6.5: Amine Fragmentation

Functional groups can have a significant effect the fragmentation patterns observed in mass spectrometry and textbooks on mass spectrometry cover a large range of common fragmentation patters for different functional groups. For a detailed discussion of this, interested readers are encouraged to look at any of the following books:

As one final example aliphatic amines often undergo cleavage at the $\alpha \mathrm{C}-\mathrm{C}$ bond to produce a relatively stable $\mathrm{CH_2NH_2}^+$ ion (Figure $6.5.1$). The resulting fragments distinguish primary, secondary, and tertiary amines.

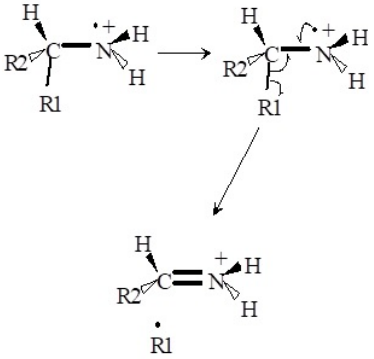

Figure $6.5.1$: α-Cleavage fragmentation of an amine.

This fragmentation is useful for distinguishing mass spectra of the three different $\mathrm{C_4H_{11}N}$ isomers. Draw the structure of 1-butanamine, 2-butanamine, 2-methyl-1-propanamine, and 2-methyl-2-propanamine. Determine the mass to charge ratio for the molecular ion, identify the site for alpha-cleavage for each molecule, and determine the mass to charge ratio for the expected fragments. After you have done this, look up the mass spectra for these four compounds in the NIST Chemistry WebBook (https://webbook.nist.gov/) which contains mass spectra for a large number of compounds.

All four compounds have the same molecular formula, $\mathrm{C_4H_{11}N}$ with an odd number of nitrogen atoms so the molecular ion has an odd mass to charge ratio. The molecular ion is observed for all four compounds at 73 *m/z* .

1-butanamine. The α-cleavage fragment for 1-butanamine produces $\mathrm{CH_2NH_2}^+$ at 30 *m/z* and $\mathrm{C_3H_7}^{\bullet}$. The $\mathrm{C_3H_7}$ fragment has a very low intensity in the mass spectrum because since the charge is retained by the nitrogen containing fragment. See NIST Webbook for the mass spectrum of 1-butanamine.

2-butanamine. There are two α-cleavage sites for 2-butanamine. Loss of $\mathrm{CH_3'}$ produces $\mathrm{C_3H_6NH_2}^+$ (58 *m/z*) and loss of $\mathrm{C_2H_5'}$ produces $\mathrm{C_2H_4NH_2}^+$ (44 *m/z*). Both of these ions are observed but the greater abundance of the 44 *m/z* signal indicates that loss of $\mathrm{C_2H_5''}$ is favored. See NIST Webbook for the mass spectrum of 2-butanamine.

2-methyl-1-propanaimne. The α-cleavage fragment for 2-methyl-1-propanamine produces $\mathrm{CH_2NH_2}^+$ at 30 *m/z* and $\mathrm{C_3H_7}^{\bullet}$. The $\mathrm{C_3H_7}$ fragment has a very low intensity in the mass spectrum because since the charge is retained by the nitrogen containing fragment. The resulting mass spectrum is very similar to 1-butanamine and distinguishing these two isomers by mass spectrometry will depend on careful comparison of the relative intensity of the molecular ion and other fragments observed in the mass spectrum. The See NIST Webbook for the mass spectrum of 2-methyl-1-propanamine.

2-methyl-2-propanaimne. The α-cleavage fragment for 2-methyl-2-propanaimne produces $\mathrm{C_3H_6NH_2}^+$ at 58 *m/z* and $\mathrm{CH_3}^{\bullet}$. The $\mathrm{CH_3}$ fragment has a very low intensity in the mass spectrum because since the charge is retained by the nitrogen containing fragment. See NIST Webbook for the mass spectrum of 1-butanamine.