

CHEM 100L Lab 4: Introduction to Mass Spectrometry

Purpose: In this virtual lab experiment, you will explore the use of infrared spectroscopy and mass spectrometry to identify five organic compounds: butyraldehyde, acetophenone, benzoic acid, 2-chloro-2-methylpropane, and diethyl ether.

Introduction: You will use the Beyond Labz virtual platform to record the IR spectrum and the mass spectrum for butyraldehyde, acetophenone, benzoic acid, 2-chloro-2-methylpropane, and diethyl ether. You will then analyze the spectra by identifying the key absorption peaks in the IR spectrum and identifying the key fragments in the mass spectrum for each of the five compounds.

IR spectroscopy:

We can identify functional groups using infrared (IR) spectroscopy. IR radiation is in the same range of frequencies ($4000\text{-}600\text{ cm}^{-1}$) as the stretching and bending vibrations of bonds in organic molecules. When the frequency of the radiation exactly matches the frequency of the bond, the molecule absorbs energy, resulting in an absorption peak in the IR spectrum. Most functional groups show absorption bands in the region of $4000\text{-}1400\text{ cm}^{-1}$.

See the handouts: Characteristic Infrared Absorption Peaks and IR Tutorial UCLA for help identifying the peaks.

Mass spectrometry:

We can get some information about the structure of a molecule from examining its mass spectrum. In a mass spectrometer, a sample is vaporized, and then ionized. The most common method of ionization is electron ionization (EI). In EI the vaporized compound is bombarded with a beam of high energy electrons (typically around 70 eV). When the electron beam first collides with the vaporized compound the compound loses one electron. This initially formed ion, the molecular ion or M^+ , has the same mass as the starting compound and so can be used to determine the molecular weight. The signals that are displayed in the mass spectrum are reported as their mass to charge ratio (m/z). In EI mass spectroscopy the charge is +1 so we can read this number as the mass of the ion. The ions formed inside the mass spectrometer are unstable and often fragment before reaching the detector. Only positively charged species are recorded in the mass spectrum. The positively charged fragments that reach the detector in the greatest abundance tend to be the fragments that are the most stable and/or are formed in the greatest quantity.

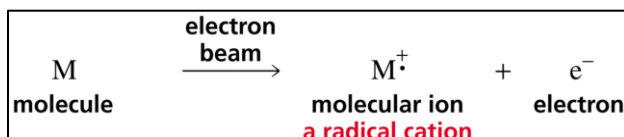


Figure 4.1 Formation of the molecular ion. (From Organic Chemistry by Bruice, 8th Ed.)

Functional groups tend to fragment in somewhat of predictable ways to form stabilized cations. In this virtual lab you will be examining the mass spectra of several carbonyl-containing molecules, an alkyl halide, and an ether.

The butyraldehyde, the acetophenone, and the benzoic acid all contain a carbonyl (C=O). A common fragmentation pathway for carbonyl-containing molecules is alpha-cleavage. The bond between the carbonyl carbon and the adjacent group cleaves to give a resonance stabilized acylium ion.

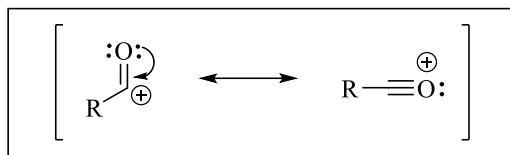


Figure 4.2 Resonance stabilized acylium ion.

The figure below shows the two alpha-cleavage pathways possible for 2-pentanone. The loss of either the propyl group or the methyl group leads to a resonance stabilized acylium ion.

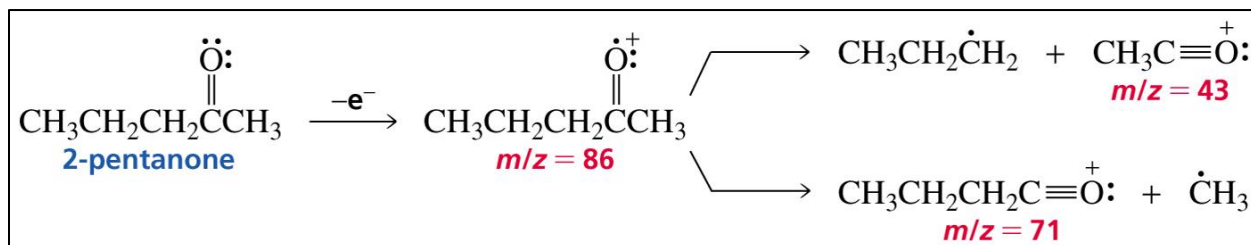


Figure 4.3 Alpha-cleavage of carbonyl containing compounds. (From Organic Chemistry by Bruice, 8th Ed.)

The 2-chloro-2-methylpropane contains a chlorine atom. Both chlorine and bromine have a high percentage of a naturally occurring isotope that is two mass units heavier than the most abundant isotope. Naturally occurring chlorine is 75.77 % chlorine-35 and 24.23 % chlorine-37. In the mass spectrum, any fragment that contains 1 chlorine atom has a peak 2 mass units higher that is 1/3 its height. Naturally occurring bromine is 50.69 % bromine-79 and 49.31% bromine-81. In the mass spectrum, any fragment that contains 1 bromine atom has a peak 2 mass units higher that is equal in height.

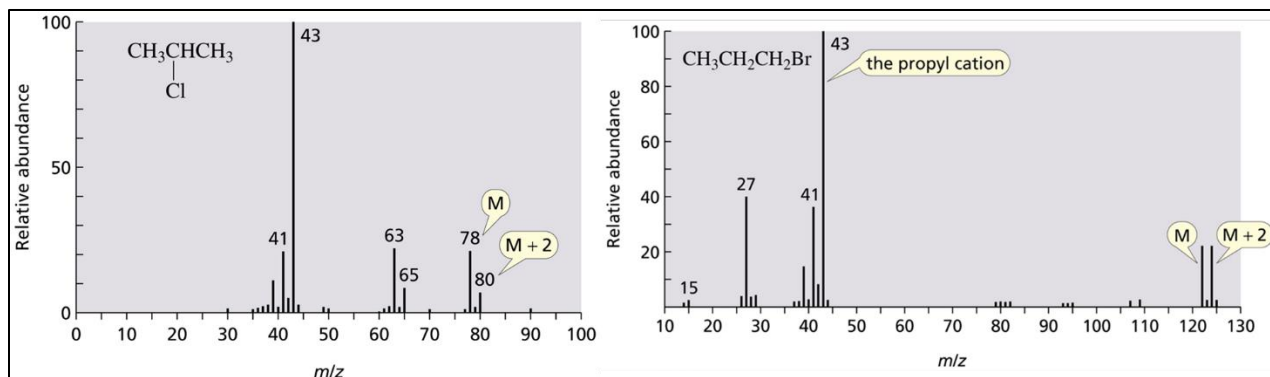


Figure 4.4 M+2 peaks for chlorine (left) and bromine (right). (From Organic Chemistry by Bruice, 8th Ed.)

Alkyl halides and ethers tend to undergo two major fragmentation patterns in EI mass spectrometry. They tend to undergo heterolytic cleavage of the carbon-halogen or carbon-oxygen bond, and they tend to undergo alpha-cleavage to form cations that are resonance stabilized.

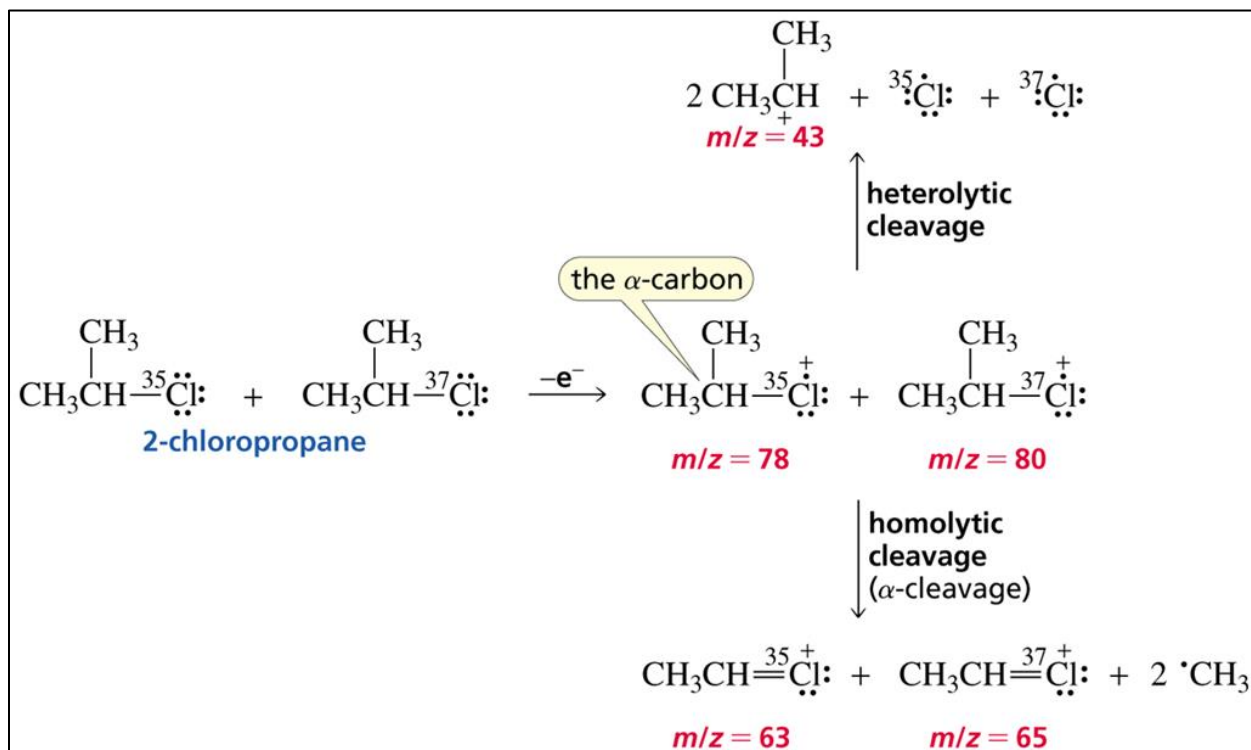


Figure 4.5 Common fragmentation patterns for alkyl halides. (From Organic Chemistry by Bruice, 8th Ed.)

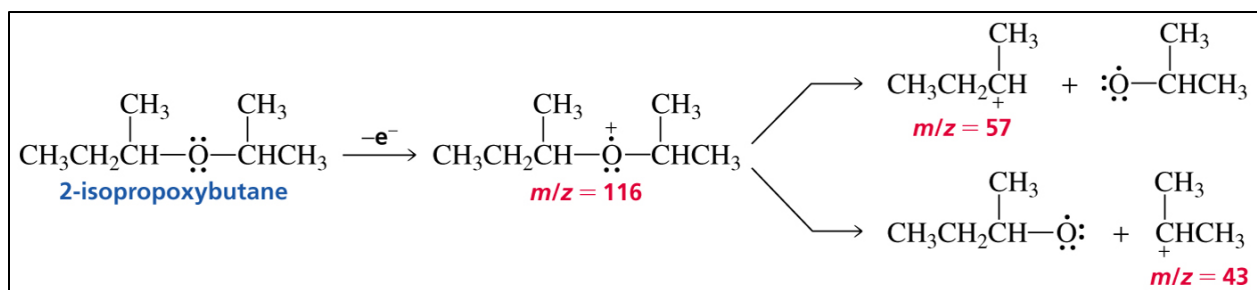


Figure 4.6 Common fragmentation patterns for ethers. (From Organic Chemistry by Bruice, 8th Ed.)



Figure 4.7 The qualitative analysis virtual lab.

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter. *Note: Reference IR spectra for the butyraldehyde, acetophenone, benzoic acid, 2-chloro-2-methylpropane, and diethyl ether are provided at the end of this handout with the key peaks clearly labeled.*

1. Open the organic chemistry lab on the Beyond Labz platform. Select “Qualitative Analysis” at the top left of the screen to open the Qualitative Analysis virtual lab.
2. Select “**Aldehydes**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **butyraldehyde** to add it to the flask.
3. Drag the flask to the cork ring support on the lab bench.
4. Record the IR spectrum by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
5. Record the mass spectrum by clicking on the mass spectrometer and dragging the sample vial icon to the flask. This will display the mass spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. To view the m/z values, mouse over each peak- the first number is the m/z value. Click ok to close the spectrum.
6. Reset the qualitative analysis lab by clicking on the waste container to “clear lab”.
7. Select “**Ketones**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **acetophenone** to add it to the flask.
8. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the acetophenone.
9. Reset the qualitative analysis lab by clicking on the waste container to “clear lab”.
10. Select “**Acids**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **benzoic acid** to add it to the flask.
11. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the benzoic acid.
12. Reset the qualitative analysis lab by clicking on the waste container to “clear lab”.
13. Select “**Halides**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **2-chloro-2-methylpropane** to add it to the flask.
14. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the 2-methyl-2-chloropropane.
15. Reset the qualitative analysis lab by clicking on the waste container to “clear lab”.
16. Select “**Ethers**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **diethyl ether** to add it to the flask.
17. Repeat steps 3-5 to record the IR spectrum and the mass spectrum for the diethyl ether.
18. Reset the qualitative analysis lab by clicking on the waste container to “clear lab”.
19. Your virtual experiment is now complete!

Lab 4 Assignment:

Points (total = 50)

- 7 pts Prelab questions
- 12 pts Butyraldehyde results
- 9 pts Acetophenone results
- 8 pts Benzoic acid results
- 7 pts 2-chloro-2-methylpropane results
- 7 pts Diethyl ether results

Prelab Questions (7 pts)

1. (5 pts) Give the structures of the 5 organic compounds that you will be studying in this experiment: butyraldehyde, acetophenone, benzoic acid, 2-chloro-2-methylpropane, and diethyl ether.
2. (2 pts) What is the m/z value of a peak in the mass spectrum and what does it tell you about the ion?

Results (43 pts) *Labeled IR spectra and solved example appear at the end of this handout.

Butyraldehyde Results (12 pts total) Complete the following tables.

Infrared spectrum (3 pts):

Absorbance peak (cm^{-1})	Bond(s)
2965-2875	
2817 & 2716	
1731	

Mass spectrum (9 pts):

m/z value	Charged Fragment	Fragment Lost
72		N/A
71		
57		
44		
29		

Acetophenone Results (9 pts total) Complete the following tables.

Infrared spectrum (4 pts):

Absorbance peak (cm^{-1})	Bond(s)
3065-3005	
2965-2865	
1685	
1600	

Mass spectrum (5 pts):

m/z value	Charged Fragment	Fragment Lost
120		N/A
105		
77		

Benzoic Acid Results (8 pts total) Complete the following tables.

Infrared spectrum (3 pts):

Absorbance peak (cm^{-1})	Bond(s)
3200-2550	
1690	
1600	

Mass spectrum (5 pts):

m/z value	Charged Fragment	Fragment Lost
122		N/A
105		
77		

2-Chloro-2-methylpropane Results (7 pts total) Complete the following tables and answer the questions.

Infrared spectrum (1 pt):

Absorbance peak (cm^{-1})	Bond(s)
2985-2930	

Mass spectrum (4 pts):

m/z value	Charged Fragment	Fragment Lost
77		
57		

1. The molecular ion is not visible in the mass spectrum of 2-chloro-2-methylpropane. At what m/z value would the molecular ion be if it were visible?
2. What evidence is there in the mass spectrum that suggests that the peak at m/z = 77 contains a chlorine atom?

Diethyl Ether Results (7 pts total) Complete the following tables.

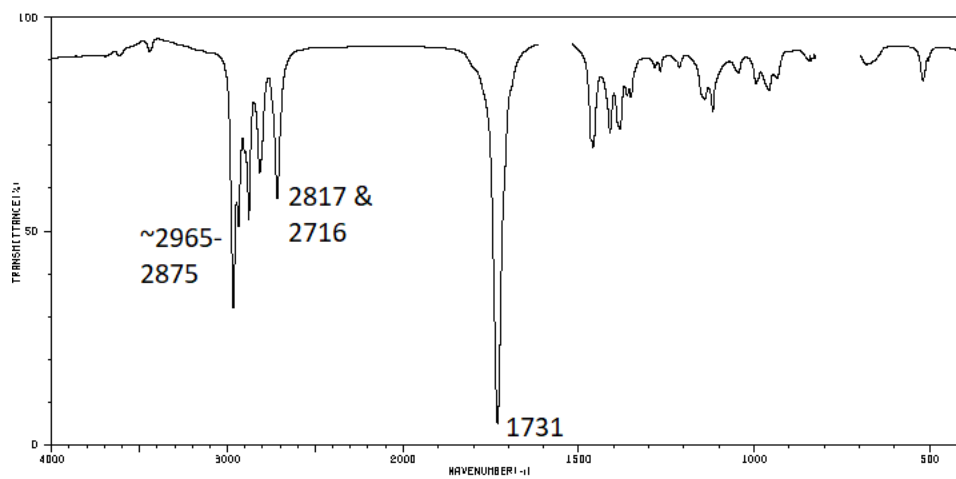
Infrared spectrum (2 pts):

Absorbance peak (cm^{-1})	Bond(s)
2990-2865	
1126	

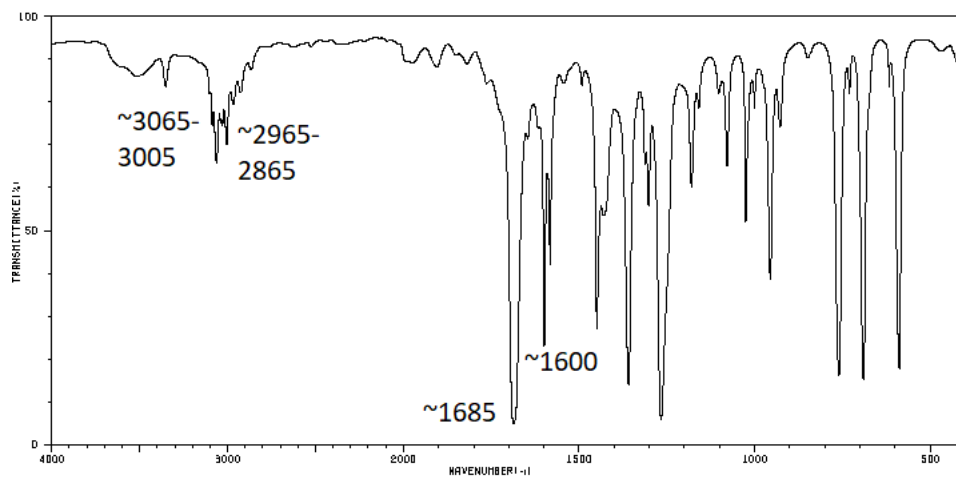
Mass spectrum (5 pts):

m/z value	Charged Fragment	Fragment Lost
74		N/A
59		
45		

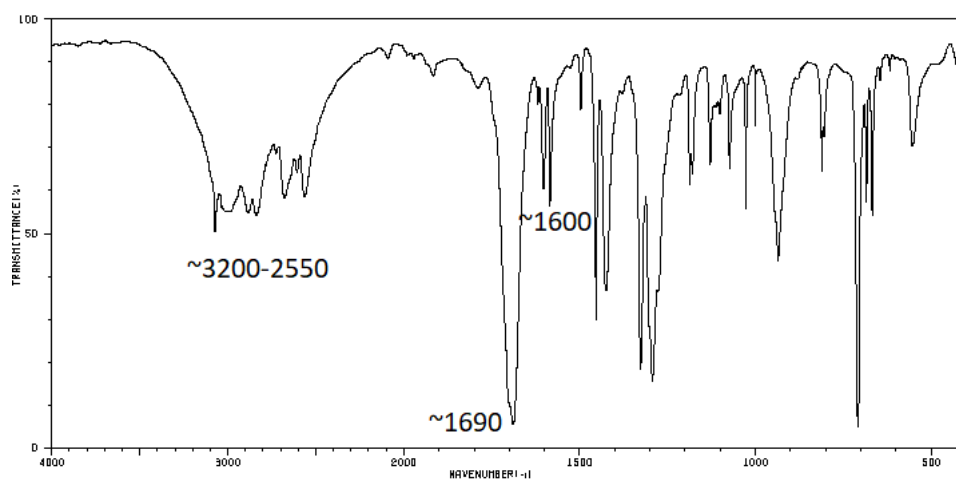
Butyraldehyde:



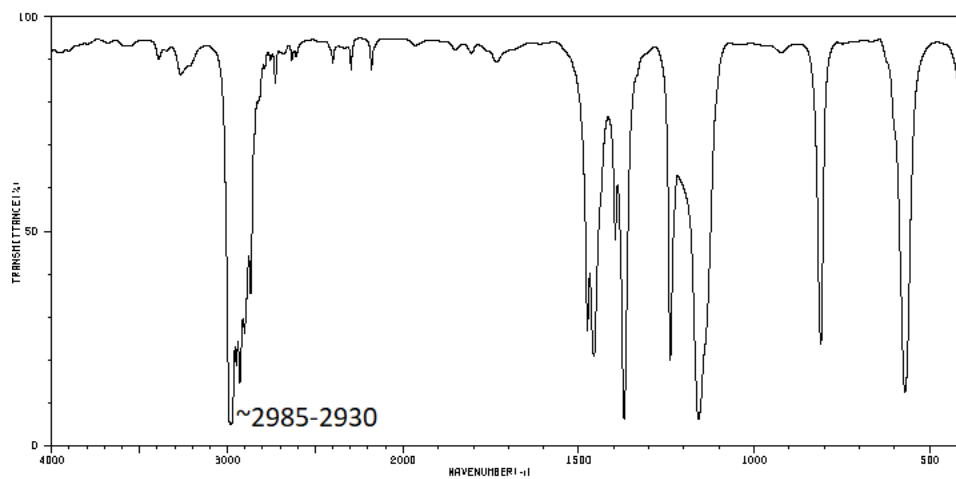
Acetophenone:



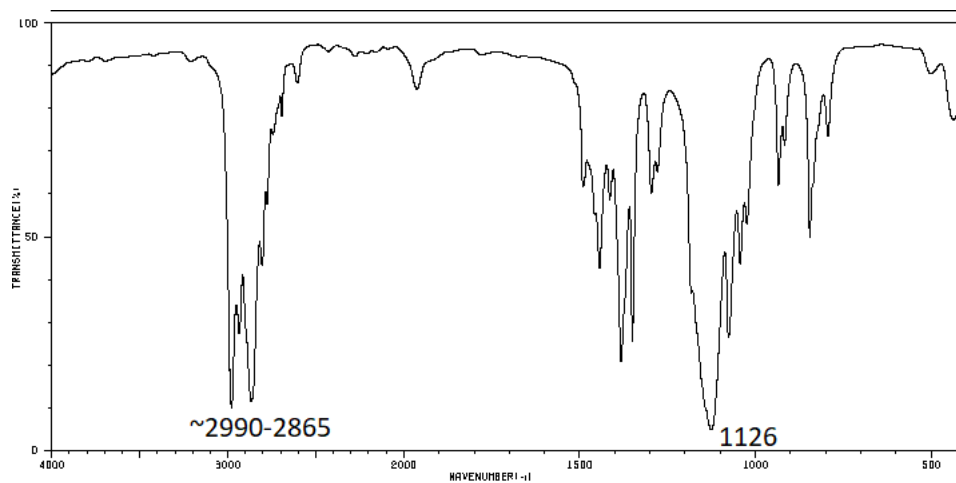
Benzoic acid:



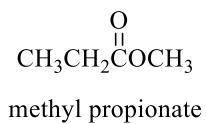
2-chloro-2-methylpropane:



Diethyl ether:



Solved example: methyl propionate (spectra appear after tables)



Infrared spectrum:

Absorbance peak (cm ⁻¹)	Bond(s)
2985-2850	sp ³ C-H
1741	C=O, saturated ester
1207	C-O, ester

Mass spectrum:

m/z value	Charged Fragment	Fragment Lost
88	$\left[\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{COCH}_3 \right]^+$	N/A
59	$\overset{\text{O}}{\parallel}\text{C}^+\text{OCH}_3$	$\cdot\text{CH}_2\text{CH}_3$
57	$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}\text{C}^+$	$\cdot\text{OCH}_3$

