2.2: Functional group

Learning Objectives

- Recognize the two basic mechanisms of bond breaking and making and draw curly arrows to show the electron movement in these steps.
- Define organic functional group and recognize it in an organic compound.

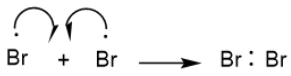
What is a chemical reaction?

A chemical reaction involves making and breaking chemical bonds. Often the elemental composition of the compound changes during a chemical reaction. Sometimes the composition remains the same; atoms rearrange, resulting in a new combination that is an isomer of the initial compound. Often making and breaking of a covalent bond is involved in organic reactions. Recall that a covalent bond is a shared pair of electrons. The bond breaking or making can happen in one of two modes: homolytic or heterolytic, as described below.

Homolytic breaking and bond-making

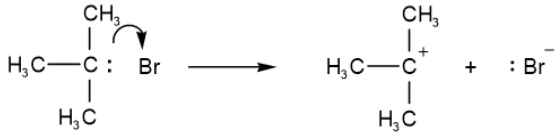
In homolytic bond breaking, each bonded atom receives one of the two electrons in a covalent bond, e.g.:

, where half-headed arrows show the movement of a single electron. The above reaction produces two atoms with one unpaired electron, i.e., free radicals. The reverse of it is hemolytic bond making, e.g.:

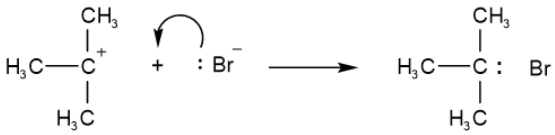


Heterolytic bond-making and breaking

In heterolytic bond breaking, the bonding electrons move to one of the bonded atoms, usually to a more electronegative atom, making a lone pair, e.g.:



, where the regular double-headed arrows show the movement of an electron pair. The formal charge changes in heterolytic bond-making and breaking. The bonded atom that receives the electrons usually becomes an anion, and the other becomes a cation in the above reaction. Revers of it is heterolytic bond making, e.g.:



What is a functional group?

> A functional group is an atom or a group of atoms that imparts a characteristic set of physical and chemical properties to the compound.

For example, alkanes with no functional group are the least reactive classes of organic compounds. Alkanes have only $\mathrm{C-C}$ and $\mathrm{C-H}$ single bonds, which are nonpolar and strong bonds. Alkenes, alkynes, and aromatic compounds are relatively reactive classes of organic compounds because they have a $\mathrm{C=C}$ bond, $\mathrm{C \equiv C}$ bond, or a benzene ring as functional groups. Although alkenes, alkynes, and aromatic hydrocarbons are nonpolar, there is a partial negative (δ^-) character in the π-bond region that attracts electrophilic reagents having δ^+ regions. Further, the π-bond is weaker than a σ-bond making it easier to break during chemical reactions.

Classification of organic compounds based on the functional groups

One primary class of organic compounds is hydrocarbons that contain only C′s and H′s, listed in Table 1, and the others are organic compounds with heteroatom/s, in their functional group/s. Hydrocarbons have been introduced in the previous section. Other classes of organic compounds containing heteratom\s in their functional groups are described next.

The heteroatom/s in the functional group can be a single bonded, i.e., sp^3-hybridized halogen, O, N, S, P, etc., listed in Table 2; a double bonded, i.e., sp^2-hybridized O, N, S, P, etc., listed in Table 3; or a combination of these, listed in Table 4.

Table 1: Classes of hydrocarbons based on their functional groups. (R-, R_1-, R_2, R_3, and R_4- represents a general alkyl group or hydrogen)

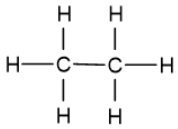
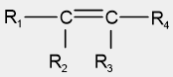
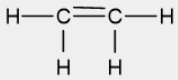
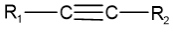
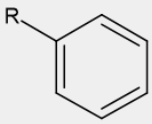
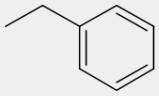
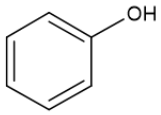
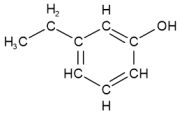
Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Alkane	Alkyl	R	R	alkyl-	-ane	 ethane
Alkene	Alkenyl		$R_2C{=}CR_2$	alkenyl-	-ene	 ethene
Alkyne	Alkynyl		$RC \equiv CR_2$	alkynyl-	-yne	 ethyne
Aromatic (benzene derivatives)	Phenyl		$R{-}C_6H_5$	phenyl-	-benzene	 ethylbenzene

Table 2: Classes of organic compounds containing an sp^3-hybridized heteroatom in functional groups. (R-, R_1-, R_2, R_3, and R_4- represent a general alkyl group or hydrogen.)

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Haloalkane	Halo	$R{-}X$, i.e., $R{-}F$, $R{-}Cl$, $R{-}Br$, or $R{-}I$	$R{-}X$ i.e., $R{-}F$, $R{-}Cl$, $R{-}Br$, or $R{-}I$	halo- i.e., fluoro-, chloro-, bromo-, or iodo-)	-	$CH_3{-}CH_2{-}Cl$ (chloroethane)
Alcohol	Alcohol	$R{-}OH$	ROH	hydroxy-	-ol	$CH_3{-}CH_2{-}OH$ (ethanol)
Phenol	Phenol		C_6H_5OH	-	-phenol	 3-ethylphenol
Ether	Ether	$R{-}O{-}R'$	ROR'	Alkoxy	-	$CH_3{-}CH_2{-}O{-}CH_2$ (ethoxyethane)

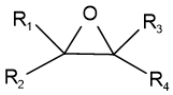
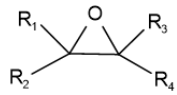
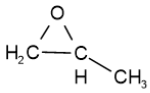
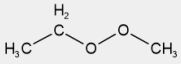
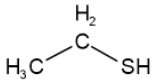
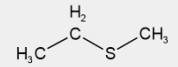
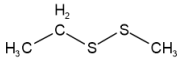
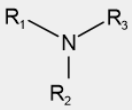
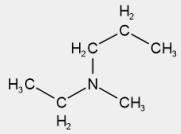
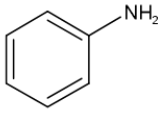
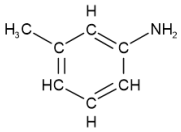
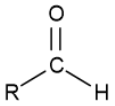
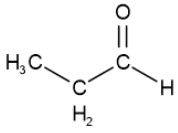
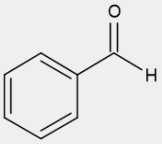
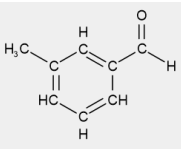
Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Epoxide	Epoxide			epoxy-	-oxirane	 2-methyloxirane, or 1,2-epoxypropane
Peroxide	Peroxy	$R-O-O-R'$	$ROOR'$	peroxy-	alkyl peroxide	 (methylperoxy)ethane
Thiol	Sulfhydryl	$R-S-H$	RSH	sulfanyl-	-thiol	 ethanethiol
Sulfide (Thioether)	Sulfide	$R-S-R'$	RSR'	sulfanyl-	-sulfide	 (methylsulfanyl)ethane
Disulfide	Disulfide	$R-S-S-R'$	$RSSR'$	disulfanyl-	-disulfide	 (methyldisulfanyl)ethane
Amine	Amine		$R_1R_2R_3N$	amino-	-amine	 ethyl(methyl)propylamine
Aniline	Aniline		$C_6H_5NH_2$	-	-aniline	 3-methylaniline

Table 3: Classes of organic compounds containing an sp^2-hybridized heteroatom in functional groups. (R-, R_1-, R_2, R_3, and R_4- represents a general alkyl group or hydrogen)

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Aldehyde	Aldehyde		$RCHO$	oxo-	-al	 propanal
Benzaldehyde	Benzaldehyde		C_6H_5COH	-	-benzaldehyde	 3-methylbenzaldehyde

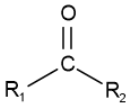
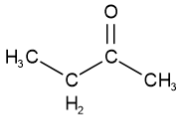
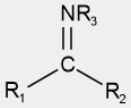
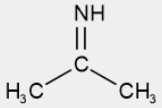
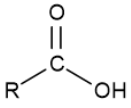
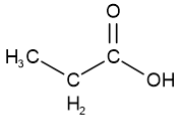
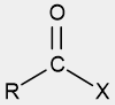
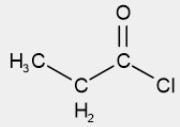
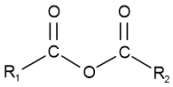
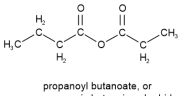
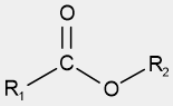
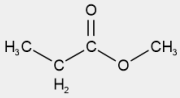
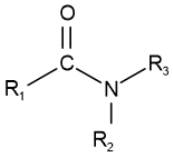
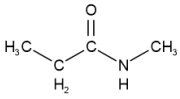
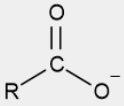
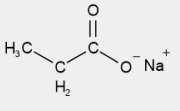
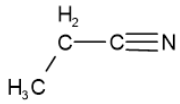
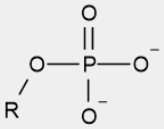
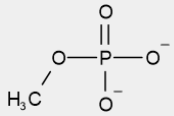
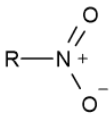
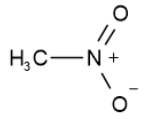
Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Ketone	Ketone		$RCOR'$	oxo-	-one	 butan-2-one
Imine	Imine		$R_1C(=NR_3)R_2$	imino-	-imine	 propan-2-imine

Table 4: Classes of organic compounds containing a mix of sp^3-, sp^2-, and sp-hybridized heteroatoms in functional groups. (R-, R_1-, R_2, R_3, and R_4-represents a general alkyl group or hydrogen)

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Carboxylic acid	Carboxyl		$R-COOH$	carboxy-	oic acid	 propanoic acid
Acyl halide	Acyl halide		$R-COX$	-	oil halide	 propanoyl chloride
Acid anhydride	Acid anhydride		$R_1-(CO)O(CO)R_2$		R1-oil R2-oat, or R1-oic R2-oic anhydride	 propanoyl butanoate, or propanoic butanoic anhydride
Easter	Easter		R_1COORR'	-	alkyl -alkanoate	 methyl propanoate
Amide	Amide		$RCONR'R''$	alkyl carbamoyl	-amide	 N-methylpropanamide
Carboxylate	Carboxylate		$RCOO^-$	-carboxy	-oate	 sodium propanoate

Class name	Group name	General structural formula	General condensed formula	Prefix	Suffix	Example
Nitrile	Nitrile	$\mathrm{R{-}C{\equiv}N}$	RCN	cyano-	-nitrile	 propanenitrile
Phosphate	Phosphate	$\mathrm{ROP(=O)(OH)_2}$		-	phosphate	 methyl phosphate
Nitro	Nitro	$\mathrm{RNO_2}$		nitro-	-	 nitromethane