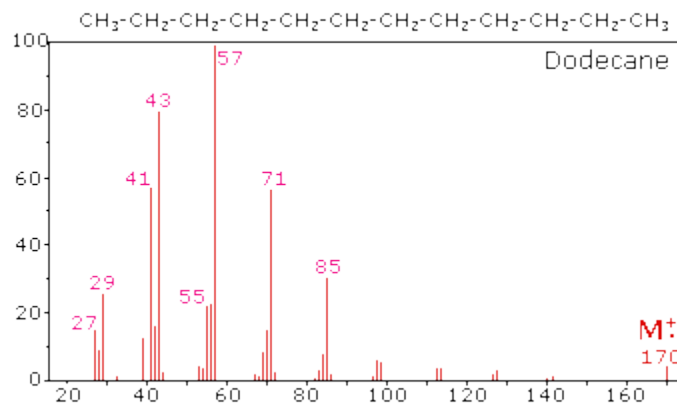


## Fragmentation Patterns

The fragmentation of molecular ions into an assortment of fragment ions is a mixed blessing. The nature of the fragments often provides a clue to the molecular structure, but if the molecular ion has a lifetime of less than a few microseconds it will not survive long enough to be observed. Without a molecular ion peak as a reference, the difficulty of interpreting a mass spectrum increases markedly. Fortunately, most organic compounds give mass spectra that include a molecular ion, and those that do not often respond successfully to the use of milder ionization conditions. Among simple organic compounds, the most stable molecular ions are those from aromatic rings, other conjugated pi-electron systems and cycloalkanes. Alcohols, ethers and highly branched alkanes generally show the greatest tendency toward fragmentation.

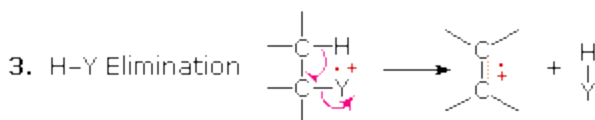
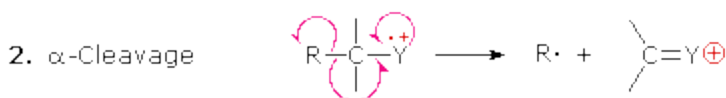
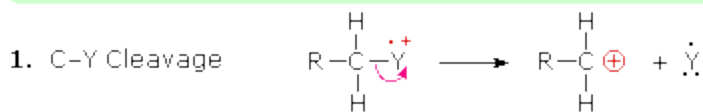
The mass spectrum of dodecane on the right illustrates the behavior of an unbranched alkane. Since there are no heteroatoms in this molecule, there are no non-bonding valence shell electrons. Consequently, the radical cation character of the molecular ion ( $m/z = 170$ ) is delocalized over all the covalent bonds. Fragmentation of C-C bonds occurs because they are usually weaker than C-H bonds, and



this produces a mixture of alkyl radicals and alkyl carbocations. The positive charge commonly resides on the smaller fragment, so we see a homologous series of hexyl ( $m/z = 85$ ), pentyl ( $m/z = 71$ ), butyl ( $m/z = 57$ ), propyl ( $m/z = 43$ ), ethyl ( $m/z = 29$ ) and methyl ( $m/z = 15$ ) cations. These are accompanied by a set of corresponding alkenyl carbocations (e.g.  $m/z = 55, 41$  &  $27$ ) formed by loss of 2 H. All of the significant fragment ions in this spectrum are even-electron ions. In most alkane spectra the propyl and butyl ions are the most abundant.

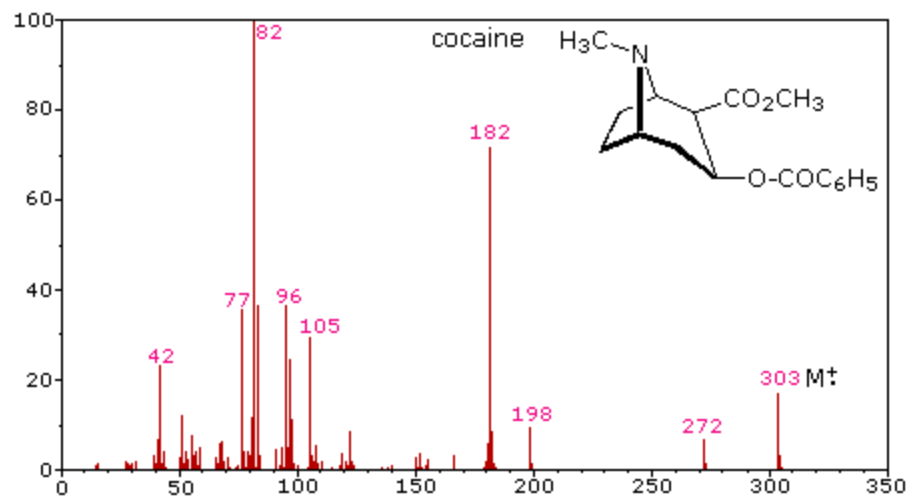
The presence of a functional group, particularly one having a heteroatom Y with non-bonding valence electrons ( $Y = \text{N}, \text{O}, \text{S}, \text{X}$  etc.), can dramatically alter the fragmentation pattern of a compound. This influence is thought to occur because of a "localization" of the radical cation component of the molecular ion on the heteroatom. After all, it is easier to remove (ionize) a non-bonding electron than one that is part of a covalent bond. By localizing the reactive moiety, certain fragmentation processes will be favored. These are summarized in the following diagram, where the green shaded box at the top displays examples of such "localized" molecular ions. The first two fragmentation paths lead to even-electron ions, and the elimination (path #3) gives an odd-electron ion. Note the use of different curved arrows to show single electron shifts compared with electron pair shifts.

molecular ions  $[M]^+$   $\equiv$   $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{Cl}}}\overset{+}{:}$  or  $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\overset{+}{-}R'$  or  $R-\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{N}}}\overset{+}{-}R'_2$  or  $R_2C=\overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}}\overset{+}{:}$



The charge distributions shown above are common, but for each cleavage process the charge may sometimes be carried by the other (neutral) species, and both fragment ions are observed. Of the three cleavage reactions described here, the alpha-cleavage is generally favored for nitrogen, oxygen and sulfur compounds. Indeed, in the previously displayed spectra of 4-methyl-3-pentene-2-one and N,N-diethylmethylamine the major fragment ions come from alpha-cleavages. Further examples of functional group influence on fragmentation are provided by a selection of compounds that may be examined by clicking the left button below. Useful tables of common fragment ions and neutral species may be viewed by clicking the right button.

The complexity of fragmentation patterns has led to mass spectra being used as "fingerprints" for identifying compounds. Environmental pollutants, pesticide residues on food, and controlled substance identification are but a few examples of this application. Extremely small samples of an unknown substance (a microgram or less) are sufficient for such analysis. The following mass spectrum of cocaine demonstrates how a forensic laboratory might determine the nature of an unknown street drug. Even though extensive fragmentation has occurred, many of the more abundant ions (identified by magenta numbers) can be rationalized by the three mechanisms shown above. Plausible assignments may be seen by clicking on the spectrum, and it should be noted that all are even-electron ions. The  $m/z = 42$  ion might be any or all of the following:  $C_3H_6$ ,  $C_2H_2O$  or  $C_2H_4N$ . A precise assignment could be made from a high-resolution  $m/z$  value (next section).



Odd-electron fragment ions are often formed by characteristic rearrangements in which stable neutral fragments are lost. Mechanisms for some of these rearrangements have been identified by following the course of isotopically labeled molecular ions.

Source : <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/Spectrpy/MassSpec/masspec1.htm#ms1>