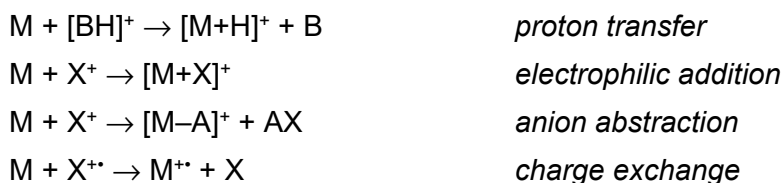## Answers 7.1 c) and d)

c) Name four processes of positive ion generation in CI and write down the corresponding general equations.

Chemical ionization may involve the transfer of an electron, proton, or other charged species between the reactants. There are four general pathways to form ions from a neutral analyte M in CI (Chap. 7.1.1):

$$M + [BH]^+ \rightarrow [M+H]^+ + B \qquad \textit{proton transfer}$$
$$M + X^+ \rightarrow [M+X]^+ \qquad \textit{electrophilic addition}$$
$$M + X^+ \rightarrow [M–A]^+ + AX \qquad \textit{anion abstraction}$$
$$M + X^{+\bullet} \rightarrow M^{+\bullet} + X \qquad \textit{charge exchange}$$

d) What role does a reagent gas play in CI?

In chemical ionization new ionized species are formed when gaseous molecules (the neutral analyte M) interact with ions from a reagent gas. The occurrence of bimolecular reactions requires a sufficiently large number of ion-molecule collisions during the dwelltime of the reactants in the ion source. This is achieved by significantly increasing the partial pressure of the reagent gas. A molecule will undergo 30–70 collisions at an ion source pressure of about 2.5×10^2 Pa. The large excess of reagent gas also shields the analyte molecules effectively from ionizing primary electrons which is important to suppress competing direct EI of the analyte.