Mechanisms of ion decomposition

Introduction

Decomposition reactions in a mass spectrometer E.I. source are unimolecular; due to the low pressures in these sources, ion-molecule interactions or other collisions are of low probability. Ions with sufficient internal energy will fragment by a variety of reactions. Each reaction will produce an ion and a neutral fragment. Ions formed during a reaction may have sufficient energy to fragment further.

\[
\text{ABC}^+ \rightarrow \text{A}^+ + \text{BC}^-
\]

or \[
\text{ABC}^+ \rightarrow \text{A}^- + \text{BC}^+
\]

followed by \[
\text{BC}^+ \rightarrow \text{B}^+ + \text{C}^-
\]

Rearrangements are also possible \[
\text{ABC}^+ \rightarrow \text{AC}^+ + \text{B}
\]

Mechanisms

1) Sigma-bond dissociation

The ionisation of alkanes causes the C-C bond lengths to increase, and the bond energy to decrease. Fragmentation takes place at these C-C bonds in saturated systems. Fragmentation occurs preferentially at the more substituted C atoms (sites of branching in branched alkanes).

2) \(\alpha\) - cleavage (radical-site initiation)

This reaction is caused by the tendency for electron pairing; the unpaired electron at the radical site is donated to create a new bond with the adjacent atom. another bond to this atom is then cleaved.

\[
e.g. \quad R \text{-----CR}_2 \text{-----Y}^+R \quad \rightarrow \quad R^- + CR_2 = Y^+R
\]

This type of reaction is a homolytic cleavage, and a single electron is transferred. The site of the unpaired electron is moved in this reaction. The probability of a radical site initiating a reaction is related to the radical site's tendency for electron donation:

\[
N > S, O, \pi > Cl, Br > H.
\]

3) Charge-site initiation (inductive cleavage)

This reaction is caused by the attraction of an electron pair:

\[
e.g. \quad R \text{-----Y}^+ \text{-----R} \quad \rightarrow \quad R^+ + Y^-R
\]

The tendency for formation of the ion \(R^+\) from the molecule \(RY\) is related to the inductive effect of the element \(Y\). Strongly eleclenegative elements have a larger inductive effect. In general, the tendency is halogens > O, S >> N, C. This cleavage is heterolytic, and requires that the charge site migrates. This means that this reaction is less favoured than radical-site reactions.

4) Decomposition of cyclic structures

To produce a fragment from a ring, 2 bonds must be broken. If only one bond is cleaved, then no change in mass occurs, but the charge and radical sites are separated. The unpaired electron at the radical site is donated to form a bond with the adjacent carbon atom, and another bond to that carbon atom is cleaved.
5) Retro-Diels-Alder reaction

In a cyclic compound containing a double bond such as cyclohexene, the pi electrons of the double bond are a favored charge and radical site. Two successive alpha cleavages produce the neutral \( \text{C}_2\text{H}_4 \); the other product is butadiene. This reaction is the mass spectrometric analogue of the retro-Diels-Alder reaction. The charge may reside with the \( \text{C}_2\text{H}_4 \) fragment, but with a low probability, since it has a higher ionization energy than butadiene. If a substituent is present, the charge may remain on the fragment containing this group, depending on the relative ionisation energies of the two products.

6) The McLafferty rearrangement

In this rearrangement, an electron is donated through space; the other electron to form the bond comes from a bond to this atom. The initial cleavage does not cause fragmentation, only rearrangement and transfer of the radical site. This new radical site then initiates an alpha cleavage, resulting in the formation of the odd-electron ion. This rearrangement occurs at unsaturated functional groups, notably carbonyls, and is common reaction in ketones, aldehydes, esters, acids, and amides.

7) Hydrogen rearrangement to a saturated heteroatom

A hydrogen molecule can transfer to a radical site on a saturated heteroatom. Following this, a charge-site reaction is favored, cleaving a bond to the heteroatom. This reaction results in loss of \( \text{H}_2\text{O} \) from alcohols. The reaction is favored for alcohols as: primary > secondary > tertiary, since alpha cleavage reactions are more competitive in the higher alcohols.