

7 Mass Spectrometry



7.1

Alkanes [1]

7.1.1

Unbranched Alkanes [2,3]

Fragmentation: Larger alkyl fragments (with $C_{n>4}$) are chiefly formed by direct cleavage. They dehydrogenate and undergo substantial H and skeleton rearrangements. Smaller alkyl fragments (C_2 to C_4) are mainly formed by secondary decomposition of higher alkyl fragments. Eliminations of groups from within the chain (and recombination of its ends) also occur.

Ion series: Consecutive peaks corresponding to C_nH_{2n+1} (m/z 29, 43, 57, 71,...), accompanied by C_nH_{2n-1} (m/z 27, 41, 55, 69,...) and C_nH_{2n} (m/z 28, 42, 56, 70,...) of lower intensity.

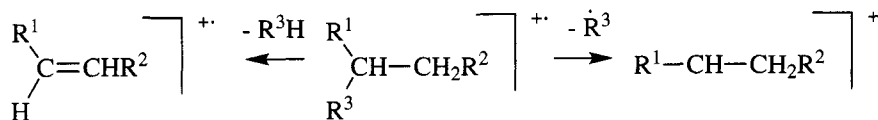
Intensities: Maximum intensity at m/z 43 or 57; with increasing masses, intensity of local maxima smoothly decreasing to a minimum at $[M-15]^+$.

Molecular ion: Medium intensity.

7.1.2

Branched Alkanes

Fragmentation: In most cases, apparently simple bond cleavages, preferably at branched C atoms. The positive charge remains mainly on the branched C atom. Mechanistically, many H and skeleton rearrangements take place. This is reflected by the fact that no specific localization of heavy isotopes is possible.



Ion series: Consecutive peaks corresponding to C_nH_{2n+1} (m/z 29, 43, 57, 71,...), accompanied by C_nH_{2n-1} (m/z 27, 41, 55, 69,...) and C_nH_{2n} (m/z 28, 42, 56, 70,...) of lower intensity.



Intensities: Local intensity maxima at those masses that result from cleavage at branched C atoms if the charge is localized there. Both C_nH_{2n+1} and (often more characteristically) C_nH_{2n} show this tendency.

Molecular ion: Intensity decreasing with increasing degree of branching. No $M^{+\cdot}$ is observed in highly branched systems.

7.1.3

References

- [1] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
- [2] K. Levsen, H. Heimbach, G.J. Shaw, G.W.A. Milne, Isomerization of hydrocarbon ions. VIII. The electron impact induced decomposition of *n*-dodecane, *Org. Mass Spectrom.* **1977**, 12, 663.
- [3] A. Lavanchy, R. Houriet, T. Gäumann, The mass spectrometric fragmentation of *n*-alkanes, *Org. Mass Spectrom.* **1979**, 14, 79.

7.2

Alkenes [1-4]



7.2.1

Unbranched Alkenes

Fragmentation: Dominant loss of alkyl residues and neutral alkenes. The position of highly substituted double bonds can be localized because in this case alkene eliminations are specific McLafferty-type reactions. Otherwise, double bonds can be localized in derivatives, such as epoxides and glycols, or by means of low energy ionization techniques. Branching effects are less characteristic than in isoalkanes. Alicyclic compounds exhibit very similar spectra.

Ion series: Consecutive peaks corresponding to $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69, 83,...), accompanied by alkyl and alkene ions, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...), mostly of lower intensity.

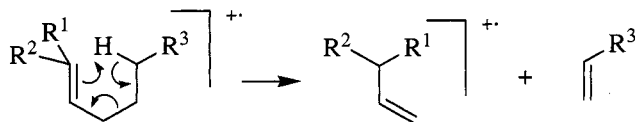
Intensities: Dominant maxima in the lower mass range, peaking around C_4 . Local even-mass maxima due to alkene eliminations if the double bond is highly substituted.

Molecular ion: Significant, but not necessarily strong.

7.2.2

Branched Alkenes

Fragmentation: Highly substituted double bonds are less easily displaced than the unsubstituted ones and give rise to specific alkene eliminations of the McLafferty type, resulting in significant local maxima corresponding to C_nH_{2n} (cf. scheme). The latter may allow to localize the double bond. With unsubstituted double bonds, no reliable localization is possible and only moderately useful branching effects can be observed. The branching position is more easily determined after reduction to an alkane (in situ in GC/MS with H_2 as carrier gas and heated Pt wool as catalyst).



Ion series: Maxima of the alkene type ($\text{C}_n\text{H}_{2n-1}$; m/z 41, 55, 69, 83,...), accompanied by weaker alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71, 85,...), in the low mass range and more significant alkene ions, C_nH_{2n} (m/z 42, 56, 70, 84,...).

Intensities: Intensive peaks in the lower mass range. Diagnostically important local maxima of even mass, frequently also in the higher mass range.

Molecular ion: Usually significant.

7.2.3

Polyenes and Polyynes

Fragmentation: The spectra of aliphatic compounds with several triple and/or double bonds are similar to those of aromatic hydrocarbons.

Ion series: Very similar to those of aromatic hydrocarbons, but fragments with higher hydrogen contents than in aromatics (m/z 54, 55; 66, 67; 79, 80) are usually found in polyenes and polyynes.

Intensities: Very similar distribution of peak intensities as for aromatic hydrocarbons.

Molecular ion: Usually strong, as in aromatic hydrocarbons.

7.2.4

References

- [1] A.G. Loudon, A. Maccoll, The mass spectrometry of the double bond. In: *The Chemistry of Alkenes*; J. Zabicky, Ed.; Interscience: London, 1970; p 327.
- [2] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
- [3] N.J. Jensen, M.L. Gross, Localization of double bonds. *Mass Spectrom. Rev.* **1987**, 6, 497.
- [4] C. Dass, Ion-molecule reactions of [ketene] $^{+}$ as a diagnostic probe for distinguishing isomeric alkenes, alkynes, and dienes: A study of the C_4H_8 and C_5H_8 isomeric hydrocarbons, *Org. Mass. Spectrom.* **1993**, 28, 940.

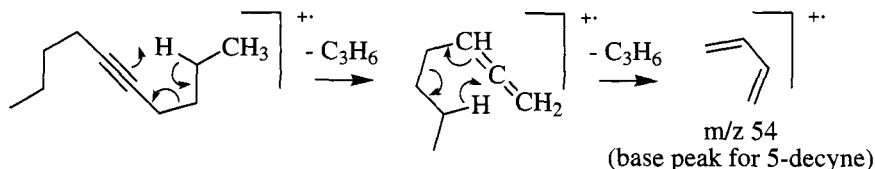
7.3

Alkynes [1]

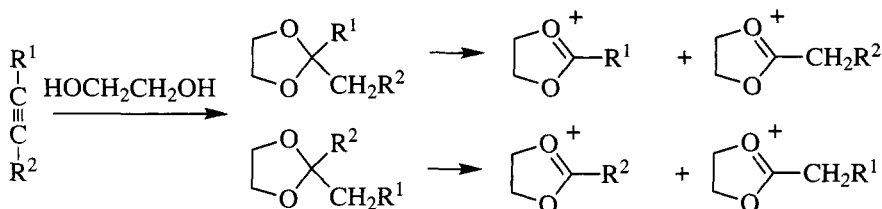
7.3.1

Aliphatic Alkynes

Fragmentation: Tendency to lose a non-acetylenic H[•] from M^{•+}. Extensive rearrangements (including consecutive McLafferty rearrangements to the triple bond) result in uncharacteristic degradation:



Rearrangement products at m/z 82 and 96 are dominant in nonbranched alkynes with $C_{n>8}$. Consecutive loss of methyl radical occurs. In general, no reliable localization of the triple bond is possible except in derivatives (as in ethylene glycol adducts [1], see scheme).



Ion series: Prominent peaks for C_nH_{2n-3} (m/z 25, 39, 53, 67, 81,...), accompanied by C_nH_{2n-1} (m/z 41, 55, 69, 83,...) and alkyl ions C_nH_{2n+1} (m/z 43, 57, 71, 85,...). Occasionally even-mass maxima for C_nH_{2n-2} (m/z 26, 40, 54, 68, 82,...).

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak or missing in spectra of smaller molecules, significant in those of larger ones. Generally, $[M-1]^+$ is present. In terminal acetylenes, it is normally more abundant than $M^{•+}$.

7.3.2

References

- [1] C. Lifshitz, A. Mandelbaum, Mass spectrometry of acetylenes. In: *The Chemistry of the Carbon-Carbon Triple Bond*; S. Patai, Ed.; Wiley: New York, 1978; p 157.

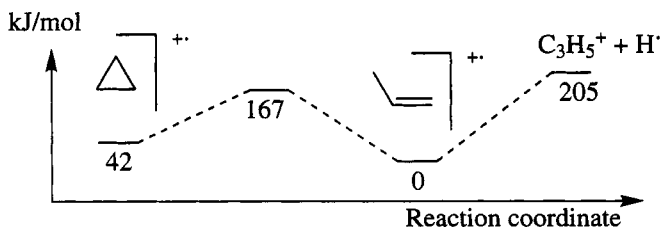
7.4

Alicyclic Hydrocarbons [1]

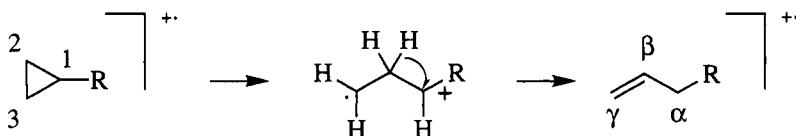
7.4.1

Cyclopropanes [2,3]

Fragmentation: Generally, spectra of cyclopropanes and alkenes are very similar because at 70 eV ionization, the ring readily isomerizes to corresponding alkene radical cations.



Preferred primary fragmentation by bond cleavage at branched C atoms. Loss of alkyl residues and of neutral alkenes dominates. The ring of monosubstituted cyclopropanes is opened exclusively at the 1,2- and not the 2,3- bond. The primarily formed double bond is predominantly (for R: OCH₃) or exclusively (for R: H, alk, COOCH₃) found in the β,γ -position (even for COOCH₃, where the α,β -unsaturation is thermodynamically more stable).



Molecular ions of cyclopropyl cyanide, allyl cyanide, methacrylonitrile, and pyrrole rearrange to one common radical ion, most likely that of pyrrole [4].

Ion series: Consecutive maxima corresponding to C_nH_{2n-1} (m/z 41, 55, 69, 83,...), accompanied by alkyl and alkenyl ions of the type C_nH_{2n+1} (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...), mostly of lower intensity.

Intensities: Dominant peaks in the low mass range, peaking around C_4 . Local even-mass maxima due to alkene eliminations if the resulting double bond is highly substituted.

Molecular ion: Significant, but not necessarily strong.

7.4.2

Saturated Monocyclic Alicyclics [5]

Fragmentation: Preferred primary fragmentation by bond cleavage at branched C atoms, followed by loss of alkyl residues and alkenes.

Ion series: Consecutive maxima corresponding to C_nH_{2n-1} (m/z 41, 55, 69, 83,...), accompanied by C_nH_{2n+1} (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...) of lower intensities. In general, the maxima are so similar to those of alkenes that no clear distinction is possible.

Intensities: Overall distribution of peaks maximizing in the lower mass range, around C_4 or C_5 . Local maxima can result from branching effects.

Molecular ion: Significant, mostly of medium intensity.



7.4.3

Polycyclic Alicyclics

Fragmentation: Most important primary cleavage at highly branched carbon atoms, followed by H rearrangements and complex fragmentations.

Ion series: With increasing number of rings, the position of unsaturated hydrocarbon fragments in the upper m/z range shifts from C_nH_{2n-1} (m/z 41, 55, 69, 83,...) to C_nH_{2n-3} (m/z 39, 53, 67, 81,...) and to C_nH_{2n-5} (m/z 51, 65, 79, 93,...). Typically, maxima in the lower m/z range have a lower degree of unsaturation than those in the upper m/z range.

Intensities: Major maxima evenly distributed, somewhat more intense in the high mass or M^{++} range.

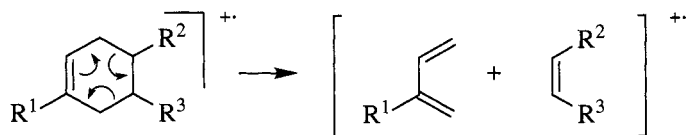
Molecular ion: Strong.

7.4.4

Cyclohexenes

Fragmentation: Loss of larger ring substituents as well as retro-Diels–Alder reaction, yielding even-mass maxima with one or two double-bond equivalents, C_nH_{2n} (m/z 42, 56, 70, 84,...) and C_nH_{2n-2} (m/z 40, 54, 68, 82,...), unless the retro-Diels–Alder product corresponds to ethylene. Somewhat unexpectedly, the base peak of cyclohexene is at $[M-15]^+$.

The retro-Diels–Alder reaction often accounts for prominent fragments of cyclohexenes and 1,4-cyclohexadienes:



However, double-bond migration may or may not occur beforehand. Also, other fragmentation pathways may dominate. Therefore, a reliable localization of the

double bond in cyclohexene derivatives of unknown structure is not necessarily possible. For example, the base peak of 1,2-dimethylcyclohexene is at m/z 68 rather than at the expected m/z 82.

Ion series: Unsaturated hydrocarbon fragments in the upper m/z range are shifted, relative to cyclohexane fragments, by two mass units to C_nH_{2n-3} (m/z 39, 53, 67, 81,...). Typically, maxima in the lower m/z range have a lower degree of unsaturation than those in the upper m/z range.

Intensities: Intensive peaks evenly distributed over whole mass range.

Molecular ion: Medium intensity (ca. 40% in cyclohexene).



7.4.5 References

- [1] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
- [2] H. Schwarz, The chemistry of ionized cyclopropanes in the gas phase. In: *The Chemistry of the Cyclopropyl Group*; Z. Rappoport, Ed.; Wiley: Chichester, 1987; p 173.
- [3] J.R. Collins, G.A. Gallup, Energy surfaces in the cyclopropane radical ion and the photo-electron spectrum of cyclopropane, *J. Am. Chem. Soc.* **1982**, 104, 1530.
- [4] G.D. Willet, T. Baer, Thermochemistry and dissociation dynamics of state-selected C_4H_4X ions. 3. $C_4H_5N^+$, *J. Am. Chem. Soc.* **1980**, 102, 6774.
- [5] E.F.H. Brittain, C.H.J. Wells, H.M. Paisley, Mass spectra of cyclobutanes and cyclohexanes of molecular formula $C_{10}H_{16}$, *J. Chem. Soc. B* **1968**, 304.

7.5

Aromatic Hydrocarbons [1-4]

7.5.1

Aromatic Hydrocarbons

Fragmentation: Weak tendency of fragmentation. Elimination of H^+ and successive H_2 eliminations, yielding $[M-1]^+$, $[M-3]^+$, and $[M-5]^+$ of decreasing intensities. In condensed aromatics, $[M-2]^+$ can be a dominating fragment. Further typical fragmentation reactions are the eliminations of acetylene (Δm 26) and C_3H_3 (Δm 39). Some CH_3 elimination frequently occurs in pure aromatic compounds. In the case of diphenyl compounds, biphenylene (m/z 152) and, if a CH_2 group is available, fluorene (m/z 165) ions are typically observed.

Ion series: C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), for polycyclic aromatics gradually changing to more highly unsaturated ions. Doubly charged ions frequently occur, increasingly with increasing number of π -electron systems.

Intensities: Weak fragments. The intensity pattern of doubly charged ions does not follow that of the corresponding singly charged ions.

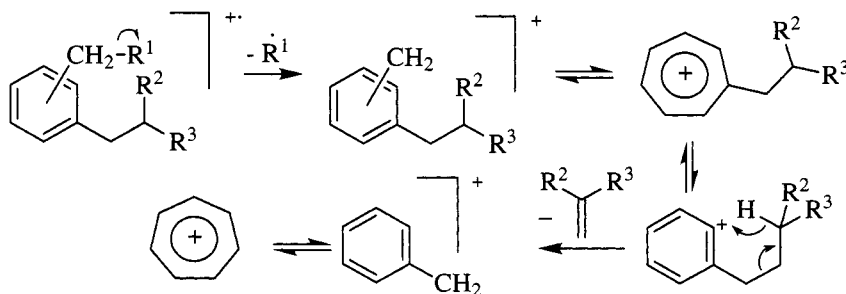
Molecular ion: Strong.



7.5.2

Alkylsubstituted Aromatic Hydrocarbons

Fragmentation: Dominant loss of alkyl residues by benzylic cleavage, followed by elimination of alkenes.



At low resolution, ethylbenzyl and β -phenylethyl are isobaric with benzoyl (m/z 105). In contrast to benzoyl, dehydrogenation products (m/z 104, 103) as well as protonated benzene (m/z 79) are also present if m/z 105 is a hydrocarbon rest.

Ion series: Aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), in the lower mass range.

Intensities: Intensive peaks mainly in the higher mass range. Maxima by benzylic cleavage.

Molecular ion: Strong or medium.

7.5.3**References**

- [1] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
- [2] W. Schönfeld, Fragmentation diagrams for elucidation of decomposition reactions of organic compounds. 1. Aromatic hydrocarbons (in German), *Org. Mass. Spectrom.* **1975**, 10, 321.
- [3] C. Lifshitz, Tropylium ion formation from toluene: Solution of an old problem in organic mass spectrometry. *Acc. Chem. Res.* **1994**, 27, 138.
- [4] M.V. Buchanan, B. Olerich, Differentiation of polycyclic aromatic hydrocarbons using electron-capture negative chemical ionization, *Org. Mass. Spectrom.* **1984**, 19, 486.



7.6 Heteroaromatic Compounds [1,2]

7.6.1 General Characteristics

Fragmentation: Mostly fragments of aromatic character with specific eliminations including heteroatoms, e.g., elimination of HCN, CO, CHO, CS, and CHS from $M^{+\cdot}$ and of HCN, CO, and CS from fragments. In the case of alkylsubstituted heteroaromatics, occurrence of benzylic-type cleavage and McLafferty rearrangements of substituents with $C_{n>1}$, as well as specific rearrangements including heteroatoms, especially in N aromatics.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...) in the lower mass range if the necessary number of C atoms is present (no such fragments, e.g., in pyrazine). Ions including heteroatoms like $HCN^{+\cdot}$ (m/z 27), CH_3CNH^+ (m/z 42), and $CS^{+\cdot}$ (m/z 44).

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Generally strong. $[M-1]^+$ is often relevant in alkylsubstituted heteroaromatics.



7.6.2 Furans [3]

Fragmentation: Oxygen can be lost from $M^{+\cdot}$ together with the neighboring C as CHO (Δm 29). In 2- or 6-methyl-furans, CH_3CO^+ (m/z 43) can be seen (base peak in 2,5-dimethylfuran). As in aromatic methyl ethers, $[M-43]^+$ is a product of a two-step reaction: $(M^{+\cdot}-CH_3^{\cdot}-CO)$. Furans substituted with an alkyl group ($C_{n>1}$): benzylic-type cleavage (to pyrylium ion $C_5H_5O^+$, m/z 81), followed by loss of CO.

Ion series: Mainly aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...).

Intensities: Intensive peaks mainly in the higher mass range. The fragments are usually stronger than in purely aromatic hydrocarbons.

Molecular ion: Strong. No pronounced tendency to protonate. Usually, $[M-1]^+$ is very strong in methylfurans.

7.6.3 Thiophenes [4]

Fragmentation: Sulfur can be lost from $M^{+\cdot}$ together with the neighboring C as CHS (Δm 45) or CS (Δm 44). Typical for thiophenes substituted with an alkyl group ($C_{n>1}$) is benzylic-type cleavage followed by loss of CS (Δm 44). Protonated thiophene (m/z 85) is a characteristic product of monoalkylated thiophenes.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...). Besides the isotope peak ($M+2$), the signals at m/z 44 and 45 (CS^+ and CHS^+) are indicators for sulfur.

Intensities: Dominant peaks for M^+ and products of benzylic-type cleavage.

Molecular ion: Strong. Characteristic S isotope signal ($[M+2]^+$ corresponds to 4.4% of M^+). No pronounced tendency of protonation. Usually, $[M-1]^+$ is very strong in methylthiophenes.

7.6.4

Pyrroles [5]

Fragmentation: HCN elimination from M^+ and from fragments. In methylpyrroles, $[M-1]^+$ is dominant. Benzylic-type cleavage in C- and N-alkylpyrroles with or without (non-specific) H rearrangements.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...).

Intensities: Dominant peaks for M^+ and products of benzylic-type cleavage.

Molecular ion: Strong (odd mass for odd number of N in the molecule). No tendency to protonate. In methylsubstituted pyrroles, $[M-1]^+$ is dominant.

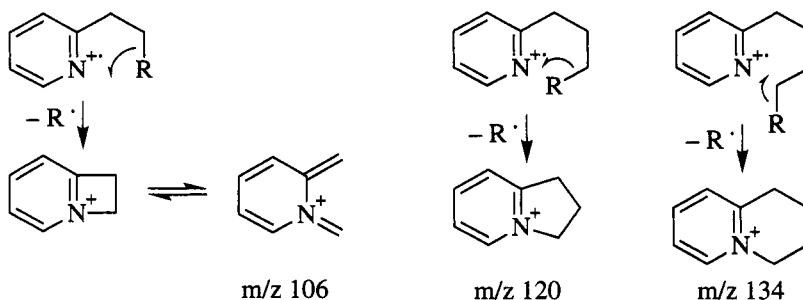


7.6.5

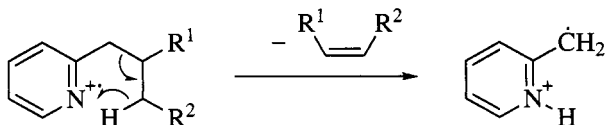
Pyridines

Fragmentation: HCN elimination (Δm 27) from fragments and the ion H_2CN^+ (m/z 28) are characteristic. Additional reactions in 2- or 6-methylpyridines are CH_3CN elimination (Δm 41) and the formation of CH_3CNH^+ (m/z 42). Benzylic cleavage is dominant for 3-alkyl-, strong for 4-alkyl-, and weak for 2-alkylpyridines. Typical rearrangements with participation of the N atom in 2- and 6-alkylpyridine derivatives.

Intramolecular N-alkylation in 2-alkyl derivatives:



McLafferty rearrangements are important in 2- and 4-alkylpyridines:



Ion series: Aromatic hydrocarbon fragments, C_nH_n , $C_nH_{n\pm 1}$ and $C_nH_{n\pm 1}N$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant peaks for $M^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong except when benzylic-type cleavage is possible. Odd mass for an odd number of N in the molecule. No tendency to protonate. $[M-1]^+$ is usually present and is strong in alkylsubstituted pyridines.

7.6.6

N-Oxides of Pyridines and Quinolines



Fragmentation: The $[M-O]^{+\cdot}$ ion, with variable intensity, is probably due to thermal decomposition. The fragments $[M-CO]^{+\cdot}$ and, if an alkyl group is present on the neighboring C atom, $[M-OH]^{+\cdot}$ are relevant for quinoline *N*-oxides. Rearrangements with ring formation including the N–O moiety if alkyl or aryl groups are present in the neighboring positions.

Ion series: As for the corresponding heteroaromatics, too, aromatic hydrocarbon fragments C_nH_n , $C_nH_{n\pm 1}$ and $C_nH_{n\pm 1}N$ (m/z 39–41, 51–54, 63–67, 75–80,...) are observed.

Intensities: Dominant peaks for $M^{+\cdot}$ and products of benzylic-type cleavage.

Molecular ion: Strong, except when $[M-O]^{+\cdot}$ dominates due to experimental conditions or when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate.

7.6.7

Pyridazines and Pyrimidines

Fragmentation: Loss of N_2 and CH_2N^{\cdot} from pyridazines to yield $M-28$. Also, loss of N_2H^{\cdot} (especially important in methylpyridazines) to give $[M-29]^+$. In pyridazine *N*-oxides, consecutive loss of NO^{\cdot} and HCN . Consecutive loss of two HCN (Δm 27) molecules from pyrimidines. In 2-, 4-, and 6-methylpyrimidines, CH_3CN is eliminated (Δm 41) and the ion $CH_3CNH^{+\cdot}$ (m/z 42) occurs.

Ion series: Aromatic hydrocarbon fragments (C_nH_n , $C_nH_{n\pm 1}$) and, for pyrimidines, $C_nH_{n\pm 1}N$, at low masses (m/z 39, 51–53).

Intensities: Dominant peak for $M^{+\cdot}$.

Molecular ion: Strong. No tendency to protonate. For pyrimidines, $[M-1]^+$ is usually observable.

7.6.8

Pyrazines

Fragmentation: Consecutive losses of two HCN (Δm 27) molecules. For methylpyrazines, elimination of CH_3CN (Δm 41) and formation of CH_3CNH^+ (m/z 42).

Ion series: No aromatic character of the spectra.

Intensities: Dominant peak for $\text{M}^{+\cdot}$.

Molecular ion: Strong. No tendency to protonate. Usually, $[\text{M}-1]^+$ is observable; it can be stronger than $\text{M}^{+\cdot}$ in alkylsubstituted ($\text{C}_{n>1}$) pyrazines.

7.6.9

Indoles



Fragmentation: Analogous to pyrrole; HCN elimination (Δm 27) from $\text{M}^{+\cdot}$ and from fragments. From $\text{M}^{+\cdot}$ also $\text{H}_2\text{CN}^{\cdot}$ (Δm 28) elimination (in one or two steps). In methylsubstituted indoles, $[\text{M}-1]^+$ is dominant. In *N*-methylindoles, $[\text{M}-15]^+$ is significant. Benzylic-type cleavage in *C*- and *N*-alkylindoles with or without (non-specific) H rearrangements.

Ion series: Aromatic ion series.

Intensities: Dominant maxima in the higher mass range.

Molecular ion: Strong. No tendency to protonate. In methylsubstituted indoles, $[\text{M}-1]^+$ is strong.

7.6.10

Quinolines and Isoquinolines

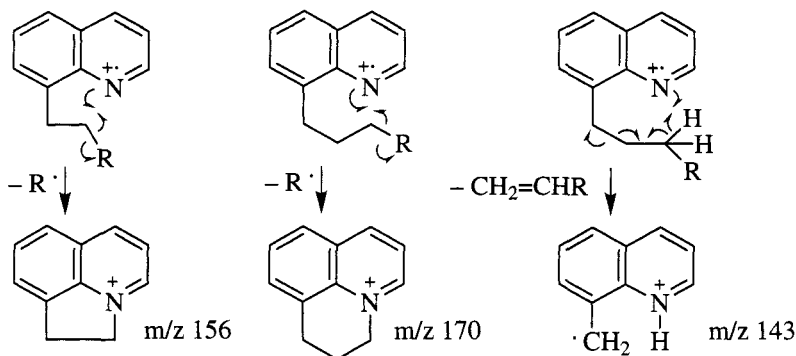
Fragmentation: Similar to pyridine: HCN elimination (Δm 27) from $\text{M}^{+\cdot}$, $[\text{M}-1]^+$, and fragments. In methylquinolines and isoquinolines also CH_3CN eliminations (Δm 41). In alkylsubstituted ($\text{C}_{n>1}$) quinolines, benzylic cleavage dominates except when neighboring effects of N can play a role. For 2- and 8-alkylquinolines, as well as 1- and 3-alkylisoquinolines, see rearrangements in pyridines.

Ion series: Aromatic hydrocarbon fragments, C_nH_n , $\text{C}_n\text{H}_{n\pm 1}$, and $\text{C}_n\text{H}_{n\pm 1}\text{N}$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant peak for $\text{M}^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong, except when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate. $[\text{M}-1]^+$ is usually present and is strong in alkylsubstituted quinolines.

Rearrangements in 8-alkylquinolines:



7.6.11

Cinnoline, Phthalazine, Quinazoline, Quinoxaline



Fragmentation: Same as for the corresponding monocyclic heteroaromatics pyridazine, pyrimidine, and pyrazine. Characteristic for pyridazine, cinnoline, and phthalazine is the elimination of N_2 (Δm 28) and of N_2H^+ (Δm 29) from their alkyl derivatives. Phthalazine loses HCN (Δm 27) twice.

Ion series: Aromatic hydrocarbon fragments (C_nH_n , $\text{C}_n\text{H}_{n\pm 1}$) and $\text{C}_n\text{H}_{n\pm 1}\text{N}$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant maximum for $\text{M}^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong, except when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate. $[\text{M}-1]^+$ is usually present and is strong in alkylsubstituted compounds.

7.6.12

References

- [1] Q.N. Porter, *Mass Spectrometry of Heterocyclic Compounds*, 2nd ed.; Wiley: New York, 1985.
- [2] D.G.I. Kingston, B.W. Hobrock, M.M. Bursey, J.T. Bursey, Intramolecular hydrogen transfer in mass spectra. III. Rearrangements involving the loss of small neutral molecules, *Chem. Rev.* **1975**, 75, 693.
- [3] R. Spilker, H.-F. Grützmacher, Isomerization and fragmentation of methylfuran ions and pyran ions in the gas phase, *Org. Mass. Spectrom.* **1986**, 21, 459.
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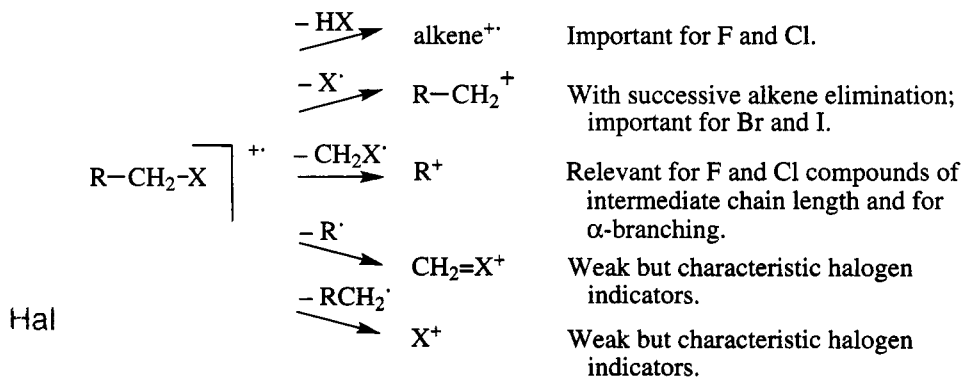
7.7

Halogen Compounds [1-3]

7.7.1

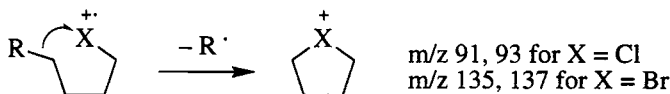
Saturated Aliphatic Halides

Fragmentation: Loss of halogen radical ($I > Br > Cl > F$) followed by elimination of alkenes. Loss of alkyl radical followed by elimination of acid HX. Loss of acid HX to give an alkene radical cation.



Ion series: The dominant hydrocarbon fragments are mainly alkenyl fragments ($\text{C}_n\text{H}_{2n-1}$) for F and Cl, mixed alkyl ($\text{C}_n\text{H}_{2n+1}$) and alkenyl fragments ($\text{C}_n\text{H}_{2n-1}$) for Br, and mainly alkyl fragments ($\text{C}_n\text{H}_{2n+1}$) for I.

Intensities: Intensive peaks mainly in the lower mass range. Characteristic maxima for Cl and Br at $\text{C}_4\text{H}_8\text{X}$ (m/z 91/93 and 135/137, respectively), which has a cyclic structure:



Alkyl substituents on the chain reduce the intensity of this fragment. If it is strong, $[\text{M}-\text{X}]^+$ is weak. In the case of iodoalkanes some I^+ and $\text{HI}^{\bullet+}$ at m/z 127, 128 is usually detectable.

Molecular ion: Strong for the smallest alkanes, with increasing intensity in the sequence F, Cl, Br, I. Decreases rapidly with increasing mass and with increasing branching. It is negligible for F and Cl if the n -alkyl chains are longer than pentyl, and for Br and I if they are longer than heptyl and nonyl, respectively. Low tendency to protonate. Characteristic isotope patterns for Cl and Br. Iodine can be detected because of its high mass; the ^{13}C signals of $\text{M}^{\bullet+}$ and its fragments are conspicuously weak.

7.7.2

Polyhaloalkanes

Fragmentation: Preferred fragmentation of the C–C bond if several halogen atoms are bonded to one of these carbon atoms. CF_3 (m/z 69) is often the base peak in terminally perfluorated alkanes, and so is CHCl_2 (m/z 83, 85, 87) in terminally dichlorinated compounds. Often, X_2 is eliminated besides the usual fragmentation of X^\cdot and HX . Interchange of halogens may occur. For example, m/z 85 (CF_2Cl) is a dominant signal (ca. 60%) for CF_3CFCI_2 .

Ion series: Most fragments are halogenated alkyl and alkenyl groups, easily detectable on the basis of the isotope signals in the cases of Cl and Br.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak, decreasing with increasing number of halogen atoms. Absent from the spectra of many polyhalogenated compounds.

7.7.3

Aromatic Halides

Fragmentation: Consecutive losses of halogen radicals and/or acid HX . In perhalogenated aromatics, decomposition down to C_x^+ , with x from 1 to 6 (m/z 12, 24, 36, 48, 60, 72). If alkylsubstituted ($\text{C}_{n>1}$), the base peak is mostly the result of benzylic cleavage. In an otherwise aromatic environment, m/z 57 is a F indicator ($\text{C}_3\text{H}_2\text{F}^+$). Elimination of CF_2 (Δm 50) from CF_3 groups attached to the aromatic ring (from $\text{M}^{+\cdot}$ or from fragments).

Ion series: Aromatic hydrocarbon fragments, C_nH_n , C_nH_{n-1} , and C_nH_{n-2} (m/z 39, 51–53, 63–65, 75–77,...). In the higher mass range: $\text{C}_n(\text{H,X})_n$.

Intensities: Dominant peaks in the $\text{M}^{+\cdot}$ region.

Molecular ion: Usually very strong. Characteristic isotope signals for Cl and Br.

7.7.4

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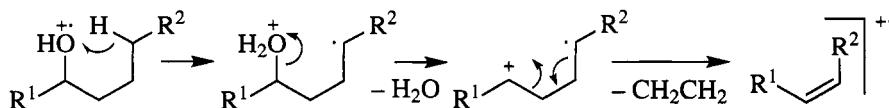
7.8

Alcohols, Ethers, and Related Compounds [1,2]

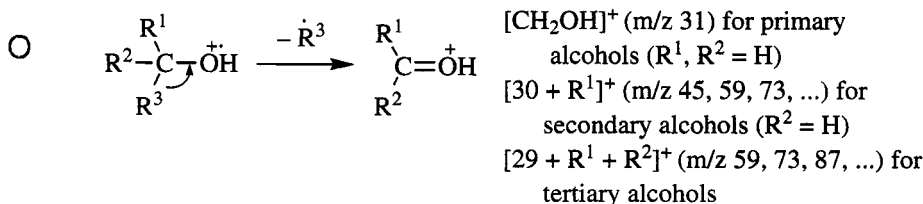
7.8.1

Aliphatic Alcohols [3]

Fragmentation: Elimination of water from $M^{+\cdot}$ and from fragments. Strong for primary alcohols. If an aliphatic H atom can be transferred in a 6-ring process, it is involved in the water elimination in 90% of the investigated cases. If a CH_2CH_2 group is attached to the O-bearing C atom, water elimination is often followed by loss of ethylene. Water elimination is dominant for long-chain alcohols, making their spectra similar to those of alkenes.



Cleavage of bonds next to the OH-bearing C atom to form oxonium ions, then elimination of water and of alkenes. The α -cleavage is often dominant. Usually, its importance increases with increasing branching at the α -carbon atom. The larger substituent is lost most readily.



Consecutive H_2O and alkene eliminations in longer chain primary alcohols lead to $[\text{M}-46]^+$, $[\text{M}-74]^+$, $[\text{M}-102]^+$, The series of fragments at $[\text{M}-15]^+$, $[\text{M}-18]^+$, and $[\text{M}-33]^+$ is frequently observed for branched alcohols.

Ion series: Dominant consecutive alkene ions corresponding to $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69, ...), C_nH_{2n} (m/z 42, 56, 70, ...), accompanied by weaker fragments, $\text{C}_n\text{H}_{2n+1}\text{O}$ (m/z 31, 45, 59, ...), with one or more local maxima in the latter series (m/z 31 dominates in primary alcohols).

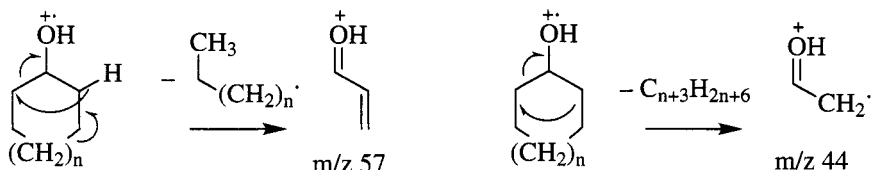
Intensities: Major peaks in the lower mass range from alkyl- and alkene-type ions with weaker maxima from ions of the sort $\text{C}_n\text{H}_{2n+1}\text{O}$.

Molecular ion: Mostly weak, often missing, especially in tertiary and long-chain alcohols. Indirect determination of $M^{+\cdot}$ is often possible from the fragments at $[\text{M}-15]^+$, $[\text{M}-18]^+$ and $[\text{M}-33]^+$. $[\text{M}+1]^+$ is often significant. In primary and secondary alcohols also $[\text{M}-1]^+$ can usually be seen. Sometimes, $[\text{M}-2]^+$ is formed because of oxidation to carbonyl compounds during sample introduction.

7.8.2

Alicyclic Alcohols [3]

Fragmentation: Elimination of water from $M^{+\cdot}$, followed by loss of alkyl or alkenyl residues. Ring cleavage at the O-bearing C atom, followed by loss of alkyl residues after H rearrangement.



Ion series: Alkene hydrocarbon fragments $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69,...), $\text{C}_n\text{H}_{2n-3}$ (m/z 39, 53, 67, 81,...), and unsaturated O fragments, $\text{C}_n\text{H}_{2n-1}\text{O}$ (m/z 43, 57, 71,...), as well as acetaldehyde and its homologues (m/z 44, 58, 72,...).

Intensities: Local maxima evenly distributed over whole mass range.

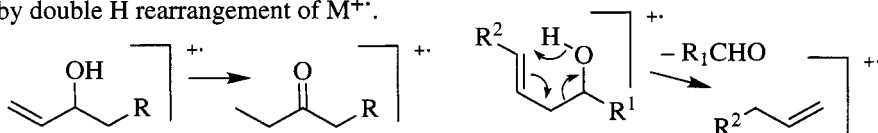
Molecular ion: Usually weak but in contrast to aliphatic alcohols practically never missing. $[M+1]^+$ usually contains a significant amount of protonated molecule ion.

7.8.3

Unsaturated Aliphatic Alcohols [3]

Allyl alcohols: The spectra are similar to those of the corresponding carbonyl compounds, which are (partly) formed by double H rearrangement of $M^{+\cdot}$.

γ,δ -Unsaturated alcohols: Aldehyde elimination through a McLafferty-type rearrangement:



7.8.4

Vicinal Glycols

Fragmentation: Cleavage of bonds next to the OH-bearing C atom (α -cleavage) dominates. Preferable fragmentation of the C–C bond between the two oxygens, the charge remaining mainly on the larger fragment. Water elimination from these fragments, but scarcely from $M^{+\cdot}$.

Ion series: Saturated and unsaturated aliphatic ions (m/z 43, 57, 71,... and 41, 55, 69,...) and intense peaks from O-containing saturated rests (m/z 45, 59, 73,...).

Intensities: Dominant peaks for the products of α -cleavages and their dehydrated derivatives.

Molecular ion: Weak.

7.8.5

Aliphatic Hydroperoxides [4]

Fragmentation: Most pronounced is the loss of the hydroperoxy radical HO_2^\cdot (Δm 33), especially when a tertiary alkyl cation is formed. Important, in decreasing order, is loss of H_2O_2 (Δm 34), H_2O (Δm 18), HO^\cdot (Δm 17), and O (Δm 16).

Ion series: Mainly saturated and unsaturated alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71,...) and $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69,...). The oxygen-indicating fragments at m/z 31 and its homologues are always present.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak.

7.8.6

Phenols

Fragmentation: Decarbonylation (Δm 28) and loss of CHO^\cdot (Δm 29) followed by elimination of acetylene. In alkyl derivatives $[\text{M}-1]^+$ and, if at least two alkyl carbons are present (dimethyl or ethyl), $[\text{M}-15]^+$ become important. Elimination of CO from the primary fragments. $[\text{M}-18]^{++}$ mainly with *ortho*-alkylphenols. In derivatives with a longer alkyl chain, benzylic cleavage and alkene elimination (McLafferty rearrangement) are the dominant primary fragmentation processes. The fragments then lose CO (Δm 28).

Ion series: Aromatic hydrocarbon fragments C_nH_n and C_nH_{n+1} (m/z 39, 51–53, 63–65, 75–77,...). The presence of some m/z 55 ($\text{C}_3\text{H}_3\text{O}$) is common. A peak at m/z 69 ($\text{O}\equiv\text{CCH}=\text{C}=\text{O}$) is characteristic of 1,3-dihydroxy substitution.

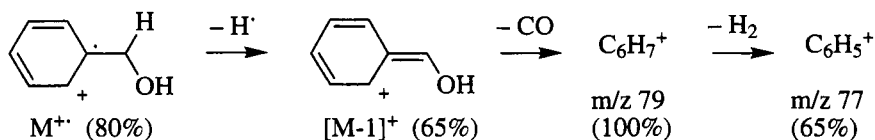
Intensities: Dominant peaks in the higher mass range.

Molecular ion: Dominant, no tendency to form $[\text{M}+\text{H}]^+$. $[\text{M}-1]^+$ is weak.

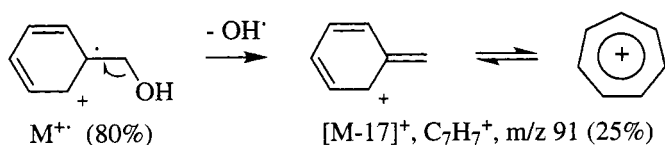
7.8.7

Benzyl Alcohols

Fragmentation: Loss of H^\cdot and consecutive elimination of CO (Δm 28) to give a protonated benzene molecule, which further loses H_2 .



Elimination of OH^\cdot (Δm 17) to yield the tropylium cation is the second important fragmentation path:



Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

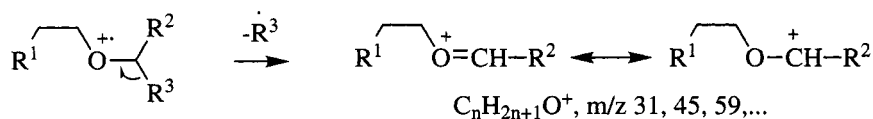
Intensities: Dominant peaks for the products described under Fragmentation. For benzyl alcohol decreasing in the sequence of $[\text{M}-29]^+$, M^+ , $[\text{M}-1]^+$, $[\text{M}-31]^+$, $[\text{M}-17]^+$.

Molecular ion: Strong.

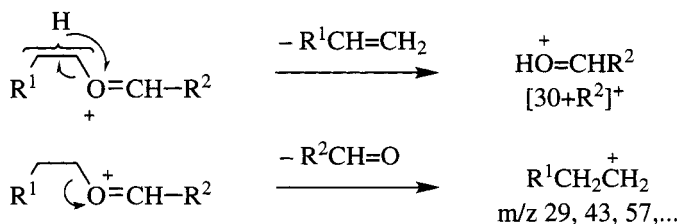
7.8.8

Aliphatic Ethers [5,6]

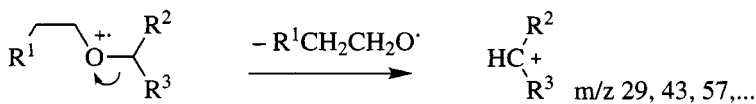
Fragmentation: Homolysis of the C–C bond next to the O atom to yield oxygen-containing fragments. Preferably, the bond at the highest substituted C atom breaks and the larger alkyl group is lost.



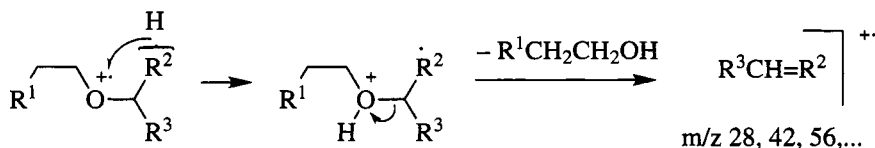
This homolysis is followed by the elimination of alkenes, carbonyls, or, less importantly, of water.



As a competing process, especially with increasing molecular weight, heterolysis at the O atom takes place to yield strong alkyl ion signals. The larger as well as the branched alkyl rests are fragmented preferably. The base peak often arises from heterolysis of the C–O bond.



In contrast to the H_2O elimination from alcohols, the H transfer involved in the elimination of $\text{RCH}_2\text{CH}_2\text{OH}$ from ethers is non-specific.



Ion series: Alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 29, 43, 57,...), with maxima due to cleavage of the C–O bond. Alkene ion series, C_nH_{2n} (m/z 28, 42, 56,...), due to elimination of alcohol. Oxygen-containing fragments $\text{C}_n\text{H}_{2n+1}\text{O}$ (m/z 31, 45, 59,...) with maxima due to cleavage of the C–C bond next to oxygen.

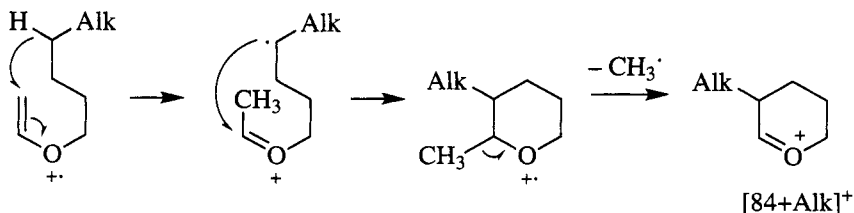
Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Significant or weak. Decreasing with increasing chain length and branching.

7.8.9

Unsaturated Ethers [7]

Fragmentation of vinylic and acetylenic alkyl ethers: Dominant homolysis of the alkyl C–C bond next to the O atom on the saturated side, leading to $\text{C}_3\text{H}_5\text{O}^+$ (m/z 57) for vinylic and $\text{C}_3\text{H}_3\text{O}^+$ (m/z 55) for acetylenic ethers of primary aliphatic alcohols. For alkyl ($\text{C}_{n>5}$) vinyl ethers, ethanol elimination after triple H transfer. $[\text{M}-15]^+$ in vinyl ethers predominantly by elimination of the vinyl CH_2 after H rearrangement.



Fragmentation of allylic ethers: Heterolysis of both C–O bonds, leading to strong C_3H_5^+ (m/z 41) and alkyl (m/z 29, 43, 57,...) cations. Formation of ionized allylic alcohol (m/z 58) by non-specific H transfer from the alkyl rest. In allylic and propargylic ethers, no cleavage of the C–C bond next to the O atom of the alkenyl group occurs. Hence, loss of vinyl or acetylenyl cannot be observed.

Ion series: $\text{C}_n\text{H}_{2n}\text{O}$ (m/z 44, 58, 72,...) for alkenyl alkyl ethers and $\text{C}_n\text{H}_{2n-2}\text{O}$ (m/z 42, 56, 70,...) for dialkenyl ethers. Unsaturated aliphatic ($\text{C}_n\text{H}_{2n-1}$; m/z 41, 55, 69,...) as well as saturated aliphatic and unsaturated oxygen-containing fragments ($\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}\text{O}$; m/z 43, 57, 71,...).

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak to medium, very weak for acetylenic ethers.

7.8.10

Alkyl Cycloalkyl Ethers

Fragmentation of methyl ethers of cycloalkanols with > 3 C atoms: After primary cleavage of the ring C–C bond next to the O atom, the prominent fragments formed are $\text{CH}_3\text{OCH}=\text{CH}_2^{+\cdot}$ (m/z 58) and, for alicyclics with > 4 C atoms, $\text{CH}_3\text{O}=\text{CHCH}=\text{CH}_2^+$ (m/z 71, rearrangement in analogy to that observed for cycloalkanols). Loss of methanol to give hydrocarbon fragments, $\text{C}_n\text{H}_{2n-2}$ (m/z 54, 68, 82,...).

Fragmentation of ethyl and higher alkyl ethers of cycloalkanols with > 3 C atoms: Alkene elimination to yield the protonated cycloalkanol (m/z 72, 86, 100,...) and heterolytic cleavage of the C–O bond to give dominating cycloalkyl ions (m/z 69, 83,...).

Ion series: Besides the fragments already mentioned, mainly unsaturated hydrocarbon fragments ($\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55, 69,...).

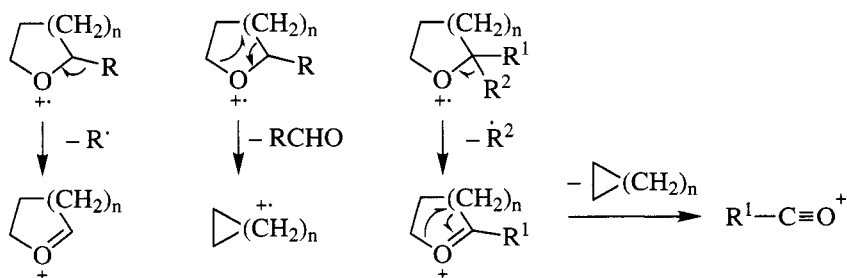
Intensities: The above mentioned fragments dominate the spectrum.

Molecular ion: Weak or intermediate.

7.8.11

Cyclic Ethers

Fragmentation: Primary ring cleavage at C–C bonds next to the O atom, followed by loss of CH_2O (Δm 30), H_2O (Δm 18), or alkyl (Δm 15, 29,...). Elimination of H^+ to give $[\text{M}-1]^+$, followed by CO elimination (Δm 28) to $[\text{M}-29]^+$. When α -substituted, dominant loss of substituents, followed by water elimination. Formation of acyl if two α -substituents are present.



Ion series: Mainly ions of the alkene type. Weak saturated, oxygen-containing fragments (m/z 31, 45,...).

Intensities: Intensive peaks evenly distributed over whole mass range.

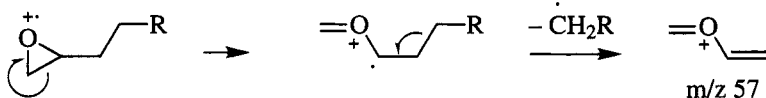
Molecular ion: Often significant but sometimes weak, especially when α -substituted. Intensity of $[\text{M}-1]^+$ usually comparable to that of $\text{M}^{+\cdot}$ if no α -substituent is present.

7.8.12

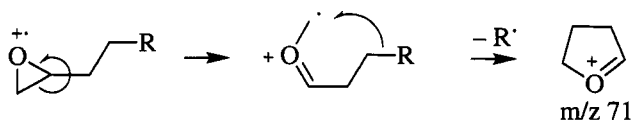
Aliphatic Epoxides [8]

Fragmentation: The most important primary fragmentation is the cleavage of C–C bonds next to the O atom (α -cleavage), resulting in complex degradation due to the related multiple choice and extensive secondary rearrangements. The products allow mass-spectrometric localization of double bonds after epoxidation.

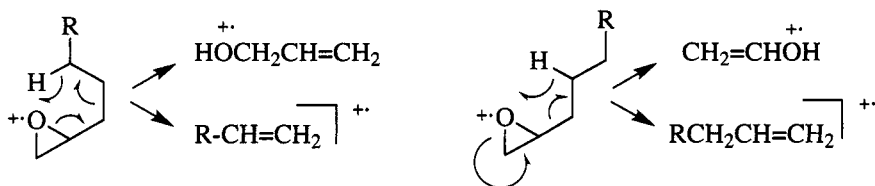
Due to ring opening prior to fragmentation, β -cleavage is as relevant as the α -cleavage.



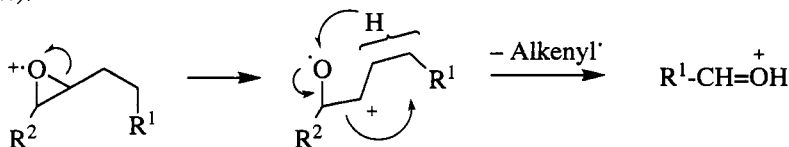
γ -Cleavage is the most important fragmentation mechanism, especially in terminal epoxides:



Mainly in terminal epoxides, rearrangement with alkene elimination, formally leading to alkene- $\text{OH}^{+\cdot}$ ($\text{C}_n\text{H}_{2n}\text{O}$, m/z 44, 58, 72,...) and alkene $^{+\cdot}$ (C_nH_{2n} , m/z 28, 42, 56,...):



Mainly in nonterminal epoxides, transannular cleavage with H transfer and elimination of an alkenyl radical, leading to $\text{C}_n\text{H}_{2n+1}\text{O}$ fragments (m/z 45, 59, 73,...):



Ion series: Mixed, not characteristic.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak.

7.8.13

Methoxybenzenes

Fragmentation: Loss of methyl radical, followed by decarbonylation to give $[M-43]^+$; elimination of formaldehyde (Δm 30) from M^{++} or from primary fragments.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the M^{++} region.

Molecular ion: Strong.

7.8.14

Alkyl Aryl Ethers [9]

Fragmentation: Commonly dominating alkene elimination to give the corresponding phenol ion (non-specific hydrogen migration), followed by decarbonylation. In the case of aryl methyl ethers, loss of CH_2O from M^{++} or from primary fragments as well as $CH_3\cdot$ elimination followed by decarbonylation.

Ion series: Mostly aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Usually maximum at the mass of the corresponding phenol. Otherwise, intensive peaks mainly concentrated in the high and medium mass range.

Molecular ion: Strong.

O

7.8.15

Aromatic Ethers

Fragmentation: Loss of $H\cdot$ (Δm 1), CO (Δm 28), and $CHO\cdot$ (Δm 29) from M^{++} . Cleavage at the C–O bond and decarbonylation of the resulting product, followed by dehydrogenation.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

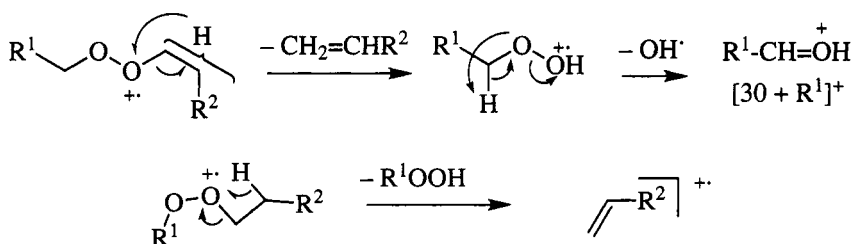
Intensities: Intensive peaks mainly in the M^{++} region.

Molecular ion: Strong.

7.8.16

Aliphatic Peroxides [4]

Fragmentation: Alkene elimination to give hydroperoxide radical cations and hydroperoxide elimination to yield alkene radical cations (dominating if larger alkyl groups are present). Alkene elimination can be followed by loss of $OH\cdot$, resulting in products that formally correspond to those obtained by O–O cleavage, which probably is not a one-step process (see scheme).



Elimination of O^\cdot or O_2 may occur in cyclic peroxides. *tert*-Butyl peroxides predominantly eliminate *tert*-butyl- OO^\cdot to give $[\text{M}-89]^+$.

Ion series: Saturated or unsaturated alkyl groups ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,...; $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...) and alkenyl ions (C_nH_{2n} , m/z 28, 42, 56,...) dominate. The fragment at m/z 31, and sometimes its homologues, indicate the presence of oxygen.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak to moderate.

7.8.17

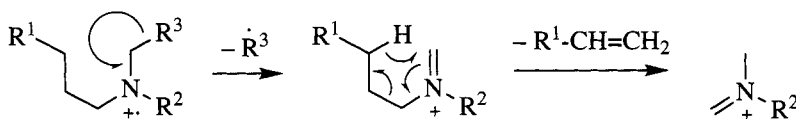
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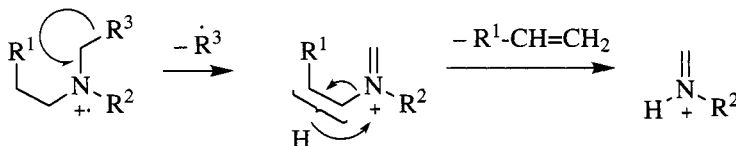
7.9 Nitrogen Compounds [1,2]

7.9.1 Saturated Aliphatic Amines [3]

Fragmentation: Dominating loss of alkyl residues by cleavage of the C–C bond next to the N atom (“N-cleavage”). Larger substituents are eliminated preferably. When a γ -H is available, subsequent elimination of alkenes by McLafferty-type reactions.



Otherwise, unspecific H transfer onto the N atom.



NH_3 , RNH_2 , and $\text{RR}'\text{NH}$ eliminations from primary, secondary, and tertiary amines, respectively, are negligible except from some multifunctional compounds (e.g., diamines and phenyl-phenoxy-substituted amines).

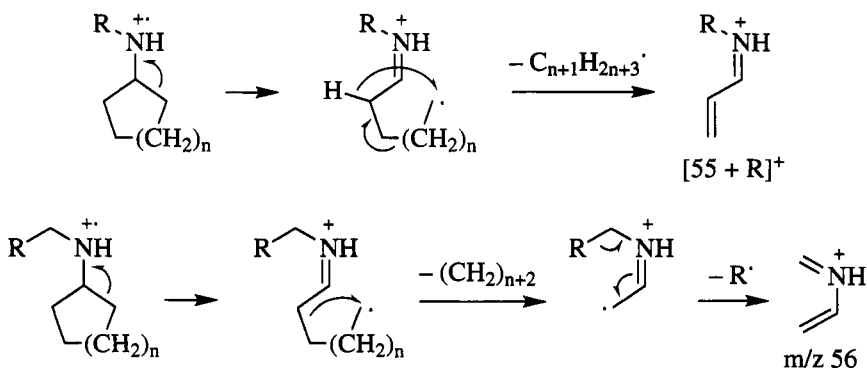
Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n+2}\text{N}$ (m/z 30, 44, 58, 72, 86,...). N

Intensities: Mainly peaks in the low mass range. Dominating base peak from “N-cleavage” at $[28 + m(\text{R}^1) + m(\text{R}^2) + m(\text{R}^4) + m(\text{R}^5)]^+$ for $\text{R}^1\text{R}^2\text{R}^3\text{CNR}^4\text{R}^5$ (e.g., m/z 30 for RCH_2NH_2 , m/z 44 for $\text{RCH}_2\text{NHCH}_3$, m/z 58 for $\text{RCH}_2\text{N}(\text{CH}_3)_2$, and m/z 86 for $\text{RCH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$). Local maximum at m/z 86 ($\text{C}_5\text{H}_{12}\text{N}^+$) for n -alk- NH_2 (protonated piperidine, 6-membered ring).

Molecular ion: Usually weak or absent, especially if the α -C atom is substituted. Decreasing intensity with increasing molecular weight. Tendency to protonate to $[\text{M}+\text{H}]^+$.

7.9.2 Cycloalkylamines

Fragmentation: The most important primary reaction is the ring cleavage next to the N atom, followed by H rearrangement and loss of an alkyl residue. Some elimination of amine, $\text{R}_1\text{R}_2\text{NH}$.



Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n}\text{N}$ (m/z 42, 56, 70, 84,...).

Intensities: Intensive local maxima evenly distributed over whole mass range.

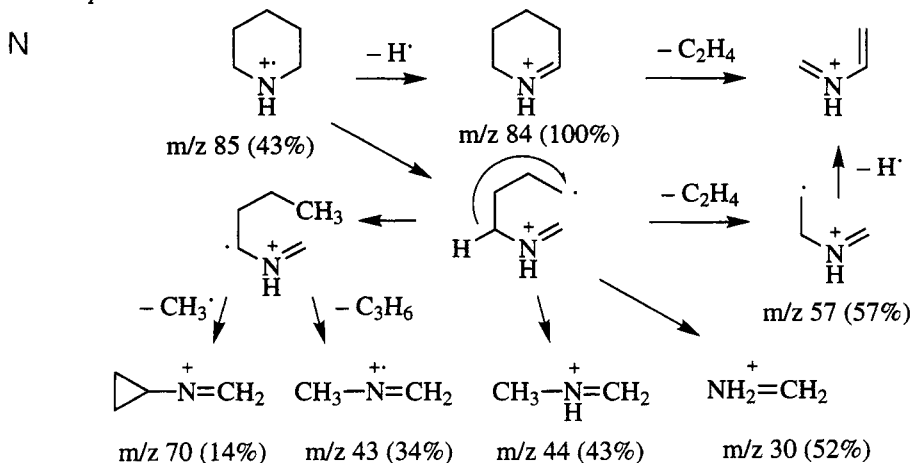
Molecular ion: Usually significant.

7.9.3

Cyclic Amines

Fragmentation: Dominating primary reaction is the cleavage of C–C bonds next to N, resulting in loss of substituents next to N or in primary ring cleavage. Primary ring cleavage is followed by H rearrangement and loss of alkenes or alkyl groups. The most important primary fragmentation for substituted cyclic amines is the loss of substituents at C atoms next to N.

Piperidine:



Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n}\text{N}$ (m/z 42, 56, 70, 84,...) and $\text{C}_n\text{H}_{2n+2}\text{N}$ (m/z 30, 44, 58,...) as well as odd-mass fragments of the type $\text{C}_n\text{H}_{2n+1}\text{N}$ (m/z 43, 57, 71, 85,...).

Intensities: Intensive local maxima evenly distributed over whole mass range if no substituent is bonded to the C atom next to N. Otherwise, dominating maxima by loss of such substituents.

Molecular ion: Significant or strong if no substituent is bonded to the C atom next to N; otherwise weak. Tendency to form $[M-H]^+$.

7.9.4

Piperazines

Fragmentation: As for cyclic amines, enhanced primary ring cleavage at C–C bonds next to the N atom.

Ion series: Even-mass fragments of the type $C_nH_{2n}N$ (m/z 42, 56, 70, 84,...) and $C_nH_{2n+2}N$ (m/z 30, 44, 58,...) as well as odd-mass series of the type $C_nH_{2n+1}N$ (m/z 43, 57, 71, 85,...).

Intensities: Intensive local maxima evenly distributed over whole mass range if no substituent is bonded to the C atom next to N. Otherwise, dominating maxima by loss of such substituents.

Molecular ion: Significant or strong if no substituent is bonded to the C atom next to N; otherwise weak. Tendency to form $[M-H]^+$.

7.9.5

Aromatic Amines

Fragmentation: Dominating cleavage of alkyl bond at N-bearing C atom (“N-cleavage”) followed by alkene elimination if aliphatic substituents with $\geq C_2$ are present. Otherwise, loss of H^\bullet from primary and secondary anilines and benzylic amines. Loss of HCN from M^+ or from fragments. A local maximum at m/z 42 is typical of an aromatically bonded dimethylamino group.

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Dominating maxima by “N-cleavage” and following alkene loss if aliphatic substituents with $C_{n>1}$ are present.

Molecular ion: Abundant if no aliphatic substituents with more than one carbon atom are present, otherwise medium or weak. No tendency to protonate. In primary and secondary aromatic and benzylic amines, $[M-H]^+$ is important.

7.9.6

Aliphatic Nitro Compounds

Fragmentation: Loss of NO^\bullet (Δm 30), NO_2^\bullet (Δm 46), and HNO_2 (Δm 47) as well as the formation of some m/z 30 as \bar{N} indicator. Spectra with only few characteristic features.

Ion series: Mixed alkyl and alkenyl fragments, C_nH_{2n+1} (m/z 43, 57, 71,...) and C_nH_{2n-1} (m/z 41, 55, 69,...).

Intensities: Dominant peaks in the lower mass range.

Molecular ion: Weak or missing.

7.9.7

Aromatic Nitro Compounds

Fragmentation: Loss of O (Δm 16), NO \cdot (Δm 30, followed by elimination of CO, Δm 28), and NO $_2\cdot$ (Δm 46) from M $^{+\cdot}$ or from a major primary cleavage product. Extensive rearrangement of the functional group to a nitroso ester.

Ion series: Aromatic hydrocarbon fragments corresponding to C $_n$ H $_n$ and C $_n$ H $_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks mainly in the upper mass range.

Molecular ion: Strong.

7.9.8

Diazo Compounds [4,5]

Diazonium: Because of the low volatility of diazo compounds, their electron impact mass spectra show thermal decomposition products. These are formed by loss of N $_2$ (e.g., an aromatic chloro compound is formed from the corresponding diazonium chloride). From a phenyl diazonium *ortho*-carboxylate zwitterion, biphenylene is formed as dimerization product.

Diazomethane and derivatives: M $^{+\cdot}$ is strong except when catalytic decomposition occurs on metal surfaces of the inlet system. Loss of N $_2$ is a dominant reaction of diazomethane and diazoketones.

N

7.9.9

Azobenzenes

Fragmentation: Cleavage at the azo group followed by loss of N $_2$, giving rise to the dominant base peak.

Ion series: Aromatic hydrocarbon fragments corresponding to C $_n$ H $_n$ and C $_n$ H $_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Dominant M $^{+\cdot}$ and azo cleavage products.

Molecular ion: Strong.

7.9.10

Aliphatic Azides [6]

Fragmentation: [M-42] $^{+}$ (N $_3\cdot$ elimination) or [M-28] $^{+\cdot}$ (N $_2$ elimination) is dominant in most cases. The spectra have the character of the corresponding aliphatic compounds.

Ion series: Aliphatic hydrocarbon series.

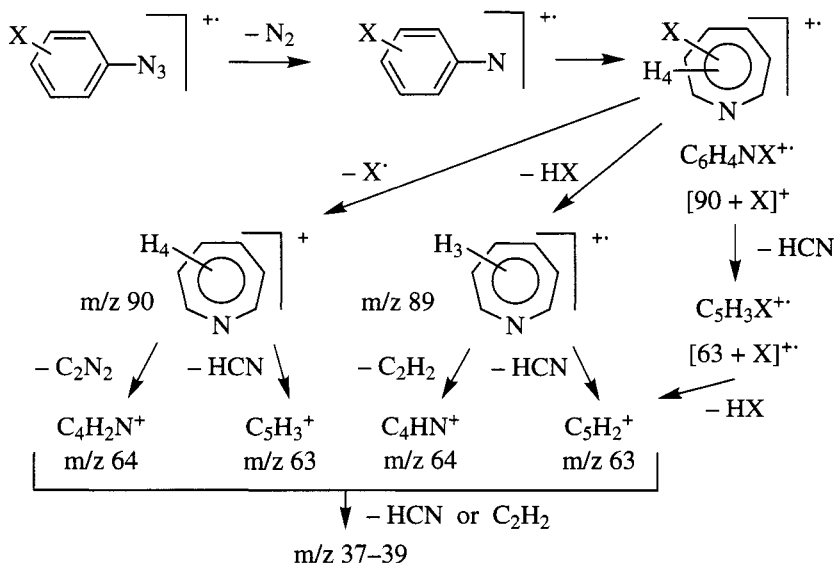
Intensities: Dominant peaks in the lower mass range, as in aliphatic compounds.

Molecular ion: Absent or weak. Odd mass for odd number of N atoms in the molecule.

7.9.11

Aromatic Azides [7]

Fragmentation: In most cases, $[M-28]^+$ (N_2 elimination) is the base peak. The next step is the elimination of HCN (Δm 27) or acetylene (Δm 26), or, if there is a substituent X on the ring, of X^\cdot or HX.



N

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51-53, 63-65, 75-77,...).

Intensities: Dominant peaks in the higher mass range: $[M-28]^+$ (N_2 elimination) and $[M-55]^+$ (N_2 and HCN elimination) are the most intense peaks.

Molecular ion: Weak. Odd mass for odd number of N atoms in the molecule.

7.9.12

Aliphatic Nitriles [4]

Fragmentation: Elimination of alkyl radicals to give $(CH_2)_nCN^+$ ions (m/z 40, 54, 68,...). McLafferty rearrangement yielding $CR_2=C=NH^+$ (m/z 41 for R: H). In most cases, C-CN cleavage and HCN elimination are not significant reactions. Complex rearrangements in unsaturated cyanides if other functional groups are present.

Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} and C_nH_{2n-1} ; m/z 29, 43, 57,... and 27, 41, 55,...). Rearrangement products corresponding to $C_nH_{2n-1}N$ contribute, to a significant extent, to the ion series m/z 41, 55, 69,... For alkyl chains with $C_{n>5}$, dominating $(CH_2)_nCN^+$ (i.e., $C_nH_{2n-2}N$, m/z 82, 96, 110,..., probably with a cyclic structure).

Intensities: Intensive peaks due to the above mentioned ions.

Molecular ion: Weak or missing. Both $[M+H]^+$ and $[M-H]^+$ are usually more intense than $M^{+\bullet}$. In some aliphatic nitriles, $[M+2H]^{++}$ is as intensive as $M^{+\bullet}$. Odd mass for odd number of N atoms in the molecule.

7.9.13

Aromatic Nitriles

Fragmentation: Consecutive elimination of HCN and acetylene.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the M^+ region.

Molecular ion: Dominant intensity, often base peak. In contrast to aliphatic and benzylic nitriles, $[M-1]^+$ is usually not important. Odd mass for odd number of N atoms in the molecule.

7.9.14

Aliphatic Isonitriles (R–NC)

Fragmentation: In general, the spectra are similar to those of the corresponding nitriles. The most important difference lies in the loss of CN^{\bullet} (Δm 26) and the higher probability of losing HCN (Δm 27). Further important fragmentations are the elimination of alkyl radicals to give $(CH_2)_nCN^+$ ions and the McLafferty rearrangement to yield $CR_2=N=CH^{+\bullet}$ (m/z 41 if R: H).

Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} , m/z 29, 43, 57,... and C_nH_{2n-1} , m/z 27, 41, 55,...). Rearrangement products corresponding to $C_nH_{2n-1}N$ contribute, to a significant extent, to the ion series of m/z 41, 55, 69,....

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Weak, decreasing with increasing chain length and degree of branching. Both $[M+H]^+$ and $[M-H]^+$ can be stronger than $M^{+\bullet}$. Odd mass for odd number of N atoms in the molecule.

7.9.15

Aromatic Isonitriles (R–NC) [4]

Fragmentation: Dominant loss of HCN ($[M-27]^{+\bullet}$). In methylphenyl and benzyl isocyanides also formation of isocyanotropylium ion, $[M-1]^+$, followed by loss of HCN to $[M-28]^+$.

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak for phenyl isocyanide. Odd mass for odd number of N atoms in the molecule.

7.9.16

Aliphatic Cyanates (R–OCN) [8]

Fragmentation: Spectra often very similar to those of the corresponding isocyanates. Cleavage of the C–C bond next to O, with the charge remaining on $\cdot CH_2OCN$ (m/z 56) for short-chain cyanates and preferably on the alkyl substituent if it has a $C_{n>2}$ chain (m/z 29, 43, 57,...). Cleavage of the C–O bond with H rearrangement to give $HCNO^{+\cdot}$ (m/z 43) or $alkene^{+\cdot}$ (m/z 42, 56, 70,...). For cyanates with $C_{n>5}$ substituents, alkene elimination to yield m/z 99.

Ion series: Saturated and unsaturated alkyl cations (C_nH_{2n+1} , m/z 29, 43, 57,... and C_nH_{2n-1} , m/z 27, 41, 55,...). Alkene radical cations (C_nH_{2n} , m/z 42, 56, 70,...) together with isobaric ions of the composition $C_nH_{2n}NCO$.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak or absent. $[M-H]^+$ is often more intense. Odd mass for odd number of N atoms in the molecule.

7.9.17

Aromatic Cyanates (R–OCN) [8]

Fragmentation: Loss of $OCN\cdot$ (Δm 42) or, to a lesser extent, of CO, with subsequent HCN elimination (Δm 28 and 27).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

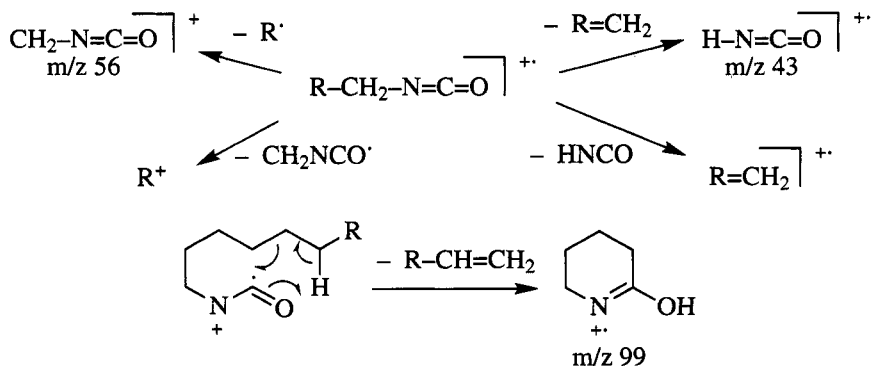
Intensities: Intensive peaks in the higher mass range.

Molecular ion: Strong. Odd mass for odd number of N atoms in the molecule.

7.9.18

Aliphatic Isocyanates (R–NCO) [8]

Fragmentation: Spectra often very similar to those of the corresponding cyanates. Cleavage of the C–C bond next to N, the charge remaining on the $\cdot CH_2NCO$ (m/z 56) for short-chain isocyanates and preferably on the alkyl substituent for compounds with a $C_{n>2}$ chain (m/z 29, 43, 57,...). Cleavage of the C–N bond with H rearrangement to give $HCNO^{+\cdot}$ (m/z 43) or $alkene^{+\cdot}$ (m/z 42, 56, 70,...) ions. For isocyanates with $C_{n>5}$ alkyl chains, alkene elimination, yielding m/z 99.



Ion series: Saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...). Alkene radical cations ($\text{C}_n\text{H}_{2n}^\cdot$, m/z 42, 56, 70,...) together with isobaric ions of the composition of $\text{C}_n\text{H}_{2n}\text{OCN}$.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak or absent. $[\text{M-H}]^+$ is often more intense. Odd mass for odd number of N atoms in the molecule.

7.9.19

Aromatic Isocyanates (R-NCO) [8]

Fragmentation: Consecutive elimination of CO (Δm 28) and HCN (Δm 27). In contrast to aromatic cyanates, practically no elimination of NCO^\cdot (Δm 42).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominating; base peak for phenyl isocyanate. Odd mass for odd number of N atoms in the molecule.

7.9.20

Aliphatic Thiocyanates (R-SCN) [8]

Fragmentation: Elimination of HCN (Δm 27) followed by loss of an alkyl group. The cleavage of the C–C bond next to SCN is unimportant except in short-chain thiocyanates.

Ion series: Saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...).

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Weak. Decreasing with increasing chain length and degree of branching; absent from the spectrum of hexyl thiocyanate. Odd mass for odd number of N atoms in the molecule. Both $[\text{M+H}]^+$ and $[\text{M-H}]^+$ are detectable.

Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.21

Aromatic Thiocyanates ($\text{R}-\text{SCN}$) [8]

Fragmentation: The most important fragmentation is the elimination of SCN^{\cdot} (Δm 58). Further elimination reactions are loss of CN^{\cdot} (Δm 26), HCN (Δm 27), and CS (Δm 44).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...). Weak signal at m/z 45 (CHS^+) indicates sulfur.

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak in phenyl thiocyanate. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.22

Aliphatic Isothiocyanates ($\text{R}-\text{NCS}$) [8]

Fragmentation: Cleavage of the C–C bond next to NCS , leading to m/z 72 (CH_2NCS) or to its homologues if the α -C atom is substituted. Loss of the alkyl residue with concomitant double hydrogen rearrangement to yield the protonated functional group (m/z 60). With a $\text{C}_{n>4}$ alkyl chain, loss of SH^{\cdot} (Δm 33). With $\text{C}_{n>5}$ alkyl chain, loss of alkene leading to m/z 115, probably according to the mechanism shown for isocyanates.

Ion series: Mainly saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...). Signal for CH_2NCS^+ (m/z 72) or its homologues (m/z 86, 100, 114,...) if the α -C atom is substituted.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Medium to weak, decreasing with increasing chain length and degree of branching. More intense than in the corresponding thiocyanates; 1% for hexadecyl isothiocyanate. Both $[\text{M}+\text{H}]^+$ and $[\text{M}-\text{H}]^+$ are relevant. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.23

Aromatic Isothiocyanates ($\text{R}-\text{NCS}$) [8]

Fragmentation: Dominant loss of NCS^{\cdot} (Δm 58). In contrast to aromatic thiocyanates, the loss of HCN (Δm 27) or CS (Δm 44) leads to very weak fragments only.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...). Weak signal at m/z 45 (CHS^+) indicates sulfur.

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak in phenyl isothiocyanate. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{++}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{++}).

7.9.24

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