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Dissociation behavior of ionized valeramide
Part III. An unprecedented temperature effect on the C_3/C_2 branching ratio and its implications for metastable ion dissociations

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Abstract

The competing formations of C_2- and C_3-fragments in the unimolecular decay of mass-selected valeramide cation-radicals are analyzed in detail. It turns out that the different branching ratios observed in the various experiments are due not only to the internal energy of the ions but also to that of the neutral precursors. The latter is manifested by a pronounced effect of the temperature of the ion source on the C_3/C_2 branching ratios in the metastable ion spectra of ionized valeramide. Exploratory studies indicate that the effect is not limited to valeramide in that similar temperature phenomena are observed for the metastable molecular ions of hexanoic acid and its amide. (Int J Mass Spectrom 214 (2002) 155–170) © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the two preceding papers [1,2], the ionization of valeramide **1** and the subsequent dissociation pathways of the cation radical $\mathbf{1}^{\bullet+}$ are explored by experimental and theoretical means. The mass spectrometric results as well as the computed potential-energy surface predict a competition between initial β-, γ-, and δ-C–H bond activations in $\mathbf{1}^{\bullet+}$ leading to the corresponding distonic ions $\mathbf{11}^{\bullet}$, $\mathbf{2}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$ and their subsequent fragmentations.[1] In addition, direct C(3)–C(4) bond cleavage to presumably yield $\mathbf{9}^{+}$ occurs at slightly elevated energies (Scheme 1).

The different experimental approaches as well as the theoretical results agree pretty well with each other in many respects, including subtle mechanistic details reflected in the product distributions upon isotopic labeling. Inter alia, the experimental findings suggest that the McLafferty rearrangement (loss of propene,

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[1] For the sake of consistency, the notation of structures **1–14** used in [1,2] is adopted here.

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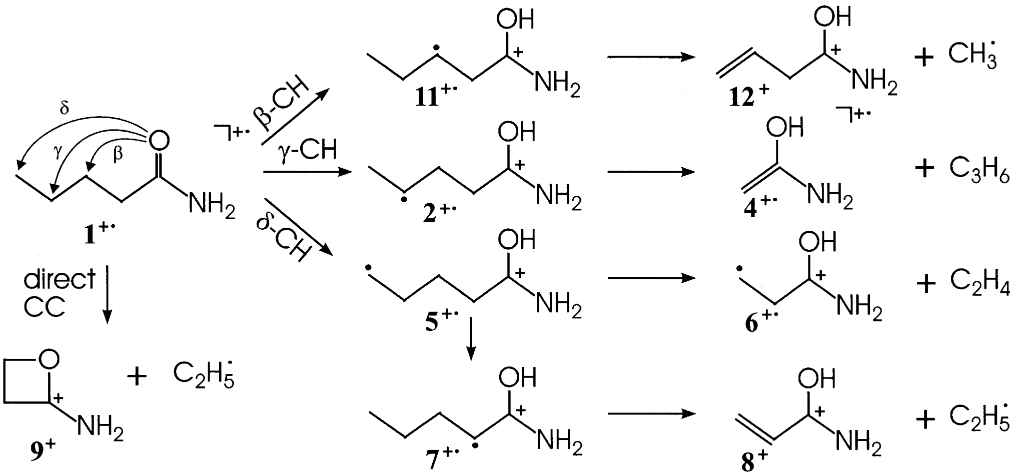

Scheme 1.

C_3-route) and the processes leading to eliminations of $C_2H_4^•$ as well as $C_2H_5^•$ (C_2-route) are effectively uncoupled from each other in that the intermediate distonic ions $\mathbf{2}^{•+}$ and $\mathbf{5}^{•+}$ do not interconvert within the timescales and energies available. Credit to this conjecture is provided by consideration of barrier heights and fragmentation thresholds derived in the computational studies. Despite the wealth of agreement, however, no consistent explanation could be provided for the differences in the branching ratios of both routes (referred to as C_3/C_2 ratio) observed in the various experiments. Thus, the metastable ion studies performed in the sector instrument yield C_3/C_2 ratios close to unity, a C_3/C_2 ratio of about 3 ± 1 is derived as a mean for the metastable traces in the threshold photoelectron–photoion coincidence (TPEPICO) data between 9.8 and 10.5 eV, and for dissociative photoionization the C_3/C_2 ratios range from ca. 5 at photon energies above 12 eV to $C_3/C_2 > 100$ close to the ionization threshold of valeramide (9.40 ± 0.03 eV, [1]). In other words, while refined insight in most of the mechanistic details is achieved, the gross product distribution is not understood. This finding points towards some fundamental difference between the various experiments and prompted substantial experimental and theoretical efforts aimed at resolving this discrepancy.

2. Experimental methods

Most experiments used the methods described in [1], and only additional aspects are mentioned here. In the sector experiments, a VG ZAB/HF/AMD 604 mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sector) [3,4] was used to ionize the samples by electrons with different kinetic energies at either a repeller voltage of ca. 30 V (electron ionization, EI) or with the repeller grounded to the source potential (chemical ionization, CI) with and without addition of CI gases. The ions of interest were accelerated to 8 keV kinetic energy and mass-selected using the magnetic and electric sectors indicated. While metastable ion (MI) spectra were generally recorded with $B(1)/E(1)$-mass-selected ions, the unimolecular dissociations of $\mathbf{1}^{•+}$ were examined in all possible field-free regions of the mass spectrometer at mass resolutions between 1500 and 6000 by the following methods [5,6]. (i) Direct analysis of the daughter ions formed in the field-free region between the ion source and the first magnet by means of a linked $B(1)/E(1)$-scan. (ii) Mass-selection of $\mathbf{1}^{•+}$ with $B(1)$ and monitoring the fragmentation occurring between $B(1)$ and $E(1)$ by scanning $E(1)$. (iii) Mass-selection using $B(1)/E(1)$ while observing the unimolecular decay between $E(1)$ and

B(2) in a *B*(2)-scan. (iv) Mass-selection of $\mathbf{1}^{\bullet +}$ with *B*(1)/*E*(1)/*B*(2) and analysis of the fragmentation processes using *E*(2). In another series of experiments, MI spectra were recorded while the kinetic energies of the ionizing electrons were varied by adjusting the voltage between the filament and the source with the repeller grounded to the source. The latter measure is important in order to avoid unintentional acceleration of the electrons entering the source towards the repeller. The ionization energy of benzene ($\mathrm{IE} = 9.24\,\mathrm{eV}$) was used as an anchor for scaling the electron-energy. Note, however, that electrons emitted from the hot filament are not at all monoenergetic, and the dependence is largely meant qualitatively. Further, the MI spectra were recorded at different temperatures of the ion source. Because the ion source is usually heated to 200 °C and not equipped with a cooling device, these experiments were performed as follows. Twelve hours prior to the actual measurements, the ion optics were optimized first and afterwards the filament and the source heater were switched off, in order to allow the source to reach room temperature. Then, the samples were introduced, and MI spectra were recorded immediately while monitoring the source temperature which increases continuously due to the heat emitted by the glowing filament. At medium filament currents, the source reaches ca. 160 °C in about half an hour. Higher temperatures were achieved by additional heating of the source block. In these temperature-dependent studies, the neutral substrates were evaporated at or close to room temperature (maximum 35 °C) by adjusting the solid probe to a position where it just does not touch the source, thereby reducing heat transfer from the source block to the sample tip. In addition, MI spectra of ionized valeramide as a function of the temperature of the ion source were performed using a Finnigan MAT 95ST mass spectrometer with 6 kV acceleration voltage and ion generation by EI (70 eV).

In the course of this collaborative study, CERISES [7] has been upgraded to MS/MS capabilities by implementing a quadrupole/octopole/quadrupole arrangement. This configuration permits to investigate uni- as well as bi-molecular reactions of mass-selected ions occurring in the octopole ion guide. In the present case, unimolecular dissociations of metastable $\mathbf{1}^{\bullet +}$ within the octopole were examined. As far as timescales are concerned, the parent ions produced in the source need about 60 μs to reach the end of the first quadrupole, and may transit for as long as 500 μs in the octopolar ion guide depending on the adjustment of the potentials. These relatively long transit times are due to the low acceleration potentials applied in the CERISES apparatus. For example, ions accelerated by 1 eV in the quadrupole filter can be decelerated to 150 meV inside of the 60 cm long octopole ion guide. Due to the relatively large time windows sampled (up to 500 μs), MI spectra are obtained in which the intensities of parent and fragment ions can reach the same order of magnitude. The photoionization spectra of hexanoic acid described below were obtained in the same manner as those of valeramide (see [1]). However, the vapor pressure of hexanoic acids is just at the borderline of practicability of the inlet systems available. As a consequence, the photoionization data for hexanoic acid show only moderate signal-to-noise ratios.

5-Iodovaleramide **15** was prepared from 5-chlorovaleric acid chloride (Aldrich) by ammonolysis and subsequent S_N2 reaction with KI in acetone. Valpronamide (2-propyl valeramide) **16** was prepared from valproic acid (Aldrich) by treatment with $SOCl_2$ followed by ammonolysis. Both products were purified by recrystallization from $CHCl_3$/hexane and spectroscopically characterized by GC–MS and ^{1}H-NMR.

3. Additional studies on ionized valeramide

In this section, additional experiments with ionized valeramide are described aimed at understanding the branching of the C_3- and C_2-routes. Let us first re-iterate the problem by means of Fig. 1 which summarizes the C_3/C_2 ratios obtained in the various kinds of experiments reported in [1]. Very large C_3/C_2 ratios >100 are obtained close to the photoionization threshold of **1**. This is perfectly consistent with the lower appearance energy (AE) of the C_3-route compared to

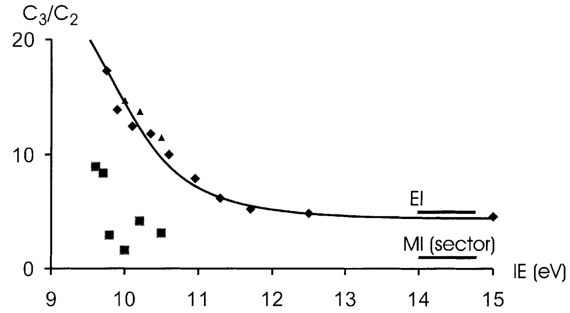

Fig. 1. C_3/C_2 ratios observed upon dissociative photoionization of valeramide at different photon energies ((◆), connected by a spline) and the TPEPICO experiments (sum of photofragments (▲) and the metastable fractions (■)). In addition, the C_3/C_2 ratios obtained in the MI mass spectra of valeramide in the sector instrument and in the EI mass spectra (taken from: http://webbook.nist.gov/chemistry/) are indicated as bold horizontal dashes.

the C_2-route (9.43 ± 0.05 vs. 9.58 ± 0.05 eV). With the AEs in mind, it is not at all surprising that the C_3/C_2 ratio decreases with increasing energy of the ionizing photons, reaching a “plateau” at $C_3/C_2 \approx 5$ for photon energies >12 eV which is in accord with C_3/C_2 ratios of about 4 in the 70 eV-EI mass spectra of 1 as well as $C_3/C_2 \approx 3$ for the metastable fractions in the TPEPICO data between 9.8 and 10.5 eV. What matters is the ca. 1:1 ratio obtained for the metastable ions examined in the sector instrument, because it leads to the counterintuitive conclusion that the more energy demanding and more complex C_2-route is able to balance with the McLafferty rearrangement. Such a situation is quite unusual and must have its origin either in instrumental effects specific for the two kinds of mass spectrometers used in this study or in the intrinsic properties of the mass-selected parent ions under investigation [8,9].

3.1. Discrimination effects

An obvious reason for variations of branching ratios in gas-phase ion chemistry is associated with discrimination effects in the collection of the product ions and/or detection efficiencies when different instruments are used. Discrimination can arise from both, mere mass effects and differences in the kinetic energies of the product ions. If, e.g., one of two competing fragmentations is associated with a large release of kinetic energy while the other is not, collection efficiencies may vary largely [10]. A similar effect could occur, if the masses of the fragment ions are quite different. Moreover, discrimination effects differ for each kind of mass analyzer and depend on the adjusted mass- and/or energy resolutions. Here, magnetic and electrostatic analyzers were used in the sector instrument, while the photoionization experiments were conducted with an octopole/quadrupole system and a quadrupole/octopole/quadrupole device after upgrading, respectively. Further, the ions’ lifetimes sampled in the different experiments may affect the apparent branching ratios between competing dissociation channels.

In the case of valeramide, however, none of these effects can account for the observed variations in the C_3/C_2 ratios. Thus, the branching ratios in the metastable ion studies with the sector instrument are barely influenced by the ion lifetimes, the adjusted mass- and/or energy resolutions, and the scanning techniques used (Table 1). While some slight trends emerge, these can by no means resolve the large discrepancy of the C_3/C_2 ratios obtained in the other experiments and are therefore not pursued any further.

Table 1
Normalized[a] MI spectra of $\mathbf{1}^{\bullet +}$ in different field-free regions of the sector mass spectrometer recorded by adequate scanning techniques

Scan	Age (μs)[b]	$-CH_3^\bullet$	$-C_2H_4$	$-C_2H_5^\bullet$	$-C_3H_6$
$B(1)/E(1)$	2	2	4	47	47
$E(1)$ LR[c]	12	2	5	45	48
$E(1)$ HR[d]	12	2	5	46	47
$B(2)$	35	2	7	42	49
$E(2)$	56	2	9	43	46
KER[e]		60	35	12	6

[a] $\Sigma = 100$.
[b] Approximate flight time of the molecular ion from the source to the center of the respective field-free region.
[c] Low resolution, $E/\Delta E \approx 1500$.
[d] High resolution, $E/\Delta E \approx 5000$.
[e] Kinetic energy releases ($T_{0.5}$) in meV of the respective fragmentations determined by means of $E(1)$ scans at $E/\Delta E \approx 5000$.

Also consistent with the view of negligible discrimination effects, we found that the kinetic energy releases (KERs) associated with the relevant fragmentations are relatively small. Note, that the small KERs also agree with the low thresholds for the unimolecular dissociation of $\mathbf{1}^{\bullet+}$ via either of the routes discussed here.

As far as the photoionization studies are concerned, already the good agreement between the C_3/C_2 ratios of the PI and TPEPICO data disputes the operation of severe discrimination effects, because the former experiments were performed at unit mass resolution of the quadrupole analyzer while the peak widths were several amu broader in the latter. In addition, the small KERs determined in the sector experiments render unlikely that the C_3/C_2 ratios are changed by backward scattering in the ion optics and the octopole ion guide. In summary, instrumental discrimination effects are excluded as the origin of the observed variations in the C_3/C_2 ratios.

3.2. *Conditions of ionization*

Another, more subtle reason for changes in branching ratios is associated with mode- and/or state-specific ionization. Thus, cross-sections and selection rules may differ for ionization by photons and electrons, respectively. While effects of this kind are well-known for dissociative ionization of small molecules (diatomics in particular), it is difficult to envision such a behavior for a long-lived molecular ion of a polyatomic sample such as valeramide. Further, comparison of the energy behavior of the photoelectron- and photoion-spectra of **1** (see Fig. 1 in [1]) do not indicate a particular state specificity of the C_3/C_2 ratios in the range of photon energies studied. In fact, the C_3/C_2 ratios $\gg$1 obtained in the PI studies agree with expectations, while it is $C_3/C_2 \approx 1$ observed in the sector experiments that constitutes the problem.

In order to probe the possible occurrence of some mode- or state-specific ionization in the sector experiments, the ionization conditions were varied systematically. The first, obvious choice is to decrease the energy of the ionizing electrons, thereby possibly changing the internal energy of $\mathbf{1}^{\bullet+}$. In fact, notable increases in the relative abundance of the molecular ions and more specific fragmentation has been observed upon ionization of amides with electrons having only 12 eV kinetic energy [11,12]. However, the C_3/C_2 ratio of ca. 1 in the MI spectra of mass-selected $\mathbf{1}^{\bullet+}$ generated by 70 eV electrons remains more or less constant until the ionization threshold is reached (IE(**1**) $= 9.40 \pm 0.03$ eV, [1]) and even tends to slightly decrease at lower electron energies (Fig. 2). Note, however, that relative to EI (70 eV) the intensity of the parent ion decreases to less than 1/1000 at electron energies below 10 eV. A rational for the smaller C_3/C_2 ratios at lowest electron energies is provided by involving a very minor amount of the enol form **7** being present in the ion source, because the enol has a much lower ionization energy than the keto (IE(**7**) $=$ 7.2 eV according to B3LYP calculations, [2]), and $\mathbf{7}^{\bullet+}$ preferentially fragments via the C_2-route. The minute fraction of neutral **7** becomes only apparent, however, when formation of $\mathbf{1}^{\bullet+}$ practically ceased at lowest electron energies. Accordingly, contribution of neutral **7** cannot explain the C_3/C_2 ratio of about 1 observed at higher electron energies where the overall ion currents increase by several orders of magnitude.

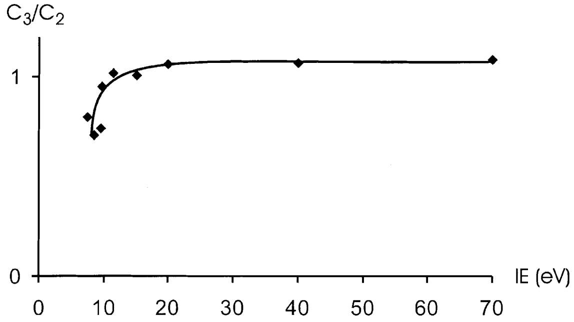

Fig. 2. C_3/C_2 ratios in the MI spectra of *B*(1)-mass-selected $\mathbf{1}^{\bullet+}$ as a function of the kinetic energy of the ionizing electrons (the solid line is a spline fit through the data).

While variation of the electron energy quite likely affects the internal energy content of metastable $\mathbf{1}^{\bullet+}$, it might not be sensitive with respect to mode- and/or state-specificity in electron ionization. Therefore, the

MI spectra of $\mathbf{1}^{\bullet+}$ were also recorded for ions generated under the conditions of chemical ionization (CI). For example, when either CO (IE = 14.0 eV) or CS_2 (IE = 10.1 eV) are used as reagent gases present in a large excess, ionization of valeramide (IE = 9.4 eV) is most likely to occur via the charge-exchange reactions (1) and (2), respectively, rather than directly by energized electrons.

$$CO^{\bullet+} + \mathbf{1} \rightarrow \mathbf{1}^{\bullet+} + CO \qquad (1)$$

$$CS_2{}^{\bullet+} + \mathbf{1} \rightarrow \mathbf{1}^{\bullet+} + CS_2 \qquad (2)$$

Because charge-exchange mass spectra often differ from EI mass spectra in many respects, changes in the C_3/C_2 ratio are to be expected, if the low ratios obtained in the EI experiments were due to mode- and/or state-specificity in ionization. Furthermore, the enhanced pressure in the CI source may allow for some thermalization of the initially formed ions via intermolecular collisions with the neutral gases, thereby possibly moderating the internal energy content of $\mathbf{1}^{\bullet+}$. Finally, CI conditions may induce the isomerization of the molecular ion $\mathbf{1}^{\bullet+}$ to distonic ions by intermolecular catalysis [13–16]. However, none of the CI experiments (in addition to self-CI, CH_4, CO, CS_2, and Ar were used as reagent gases) led to a significant deviation from $C_3/C_2 \approx 1 \pm 0.1$ obtained in the MI spectra of EI generated, mass-selected $\mathbf{1}^{\bullet+}$.

Accordingly, neither the energy of the ionizing electrons nor the mode of ionization (EI vs. CI) account for the low C_3/C_2 ratios in the sector experiments in comparison to the PI measurements. In order to probe this aspect even more directly, the newly implemented MS/MS capability of CERISES was used to examine the unimolecular decay of $\mathbf{1}^{\bullet+}$ generated by EI. To this end, an electron gun was mounted to the ion source which allows to operate CERISES in the EI mode at variable electron energies. The molecular ion $\mathbf{1}^{\bullet+}$ was then mass-selected using the first quadrupole analyzer, allowed to dissociate during the traverse of the octopole ion guide, and the products were recorded by scanning the second quadrupole analyzer. The resulting MI spectra probe metastable $\mathbf{1}^{\bullet+}$ having lifetimes between 60 and 300 μs. Irrespective of the ion lifetimes, however, C_3/C_2 ratios of about 4 ± 1 were found in these experiments, consistent with the TPEPICO data, but again beyond the error margin of the sector experiments.

3.3. *Uncoupling of C_2- and C_3-routes*

The experimental and theoretical results reported in [1,2] of this study indicate that the C_2- and C_3-routes are uncoupled from each other in that the intermediates initially formed via both routes do not interconvert prior to dissociation. Before addressing the possible consequences of such an uncoupling on the C_3/C_2 ratios, it should be probed experimentally whether or not the uncoupled intermediates can be generated via independent methods.

With respect to specific access to the C_3-route, it is obviously sufficient to lower the ions' internal energy below the threshold of the C_2-channel (AE = 9.58 ± 0.05 eV). Thus, the photoionization spectrum of valeramide recorded at 9.5 eV contains negligible amounts of C_2-fragments; a C_3/C_2 ratio of >100 can be derived at the noise level. Likewise, the TPEPICO experiments conducted below 9.6 eV show very large C_3/C_2 ratios.

In order to specifically access the C_2-route, two different approaches were pursued. The first idea is derived from work of Smith and Kenttämaa on distonic aromatic ions [17]. Thus, protonation of valeramide having a suitable homolytically cleavable leaving group X at C(5) in an exothermic reaction may provide enough excess energy to promote C–X bond homolysis. To this end, 5-iodovaleramide **15** was subjected to chemical ionization (CI) with CH_4 as reagent gas. Using the proton affinities $PA(CH_4) = 130$ kcal/mol [18] and $PA(\mathbf{15}) \approx PA(\mathbf{1}) = 211$ kcal/mol [19],[2] protonation of **15** by $CH_5{}^+$, as the predominating Brønsted acid in a CH_4 plasma, has an exothermicity of ca. 80 kcal/mol which largely exceeds the typical dissociation energies of C–I bonds (52 kcal/mol [20]). Assuming that the majority of the excess energy remains

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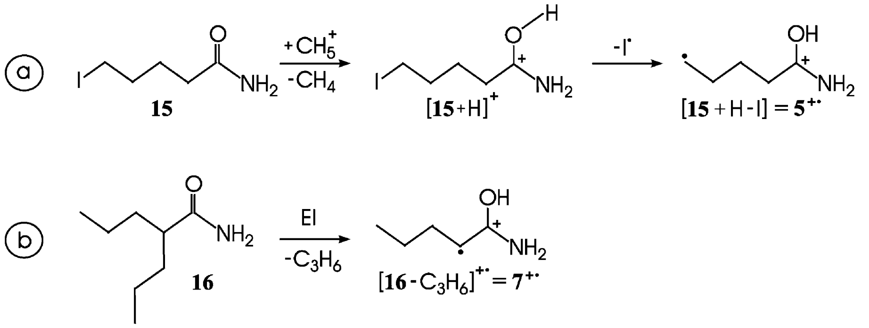
[2] Taken as the average of the PAs of butyramide and hexanamide given in [19].



Scheme 2.

in the protonated amide, at least from an energetic point of view, subsequent homolytic cleavage of the C–I bond is feasible to yield the distonic ion **5**$^{\bullet+}$ with $m/z = 101$ (Scheme 2). However, other reactions of [**15** + H]$^+$, such as losses of ammonia as well as HI, compete efficiently. Moreover, dissociative ionization of **15** gives rise to an intense peak due to [**15** – I]$^+$ ($m/z = 100$) along with its isotope [$^{13}C_1$ – **15** – I]$^+$ ($m/z = 101$), where the latter is isobaric with the ion of interest. Nevertheless, the signal at $m/z = 101$ generated from **15** increases upon addition of methane in that the ca. 100:6 ratio of $m/z = 100$ and 101 obtained under EI conditions changes to about 100:10 under CI conditions. To a first approximation, the resulting mixture of ions upon mass selection of $m/z = 101$ can be deconvoluted by continuously changing from EI to CI conditions where the former is assumed to only yield [$^{13}C_1$ – **15** – I]$^+$, while the latter also affords [**15** + H – I]$^{\bullet+}$ as a putative isomer of ionized valeramide, i.e., **5**$^{\bullet+}$. In fact, an additional fragment due to $\Delta m = -29$ appears in the MI spectra of the $m/z = 101$ ion generated under CI conditions (Table 2). Deconvolution of the components leads to a C_3/C_2 ratio of <0.2, indicating a selective access to intermediate **5**$^{\bullet+}$ of the C_2-route. These results are further supported by the experimentally observed loss of $C_2H_5^\bullet$ from the [**15** + D – I]$^{\bullet+}$ species generated upon CI of **15** with D_2 as reagent gas.

Table 2
Mass differences[a] in the MI spectra[b] of **1**$^{\bullet+}$ and its putative isomers generated from the precursors indicated

	m/z	Δm					
		−15	−17	−18	−28	−29	−42
1$^{\bullet+c}$	101	4	4	<1	14	86	100
[$^{13}C_1$ – 15 – I]$^{+c}$	101	4	30^f	15	<1	<1	100
[**15** + H – I]$^{\bullet+d,e}$	101		<2^f	<4^{f,g}	10	100	<20^f
[**15** + D – I]$^{\bullet+h}$	102		<10^f	<4^{f,g}	4	100	<25^f
[**16** – C_3H_6]$^{\bullet+c}$	101		3	<1		100	2

[a] Most probably, the mass differences Δm correspond to losses of CH_3, NH_3, H_2O, C_2H_4, $C_2H_5^\bullet$, and C_3H_6, respectively.
[b] Given intensities relative to the base peak (100%).
[c] EI (70 eV).
[d] CI with CH_4 as reagent gas.
[e] Corrected for isobaric interferences by ^{13}C isotopes of [**15** – I]$^+$.
[f] Upper limit derived from the correction of overlapping isobaric species.
[g] At highest CI pressures, a third, unknown isobaric ion is formed which gives rise to an increase of $\Delta m = -18$.
[h] CI with D_2 as reagent gas.

The second approach takes advantage of the selectivity of the McLafferty rearrangement by specifically generating the ionized enol of valeramide $\mathbf{7}^{\bullet+}$ via loss of propene from ionized valpronamide **16** (Scheme 2). The MI spectrum of mass-selected $[\mathbf{16} - C_3H_6]^{\bullet+}$ is largely dominated by $\Delta m = -29$ (eliminations to loss of $C_2H_5^{\bullet}$) along with minor peaks due to $\Delta m = -17$ and -42 (assigned to losses of NH_3 and C_3H_6, respectively). Thus, we conclude that the associated C_3/C_2 ratio of the ionized enol $\mathbf{7}^{\bullet+}$ amounts to only about 0.02, thereby strongly supporting the uncoupling of the C_2- and C_3-routes in the dissociation of ionized valeramide. We note in passing that the absence of $\Delta m = -28$ in the MI spectrum of $[\mathbf{16} - C_3H_6]^{\bullet+}$ nicely confirms that loss of ethene proceeds as a direct C(3)–C(4) bond cleavage of $\mathbf{5}^{\bullet+}$ as deduced from the labeling studies (see [1]).

In order to evaluate the possible effects of this uncoupling on the C_3/C_2 ratios, let us first consider a system of isomeric ions which interconvert into each other within the ions' lifetime. In such case of a coupled system, competitive ion dissociation is determined by the relative energy demands of the associated fragmentation channels. Note that this statement is a key assumption in the various variants of the kinetic method developed by Cooks and Wong which is a nowadays widely applied, rather useful and versatile thermokinetic scheme in mass spectrometry [21]. More specifically for the present case, application of the kinetic model would imply that the various distonic ions generated via C–H bond activations of $\mathbf{1}^{\bullet+}$ easily isomerize into each other. Accordingly, the C_3-route as the reaction with the lowest energy demand is assumed to predominate at all internal energies, unless particular kinetic restrictions apply. The latter appear unlikely because the McLafferty rearrangement of $\mathbf{1}^{\bullet+}$ is primarily rate determined by the accessibility of the appropriate conformers, while neither the 1,5-H-transfer nor the exit channel play a role at room temperature (see theoretical results, [2]).

In an uncoupled case, the distonic ions $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ formed from metastable $\mathbf{1}^{\bullet+}$ do not interconvert into each other within the microsecond timescale. Accordingly, at least two different kinds of "parent ion" populations evolve. The low kinetic isotope effects upon deuteration as well as the theoretical data suggest that regioselectivity of the initial C–H bond activation is determined by conformational effects. For the sake of the argument, let us assume the same propensity for either γ-C–H and δ-C–H bond activation occurring rapidly after ionization. According to the PI experiments and the theoretical results, the barriers en route to the intermediates as well as the products of the C_2-route have slightly higher energy demands than the C_3-route. Moreover, the lowest-lying exit channel of the C_2-route requires a second rearrangement ($\mathbf{5}^{\bullet+} \rightarrow \mathbf{7}^{\bullet+}$) such that the C_2-route is in fact expected to be disfavored entropically. If both routes were accessed from $\mathbf{1}^{\bullet+}$ having a certain internal energy content, the C_3-route will therefore, exhibit a larger unimolecular rate constant than the C_2-route. With respect to the metastable ions sampled in the experiments, the hypothetical 1:1 population of $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ formed upon ionization will accordingly change in favor of the intermediate $\mathbf{5}^{\bullet+}$ (as well as isomeric $\mathbf{7}^{\bullet+}$) proportional to the time required for mass selection. This would give rise to a de-mixing of $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ which might be used to explain the lower C_3/C_2 ratios in the metastable ion studies at the sector instrument; for a related reasoning and similar arguments, see [22]. In fact, many isomeric ions can be distinguished by means of their MI spectra [12,23], and the independent generation of the enol cation $\mathbf{7}^{\bullet+}$ may serve as an example (see above). Although this argument seems quite appealing, it bears a logical flaw [24] when both isomers are generated from a common precursor as in the present case. Thus, for a mixture of non-interconverting isomers, a metastable ion experiment does not sample different decay rates of ions having identical internal energies relative to the common precursor, but similar dissociation rates of ions having different internal energies. Accordingly, if intermediate $\mathbf{5}^{\bullet+}$ of the C_2-route decays more slowly than $\mathbf{2}^{\bullet+}$, a direct consequence is that the internal energy content of long-lived $\mathbf{5}^{\bullet+}$ exceeds that of $\mathbf{2}^{\bullet+}$, thereby compensating for the different rate constants at a given energy. Except unusual situations, this compensation qualitatively holds true for all kinds of processes and to a first approximation is independent of the actual internal energy of the mass-selected ion until the internal energy decreases close to the threshold of the reaction with higher energy demand. This line of reasoning is supported by the energy behavior of the C_3/C_2 ratio for the metastable ions sampled in the TPEPICO experiments (Fig. 1). Thus, from C_3/C_2 ratios of about 8 in the vicinity of the appearance energy of the C_2-route, the ratio reaches a level of about 3 ± 1 at photon energies between 9.8 and 10.5 eV.

In conclusion, uncoupling itself does not provide an explanation for the low C_3/C_2 ratios ($\approx$1) in the metastable ion studies conducted in the sector instrument. Further, the negligible changes in the C_3/C_2 ratios observed for ions having different lifetimes (Table 1) would not support such a scenario because significant changes are to be expected otherwise.

3.4. Source temperature

While the effects of various experimental parameters on the C_3/C_2 ratio were considered in the previous sections, none of them is able to account for the unusually low C_3/C_2 ratios observed for metastable $\mathbf{1}^{\bullet+}$ in the sector studies. Because mere discrimination effects in the two instruments appear unlikely in this case (see above), we finally addressed the temperature of the ion source (T_s) as the only difference which remained between the two machines. Thus, the ion source of CERISES is operated at room temperature, whereas conventional EI sources, such as the one installed in our sector instrument, are usually maintained at elevated temperature (typically 200 °C) in order to reduce memory effects and to avoid temperature drifts caused by the glowing filament which effectively acts as a heater. While the temperature of the ion source is known to affect EI mass spectra [11,12] as well as the fragmentation patterns upon collisional activation [25,26], temperature effects on intensity ratios in metastable ion spectra are usually small for the reasons outlined above [27–32]. Recently, a thorough study of Norrman and McMahon further corroborated these ideas [33]. In fact, these authors even concluded that the internal energy of metastable ions (proton-bound dimers were studied) decreases with increasing T_s. Thus, the product branching ratios typically increased by about 50% in favor of the thermodynamically favored product when increasing T_s from 50 to 300 °C. Because a similar, or even negligible temperature behavior was also expected for ionized valeramide, we were rather surprised to observe a pronounced effect of the source temperature on the C_3/C_2 ratios in the MI spectra of $\mathbf{1}^{\bullet+}$ (Fig. 3).

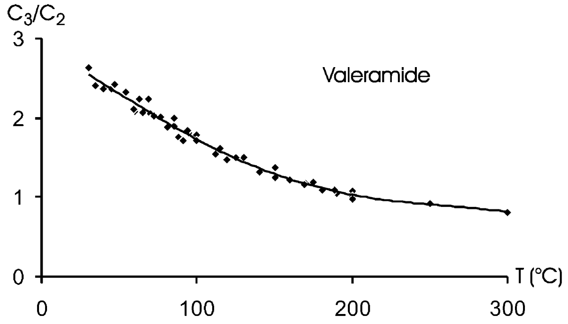


Fig. 3. C_3/C_2 ratios in the MI spectra of mass-selected $\mathbf{1}^{\bullet+}$ as a function of the temperature of the ion source (the solid line is a polynom fit through the data). Note that two independently performed experiments are superimposed.

All experiments with the sector instrument described so far were performed at $T_s = 200\,^\circ\mathrm{C}$ at which C_3/C_2 ratios of about 1 ± 0.1 were obtained in all kinds of experiments conducted with metastable $\mathbf{1}^{\bullet+}$. Upon lowering T_s, however, the C_3/C_2 ratios increases notably and in fact reaches a value of ca. 3 at the lowest temperature achieved (Appendix A). Hence, after all it is effectively the source temperature which gives rise to the variations in the C_3/C_2 ratios in the two kinds of instruments. We are not aware of any similar effect of this magnitude in previous metastable ion studies [34]. Compared to the results of Norrman and McMahon [33], the effect is much more pronounced (ca. 300%) and works in the opposite direction, i.e., the high-energy channels are favored at higher source temperatures. Because this effect deemed quite surprising, the experiment was also repeated on an analytical Finnigan MAT 95ST, where again a notable change of the C_3/C_2 ratios was observed in the MI spectra of $\mathbf{1}^{\bullet+}$ from ca. 2 at 200 °C to about 5 at the lowest temperature achievable (50 °C).

Next, four possible rationalizations of the pronounced temperature effect are discussed of which two are associated with the properties of the neutral precursor and two originate from the behavior of the ionic species.

For a carbonyl compound, an obvious explanation of the temperature effect is provided by involvement of keto/enol tautomerization of the neutral precursor. In fact, temperature effects have been observed in the metastable mass spectra of ionized 1,3-diones which easily undergo enolization [29,30]. For the case of valeramide, this would imply that increasing temperatures favor formation of the neutral enol **7** which is, in turn, much easier to ionize than **1** (see above). Hence, the C_3/C_2 ratio of about 1 at 200 °C might be explained by involving the formation of a mixture of $\mathbf{1}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$ upon ionization, because the former contributes to both routes while the latter decays via the C_2-channel almost exclusively. Moreover, the enol has a significantly lower ionization energy than the keto and the corresponding cation radical $\mathbf{7}^{\bullet+}$ resides in a much deeper well than $\mathbf{1}^{\bullet+}$. Accordingly, an enrichment of the enol cation in the mass-selected ion is to be expected. Therefore, keto/enol tautomerization of the neutral would provide an intuitive and straight forward explanation for the observed temperature dependence of the MI spectra. However, the computed stability difference of ca. 25 kcal/mol in favor of **1** [2] disputes involvement of neutral **7**. Even if keto/enol tautomerism is effectively catalyzed by termolecular or surface reactions, the computed energy differences suggest a keto/enol ratio of about 10^{18} at room temperature, and still about 10^{11} at 200 °C. These ratios appear much too large, and hence this explanation is considered unlikely. Another experimental observation disfavors keto/enol tautomerization of the neutral precursors. Thus, while the data shown in Fig. 2 indicate that a minute amount of neutral $\mathbf{7}^{\bullet+}$ might contribute at electron energies below the ionization threshold of **1** (see above), the behavior above $\mathrm{IE}(\mathbf{1}) = 9.40 \pm 0.03\,\mathrm{eV}$ is incompatible with involvement of $\mathbf{7}^{\bullet+}$.

The second explanation is much more difficult to address. As stated, the regioselectivities of the initial C–H bond activations are primarily determined by the accessibility of the appropriate conformations. Therefore, it is conceivable that the population of the neutral conformers required for access to the C_2-route increases at elevated temperatures; in fact, complete flexibility of the alkyl backbone might be reached at 200 °C. Moreover, δ-C–H bond activation is favored on statistical grounds because there exist three δ-C–H but only two γ-C–H bonds. However, the experimental and theoretical data clearly indicate that the C_2-route is more complex than the McLafferty rearrangement. For the time being, we are unable to address this aspect because this would require to screen the entire conformational space of neutral valeramide by B3LYP calculations (molecular modeling does not suffice, see [2]) and a subsequent examination of the non-negligible conformational changes occurring upon ionization at this level of theory. Further, a comprehensive description of such a scenario must also account for the different trajectories involved in γ-C–H and δ-C–H bond activations by means of dynamic considerations.

The third explanation takes us back to the uncoupling of the ionic intermediates $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ of the C_3- and C_2-routes, respectively. As stated, uncoupling alone is not expected to affect the branching ratios of metastable ion dissociations in any but unusual situations. However, we may encounter precisely such a situation here. Thus, the above considerations are based on the assumption that the metastable ions are a small fraction of the mass-selected ions such that depletion of the parent can be neglected. In the present case, however, the appearance energy of the C_3-route is very close to the ionization threshold of **1**, indicating rather low thermochemical and kinetic restrictions of this particular fragmentation. Consequently, it is quite conceivable that the population of intermediate $\mathbf{2}^{\bullet+}$ is effectively depleted at elevated temperatures in that a significant fraction of $\mathbf{2}^{\bullet+}$ formed upon ionization of **1** and subsequent hydrogen migration already dissociates before mass-selection is achieved. In such a case, the above discussed compensation of rate constants and internal energies is not valid anymore. Instead, the

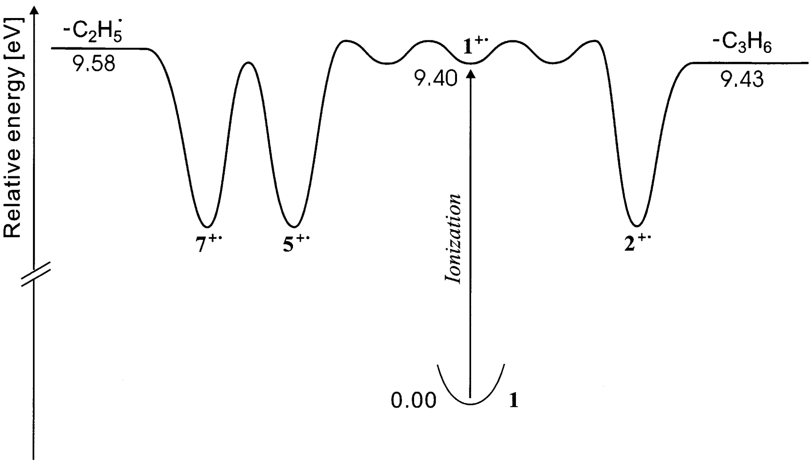


Fig. 4. Strongly simplified potential-energy surface for the competitive dissociation of $\mathbf{1}^{\bullet+}$ via the C_2- and C_3-routes, respectively. For example, the conformational barriers near $\mathbf{1}^{\bullet+}$ and the distonic intermediates, respectively, are deliberately assigned to have equal energy demands. See [2] for a more elaborate representation.

unexpectedly low C_3/C_2 ratio of about 1 in the experiments conducted at a source temperature of 200 °C can be explained through an enrichment of $\mathbf{5}^{\bullet+}$ relative to $\mathbf{2}^{\bullet+}$. To further illustrate this particular effect of uncoupling in a fragile molecular ion, let us refer to the very schematic potential-energy surface of ionized valeramide depicted in Fig. 4. Thus, ionization of **1** leads to the cation radical $\mathbf{1}^{\bullet+}$ which is only stabilized by conformational barriers towards C–H bond activations. Once the distonic ion $\mathbf{2}^{\bullet+}$ is formed, C–C bond rupture leads to the McLafferty products in a more or less thermoneutral process. Due to the entropic preference of dissociation, $\mathbf{2}^{\bullet+}$ therefore, is unlikely to return to structure $\mathbf{1}^{\bullet+}$. While the very same applies for intermediate $\mathbf{5}^{\bullet+}$ formed by δ-C–H bond activation, its dissociation requires yet another hydrogen transfer ($\mathbf{5}^{\bullet+} \rightarrow \mathbf{7}^{\bullet+}$), which also is facile at the energy available, but nevertheless extends the average lifetimes of energized $\mathbf{5}^{\bullet+}$ and $\mathbf{7}^{\bullet+}$. The increased internal energy imparted upon heating the neutrals in the source may therefore cause more or less prompt dissociation of $\mathbf{2}^{\bullet+}$ while a significantly larger fraction of $\mathbf{5}^{\bullet+}$ and/or $\mathbf{7}^{\bullet+}$ can survive the mass selection. Note that this scenario can only apply, if the initially formed molecular ion is energetically above or close to the energy demand of the competing dissociation channels. For endothermic reactions, a regular behavior is to be expected.

The fourth explanation simply involves an enhanced propensity for the formation of a long-lived $\mathbf{1}^{\bullet+}$ upon ionization of neutral valeramide at low temperatures. Contribution of some amount of genuine $\mathbf{1}^{\bullet+}$ to the mass-selected ion beam would result in a preference for the energetically favored McLafferty route, and this scenario can thereby account for the observed temperature behavior as well.

While we can presently not unambiguously decide between these options, it is important to point out that the inclusion of the temperature effect provides an internally consistent picture of the complete fragmentation pattern of ionized valeramide which comprises all experimental and theoretical aspects treated in this series of studies. Further, it is not surprising that besides the overall branching ratios of the different channels also their separate components show variations due to the temperature of the ion source. For example, the ratio of the isotopic McLafferty fragments $m/z = 59$ and 60 unimolecularly formed from the molecular ion of *rac*-[4-D_1]-valeramide via C–H and C–D bond activation, respectively, changes from about 2 at $T_S = 45\,°C$ to ca. 1.2 at $T_S = 300\,°C$. Note, however, that these figures do not directly reflect a particular kinetic isotope effect because partial H/D exchange processes are involved in the McLafferty rearrangement and the extent of H/D equilibration will also depend on the internal energy. This finding further implies that the kinetic modeling described in [1] is only valid for those particular ions generated at $T_S = 200\,^\circ\text{C}$. Nevertheless, it is expected that the general model applies for all temperatures while the actual parameters certainly differ.

4. Related compounds

As noted in [1], the present studies were motivated by a report of Kreft and Grützmacher [35] about unusually large differences between the EI and MI mass spectra of the molecular ions of hexanamide **17** and the corresponding acid **18**. Therefore, it was obvious to investigate these two molecules in order to probe whether the temperature dependence of the C_3/C_2 ratio in the fragmentation of ionized valeramide is an exceptional curiosity or is of more general relevance.

The metastable ion spectrum of hexanamide has been discussed in detail by Kreft and Grützmacher [35]. The most pronounced fragments are due to losses of the alkyl radicals $C_2H_5^\bullet$ and $C_3H_7^\bullet$ leading to fragment ions with $m/z = 86$ and 72, respectively, as well as the McLafferty rearrangement to afford the ionized enol of acetamide at $m/z = 59$ concomitant with loss of the C_4-fragment butene. By and large, our present results obtained at a source temperature of $200\,^\circ\text{C}$ agree with those reported by Kreft and Grützmacher. Therefore, only the effect of the source temperature on the branching ratio is discussed, where the ratio of C_4H_8 and $C_2H_5^\bullet$ losses is used as a diagnostic (referred to as C_4/C_2 ratio). Very similar to the valeramide ion, a pronounced dependence of the C_4/C_2 ratio on T_S is observed (Fig. 5a). Thus, the C_4/C_2 ratio decreases from about 0.8 close to room temperature to less than 0.2 at $T_S = 300\,^\circ\text{C}$. Without further discussing the mechanistic consequences of this result for the dissociation behavior of ionized hexanamide, we conclude that the surprising temperature effect found for ionized valeramide is not restricted to this particular compound.

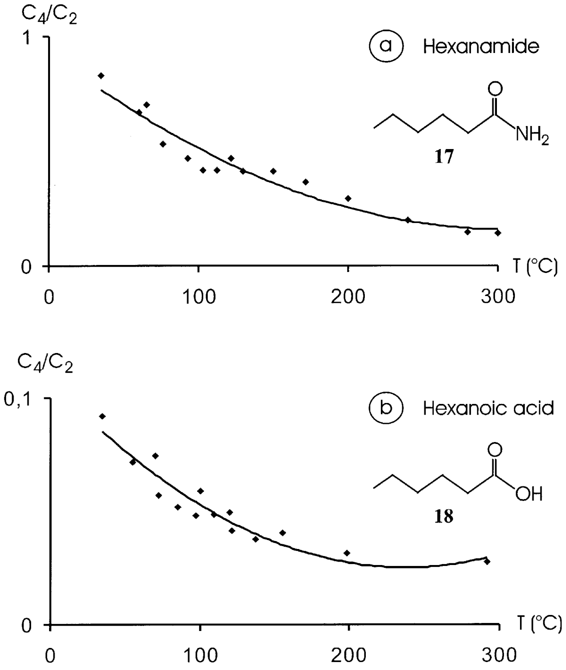


Fig. 5. (a) C_4/C_2 ratios in the MI spectra of $B(1)/E(1)$-mass-selected $\mathbf{17}^{\bullet+}$ as a function of the temperature of the ion source (the solid line is a polynom fit through the data). (b) C_4/C_2 ratios in the MI spectra of mass-selected $\mathbf{18}^{\bullet+}$ as a function of the temperature of the ion source (the solid line is a polynom fit through the data).

The molecular ions of carboxylic acids have been studied in great detail about two decades ago [8,36], and particularly for hexanoic acid **18** and its fragments a solid set of experimental data is available [37–41]. Similar to ionized valeramide, the McLafferty rearrangement of $\mathbf{18}^{\bullet+}$ competes with expulsions of alkyl radicals, i.e., loss of $C_2H_5^\bullet$ concomitant with a fragment ion at $m/z = 87$ and loss of $C_3H_7^\bullet$ concomitant with a fragment ion at $m/z = 73$. Note that the McLafferty reaction of $\mathbf{18}^{\bullet+}$ leads to three different products: (i) loss of butene affords the ionized enol of acetic acid ($m/z = 60$), (ii) loss of acetic acid affords the ionized butene ($m/z = 56$), and (iii) abstraction of an allylic hydrogen within the intermediate ion/neutral complex leads to protonated acetic acid ($m/z = 61$)

Table 3
Neutral molecules lost[a] in the various types of mass spectra[b] of hexanoic acid **17**

	m/z				
	87 $-C_2H_5^{\bullet}$	73 $-C_3H_7^{\bullet}$	61 $-C_4H_7^{\bullet}$	60 $-C_4H_8$	56 $-C_2H_4O_2$
EI[c]	10	45	9	100	8
MI[d]	100	3	1	<1	4
MI[e]	100	1	1	<1	5
MI[f]	100	1	<1	<1	3
PI[g] 11.5 eV	4	19	30	100	35
16.0 eV	4	22	14	100	15
25.0 eV	3	20	16	100	13

[a] Assignments based upon the extensive labeling studies reported in [37].

[b] Given intensities relative to the base peak (100%).

[c] Taken from: http://webbook.nist.gov/chemistry/.

[d] Taken from [35].

[e] Taken from: T. Weiske, Diplomarbeit, TU Berlin, 1981.

[f] $B(1)/E(1)$-mass-selected ions recorded in this work at $T_s = 200\,^{\circ}C$.

[g] Photoionization mass spectra recorded with CERISES at the photon energies indicated.

concomitant with a butenyl radical [37]. For the sake of the argument, we only discuss the sum of these three channels in the context of the competition between the McLafferty rearrangement and other fragmentations occurring.

For hexanoic acid, the difference between the EI and MI mass spectra (Table 3) is even more pronounced than for valeramide and hexanamide. Thus, the losses of $C_2H_5^{\bullet}$ and $C_3H_7^{\bullet}$ and the sum of the McLafferty products behave as ca. 8:38:100 in the EI spectrum, whereas a ca. 100:2:5 pattern evolves from the metastable ion studies. Again, the PI spectra are qualitatively similar to those obtained upon EI with some interesting dependence of the product pattern of the McLafferty route from the photon energy in that the amount of ionized butene ($m/z = 56$) increases at lowest energies. As far as appearance energies are concerned, single-ion monitoring in the PI experiments yields $\text{AE}(m/z = 56) = 10.25 \pm 0.05$ eV, $\text{AE}(m/z = 60) = 10.55 \pm 0.1$ eV, $\text{AE}(m/z = 61) = 10.4 \pm 0.1$ eV, $\text{AE}(m/z = 73) = 10.8 \pm 0.1$ eV, and $\text{AE}(m/z = 87) = 10.4 \pm 0.1$ eV. As far as the corresponding C_4/C_2 ratio is concerned, the results of the MI spectra again contradict the thermochemical ordering of the exit channels. Quite remarkably, the intensity of the molecular ion **18**$^{\bullet+}$ did not even reach 1% relative to $m/z = 60$ at the photon energies examined. In view of the arguments raised above, the negligible intensity of **18**$^{\bullet+}$ in the PI experiments can be attributed to the even more facile occurrence of bond activations in the ionized acid as observed for the amides.

Fig. 5b shows the corresponding C_4/C_2 ratio for the metastable ion of hexanoic acid as a function of the temperature of the ion source. Again, significant increase of the McLafferty channel is observed at lower temperatures of the ion source. Nevertheless, even close to room temperature, the C_4/C_2 ratio is far from those in the EI and PI spectra. A rational is the even lower stability of the molecular ion **18**$^{\bullet+}$ relative to the ionized amides as far as the various C–H bond activations possible are concerned, such that already at ambient temperatures the majority of the corresponding McLafferty intermediates undergo dissociation during mass selection, whereas a larger fraction of the other distonic intermediates can survive this procedure. Decreased stability of **18**$^{\bullet+}$ compared to **1**$^{\bullet+}$ and **17**$^{\bullet+}$ is attributed to the electron-withdrawing character of the hydroxy group in the acid which increases the ionization energies of the acids relative to the amides, e.g., IE(**1**) = 9.4 eV [1] vs. IE(**18**) = 10.1 eV [42].[3] According to Fig. 4, the hydroxy group elevates the energetic location of the molecular ion such that dissociation becomes even faster. Accordingly, a C_4/C_2 ratio similar to those in the EI and PI mass spectra can only be foreseen for metastable **18**$^{\bullet+}$ produced at much lower temperatures.

5. Conclusions

Collaborative experimental and theoretical investigations help to elucidate the dissociation behavior of ionized valeramide which is primarily characterized

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[3] Based on the PI experiments, we are tempted to better assign IE(**18**) as 10.25 ± 0.05 eV.

by facile C–H bond activations of the alkyl backbone. Among other observations, a pronounced dependence of the C_3/C_2 ratio in the fragmentation of ionized valeramide from the temperature of the ion source is found to be responsible for the otherwise non-explicable variations in the branching ratios. This effect is indeed quite unexpected and seems to have escaped attention in the numerous previous investigations dealing with the McLafferty rearrangement. Specifically, this effect may account for the seemingly vanishing McLafferty fragments in the metastable ion spectra of various types of carbonyl compounds [8,35,37–41,43]. It is to be probed in future, whether this effect is restricted to some specific types of carbonyl compounds (i.e., amides and acids) or forms a more general phenomenon in metastable ion spectra. In this context, additional research of other groups equipped with mass spectrometers better suited for variations of the ion source temperatures is very much encouraged.

Acknowledgements

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Appendix A. Ion source temperature

As stated in the text, we observe pronounced effects of the temperature of the ion source (T_s) on the unimolecular fragmentations of mass-selected metastable ions of several carbonyl compounds. However, the temperatures mentioned must not directly correspond to those of the neutral samples just before ionization. To illustrate this aspect, a more detailed consideration of the ion source is required (Fig. 6).

The source temperatures given in the text refer to the readings from a thermocouple mounted on the massive source block made of stainless steel. The exit-slit plate as well as the repeller, both also made from stainless steel and mounted directly on the source block, can safely be assumed to have the same temperature.

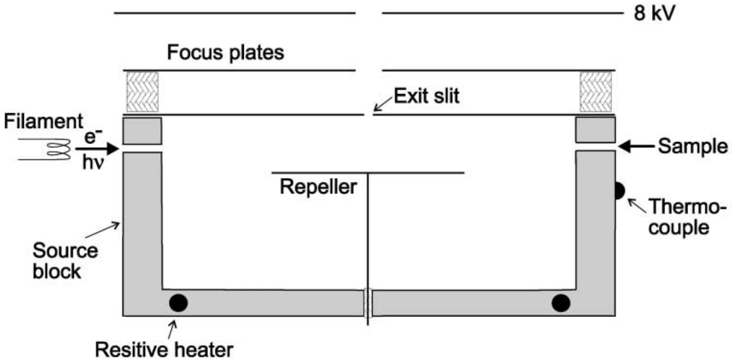

Fig. 6. Schematic drawing of the VG ZAB ion source used in the selection-experiments.

When the filament and heaters are switched off, the source block reaches ambient temperature during several hours. Once the filament is turned on, however, T_S increases rapidly due to the heat emitted, reaching $T_S \approx 160\,^\circ$C after about half an hour. Therefore, all spectra were effectively recorded at temperature gradients, and the values given refer to the averages of the temperature readings at the begin and end of the accumulations. Also, note that there is hardly any time for re-focusing in this period. After ca. $160\,^\circ$C have been reached, higher temperatures can be achieved by additional heating.

The actual temperature of the gaseous neutrals before ionization is more difficult to assess, however. In these experiments, the neutral samples were always evaporated at (or close to) room temperature. The vapors enter the source block through a bore of ca. 1 mm diameter and 10 mm length, such that collisions with the surface are likely to occur. Nevertheless, the EI source used in these experiments is not particularly sealed against the high-vacuum in the source chamber (ca. 3×10^{-6} mbar when samples were present). Therefore, the temperature of the gaseous neutral can in fact be somewhat lower than that of the source block, due to incomplete coupling between the gas phase and the surfaces. On the other hand, however, the neutrals could also exhibit temperatures higher than that of the surrounding source block because in addition to electrons, the filament emits bright light which enters the source as well and can interact with the neutrals in the very same volume where ionization is most likely to occur under EI conditions. Consequently, the effects on the branching ratios reported here are obviously proportional to T_S, while the actual internal energy of the neutrals must not coincide with T_S. Considering the experimental conditions, it is in fact quite likely that not only the ions, but also the neutral precursors exhibit broadened, non-Boltzmann energy distributions [12].

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