

Characterization of Ion Fragmentations of Fatty Acids

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Ion fragmentations of fatty acids such as stearic acid, palmitic acid, myristic acid, and lauric acid were studied using mass spectrometry and semiempirical calculations. The mass spectra of fatty acids showed the distributions of $\text{CH}_3(\text{CH}_2)_n^+$ and $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ fragment ions. The relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ showed the local maxima at $n=6, 10,$ and 14 . The local maximum phenomena were also found in the mass spectra of methyl stearate but not in those of normal alcohols. These local maxima could be explained not by heats of reaction for fragmentation but by the cyclic structures of the molecular ions. The AM1 semiempirical calculations for fatty acids clearly show that the linear structures are more favorable than the cyclic ones for neutral molecules while the cyclic structures are more favorable than the linear ones for ionic molecules. The distances between carboxyl group and methylene of the cyclic structures of ionized fatty acids were calculated. The methylene carbons with $n=6, 10,$ and 14 were closer to the carboxyl group than adjacent ones.

Introduction

Molecules with specific functional group undergo typical fragmentation patterns which is used to obtain structural information. For example, the mass spectra of ethers show prominent ions of general formula $\text{C}_n\text{H}_{2n+1}\text{O}^+$.^{1,2} Ionized alcohols are fragmented and rearranged by loss of water molecule.^{3,4} Keough⁵ investigated mass spectra for chemical ionization of alkanes, alkenes, aldehydes, ketones, acids, esters, and alcohols. Formations of $[\text{M}-\text{OH}]^+$ and $[\text{M}-\text{OR}]^+$ with acids and esters, respectively, were observed. He reported that the spectra of the normal alkanes exhibit a distribution of intense $\text{CH}_3(\text{CH}_2)_n^+$ fragment ions. Wysocki and coworkers⁶ studied chemical ionization of $\text{CH}_3(\text{CH}_2)_n\text{R}$ using isobutane as a reagent gas and investigated the loss of $\text{C}_n\text{H}_{2n+2}$ from parent ion. The results have proven that the mass spectrum of the stearate anion shows a distribution of intense $\text{CH}_3(\text{CH}_2)_n$ fragment ions.

Efficiencies for typical fragmentations of molecular ion are usually based on heats of reactions. The less energies for fragmentations were required, the more abundant fragment ions were observed. For example, among fragmentations of $\text{HOCH}_2\text{CH}_2\text{NH}_2^+$, the most abundant fragment ion is $\text{H}_2\text{C}=\text{NH}_2^+$ which is the most favorable fragment in view of the heats of reaction.⁷ Ionized methyl ethyl ketone, $\text{CH}_3\text{COCH}_2\text{CH}_3^+$ can be mainly dissociated into $\text{CH}_3\text{CH}_2\text{CO}^+\text{CH}_3$ or $\text{CH}_3\text{CO}^+\text{C}_2\text{H}_5$. The $\text{CH}_3\text{CH}_2\text{CO}^+$ was more abundant than CH_3CO^+ in the mass spectrum.⁸ Heats of reaction for the dissociation into $\text{CH}_3\text{CH}_2\text{CO}^+\text{CH}_3$ and $\text{CH}_3\text{CO}^+\text{C}_2\text{H}_5$ were 58 and 96 kJ/mol, respectively. Thus, the formation of $\text{CH}_3\text{CH}_2\text{CO}^+$ is more favorable than that of CH_3CO^+ .

Goto and coworkers⁹ studied fragmentation patterns of various derivatives for carboxyl group of stearic acid. The mass spectrum of methyl stearate exhibited a distribution of intense $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$ fragment ions and local maxima at $n=6, 10$ and 14 . And the formation of $[(\text{CH}_2)_n\text{CO}_2\text{R}]^+$ ions with $\text{R}=\text{H}$ or CH_3 from fatty acids and fatty acid methyl esters and the particular enhancement of this species with $n=6$

and 10 has been known for many years.¹⁰ However, unfortunately the reasons for the local maxima were not explained.

In the present work, fragmentation patterns of fatty acids such as stearic, palmitic, myristic, and lauric acids were studied using a quadrupole mass spectrometer. Fragmentations of methyl stearate and normal alcohols were also investigated to compare with those of fatty acids. The specific ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ were explained by the structures of molecular ions and heats of formation by AM1 semiempirical calculations.

Experimental

All the experiments were carried out using an Extrel ELQ 400 quadrupole mass spectrometer. The instrument is equipped with two diffusion pumps attached to source and analyzer chambers. The base pressures of the source and analyzer chamber are lower than 1×10^{-6} and 1×10^{-7} Torr, respectively. All the reagents were obtained commercially and used without further purification. Samples were introduced into the ion volume through solids probe, which can be temperature controlled, for direct injection. Electron impact energy was 70 eV and applied voltage to channel electron multiplier was -1200 V.

The heats of formation for product ions which were not available from literature¹¹ were estimated by AM1 semiempirical calculations¹²⁻¹⁴ to investigate stabilities of product ions and favorabilities of fragmentations. This calculated results were used to elucidate the fragmentations depending on the structure of molecular ion. And linear and cyclic structures of neutral and ionized molecules of fatty acids were also calculated by AM1 semiempirical method.

Results and Discussion

Fatty acids with general formulae of $\text{CH}_3(\text{CH}_2)_n\text{CO}_2\text{H}$ have a long linear hydrocarbon chain. In this work, fatty acids such as stearic acid, palmitic acid, myristic acid, and

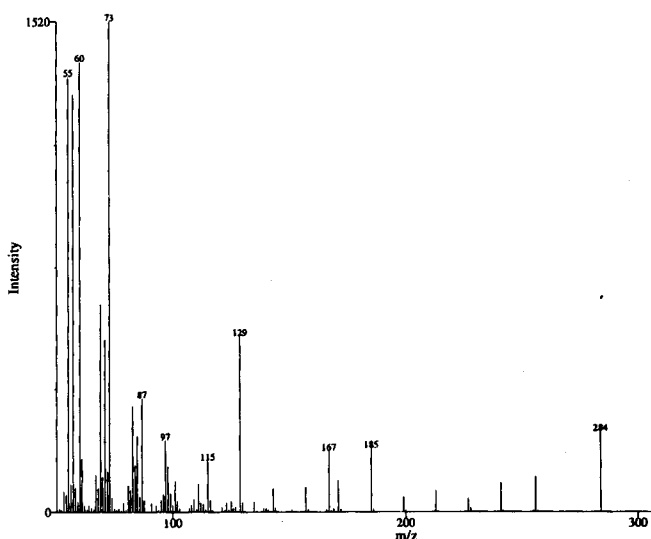


Figure 1. Mass spectrum of stearic acid. Electron impact energy is 70 eV.

lauric acid with formulae of $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, $\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$, $\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$, and $\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$, respectively, were used. Figure 1 is the mass spectrum of stearic acid obtained by electron impact ionization. The most abundant ion in Figure 1 was m/z 73 having an ion formula of $[(\text{CH}_2)_6\text{CO}_2\text{H}]^+$. And the relative ion abundances of observed ions of stearic acid were listed in Table 1. The mass spectrum of stearic acid was composed of $\text{CH}_3(\text{CH}_2)_n^+$ (m/z $15+14n$) and $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ (m/z $45+14n$) ion distributions as shown in Figure 1 and Table 1. The m/z 167 is a noise peak from impurity. The relative ion abundances of $\text{CH}_3(\text{CH}_2)_n^+$ decrease continuously by increasing the number of carbon chain of n . The relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ show a specific pattern as shown in Figure 1, which show local maxima at $n=6, 10,$ and 14 . It was very interesting that the relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ show local maxima at $n=6, 10,$ and 14 . Fragmentations of other fatty acids such as palmitic acid, myristic acid, and lauric acid were also investigated. The

$\text{CH}_3(\text{CH}_2)_n^+$ and $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ series were also observed in the mass spectra of the other fatty acids as shown in Figure 2. The relative ion abundances of observed ions of palmitic acid, myristic acid, and lauric acid were listed in Table 1. The relative ion abundances of $\text{CH}_3(\text{CH}_2)_n^+$ of palmitic acid, myristic acid, and lauric acid decrease continuously by increasing the number of carbon chain of n and the relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ show the local maxima as similar to stearic acid. The relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ show the local maxima at $n=6$ and 10 for palmitic acid and myristic acid and at $n=6$ for lauric acid as shown in Figure 2.

Fragmentations of methyl stearate and normal alcohols such as 1-octadecanol, 1-tetradecanol, 1-tridecanol, and 1-dodecanol were investigated to study the effect of functional group on the local maxima. The relative ion abundance distributions of methyl stearate was similar to that of stearic acid. The mass spectrum of methyl stearate was composed of $\text{CH}_3(\text{CH}_2)_n^+$ (m/z $15+14n$) and $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$ (m/z $45+14n$) ion distributions as shown in Figure 3 and Table 1. The relative ion abundance distributions of $\text{CH}_3(\text{CH}_2)_n^+$ decrease continuously by increasing the number of carbon chain, while those of $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$ show the local maxima at $n=6, 10,$ and 14 . The local maxima in ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$ of methyl stearate were also shown in the mass spectrum with low electron impact energy of 30 eV.⁹ Thus, for fatty acids and methyl esters, these local maxima are typical phenomena independently of the strength of electron impact energy.

Mass spectra of normal alcohols such as 1-octadecanol, 1-tetradecanol, 1-tridecanol, and 1-dodecanol with formulae of $\text{CH}_3(\text{CH}_2)_{17}\text{OH}$, $\text{CH}_3(\text{CH}_2)_{13}\text{OH}$, $\text{CH}_3(\text{CH}_2)_{12}\text{OH}$, $\text{CH}_3(\text{CH}_2)_{11}\text{OH}$, respectively, were shown in Figure 4. Typical fragments of normal alcohols are $[\text{M}-\text{H}_2\text{O}]^+$ formed by loss of water.^{3,4} The relative ion abundances of observed ions of normal alcohols were listed in Table 1. Mass spectra of normal alcohols were very different with those of fatty acids and methyl stearate. The mass spectra of normal alcohols were mainly composed of a series of $\text{C}_n\text{H}_{2n-1}^+$ and $\text{C}_n\text{H}_{2n}^+$ fragment ions as shown in Figure 4 and Table 1, while the mass spectra of fatty acids and methyl stearate were mainly

Table 1. Relative ion abundances of observed ions from ionization of fatty acids, methyl stearate, and normal alkyl alcohols

Stearic acid:	55(88.8), 57(85.5), 59(2.1), 60(91.7), 69(42.4), 71(35.3), 73(100.0), 83(21.5), 85(15.3), 87(23.1), 99(3.8), 101(6.2), 113(1.6), 115(10.3), 127(1.0), 129(35.7), 141(0.5), 143(4.7), 157(5.0), 171(6.4), 185(12.8), 199(3.0), 213(4.2), 227(2.7), 241(5.9), 255(0.4), 284(16.2)
Palmitic acid:	57(95.7), 59(1.8), 73(100.0), 87(32.3), 97(14.0), 101(9.0), 115(14.0), 129(49.0), 143(7.5), 157(12.6), 171(13.7), 185(14.8), 199(3.9), 213(14.6), 227(2.2), 256(26.4)
Myristic acid:	55(100.0), 59(3.0), 60(71.5), 69(41.7), 73(80.5), 83(20.9), 87(79.8), 97(11.6), 101(9.4), 115(14.7), 129(92.2), 143(14.1), 157(6.1), 171(11.6), 185(35.4), 199(2.6), 228(19.6)
Lauric acid:	55(100.0), 59(4.9), 73(89.3), 87(51.1), 101(27.3), 115(20.9), 129(59.5), 143(10.2), 157(32.8), 171(7.0), 200(16.9)
Methyl stearate:	55(48.0), 57(17.8), 69(21.0), 71(7.7), 73(57.3), 74(100.0), 85(4.8), 87(41.8), 99(0.7), 101(8.5), 115(2.9), 129(8.5), 141(1.3), 143(38.8), 157(6.1), 171(2.4), 185(6.2), 199(21.6), 213(6.6), 227(0.8), 241(2.1), 255(8.4), 269(0.3), 298(42.8)
1-Octadecanol:	54(10.3), 55(100.0), 57(19.0), 67(13.4), 68(14.5), 69(63.8), 71(2.2), 82(9.9), 83(50.5), 97(36.1), 111(17.1), 125(7.3), 139(2.1), 154(1.0), 168(0.6), 182(0.4), 195(0.2), 209(0.1), 224(0.6), 252(1.1)
1-Tetradecanol:	54(8.0), 55(10.2), 56(100.0), 57(49.1), 58(44.8), 68(26.1), 69(41.5), 70(63.5), 71(38.8), 72(10.9), 82(12.9), 83(48.4), 84(58.4), 85(17.7), 86(5.6), 97(15.7), 98(32.5), 99(10.8), 111(5.4), 112(16.8), 113(5.7), 125(2.9), 126(6.5), 140(1.6), 154(0.5), 169(2.2), 197(2.9)
1-Tridecanol:	54(15.8), 55(100.0), 67(5.4), 68(15.9), 69(55.7), 82(7.1), 83(34.4), 97(17.4), 111(6.0), 125(3.7), 139(0.8), 155(0.5), 183(0.9)
1-Dodecanol:	54(10.5), 55(100.0), 56(14.4), 67(4.6), 68(20.5), 69(33.7), 70(5.7), 82(22.0), 83(6.1), 97(18.3), 111(10.5), 125(0.1), 140(4.8)

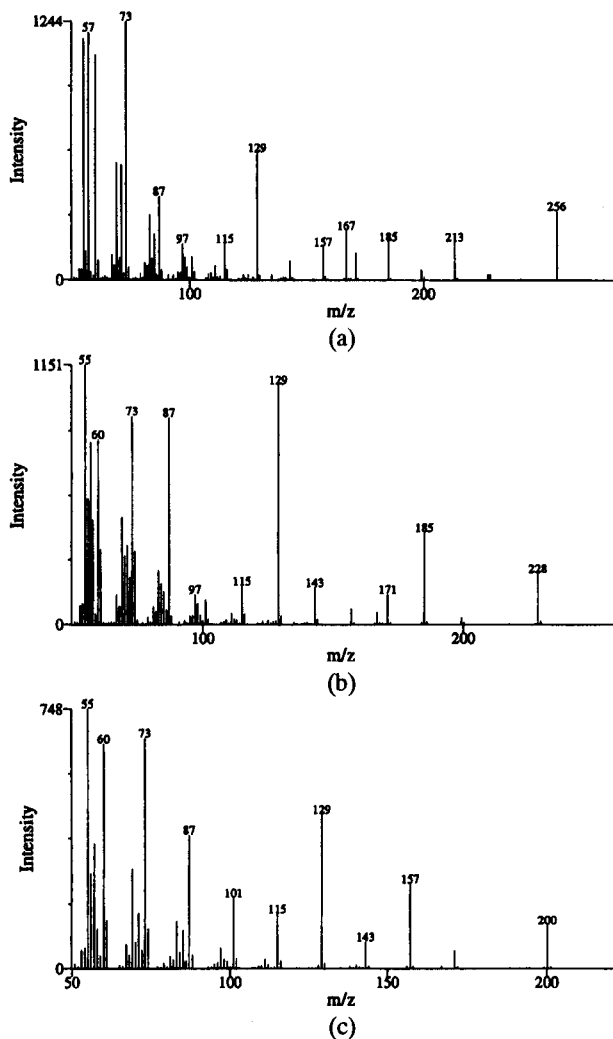


Figure 2. Mass spectra of fatty acids: (a) palmitic acid, (b) myristic acid, and (c) lauric acid. Electron impact energy is 70 eV.

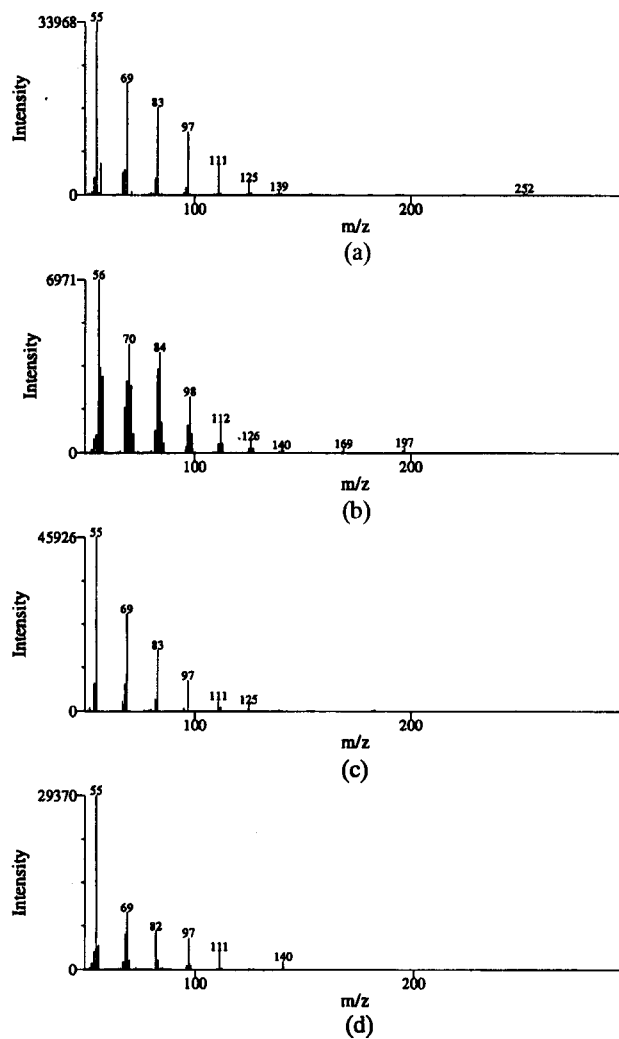


Figure 4. Mass spectra of n-alkyl alcohols: (a) 1-octadecanol, (b) 1-tetradecanol, (c) 1-tridecanol, and (d) 1-dodecanol. Electron impact energy is 70 eV.

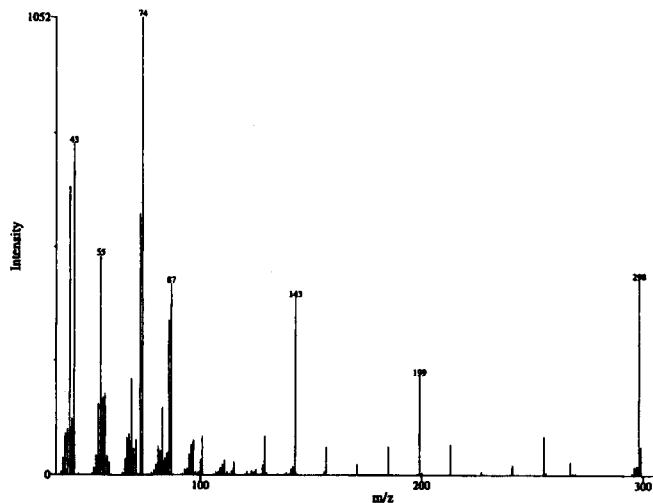


Figure 3. Mass spectrum of methyl stearate. Electron impact energy is 70 eV.

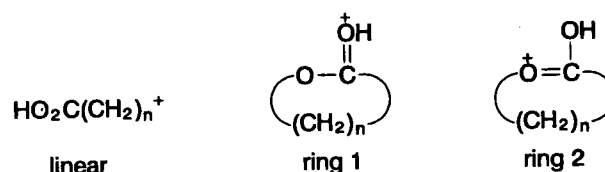
composed of a series of $\text{CH}_3(\text{CH}_2)_n^+$ and $[(\text{CH}_2)_n\text{CO}_2\text{R}]^+$, R is H or CH_3 , as shown in Figures 1-3 and Table 1. The HO

$(\text{CH}_2)_n^+$ ($m/z\ 17+14n$) were not observed in all of mass spectra of 1-octadecanol, 1-tetradecanol, 1-tridecanol, and 1-dodecanol as shown in Figure 4.

From the above results, it was found that the mass spectra of alkyl compounds with acids or methyl esters show the local maxima in relative ion abundance distributions but those with alcohols do not show the local maxima. Here, there are some questions. Why do the relative ion abundance distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ of fatty acids show the local maxima at $n=6, 10, \text{ and } 14$? Are the local maximum phenomena mainly due to a role of a functional group? It can be considered that the carboxyl group of fatty acids could stabilize $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ ions, especially ones with $n=6, 10, \text{ and } 14$.

Typical fragmentations of molecular ion usually are based on heats of formation for fragment ions and heats of reaction for fragmentations.^{7,8} Usually the less the energies for fragmentations were required, the more abundant fragment ions were formed. Heats of formation for fragment ions, $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ and $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$, and counter radicals of $\text{CH}_3(\text{CH}_2)_m$ were calculated by AM1 semiempirical cal-

culations. In order to try to explain the local maximum phenomena in terms of thermodynamic data, heats of reaction for fragmentations of ionized stearic acid and methyl stearate were calculated. The results are summarized in Tables 2 and 3. Heats of reaction for the fragmentations are 80-110 kJ/mol for both of stearic acid and methyl stearate. From the heats of reaction for the fragmentations, it was not found that favorabilities for the formations of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ and $[(\text{CH}_2)_n\text{CO}_2\text{CH}_3]^+$ with $n=6, 10,$ and 14 . Thus, the reasons of the local maxima are not due to the heats of reaction for the fragmentations. The $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ fragment ions can have structures with one linear and two ring structures¹⁵ as shown in Scheme 1. The calculational results for the heats of formation of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n=3-14$ were summarized in Table 4. The ring structures were much more stable than the linear one. And ring 1 structure was more stable than ring 2 one. But, it could not be found that



Scheme 1. Plausible structures of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$.

the $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ fragment ions with $n=6, 10,$ and 14 have specific structural stabilities. The heats of formation of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ continuously decrease with the increase of the cationic size independently of their structures. Thus, the local maximum phenomena could not be also explained by the heats of formation for fragment ions. What is the reason of the local maxima?

Stearic acid and methyl stearate have a long linear hydrocarbon chain. Energetic favorabilities between linear and cyclic structures of neutral and ionized molecules for stearic acid and methyl stearate were compared in terms of heats of formation. Heats of formation for neutral molecules with linear and cyclic structures of stearic acid were -885 and -828 kJ/mol, respectively, and those of methyl stearate were -836 and -794 kJ/mol, respectively. Neutral molecules with linear structures are more stable than those with cyclic structures by 57 and 42 kJ/mol for stearic acid and methyl stearate, respectively. However, for ionized molecules, the aspect is reverse to neutral molecules. Heats of formation for molecular ions with linear and cyclic structures of stearic acid were 171 and -15 kJ/mol, respectively, and those of methyl stearate were 181 and 145 kJ/mol, respectively. Molecular ions with cyclic structures are more favorable than those with linear structures by 186 and 36 kJ/mol for stearic acid and methyl stearate, respectively. Therefore, stearic acid and methyl stearate will be linear forms when they are neutral, while they will have cyclic structures when they are ionized.

From the result above, it can lead to a conclusion that neutral molecules of stearic acid and methyl stearate with linear structures are ionized by electron impact, then the structures of ionized molecules are changed into cyclic ones. From the mass spectra and the AM1 semiempirical calculations, it can be found that the distances between car-

Table 2. Heats of reaction for fragmentations of stearic acid. Values in parentheses are heats of formation in kJ/mol. All of molecular ion, fragment ions, and radicals have linear structures

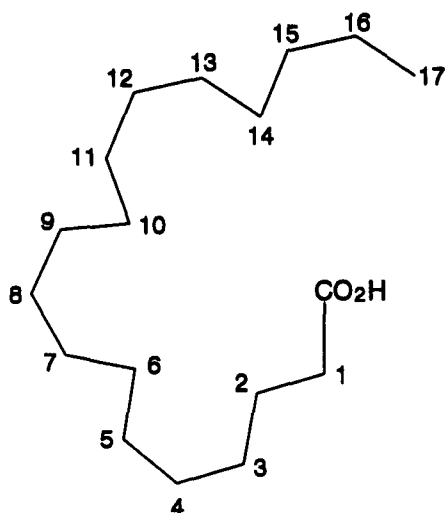
Fragmentation	ΔH (kJ/mol)
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}^+$ (171)	
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{16}^+$ (149) + CH_3 (131)	109
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{15}^+$ (177) + CH_2CH_3 (76)	82
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{14}^+$ (206) + $(\text{CH}_2)_2\text{CH}_3$ (51)	86
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{13}^+$ (236) + $(\text{CH}_2)_3\text{CH}_3$ (23)	88
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{12}^+$ (265) + $(\text{CH}_2)_4\text{CH}_3$ (-6)	88
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{11}^+$ (295) + $(\text{CH}_2)_5\text{CH}_3$ (-35)	89
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_{10}^+$ (325) + $(\text{CH}_2)_6\text{CH}_3$ (-63)	91
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_9^+$ (356) + $(\text{CH}_2)_7\text{CH}_3$ (-92)	93
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_8^+$ (387) + $(\text{CH}_2)_8\text{CH}_3$ (-121)	95
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_7^+$ (420) + $(\text{CH}_2)_9\text{CH}_3$ (-149)	100
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_6^+$ (454) + $(\text{CH}_2)_{10}\text{CH}_3$ (-178)	105
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_5^+$ (481) + $(\text{CH}_2)_{11}\text{CH}_3$ (-207)	103
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_4^+$ (494) + $(\text{CH}_2)_{12}\text{CH}_3$ (-235)	88
$\longrightarrow \text{HO}_2\text{C}(\text{CH}_2)_3^+$ (538) + $(\text{CH}_2)_{13}\text{CH}_3$ (-264)	103

Table 3. Heats of reaction for fragmentations of methyl stearate. Values in parentheses are heats of formation in kJ/mol. All of molecular ion, fragment ions, and radicals have linear structures

Fragmentation	ΔH (kJ/mol)
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{CH}_3^+$ (181)	
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{16}^+$ (156) + CH_3 (131)	106
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}^+$ (196) + CH_2CH_3 (76)	91
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{14}^+$ (223) + $(\text{CH}_2)_2\text{CH}_3$ (51)	93
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{13}^+$ (249) + $(\text{CH}_2)_3\text{CH}_3$ (23)	91
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{12}^+$ (271) + $(\text{CH}_2)_4\text{CH}_3$ (-6)	84
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{11}^+$ (306) + $(\text{CH}_2)_5\text{CH}_3$ (-35)	90
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{10}^+$ (336) + $(\text{CH}_2)_6\text{CH}_3$ (-63)	92
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_9^+$ (366) + $(\text{CH}_2)_7\text{CH}_3$ (-92)	93
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_8^+$ (392) + $(\text{CH}_2)_8\text{CH}_3$ (-121)	90
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_7^+$ (430) + $(\text{CH}_2)_9\text{CH}_3$ (-149)	100
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_6^+$ (455) + $(\text{CH}_2)_{10}\text{CH}_3$ (-178)	96
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_5^+$ (475) + $(\text{CH}_2)_{11}\text{CH}_3$ (-207)	87
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_4^+$ (510) + $(\text{CH}_2)_{12}\text{CH}_3$ (-235)	92
$\longrightarrow \text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_3^+$ (553) + $(\text{CH}_2)_{13}\text{CH}_3$ (-264)	101

Table 4. Heats of formation for $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ fragment ions. Cationic types were shown in Scheme 1. Units are kJ/mol

Carbon Number n	Cationic type		
	linear	ring 1	ring 2
3	538	338	353
4	494	271	297
5	481	253	276
6	454	225	262
7	420	210	246
8	387	185	232
9	356	163	198
10	325	121	156
11	295	95	121
12	265	84	100
13	236	56	75
14	206	21	51



Scheme 2. Skeletal structure for cyclic molecular ion of stearic acid.

boxyl group and methylene with $n=6, 10,$ and 14 are closer than those of the adjacent methylene in the structures of ionized molecules of fatty acids as shown in Scheme 2. The $[(CH_2)_nCO_2H]^+$ fragment ions can be formed from molecular ion by C-C bond breakings or rearrangements to form cyclic fragment ions. Scheme 2 is a carbon skeletal structure of molecular ion of stearic acid. Carbons of methylene were numbered from 1 to 17. The carbon number 1 indicates a methylene carbon bonded to carboxyl group. The structures of molecular ion of fatty acids were studied in detail to investigate the distances between carboxyl group and methylene. Heats of formation for cyclic molecular ion of fatty acids obtained from AM1 calculations were $-15, 41, 87,$ and 141 kJ/mol for stearic acid, palmitic acid, myristic acid, and lauric acid, respectively. Figures 5-8 were cyclic structures of lauric acid, myristic acid, palmitic acid, and stearic acid, respectively, obtained from AM1 calculations. It was found that the distances between carboxyl carbon and methylene carbon with carbon number of $n=6, 10,$ and 14

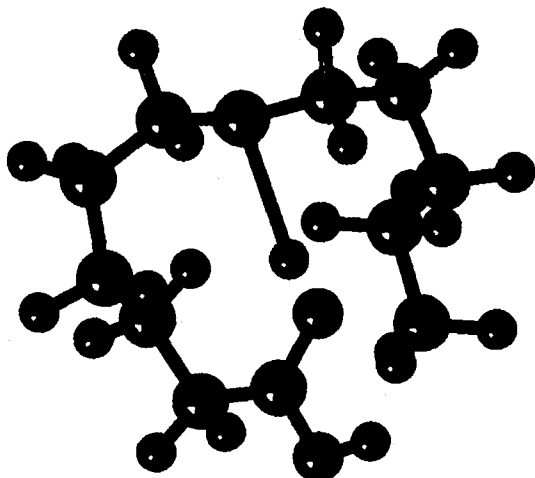


Figure 5. A cyclic structure of molecular ion of lauric acid obtained from AM1 semiempirical calculation. The heat of formation for this structure was 141 kJ/mol.

were closer than those of the other methylene as shown in Figures 5-8.

The distances between carboxyl carbon and methylene carbon were obtained from Figures 5-8 and listed in Table 5. These local maximum phenomena could be explained by the cyclic structure of ionized molecule and the distances between carboxyl group and methylene of molecular ion. The distances between carboxyl carbon and methylene carbon of the ionized fatty acids increase from about 1.5 to 4.3 Å with the increase of the methylene carbon number, $n,$ from 1 to 4 (or 5) and decrease to about 4.0-4.1 Å with the increase of n from 5 to 6. The ion intensities of $[(CH_2)_nCO_2H]^+$ with $n=2$ are the most abundant among those of $[(CH_2)_nCO_2H]^+$. The ion intensities decrease with the increase of the methylene chain from $n=2$ to 5 and remarkably increase at $n=6$ as listed in Table 1. The distances increase again from about 4.0-4.1 to 4.9-5.3 Å by increasing n from 6 to 8 and decrease to about 3.9-4.4 Å by increasing n from 8 to 10. The ion intensities notably decrease as the

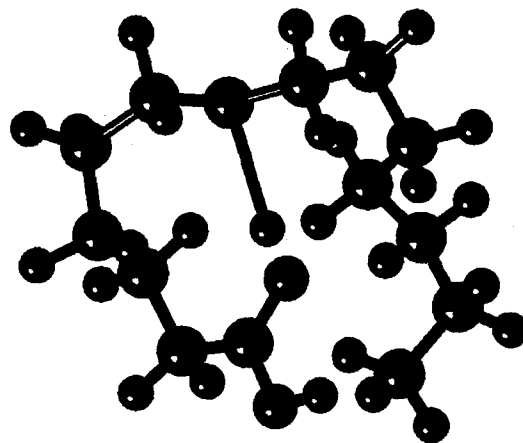


Figure 6. A cyclic structure of molecular ion of myristic acid obtained from AM1 semiempirical calculation. The heat of formation for this structure was 87 kJ/mol.

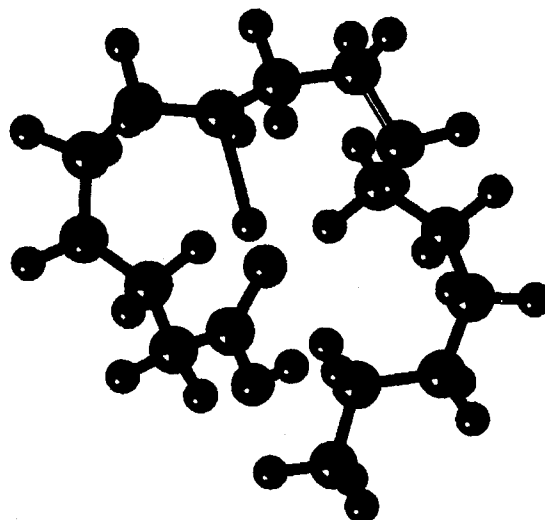


Figure 7. A cyclic structure of molecular ion of palmitic acid obtained from AM1 semiempirical calculation. The heat of formation for this structure was 41 kJ/mol.

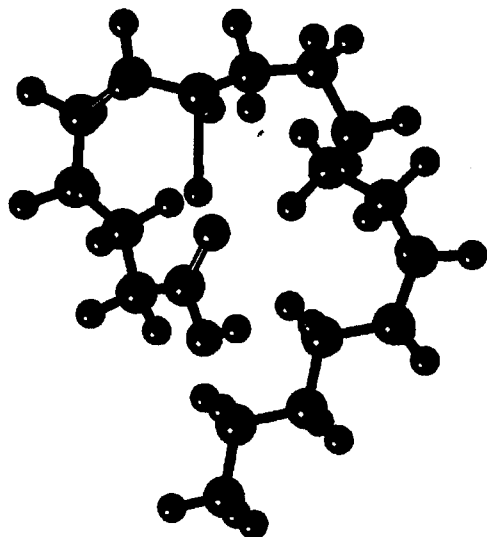


Figure 8. A cyclic structure of molecular ion of stearic acid obtained from AM1 semiempirical calculation. The heat of formation for this structure was -15 kJ/mol.

size of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ increases from $n=6$ to 7 and, after $n=7$, slightly increase or decrease until $n=9$. The ion intensities increase with the increase of n from 9 to 10 so that the ion intensity distributions show the local maxima at $n=10$ for myristic, palmitic, and stearic acids. The distances notably increase with the increase of n from 10 to 11, while the ion intensities remarkably decrease with the increase of n from 10 to 11. By increasing n from 11 to 14, the distances decrease and the ion intensity distribution for stearic acid shows the local maximum at $n=14$. Thus, the results lead to a conclusion that the local maxima in the ion intensity distributions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ of the fatty acids are closely related with the distances between carboxyl group and methylene of the cyclic structures of ionized molecules.

The $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ can have either cyclic or ring structure. The local maxima were not explained only by the heats of formation for the fragmentations when the fragment ions have only one type of linear or ring structure as discussed previously. But, it can be explained with ease if the $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n=6, 10,$ and 14 have ring structures and the other $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ have linear structures. The ring structures are energetically much more favorable than the linear ones by over 150 kJ/mol as listed in Table 4. Since the distances between carboxyl group and methylene with $n=6, 10,$ and 14 in the ionized fatty acids are short, it can be possible to form the ring structure. The other plausible explanation is based on loose transition state. If all of the $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ fragment ions have ring structures, the shorter the distance between carboxyl group and methylene is the more favorable the fragmentation is. It can be considered that the formations of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n=6, 10,$ and 14 have loose transition states since the distances between carboxyl group and methylene are so short that the geometry of the fragment ion is similar to that of the ionized molecule. On the other hand, the formations of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n \neq 6, 10,$ and 14 can have activation barriers to rearrange into a ring form since the distances between carboxyl group and methylene are long. Thus, the forma-

Table 5. Distances between carboxyl and methylene carbons of fatty acids such as lauric acid, myristic acid, palmitic acid, and stearic acid. Values were obtained from AM1 semiempirical calculations. Carbon number was shown in Scheme II. Units are Å

Carbon Number n	Cationic type			
	lauric	myristic	palmitic	stearic
1	1.477	1.484	1.479	1.486
2	2.528	2.507	2.545	2.497
3	3.098	3.102	3.317	3.190
4	4.254	4.289	4.339	4.336
5	4.397	4.397	4.335	4.294
6	4.110	4.084	3.993	4.057
7	4.444	4.474	4.437	4.550
8	4.921	5.144	5.126	5.260
9	4.176	4.548	4.549	4.756
10	3.892	4.152	4.322	4.417
11	3.548	4.754	5.074	5.376
12		4.400	4.711	5.291
13		3.507	4.566	5.091
14			3.421	3.801
15			4.070	4.390
16				3.814
17				5.034

tions of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n=6, 10,$ and 14 can be more favorable than those of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n \neq 6, 10,$ and 14 . And it can be shown that the relative ion intensities of $[(\text{CH}_2)_n\text{CO}_2\text{H}]^+$ with $n=6, 10,$ and 14 are more intensive than the other ones.

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