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Charge-Remote Metastable Ion Decomposition of Free Fatty Acids under FAB MS: Evidence for Biradical Ion Structures

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Classical charge-remote fragmentation (CRF) of a series of long-chain saturated and monounsaturated fatty acid anions, a well-known phenomenon under collisional activation conditions, is observed for the first time during fast atom bombardment of the analyte–matrix mixture without collisional activation. The process is efficient enough to allow collision-induced dissociation and metastable ion decomposition MS/MS spectra of any charge-remote $[M - H_2 - (CH_2)_n]^-$ fragments as well as spectra of neutral losses to be recorded. The results obtained are in contradiction to the generally accepted theory that CRF results exclusively in terminally unsaturated carboxylate anions. The new results indicate that a multistep radical mechanism is involved in CRF ion formation. The first step of the process appears to be accompanied by hydrogen elimination that occurs randomly throughout the molecule. The primary fragment radical ions formed can decompose further with the formation of the next generation of CRF ions.

Charge-remote fragmentation (CRF), as an analytically useful and fundamentally interesting gas-phase reaction, was first observed in high-energy collision-induced dissociation (CID) mass-analyzed ion kinetic energy spectra of fatty acid carboxylate anions and their methyl esters.^{1,2} Since that time, several groups have carried out investigations of this phenomenon using experimental approaches that include different functionalities and isotope labeling,³ changing the internal energy content of precursor ions,⁴ and analysis including quantum chemical calculations.⁵ This list is far from comprehensive; the interested reader is referred to recent review articles for further details.⁶ These past efforts have led to the conclusion that high-energy collisions are generally necessary for CRF to occur; however, no consensus about the mechanism of CRF has been reached, and investigation of this phenomenon continues.

The instrumental configuration for collisional activation, which assumes the use of multianalyzer instruments, imposes limitations

on studying CRF. There are, however, three instances in which CRF reactions have been observed under regular FAB conditions without CID. Boyd and co-workers^{3b,c} noted that FAB or, more appropriately, liquid secondary ion mass spectrometry positive ion mass spectra of quaternary ammonium ions contained complete sets of CRF ions, in which the most intense fragment ion's abundance was 4–5% relative to the parent quaternary ammonium ion. Traldi and co-workers^{3b,7} observed that alkyltrimethylammonium halides apparently undergo CRF during positive ion FAB just as they do when subjected to CID and, furthermore, that alkyltrimethylammonium halides can be characterized by FAB analysis without tandem mass spectrometry. In attempting to locate epoxides in acetogenin, Laprévotte et al.⁸ found that the linked scan FAB spectrum of lithium-cationized long-chain acetogenin exhibited the same fragment ion peaks in the absence of a collision gas as in the presence of gas, although with appreciably lower intensity.

As far as fatty acids (FA) are concerned, it has been observed in experiments with ESI,⁹ negative ion chemical ionization,¹⁰ and resonance electron capture (REC)¹¹ that carboxylate anions are stable species and do not dissociate without collisional activation. Furthermore, CRF of carboxylate anions has not been observed

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- (1) Tomer, K. B.; Crow, F. W.; Gross, M. L. *J. Am. Chem. Soc.* **1983**, *105*, 5487.
- (2) M. Bambagiotti-Alberti, M.; Coran, S. A.; Giannellini, V.; Vincieri, F. F.; Daolio, S.; Traldi, P. *Org. Mass Spectrom.* **1983**, *18*, 133.

- (3) (a) Bowie, J. H. *Int. J. Mass Spectrom. Ion Phys.* **2001**, *212*, 249. (b) Seto, C.; Grossert, J. S.; Waddle, D. S.; Curtis, J. M.; Boyd, R. K. *Int. J. Mass Spectrom. Ion Phys.* **1999**, *188*, 27. (c) Seto, C.; Grossert, J. S.; Waddle, D. S.; Curtis, J. M.; Boyd, R. K. *J. Am. Soc. Mass Spectrom.* **2001**, *12*, 571. (d) Contado, M. J.; Adams, J.; Jensen, N. J.; Gross, M. L. *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 180. (e) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1863. (f) Huysmans, L.; Nizigiyimana, L.; Van, den Heuvel, H.; Claeys, M. *Int. J. Mass Spectrom.* **1999**, *188*, 39. (g) Denekamp, C.; Van den Heuvel, H.; Voinov, V. G.; Claeys, M.; Seto, C.; Grossert, J. S.; Waddell, D. S.; Curtis, J. M.; Boyd, R. K. *Rapid Commun. Mass Spectrom.* **2000**, *14*, 1035. (h) Bambagiotti-Alberti, M.; Coran, S. A.; Benvenuti, F.; LoNostro, P.; Catinella, S.; Favretto, D.; Traldi, P. *J. Mass Spectrom.* **1995**, *30*, 1742.
- (4) Griffiths, W. J.; Brown, A.; Reimendal, R.; Yang, Y.; Zhang, J.; Sjövall, J. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1169.
- (5) Siegel, M. M.; Colthup, N. B. *Appl. Spectrosc.* **1988**, *42*, 1214.
- (6) (a) Cheng, C.; Gross, M. L. *Mass Spectrom. Rev.* **2000**, *19*, 398. (b) Gross, M. L. *Int. J. Mass Spectrom.* **2000**, *200*, 611.
- (7) Bambagiotti-Alberti, M.; Coran, S.; Giannellini, V.; Favretto, D.; Traldi, P. *Rapid Commun. Mass Spectrom.* **1994**, *8*, 439.
- (8) Laprévotte, O.; Girard, C.; Das, B.; Laugel, T.; Roblot, F.; Leboeuf, M.; Cavé, A. *Int. Commun. Mass Spectrom.* **1992**, *6*, 352.
- (9) Griffiths, W. J.; Yang, Y.; Lindgren, J. Å.; Sjövall, J. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 21.
- (10) Bambagiotti-Alberti, M.; Coran, S.; Vincieri, F. F.; Petrucciani, T.; Traldi, P. *Org. Mass Spectrom.* **1986**, *21*, 485.
- (11) Voinov, V. G.; Claeys, M. *Int. J. Mass Spectrom.* **2000**, *198*, 23.

under FAB^{1,6b} or static SIMS¹² conditions. In contrast to these previous findings, it is demonstrated in the present report that FA carboxylate anions formed under FAB desorption/ionization conditions can undergo CRF reactions without activation in a collision cell. The occurrence of CRF under regular FAB conditions provides an opportunity to study these reactions on double-sector instruments operating in linked scan modes.^{3b,h} Although the high chemical background usually present in FAB spectra poses a potential problem, the present results show that interference from the matrix is to a large degree suppressed.¹³

Although there is currently no agreed upon mechanism for CRF, it seems commonly accepted that these reactions result in terminally unsaturated fragment ions.¹⁴ In the present work, this concept was tested by monitoring the various CRF ions generated in the source of a double-focusing, sector (Nier-Johnson *E*, *B* geometry) mass spectrometer in a straight scanning mode, i.e., scanning the magnetic field (*B*), or in linked scanning¹⁵ mode, i.e., simultaneously scanning the electric (*E*) and magnetic fields according to one of the following mathematical relationships: $B/E = \text{constant}$ (to obtain product ion spectra) or $(B/E)(1 - E)^{1/2} = \text{constant}$ (to obtain neutral loss spectra). The results from the experiments unambiguously indicate that carboxylate anions can form not only as terminally unsaturated species but also as biradical fragments.

EXPERIMENTAL SECTION

The fatty acids, octadecanoic (stearic) $C_{18:0}$ (>99%), *cis*-9-octadecenoic (oleic) $C_{18:1}$ (99%), *cis*-13-docosenoic (erucic) $C_{22:1}$ ($\geq 99\%$), *trans*-13-docosenoic (brassicic) $C_{22:1}$ (99%), and 10-undecenoic $C_{11:1}$ (98%), and the compounds, triethanolamine (TEA; $\geq 99\%$), diethanolamine (DEA; $\geq 98\%$), nitrobenzyl alcohol (NBA; 98%), and glycerol (>99.5%) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO) and used as received.

All the experiments were performed on a JEOL 600H mass spectrometer equipped with a FAB source. The energy of the Xe atoms was 4 keV, and the Xe flux was equivalent to 5 mA. TEA, DEA, NBA, and glycerol were used as matrixes. Small amounts of fatty acid samples were mixed with matrix on the tip of the stainless steel FAB probe. The ion accelerating voltage was 3 kV. The temperature of the ionization chamber was maintained below 50 °C. Negative ion (NI) spectra of ions produced by unimolecular decompositions in the ion source were recorded in the normal magnetic scan mode. Product ion spectra of ions originating in the first field-free region (FFR) located between the ion source and the electric sector, whether by metastable decomposition or CID, were recorded by linked scanning¹⁵ with B/E held constant, and neutral loss spectra were recorded by linked scanning¹⁵ with $(B/E)(1 - E)^{1/2}$ held constant. Helium was used as collision gas, and the pressure of the helium was adjusted until the intensity of the precursor ion signal was reduced by 50%.

RESULTS

FAB of Fatty Acids in the Negative Ion Mode, Magnet Scanning. The NI FAB spectrum of stearic acid (Figure 1a), a typical representative of saturated long-chain hydrocarbon compounds, closely resembles a standard CID spectrum (Figure 1b)

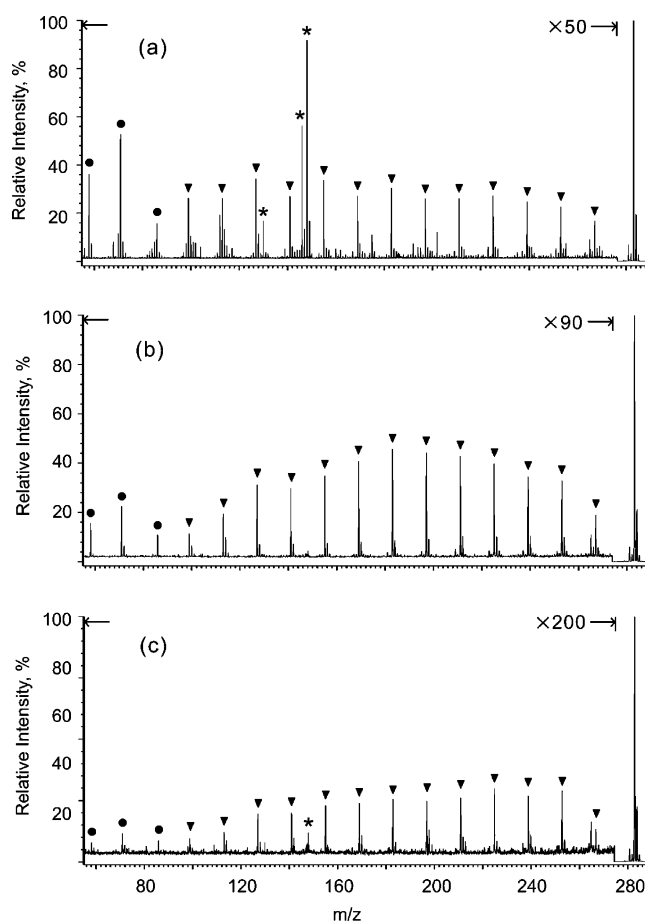


Figure 1. NI FAB mass spectra of stearic acid: full magnetic scan (a); CID product spectrum of $[M - H]^-$ (b); metastable ion decomposition mass spectrum of $[M - H]^-$ (c). TEA was used as matrix in all three cases. Peaks marked with triangles and dots represent ions from charge-remote and charge-driven processes, respectively. The peaks marked with asterisks originate from matrix.

except for the presence of three peaks in the former (marked with asterisks) that originate from the matrix. The intensities of the CRF ions in both spectra are about the same and are generally equal to 1% of the precursor ion intensity, which is the normal efficiency for CID of carboxylate anions.¹⁶ Oleic $C_{18:1}$ and erucic $C_{22:1}$ acids, representatives of monounsaturated compounds, yield spectra (Figure 2) that are practically the same as those produced by standard CID^{16,17} and, therefore, allow the positions of double bonds to be easily determined. The same CRF patterns were observed for all matrixes used without noticeable effect on CRF efficiency.

FAB of Fatty Acids in the Negative Ion Mode, B/E -Linked Scanning (Product Ion Spectra). The spectrum of the decomposition products of the metastable ion $[M - H]^-$ for stearic acid in the first FFR (Figure 1c) consists of a full set of CRF ion peaks and differs from its CID counterpart (Figure 1b) by a shift in the envelope maximum to a higher mass range, in accordance with the amount of internal energy deposited. Downstream in the

(12) Stapel, D.; Brox, O.; Benninghoven, A. *Appl. Surf. Sci.* **1999**, *140*, 156.

(13) Shiea, J.; Sunner, J. *Int. J. Mass Spectrom. Ion Phys.* **1991**, *109*, 265.

(14) In a recent review, a new "charge-assisted" mechanism is suggested that leads to terminally unsaturated CRF ions with resonance-stabilized structures: Harvey, D. J. *J. Am. Soc. Mass Spectrom.* **2005**, *16*, 280.

(15) Boyd, R. K. *Mass Spectrom. Rev.* **1994**, *13*, 359, and references therein.

(16) Jensen, N. J.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 2018.

(17) Voinov, V. G.; Claeys, M. *Int. J. Mass Spectrom.* **2001**, *205*, 57.

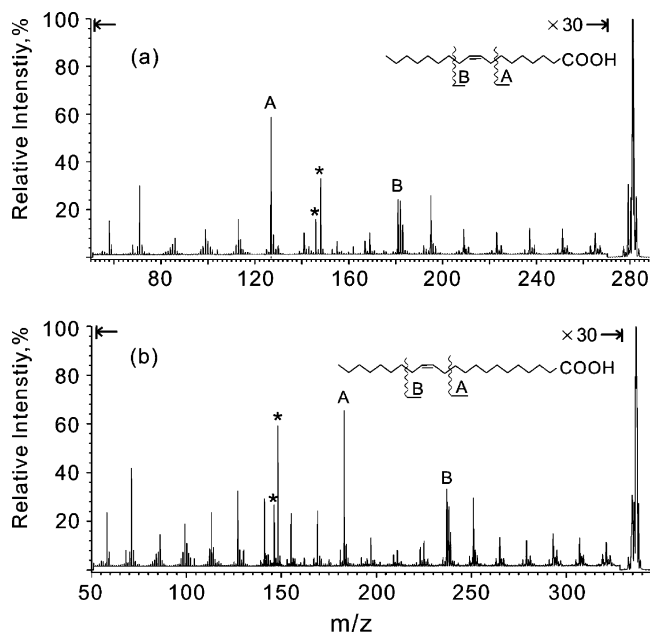


Figure 2. NI FAB mass spectra of oleic (a) and erucic acid (b). TEA was used as matrix in both cases. The peaks marked with asterisks originate from matrix.

second FFR (between the electric and magnetic sectors), no ion peaks corresponding to metastable ion decomposition were observed, neither with (Figure 1b) nor without (Figure 1c) collisional activation in the first FFR.

The fact that free fatty acids experience CRF reactions in the ion source makes it possible to investigate the structure of CRF ions with a double-sector instrument using *B/E*-linked scanning. The CID mass spectrum of the stearic acid fragment ion m/z 183 (Figure 3a) and that of the $[M - H]^-$ of 10-hendecenoic acid (Figure 3b), which is the terminally unsaturated counterpart of stearic acid's CRF ion m/z 183, clearly show different fragmentation patterns. Both spectra contain numerous CRF ion peaks, but only the spectrum of 10-hendecenoic acid has a gap between precursor and m/z 141; this gap is known from previously reported results to be characteristic of a terminal double bond.¹⁸ By contrast, no double bond gap can be seen in the spectra of stearic acid's CRF m/z 183 ion (Figure 3a and c); instead, peaks corresponding to $[M_P - CH_2]^-$ and $[M_P - C_2H_4]^-$ at m/z 169 and 155, respectively, are distinctly present where the gap would be if this structure terminated in a double bond.

Spectra obtained from the metastable ion decomposition of stearic acid's m/z 183 fragment (Figure 3c) and of $[M - H]^-$ of 10-hendecenoic acid exhibit the same fragmentation patterns seen in the CID spectrum. Specifically, the latter spectrum (not shown because it is identical to the CID spectrum) has the same gap as seen in its CID spectrum (Figure 3b). The spectrum of metastable ion decomposition of stearic acid's fragment ion at m/z 183 again consists of a full set of CRF ions including ones with m/z 155 and 169 (Figure 3c). In comparison with the CID spectrum, the relative abundances of the ions at m/z 155 and 169 are much higher in the metastable ion spectrum. This difference in intensity distribution of CRF ions between CID and metastable ion spectra was further studied by varying the collision gas pressure. The

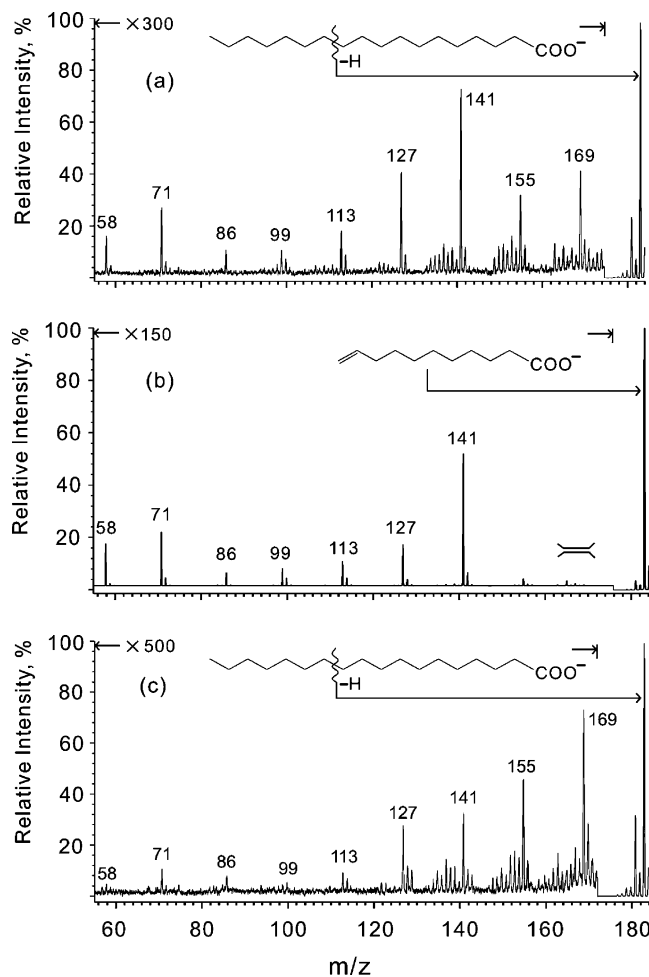


Figure 3. Linked scan CID (a) and metastable ion decomposition (c) spectra of stearic acid's CRF fragment ion with m/z 183 and linked scan CID mass spectrum of $[M - H]^-$ ion of 10-hendecenoic acid (b). Symbol for double bond is shown at location where fragment ion formed by cleavage at double bond would be seen. DEA was used as matrix in all three cases.

abundances of these particular ions gradually decrease with pressure and ultimately disappear at a pressure that suppresses 90% of the precursor ion signal. The same patterns, namely, the presence of peaks that should be absent were the terminal double bond present, were observed for different CRF ions for all the fatty acids studied (data not shown).

In order to rule out the possibility that the linked scan mode might not be sensitive to the presence of double bonds in CRF fragment ions, a CRF fragment ion of brassidic acid with m/z 279 was selected as a precursor ion, and its CID spectrum was recorded (Figure 4). There is clearly a gap between the peaks at m/z 183 and 237 corresponding to the native double bond at the C-13 position, but there is no gap corresponding to a terminal double bond. Signals at m/z 265 and 255, corresponding respectively to $[M_P - CH_2]^-$ and $[M_P - C_2H_4]^-$, are both clearly present.

FAB-MS of Fatty Acids in Negative Ion Mode, (*B/E*)(1 - *E*)^{1/2}-Linked Scanning (Neutral Loss). Spectra due to neutral losses in the first FFR were recorded to follow metastable ion decay and collision-induced decomposition. No significant difference in the pattern of peaks was observed between the spectra obtained with and without collision gas, but adding gas did result in higher dissociation efficiency and better S/N. The mass window

(18) Adams, J.; Gross, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 435.

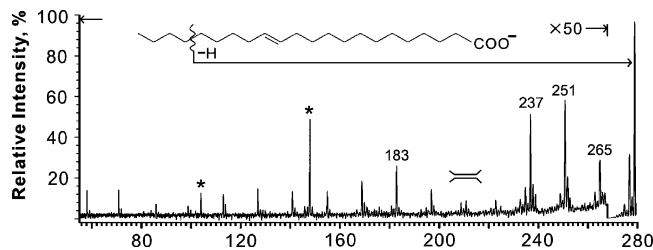


Figure 4. CID B/E -linked scan spectrum of brassidic acid's CRF ion with m/z 279. DEA was used as matrix. The peaks marked with asterisks originate from matrix. Symbol for double bond is shown at location where fragment ion formed by cleavage of double bond would be seen.

created by the JEOL 600H in a $(B/E)(1 - E)^{1/2}$ -linked scan mode extends broadly (up to ± 5 Th in separate tests) about the selected neutral loss rather than narrowly as it would in a true tandem mass spectrometer. The results are a series of spectra similar to those shown in Figure 5. The CID spectra for neutral losses of 14 and 42 Th from stearic acid, in addition to a series of CRF ion peaks corresponding to losses from the termini of the precursor CRF ions, contain the ions formed by elimination, respectively, of the terminal units 16 and 44 Th from the precursor $[M - H]^-$. The mass assignments in these spectra were confirmed by increased absolute and relative intensities of these signals in the spectra of losses of 16 and 44 Th.¹⁹ The appearance of these series of ions is further evidence that CRF anions of fatty acids are unstable structures that dissociate into second-generation CRF ions.

DISCUSSION

Although FAB is a soft ionization technique that provides information mainly about molecular mass, there are many instances in which FAB spectra exhibit structurally significant metastable ion fragmentation. The observations of CRF reactions under FAB conditions cited in the introduction^{3b,c,h,7,8} are excellent cases in point. The present finding that anions of fatty acids produced by FAB undergo extensive CRF would appear to be just one more such example were it not for the fact that it was demonstrated several years ago that CRF^{1,6b} and metastable ion decomposition²⁰ of carboxylate anions does not occur under FAB conditions—the latter studies were conducted on a Kratos mass spectrometer. At least one other situation of this sort exists in the literature—in an earlier study of alkyltrimethylammonium halides using a Kratos instrument,²¹ no CRF ions were observed, but in a later study using a ZAB-2F instrument,⁷ CRF ions of the same compounds were found. Unfortunately, the disparity in such instances cannot be readily resolved by experimental means. In a Kratos source, such as was used in the earlier studies in question, the axis of the atom gun is perpendicular to the direction of ion extraction, whereas in the JEOL source used in the present study, the atom gun's axis is at an angle of $\sim 75^\circ$ relative to the direction of ion extraction. Experimentally, it would be impractical to determine whether this difference of 15° in incidence has a significant effect on CRF reactions of carboxylate anions by

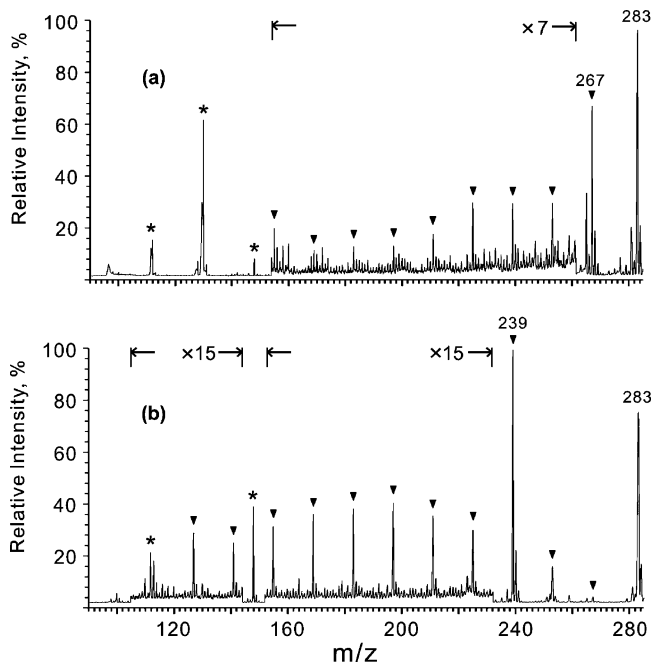


Figure 5. CID $B/E(1 - E)^{1/2}$ -linked scan spectra of stearic acid for the neutral losses $m_n = 14$ (a) and 42 (b). TEA was used as matrix in both cases. Peaks marked with triangles represent ions from charge-remote processes. The peaks marked with asterisks originate from matrix.

changing the FAB gun's position because the JEOL's ion source is rigidly constructed and its use is shared. Regardless of the reason for the disparity, the unexpected phenomenon found in the present study that carboxylate anions undergo extensive metastable ion decomposition helps to explain discrepancies between data reported by different laboratories and also makes the determination of CRF kinetics of FAB formed ions tricky.

The results of the present study provide both indirect and direct evidence that CRF produces, in addition to terminally unsaturated species, radical fragment ions. The spontaneous decomposition of CRF ions in the first FFR of the mass spectrometer provides the indirect evidence in favor of radical fragment ions. If the CRF ions were unsaturated at the termini of the carboxylate anions, they would require extra excitation energy for decomposition; however, the spectra of metastable ion decomposition (Figure 3c) and neutral losses (Figure 5) clearly show that CRF ions are not stable species. These spectra indicate a chain of events in which metastable radical ions, resulting from CRF ions formed by FAB, are in turn stabilized by subsequent decomposition into second-generation, stable carboxylate anions. Though the formation of the second-generation CRF ions is of itself a relatively minor process, the effect integrated over all fragments produced by long-chain molecules can be considerable in terms of data interpretation. The presence of peaks corresponding to $[M_p - CH_2]^-$ and $[M_p - C_2H_4]^-$ in the CID (Figure 3a) and metastable (Figure 3c) spectra of CRF ions is direct evidence for a radical structure. If the product ions of CRF terminated in double bonds, their CID and metastable spectra should exhibit characteristic double bond gaps as does the CID spectrum of $[M - H]^-$ of 10-undecenoic acid (Figure 3b). The formation of terminally unsaturated ions by the 1,4-elimination of H_2 and neutral alkenes was validated by Adams and Gross with the results they

(19) Haddon, W. F. *Org. Mass Spectrom.* **1980**, *15*, 539–543.

(20) Adams, J.; Gross, M. L. *J. Am. Chem. Soc.* **1986**, *108*, 6915.

(21) Lyon, P. A.; Crow, F. W.; Tomer, K. B.; Gross, M. L. *Anal. Chem.* **1984**, *56*, 2278.

obtained from a study of lithiated fatty acids.¹⁸ In that work, the MS/MS spectra of pairs of ions with m/z 141, of which one was a fragment of lithiated 10-undecenoic acid and the other was its terminally unsaturated counterpart $[M + 2Li - H]^+$ of 6-heptenoic acid, were compared and found identical. The CRF precursor ion in that comparison was so short, however, that it must be regarded as a special case that does not necessarily rule out the formation of radical CRF ions. In a study by Dua et al., it was clearly demonstrated that the short CRF ions are special cases.²² By systematically analyzing nona-8-enoic acid with deuterium and carbon-13 labeling, those investigators showed that the fragment ion with m/z 113, which can be formally assigned to terminally unsaturated CRF ions such as $CH_2=CH(CH_2)_3CO_2^-$ hex-1-enoic carboxylate anion, is in fact the cyclopentyl carboxylate anion. In the study by Adams and Gross, the lithiated CRF ion with m/z 141, which corresponds to m/z 127 for the nonlithiated fatty acid carboxylate anion, only has seven carbon atoms in its chain; i.e., it is even shorter than the structure analyzed by Dua et al. If formation of radical ions is initiated through random elimination of a H-atom from the chain, there can be no other fragment ions except those that were observed by Adams and Gross.¹⁸ Hence, the use of a short precursor ion by Adams and Gross demonstrated formation of the terminal unsaturated ion but did not rule out formation of radical fragment ions. In the present study, starting from the next CRF ion of m/z 141, peaks corresponding to $[M_p - CH_2]^-$ and $[M_p - C_2H_4]^-$ are always present.

Radical mechanisms have been proposed by Wysocki and Ross²³ and extensively studied later by Claeys.²⁴ The evidence found in the present work that the CRF ions do not lead exclusively to terminally unsaturated carboxylate anions clearly supports a radical mechanism with hydrogen atom elimination along the carbon chain, very likely with the same probability distribution as the one that takes place under REC conditions.^{11,25} Similar evidence for a radical mechanism was obtained by Wysocki

and Ross,^{23,26} who found that a series of second-generation fragment ions corresponding to the loss of C_nH_{2n} was produced when CRF ions with m/z 218 and 219 generated from protonated 2-pentadecylpyridine by collisions with Ar were allowed to collide with Xe target gas. In the present case, the second-generation CRF ions are observed without collisional activation; this is the result of both different compound type and different experimental approach. Specifically, in the latter case, the primary CRF ions were formed in source and, therefore, required about one-tenth of the time to arrive in the first FFR that those CRF ions formed in the first FFR required to arrive in the second FFR.²⁷ As a result, not only terminally unsaturated but also radical CRF ions arrive in the first FFR. Hence, both the CID and spontaneous decomposition spectra recorded consist of $[M_p - CH_2]^-$ and $[M_p - C_2H_4]^-$ ions. The fact that metastable ion decomposition is observed in the first FFR and not at all in second FFR shows how critically CRF reactions depend on instrumental time scale.

CONCLUSION

It is found that fatty acid carboxylate anions experience CRF reactions under regular FAB conditions, without collisional activation. The efficiency of CRF is sufficiently high to allow analysis of the resulting $[M - H_2 - (CH_2)_n]^-$ fragments by linked scanning in conjunction with CID and metastable ion decomposition.

Results obtained in the present work clearly indicate that CRF of fatty acid anions must involve formation of radical anions in addition to terminally unsaturated fragment ions, i.e., those having stable carboxylate anion structures. The latter are unique in the sense that they are the last to be formed in the decomposition process. If radical ions are formed, they are further stabilized by decomposition to the second-generation CRF ions, which in their turn, can be radical ions and decompose to the third generation and so on until stable carboxylate anions are finally produced. Distinguishing between the first and subsequent generations of CRF ions in CID spectra is not a trivial task, because all have the same mass and eventually the same structure. Additional experiments with different standards, including deuterium-labeled compounds, need to be performed in order to clarify the mechanism of CRF reactions.

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- (22) Dua, S.; Bowie, J. H.; Cerda, B. A.; Wesdemiotis, C.; Raftery, M. J.; Kelly, J. F.; Taylor, M. S.; Blanksby, S. J.; Buntine, M. A. *J. Chem. Soc. Perkin Trans. 2* **1997**, 4, 695.
- (23) Wysocki, V. H.; and Ross, M. M. *Int. J. Mass Spectrom. Ion Phys.* **1991**, 104, 179.
- (24) (a) Claeys, M.; Nizigiyimana, L.; Van den Heuvel, H.; Derrick, P. J. *Rapid Commun. Mass Spectrom.* **1996**, 10, 770. (b) Nizigiyimana, L.; Rajan, P. K.; Haemers, A.; Claeys, M.; Derrick, P. J. *Rapid Commun. Mass Spectrom.* **1997**, 11, 1808. (c) Claeys, M.; Nizigiyimana, L.; Van den Heuvel, H.; Vedernikova, I.; Haemers, A. *J. Mass Spectrom.* **1998**, 33, 631. (d) Huysmans, L.; Nizigiyimana, L.; Van den Heuvel, H.; Claeys, M. *Int. J. Mass Spectrom.* **1999**, 188, 39.
- (25) Voinov, V. G.; Van den Heuvel, H.; Claeys, M. *J. Mass Spectrom.* **2002**, 37, 313.
- (26) Wysocki, V. H.; Ross, M. M.; Horning, S. R.; Cooks, R. G. *Rapid Commun. Mass Spectrom.* **1988**, 2, 214.
- (27) Holmes, J. L. *Org. Mass Spectrom.* **1985**, 20, 169.