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Effect of variations of the size and structure of the principal alkyl group on alkene elimination from the immonium ions $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$

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Abstract

The reactions of three homologous series of metastable immonium ions of general structure, $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$, [$m = 1-3$; $\text{R} = n\text{-C}_n\text{H}_{2n+1}$, $n = 1-10, 12, \text{ and } 14$, iso- C_5H_{11} , $\text{CH}_2\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$, neo- C_5H_{11} , and $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$] are reported and discussed. The first member of each homologous series is anomalous in undergoing several reactions, including elimination of molecular hydrogen and a methyl radical. In contrast, higher members of all three series expel either or both alkenes, C_nH_{2n} or $\text{C}_{n-1}\text{H}_{2n-2}$ derived from the principal alkyl group, R. The influence of the size and structure of R on these alkene eliminations is analysed. Loss of C_nH_{2n} produces an approximately Gaussian metastable peak; the associated kinetic energy release is relatively small and varies only slightly as the homologous series are ascended. In contrast, $\text{C}_{n-1}\text{H}_{2n-2}$ elimination releases a much larger amount of kinetic energy, particularly for $n = 3$, when the associated metastable peak is dish; but the kinetic energy release declines dramatically on ascending the homologous series. Loss of $\text{C}_{n-1}\text{H}_{2n-2}$ is favoured by branching at the γ -carbon atom, provided there is a γ -hydrogen atom, but it does not occur when $\text{R} = \text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ because γ -hydrogen transfer is impossible. (Int J Mass Spectrom 199 (2000) 189–200) © 2000 Elsevier Science B.V.

Keywords: Metastable ions; Degree of freedom effects; Immonium ions; Alkene elimination; kinetic energy release

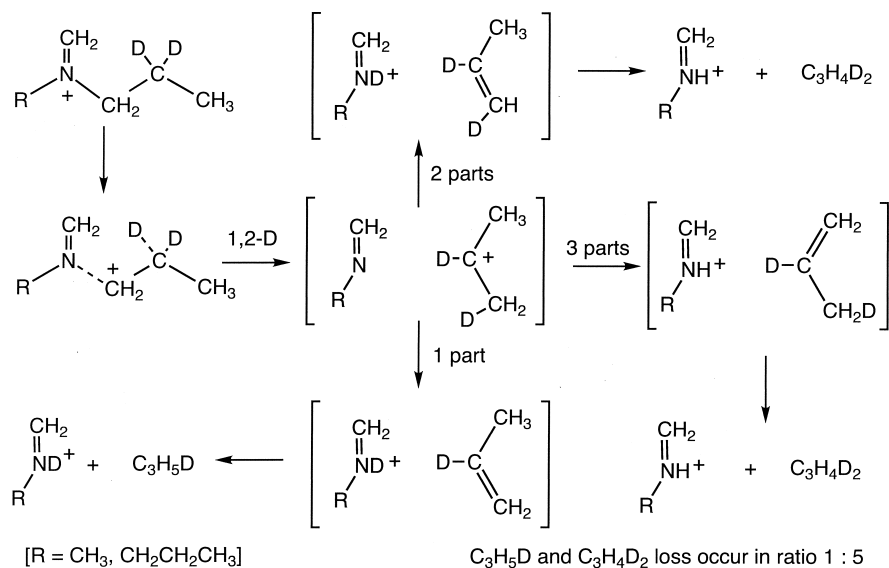
1. Introduction

The structure and reactivity of ionic species may be conveniently investigated by studying the behaviour of metastable ions [1,2], which have sufficiently long av-

erage lifetimes [3] that the observed reactions normally occur in competition with one another from the ground electronic state, except in very rare cases [4]. Moreover, the relative rates of these competing processes normally depend upon their critical [5] energies and the reactions with the lowest critical energies are usually dominant [1–3,6], as is illustrated by the frequent intervention of isotope effects, some of which are extraordinarily large [7–10] in the fragmentation of small metastable ions.

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Dedicated to Professor Henri Edouard Audier on the occasion of his 60th birthday.



Scheme 1.

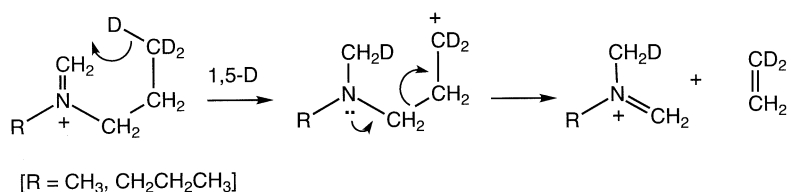
Extensive studies of oxonium ions of general formula $C_nH_{2n+1}O^+$ were important in the development of many concepts which are now routinely used to describe the behaviour of ions in the gas phase [11,12]. In contrast, the analogous immonium ions, $C_nH_{2n+2}N^+$, have received much less attention [13].

The characteristic reaction of these immonium ions is alkene loss. Two distinct general routes are found for expulsion of an alkene from the principal *N*-alkyl group, R (C_nH_{2n+1}). Elimination of C_nH_{2n} gives rise to an approximately Gaussian metastable peak corresponding to a relatively small kinetic energy release. This process has been interpreted in terms of species in which the initial N–R bond has been stretched, thus permitting hydrogen transfer to occur between the developing products [14]. Rearrangement of the incipient cation to a more stable isomer may occur, with the 1,2-H or 1,2-alkyl shift probably taking place as the N–R bond is stretched, as illustrated for $CH_2=N^+(CH_3)CH_2CD_2CH_3$ in Scheme 1. The hydrogen atom that is transferred to nitrogen originates mainly from either the α - or γ -carbon atom, rather than from the β position [15–17]. Specific β -hydrogen transfer would be anticipated on the basis of the traditional “four-centre” mechanism, Eq. (1).



Expulsion of an alkene, typically $C_{n-1}H_{2n-2}$, containing fewer carbon atoms than R involves a different mechanism: specific γ -hydrogen transfer is observed and the metastable peak is considerably broader, thus indicating the presence of a substantial reverse critical energy. Thus, $C_2H_2D_2$ is lost with high selectivity from $CH_2=N^+(CH_3)CH_2CH_2CD_3$ [15–17], and the associated metastable peak is dish-shaped [14]. This process is formally isoelectronic with the retro-Alder “ene” reaction [18] and it may be interpreted in terms of hydrogen transfer through a six-membered ring transition state to give a high-energy, open-chain carbonium ion, which then fragments with a substantial kinetic energy release, Scheme 2.

The kinetic energy release for $C_{n-1}H_{2n-2}$ loss from $CH_2=N^+(CH_3)C_nH_{2n+1}$ decreases as n increases [19]. However, although the competition between $C_{n-1}H_{2n-2}$ and C_nH_{2n} elimination from some relatively small immonium ions has been considered [13,20], no systematic study of the influence of the size and structure of the C_nH_{2n+1} group on the ratio of $C_{n-1}H_{2n-2}$ to C_nH_{2n} loss from larger immonium ions has been made. In the course of studies on ionised tertiary amines [21], three



Scheme 2.

series of immonium ions of general structure CH₃(CH₂)_mCH=N⁺(CH₃)R, *m* = 1–3, were generated, so allowing these influences to be investigated.

2. Experimental

All mass spectra were recorded on the VG Analytical ZAB-R mass spectrometer. Details of the geometry of this three-sector (BE₁QE₂) instrument have been reported elsewhere [22]. Data on the dissociation of metastable ions in the second field-free region were obtained by the mass-analysed ion kinetic energy spectra (MIKES) technique [3]. The quoted spectra are integrated data, compiled from 2–5 individual scans. Typical operating conditions were 70 eV ionising electron energy and 7910 V accelerating voltage. The kinetic

energy releases were estimated from the width at half-height of the appropriate metastable peak, by means of the standard one-line equation [3,23]; no correction [24] was applied for the width at half-height of the main beam.

The immonium ions were generated by ionisation and α -cleavage of the tertiary amines, CH₃CH₂CH₂(CH₃CH₂)CHN(CH₃)(C_nH_{2n+1}) and CH₃CH₂CH₂CH₂(CH₃CH₂CH₂)CHN(CH₃)(C_nH_{2n+1}). The synthesis of these amines has been described elsewhere [21].

3. Results and discussion

The reactions of metastable immonium ions of general structure CH₃(CH₂)_mCH=N⁺(CH₃)(*n*-

Table 1
Reactions of metastable immonium ions of general structure CH₃CH₂CH=N⁺(CH₃)R

R	Alkene lost				Ratio of alkene loss C _{n-1} H _{2n-2} :C _n H _{2n}
	C _n H _{2n}		C _{n-1} H _{2n-2}		
	RA ^a	T _{1/2} ^b	RA ^a	T _{1/2} ^b	
CH ₃ ^c	0		0		
C ₂ H ₅ ^d	100	3.8	0		
<i>n</i> -C ₅ H ₁₁	61.0	4.6	39.0	37.2	0.64
<i>n</i> -C ₆ H ₁₃	56.2	4.1	43.8	25.3	0.78
<i>n</i> -C ₇ H ₁₅	47.6	4.5	52.4	17.0	1.10
<i>n</i> -C ₈ H ₁₇	45.5	4.9	54.5	16.7	1.20
<i>n</i> -C ₉ H ₁₉	39.8	5.2	60.2	16.7	1.51
<i>n</i> -C ₁₀ H ₂₁	37.9	5.9	62.1	13.4	1.64
<i>n</i> -C ₁₂ H ₂₅	37.3	6.2	62.4	12.9	1.68
<i>n</i> -C ₁₄ H ₂₉	35.5	6.2	64.2	11.8	1.79

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol⁻¹, estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^c Neither C_nH_{2n} nor C_{n-1}H_{2n-2} may be lost from this ion [the actual reactions include: loss of CH₃· (RA 20, T_{1/2} 5.0), C₂H₄ (RA 1.5, T_{1/2} 95) and C₃H₆ (RA 74, T_{1/2} 6.4)].

^d C_nH_{2n}, but not C_{n-1}H_{2n-2}, may be lost from this ion.

Table 2

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{R}^a$

R	Alkene lost,														
	C_nH_{2n}						$\text{C}_{n-1}\text{H}_{2n-2}$						Ratio of alkene loss $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$		
	RA ^a			$T_{1/2}$ ^b			RA ^a			$T_{1/2}$ ^b					
	<i>H</i> ^h	<i>O</i> ^o	<i>A</i> ^m	<i>H</i> ^h	<i>O</i> ^o	<i>A</i> ^m	<i>H</i> ^h	<i>O</i> ^o	<i>A</i> ^m	<i>H</i> ^h	<i>O</i> ^o	<i>A</i> ^m	<i>H</i> ^h	<i>O</i> ^o	<i>A</i> ^m
CH_3^c	0	0	0				0	0	0						
C_2H_5^d	100	100	100	5.4	5.8	5.6	0	0	0						
<i>n</i> - C_3H_7		95.0	95.0		4.2	4.2		5.0	5.0		67.2	67.2		0.05	0.05
<i>n</i> - C_5H_{11}	72.2		72.2	4.4		4.4	27.8		27.8	35.7		35.7	0.38		0.38
<i>n</i> - C_6H_{13}	62.1	60.0	61.1	4.0	4.5	4.3	37.9	40.0	38.9	23.1	24.7	23.9	0.61	0.67	0.64
<i>n</i> - C_7H_{15}	51.3	50.4	50.9	4.3	4.6	4.5	48.7	49.6	49.1	17.4	17.4	17.4	0.95	0.98	0.96
<i>n</i> - C_8H_{17}	52.2	51.7	52.0	4.7	4.8	4.8	47.8	48.3	48.0	16.5	15.6	16.1	0.92	0.93	0.93
<i>n</i> - C_9H_{19}	51.0	48.7	49.8	5.0	4.8	4.9	49.0	51.3	50.2	14.2	12.9	13.6	0.96	1.05	1.00
<i>n</i> - $\text{C}_{10}\text{H}_{21}$	47.0	43.2	45.1	4.9	5.8	5.4	53.0	56.8	54.9	12.1	12.9	12.5	1.13	1.31	1.21
<i>n</i> - $\text{C}_{12}\text{H}_{25}$	41.9	39.1	40.5	4.6	5.1	4.9	58.1	60.9	59.5	9.8	12.7	11.3	1.38	1.56	1.47
<i>n</i> - $\text{C}_{14}\text{H}_{29}$	41.6	43.5	42.5	4.7	6.5	5.6	58.4	56.5	57.5	9.0	11.1	10.1	1.41	1.30	1.36

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^h *H* = immonium ion generated from appropriate 3-hexylamine; ^o *O* = immonium ion generated from appropriate 4-octylamine; ^m *A* = average value from data from immonium ions generated from appropriate 3-hexylamine and 4-octylamine.

^c Neither C_nH_{2n} nor $\text{C}_{n-1}\text{H}_{2n-2}$ may be lost from this ion [the actual reactions include: loss of $\text{CH}_3\cdot$ (RA 8, $T_{1/2}$ 2.8), $\text{C}_2\text{H}_5\cdot$ (RA 11, $T_{1/2}$ 5.2), $\text{C}_2\text{H}_7\text{N}$ (RA 6, $T_{1/2}$ 3.3), C_3H_6 (RA 52, $T_{1/2}$ 48), C_4H_8 (RA 7, $T_{1/2}$ 6.1), and C_4H_6 (RA 6, $T_{1/2}$ 3.5)].

^d C_nH_{2n} , but not $\text{C}_{n-1}\text{H}_{2n-2}$, may be lost from this ion.

Table 3

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$

R	Alkene lost										
	C_nH_{2n}					$\text{C}_{n-1}\text{H}_{2n-2}$					Ratio of alkene loss $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$
	RA ^a		$T_{1/2}$ ^b			RA ^a		$T_{1/2}$ ^b			
CH_3^c	0					0					
C_2H_5^d	100		4.9			0					0
<i>n</i> - C_3H_7	94.3		4.4			5.7		69.5			0.06
<i>n</i> - C_6H_{13}	69.6		4.6			30.4		23.9			0.44
<i>n</i> - C_7H_{15}	54.0		4.8			46.0		16.9			0.85
<i>n</i> - C_8H_{17}	51.7		4.2			48.3		15.2			0.93
<i>n</i> - C_9H_{19}	51.2		4.3			48.8		13.1			0.95
<i>n</i> - $\text{C}_{10}\text{H}_{21}$	50.8		5.3			49.2		11.8			0.97
<i>n</i> - $\text{C}_{12}\text{H}_{25}$	43.6		5.0			56.4		11.0			1.29
<i>n</i> - $\text{C}_{14}\text{H}_{29}$	39.7		5.5			60.3		10.4			1.52

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^c Neither C_nH_{2n} nor $\text{C}_{n-1}\text{H}_{2n-2}$ may be lost from this ion [the actual reactions include: loss of $\text{C}_3\text{H}_7\cdot$ (RA 7, $T_{1/2}$ 8.4), $\text{C}_2\text{H}_7\text{N}$ (RA 14, $T_{1/2}$ 3.7), C_3H_6 (RA 31, $T_{1/2}$ 5.9), and C_4H_8 (RA 46, $T_{1/2}$ 31)].

^d C_nH_{2n} , but not $\text{C}_{n-1}\text{H}_{2n-2}$, may be lost from this ion.

Table 4

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{C}_5\text{H}_{11}^{\text{a}}$

Ion structure	Alkene lost				Ratio of alkene loss $\text{C}_4\text{H}_8:\text{C}_5\text{H}_{10}$
	C_5H_{10}		C_4H_8		
	RA ^a	$T_{1/2}^{\text{b}}$	RA ^a	$T_{1/2}^{\text{b}}$	
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	61.0	4.6	39.0	36.2 ^e	0.64
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	12.6	5.0	87.4	35.7 ^e	6.9
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	90.7	3.4 ^f	9.3	37.5 ^f	0.10
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$	98.2	3.2	<1.8	W ^w	<0.02

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^c composite metastable peak; composite metastable peak with a flat-topped component; W^w = metastable peak too weak to permit a meaningful KE release to be estimated.

$\text{C}_n\text{H}_{2n+1}$), $m = 1-3$, are reported in Tables 1–3, respectively. Data on the reactions of metastable $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)\text{R}$ ions in which R is a pentyl and hexyl group with various degrees of branching in the alkyl chain are presented in Tables 4–8. The reactions of metastable $\text{CH}_2=\text{N}^+(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ are reported in Table 9.

Elimination of C_nH_{2n} and/or $\text{C}_{n-1}\text{H}_{2n-2}$ dominates the chemistry of each member of all three series of immonium ions apart from the $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)_2$ ions which contain two N-methyl groups. These ions are atypical because elimination of either C_nH_{2n} or $\text{C}_{n-1}\text{H}_{2n-2}$ from the principal alkyl group is impossible when $n = 1$. Instead, a variety of other reactions is observed, including loss of molecular hydrogen, a methyl radical and an alkene derived from the $\text{CH}_3(\text{CH}_2)_m\text{CH}$ entity.

Similarly, the three $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_3$ immonium ions show essentially only loss of C_nH_{2n} , without significant competition from $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion, because the only alkene that may be lost from an *N*-ethyl group is C_2H_4 .

In contrast, once $n = 3$, both routes for alkene loss become viable; however, elimination of $\text{C}_{n-1}\text{H}_{2n-2}$ competes poorly with C_nH_{2n} loss. The ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ loss from $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(n-\text{C}_n\text{H}_{2n+1})$ is 0.05 and 0.06 when $m = 2$ and 3, respectively. These ratios are taken from metastable peak heights, which systematically underestimates $\text{C}_{n-1}\text{H}_{2n-2}$ elimination because the peak for this fragmentation is invariably wider than that for C_nH_{2n} loss.

Unfortunately, no data for the reactions of $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(n-\text{C}_4\text{H}_9)$ are available because these immonium ion could not be unambigu-

Table 5

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{C}_6\text{H}_{13}^{\text{a}}$

Ion structure	Alkene lost				Ratio of alkene loss $\text{C}_5\text{H}_{10}:\text{C}_6\text{H}_{12}$
	C_6H_{12}		C_5H_{10}		
	RA ^a	$T_{1/2}^{\text{b}}$	RA ^a	$T_{1/2}^{\text{b}}$	
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	56.2	4.1	43.8	25.3	0.78
$\text{CH}_3\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$	>99.9	3.8	<0.1	W ^w	<0.001

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

W^w = metastable peak too weak to permit a meaningful KE release to be estimated.

Table 6

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{C}_5\text{H}_{11}$

Ion structure	Alkene lost				Ratio of alkene loss $\text{C}_4\text{H}_8:\text{C}_5\text{H}_{10}$
	C_5H_{10}		C_4H_8		
	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	72.2	4.3	27.8	35.7	0.38
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	21.0	4.4	79.0	33.5	3.76
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	93.5	3.4	6.5	36.5	0.07
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_3$	99.3	3.2	<1	^w W	<0.01

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^w W = metastable peak too weak to permit a meaningful KE release to be estimated.

ously generated: propyl radical loss could occur by α -cleavage the butyl group as well as the 3-hexyl or 4-octyl substituent in the parent ionised amines. However, when $n = 5$, the ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ elimination is much greater (0.38 and 0.44 for $m = 2$ and 3, respectively) than when $n = 3$. Moreover, as n increases further from 6 to 14, this ratio steadily rises and $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion eventually becomes dominant.

The ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ loss from $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(n-\text{C}_n\text{H}_{2n+1})$ is generally higher for lower values of m , Fig. 1. Although these differences are not pronounced, they appear to be quite general and similar trends are evident in the data of Tables 4–8. One reason for this slightly increased

preference for eliminating the smaller alkene ($\text{C}_{n-1}\text{H}_{2n-2}$) from smaller immonium ions is that rotational effects [25,26] may favour loss of the larger alkene (C_nH_{2n}) from the larger immonium ions. This explanation is tentative, however, and the precise origins of any such rotational effects remain to be elucidated.

The trends in the ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ loss are broadly consistent with earlier mechanistic interpretations. In particular, $\text{C}_{n-1}\text{H}_{2n-2}$ loss involves an open-chain carbonium ion (or a structure resembling this species) as a transition state. Consequently, when $n = 3$, $\text{C}_{n-1}\text{H}_{2n-2}$ elimination must proceed via a primary carbonium ion. However, once $n \geq 4$, $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion may proceed via a more stable

Table 7

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{C}_6\text{H}_{13}$

Structure of C_6H_{13} group	Alkene lost									Ratio of alkene loss $\text{C}_5\text{H}_{10}:\text{C}_6\text{H}_{12}$					
	C_6H_{12}			C_5H_{10}											
	RA ^a			$T_{1/2}$ ^b			RA ^a			$T_{1/2}$ ^b					
	H^h	O^o	A^m	H^h	O^o	A^m	H^h	O^o	A^m	H^h	O^o	A^m	H^h	O^o	A^m
$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	62.1	60.0	61.1	4.0	4.3	4.2	37.9	40.0	38.9	23.1	24.5	23.8	0.61	0.67	0.64
$\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$	>99.6	>99.3	>99.4	4.0	4.1	4.1	<0.4	<0.7	<0.6	^w W	^w W	^w W	<0.01	<0.01	<0.01

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^hH = immonium ion generated from appropriate 3-hexylamine; ^oO = immonium ion generated from appropriate 4-octylamine; ^mA = average value from data from immonium ions generated from appropriate 3-hexylamine and 4-octylamine; ^ww = metastable peak too weak to permit a meaningful KE release to be estimated.

Table 8

Reactions of metastable immonium ion ions of general structure $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{C}_6\text{H}_{13}$

Alkene loss ion structure	Alkene lost				Ratio of $\text{C}_5\text{H}_{10}:\text{C}_6\text{H}_{12}$
	C_6H_{12}		C_5H_{10}		
	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	69.6	4.6	30.4	23.4	0.44
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{N}^+(\text{CH}_3)\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$	99.3	4.0	<0.7	W ^w	<0.01

^a RA = relative abundance measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

^w W = metastable peak too weak to permit a meaningful KE release to be estimated.

secondary cation because the chain length is sufficient to permit γ -hydrogen transfer to occur from a secondary position. Consequently, $\text{C}_{n-1}\text{H}_{2n-2}$ loss competes very much more effectively with C_nH_{2n} expulsion once $n \geq 4$ than when $n = 3$; however, the ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ elimination does not increase so dramatically once $n > 4$ because $\text{C}_{n-1}\text{H}_{2n-2}$ loss still involves a secondary cation.

Further evidence for a two-step mechanism is found in the trends in the $T_{1/2}$ value for $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion, which is always greater than that for C_nH_{2n} loss. The differences are most dramatic for the lower members of the series. Thus, the $T_{1/2}$ values for C_2H_4 loss from $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(n-\text{C}_3\text{H}_7)$ are 67 and 69 kJ mol^{-1} , respectively, when $m = 2$ and 3. The associated metastable peaks are extremely broad and dish-topped, indicating that a comparatively well-

defined kinetic energy release accompanies these reactions. In contrast, although C_4H_8 expulsion from $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(n-\text{C}_5\text{H}_{11})$ produces metastable peaks that are broad and flattened at the top, the $T_{1/2}$ values of 37 and 36 kJ mol^{-1} , respectively, for $m = 1$ and 2 are greatly reduced. This great reduction is intelligible because the reverse critical energy is diminished if the transition state is a secondary cation ($n \geq 4$), rather than a higher-energy primary cation ($n = 3$). Furthermore, the $T_{1/2}$ value for $\text{C}_{n-1}\text{H}_{2n-2}$ loss decreases steadily as n increases further, but there is no dramatic decline which might reflect a further change in the nature of the transition state.

The degree of substitution at the γ -carbon atom strongly influences the ratio of $\text{C}_{n-1}\text{H}_{2n-2}:\text{C}_n\text{H}_{2n}$ elimination. Branching at the γ -carbon atom favours $\text{C}_{n-1}\text{H}_{2n-2}$ loss over C_nH_{2n} expulsion. Thus, the ratio of $\text{C}_4\text{H}_8:\text{C}_5\text{H}_{10}$ loss from isomeric $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(\text{C}_5\text{H}_{11})$ species increases from 0.64 when the N -alkyl group is $n-\text{C}_5\text{H}_{11}$ to 6.9 when it is iso C_5H_{11} for $m = 1$; the corresponding ratios for $m = 2$ are 0.38 and 3.8, respectively. This increase reflects the fact that the cation involved in C_4H_8 loss from the isomer containing the iso C_5H_{11} group has a tertiary structure and is more readily formed than the isomeric secondary cation that is involved in the analogous reaction of the isomeric immonium ion containing an $n-\text{C}_5\text{H}_{11}$ group. On the other hand, the immonium ions in which the pentyl group has the neo- C_5H_{11} structure eliminate almost no C_4H_8 because the cation involved in C_4H_8 loss has

Table 9

Reactions of the metastable immonium ion $\text{CH}_2=\text{N}^+(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$

Alkene lost		C_4H_8		C_5H_{10}		C_6H_{12}	
RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b	RA ^a	$T_{1/2}$ ^b
31.6	50.9	2.6	54.2	3.2	3.9	61.9	2.6

^a RA = relative abundances measured by metastable peak heights for ions dissociating in the second field-free region of the ZAB-R research mass spectrometer and normalised to a total metastable ion current of 100 units.

^b KE = kinetic energy release, in kJ mol^{-1} , estimated from the width at half-height of the associated metastable peak. Some values are quoted to one decimal place to avoid introducing rounding errors, but this figure is unlikely to be significant.

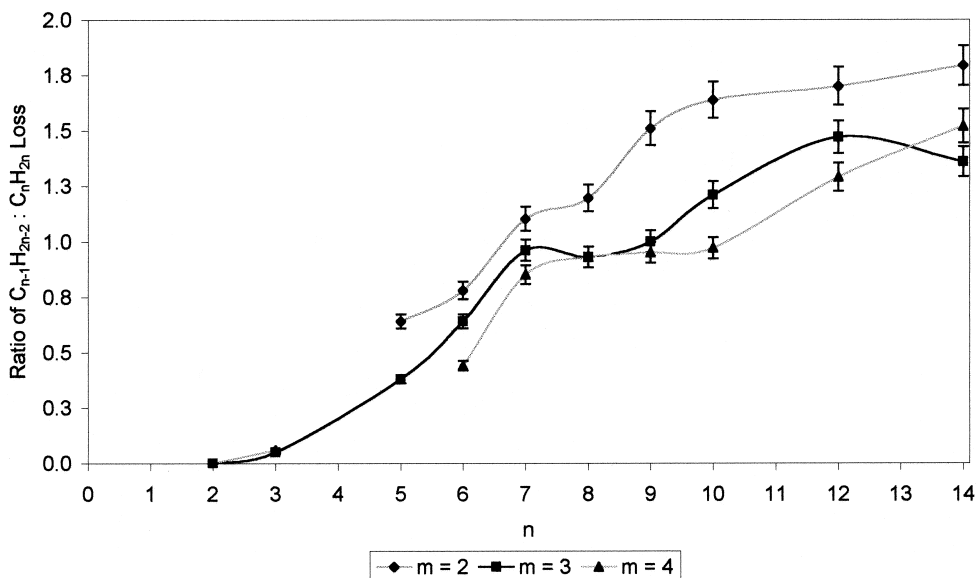


Fig. 1. Variation of the ratio of $C_{n-1}H_{2n-2}:C_nH_{2n}$ loss from three series of $CH_3(CH_2)_mCH=N^+(CH_3)C_nH_{2nH}$ immonium ions.

an unfavourable primary structure, so C_5H_{10} loss dominates.

A concerted mechanism for $C_{n-1}H_{2n-2}$ loss cannot explain any of these trends. Nor can it account for alkene elimination by this route from immonium ions in which hydrogen transfer may occur in competition from primary, secondary and tertiary sites. The hydrogen is always abstracted from the most substituted position, as would be expected if a cationic site was being formed by hydride anion transfer. Thus, $CH_2=N^+(CH_3)CH(CH_2CH_3)CH_2CH_2CH_3$ loses C_3H_6 rather than C_2H_4 .

An interesting conclusion follows from the variation in the ratio of $C_{n-1}H_{2n-2}:C_nH_{2n}$ loss from isomeric $CH_3(CH_2)_mCH=N^+(CH_3)(C_6H_{13})$ ions. Elimination of C_5H_{10} is entirely suppressed when the γ -carbon atom of the hexyl group has a quaternary structure. Thus, all three $CH_3(CH_2)_mCH=N^+(CH_3)CH_2CH_2C(CH_3)_3$ species expel essentially only C_6H_{12} . In contrast, the ratio of $C_5H_{10}:C_6H_{12}$ loss from the $CH_3(CH_2)_mCH=N^+(CH_3)(n-C_6H_{13})$ ions is 0.78, 0.64, and 0.44, respectively, for $m = 1, 2,$ and 3 . This pronounced trend is consistent with specific γ -hydrogen transfer because the $CH_3(CH_2)_m$

$CH=N^+(CH_3)CH_2CH_2C(CH_3)_3$ species have no γ -hydrogen and C_5H_{10} elimination is blocked.

No consistent trend is evident in the $T_{1/2}$ value for C_nH_{2n} loss from the $CH_3(CH_2)_mCH=N^+(CH_3)(n-C_nH_{2n+1})$ ions. For $m = 1$, there is a gradual rise, from 3.8 ($n = 2$) to 6.2 ($n = 14$) kJ mol^{-1} . However, when $m = 2$ or 3 , the variations are barely perceptible and only comparable to the experimental errors.

The sole deduction which may safely be made from the $T_{1/2}$ values for C_nH_{2n} expulsion is that this reaction is clearly different from $C_{n-1}H_{2n-2}$ loss. The $T_{1/2}$ value is much smaller for C_nH_{2n} loss, especially when n is small, and the absence of a clear trend is consistent with a transition state with imprecisely defined geometry. This conclusion is compatible with a mechanism involving species in which incipient neutral and cationic fragments are held together by ionic forces [15,27–33]. Stretching of the C–N bond precedes the hydrogen transfer from carbon to nitrogen which occurs at a late stage on the reaction coordinate. Consequently, partitioning of excess internal energy as translation when dissociation finally occurs is relatively inefficient, the metastable peak is of Gaussian profile and the $T_{1/2}$ value is

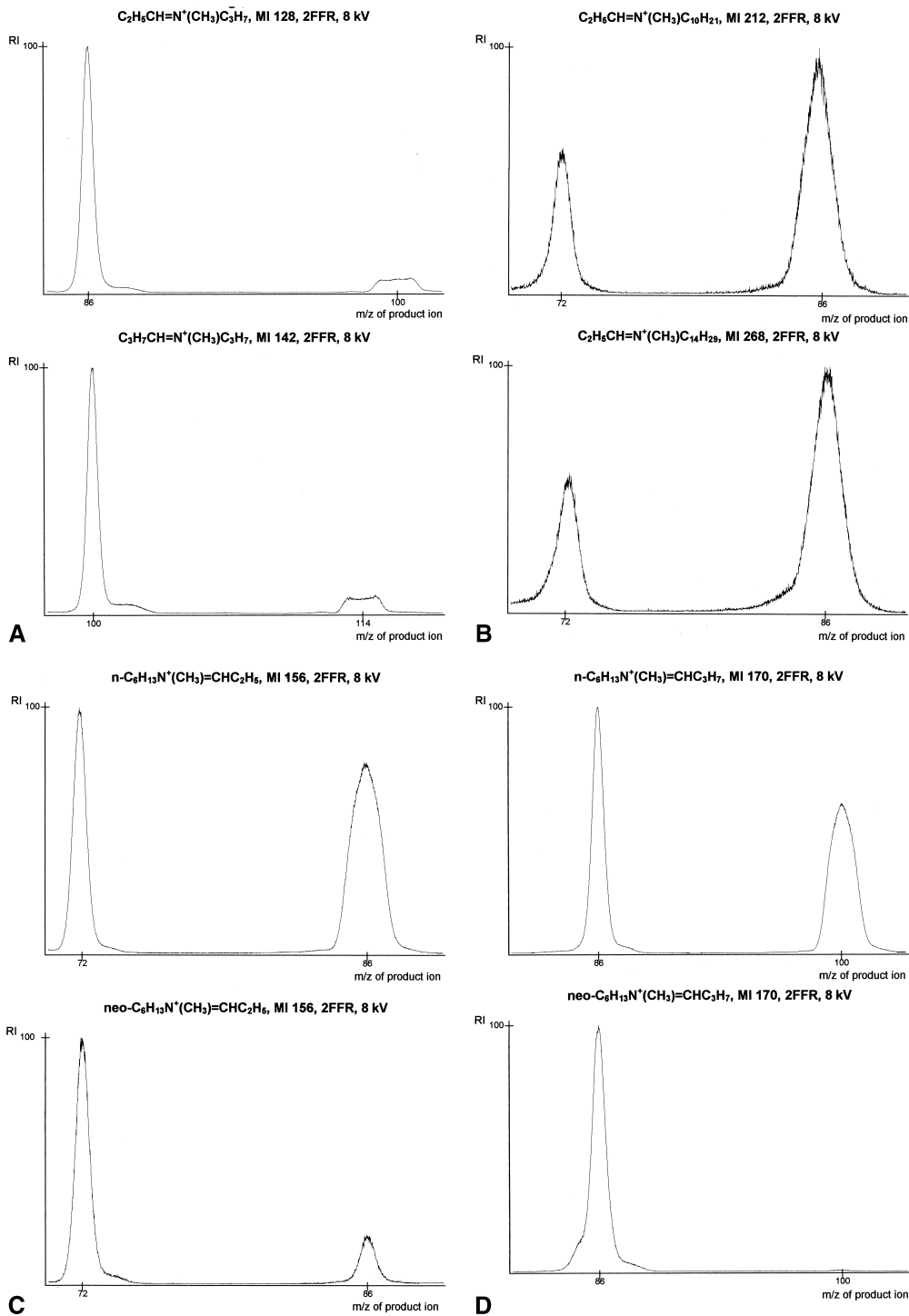
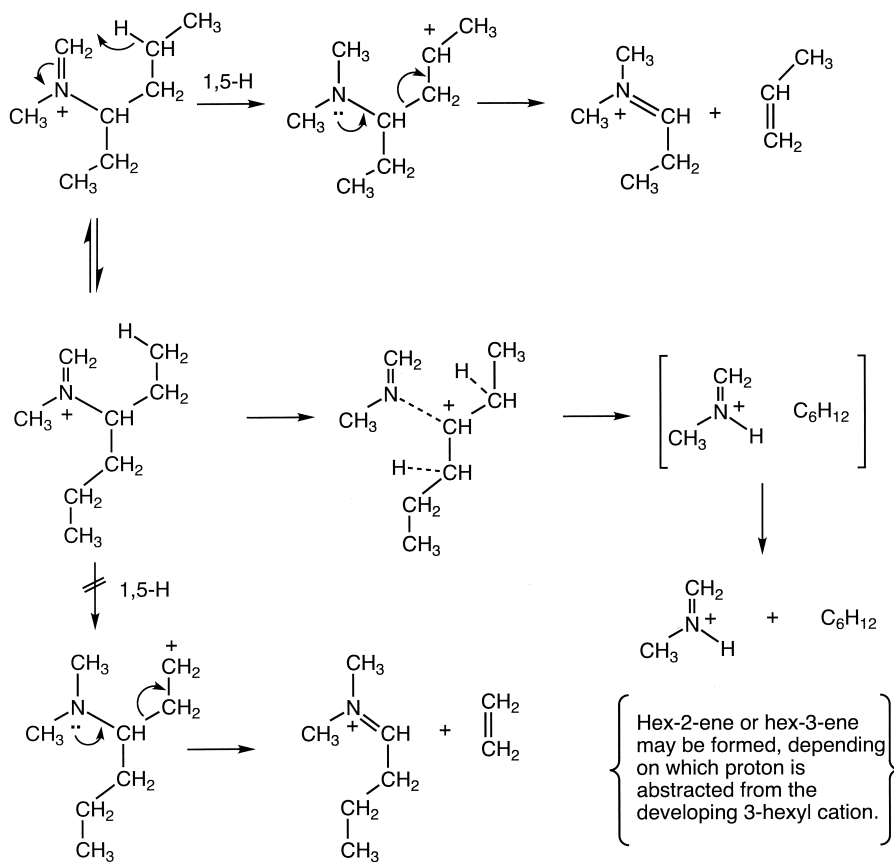


Fig. 2. MIKE spectra of representative $CH_3CH_2CH=N^+(CH_3)R$ and $CH_3CH_2CH_2CH=N^+(CH_3)R$ immonium ions. The m/z scale in these spectra is not uniform but has been expanded in the region of each of the metastable peaks in order to show their shapes more clearly.



comparatively small. In contrast, $C_{n-1}H_{2n-2}$ loss is initiated by a specific 1,5-hydrogen transfer between two carbon atoms via a transition state with a well-defined geometry. Therefore, there is more opportunity for internal energy released in the final step to be partitioned as translation. Since this reverse critical energy is relatively large, the metastable peak assumes a dish-shaped or flat-topped appearance when n is small. Illustrative examples of the MIKE spectra of representative $CH_3CH_2CH=N^+(CH_3)R$ immonium ions are shown in Fig. 2.

Finally, the behaviour of $CH_2=N^+(CH_3)CH(CH_2CH_3)CH_2CH_2CH_3$ is instructive. The two main reactions of this ion are loss of C_6H_{12} and C_3H_6 .

The first process is C_nH_{2n} loss, which produces a Gaussian metastable peak. The kinetic energy release is small; indeed, the $T_{1/2}$ value of 2.6 kJ mol^{-1} is

noticeably lower than any of those measured for C_6H_{12} expulsion from immonium ions containing an $N-(n-C_6H_{13})$ substituent. This reduction in the $T_{1/2}$ value is significant and may reflect the absence of rearrangement of the developing 3-hexyl cation, which cannot isomerise to a more stable tertiary isomer by a single 1,2-hydride or alkyl shift. Consequently, there is no release of internal energy occasioned by exothermic isomerisation of the developing cation, so the kinetic energy release is smaller [13] than for immonium ions with an $N-(n-C_6H_{12})$ group.

The second process corresponds to $C_{n-3}H_{2n-6}$ loss, which actually is analogous to $C_{n-1}H_{2n-2}$ expulsion. Thus, C_3H_6 elimination gives rise to a broad dish-topped metastable peak and the associated kinetic energy release is much larger ($T_{1/2} = 51 \text{ kJ mol}^{-1}$). There are two sets of γ -hydrogen atoms in the N -(3-hexyl) group.

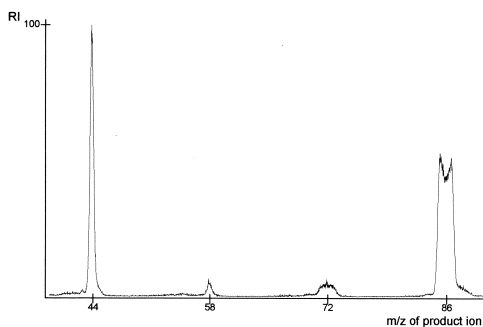


Fig. 3. MIKE spectrum of the immonium ion $\text{CH}_2=\text{N}^+(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$. The m/z scale in this spectrum is not uniform but has been expanded in the region of each of the metastable peaks in order to show their shapes more clearly.

Hydrogen transfer from the less distant of the two methyl groups would result in C_2H_4 loss, but this reaction would proceed via a primary open-chain cation. In contrast, hydrogen transfer from the most distant methylene group would lead to C_3H_6 elimination via a secondary cation, Scheme 3. The latter is preferred and is observed in competition with C_6H_{12} loss, but C_2H_4 elimination does not occur. The MIKE spectrum of $\text{CH}_2=\text{N}^+(\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$ is shown in Fig. 3.

4. Conclusions

The reactions of metastable $\text{CH}_3(\text{CH}_2)_m\text{CH}=\text{N}^+(\text{CH}_3)(\text{C}_n\text{H}_{2n+1})$ immonium ions are dominated by alkene elimination once $n \geq 2$. Loss of C_nH_{2n} gives rise to a Gaussian metastable peak, the associated kinetic energy release is comparatively small and varies only slightly with n . In contrast, loss of $\text{C}_{n-1}\text{H}_{2n-2}$ produces a much broader metastable peak, which is dished when $n = 3$, the associated kinetic energy release is considerably greater and decreases as n increases. The ratio of $\text{C}_{n-1}\text{H}_{2n-2}$: C_nH_{2n} loss rises as n increases, from ~ 0.05 when $n = 3$ to ~ 1.5 when $n = 14$. Branching at the γ -carbon atom also favours $\text{C}_{n-1}\text{H}_{2n-2}$ elimination relative to C_nH_{2n} loss; but if there is no γ -hydrogen atom, $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion is entirely suppressed because the initial 1,5-hydrogen transfer is no longer

possible. These trends are consistent with contrasting mechanisms for C_nH_{2n} and $\text{C}_{n-1}\text{H}_{2n-2}$ expulsion. Cleavage of the carbon–nitrogen bond occurs at an early stage in the route for C_nH_{2n} loss, but hydrogen transfer from carbon to nitrogen takes place at a later stage. In contrast, a 1,5-hydrogen transfer from carbon to carbon takes place at an early stage in the mechanism for $\text{C}_{n-1}\text{H}_{2n-2}$ loss, followed by carbon–carbon bond cleavage, and the geometry of the cyclic transition state is well defined.

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