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The Importance of Intramolecular Associations in the Chemical Ionization Mass Spectra of Monoenoic and Monoepoxy Fatty Acid Methyl Esters

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Abstract: The isobutane chemical ionization mass spectra are reported for some monoenoic fatty acids, methyl esters, and monoepoxy methyl esters. The enhanced fragmentation observed in the epoxy methyl esters is explained in terms of exothermic intramolecular hydrogen bond formation in the protonated molecular ions. The presence of intramolecular hydrogen bonding in bifunctional ions is supported by the observed efficient gas phase hydrolysis and transesterification reactions of the epoxy methyl esters when water and deuteriomethanol are used as reagent gases. The spectra of the epoxide derivative indicate the position, but not the stereochemistry, of the double bond in the olefinic side chain.

This study of the chemical ionization spectra of unsaturated fatty acids was initiated as an effort to determine the position and stereochemistry of the double bond in the alkyl chain. The data presented here demonstrate that the epoxide derivative can be useful in determining the position of the double bond. On protonation, extensive cleavage of the alkyl chain occurred at the epoxide ring by way of a long range interaction between the epoxide and carboxymethyl functions, but the subtle energy difference between the epoxide stereoisomers was not sufficient to influence the fragmentation pattern. This paper is directed toward understanding the nature of these long range interactions and how they play such a dominant role in the fragmentation of bifunctional molecules.

Chemical ionization induced fragmentation of monofunctional molecules appears to occur as a unimolecular dissociation of the protonated molecules, while intramolecular interactions in polyfunctional molecules have been reported to stimulate fragmentation or to stabilize the protonated molecular ion. Protonated alkyl esters have been shown to fragment by unimolecular mechanisms to give RCO^+, $RCO_2H_2^+$, and alkyl ions from the alcohol chain.[1] The relative abundance of the protonated molecular ion and its fragments are controlled in simple esters by the size and complexity of the alcohol group.[2-6] The dissociations leading to $RCO_2H_2^+$ and alkyl (CH_3^+) ions are endothermic for methyl esters and are not observed for these compounds.[1]

Chemical ionization mass spectra of dibasic acid esters fragment by the same mechanisms.[7] In addition, cyclic fragment ions are observed when the carboxyalkyl functions can become sterically proximate. For example, the protonated cyclic anhydride ion, *m/e* 149, was found only in the orthophthalate esters. The dominant feature of the ortho isomer spectrum, however, is the increased stability of the protonated molecular ion relative to the meta and para isomers.[7]

Carboxylic acids fragment on protonation to give the acylonium ion, RCO^+, with loss of water. Loss of CO_2H_2 occurs when it leads to the formation of a stable ion such as the immonium ion, $RCH{=}NH_2^+$, observed in α-amino acid spectra.[8,9] The amount of amino acid fragmentation is also increased through bifunctional interactions such as those observed in the aromatic amino acids.[8,9]

The isobutane chemical ionization induced fragmentation of monoenoic long chain carboxylic acids and methyl esters yields the acylonium ion with loss of water or alcohol as the only significant cleavage product. These observations are analogous to the simple carboxylic acids and methyl esters previously reported.[1] The epoxy derivatives, however, undergo more extensive fragmentation through pathways not available to the isolated functions. The data presented suggest a long range interaction between the epoxy and carboxymethyl functions which is explained by way of a proton complex postulate in which the epoxy and carboxymethyl oxygens act as ligands. The heat of formation

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of this complex can provide the energy potential for subsequent fragmentation. The role of the epoxy ester as a bidentate ligand is supported by the observation of gas phase hydrolysis and transesterification products when water or deuteriomethanol was used as the reagent gas.

Experimental Section

The experiments were carried out using an AEI MS-902 high resolution mass spectrometer which has been modified to operate under chemical ionization conditions. Details of the ion source modification have been described elsewhere.[10] Sample introduction was by way of an unheated direct insertion probe in which the sample was carried into the ionization chamber by the reagent gas flow.

The fragmentation patterns of the compounds reported here were sensitive to changes in the temperature[5] and pressure of the reagent gas in the ion chamber. With higher temperatures and lower reagent gas pressures (>0.5, <0.9 Torr) the spectra showed substantially greater fragmentation. Care was taken, therefore, to maintain consistent ion chamber conditions of 200° and approximately 0.6 Torr for those samples in which isobutane was used as the reagent gas. With these precautions duplicate runs gave reproducible data. The comparative significance of these spectra was supported by spectra of 1:1 mixtures of C_{16} and C_{18} epoxy esters. The relative ion abundances present in the mixtures were within 2% of those in the spectra of the pure compounds. Reported spectra indicate peaks of more than 1% relative abundance.

The H_2O, D_2O, and $DOCD_3$ spectra were obtained by bleeding these reagents into a stream of methane which then entered the ionization chamber at a pressure maintained at 0.6 Torr. The concentration of the additives in the methane was the minimum required to quench the methane ionization products to <1% total ion current. In each case the isotopic purity of the deuterio additive ions in the plasma was greater than 80% as evidenced by relative ion abundance measurements. Under these conditions the relative concentration of the additive was minimized as were ions formed by their association.

The fatty acids and fatty acid esters were chromatographically pure when analyzed under conditions that were capable of separating homologs and stereoisomers. The epoxides of these methyl esters were prepared by oxidation with excess *m*-chloroperbenzoic acid in hexane at room temperature for 24 hr. The reaction mixture was treated with sodium bisulfite to destroy the peroxide and extracted with aqueous potassium bicarbonate to remove the *m*-chlorobenzoic acid. The organic soluble material was chromatographed on silica gel with benzene. The chromatographic conditions were capable of separating the epoxy ester from unreacted enoic ester as well as the respective carboxylic acids. The epoxides were eluted from the silica gel with methylene chloride and the spectra taken.

The deuteriomethyl esters were prepared from the epoxy acid and deuteriodiazomethane using the reported procedure.[11] Proton exchange of the methylene hydrogens α to the carboxymethyl function was achieved by treatment of the epoxy methyl ester with sodium methoxide in anhydrous methanol-*O*-d_1 for 7 days at room temperature; 80% exchange was achieved and no evidence of sample degradation could be found on tlc or in the mass spectra.

Results

The isobutane chemical ionization spectra of some monoenoic fatty acids and their methyl esters are shown in Table I. In each spectrum the base peak was the protonated molecular ion (MH^+). Loss of water or methanol to give an acylonium ion was less than 10% of MH^+. Cleavage of the alkyl portion of the molecule resulting from protonation of the double bond totaled less than 15% of the total ion current for each compound. The carbon–carbon bond cleavage was nearly random due to extensive charge migration and no correlation with the original position of the double bond could be made.

Table I. Isobutane Chemical Ionization Spectra of Monoenoic Fatty Acids and Methyl Esters at 200°

Compound	Rel intensities		
	MH^+	$-H_2$	$-HOR^a$
cis-Octadec-9-enoic acid	100	10	6
trans-Octadec-9-enoic acid	100	7	5
Methyl *cis*-octadec-6-enoate	100	2	2
Methyl *cis*-hexadec-9-enoate	100	3	6
Methyl *cis*-octadec-9-enoate	100	1	6
Methyl *trans*-octadec-9-enoate	100	4	5
Methyl *cis*-octadec-11-enoate	100	3	8
Methyl *trans*-octadec-11-enoate	100	3	5

[a] R = H or CH_3 for carboxylic acids and methyl esters, respectively.

The isobutane chemical ionization spectra of some monoepoxy fatty acid methyl esters is shown in Table II. In each spectrum the most intense peak was that of the protonated molecule. The ions with the intact molecular structure carried about 30% of the total ion current in the epoxide relative to 70% of the total current in the corresponding olefinic methyl esters. Methanol loss in the epoxy ester was enhanced relative to the corresponding enoic ester in respect to the percent of base and percent of total ion current; water loss was also enhanced relative to that observed in an epoxy alkane. The isobutane chemical ionization spectrum of epoxy 1,2-dodecane at 200°, for example, shows loss of water with a relative abundance of 9% of the protonated molecular ion. There was no evidence of fragments resulting from carbon–carbon bond cleavage in this spectrum.

In addition to the enhanced losses of water and methanol the epoxy ester spectra show a number of ions apparently resulting from participative interaction between two functional groups. Three ions were formed from cleavage of the carbon–carbon bond in the epoxide ring. These correspond to loss of the elements of neutral alkene, acyclic alkane, and aldehyde. The charge in each case was retained by the carboxymethyl side of the epoxide. No ions from the alkyl side were observed. Each of the ions formed upon epoxide ring cleavage can undergo further fragmentation. The major pathways involve loss of the alkene (4–18% MH^+) or aldehyde (2–24% MH^+) and each of these epoxide cleavage products can lose methanol.

The ion resulting from initial loss of water from the epoxide function fragments further with loss of methanol from the ester function. This ion can then lose another molecule of water. Similarly, initial loss of methanol from the methyl ester can sequentially lose two molecules of water.

Discussion

Intramolecular interactions in which acid-catalyzed bond cleavage is facilitated by nucleophilic displacement by an adjacent functional group are well known in solution chemistry.[12] Similar bifunctional interactions have been observed in electron impact mass spec-

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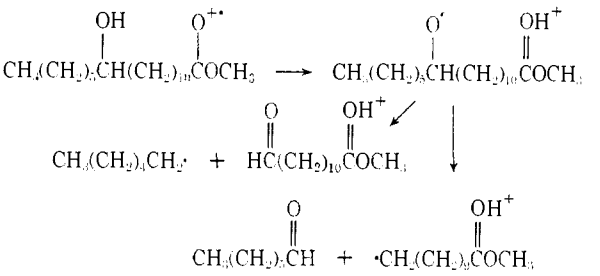
Table II. Isobutane Chemical Ionization Spectra of Epoxy Fatty Acid Methyl Esters at 200°

Compound	Rel intensity											
	MH^+	$-H_2$	$-H_2O$	$-HOCH_3$	$-H_2O$, $HOCH_3$	$-2H_2O$, $HOCH_3$	$-CHR^a$	$-CH_3R$	$-OCHR$	$(MH - CH_3R)^+$ $-CO$	$(MH - CHR)^+$ $-HOCH_3$	$(MH - OHCR)^+$ $-HOCH_3$
Methyl *cis*-7,8-epoxyoctadecanoate	100	2	27	30	4	<1	4	<1	2	<1	1	1
Methyl *cis*-9,10-epoxyhexadecanoate	100	3	85	27	11	1	18	2	15	3	3	1
Methyl *cis*-9,10-epoxyoctadecanoate	100	3	71	18	7	1	13	3	14	3	2	1
Methyl *trans*-9,10-epoxyoctadecanoate	100	3	73	22	8	1	6	3	6	3	2	1
Methyl *cis*-11,12-epoxyoctadecanoate	100	2	80	22	7	1	11	2	21	2	2	<1
Methyl *trans*-11,12-epoxyoctadecanoate	100	3	100	25	10	1	14	2	24	3	2	1

[a] R = $(CH_2)_6CH_3$.

trometry[13-17] when the parent ion has a lifetime sufficiently long to allow the conformational changes leading to functional group interactions. In general, this type of long range interaction is optimal when it occurs through a five-, six-, or seven-membered ring,[13] but can occur through larger cyclic intermediates.[13,18] Another type of long range interaction involves transfer of an atom or atoms through a cyclic intermediate leading to fragmentation pathways not open to the isolated functions. A long range proton transfer has been observed in the electron impact spectrum of methyl 12-hydroxyoctadecanoate which leads to radical cleavage adjacent to the hydroxyl function.[19]



Chemical ionization induced fragmentation of monofunctional molecules proceeds through protonation of the functional group by the reactant ion with energy transfer related to the relative proton affinities of the respective conjugate bases.[20] Molecular cleavage occurs if the transferred energy is sufficient to provide the necessary activation energy for the fragmentation process with the rate of decomposition qualitatively following the stability of the ions produced.[2] The relative rate of a given cleavage reaction should, therefore, be increased by an intramolecular reaction that would stabilize the ionic product. The chemical ionization induced fragmentation of polyfunctional amino acids[8,9] and amphetamines[21] can be correlated to the electronic properties of neighboring groups. For example, loss of ammonia is a minor feature in the spectra of alkylamines but it assumes greater importance as aromatic groups are introduced which can participate in stabilizing the ion formed on ammonia loss.[21] Intramolecular interactions have been observed in protonated diamino-,[22] dihydroxy-, and dithioalkanes[23] which increase the stability of the protonated molecular ion relative to that of their monofunctional analogs.

The isobutane chemical ionization spectra of epoxy methyl esters are dominated by the effects of long range bifunctional interactions. Since the participating func-

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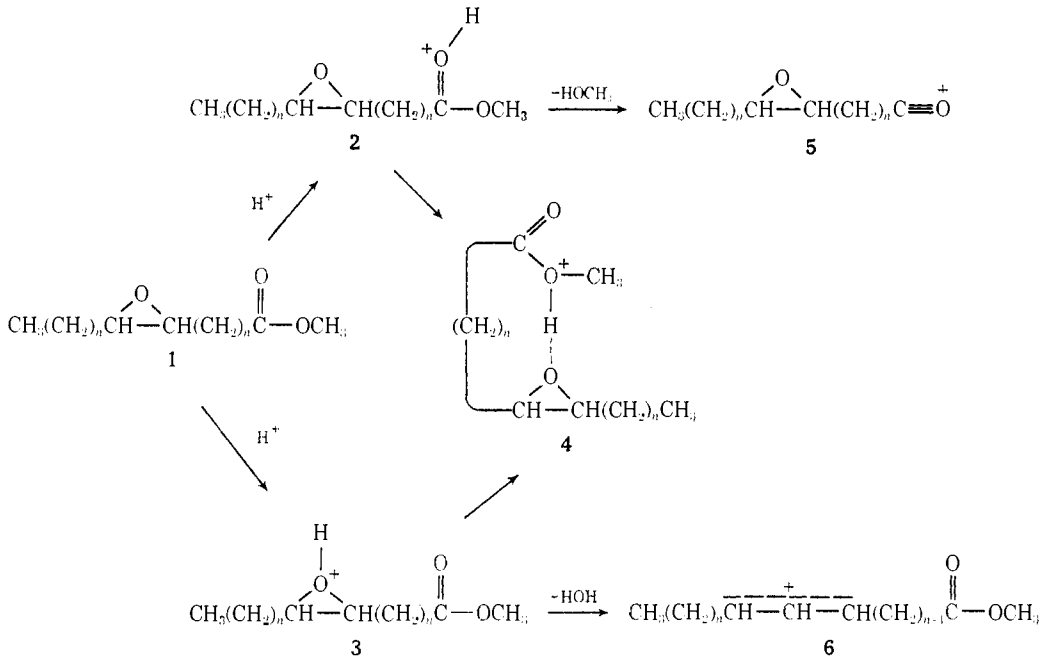

(1)

tional groups were separated in some cases by nine methylene units the extent of their interactions was more prevalent than expected. A nucleophilic cyclization mechanism may operate in which a nonbonded electron pair of the epoxide associates with the electron deficient region of the protonated methyl ester function. This could lower the activation energy of the methanol loss or stabilize the resultant ion thus enhancing the probability of methanol cleavage. Nucleophilic interactions, however, become less significant as the separation between groups increases so that a group tends to act as an isolated function. These exceptionally effective long range interactions could be rationalized by postulating a gas phase conformation for these fatty acids in which the molecule folded back upon itself so that the functional groups became spacially proximate.[24] Since long chain molecules may well populate folded gas phase conformations there is no reason to exclude nucleophilic interactions as a possible mechanism of fragmentation in this system.

Nevertheless, this mechanism could be superseded by another mechanism involving the formation of a proton complex with the epoxide and ester oxygens complexing with the hydrogen ion. The following discussion of fragmentation pathways describes how this mechanism could operate.

Equation 1 represents the initial protonation of an epoxy ester **1** in which proton transfer can occur at either of the separated functions leading to ions **2** or **3** or, if a folded conformation exists, proton complex **4** could form directly.

Ions **2** or **3** may fragment without any intramolecular hydrogen bonding and eliminate methanol or water, to give **5** or **6**, respectively. In each case such unassisted cleavage should lead to ions with an intensity of less than 10% of MH^+ from comparison with the corresponding monofunctional compounds. The initial elimination of methanol and water from ions **2** and **3** could be facilitated nucleophilic displacement by the epoxy or ester functions. The sequential eliminations of two molecules of water following methanol eliminations from **2**, for example, would be inhibited if the initial fragment ion were stabilized so that this does not appear to be the sole mechanism leading to facilitated fragmentation.

Indeed, intramolecular hydrogen bonding to form the cyclic proton complex **4** appears more probable than nucleophilic displacement. The electron pair of an epoxy oxygen approaching a protonated ester function could associate by forming a hydrogen bond with the H–O proton or by donating electron density to the deficient p orbital of the carbonyl carbon. The most exothermic interaction available to the approaching epoxy oxygen would be hydrogen bonding allowing the positive charge to be linearly distributed. Further, the steric requirement for the formation of hydrogen bonds is less than that required for σ-bonding with a $p-\pi$ orbital.[25] This would be augmented to the extent that electric field effects of the nonsolvated protonated carboxy function could direct the spacial orientation of the approaching epoxide dipole.

The exothermic proton complex formation may in fact occur with an enthalpy greater than that of the initial proton transfer. The proton affinity of methyl esters has been found to be -205 ± 3 kcal/mol.[26] The net enthalpy change for proton transfer from *t*-$C_4H_9^+$ ion to an isolated ester function was calculated to be -10 kcal/mol (eq 2). This energy is distributed between the product isobutylene and protonated ester molecules as kinetic, rotational, or vibrational energy. The enthalpy change on hydrogen bond formation between a protonated ester and the nonbonded electron pair of the oxygen in water was found to be -14 kcal/mol[2] (eq 3). The enthalpy of formation of

$$RCOOR' + t\text{-}C_4H_9^+ \longrightarrow RCOOR'H^+ + i\text{-}C_4H_8 \qquad \Delta H = -10 \text{ kcal/mol} \quad (2)$$

$$RCOOR'H^+ + HOH \longrightarrow (RCOOR'H{-}HOH)^+ \qquad \Delta H = -14 \text{ kcal/mol} \quad (3)$$

(24) S. Meyerson and L. C. Leitch, *J. Amer. Chem. Soc.*, **93**, 2244 (1971).

(25) P. A. Kollman and L. C. Allen, *Chem. Rev.*, **72**, 285 (1972).

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ion **4** by hydrogen bond formation between the protonated ester and epoxy oxygen of **2** should be of the same magnitude. Since this heat of complex formation would be significantly greater than an entropy requirement as demanding as $\Delta S = -10$ eu, hydrogen bond formation would be a driving force in the direction of complex formation. The energy released into the molecular structure as vibrational energy would be available to provide the activation energy leading to the observed fragment ions until dissipated through an ion molecule collision in the ion source or until the hydrogen bond is broken. This internal potential energy can be utilized in fragmentation if the rate-determining step in the fragmentation process occurs prior to cleavage of the hydrogen bond. This condition cannot be met in the case of the bifunctional 1,10-diamino-, dihydroxy-, and dithiodecanes.[23] The protonated molecular ions of these molecules can either ring open or dissipate their internal vibrational energy through collision[27] leading to the observed stabilization.

Epoxy esters also appear to act as bidentate ligands with reagent gases that can participate in hydrogen bond formation.[28] The ion D_3O^+ was the major component of the ion plasma formed in the chemical ionization source when D_2O was used as the reagent gas. Ionization of methyl *cis*-9,10-epoxyhexadecanoate with D_3O^+ yields a spectrum (Table III) which shows the same fragmentation pattern in the isobutane spectrum of Table II. An additional ion, *m/e* 273, was present with an abundance 20% of the deuterated molecular ion (MD^+) and a precise mass corresponding to that of the deuterated epoxy acid. Similarly, when methanol-d_4 was used as the reagent gas (eq 4, R = CD_3) an ion having a mass 3 amu higher than the deuterated epoxy methyl ester was present in the spectrum (Table III).

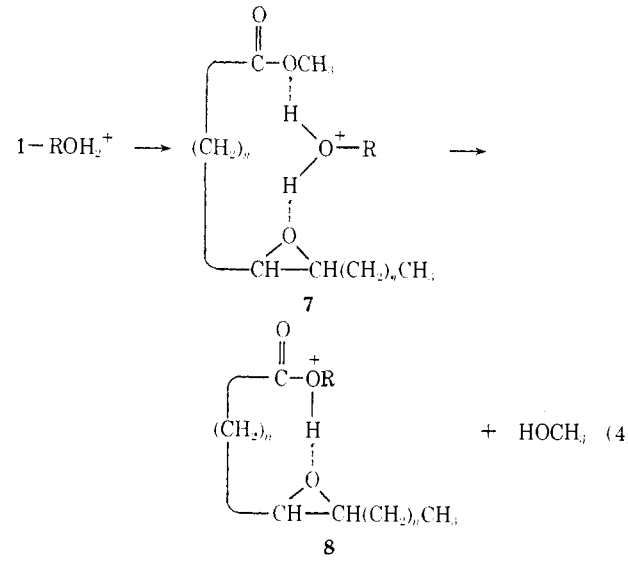
Table III. Methyl *cis*-9,10-Epoxyhexadecanoate Chemical Ionization Spectra with D_2O and $DOCD_3$

Ion[a]	*m/e*	Rel abundance D_2O (50°)	Rel abundance $DOCH_3$ (90°)
$MD^+ + 3$	289		40
MD^+	286	71	100
MH^+	285	15	21
$MD^+ - 13$	273	20	
	272	9	
	270	7	10
$MD^+ - HOD$	267	100	96
$MD^+ - CH_3OD$	253	71	71
$MD^+ - HOD(H), CH_3OH(D)$	235	73	64
$MD^+ - HOD(H), HOH, CH_3OH(D)$	217	14	16
	191		16
$MD^+ - CHR^b$	188	17	17
	187	5	6
$MD^+ - CH_2DR$	185	7	3
$MD^+ - OHCR$	172	17	16
$MD^+ - ODCR$	171	14	15
$(MD - CHR)^+ - DOCH_3$	157	6	4
$(MD - CH_2R)^+ - CO$	155	16	13
$(MD - CH(D)OR)^+ - D(H)OCH_3$	139	9	6

[a] Represented for ions formed from D^+ transfer. [b] R = $(CH_2)_5CH_3$.

This ion corresponded to the trideuteriomethyl ester and was present as 40% of MD^+ at a source temperature of 90° and as 100% of MD^+ at 300°. Under the same conditions the D_2O and deuteriomethanol chemical ionization spectra of methyl *cis*-hexadec-9-enoate showed no evidence of gas phase hydrolysis or transesterification.

This suggests that the collision complex between the ester function and H_3O^+ which could normally lead to proton transfer to the ester group could have interacted with the epoxy oxygen by formation of a hydrogen bond as shown in eq 4. The indicated reactant ion



complex **7** could have a sufficient lifetime and energy potential to transfer a proton to the $COOCH_3$ function while maintaining the hydrogen bond to the HOR molecule, eliminate methanol, and reform a carbonyl oxygen bond with HOR to give the gas phase hydrolysis product, **8**, R = H. No significant ion current corresponding to the nominal mass of **7** was observed under the ionization conditions employed in this experiment. The factors influencing gas phase hydrolysis and transesterification reactions will be discussed in more detail in a later publication.[27]

Discussion of the fragmentation process leading from the proton complex **4** was based on the presence of the relevant metastable ions (Table IV) and precise mass measurements of fragment ions. Chemical ionization induced fragmentation of methyl *cis*-9,10-epoxyhexade-

Table IV. Metastable Ions from Methyl *cis*-9,10-Epoxyoctadecanoate at 200° Using Isobutane

Ion	*m/e*[a]	Transition	Calcd M*	Obsd M*
$MH^+ - H_2O$	295	313 → 295	278.0	278.0
$MH^+ - HOCH_3$	281	313 → 281	252.3	252.3
$(MH - H_2O)^+ - HOCH_3$	263	295 → 263	234.5	234.7
$(MH - HOCH_3)^+ - H_2O$	263	281 → 263	246.2	246.1
$(MH - H_2O,HOCH_3)^+ - H_2O$	245	263 → 245	228.2	228.2
$MH^+ - C_9H_{18}$	187	313 → 187	111.7	
$MH^+ - C_9H_{20}$	185	313 → 185	109.3	109.3
$MH^+ - C_9H_{18}O$	171	313 → 171	93.4	
$(MH - C_9H_{18})^+ - HOCH_3$	155	187 → 155	128.6	128.6
$(MH - C_9H_{18}O)^+ - HOCH_3$	139	171 → 139	113.0	113.0

[a] Precise mass determinations of the parent and fragment ions were determined with deviations less than 1 mmu from the calculated ionic formulas indicated above.

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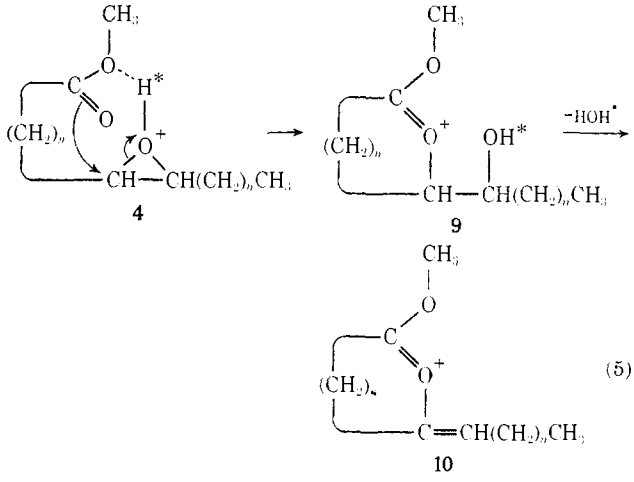
(28) D. F. Hunt, C. N. McEwen, and R. N. Upham, *Anal. Chem.*, 44, 1292 (1972).

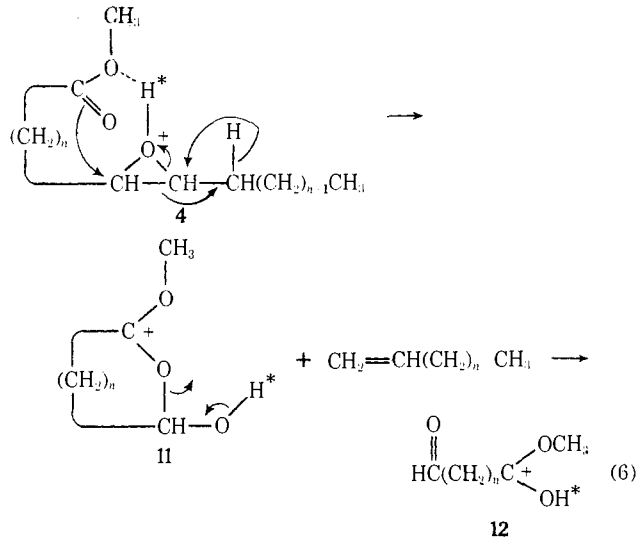
canoate-2,2′-^2H showed no loss of deuterium and the movement of the initial ionizing atom was followed by using D_3O^+ as the ionizing species. Although these data suggest some features of the fragmentation process they do not permit delineation of unambiguous fragmentation mechanisms for these epoxy methyl esters. Some general features are given in the following examples. All of the observed fragments can be derived from the intermediate **4** by going through an initial rearrangement to form an oxygen–carbon bond between the carbonyl oxygen and a carbon of the epoxide. An example is given in eq 5 which shows rearrangement of **4** to **9** and subsequent elimination of water with the ionizing proton H*. Methanol elimination from **10** can occur through a mechanism analogous to alcohol elimination from an alkylated ester.[1] Metastable transitions indicated that the elimination sequence can be reversed. In either case the third oxygen atom in the molecules can be eliminated as H_2O to give an alkyl ion $(C_nH_{2n-7})^+$ as a minor fragment.



(5)

The alkyl chain of the epoxy esters was cleaved at the epoxide through three pathways; in each case the charge was retained on the carboxy side of the epoxide. The carbon originally on the alkyl side of the epoxide ring, carbon 10 of a 9,10-epoxide, was lost as part of a neutral alkene, methyl, or aldehyde function. The alkene may be lost with the initial rearrangement of **4** leading to C–C bond cleavage at the epoxide as shown in eq 6. The resulting cyclic ion **11** was found to lose methanol containing the ionizing atom. This elimination would occur from **12** which may be derived from **11** by a proton abstraction mechanism as proposed by Munson and Field to give the $RCO_2R'H^+$ ion from alkylated alkyl esters.[1] Mechanisms of similar speculative quality can be conceived for the other alkyl cleavage processes.

The discussion of spectral data has considered the epoxy esters as a group (Table II). Indeed, the only systematic variation in ion abundance with molecular structure was the increased $MH^+ - H_2O$ ion as the epoxy function was moved further from the carboxy ester, as the relative intensities of all ions in the spectra were modified by small changes in ion chamber temperature and reagent gas pressure; this structural variation was probably the result of kinetic and thermodynamic factors operating simultaneously. An interesting feature concerned the variation in fragmentation with reagent gas pressure as this was not observed with benzyl acetate.[2]



(6)

Differences in nonbonded interactions between cis and trans epoxide groups could affect the equilibrium of internal energy of the proton complex **4**. But these energy differences were small compared to the heat of formation of the complex so that no spectral differences were observed. The alkyl cleavage fragments indicate the position of the epoxide ring in the fatty acid chain, and consequently the position of the olefenic bond from which it was prepared.

Conclusion

The isobutane chemical ionization spectra of monoenoic fatty acids, their methyl esters, and aliphatic epoxides result from protonation of the functional group which then fragments to a modest extent with loss of water or methanol from the protonated function. The spectra of the epoxy esters taken under the same conditions were dominated by participative interaction between the two functional groups. While loss of water and methanol may result, in part, from protonation and fragmentation of the isolated functional groups, the major spectral characteristics result from long range functional group interactions.

These observations were explained in terms of a proton complex formed from the protonated molecular ion. The enhanced fragmentation present in these molecules results from the spacially proximate configuration of the functional groups in the complex and the large heat of formation associated with gas phase hydrogen bonding.

The nature of the interactions required for proton complex formation suggests that analogous structures may be involved in the fragmentation of many polyfunctional molecules under chemical ionization conditions. Some of the more prominent implications of complex formation are that group interactions may occur through very large cyclic intermediates and that a certain amount of energy, the heat of complex formation, would be available within the molecule to promote ion fragmentation which is independent of the amount of energy transferred on ionization by the reagent gas. A hydrogen bond formed prior to protonation, however, could stabilize the molecule to fragmentation.