been performed using DFT calculations [13,14], binary-encounter-Bethe (BEB) model procedure [15] and the Schwinger multichannel method [16]. In our laboratory we have been focused on electron transfer studies in potassium collisions with biologically relevant molecules [17–20].

Here we report negative ion formation in electron transfer processes by collisions of neutral potassium atoms with alanine and

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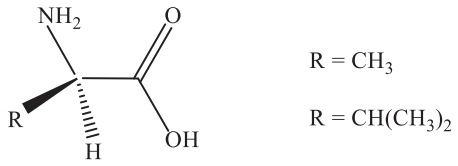

Fig. 1. Chemical structure of alanine and valine.

valine. Fragmentation patterns are discussed in terms of the amino acids side chain effect (Fig. 1) as well as on the available energy in the centre-of-mass frame.

2. Experimental set-up

The negative ion time-of-flight (TOF) mass spectra were obtained in collisions of neutral potassium atoms with alanine and valine in a crossed beam set-up described elsewhere [21]. Briefly, an effusive molecular beam crosses a primary beam of fast neutral potassium (K) atoms. K^+ ions produced by a potassium ion source were accelerated to 15–100 eV, before passing through an oven where they resonantly charge exchange with neutral potassium to produce a beam of fast (hyperthermal) atoms. Residual ions from the primary beam were removed by electrostatic deflecting plates outside the oven. The intensity of the neutral potassium beam was monitored using a Langmuir–Taylor ionisation detector, before and after the collection of each TOF mass spectra.

The effusive beam of amino acids was then introduced into a 1 mm diameter source where it was crossed with the neutral hyperthermal potassium beam between two parallel plates with 1.2 cm separation. The anions produced were extracted by a 250 V cm^{-1} pulsed electrostatic field. The typical base pressure in the collision chamber was 6×10^{-5} Pa and the working pressure was 4×10^{-4} Pa. Mass spectra (resolution $m/\Delta m \approx 125$) were obtained by subtracting the background measurements (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 nitromethane molecule [21].

The solid samples of valine and alanine were purchased from Sigma–Aldrich with a minimum purity of ≥98%. They were used as delivered. The samples were heated up to 410 K for alanine and 375 K for valine and the temperatures were controlled using a PID unit. In order to test for any thermal decomposition, the spectra were recorded at different temperatures. No differences were observed in relative peak intensities as a function of temperature. The extraction region and the TOF system were heated during the measurements in order to prevent any sample condensation and thus charge accumulation on the electrodes.

3. Results and discussion

The negative ion mass spectra for alanine and valine collected at 15 and 100 eV laboratory collision energies are shown in Fig. 2, and fragment anions assigned in Table 1. We will now discuss the formation mechanisms of each anion observed in the TOF spectra and critically compare them against gas phase DEA measurements.

3.1. Dehydrogenated parent anions $[A–H]^-$ (88 a.m.u.) and $[V–H]^-$ (116 a.m.u.)

The dehydrogenated close shell anions are formed through direct decay of the transient negative ion (TNI), according to reactions (1) and (2) for alanine and valine, respectively:

$$K^+ + [C_3H_7NO_2]^{\#-} \rightarrow C_3H_6NO_2{}^- + H + K^+ \quad (1)$$

Table 1
Anionic fragmentation assignment for alanine (A) and valine (V) at 15 and 100 eV.

Energy (eV)		Mass (a.m.u.)	Anionic fragments
15	100		
A/V	A/V	1	H^-
A/V	A/V	12	C^-
A/V	A/V	13	CH^-
–	A/V	14	$CH_2{}^-$
A/V	A/V	16	$O^-/NH_2{}^-$
A/V	A/V	17	OH^-
A/V	A/V	24	$C_2{}^-$
A/V	A/V	25	C_2H^-
A/V	A/V	26	$C_2H_2{}^-/CN^-$
A/V	A/V	41	$CHCO^-$
–	A	45	$COOH^-/CHOO^-$
A/V	V	48	Metastable decay
A/V	V	71	$C_3H_3O_2{}^-/C_4H_9N^-$
A	A	88	$CH_3CH(NH_2)COO^-/[A–H]^-$
V	V	116	$C_3H_5O_2{}^-/[V–H]^-$

$$K^+ + [C_5H_{11}NO_2]^{\#-} \rightarrow C_5H_{10}NO_2{}^- + H + K^+ \quad (2)$$

In the case of alanine, this fragment is predominant at low collision energies, decreasing in intensity with increasing energy whereas for valine it is never the most intense anionic fragment. At a first glance, one would be tempted to attribute such behaviour to the role of the potassium cation after electron transfer in the vicinity of the TNI. Such coulombic interaction in the collision complex could allow for dissociation to successfully compete with autodetachment especially in the low collision regime due to a longer K^+ transit time. However, such hypothesis fails since K^+ is present for both molecules. Though, differences can be rationalised in terms of the molecules' degrees of freedom, in particular due to the side chain effect. In the case of alanine, the side chain is a methyl group in the α-position, whereas for valine is an isopropyl group. In atom–molecule collisions above threshold, the excess energy may be channelled into the available degrees of freedom [22].

In DEA unimolecular decomposition process yielding the dehydrogenated parent anion, the considerable high values of the $EA(C_3H_6NO_2) = 3.68$ eV and $EA(C_5H_{10}NO_2) = 3.78$ eV [23] may be a driving force to form low energy resonance. For both molecules, Ptasinska et al. [4] and Denifl et al. [8] report such resonances peaking at ~1.2 eV. Interesting to note that, at low energies, the reactions yielding such anion formation can not only explain the differences observed in potassium collisions in terms of the electron affinity but also to a structural effect attributed to the aminoacids' side chain.

The dehydrogenation effect in the carboxylic group has been reported in different compounds with particular attention to several acids. Rescigno et al. [24] have shown that in formic acid the extra electron is captured into a π^* orbital of the carboxylic group, leading to a close shell dehydrogenated parent anion. This has also been suggested in DEA studies on formic [25] and acetic acids [26], where the incoming electron is captured in shape resonances at 1.2 and 1.5 eV, respectively. Moreover, Rescigno et al. [24] have also proposed that H abstraction may proceed through a strong π^*/σ^* coupling leading to O—H bond rupture. This has been recently shown in electron transfer from potassium atoms to oriented acetic acid molecules [27]. Recently, Viscaino et al. [28], have suggested that H abstraction from aminobutanoic acids isomers upon electron capture, is due to the electron capture into the σ^* orbital (OH).

In the case of DEA studies in valine, this fragmentation process was observed as a contribution of a shape resonance at 1.2 eV and a core excited resonance located at 5.3 eV [8]. Regarding alanine, DEA studies have shown that the electron is captured via shape resonances located at 1.3, 1.4 and core excited resonances at 5.5 eV [4]. In the present study at 15 eV collision energy the available energy in the centre-of-mass frame is 5.8 eV for valine and 5.0 eV