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Charge-remote and charge-proximate fragmentations in deuterium-labeled *n*-hexadecyltriphenylphosphonium cations upon high-energy collisional activation: evidence for the involvement of a phenyl biradical

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Abstract

The charge-remote fragmentation mechanism for *n*-alkyltriphenylphosphonium cations was examined through the use of high-energy collision-induced dissociation experiments on specifically deuterium-labeled isotopomers. In addition to the study of the charge-remote fragmentation mechanism other ions in the spectra, formed by so-called charge-proximate fragmentations, have also been studied. It was found that different processes are responsible for the formation of the ions in the spectra. A deuterium–hydrogen isotope effect of approximately 2 was measured for the 3,3-$^2H_2$ and 9,9-$^2H_2$ isotopomers, indicating that a C–H cleavage is a rate-determining step in the formation of corresponding charge-remote product ions as was reported for alkali-cationized fatty acid esters. Substantial insertion of hydrogens from the triphenylphosphine moiety into the fully labeled alkyl chain upon high-energy collision-induced dissociation points to the involvement of an excited state biradical in the processes which take place upon high-energy collision-induced dissociation. (Int J Mass Spectrom 188 (1999) 163–175)

Keywords: *n*-Alkyltriphenylphosphonium salts; Collision-induced dissociation; Charge-remote fragmentation; Fast atom bombardment; π-Complex; excited state

1. Introduction

Ion fragmentation mechanisms can be classified into reactions which are initiated by a radical site or by a charge. Closed-shell ions such as protonated, alkali-cationized, or deprotonated molecules that are generated by soft ionization techniques (i.e., fast atom bombardment, electrospray ionization, and matrix-assisted laser desorption ionization) generally fragment by routes which are initiated by a charge. This behavior also holds for collision-induced fragmentation, but, in addition, a new class of fragmentation reactions which have been termed "charge-remote fragmentations" (CRF) have been described by Adams [1] and Gross [2]. These workers found that in closed-shell ions containing a stable charge center, which are submitted to high-energy collision-induced dissociation (CID), fragmentation occurs at sites remote from the charge. Because similar fragmentation

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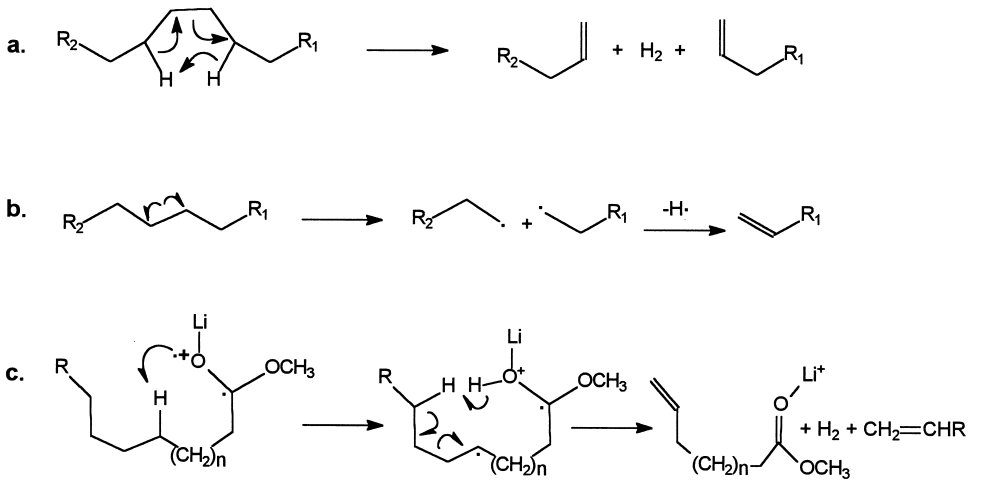


Scheme 1. Mechanistic proposals for the CRF process. (a) Concerted 1,4-hydrogen elimination, (b) initial C–C cleavages, and (c) initial C–H cleavages. The group R_1 contains a localized charge.

was noted for both positively and negatively charged closed-shell fatty acid molecular ions, the logical assumption was made that the charge is not involved in CRF reactions. In the case of long-chain alkyl compounds the CRF are characterized by a homologous series of product ions due to the loss of elements of C_nH_{2n+2}. Several mechanisms have been advanced to account for these CRF: the most cited mechanism is that proposed by Jensen et al. [3] [Scheme 1(a)] which corresponds to a cyclic concerted 1,4-elimination of molecular hydrogen and ω-alkenes to form a homologous series of ω-unsaturated product ions. However, this mechanism has been questioned and a homolytic mechanism involving initial C–C cleavage has been proposed by Wysocki and Ross [4] [Scheme 1(b)], and a similar homolytic mechanism starting with C–H cleavage has been described by Claeys and co-workers [5–7] [Scheme 1(c)], to yield the same homologous series of ω-unsaturated product ions. Furthermore, Dua et al. [8] examined the CRF mechanism in adamantane anions containing a carboxylate and an alkyl group that could not approach each other but were unable to support the 1,4-H_2-elimination mechanism proposed by Jensen et al. [3]. In a recent study, a comprehensive mechanism has been formulated for high-energy CID of alkali-cationized fatty acid esters involving electronic excitation of the ester carbonyl bond with formation of a biradical that gives rise to homolytic C–H and C–C cleavage reactions and subsequently expels two hydrogen radicals [9] or molecular hydrogen [10] and an ω-alkene to form the ω-unsaturated product ions. It is pointed out that the elimination of ω-alkenes as neutrals was proved by Cordero and Wesdemiotis [11] in neutralization–reionization experiments and is in agreement not only with the cyclic 1,4-H_2-elimination mechanism but also with the homolytic mechanism involving initial C–H cleavage, which in fact corresponds to a formal 1,4-H_2-elimination with participation of the functional group. The involvement of an excited electronic state in CRF reactions has first been reported by Voinov et al. [12,13]. These workers demonstrated that saturated fatty acids form $[M–H]^-$ ions by electron capture in two energy regions, 1.2 and 7 eV, and that those formed by electron capture at 7 eV exhibit CRF behavior. Further, it is worth mentioning that a biradical mechanism has been proposed by Whalen et al. [14] to rationalize the mixed-site fragmentation pathway for *n*-alkyltrimethylammonium ions, which is competitive with the CRF pathway.

The objective of the present work was to re-examine the CRF mechanism for *n*-alkyltriphenylphosphonium cations through the use of high-

energy CID experiments on specifically deuterium-labeled isotopomers. In this way we hoped to prove that the CRF mechanism proposed earlier for lithium-cationized fatty acid esters [5–7,9,10] with participation of the functional group is also valid for other functionalized long-chain alkanes. In addition to the study of the CRF mechanism other ions in the spectra, the ions formed by so-called charge-proximate fragmentations, have also been examined.

Alkyltriphenylphosphonium salts are regularly used in the synthesis of alkenes from carbonyl compounds and the need for structural determination of phosphonium salts was the motivation for several mass spectral investigations of these compounds [15–20]. Phosphonium salts cannot be ionized by gas-phase methods because of their low volatility and other techniques such as liquid secondary ion mass spectrometry (LSIMS) or fast atom bombardment (FAB) are used in order to generate the intact phosphonium cation. High-energy CID of the alkyltriphenylphosphonium cations was found to be useful for the structure determination of the alkyl group [20]. The positive-ion FAB mass spectra of phosphonium salts containing an aliphatic hydrocarbon substituent show intense signals of the molecular cations; elimination of the alkyl chain yields the stable triphenylphosphine (molecular) ion (*m/z* 262) and this triphenylphosphine ion shows further loss of a phenyl radical (*m/z* 185) and H_2 (*m/z* 183). Other fragmentations occur within the alkyl chain; the ion at *m/z* 199 was attributed to the loss of a phenyl radical from the molecular cation followed by α-cleavage of the alkyl substituent. The FAB spectrum also contains a series of low abundant fragment ions which result from losses of C_nH_{2n+2} neutrals. This set of fragments originates from the fission of each C–C bond in the alkyl chain and can be directly correlated with the structure of the aliphatic alkyl group. The significant higher abundance of the ions at *m/z* 289 and 275 compared with those corresponding to elimination of the shorter chain alkanes was explained by the fact that these fragmentations occur proximate to the site of ionization and are directed by the charge. The other $[Cat–C_nH_{2n+2}]^+$ ions (Cat is the molecular cation) are of very low abundance and are better observed in the high-energy CID spectrum of the phosphonium cation. The CID spectrum of the molecular cation $[Ph_3PC_{12}H_{25}]^+$ was reported as an example of the extensive fragmentation of an alkyl chain attached to a triphenylphosphonium group upon high-energy CID [20]. All possible alkene losses (n = 1–11) were observed (accompanied by H_2 elimination). The high-energy CID tandem mass spectrometry experiment again showed that two different sets of fragments are formed with different ion stability: ions at *m/z* 262, 275, and 289 with higher abundances than the $[Cat–C_{n-3}H_{2n-4}]^+$ ($n > 4$) series. The first group of fragmentations occur proximate to and are directed by the charge site, while the second set of ions were considered as CRF.

As in previous studies dealing with fragmentations in lithium-cationized fatty acid esters [6,7] specifically deuterium-labeled isotopomers were used to examine charge-remote and charge-proximate fragmentations in the *n*-hexadecyltriphenylphosphonium cation. The mechanistic proposal for CRFs of cationized fatty acid esters [9] was supported by the comparison of the high-energy CID spectra of the lithium-cationized fatty acid esters with the spectra of specifically deuterium-labeled isotopomers [7] and determination of an isotope effect of 2.9 in the corresponding fragmentation. These findings imply that a C–H cleavage is a rate-determining step in the CRF process. In view of new insights in the CRF mechanism operating in alkali-cationized fatty acid esters, which point to an interaction between the charge site and C–H bonds (and C–C bonds to a lesser extent) in the long-chain alkyl group, the term “charge-remote” fragmentation may be misleading; the term “mixed-site” fragmentation (MSF) introduced by Tuinman et al. [21,22] to describe fragmentations in deuterium-labeled *n*-alkyltrimethylammonium ions which are competitive with the *n*-alkane losses in the *n*-alkyl group would be more appropriate. Indeed, as will be shown in the present study, mixed-site fragmentation also appears to occur in the *n*-hexadecyltriphenylphosphonium cation.

2. Experimental

2.1. Mass spectrometry

The LSIMS and high-energy CID spectra were obtained on a VG70SEQ hybrid mass spectrometer of EBQ_1Q_2 design equipped with a cesium ion source (Fisons, Manchester, UK). Cesium ions with an impact energy of approximately 18 keV and a beam flux of 0.3 μA were used as the ionization beam. The accelerating voltage in the source was 8 kV. For recording high-energy CID spectra the helium pressure in the collision cell of the first field-free region was adjusted until the mass-selected ion beam was reduced to approximately 50% of its original value. The product-ion spectra were acquired by linked scanning at constant B/E at a scan rate of 8 s per decade. The samples were dissolved in dichloromethane (5 mg ml^{-1}) and 2 μl of the solution was mixed with $\sim$1 μl glycerol on the stainless-steel probe tip. High-energy CID spectra were also recorded on a VGZAB-T (Micromass, Manchester, UK) four-sector ($B_1E_1B_2E_2$ geometry) tandem mass spectrometer equipped with a wide energy gap, inhomogeneous field electrostatic analyser and a 2048 microchannel photo-diode (MCP) array detector. The configuration of the instrument is with a reverse Mattauch-Herzog geometry of MS2. The precursor ion peak in this case was selected by the first two sectors and passed to the variable potential collision cell placed after E_1 to obtain product ion spectra. Argon was used as collision gas until 75% attenuation of the precursor ion beam. The collision cell was floated at 4 kV potential. The angle of the face of the MCP relative to the incoming ion beam was set to 30° corresponding to a mass ratio of 1.22:1 for one exposure. The exposure time was 0.5 s. With this arrangement a product ion resolution around 1000 was achieved (full width at half height, FWHW resolution). The mass accuracy in the product ion spectra was better than 0.3 Da. The mass range was set from *m/z* 50 to the mass of the selected precursor ion. Only the monoisotopic (^{12}C) precursor ion was selected for the high-energy CID tandem mass spectral analysis. The spectra were recorded in the positive ion mode at 8 kV accelerating potential. Data acquisition and processing were performed using the OPUS V3.1X software. All scans were acquired in the continuum mode of the data system.

The relative abundance (RA) values given in the text were derived from measurements performed with the VG70SEQ hybrid mass spectrometer. These measurements were repeated five times and averaged. The spectra obtained on the VGZAB-T are presented in Figs. 1–5. Although the ion ratio values are notably different for the high-energy CID spectra obtained on the two instruments (since a different collision gas and attenuation were used) the same labeling effect was observed. Low-energy CID spectra (200 eV) were recorded using the VG70SEQ hybrid mass spectrometer by activating the ions in the quadrupole collision cell using argon as collision gas and by scanning the quadrupole mass analyser to separate the collision products. The collision gas pressure was approximately 8×10^{-6} mbar (measured in the quadrupole housing).

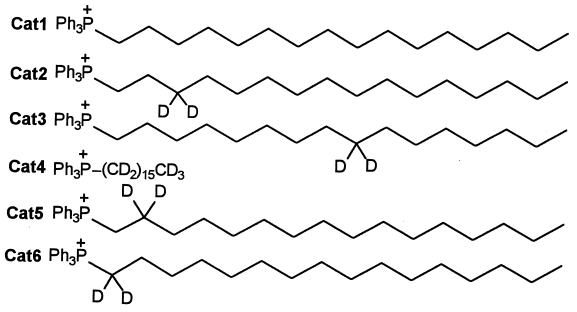
2.2. Synthesis

Palmitic acid was purchased from Sigma Chemical Company (St. Louis, MO, USA), 2,2-$^2H_2$-palmitic, 3,3-$^2H_2$-palmitic, 9,9-$^2H_2$-palmitic acids and fully labeled $C_{16}D_{32}O_2$-palmitic acid were purchased from CDN Isotopes (Point Claire, Canada). $LiAlH_4$ and $LiAlD_4$ were purchased from Aldrich. *n*-Alkyltriphenylphosphonium bromides were synthesized from the corresponding acids by standard procedures. The acids were reduced to the alcohols with $LiAlH_4$ or $LiAlD_4$ in diethyl ether, the bromides were obtained from the alcohols by treatment with phosphorus red and molecular bromine at 200 °C and the Wittig salts were prepared from the bromides in benzene with triphenylphosphine (48 h reflux). The products were analysed by LSIMS.

3. Results and discussion

3.1. Charge-remote fragmentations

LSIMS-produced *n*-hexadecyltriphenylphosphonium cations Cat1–Cat6 (Scheme 2) were studied



Scheme 2. List of the *n*-hexadecyltriphenylphosphonium cation isotopomers studied in this work.

under high-energy CID conditions. As expected they undergo charge-remote fragmentations along the alkyl chain. Fig. 1(a) and (b) illustrate the high-energy CID spectrum obtained for the molecular cation $[n\text{-}C_{16}H_{33}PPh_3]^+$ Cat1 (*m/z* 487) revealing a very clear homologous CRF ion series. It is worth noting that the spectrum also contains a $[Cat–CH_4]^+$ (*m/z* 471) ion [Fig. 1(b)]; the formation of this ion in the CRF process is inconsistent with the proposed mechanism for CRF involving loss of alkenes and molecular hydrogen [Scheme 1(a) and (c)]. The high-energy CID spectrum contains very low abundant MSF product ions as well. The MSFs correspond to losses of C_nH_{2n+1} moieties together with the loss of a phenyl group. We could not determine whether the two groups are lost together (genuine MSF [21,22]) or stepwise (loss of a phenyl to afford the ion at *m/z* 410 followed by the loss of alkyl radicals from this precursor).

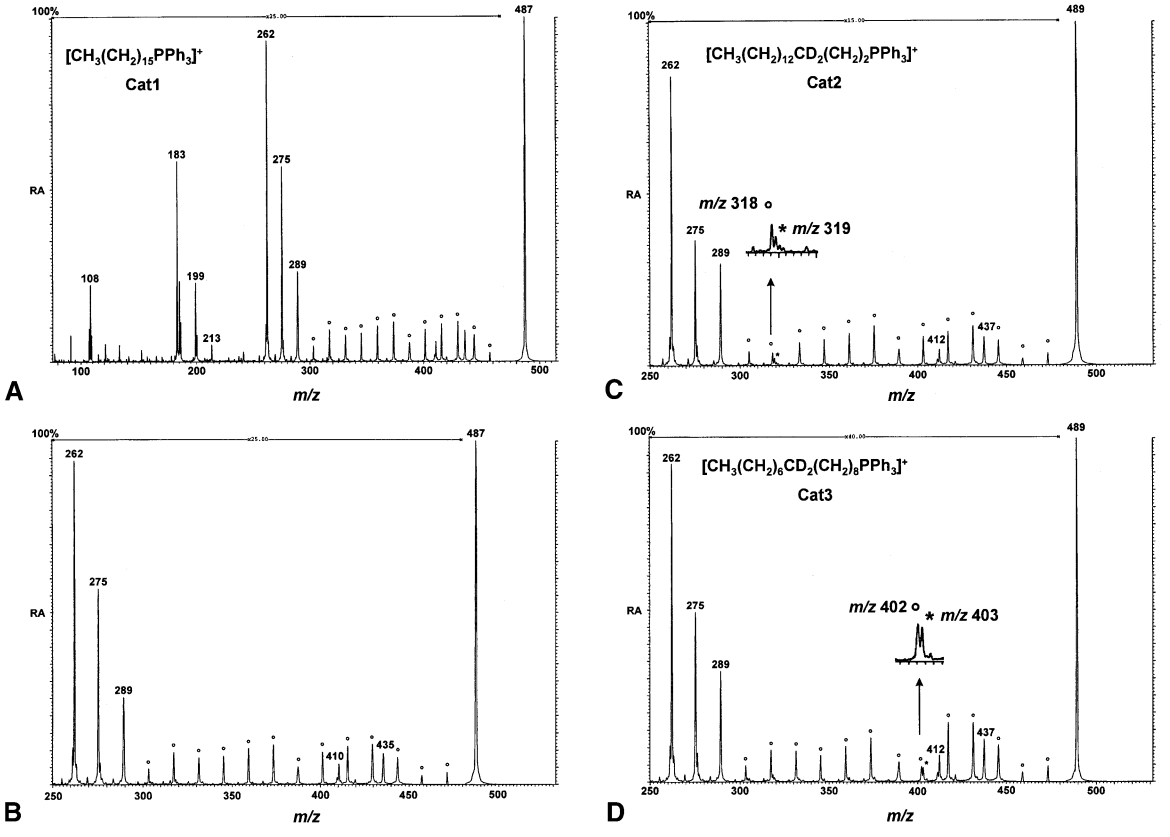
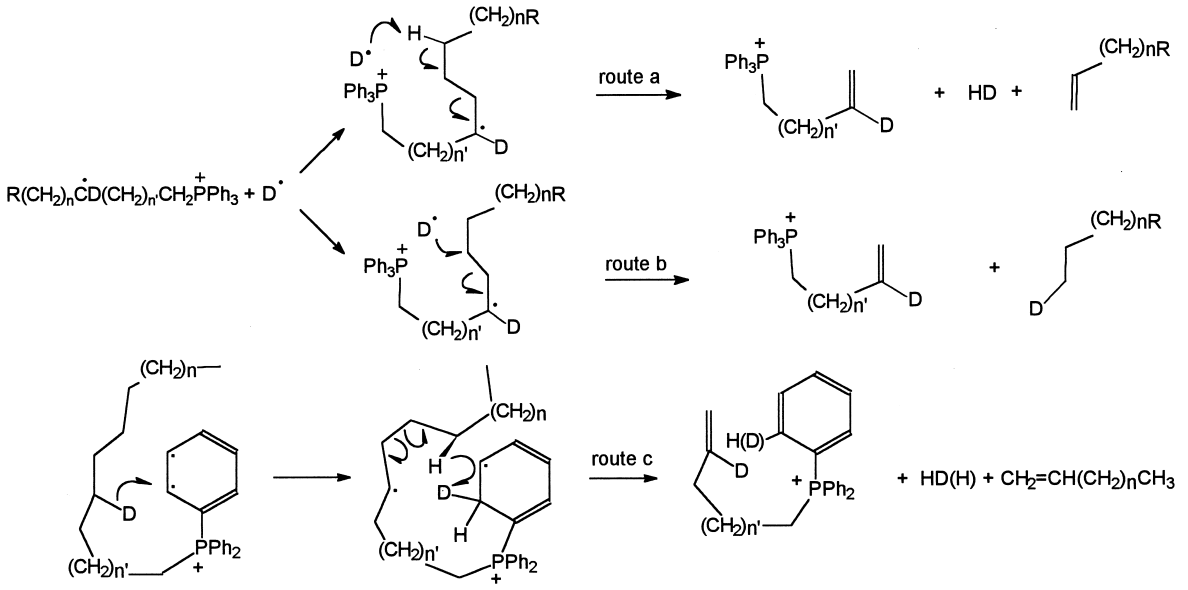


Fig. 1. (a) The high-energy CID spectrum of the *n*-hexadecyltriphenylphosphonium cation Cat1. (b) Enlargement of part of the spectrum presented in (a). (c) The high-energy CID spectrum of the 3,3-$^2H_2$–*n*-hexadecyltriphenylphosphonium cation Cat2. (d) The high-energy CID spectrum of the 9,9-$^2H_2$–*n*-hexadecyltriphenylphosphonium cation Cat3.



Scheme 3. Possible routes of fragmentation involving initial C–H cleavage.

The high-energy CID spectrum of the labeled $[3,3\text{-}^2H\text{–}n\text{-}C_{16}H_{31}PPh_3]^+$ cation Cat2 [Fig. 1(c)] shows that the $[C_{16}H_{31}D_2PPh_3\text{–}C_{12}H_{25}D]^+$ ion *m/z* 318 has a decreased relative abundance (8.8 ± 1.0% for the $[C_{16}H_{33}PPh_3\text{–}C_{12}H_{26}]^+$ (*m/z* 317) in the CID spectrum of the undeuterated molecular cation Cat1 versus 4.7 ± 0.3% in the case of the deuterated Cat2, an isotope effect of 1.9). The same result was obtained for the $[9,9\text{-}^2H_2\text{–}n\text{-}C_{16}H_{31}PPh_3]^+$ ion Cat3 [Fig. 1(d)]. The $[C_{16}H_{31}D_2PPh_3\text{–}C_6H_{13}D]^+$ ion *m/z* 402 has a decreased relative abundance (14.7 ± 1.9% for the *m/z* 401 in the CID spectrum of the undeuterated molecular cation Cat1 versus 7.0 ± 0.4% for the deuterated cation Cat3, an isotope effect of 2.1). These observations indicate that there is a kinetic ^2H-isotope effect for the formation of these ions, suggesting that a C–H cleavage is a rate-determining step in the formation of the CRF ions upon high-energy CID of the phosphonium cations, analogous to what was found in the case of alkali-cationized fatty acid esters [Scheme 1(c)] [5–7,9,10]. An equivalent mechanism suitable for the *n*-alkyl phosphonium salts is presented in Scheme 3 (route a).

The mechanism proposed by Jensen et al. [3] involves concerted dissociation of two C–H bonds. In case this were the process which takes place during high-energy CID, reduction in the RAs of two CRF fragments 28 mass units apart is expected as a result of the labeling at one position. The results of the high-energy CID measurements (Fig. 1) however show that the labeling at a specific position affects the relative abundance of only one ion in the spectrum. Other mechanisms involving a C–H cleavage as rate-determining step are also possible, for example, the mechanism illustrated in Scheme 3 (route b) which can account for the loss of CH_4 as observed in several CRF series. In the mechanisms presented in Scheme 3 (routes a and b) it is suggested that the cleaved off hydrogen radical remains associated with the phosphonium group prior to the elimination of alkane or alkene moieties, yet the structure of this intermediate is unclear. In the case of Li^+-cationized fatty acid esters it was argued that the formation of an oxygen-hydrogen bond via an excited state biradical $(C^{\cdot}\text{–}O^{\cdot})^*$ is involved in the first step of the mechanism describing the formation of the CRF ions [10]. An excited state could be involved in this process during high-energy CID of triphenylphosphonium cations as well and a C–H bond between the expelled hydrogen and one of the phenyl rings (via a biradical excited

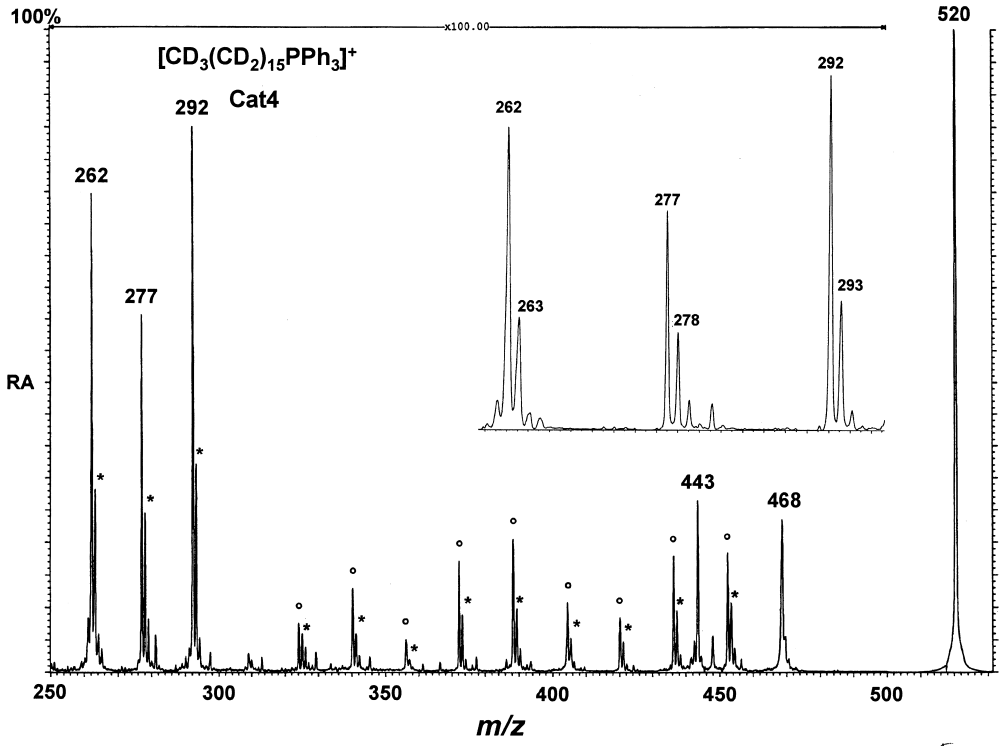
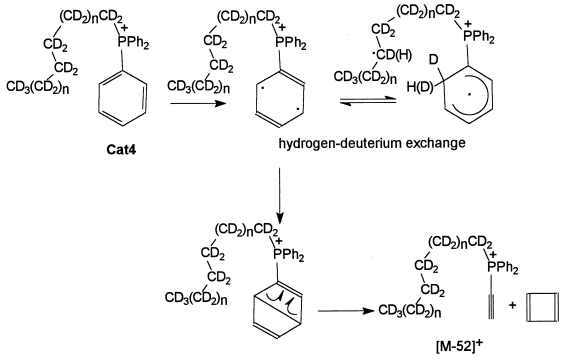


Fig. 2. The high-energy CID spectrum of the fully labeled $[C_{16}D_{33}PPh_3]^+$ cation Cat4.

state, Scheme 3, route c) may be formed. In the following discussion arguments in favor of a phenyl biradical are advanced. Formation of an excited state biradical during high-energy CID should be manifested by exchange between hydrogen atoms on the chain and those on the phenyl rings. The high-energy CID of the molecular cation Cat4 (*m/z* 520) which contains a fully labeled alkyl chain reveals the following: the ions at *m/z* 262, 277, and 292 are all accompanied by ions at *m/z* 263, 278, and 293, respectively one mass unit higher (the ion ratio $F^+/[F + 1]^+$ is roughly 1.5) and by (weak) ions two mass units higher (Fig. 2). This indicates an interchange between hydrogen atoms on the chain and those on the phenyl rings and supports the hypothesis that an excited-state biradical is formed in this process. The labeling effect on the CRF ions in the CID spectrum of Cat4 is more complicated. Yet the ions in this series are followed by an ion one mass unit higher as was observed for the more highly abundant fragments at *m/z* 262, 277, and 292.

The CID spectra of the labeled compounds Cat2 and Cat3 also reveal fragments one mass unit higher relative to the CRF ions (CRF ions in Fig. 2 are marked with a circle and the ions one mass unit higher with a star). The mechanisms proposed in Scheme 3 (routes a and c) rationalize the loss of the hydrogen which is involved in the initial C–H dissociation within the neutral product(s); this is in agreement with the observation that the labeled compounds Cat2 and Cat3 yield the CRF fragments at *m/z* 318 and 402 only one mass unit higher than the unlabeled *m/z* 317 and 401 (Fig. 1). The formation of the ions at *m/z* 319 and 403 (one mass unit higher) is consistent with rearrangements occurring within the cation prior to fragmentation which enable elimination of hydrogen instead of deuterium (Scheme 3 route c and Scheme 4). The relatively high abundances of these ions in the



Scheme 4. Indications for the formation of a biradical: H/D exchange and elimination of neutral C_4H_4.

high-energy CID spectrum of the fully labeled molecular cation Cat4 indicates that these rearrangements occur with the phenylic hydrogens. It cannot be ruled out that hydrogen–deuterium exchange occurs as a result of deuterium labeling in the alkyl chain which inhibits the initial C–H cleavage process. This is supported by the relative stability of the molecular cation Cat4 where the fragmentation yield is lower compared to the unlabeled Cat1. Another indication for the formation of a biradical is the ion $[C\text{-}52]^+$ (*m/z* 411 in the case of Cat1) which corresponds to an elimination of cyclobutadiene or methylene cyclopropene as illustrated in Scheme 4. The formation of the cation $C_4H_4^{\cdot+}$ at *m/z* 52 from phenyls upon electron ionization (EI) conditions is well known [23]. The possible pathways for the formations of the $C_4H_4^{\cdot+}$ fragment from the benzene radical were studied by calculation and it was predicted to be methylene cyclopropene [24]. In the case of the alkyl phosphonium cations elimination of a neutral C_4H_4 takes place but the structure of this moiety is unclear.

3.2. Charge-proximate fragmentations

Fragments not belonging to the CRF series were observed in all the high-energy CID spectra of *n*-alkyltriphenylphosphonium cations. These fragments correspond to elimination of the alkyl group to afford the triphenylphosphine cation at *m/z* 262 and elimination of a phenyl group (e.g. $[C\text{-}77]^+$) or C_4H_4 (e.g. $[C\text{-}52]^+$) from the triphenylphosphine group. Other fragmentations involving dissociations within the alkyl chain, proximate to the charge were mentioned briefly in the introduction (e.g. ions at *m/z* 199, 275, and 289). The high-energy CID experiment on the molecular cation Cat1 was repeated with 5% attenuation of the precursor signal (Fig. 3). Comparing the 5% attenuation spectrum of Cat1 with that shown previously, which was performed with 75% attenuation of the precursor signal, it is evident that the intensity of all the ions in the spectrum is significantly lowered. However the RA of the ions remains roughly the same. The MS/MS experiment on the molecular cation Cat1 was further repeated under low-energy CID (not shown). Under these conditions the RA of the CRF ions is very low and other fragments (e.g. ions at *m/z* 108, 183, 185, 199, 262, and 263) dominate the spectrum. The high-energy CID of the *n*-octadecyltriphenylphosphonium cation (*m/z* 515) was also performed with both 8 and 4 kV acceleration voltage (not shown). The effect of the acceleration potential resembles the effect of the collision gas pressure presented before (attenuation of the precursor ion). Upon lower acceleration potential the intensity of all the ions in the spectrum is significantly lowered but the RA of the ions remains roughly the same. The low-energy CID had a different effect on the two sets of peaks yet reduction of the collision energy from 8 to 4 keV by variation of the acceleration voltage or use of a lower collision gas pressure had the same effect on all ions in the spectrum.

In order to study the mechanisms involved in the various processes which take place upon high-energy CID of the phosphonium cations (in addition to the CRF process discussed before) other labeled isotopomers were examined. The CID spectrum of 2,2-$^2H_2$–*n*-hexadecyltriphenylphosphonium Cat5 (*m/z* 489) gives rise to an abundant *m/z* 291 ion (containing two deuterium atoms), *m/z* 275 (not labeled) and *m/z* 262 triphenylphosphine cation (Fig. 4), while the CRF ions all contain two deuterium atoms.

Examination of the CID spectrum of 1,1-$^2H_2$–*n*-hexadecyltriphenylphosphonium Cat6 (*m/z* 489), presented in Fig. 5, reveals that the RA of the ion *m/z* 290 (corresponding to *m/z* 291 in the spectrum of Cat5) is substantially decreased. The RA of this ion (*m/z* 289)

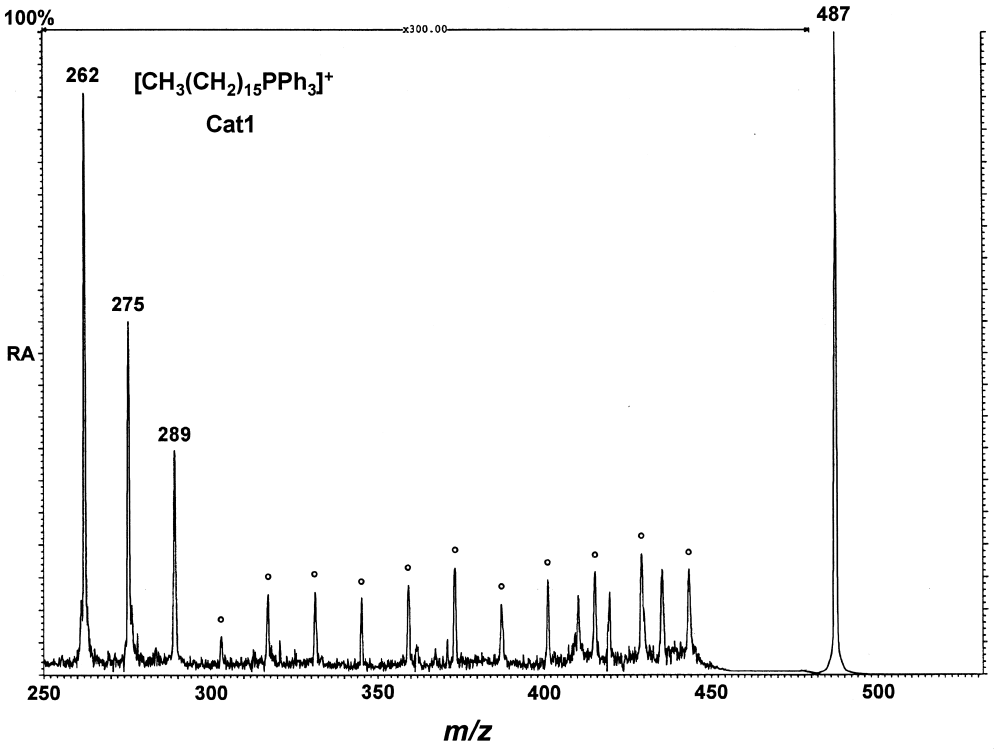


Fig. 3. The high-energy CID spectrum of the *n*-hexadecyltriphenylphosphonium cation Cat1 at low attenuation.

in the spectrum of the unlabeled molecular cation Cat1 is 56.2 ± 2.2% versus 36.5 ± 3.4% in the CID spectrum of the labeled molecular cation Cat6 (*m/z* 290), which corresponds to an isotope effect of 1.5. Both the isotope effect and the mass of this fragment (*m/z* 290 indicating loss of one deuterium) point out that the first step in the process in which the ion *m/z* 289 is formed involves a C1–H cleavage (C1 is the first carbon of the alkyl chain). It is not clear however whether the C1–H dissociation occurs as part of a 1,2-syn elimination of an alkane (Scheme 5), 1,4-hydrogen elimination accompanied by alkene formation or via a multistep rearrangement (Scheme 6, route a). The consecutive fragmentations of the ion at *m/z* 291 (Scheme 5) indicate that the deuterium atoms both remain attached to the C2 carbon (the second carbon in the alkyl chain) after the formation of the ion *m/z* 291 since they are not lost during the first step benzyne elimination but are expelled during the second step during the formation of the ion at *m/z* 183.

In the spectrum of the labeled molecular cation Cat5 all the CRF ions as well as the *m/z* 305 ion contain two deuterium atoms. As was described formerly the labeling of a specific position (with two deuterium atoms) along the alkyl chain resulted in a shift of one unit in the mass of the corresponding ion in the spectrum indicating the loss of one deuterium atom during fragmentation [Fig. 1(b) and (c)]. Apparently a different process is responsible for the formation of the ion at *m/z* 305 (*m/z* 303 in the CID) spectrum of the unlabeled compound Cat1) and the other CRF ions. Both the hydrogen atoms at position 1 and the hydrogen atoms at position 2 of the alkyl chain are not lost during the formation of the ion *m/z* 303 as revealed by the CID spectra of the molecular cations Cat5 and Cat6 which both contain the ion *m/z* 305 with the two deuterium atoms retained. These findings indicate that a hydrogen from the triphenylphosphonium moiety is lost in this process which is not analogous to the general CRF mechanism

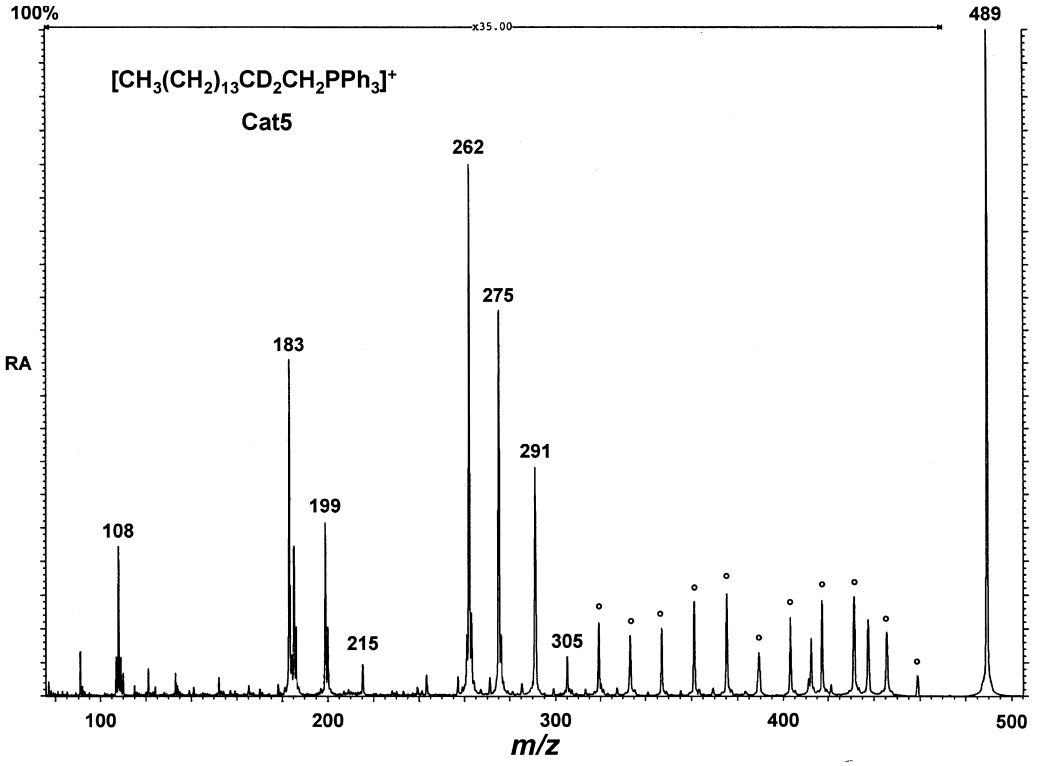


Fig. 4. The high-energy CID spectrum of the 2,2-$^2H_2$–*n*-hexadecyltriphenylphosphonium cation Cat5.

presented in Scheme 3. It is therefore concluded that the mechanisms proposed for the formation of the CRF fragments (Scheme 3) are adequate for the series $[Cat–C_nH_{2n+2}]^+$, $n \geq 12$ but that other processes are responsible for the formation of the ions at *m/z* 303, 275, and 289. A proposed structure for the *m/z* 303 ion is presented in Scheme 6 (route c).

Further examination of the CID spectrum of the labeled molecular cation Cat5 reveals that the RA of the ion *m/z* 262 is decreased in comparison with the RA of this ion in the CID spectrum of the unlabeled cation Cat1 [Fig. 1(a)]. This isotope effect (of 1.5 ± 0.1) indicates that the homolytic C1–P (C1 is the first carbon in the alkyl chain) cleavage during the formation of an alkyl radical is accompanied by a hydrogen rearrangement and formation of a secondary radical (see Scheme 5).

The CID spectrum of 1,1-$^2H_2$–*n*-hexadecyltriphenylphosphonium Cat6 (*m/z* 489) (Fig. 6) shows an abundant *m/z* 277 ion containing two deuterium atoms, corresponding to *m/z* 275 in the CID spectrum of the unlabeled molecular cation Cat1 [Fig. 1(a)]. It is evident that the phenyl rings are involved in the mechanism which holds for the formation of the ion at *m/z* 275. A proposed mechanism for this process is presented in Scheme 6 (route b). As the loss of the alkyl moiety is accompanied by the loss of hydrogen from one of the phenyl rings it is reasonable to assume former interaction between the alkyl and phenyl substituents. Interaction of that kind can be rationalized by formation of a π complex as presented in Scheme 6. Ion/neutral complexes and π complexes have been repeatedly used in the description of fragmentation processes involving phenyl moieties [25–27]. The rearrangement which allows the interaction between a hydrogen from the phenyl ring and the alkyl chain could be initialized by cleavage within the alkyl chain or by rearrangement of the triphenylphosphonium component. It is impossible to determine the structure of this intermediate from the

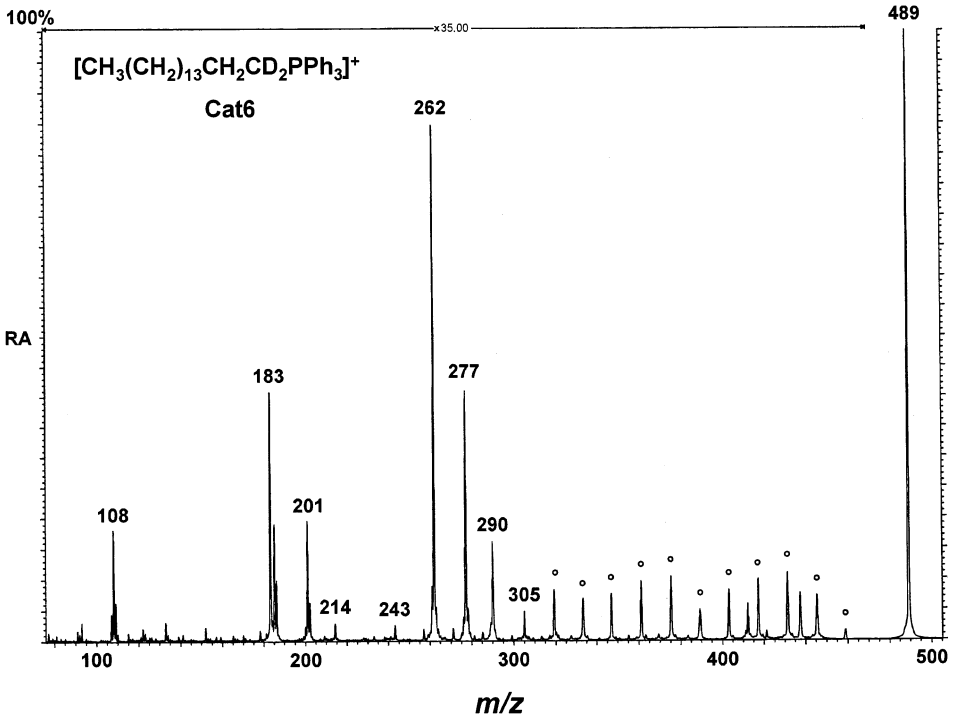
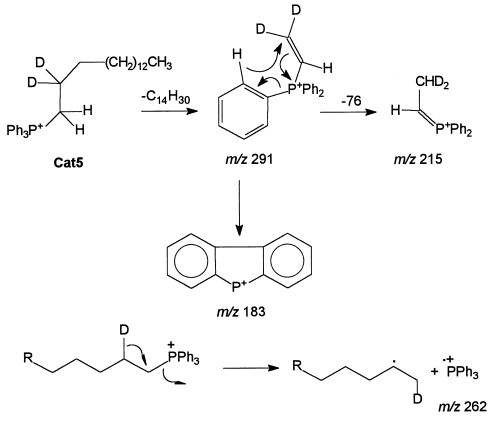


Fig. 5. The high-energy CID spectrum of the 1,1-$^2H_2$–*n*-hexadecyltriphenylphosphonium cation Cat6.

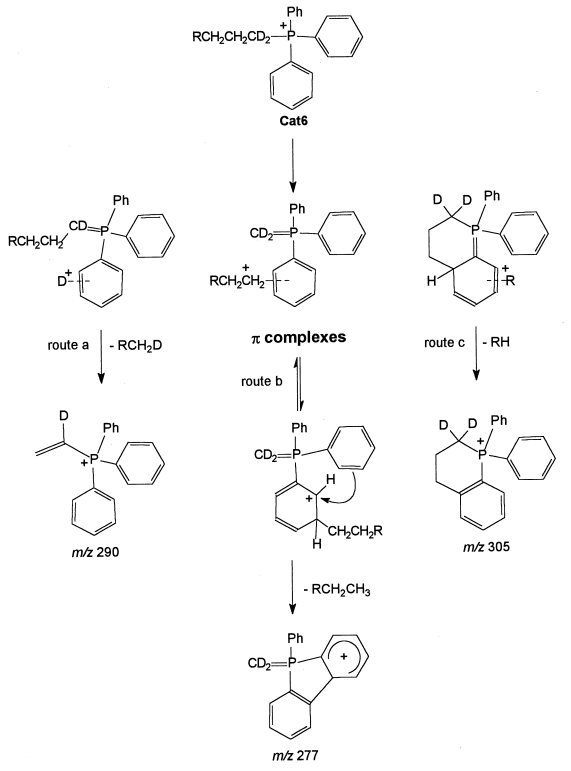
experimental results. Different possible structures are presented in Scheme 6. It is illustrated how part of the fragments in the high-energy CID spectra can arise from different π-complex intermediates. Further fragmentation of the ion at *m/z* 277 via elimination of neutral benzyne to give ion *m/z* 201 also indicates that the CD_2 moiety is retained during the formation of the ion at *m/z* 277.



Scheme 5. Fragmentation of the 2,2-^2H–*n*-hexadecyltriphenylphosphonium cation Cat5.

4. Conclusions

The examination of the high-energy CID spectra of the isomeric $^2H_2$–*n*-hexadecyltriphenylphosphonium cations in comparison with the high-energy CID spectra of the unlabeled and fully labeled *n*-hexadecyltriphenylphosphonium cation analogs bring about the following conclusions. (1) Different processes are responsible for the formation of ions at *m/z* 262, 275, 289, 303, and the CRF series. This is evident from the labeling effect (e.g. isotope effect and retention versus elimination of the deuterium atoms) which differs between these fragments. It is therefore proposed that several competing processes take place during the high-energy CID of these compounds. (2) The isotope effect in the formation of the two CRF fragments



Scheme 6. Proposed π complexes which might be formed during high-energy CID of *n*-alkyltriphenylphosphonium cations and could account for part of the charge-induced fragmentation products.

corresponding to labeled positions indicates that a C–H cleavage is a rate-determining step in the formation of the CRF ions as was suggested for alkali-cationized fatty acid esters. (3) The insertion of hydrogens from the triphenylphosphine moiety into the fully labeled alkyl chain upon high-energy CID as revealed by the substantial abundances of ions one mass unit higher following the normal ion sequence (indicating loss of H instead of D) point out that an excited state biradical may be involved in the processes that take place upon high-energy CID.

Particular molecular rearrangement processes appear to be triggered by the input of high amounts of energy into closed-shell ions and can be rationalized by fragmentation induced by an isolated excited electronic state. In the case of relatively small ions, fragmentation from isolated electronic states has been reported, for example, for acetone [28,29]. Very recently, the concept of "nonergodic" polyatomic ions (or ions showing nonstatistical behavior in which internal energy is not randomized prior to fragmentation) has been supported by Diau et al. [30] using activation of cyclic ketones at the femtosecond time scale. Nonstatistical behavior of Li^+ adducts of small organic molecules (i.e. alcohols, aldehydes, and ketones) upon high-energy CID was already considered in an early study by Röllgen et al. [31]. The possibility of macromolecular ions showing nonergodic fragmentation following high-energy CID was also addressed in detail in a review article by Derrick et al. [32]. Remacle et al. [33] reported that for linear chains positively charged at one end reactivity follows the charge, using calculations. They predicted that the migration of the charge is more efficient than the statistical energy distribution.

The high-energy CID behavior of functionalized alkanes is not only interesting because peculiar and structurally informative fragmentation has been observed but also because new insights have been obtained on the mechanism by which energy is imparted into polyatomic ions and leads to dissociation.

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