# CHM 103: Organic Chemistry I

Presented by:

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# Reactions of alkanes

1. Oxidation Reactions of Alkane
2. Substitution Reactions of Alkanes

## 1. Oxidation Reactions of Alkane

Oxidation of alkanes gives different products under different conditions.
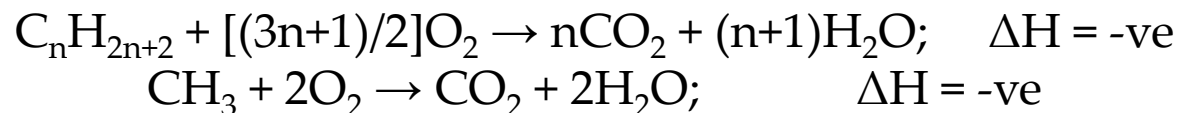
i. **Complete oxidation or combustion**          iii. **Catalytic oxidation**

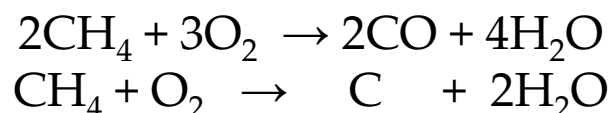ii. **Incomplete oxidation**                             iv. **Chemical oxidation**

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**i.** **Complete oxidation or combustion:** Alkanes burn readily with non-luminous flame in presence of air or oxygen. They are fuels
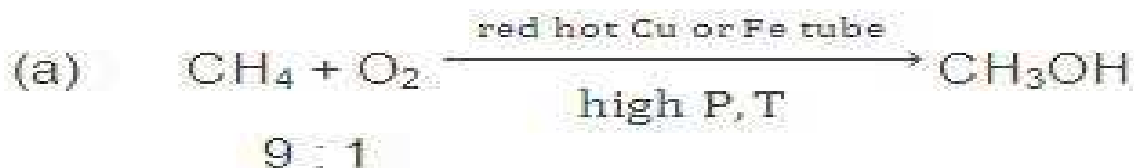


$$C_nH_{2n+2} + [(3n+1)/2]O_2 \rightarrow nCO_2 + (n+1)H_2O; \quad \Delta H = \text{-ve}$$
$$CH_3 + 2O_2 \rightarrow CO_2 + 2H_2O; \quad \Delta H = \text{-ve}$$

**ii. Incomplete oxidation:** Incomplete oxidation of alkanes in limited supply of air gives carbon black and carbon monoxide.

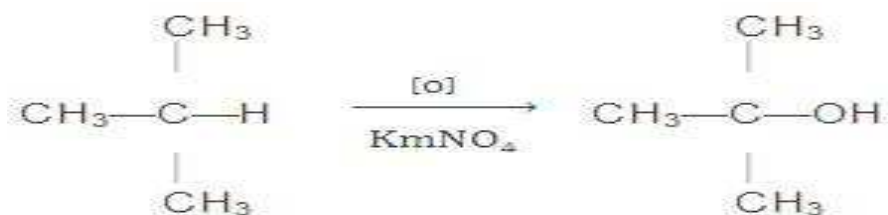$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$$
$$CH_4 + O_2 \rightarrow C + 2H_2O$$

**iii. Catalytic oxidation:**

Lower alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

(a) $\quad CH_4 + O_2 \xrightarrow[\text{high P, T}]{\text{red hot Cu or Fe tube}} CH_3OH$

$\qquad 9 : 1$

(b) $\quad CH_4 + O_2 \xrightarrow{MoO_3} HCHO + H_2O$

$\quad C_2H_6 \xrightarrow{\text{controlled oxidation}} CH_3CHO$

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**iv.** **Chemical oxidation:** Tertiary alkanes are oxidized to tertiary alcohols by $KMnO_4$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H \xrightarrow[KmNO_4]{[o]} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$$
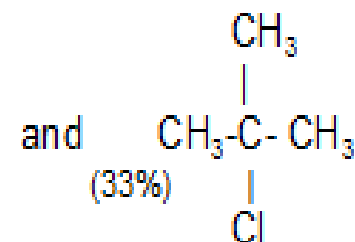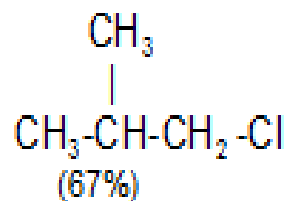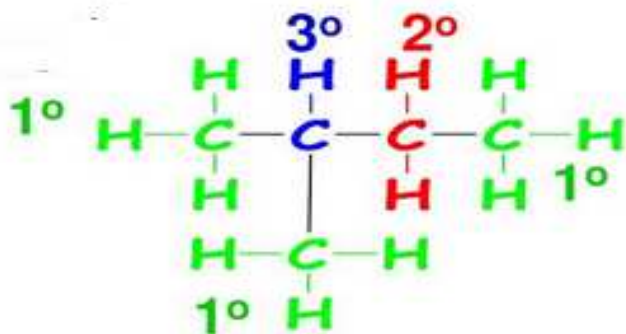
## 2. Substitution Reactions of Alkanes

**i.** **Halogenation of Alkanes:** Chlorination is

- Initiated by photo irradiation, heat or catalysts,
- and the extent of chlorination depends largely on the amount of chlorine
- to give a mixture of all possible isomeric monochlorides.
- The isomers(products) are formed in unequal amounts, due to difference in reactivity of primary, secondary and tertiary hydrogen atoms. The order of ease of substitution is *Tertiary Hydrogen > Secondary Hydrogen > Primary Hydrogen*

❑ Chlorination of isobutane at 300 °C gives a mixture of two isomeric monochlorides

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Cl \quad (67\%)$$

and

$$CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \quad (33\%)$$

The mechanism of methane chlorination is:

**Initiation Step**

$$Cl : Cl \xrightarrow[or \triangle]{uv} 2Cl \cdot \qquad DH = + 243 \text{ KJ mol}^{-1}$$

The required enthalpy comes from ultraviolet (uv) light or heat.

**Propagation Step**

i). $H_3C : H + Cl \cdot \longrightarrow H_3C \cdot + H : Cl \qquad \triangle H = - 4 \text{KJ mol}^{-1}$ (rate determining)

ii). $H_3C \cdot + Cl : Cl \longrightarrow H_3C : Cl + Cl \cdot \qquad \triangle H = - 96 \text{ KJ mol}^{-1}$

The sum of the two propagation steps in the overall reaction,

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl \qquad \triangle H = - 100 \text{ KJ mol}^{-1}$$

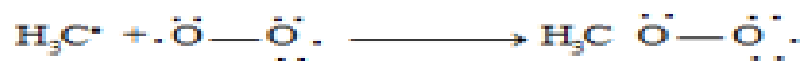**Termination step**

Chains terminate on those rare occasions when two free-radical intermediates form a covalent bond.

$$Cl \cdot + Cl \cdot \longrightarrow Cl_2 ;$$

$$H_3C \cdot + Cl \cdot \longrightarrow CH_3 : Cl$$

$$H_3C \cdot + \cdot CH_3 \longrightarrow H_3C : CH_3$$
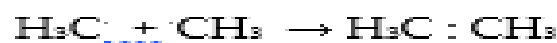
Inhibitors stop chain propagation by reacting with free radical intermediates, e.g.

$$H_3C \cdot + \cdot \ddot{O} - \ddot{O} \cdot \longrightarrow H_3C \, \ddot{O} - \ddot{O} \cdot$$

Three factors affect the product yield obtained from the halogenation of complex alkanes:

i.   probability factor
ii.  reactivity of hydrogen
iii. reactivity of halogen

**Probability Factor:** This factor is based on the number of each kind of H atom in the molecule. E.g, in $CH_3CH_2CH_2CH_3$ there are six equivalent $1^o$ H's and four equivalent $2^o$ H's. The ratio of abstracting a $1^oH$ are thus 6 to 4, or 3 to 2.

**Reactivity of H$^.$ :** The order of reactivity of H is $3^o > 2^o > 1^o$.

**Reactivity of halogen $^.$ :** The more reactive Cl$^.$ is less selective and more influenced by the probability factor. The less reactive Br$^.$ is more selective and less influenced by the probability factor, as *summarized* by the **Reactivity-Selectivity Principle**.
If the attacking species is more reactive, it will be less selective, and the yields will be closer to those expected from the probability factor.

At room temperature, for example, the relative rate per hydrogen atom are 5.0:3.8:1.0. Using these values, we can predict quite well the ratio of isomeric chlorination products from a given alkane. *For example:*
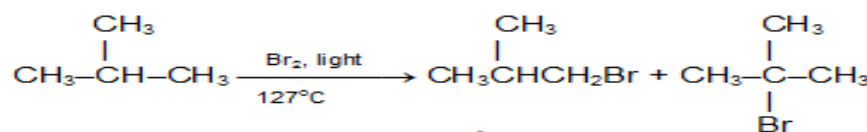
$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{light, 25°C}]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$
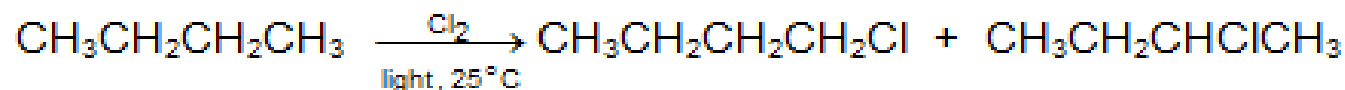
$$\frac{n-butyl\,chloride}{sec-butyl\,chloride} = \frac{no.of\,1°H}{no.of\,2°H} \times \frac{reactivity\,of\,1°\,H}{reactivity\,of\,2°\,H}$$

$$= \frac{6}{4} \times \frac{1.0}{3.8} = \frac{6}{15.2}\,equivalent\,to\,\frac{28\%}{72\%}$$

Inspite of these differences in reactivity, chlorination rarely yields a great excess of any single isomer.

The same sequence of reactivity, $3° > 2° > 1°$, is found in bromination, but with enormously larger reactivity ratios. At 127°C, for example, the relative rates per hydrogen atom are 1600:82:1. Here, differences in reactivity are so marked as vastly to outweigh probability factors. Hence, bromination gives selective product.

$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3 \xrightarrow[\text{127°C}]{Br_2,\,light} CH_3CHCH_2Br + CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Br}{|}}{C}}-CH_3$$

$$\frac{Isobutyl\,bromide}{tert-butyl\,bromide} = \frac{no.of\,1°\,H}{no.of\,3°H} \times \frac{reactivity\,of\,1°H}{reactivity\,of\,3°\,H}$$

$$= \frac{9}{1} \times \frac{1}{1600}$$

$$= \frac{9}{1600}$$

Hence, tert-butyl bromide happens to be the exclusive product (over 99%).

**Alkenes**

- ❑ Alkenes are a class of hydrocarbons
- ❑ unsaturated compounds with at least one carbon-to-carbon double bond.
- ❑ Described as olefins.
- ❑ more reactive than alkanes due to the presence of the double bond.
- ❑ molecular formulas of these unsaturated hydrocarbons reflect the multiple bonding of the functional groups:

**$C_nH_{2n}$**

Here is a chart containing the systemic name for the first twenty straight chain alkenes.

| Name | Molecular formula | Name | Molecular formula |
|---|---|---|---|
| Ethene | $C_2H_4$ | Undecene | $C_{11}H_{22}$ |
| Propene | $C_3H_6$ | Dodecene | $C_{12}H_{24}$ |
| Butene | $C_4H_8$ | Tridecene | $C_{13}H_{26}$ |
| Pentene | $C_5H_{10}$ | Tetradecene | $C_{14}H_{28}$ |
| Hexene | $C_6H_{12}$ | Pentadecene | $C_{15}H_{30}$ |
| Heptene | $C_7H_{14}$ | Hexadecene | $C_{16}H_{32}$ |
| Octene | $C_8H_{16}$ | Heptadecene | $C_{17}H_{34}$ |
| Nonene | $C_9H_{18}$ | Octadecene | $C_{18}H_{36}$ |
| Decene | $C_{10}H_{20}$ | Nonadecene | $C_{19}H_{38}$ |
| | | Eicosene | $C_{20}H_{40}$ |

## i.  Bonding in the alkenes

The double bond between the carbon atoms is,

❑ two pairs of shared electrons.

- One of the pairs of electrons is held on the line between the two carbon nuclei
- the other is held in a molecular orbital above and below the plane of the molecule.
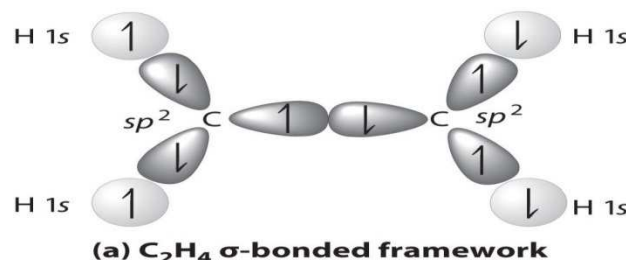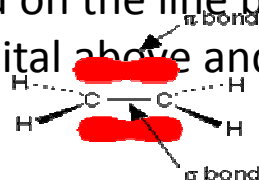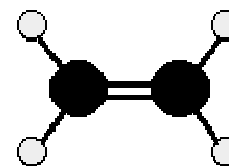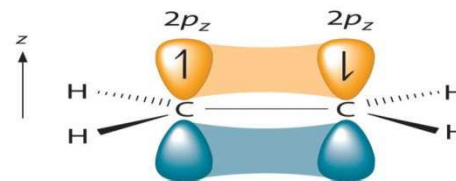


(a) C₂H₄ σ-bonded framework          (b) C₂H₄ π bonding

❑ In this diagram, the line between the two carbon atoms represents a normal bond - sort of bond is called a **sigma bond.**

❑ The other pair of electrons is found somewhere in the shaded part above and below the plane of the molecule. This bond is called a **pi bond**.

The pi electrons are not as fully under the control of the carbon nuclei as the electrons in the sigma bond and, because they lie exposed above and below the rest of the molecule, they are relatively open to attack .

## ii.    Common names

Remove the -ane suffix and add -ylene. There are a couple of unique ones like ethenyl's common name is vinyl and 2-propenyl's common name is allyl. That you should know are...

- vinyl substituent H2C=CH-
- allyl substituent H2C=CH-CH2-
- allene molecule H2C=C=CH2
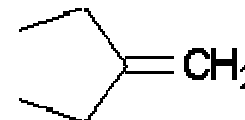- isoprene

**Endocyclic Alkenes**

Endocyclic double bonds have both carbons in the ring          Cyclopentene

**Exocyclic Alkenes**

Exocyclic double bonds have only one carbon as part of the ring.          Methylenecylopentane