Alkanes

In alkanes, the C-C bonds are weaker than the C-H bonds. Ionisation of the molecule results in greatly reduced bond strengths. Due to the delocalised nature of the charge, all bonds are weakened equally. The mass spectra of unbranched alkanes show groups of ions separated by 14Da. This separation is not caused by CH_2 elimination, but by fragmentation at different points in the chain of both molecular and fragment ions. The composition of the fragment ions is C_nH_{2n+1} , together with a series of less intense peaks at C_nH_{2n-1} , due to elimination of H_2 from the higher fragment ions. The molecular ion is of low or zero abundance, falling in intensity with increasing molecular weight.

Branched alkanes exhibit lower molecular ion abundancies and fragment preferentially at the points of branching. This is due to the increasing stability of primary, secondary and tertiary carbonium ions. Mass spectrometry may thus be used to determine branching points in alkanes.

Alkenes

Alkenes give more abundant molecular ions than alkanes, increasing in intensity with increasing number of double bonds. Allylic cleavages are favoured, and the ion series C_nH_{2n-1} and C_nH_{2n} are important. Isomerisation through migration of the double bond also occurs after ionisation, making it difficult to distinguish between alkene isomers.

Cycloalkanes

Saturated cyclic hydrocarbons show more intense molecular ion peaks than alkanes, but, once the ring is broken, show similar spectra as for the corresponding alkane. Ion series of masses separated by 14 Da are observed, corresponding to $C_nH_{2n+1-2r}$, where r is the number of rings.

Cycloalkenes

As discussed earlier, cyclohexene undergoes a retro-Diels-Alder reaction. This is a common reaction of cycloalkenes with a double bond in a six-membered ring.

Aromatic hydrocarbons

Aromatic hydrocarbon spectra generally show abundant molecular ions and few fragments. Cleavage of the aromatic ring to give $[M-C_2H_2]^+$ is observed, as are relatively abundant (1% - 5%) doubly-charged molecular ions. If a benzylic group is present (e.g. if there is an alkyl substituent), then a prominent peak at m/z 91, corresponding to C_7H_7, will be observed. In this case, an ion series consisting of ions at m/z 91,105,119.... is also observed, corresponding to $C_6H_5(CH_2)_n$

Saturated aliphatic alcohols

The addition of an OH group to an alkane lowers the ionisation potential, and causes the charge to be localised on one of the non-bonding electrons of the oxygen atom. This charge and radical site initiates reactions, of which alpha cleavage is the most prominent. Molecular ions are of low or zero abundance. In secondary or tertiary alcohols, the most abundant fragment ions are due to loss of the largest substituent on the alpha carbon atom. Peaks at $[M-2]^+$ and $[M-18]^+$ are often observed, but are frequently due to thermal or catalytic dehydrogenation and dehydration. $[M-H_2O]^+$ peaks are, however observed due to electron impact, especially in long-chain primary alcohols.

Cyclic aliphatic alcohols

Alpha cleavage initiated at the radical site on the oxygen atom is a favoured fragmentation pathway of cyclohexanols. This gives rise to the characteristic peaks at m/z 44, 57 and 71
Loss of H_2O from these compounds provides another pathway for fragmentation .

Phenols

Phenols show strong molecular ions, usually accompanied by a large $[M-1]^+$ ion. $[M-28]^+$ and $M-29]^+$ peaks are also observed, corresponding to loss of CO and CHO. If a substituent is present in the ortho- position to the OH group, loss of H_2O can occur by labile hydrogen migration (the ortho effect).

Aliphatic aldehydes and ketones

Molecular ions of aliphatic ketones are usually observed, but those of aliphatic aldehydes are often small, or absent for larger molecules. The McLafferty rearrangement discussed earlier is observed for these compounds, as is alpha cleavage of the bond adjacent to the carbonyl group. These compounds show ion series corresponding to $C_nH_{2n-1}O^+$.

Aromatic aldehydes and ketones

Benzaldehydes show losses of H and CHO; good molecular ions are also observed. Endocyclic ketones, such as anthraquinone, lose CO.

Aliphatic esters

Both oxygen atoms (the carbonyl oxygen and the saturated oxygen) of esters provide favourable sites for reactions. Both alpha and inductive cleavage are observed in methyl esters, giving ions at $[M-31]+$ and m/z 59 ($O=C-OCH_3$). The McLafferty rearrangement yields a strong peak at m/z 74. Esters also undergo the "McLafferty+1" rearrangement of 2 hydrogen atoms, resulting an an ion series of $[M-C_nH_{2n-1}]^+$ ions. Straight-chain alkanoates show an ion series corresponding to $CH_3OCO(CH_2)_n$, yielding peaks at m/z 87,101,115.....

Aromatic esters

Similar reactions as those for aliphatic esters are observed for aromatic esters. During fragmentation, charge retention is favoured on the fragment containing the aryl group.

Aliphatic ethers

Molecular ion abundancies for aliphatic ethers are of low abundance. both alpha and inductive cleavages initiated at the oxygen atom are observed, but the more abundant ions are due to inductive cleavage. Ion series consisting of $C_nH_{2n+1}O^+$ at m/z 31,45,59.... are also observed. Ethers containing higher straight-chain alkyl groups show ion series at C_nH_{2n}.

Thiols and sulphides

Spectra of thiols and sulphides are similar to those of alcohols and ethers, except that the molecular ions are usually more abundant. The C-S sigma bond can be cleaved, with the charge remaining on the sulphur containing fragment. Ion series resulting from $C_nH_{2n+1}S^+$ ions are observed.

Amines

Aliphatic amines show weak or zero molecular ion intensity, due to the nitrogen atom providing a strong driving force for alpha cleavage. This alpha cleavage reaction usually leads to the base peak in alkyl amines at m/z 30, and also accounts for the base peak in substituted amines. Ion series of $C_nH_{2n+2}N^+$ are observed.