Interconversions of $C_5H_{10}O^{+}$ Ions with the Oxygen on the First, Second and Third Carbons: Approximately 60 Communicating Isomers

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The structures of the $C_4H_7O^+$ and $C_3H_6O^{++}$ dissociation products from selected $C_5H_{10}O^{++}$ isomers with the oxygen on the first, second and third carbons were determined. The first product is $CH_3C(OH)CH=CH_2^+$ and the second is $CH_3C(OH^+)CH_2^-$ and $CH_3^-CHCHOH^+$ in various proportions. These results demonstrate that ions with the oxygen on the first and third carbons isomerize partially to isomers with the oxygen on the second carbon. This and $C_5H_{10}O^{++}$ isomers expected to be accessible to each other suggest that there are traversable pathways between about 60 $C_5H_{10}O^{++}$ isomers, demonstrating how extensive interconversions of aliphatic radical cations can be.

INTRODUCTION

 $C_nH_{2n}O^+$, $C_nH_{2n}O_2^+$ and related ions isomerize extensively.¹ For example, interconversion of more than a dozen $C_5H_{10}O^{+}$ isomers with the oxygen on the second carbon [C(2) ions] has been proposed,² and a comparable number of additional structures are known to be accessed by $C_5H_{10}O^{+\bullet}$ ions with the oxygen on the first³ [C(1) ions] and third⁴ [C(3) ions] carbons. Losses of methyl from $C(1)^3$ and $C(3)^4$ ions to form $CH_3C(OH)CH=CH_2^+$ (a) suggests that fractions of those ions isomerize to species with the oxygen on the second carbon. If so, most $C_5H_{10}O^{+}$ isomers other than cyclic and unsaturated ether ions are accessible to each other, at least in one direction. We investigated whether C(1) and C(3) isomers access C(2) structures, primarily to determine the scope of the interconversion of $C_5H_{10}O^{+}$ isomers and thereby to obtain an indication of how extensively aliphatic radical cations can isomerize in the gas phase. Another objective was to characterize better shifts that occur in the position of oxygen in $C_n H_{2n} O^{+}$ isomers.^{3,5}

RESULTS

Metastable dissociation spectra of the distonic C(1) isomers CH_3 'CHCH(CH_3)CHOH⁺ (1) and $CH_3CH_2CH(CH_2)$ 'CHOH⁺ (2) are given in Table 1. These ions are previously uncharacterized species which, by analogy with mechanisms proposed for related isomerizations,^{3,5} are expected to be important in the conversions of C(1) to C(2) and C(3) ions. Metastable 1 and metastable 2 both dissociate to m/z 71

 $(-CH_3)$, m/z 68 $(-H_2O)$, m/z 58 $(-C_2H_4)$ and m/z 57 $(-C_2H_5)$. Previous studies^{3.4} found that both C(1) and C(3) ions other than ionized pentan-3-one dissociate to products at m/z 71, 68, 58 and 57 [ionized pentan-3-one dissociates almost exclusively to m/z 56 on metastable decomposition because it lacks enough energy to undergo the reactions observed for the other C(3) ions, which dissociate primarily following energized isomerizations to ionized pentan-3-one⁴]. C(2) ions dissociate to m/z 71 and 58.² The metastable dissociation patterns of both 1 and 2 differ quantitatively from those previously reported³ for the C(1) isomers ionized cyclopentanol, CH₃CH₂CH₂CH₂CHOH⁺, CH₃CH₂CH(CH₃)CHOH⁺, (CH₃)₂CHCH₂CHO⁺ and (CH₃)₃CHO⁺, and from those for C(3) structures.⁴ This is evidence that 1 and 2 are generated as unique structures.

Ions 1 and 2 were obtained by ionizing 2,3,4,5tetramethyl- and 2,5-diethylcyclopentanol. Homologous ions have been generated by dissociations of other substituted cyclopentanol ions.^{2,6} β -Distonic ions are generated from cyclopentanols by the general reaction shown in Scheme 1, where R = H or C_nH_{2n+1}. A related pathway forms 'CH₂CH₂CO⁺ from ionized cyclopentanone.⁷

To obtain information on the structures of dissociating ions, collisionally activated dissociation (CAD)

Table	1. Field-free region diss ions	sociations of C ₅ H ₁₀ O ^{+·}
m/z	CH ₃ ·CHCh(CH ₃)CHOH ⁺ (1)	CH ₃ CH ₂ CH(CH ₂ ·)CHOH ⁺ (2)
56	1	4
57	15	93
58	25	37
68	82	100
71	100	93

Received 17 May 1994 Revised 14 July 1994 Accepted 27 July 1994

^{*} Paper prepared for publication in Organic Mass Spectrometry.



spectra of fragments of some C(1) and C(3) ions were recorded, together with spectra of reference ions, to determine the identities of those products. To ensure that fragments studied were from $C_5H_{10}O^{+}$ precursors, CAD spectra of products of first field-free region dissociations were obtained. Such spectra are not presented for dissociation products of 2 because the spectra for m/z 58 and 71 were too low in intensity to be useful. In some instances, only characteristic regions of the spectra were scanned to obtain useful signal-to-noise ratios. Any value greater than 25% relative abundance is estimated to be accurate to within 20% of the reported abundance.

CAD spectra of pertinent $C_4H_7O^+$ ions are given in Table 2. The CAD spectra of the products of methyl loss from 1 and CH₃'CHC(OH⁺)CH₂CH₃ (3) match reasonably that for *a*, and are distinct from the spectra of CH₃CH₂CH₂CO⁺ (not shown, but has^{2,3} much less intense peaks at *m/z* 31, 53, 55 and 70 than the observed spectra), CH₃CH=CHCHOH⁺ (which has a substantially less abundant *m/z* 43) and CH₂=C(CH₃)CHOH⁺ (which has a more abundant m/z 51 and a less abundant m/z 70). However, the matches are not perfect, and it is possible that a fraction of the dissociations of 1 and 2 produce C₄H₇O⁺ isomers other than *a*.

CAD spectra of $C_3H_6O^+$ products are given in Table 3. $CH_3C(OH^+)CH_2$ (b) and CH_3 CHCHOH⁺ (c) are the likely $C_3H_6O^+$ products of low-energy $C_5H_{10}O^+$ dissociations.^{2,3} Other structures are theoretically possible,⁸⁻¹⁰ but b and c are the most stable possibilities and therefore the most likely products of metastable decompositions. Furthermore, b and c are mechanistically the most plausible $C_3H_6O^+$ products. Spectra of b and c formed in the ion source (the last two entries in Table 3) provide reference spectra. A very intense peak at m/z 43 and a substantial peak at m/z 42 are present in the CAD spectrum of b, whereas the relative intensities of these peaks in the CAD spectrum of c are 4% and 6%, respectively, of that of m/z 57. There is probably a small contribution of b to the reference spectrum of c because published abundances³ of m/z 42 and 43 for c are both 2% of m/z 57. Intense peaks at m/z 42 and 43 relative to m/z 39 in the CAD spectra of $C_3H_6O^+$ formed from 1 and $CH_3CH_2C(CH_3)CHOH^+$ (4) demonstrate that those isomers dissociate mostly to b. The peaks at m/z 42 and 43 are of low intensity in the CAD spectrum of $C_3H_6O^{++}$ from the C(1) ion $CH_3CH_2CH_2CH_2CHO^{++}$,

Table 2. Collisionally activated spectra of C4H7O⁺ ions

Precursor									
m/z	CH3 CHCH(CH3)CHOH+ a (1)	CH ₃ [·] CHC(OH ⁺)C ₂ H ₅ (3) ^b	$CH_3COH^+CH=CH_2(a)^c$	сн₃сн − снснон⁺ ₫	CH₂ ∞ C(CH₃)CHOH+ ^e				
27	46	38	39	27	21				
29	16	13	9	26	11				
31	13	12	7	6					
39	39	31	23	50	33				
41	32	18	28	51	27				
43	100	100	100	25	100				
51	≤11		7	13	59				
53	26	34	19	50	16				
55	33	25	54	24	11				
69	16	15	22	77	23				
70	58	37	65	100	13				

Precursors of ions were: ^a 2,3,4,5-tetramethylcyclopentanol; ^b 4-methyl-3-heptanone; ^c methane chemical ionization (CI) of but-3-en-2-one; ^d methane CI of but-2-enal; ^e methane CI of 2-methylprop-2-enal.

Fable 3. Collisionally activated spectra of $C_3H_6O^+$	ions
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	m/z							
Precursor	27	29	31	39	42	43	55	57
CH ₃ ⁻ CHCH(CH ₃)CHOH ⁺ (1) ^{a,b}				31	42	100		
CH ₃ (CH ₂) ₃ CHO ⁺⁺ ^c	10	44	16	10	4	7	15	100
CH ₃ CH ₂ CH ₂ CHCHOH ⁺ ^{a,d}				100	40	60		
CH ₃ CH ₂ ·C(CH ₃)CHOH ⁺ ^e (4)	7	47	23	45	35	100	12	36
CH ₃ [•] CHC(OH ⁺)CH ₂ CH ₃ (3) ^{a,f}				70	60	100		
(CH ₃) ₂ CHCH ₂ CHO ⁺⁺ ⁹	28	59	25	27	9	16	24	100
CH ₃ C(O ⁺⁺)CH ₂ CH ₂ CH ₃ h ₃	17	42	21	36	34	100	6	12
CH ₃ CH ₂ CH(CH ₃)CHO ⁺ ···	17	40	17	18	6	4	14	100

^a Scanned only from m/z 38 to 44.

Sources of ions were: ^b 2,3,4,5-tetramethylcyclopentanol; ^c *n*-pentanal; ^d 2-propylpentanal; ^e enol acetate of 2-methylbutanal; ^f 4-methylheptan-3-one; ^g 3-methylbutanal; ^h pentan-2-one; ⁱ 2-methylbutanal; ⁱ product of ion source decomposition; all other results are for products of first field-free region dissociations.

demonstrating that this product is largely c. Elevations in the abundances of m/z 42 and 43 indicate that variable amounts of b are formed from most other C(1) isomers. CH₃·CHC(OH⁺)CH₂CH₃, the only C(3) ion from which m/z 58 was examined, produced predominantly b.

A CAD spectrum of the m/z 57 product of the metastable decomposition of 2 was obtained. This spectrum had its most intense peak at m/z 29 and an undetectable (less than 10% of the intensity of the m/z 29 peak) m/z31. Hence this product was CH₃CH₂CO⁺ rather than CH₂=CHCHOH⁺,¹¹ supporting conversion of C(1) to C(3) ions by $2 \rightarrow CH_2$ =CHCH(OH)CH₂CH₃⁺.

DISCUSSION

One of our goals was to identify better the mechanisms whereby oxygen shifts position in $C_n H_{2n} O^+$ ions. $CH_3C(OH)CH=CH_2^+$ is formed on methyl loss from 1, C(2) ions,² the C(1) isomers ionized cyclopentanol and 3-methylbutanal elsewhere,³ and 3, that is, in all examined methyl losses from metastable $C_5H_{10}O^+$ ions that have been examined. This product can only be CH₃C(OH⁺)[•]CHCH₂CH₃, directly from formed $CH_3C(OH^+)CH(CH_3)CH_2$ or $(CH_3)_2COHCH=CH_2^+$ all C(2) ions. This therefore argues that C(1) and C(3) isomers rearrange to a C(2) structure or structures before losing methyl. Oxygen shifts position in $C_nH_{2n}O^+$ ions by alkyl rather than O shifts,⁵ but the pathways are not clearly characterized.¹²

One observation that must be accommodated in proposing pathways to methyl loss from C(1) ions is that ionized cyclopentanol-O,2,2,5,5- d_5 loses nearly identical amounts of CD₃ and CH₂D and smaller amounts of CHD₂ and CH₃.³ Isomerization of ionized cyclopentanol to 1, followed by interconversion of 1 with itself, would equalize the two major methyl losses (Scheme 2). Analogous isomerizations are well established in other C_nH_{2n}O⁺⁺ and related systems.¹³⁻¹⁵ Methyl loss from ionized cyclopentanol produces a,³ consistent with 1 being in the pathway to that methyl loss. Ionized cyclopentanol also undergoes substantial conversion to C(3) structures following ring opening, supporting the intermediacy of 2 proposed in Scheme 2.

Another important clue to the pathway from C(1)and C(3) to C(2) ions is that 1 and 4 are the only C(1)ions examined which dissociate predominantly to b rather than to c. Other C(1) ions for which results are available (Table 3 and Ref. 3) produce predominantly c on losing ethene, demonstrating that those dissociations occur primarily from C(1) structures. The latter dissociations probably occur by

$$CH_2CH_2CH(CH_3)CHOH^+ \rightarrow$$

$$CH_3$$
 CHCHOH⁺ + $CH_2 = CH_2$
c

However, the presence of elevated m/z 43 peaks in all of the C₃H₆O⁺⁺ products of first field-free region decompositions examined suggests that varying fractions of the ions undergoing those dissociations do isomerize to C(2) structures before eliminating ethene.



The more specific formation of b from 1 than from most other C(1) ions implies that 1 is close to the point of conversion of C(1) to C(2) ions. This supports the proposal (Scheme 2) that C(1) ions convert to C(2) ions by $1 \rightarrow CH_3CHOHCH=CHCH_3^+$. The enol ion 4, an intermediate inferred in the equilibration of the methyls in ionized cyclopentanol-O,2,2,5,5-d₅ (Scheme 2), also produces predominantly b. This is consistent with the interconversion of 1 and this ion, and with generally observed interconversions of enol and β -distonic ions.

Preferential dissociations to b or c demonstrate a division of metastable C(1) ions in the degree to which they isomerize to C(2) ions. CH_3CH_2 C(CH₃)CHOH⁺ and 1 probably do not dissociate to c because they would have to do so through their carbonyl isomers, and β -distonic ions often do not isomerize to carbonyl isomers.^{6,16} Also, some carbonyl isomers are less able to reach their β -distonic isomers than their γ -distonic isomers near the thresholds for decomposition,^{16b} a pattern that the dissociation of the C(1) carbonyl ions predominantly to c rather than b shows is repeated here.

Other information consistent with Scheme 2 is (1) ionized cyclopropanols and related species, such as that in the degenerate interconversion in Scheme 2, are common intermediates or transition states, 5,14,15 (ii) the methyl shift proposed to convert C(1) to C(2) ions is similar to an ethyl shift that has been proposed to convert C(1) to C(3) ions³ and a methyl shift suggested to rationalize a similar process in C₄H₈O⁺⁺ isomers⁵ and (iii) the proposed immediate product of the $1 \rightarrow C(2)$ isomerization, i.e. CH₃CH(OH)CH=CHCH₃⁺⁺, dissociates to $b.^2$

The C(3) ion 3 dissociates to a and b. $C_4H_7O^+$ and $C_3H_6O^{+*}$ are also produced by other C(3) isomers.⁴ C(3) ions, including 3, undergo identical dissociations,⁴ so all C(3) ions that lose methyl and ethene probably do

so through C(2) ions. There is not an obvious pathway directly from C(3) to C(2) ions, as no such isomerization can form a vinylic alcohol ion. The isolation of b and c from each other¹⁷ supports the non-existence of pathways such as a direct C(1) \rightarrow C(3) interconversion. Therefore, C(3) ions probably isomerize to C(2) ions by way of C(1) ions.

The demonstration here that C(1) and C(3) ions rearrange to C(2) ions, in combination with previous conclusions regarding the dissociations of these three groups of ions,^{2-4,18,19} leads to Scheme 3 for the isomerizations of $C_5H_{10}O^{+*}$ ions. Scheme 3 contains 34 isomers.

A variety of ions not shown in Scheme 3 probably enter the pathways depicted there. A list of such species is given in the Appendix. Of these, the metastable 3methylbutanal ion clearly enters the Scheme 3 pathways because it has a typical C(1) pattern,³ so presumably the 3-methyl distonic and enol C(1) ions would also. There are seven $C_5H_{10}O^+$ unsaturated alcohol ions in the Appendix that are not shown in Scheme 3. Some of these undergo reactions shown in Scheme 3,18,19 and it is likely that the others do also. Some of the C(1)unsaturated alcohol ions also isomerize through one or more intermediates (for example, the O'-containing species in the Appendix) to the structures in Scheme 3 by pathways similar to the isomerization of ionized pent-4-en-2-ol to the pentan-2-one ion (top right of Scheme 3). All C(1) and C(3) ions (except ionized pentan-3-one) lose water.^{3,4} This probably involves the OH₂⁺-containing species in the Appendix. The Appendix also contains five cyclic alcohol ions that would be expected to access the pathways in Scheme 3. Adding the 31 species in the Appendix to the 34 strucures in Scheme 3 gives 65 $C_5 H_{10}O^{+}$ isomers that may be accessible to each other near the thresholds for their lowest energy unimolecular dissociations. Even if some of the listed species do not access Scheme 3, approximately 60 $C_5H_{10}O^{+}$ isomers must be in communication with each other. This is undoubtedly the most

elaborate set of mutually accessible isomerizations ever proposed in gas-phase ion chemistry.

Some unsaturated $C_5H_{10}O^{+}$ ether ions do not undergo reactions in Scheme 3,²⁰ demonstrating that not all $C_5H_{10}O^{+}$ ions access common pathways.

The complexity of the $C_5H_{10}O^{+\cdot}$ reactions arises from a combination of a relatively small number of types of reactions, five- and six-membered ring Htransfers, 1,2-H and C shifts between O-bearing carbons, between carbons α and β to the O and to carbons formally bearing the charge and ring openings and closings interconverting distonic and cyclic structures. The occurrence of these reactions and the absence of others that might be proposed (e.g., four-membered ring H-transfers and 1,2-shifts between β and more distant carbons) has been summarized.²¹

There are eleven distonic ions (ions with the charge and free electron formally on different atoms) in Scheme 3. The intermediacy of such species in systems similar to that described here was well established²² before they were given a name.²³

EXPERIMENTAL

Spectra were obtained on a mass spectrometer of EBE geometry (Kratos MS50TA²⁴) using established procedures. Spectra were signal-averaged for up to 150 scans to obtain acceptable signal-to-noise ratios. 2,3,4,5-Tetramethylcyclopentanol was prepared starting by reacting 1,1-dimethylhydrazine with 3,4-dimethyl-cyclopentanone. The resulting dimethylhydrazone was methylated with two equivalents of lithium diisopropylamide and two equivalents of methyl iodide.²⁵ The product was oxidized to the ketone with periodate and reduced to the alcohol with lithium aluminum hydride. 2,5-Diethylcyclopentanone and using ethyl bromide as the



Scheme 3

alkylating agent. Other compounds used were obtained from commercial sources.

and the Midwest Center for Mass Spectrometry for the use of the MS50TA mass spectrometer.

Acknowledgement

We thank Ms Debbie Pavlu for typing, the Robert A. Welch Foundation for financial support (Grant H-609) and Professor Michael Gross

REFERENCES

- (a)G. Bouchoux, Mass Spectrom. Rev. 7, 1 (1988); (b) G. Bouchoux, Mass Spectrom. Rev. 7, 203 (1988); (c) S. Hammerum, Mass Spectrom. Rev. 7, 123 (1988); (d) D. J. McAdoo, C. E. Hudson, M. Skyiepal, E. Broido and L. L. Griffin, J. Am. Chem. Soc. 109, 7648 (1987); (e) L. L. Griffin, K. Holden, C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 21, 175 (1986).
- 2. D. J. McAdoo, C. E. Hudson, F. W. McLafferty and T. E. Parks, Org. Mass Spectrom. 19, 353 (1984).
- C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 19, 1 (1984).
- D. J. McAdoo, W. Farr and C. E. Hudson, J. Am. Chem. Soc. 102, 5165 (1980).
- 5. C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 20, 402 (1985).
- D. J. McAdoo, C. E. Hudson and D. N. Witiak, Org. Mass Spectrom. 14, 350 (1979).
- 7. J. C. Traeger, C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 24, 230 (1989).
- W. J. Bouma, J. K. MacLeod and L. Radom, J. Am. Chem. Soc. 102, 2246 (1980).
- 9. G. Bouchoux and J. Tortajada, Rapid Commun. Mass Spectrom. 1, 86 (1987).
- 10. C. E. Hudson and D. J. McAdoo, Tetrahedron 46, 331 (1990).
- C. E. Hudson and D. J. McAdoo, Org. Mass Spectrom. 17, 366 (1982).
- J. C. Traeger and D. J. McAdoo, Int. J. Mass Spectrom. Ion Processes 68, 35 (1986).
- 13. R. D. Bowen and A. G. Harrison, J. Chem. Soc., Perkin Trans. 2 1483 (1989).

- (a) P. H. Hemberger, J. C. Kleingeld, K. Levsen, N. Mainzer, A. Mandelbaum, N. M. M. Nibbering, H. Schwarz, R. Weber, A. Weisz and C. Wesdemiotis, J. Am. Chem. Soc. 102, 3736 (1980); (b) G. Bouchoux and Y. Hoppilliard, Int. J. Mass Spectrom. Ion Processes 55, 47 (1983–84).
- D. J. McAdoo, C. E. Hudson, J. J. Zwinselman and N. M. M. Nibbering, J. Chem. Soc., Perkin Trans. 2, 1703 (1985).
 (a) D. J. McAdoo and C. E. Hudson, J. Am. Chem. Soc. 103,
- (a) D. J. McAdoo and C. E. Hudson, J. Am. Chem. Soc. 103, 7710 (1981);
 (b) C. E. Hudson, T. Lin and D. J. McAdoo, Org. Mass Spectrom. 22, 311 (1987).
- 17. D. J. McAdoo and D. N. Witiak, J. Chem. Soc., Perkin Trans. 2 770 (1981).
- J. J. Zwinselman, N. M. M. Nibbering, N. E. Middlemiss, J. H. Vajda and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.* 38, 163 (1981).
- R. D. Bowen and A. G. Harrison, Org. Mass Spectrom. 24, 525 (1989).
- R. D. Bowen, A. D. Wright, A. W. Colburn and P. J. Derrick, Int. J. Mass Spectrom. Ion Processes 116, 193 (1992).
- 21. D. J. McAdoo, Org. Mass Spectrom. 23, 350 (1988).
- (a) J. S. Smith and F. W. McLafferty, Org. Mass Spectrom. 5, 483 (1971); (b) D. J. McAdoo, F. W. McLafferty and T. E. Parks, J. Am. Chem. Soc. 94, 1601 (1972).
- B. F. Yates, W. J. Bouma and L. Radom, J. Am. Chem. Soc. 106, 5805 (1984).
- M. L. Gross, E. K. Chess, P. A. Lyon and F. W. Crow, Int. J. Mass Spectrom. Ion Phys. 42, 243 (1982).
- 25. E. J. Corey and D. Enders, Tetrahedron Lett. 3 (1976).

APPENDIX

Additional $C_5H_{10}O^{+}$ isomers not included in Scheme 3, but likely to access some portion of that scheme 3-Methyl C(1) ions:

 $(CH_3)_2CHCH_2CHO^+$, $CH_2CH(CH_3)CH_2CHOH^+$, $(CH_3)_2CHOH^+$, $(CH_3)_2CHCHOH^+$, $(CH_3)_2CHCHCHOH^+$, Unsaturated alcohol ions:

 $CH_3CH = C(CH_3)CH_2OH^+$, $CH_2 = C(CH_3)CH_2CH_2OH^+$, $CH_2 = CHCH_2CH_2CH_2OH^+$,

 $CH_3CH = CHCH_2CH_2OH^+$, $CH_3CH_2CH = CHCH_2OH^+$, $(CH_3)_2C = CHCH_2OH^+$,

 $CH_2 = C(CH_3)CH(OH)CH_3^+$

Cyclic alcohol ions:

 $(CH_2)CH_2(CH_2)CH(OH^+)CH_3$, $(CH_2)CH_2CH_2(CH)CHOH^+$, $(CH_2)CH(CH_3)CH_2(CH)OH^+$, $CH_3(CH)CH_2(CH)CH_2OH^+$, $(CH_2)CH_2(CH)CH_2OH^+$,

Intermediates in water eliminations or in isomerizations of unsaturated alcohol ions:

 $CH_3CHC(CH_2)CH_2OH_2^+$, $CH_2CHC(CH_3)CH_2OH_2^+$, $CH_3CH_2^+C(CH_3)CH_2O^+$, $CH_3CH_2^+$, $CH_3CH_2^+C(CH_3$

 $CH_{3}^{+}CHCH(CH_{3})CH_{2}O', \quad CH_{2}C(CH_{2})CH_{2}OH_{2}^{+}, \quad CH_{2}CH(CH_{3})^{+}CHCH_{2}OH, \quad (CH_{3})_{2}^{+}CCH_{2}CH_{2}O',$

(CH₃)₂CH⁺CHCH₂O⁺, CH₂CHCHCH₂CH₂OH₂⁺, CH₃CHCHCHCH₂OH₂⁺, CH₃CH₂⁺CHCH₂CH₂O⁺,

(CH₃)₂CH⁺CHCH₂O', (CH₃)₂⁺CCH₂CH₂O', CH₃CH₂CH₂⁺CHCH₂O', CH₃CH₂CHCHCHOH₂⁺