Studies of mixed-site and charge-site-remote fragmentations of quaternary ammonium ions. II: Effects of chain length

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Abstract

The objective of the present work was to investigate further the charge-site-remote (CSR) and mixed-site-fragmentation (MSF) mechanisms through the use of high-energy tandem mass spectrometry (MS/MS) and MS/MS/MS experiments on the specifically deuterated tetra-alkyl ammonium ions $(C_2D_5)_3N^+(C_{14}H_{29})$ (**1**), $(C_2D_5)_2N^+(C_{14}H_{29})_2$ (**2a**) and $(CD_3)_2N^+(C_{14}H_{29})_2$ (**2b**). The work reported here shows unequivocally that the MSF process proceeds only at carbon atoms directly bonded to the nitrogen charge site. Both the short and long alkyl chains could participate in the MSF process, which is best rationalized in terms of diradical intermediate species, necessitating the uptake of large amounts of internal energy. MS/MS experiments on first-generation CSR ions produced from **2a** showed a second series of CSR and MSF ions arising from the intact long chain, whereas first-generation MSF ions showed quite different behaviour under the same experimental conditions. A remarkably diverse set of molecular processes is triggered by the input of substantial amounts of energy into these closed-shell ions. (Int J Mass Spectrom 188 (1999) 27–38 Crown copyright © 1999

Keywords: Long-chain quaternary ammonium ions; Charge-remote fragmentation reactions

1. Introduction

In the 1980's, Gross and his co-workers [1,2] discovered and characterized the charge-site remote (CSR) decomposition pathway for closed-shell, even-electron ions of long-chain alkyl compounds. Fragmentations of this type have been used to characterize peptides, surfactants [3,4], oxofatty acids [5,6], fatty

alcohols, fatty acids and their esters [3,4], as well as the positions of double bonds [1–3]. The CSR fragmentations are characterized by a series of fragment ions because of the loss of the elements C_nH_{2n+2} from the alkyl terminus. The accumulated evidence [2–4] appears to favor a mechanism involving 1,4-elimination of H_2 to form two ω-unsaturated fragments, as illustrated in Scheme 1 for long-chain tetra-alkylammonium ions, the example of interest in the present work. However, Wysocki and Ross [7] proposed a mechanism involving homolytic C–C cleavage to form a neutral radical plus a distonic radical cation that subsequently expels a hydrogen atom to form the ω-alkenyl cation of the type shown in Scheme 1. A
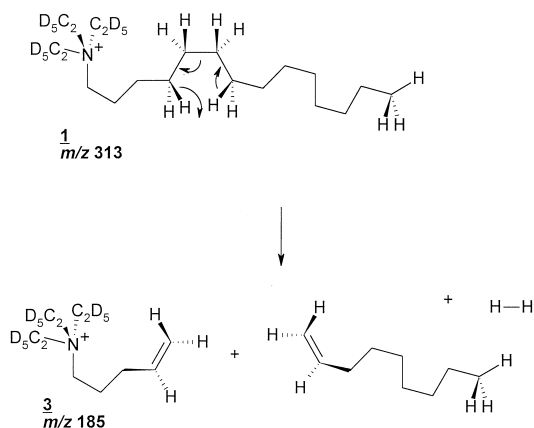
Scheme 1. Mechanisms for CSR fragmentations involving 1,4-elimination of H_2, as proposed in [2].

Scheme 2. Proposed mechanism for MSF reaction of **1** in which a diradical ion **4** is the initial product ion, as proposed in [12].

similar mechanism, but initiated by homolytic C–H cleavage, has been proposed by Claeys et al. [8]. More recently [9], these workers have proposed another alternative CSR mechanism for alkali-cationized fatty acid esters involving formation of a diradical cation that expels two hydrogen radicals and an ω-unsaturated fragment to form the ω-alkenyl cation.

In the early 1990s, Tuinman et al. [10,11] discovered the mixed-site-fragmentation (MSF) fragmentation pathway for trimethylalkylammonium ions $[(CH_3)_3N^+C_nH_{2n+1}]$, which is competitive with the CSR pathway. The MSF pathway can only be observed as distinct from CSR when the methylene groups in the long chain are distinguishable from those in the short chain. In the original work [10,11] this was achieved by incorporating perdeuteromethyl groups that permitted demonstration of incorporation of one of the methyl groups in the neutral fragment. It was proposed [11] that the fixed charge site on the nitrogen atom interacted in some way with the backbone σ bonds in a cyclic transition state, resulting in an assumed cyclic fragment ion plus a saturated alkane. Whalen et al. [12] repeated and extended this earlier work, and proposed a mechanism for the MSF reactions that involves a diradical ion intermediate that undergoes rearrangement reactions (Schemes 2 and 3) as well as cyclization to a stable cyclic structure. These rearrangements include structural elements corresponding to all of the observed second-generation fragment ions in MS/MS/MS experiments [12].

The objective of the present work was to investigate further the CSR and MSF mechanisms [10–12] through the use of high-energy tandem mass spectrometry (MS/MS) and MS/MS/MS experiments on the deuterated tetra-alkyl ammonium ions $(C_2D_5)_3N^+(C_{14}H_{29})$ (**1**), $(C_2D_5)_2N^+(C_{14}H_{29})_2$ (**2a**), and $(CD_3)_2N^+(C_{14}H_{29})_2$ (**2b**). These compounds were synthesized (as their iodide salts) in order to provide data that are complementary to those reported in the previous study [12] of the ions $(CD_3)_3N^+(C_{14}H_{29})$ and $(CH_3)_3N^+(C_{14}D_{29})$. In this way we hoped to investigate further the proposed MSF mechanism involving a diradical intermediate, and perhaps reveal some indication of the site of the reaction.

The studies described in this article provide further evidence for the CSR and MSF reactions that have been described in the literature [1–15]. In addition, the data presented here provide evidence for the equivalent competing processes that occur when *two* long chains are attached to a charge anchor, which to our knowledge has not been reported previously.

2. Experimental

2.1. Instrumental

All experiments reported here used a Micromass (Manchester, UK) AutoSpec-oaTOF instrument that
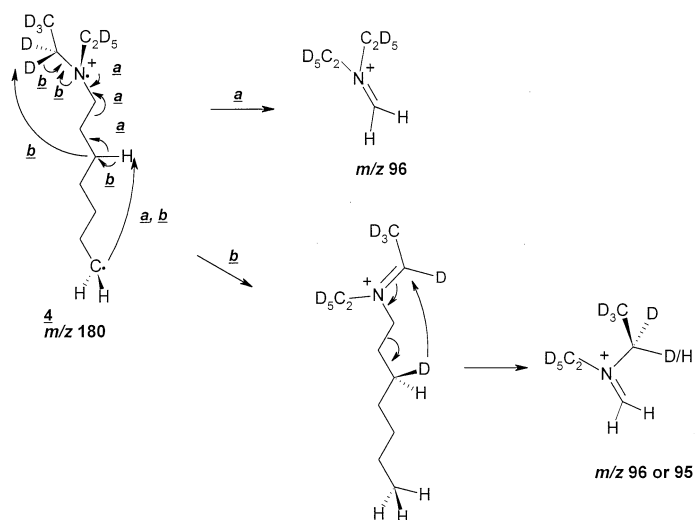
Scheme 3. Proposed reaction pathways for the formation of some third-generation ions from the second-generation MSF ions **4**, derived from **1**.

is comprised [16] of a double-focusing stage of *EBE* configuration coupled to an orthogonal acceleration time-of-flight (oaTOF) analyzer for MS/MS experiments. Liquid secondary ionization mass spectrometry (LSIMS) ionization used a glycerol matrix and a primary beam of cesium ions of effective incident energy 17 keV. At the normal ion source potential of 8 kV, the laboratory frame collision energy in the collision cell preceding the oaTOF analyzer was 800 eV. In all MS/MS experiments using the oaTOF, Xe collision gas was used at an indicated pressure of 3×10^{-7} mbar measured in the oaTOF housing.

For MS/MS/MS experiments, the precursor ion, together with the first-generation fragment ion formed in the first field-free region (FFR1), were selected by setting the analyzer fields of the double-focusing stage to static values determined by the appropriate linked-scan law at constant *B*/*E* [17]. Argon collision gas was used in the collision cell in FFR1, at a pressure resulting in 50% attenuation of the precursor ion intensity. A laboratory-frame collision energy of 8 keV was used in this first MS/MS stage. The collision energy in the oaTOF collision cell is linked to the ion energy determined by the field in the second electric sector of the *EBE* analyzer, in order to accommodate the full fragment ion mass range on the channel plate detector of the oaTOF [16].

In characterizing the synthesized compounds, infrared spectra were recorded by using a Philips Pye Unicam (Cambridge, UK) SP3-200 infrared (IR) spectrometer and nuclear magnetic resonance (NMR) spectra were recorded by using a Bruker (Karlsruhe, DE) AC 250F NMR spectrometer.

2.2. Materials and synthesis

All solvents were purified prior to use. Tetrahydrofuran (THF) was dried by allowing reagent grade THF to stand over P_2O_5 overnight. The solvent was decanted, distilled from fresh P_2O_5, and refluxed for 1–2 h over lithium aluminum hydride under a dry nitrogen atmosphere. THF was distilled into reaction flasks under nitrogen immediately before use. Triethylamine was distilled from KOH. All organic layers were dried with anhydrous $MgSO_4$ unless otherwise stated.

The iodide salt of $[(C_2D_5)_3N^+C_{14}H_{29}]$ was synthesized by heating 1-aminotetradecane (Aldrich Chemical, Milwaukee, WI) with an excess of pentadeuteroiodoethane (CDN Isotopes, Montréal, Canada). The identity of the product was confirmed by ^{1}H NMR and by LSIMS. Preparation of the iodide salts of $[(CD_3)_2N^+(C_{14}H_{29})_2]$ and $[(C_2D_5)_2N^+(C_{14}H_{29})_2]$ was carried out in several steps. In a typical experiment, tetradecanoic acid (Aldrich) was stirred overnight

with excess purified thionyl chloride [18] in benzene. The excess thionyl chloride and benzene were evaporated off to yield tetradecanoyl chloride. The identity of the product was checked with infrared spectroscopy. The tetradecanoyl chloride was then diluted with dichloromethane and 1-aminotetradecane (Aldrich), dissolved in dichloromethane, was added slowly. Once all of the amine was added the reaction mixture was cooled and distilled triethylamine was added dropwise. After the mixture had been stirred overnight, the mixture was diluted with dichloromethane and washed with 5% HCl, then 5% NaHCO$_3$, and then with water. The organic layer was then dried and evaporated to yield crude *N*-tetradecyltetradecanamide. The identity of the product was confirmed by ^{1}H and ^{13}C NMR as well as infrared spectroscopy. The amide was then refluxed, under nitrogen, in dry THF with an excess lithium aluminum hydride (Aldrich). After 72 h, the unreacted hydride was destroyed with water and the reaction mixture was filtered through Celite 545 (Fisher Chemical, Nepean, Ont.). The organic layer was dried and evaporated to yield crude ditetradecylamine. The identity of the product was checked by ^{1}H NMR. The iodide salts of [(CD$_3$)$_2$N$^+$(C$_{14}$H$_{29}$)$_2$] and [(C$_2$D$_5$)$_2$N$^+$(C$_{14}$H$_{29}$)$_2$] were then synthesized by heating ditetradecylamine with trideuteroiodomethane (CDN) and pentadeuteroiodoethane (CDN), respectively. The identity of the products was checked by ^{1}H NMR and LSIMS.

3. Results and Discussion

3.1. Effects of chain length on the MS/MS spectra of long-chain tetra-alkyl ammonium ions

In accord with previous findings, the LSIMS spectra (not shown) of the halides of **1**, **2a**, and **2b** were found to contain abundant fragment ions attributable to both CSR and MSF reactions, in addition to intense signals corresponding to **1**, **2a**, and **2b** themselves. Figs. 1–3 show fragment ion spectra for **1**, **2a**, and **2b** obtained by using Xe collision gas at a laboratory-frame collision energy of 800 eV. In all three spectra, the CSR fragment ions are generally much more intense than the MSF fragment ions, as observed previously [10–15]. Comparing the MS/MS spectrum of **1** with that shown previously for the analogous trimethylalkylammonium ion [12], it is evident that the abundance of MSF ions is greater for the tri*ethyl*-alkylammonium ion. This trend was checked by repeating the experiment on the trimethyl compound under the present conditions. We currently have no convincing explanation for this observation.

The present discussion on both the MS/MS and MS/MS/MS processes will focus on those from **1** and from the di-perdeuteroethyl ion **2a**, but the arguments are equally applicable to the dimethyl homologue **2b**. In the fragment ion spectrum of **1** (Fig. 1) the series of peaks at *m/z* 269, 255, 241, etc. and in the spectrum of **2a** (Fig. 2) the series at *m/z* 432, 418, 404, etc. are a result of the CSR expulsions of the elements of (C$_k$H$_{2k+2}$). In the previous studies [10–12] of MSF reactions of deuterated analogs of trimethylalkylammonium ions, it was shown that MSF fragmentation involves the incorporation of one of the methyl groups into the neutral fragment. In the case of **1**, the series of peaks at *m/z* 264, 250, 236, etc. corresponds to the MSF fragmentations that involved the incorporation of one of the ethyl-d$_5$ groups into the neutral fragment. The mechanism proposed previously [12] to account for the MSF reaction is reproduced in Scheme 2 for the case of **1**. (Note that structure **4** in Scheme 2 is the analogue of structure **5′** in [12].) The diradical **4** can undergo radical-site-initiated rearrangements to account for the second-generation fragment ions of the first-generation MSF fragments of **1**, as discussed below. The more stable long-lived MSF fragment ions are probably formed by simple cyclization of the diradical **4** to form a cyclic quaternary ammonium ion. An alternative possible mechanism for this process involving an initial simple homolytic cleavage of a C–N$^+$ bond to form a molecular radical cation of a tertiary amine, followed by an expulsion of an alkyl radical, is considered less likely as it cannot readily account for the trends observed here and previously [12]. For example, electron ionization (EI) spectra of long-chain tertiary amines R$_1$R$_2$N–CH$_2$–R$_3$ include abundant ions R$_1$R$_2$N$^+$=CH$_2$ resulting from α cleavage [19], but no such ions were observed here.
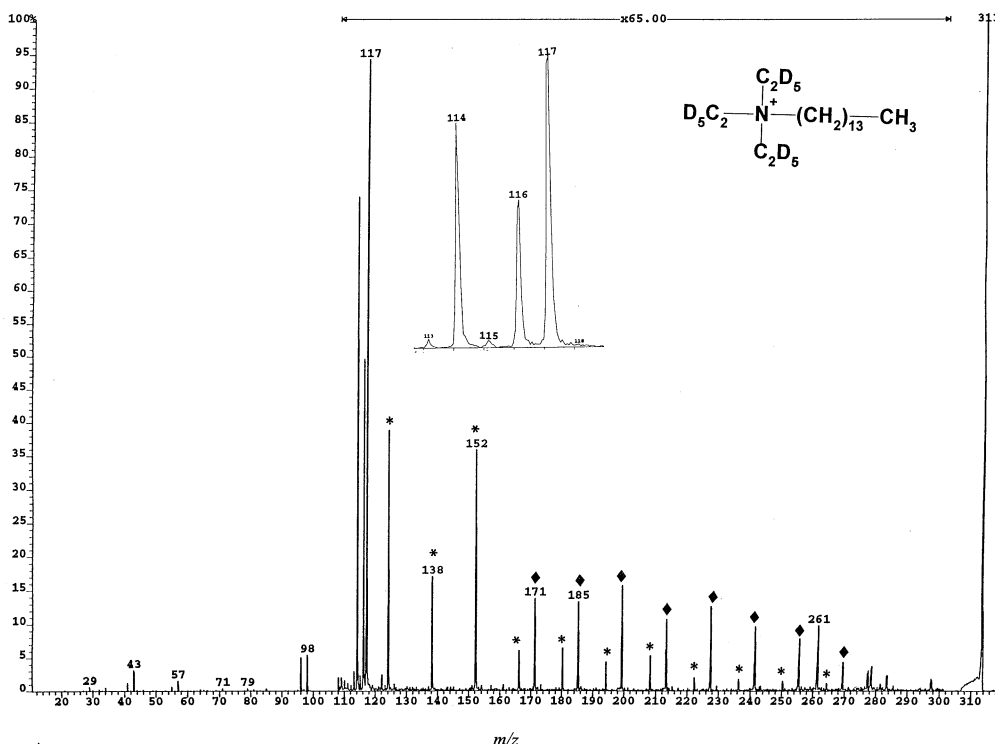
Fig. 1. MS/MS spectrum of $(C_2D_5)_3N^+C_{14}H_{29}$ (**1**), obtained by using the AutoSpec-oaTOF instrument, with conditions described in Sec. 2. (◆ CSR ions; * MSF ions.)

The MSF process is also observed when two long-chain alkyl groups are present, such as for **2a**. Thus, in the fragment ion spectrum of **2a** (Fig. 2), the series of peaks at m/z 427, 413, 399, etc. corresponds to incorporation of one of the ethyl-d_5 groups in the neutral fragment. However, another MSF process is also apparent in the fragment ion spectrum of **2a**. The series of peaks at lower m/z values 124, 138, 152, etc. corresponds to the incorporation of the *second* tetradecyl group into the neutral fragment arising from the MSF process derived from loss of part of the *first* tetradecyl group, a process that to our knowledge has not been described previously. The two series of MSF processes seen in the MS/MS spectrum of **2a** (Fig. 2) indicate that the MSF mechanism involves cleavage between the charge-bearing N-atom and the adjacent C-atom on either the ethyl-d_5 group or on the second C_{14} alkyl chain, but not

between two C atoms, e.g. the methylene-d_2 and terminal methyl-d_3 groups.

In order to investigate the MSF mechanism further, and to obtain structural information on the fragment ions formed, MS/MS experiments were performed on a range of first-generation fragment ions (i.e., MS/ MS/MS experiments), as described below.

3.2. Interpretation of second-generation fragments

Table 1 summarizes fragment ion spectra, obtained in MS/MS/MS experiments for first-generation fragment ions of both the CSR and MSF types, formed in FFR1 from **1**. The interpretations proposed in Table 1 are analogous to those derived previously [12] for similar ions, based on comparisons between MS/ MS/MS spectra of $(CD_3)_3N^+C_{14}H_{29}$ and of $(CH_3)_3N^+C_{14}D_{29}$. Figs. 4 and 5 show MS/MS/MS
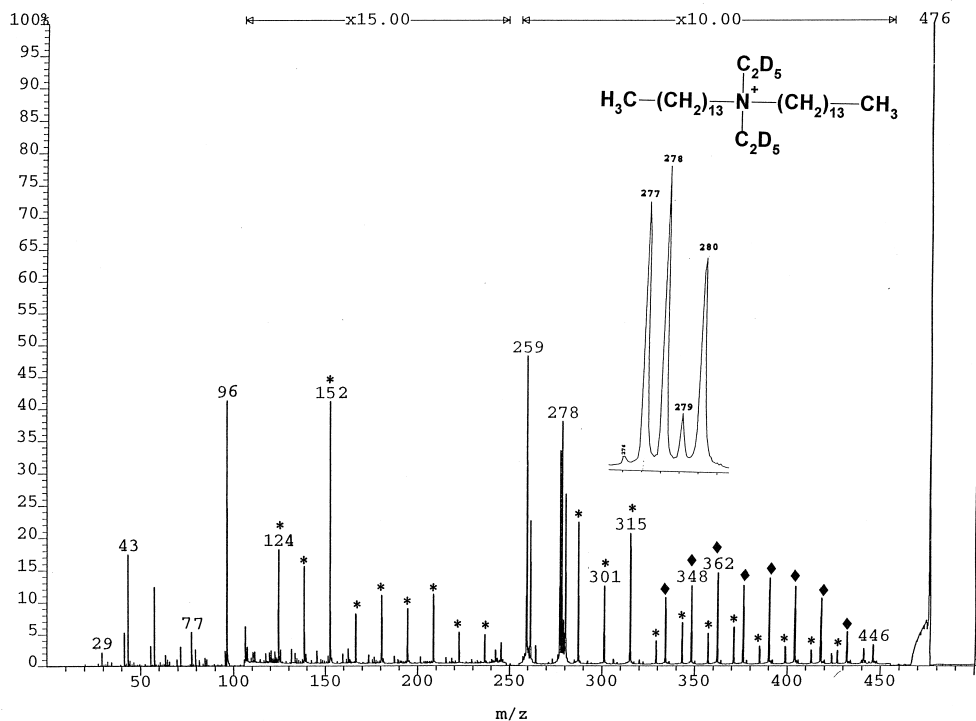
Fig. 2. MS/MS spectrum of $(C_2D_5)_2N^+(C_{14}H_{29})_2$ (**2a**), obtained by using the AutoSpec-oaTOF instrument, with conditions described in Sec. 2. (◆ CSR ions; * MSF ions.)

spectra obtained for **2a**, for CSR and MSF first-generation fragments, respectively. The two CSR fragments, selected as being representative examples for the purposes of discussion, are the ions at m/z 185 from **1** having the structure $(C_2D_5)_3N^+(CH_2)_3CH=CH_2$ (**3**, see Table 1), and the ion at m/z 376 from **2a** of structure $(C_2D_5)_2(C_{14}H_{29})N^+(CH_2)_5CH=CH_2$ (**5**, see Fig. 4). The MSF fragments selected are the ion at m/z 180 from **1**, with structure $[(C_2D_5)_2N(C_7H_{14})]^+$ (**4**, see Table 1), i.e. presumably initially formed as a cation diradical (Scheme 2), as proposed previously [12], and the ion at m/z 371 from **2a**, of structure $[(C_2D_5)(C_{14}H_{29})N(C_9H_{18})]^+$ (**6**, see Fig. 5), i.e. closely analogous to **4** in that it is formed via loss of a ethyl-d_5 group as part of the neutral fragment.

The proposed interpretation of the MS/MS spectrum of the CSR fragment ion **3**, shown in Table 1, is consistent with the open-chain structures proposed for this type of even-electron ion. The fragmentations of **3** appear to be charge-site initiated, which is consis-

tent with previous findings [12]. In contrast to the facile cleavage processes in the fragment ion spectrum of **3**, the MSF fragment ion **4** gave rise to a relatively sparse MS/MS spectrum (Table 1). Fragmentation of MSF ions such as **4** had been assumed to proceed via a cyclic transition state [11], but only a few of the ions listed in Table 1 can be readily derived by plausible mechanisms directly from cyclic structures [12]. However, radical-site-initiated rearrangements of the diradical ion intermediate **4** can be proposed [12] giving rise at least to structural elements corresponding to some of the observed second-generation fragments, exemplified in Scheme 3. Presumably, cyclic MSF fragments can be reopened to the diradical form upon collisional activation.

The fragment-ion spectra of the two CSR fragments, **3** $[(C_2D_5)_3N^+(CH_2)_3CH=CH_2]$ derived from **1** (Table 1) and **5** $[(C_2D_5)_2(C_{14}H_{29})N^+(CH_2)_5CH=CH_2]$ derived from **2a** (Fig. 4) are clearly different. It appears that the introduction of a second long-chain
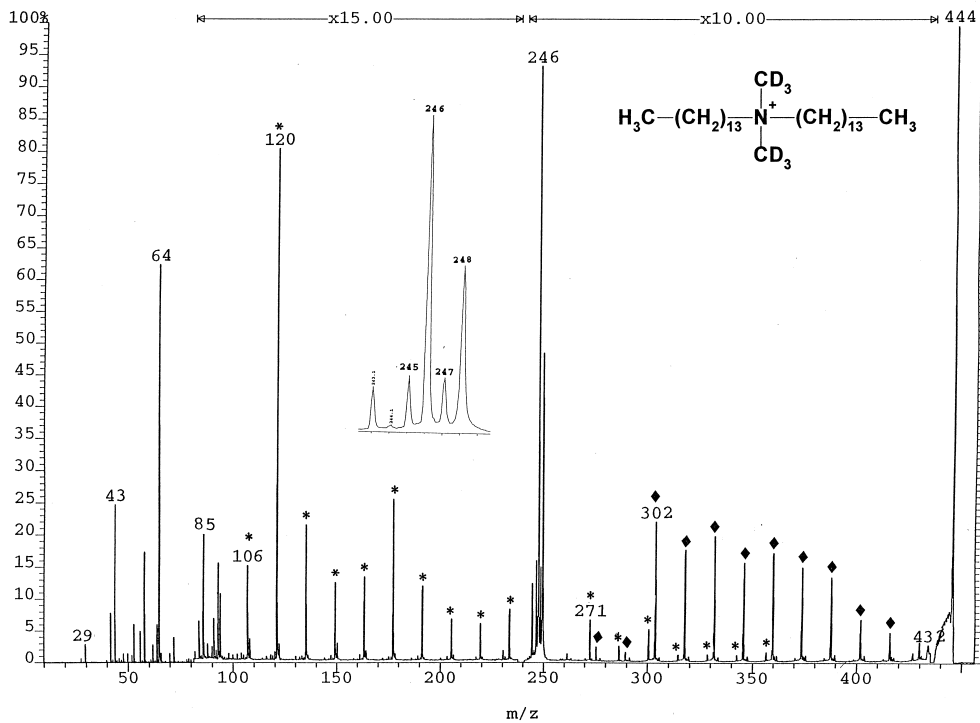
Fig. 3. MS/MS spectrum of $(CD_3)_2N^+(C_{14}H_{29})_2$ (**2b**), obtained by using the AutoSpec-oaTOF instrument, with conditions described in Sec. 2. (◆ CSR ions; * MSF ions.)

Table 1
Interpretation of fragment ion spectra obtained by MS/MS/MS experiments on **1** with m/z 185 and m/z 180, respectively, as the first-generation fragments presumed to have been formed in CSR and MSF reactions, respectively

CSR **1** → **3** $[(C_2D_5)_3NCH_2(CH_2)_2CH=CH_2, m/z\ 185]^+ \to X^a$		MSF **1** → **4** $[(C_2D_5)_2N(C_7H_{14}), m/z\ 180]^+ \to Y^b$	
2nd generation X, m/z (R.I.)[c]	Interpretation of X	2nd generation Y, m/z (R.I.)[c]	Interpretation of Y
34 (24)	$C_2D_5^+$	29 (50)	$C_2H_5^+$
41 (41)	$C_3H_5^+$	43 (64)	$C_3H_7^+$
69 (45)	$C_5H_6^+$	44 (47)	$H_2N^+=CH(CH_3)$
96 (100)	$(C_2D_5)_2N^+=CH_2$	57 (56)	$C_4H_9^+$
98 (93)	$(C_2D_5)_2N^+=CD_2$	58 (75)	$C_4H_{10}^{+\cdot}$ or $H_2N^+=CH(C_2H_5)$ or $D_2C=N^+=CH(CH_3)$
114 (30)	$(C_2D_5)_2N^+=CD(CD_3)$	62 (72)	$(C_2D_5)N^{+\cdot}=CH_2$
117 (69)	$(C_2D_5)_3N^+H$	81 (100)	$(C_2D_5)N^+H=CD(CD_3)$
		95 (67)	$C_2D_5\{(CD_3)CDH\}N^+=CH_2$
		96 (58)	$(C_2D_5)_2N^+=CH_2$

[a] Ions clearly defined intensities; all ions ≥4 times background noise levels.

[b] Spectrum relatively noisy; least intense ions ≥2 times background noise levels.
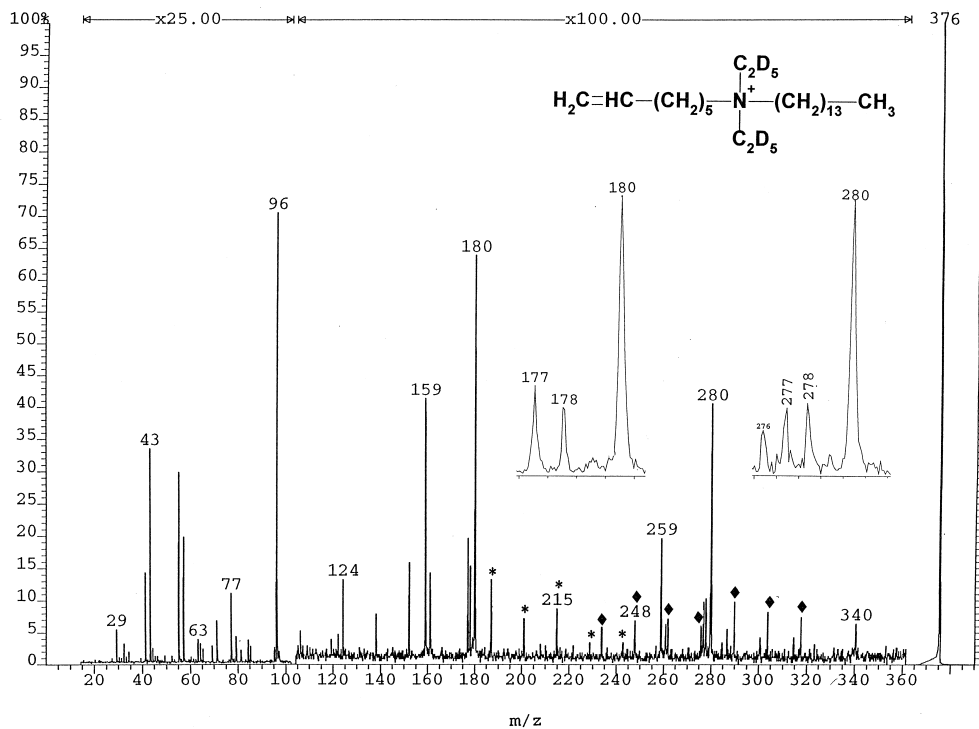
[c] Relative intensity.

Fig. 4. MS/MS spectrum of the CSR fragment ion **5** at m/z 376 observed in the MS/MS spectrum of the iodide of **2a**. See Sec. 2 for details of this MS/MS/MS experiment. (◆ CSR ions; * MSF ions.)

alkyl (tetradecyl) group allows the first-generation CSR fragment ion **5** of **2a** to undergo *both* CSR and MSF fragmentations presumably from the C_{14} chain not involved in the primary fragmentation. In Fig. 4, the ion series occurring at m/z 318, 304, 290, etc. is the result of CSR expulsions of the elements of (C_kH_{2k+2}) from the tetradecyl group. It is not possible to determine unequivocally whether any of these second-generation fragment ions are derived from the ω-olefin chain of **5**. It is likely that the presence of the double bond modifies the reactivity of the olefin chain relative to that of the intact alkyl chain, and experiments designed to probe these effects are in progress. These sequential CSR/MSF fragmentations give rise to much of the complexity evident in Figs. 2–4.

In marked contrast, the MSF fragment **6** at m/z 371, derived from **2a** by transfer of an ethyl-d_5 group to the neutral fragment, in turn, dissociates to yield a remarkable series of even-electron ions, shown in Fig. 5. At first glance these ions appear to be a CSR series.

However, on closer inspection, it becomes apparent that it is not a CSR series because larger neutral fragments (overall compositions corresponding to alkanes) are being lost than can be accounted for by the length of the chain. The CSR series of other ions regularly begin with the loss of a one-carbon fragment, but this series begins with the loss of a two-carbon fragment. Also, the absence of the expected m/z 243 fragment from Fig. 5 is puzzling. The formation of this ion series can be rationalized as outlined in Scheme 4. If the concept of **6** being formed initially as a cation diradical, **6′**, is valid; it requires only two hydrogen atom migrations, both via six-membered transition states, to arrive at the even-electron form **6″**. If **6′** is indeed a radical cation, it may be expected to show some of the fragmentation processes as seen in the EI mass spectra of long-chain alkyl-amines. These processes are characterized by an α cleavage adjacent to a nitrogen radical cation site, and by a series $[C_nH_{2n+1}]^+$ together with
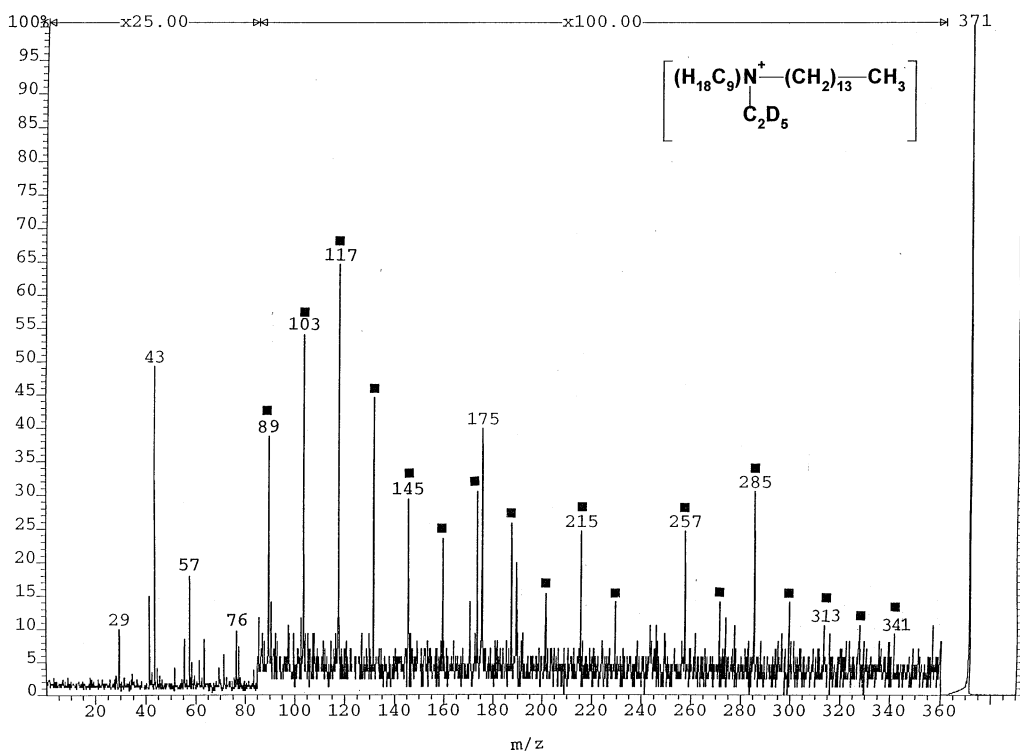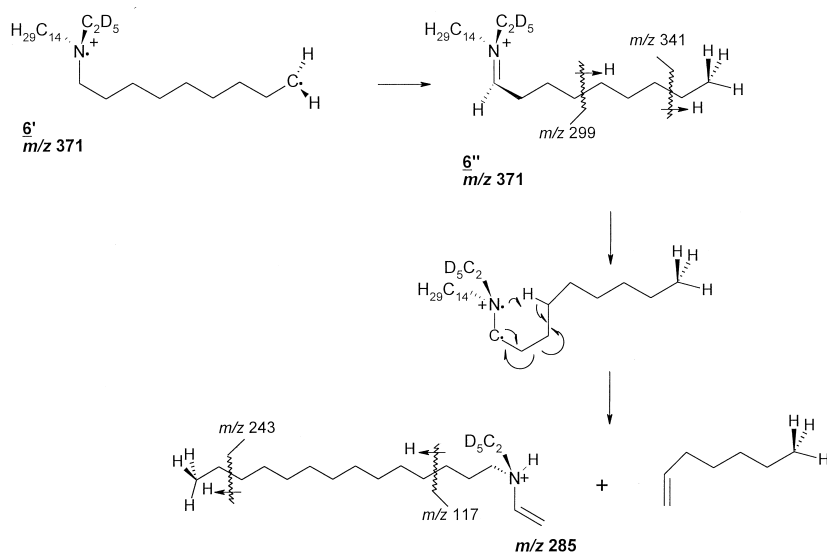
Fig. 5. MS/MS spectrum of the MSF fragment ion **6** at *m/z* 371 observed in the MS/MS spectrum of the iodide of **2a**. See Sec. 2 for details of this MS/MS/MS experiment. [■ Ions first believed to be a CSR fragment series (see text).]

Scheme 4. Proposed rearrangement and fragmentations of the second-generation MSF ions **6**, derived from **2a**.

Table 2
Interpretation of some fragment ions other than CSR and MSF types, obtained by MS/MS experiments on **1**, **2a**, and **2b**

1 → X		2a → Y		2b → Z	
1st generation		1st generation		1st generation	
X, m/z (R.I.)	Interpretation of X	Y, m/z (R.I.)	Interpretation of Y	Z, m/z (R.I.)	Interpretation of Z
117 (100)	$(C_2D_5)_3N^+H$ (**7**)	280 (68)	$(C_2D_5)_2(C_{14}H_{29})N^+H$	248 (52)	$(CD_3)_2(C_{14}H_{29})N^+H$
116 (52)	$(C_2D_5)_3N^{+\cdot}$ (**8**)	279 (18)	$(C_2D_5)_2(C_{14}H_{29})N^{+\cdot}$	247 (17)	$(CD_3)_2(C_{14}H_{29})N^{+\cdot}$
		278 (100)	$(C_2D_5)_2N^+=CH(C_{13}H_{27})$	246 (100)	$(CD_3)_2N^+=CH(C_{13}H_{27})$
114 (79)	$(C_2D_5)_2N^+=CD(CD_3)$ (**9**)	277 (88)	$(C_2D_5)(C_{14}H_{29})N^+=CD(CD_3)$	245 (17)	$(CD_3)(C_{14}H_{29})N^+=CD_2$

$[C_nH_{2n-1}]^+$ fragments from long-chain alkyl groups [19]. However, neither α cleavage nor $[C_nH_{2n-1}]^+$ fragments are observed, which suggest that the ions **6** being sampled in the MS/MS/MS experiments (Fig. 5) are acyclic even-electron species like **6″**. The series of ions at m/z 341, 327, 313, and 299 can be explained by eliminations of alkane moieties from the shorter alkyl chain in **6″**. It is conceivable that prominent m/z 285 derives from a McLafferty-type process [20] shown in Scheme 4. This ion could lose alkane moieties up to C_{14} leading to the ion series m/z 271 . . . 89 (Fig. 5).

The MS/MS/MS spectra of **2a**, for intermediate ions of the MSF type formed by transfer of one of the C_{14} chains to the other to form the neutral fragment (not shown), were very similar to those observed for MSF fragments formed from precursors like **1** with only one C_{14} chain to begin with.

3.3. Other ions in the MS/MS spectra of 1, 2a, 2b, and 5

In Figs. 1–3, there are several predominant ions that do not arise from CSR or MSF reactions, e.g. in the MS/MS spectrum of **1**, the ions at m/z 117, 116, and 114, which are here labelled as **7**, **8**, and **9**. These ions, and the analogous ions from the MS/MS spectra of **2a** and **2b**, are listed and described in Table 2. A plausible mechanism for the formation of the even-electron ions in these series is outlined in Scheme 5. An understanding of the formation of these ions is relevant to understanding the overall picture, including the CSR and MSF processes.

The formation of **7** can be explained as the loss of the long-chain alkyl group, while a hydrogen atom is simultaneously transferred from the chain to the charged nitrogen atom, as proposed in route b of Scheme 5. In the MS/MS spectrum of the fragment ion **7** (not shown), there are major ions at m/z 85 (**7**−C_2D_4), 65 (**7**−C_3D_8), and 34 ($^+C_2D_5$). These three second-generation ions are consistent with the structure of **7** proposed in Table 2. The proposed formation mechanism and structure of **7** are further supported by the presence of the ions at m/z 280 and 248 from **2a** and **2b**, which can be assigned as the equivalent protonated amines.

The ion **8**, a radical cation, can be derived via the loss of the long-chain alkyl group as a radical. In the
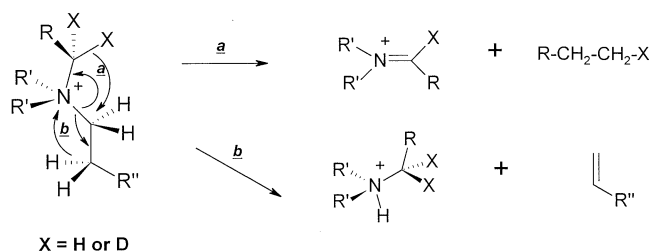
Scheme 5. Proposed fragmentation pathways of **1**, **2a**, and **2b** leading to intense second-generation ions that are not part of the regular CSR and MSF series.

Table 3
Interpretation of some fragment ions other than CSR and MSF types obtained by MS/MS/MS experiments on **2a** via the intermediate CSR fragment **3**

2a → **3** $[(C_2D_5)_2(C_{14}H_{29})N^+(CH_2)_5CH=CH_2, \ m/z \ 376] \rightarrow X \ or \ Y$

2nd generation X, m/z (R.I.)	Interpretation of X	2nd generation Y, m/z (R.I.)	Interpretation of Y
180 (100)	$(C_2D_5)_2\{CH_2=CH(C_5H_{10})\}N^+H$	280 (100)	$(C_2D_5)_2(C_{14}H_{29})N^+H$
179 (6)	$(C_2D_5)_2\{CH_2=CH(C_5H_{10})\}N^{+\cdot}$	279 (5)	$(C_2D_5)_2(C_{14}H_{29})N^{+\cdot}$
178 (23)	$(C_2D_5)_2N^+=CH((C_5H_{10})CH=CH_2)$	278 (26)	$(C_2D_5)_2N^+=CH(C_{13}H_{27})$
177 (30)	$(C_2D_5)\{CH_2=CH(C_5H_{10})\}N^+=CD(CD_3)$	277 (23)	$(C_2D_5)(C_{14}H_{29})N^+=CD(CD_3)$

MS/MS spectrum of the fragment ion **8** (not shown), there is one major fragment ion at m/z 98, which corresponds to the loss of the $\cdot CD_3$ radical, a typical α-cleavage process as seen in the EIMS of amines [19]. The proposed structure of **8** is supported by the presence of the ions at m/z 279 and 247 from **2a** and **2b**, which can be assigned structures of the equivalent radical cations. The MS/MS spectrum of the fragment ion m/z 279 (not shown) is dominated by the loss of the largest fragment to give m/z 96 (**8** − $\cdot C_{13}H_{27}$) and the same process is also observed in the MS/MS spectrum of the fragment ion m/z 247 (not shown).

The ion **9** found at m/z 114 in the MS/MS spectrum of **1**, together with m/z 277 and 245 from **2a** and **2b**, appear to be even-electron species. Like the ions at m/z 278 and 246, these ions are apparently also relatively stable iminium cations, but arise from an expulsion of the long chain plus a deuterium atom (route a, Scheme 5). In the MS/MS spectrum of the fragment ion **9** (not shown), there are two major ions, m/z 82 (**9**−C_2D_4) and 34 ($^+C_2D_5$). These ions indicate that the proposed formation mechanism and structure of **9** are plausible.

In the MS/MS spectra of **2a** and **2b**, there are intense ions at m/z 278 and 246 arising from expulsion of one of the long alkyl chains as an alkane that again requires a simultaneous hydrogen transfer. This process cannot occur in the case of **1**, because it lacks the second long chain, and indeed it is not observed in this case (see Fig. 1). The MS/MS spectrum of the fragment ion at m/z 278 shows significant ions at m/z 122 (278−$C_{11}H_{24}$), 96

(278−$C_{13}H_{26}$), and 43 ($^+C_3H_7$), as well as many minor ions.

All of the observations and proposals described above are further supported by the double series of ions found at m/z 280, 279, 279, 277, 180, 179, 178, and 177 in the MS/MS spectrum of the fragment ion **5** (Fig. 4). These eight ions are listed and interpreted in Table 3. The relative intensities of the ions in these two series mirror each other, but are quite different from the ions listed in Table 2. The observation of the radical cation at m/z 279 as both a first- and second-generation fragment may provide information on its precollision internal energy, which merits further study.

The MS/MS spectrum of the fragment ion **5** (Fig. 4) also includes significant ions at m/z 259, 159, and 96. These ions are also present in the MS/MS spectrum of **2a** (Fig. 2) and can be assigned as the structures $(C_2D_5)(C_{14}H_{29})N^+=CH_2$, $(C_2D_5)\{CH_2=CH(CH_2)_5\}N^+=CH_2$ and $(C_2D_5)_2N^+=CH_2$, respectively. The formation of these species can readily be explained by a process similar to those outlined in Scheme 5.

4. Conclusions

There are several conclusions that can be drawn from these observations. Thus, all of the present observations on CSR fragment ions are consistent with the open-chain ω-olefin structures that have long been proposed (Scheme 1), although these experi-

ments do not shed much additional light on the details of the CSR mechanism(s). The MSF reactions are believed to proceed via a cyclic transition state, and some of the present observations are consistent with a cyclic structure for at least the long-lived MSF fragments. However, the second-generation fragment ions formed from these MSF fragments are difficult to rationalize in terms of a stable cyclic structure, and the diradical structures shown in Schemes 2 and 3 seem necessary to account for the observed MS/MS/MS spectra, in agreement with previous proposals [12]. The work reported here also shows unequivocally that the MSF process proceeds only at carbon atoms directly bonded to the nitrogen charge site. The process is best rationalized in terms of diradical species, necessitating the uptake of large amounts of internal energy, and hence high energy collisional activation with massive target species as employed in this work. The observation of extensive CSR or MSF fragmentation from first generation fragments of much lower mass than the precursor ion (and that have proportionately lower collision energies) may imply an effect of precollision internal energy, i.e. the first generation fragment ions may have enhanced internal energies per vibrational mode, relative to the original precursor ion, prior to entering the second collision cell.

The studies reported in the present work, taken together with the previous literature, now begin to provide a fascinating insight into the remarkably diverse set of molecular processes triggered by the input of substantial amounts of energy into these closed-shell ions. The question of the nature of the molecular orbitals involved in these transition states has not been addressed at all.

Acknowledgements

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