3.3.3 Halogenoalkanes

3.3.3.1 *Nucleophilic substitution with OH■, CN■ and NH3. Mechanisms. Bond enthalpy and rate.*

Halogenoalkanes have polar C–X bonds (δ+C attracts nucleophiles).

With OH■ (aq KOH, reflux): R–X + OH■ → R–OH + X■ (alcohol).

With CN■ (KCN in ethanol/water, reflux): R–X + CN■ → R–CN + X■ (nitrile; chain extended by 1C).

With NH3 (excess, heat in sealed tube): R–X + 2NH3 → R–NH2 + NH4X (primary amine).

Mechanism (SN2 for primary): curly arrow from nucleophile lone pair to δ+C; simultaneously C–X bond breaks.

Reactivity: C–I > C–Br > C–Cl (C–I has lowest bond enthalpy; easiest to break).

3.3.3.2 *Elimination with KOH in ethanol. Role of OH■ as base.*

With ethanolic KOH (reflux): R–X + KOH → alkene + H2O + KX (elimination).

OH■ acts as a base — removes H■ from the carbon adjacent to C–X.

Competing reactions: aqueous KOH → substitution (alcohol); ethanolic KOH → elimination (alkene). Solvent determines the pathway.

Mechanism: curly arrow from OH■ to H on adjacent C; C–H bond breaks; electrons form C=C; C–X bond breaks simultaneously.

3.3.3.3 *Ozone depletion: CFCs, Cl radicals, legislation and alternatives.*

Ozone (O3) in upper atmosphere absorbs harmful UV radiation.

CFCs release Cl• radicals under UV (homolytic fission of C–Cl bond):

Cl• + O3 → ClO• + O2

ClO• + O3 → 2O2 + Cl•

Cl• is a catalyst — regenerated, destroys thousands of O3 molecules per radical.

Scientific evidence led to the Montreal Protocol and international legislation banning CFCs.

Replaced by HFCs (chlorine-free, less ozone-depleting).