Alkanes

Presented by

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Alkanes

- Hydrocarbon family
- First member of the alkane family is methane.
- These hydrocarbon has been assigned to the same family as methane on the basis of their structure, and on the whole their properties follow the pattern laid down by the methane.

Ethane

Next to methane second member of alkane family.

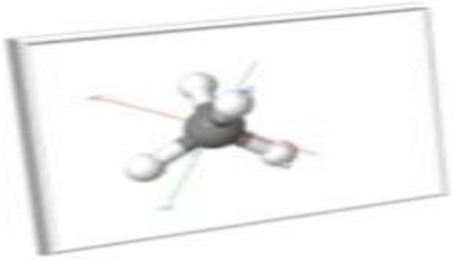
- *Structure of ethane:*

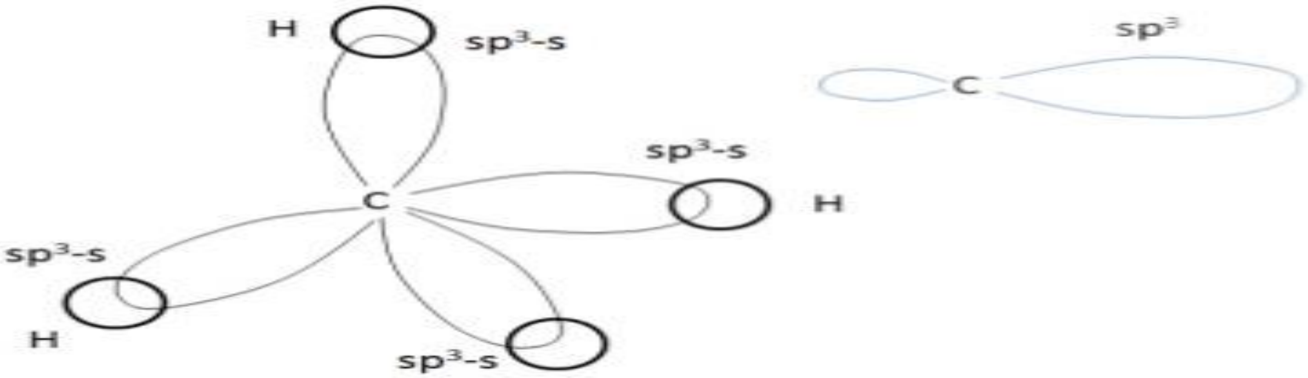
Ethane

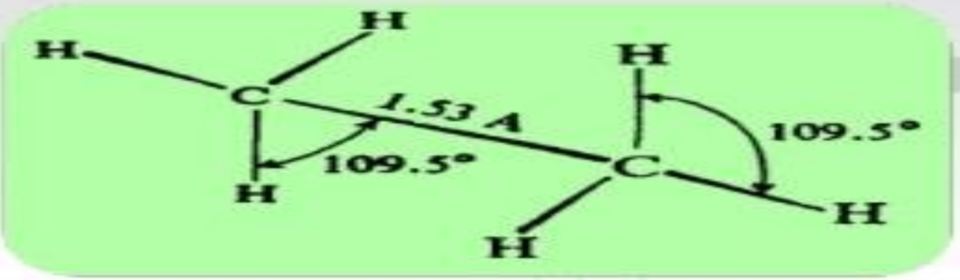
- The carbon-hydrogen bonds result from overlap of these sp^3 orbitals with the s orbitals of the hydrogens. The carbon-carbon bond arises from overlap of two sp^3 orbitals.
- Each carbon atom is bonded to four other atoms, its bonding orbitals (sp^3 orbitals) are directed toward the corners of a tetrahedron.

Bonding in Methane (CH_4)

Bonding in Methane : Carbon uses sp^3 hybridized orbital to form 4 covalent bond with hydrogen in methane.







- In ethane, then, the bond angles and carbon-hydrogen bond lengths are about 109.5 and about 1.10 A respectively.
- Bond angles is 109.5°, C-H length is 1.10 A°,C-C length is 1.53A°. These values are quite characteristic of carbon-hydrogen and carbon-carbon bonds and of carbon bond angles in alkanes.

Summary

- sp^3 hybridization occurs when a C has 4 attached groups
- sp3 hybrid orbital has 25% s and 75% p character
- the 4 sp^3 hybrids point towards the corners of a tetrahedron at 109.28° to each other
- each sp^3 hybrid orbital is involved in σ bond foprmation.

Nomenclature

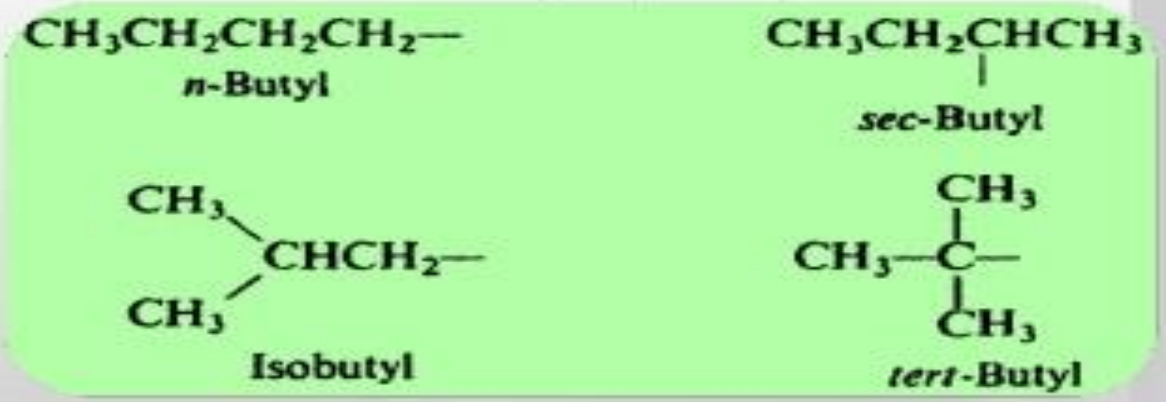
Names of Alkanes

CH_4	methane	C_9H_{20}	nonane
C_2H_6	ethane	$C_{10}H_{22}$	decane
C_3H_8	propane	$C_{11}H_{24}$	undecane
C_4H_{10}	butane	$C_{12}H_{26}$	dodecane
C_5H_{12}	pentane	$C_{14}H_{30}$	tetradecane
C_6H_{14}	hexane	$C_{16}H_{34}$	hexadecane
C_7H_{16}	heptane	$C_{18}H_{38}$	octadecane
C_8H_{18}	octane	$C_{20}H_{42}$	eicosane

- The butanes and pentanes are distinguished by the use of prefixes: n-butane and isobutane, n-pentane, isopentane, and neopentane

Alkyl group

- The general formula for an alkyl group is C_nH_{2n+1} since it contains one less hydrogen than the parent alkane, C_nH_{2n+2}
- The designations given are n- (normal), sec- (secondary), iso -, and tert- (tertiary) like this



Physical properties

- Alkane molecule is either non-polar or very weakly polar.
- Stronger intramolecular forces are there.

- Except for the very small alkanes, the boiling point rises 20 to 30 degrees for each carbon that is added to the chain.
- The first four alkanes are gases the next 13 (C_5-C_{17}) are liquids, and those- containing 18 carbons or more are solids.

Preparation of alkane

1. Hydrogenation of alkenes.

$$\underset{\text{Alkene}}{C_nH_{2n}} \xrightarrow{H_2 + Pt,\ Pd,\ or\ Ni} \underset{\text{Alkane}}{C_nH_{2n+2}}$$

2. Reduction of alkyl halides

(a) Hydrolysis of Grignard reagent.

$$RX + Mg \longrightarrow \underset{\text{Grignard reagent}}{RMgX} \xrightarrow{H_2O} RH$$

(b) Reduction by metal and acid.

$$RX + Zn + H^+ \longrightarrow RH + Zn^{++} + X^-$$

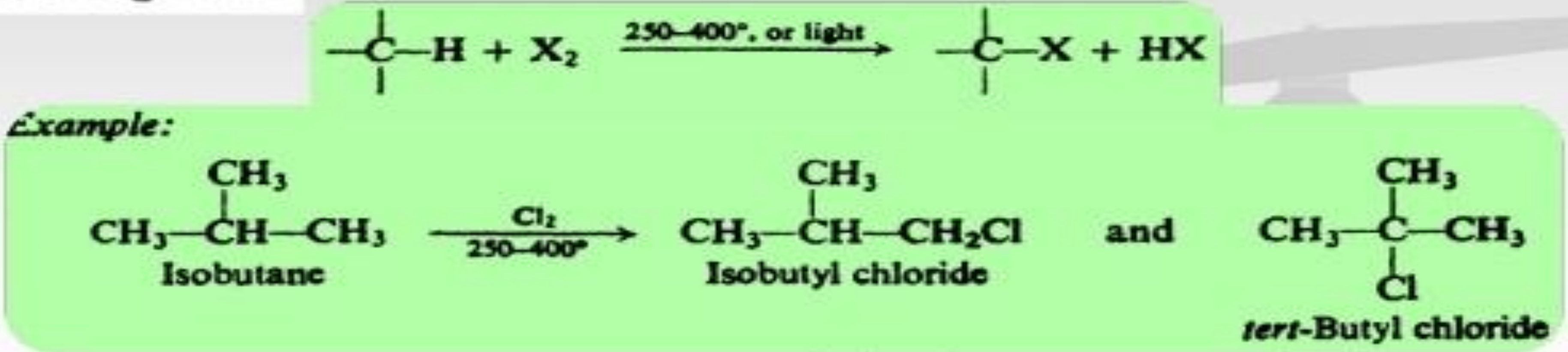
3. Coupling of alkyl halides with organometallic compounds

$$\underset{\substack{\textit{May be}\\ 1^\circ,\ 2^\circ,\ 3^\circ}}{RX} \xrightarrow{Li} \underset{\text{Alkyllithium}}{RLi} \xrightarrow{CuX} \underset{\substack{\text{Lithium}\\ \text{dialkylcopper}}}{R_2CuLi}$$

$$R_2CuLi + \underset{\textit{Should be } 1^\circ}{R'X} \longrightarrow R—R$$

Reactions

1. Halogenation.



2. Combustion.

$$C_nH_{2n+2} + \text{excess } O_2 \xrightarrow{\text{flame}} nCO_2 + (n+1)H_2O$$

ΔH = heat of combustion

Example:

$$n\text{-}C_5H_{12} + 8\,O_2 \xrightarrow{\text{flame}} 5CO_2 + 6H_2O \qquad \Delta H = -845 \text{ kcal}$$

3. Pyrolysis (cracking).

$$\text{alkane} \xrightarrow[\text{without catalysts}]{400\text{–}600°\text{; with or}} H_2 + \text{smaller alkanes} + \text{alkenes}$$

Halogenation

- Under the influence of ultraviolet light, or at 250-400, chlorine or bromine converts alkanes into chloroalkanes (alkyl chlorides) or bromoalkanes (alkylbromides).

- An equivalent amount of hydrogen chloride or hydrogen bromide is formed at the same time.

Depending upon which hydrogen atom is replaced, any of a number of isomeric products can be formed from a single alkane.

$$CH_3CH_3 \xrightarrow[\text{light, }25^\circ]{Cl_2} CH_3CH_2{-}Cl$$

Ethane → b.p. 13°, Chloroethane, Ethyl chloride

$$CH_3CH_2CH_3 \xrightarrow[\text{light, }25^\circ]{Cl_2} CH_3CH_2CH_2{-}Cl \quad \text{and} \quad CH_3CHCH_3 \text{ (Cl below C-2)}$$

Propane → $CH_3CH_2CH_2{-}Cl$: b.p. 47°, 1-Chloropropane, *n*-Propyl chloride, *45%*; and CH_3CHCH_3 (Cl): b.p. 36°, 2-Chloropropane, Isopropyl chloride, *55%*

Bromination gives the corresponding bromides but in different proportions:

$$CH_3CH_3 \xrightarrow[\text{light, }127^\circ]{Br_2} CH_3CH_2Br$$

Ethane

$$CH_3CH_2CH_3 \xrightarrow[\text{light, }127^\circ]{Br_2} CH_3CH_2CH_2Br \quad \text{and} \quad CH_3CHCH_3 \text{ (Br below C-2)}$$

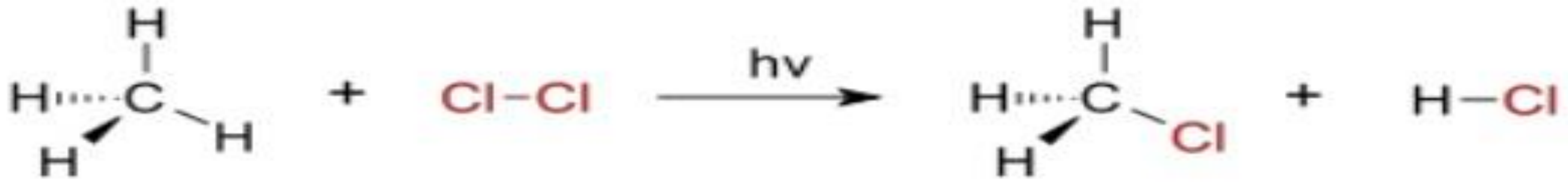
Propane → $CH_3CH_2CH_2Br$ *3%*; and CH_3CHCH_3 (Br) *97%*

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, }127^\circ]{Br_2} CH_3CH_2CH_2CH_2Br \quad \text{and} \quad CH_3CH_2CHCH_3 \text{ (Br below C-2)}$$

n-Butane → $CH_3CH_2CH_2CH_2Br$ *2%*; and $CH_3CH_2CHCH_3$ (Br) *98%*

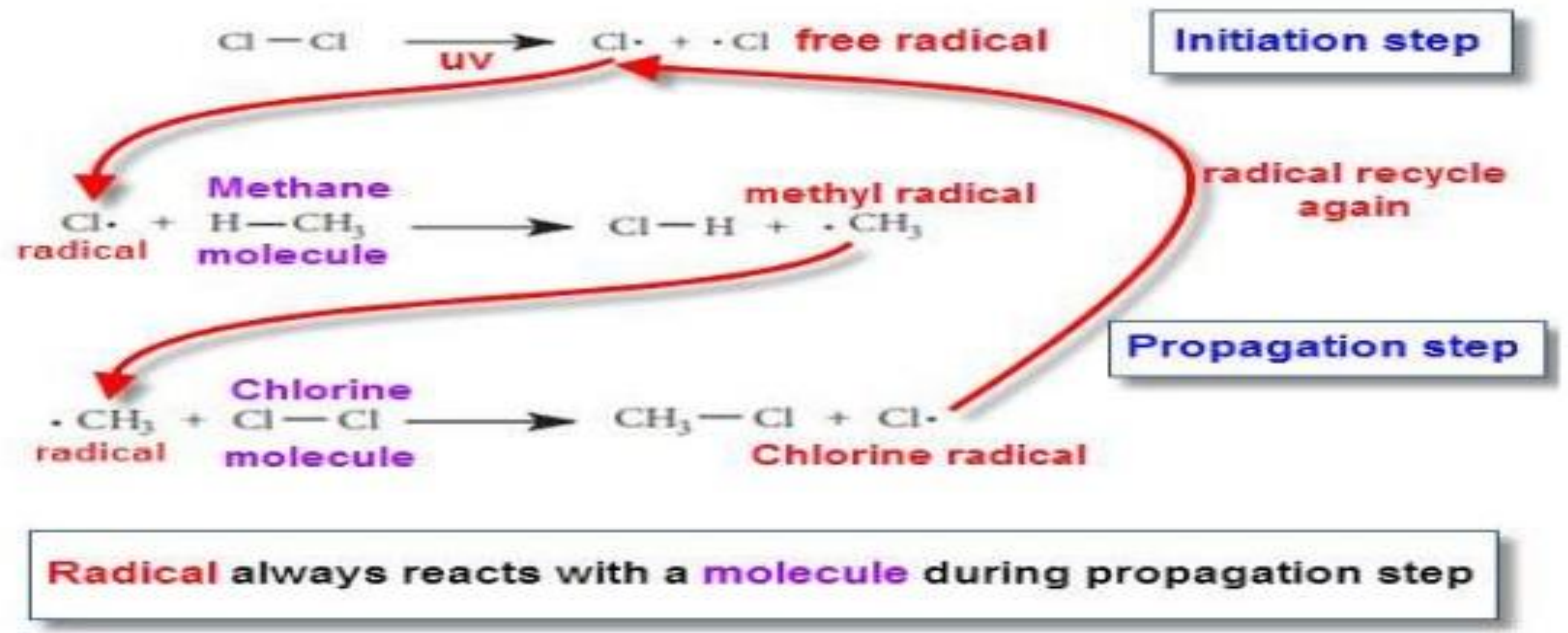
Free Radical Substitution

- Radical substitution reactions are initiated by radicals in the gas phase or in non-polar solvents.
- For example, **methane** and **chlorine** react in presence of sunlight or heat to give **methylchloride**

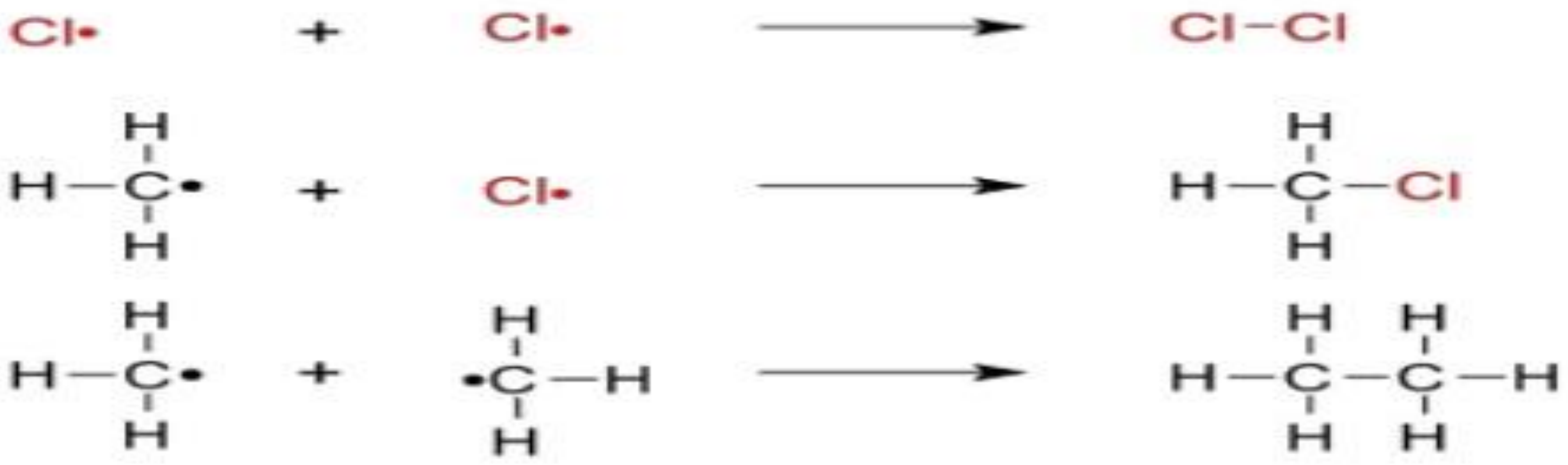


Mechanism of free radical substitution

- Light energy or heat causes homolytic fission of chlorine producing chlorine radicals which attack methane to form methylchloride.



Termination by formation of stable molecules:



- When the ratio of methane to chlorine is high, methylchloride is formed predominantly.
- When chlorine is in excess, all hydrogens are replaced to give carbon tetrachloride.