

ALKANE FORMULA

• Four carbon/or hydrogen atoms bonded to each carbon atom

• All C-C single bonds

• Ratio: C_nH_{2n+2}

NOTE: always an even number of hydrogen atoms in a hydrocarbon

• Alkane homologs : each member in a alkane series different from the next member by a CH_2 group

Sources of Alkanes

- Major sources: Natural Gas and Petroleum
- Natural gas consists of about 90-95% methane, 5-10% ethane, and some propane, butane, and 2-methylpropane
- Petroleum is a thick, viscous liquid mixture of 1000's of compounds, most of them hydrocarbons, formed from the decomposition of marine plants and animals

Major Uses of Alkanes

- C_1 - C_2 : gases (natural gas)
- C_3 - C_4 : liquified petroleum (LPG)
- C_5 - C_8 : gasoline
- C_9 - C_{16} : diesel, kerosene, jet fuel
- C_{17} -up: lubricating oils, heating oil
- Origin: petroleum refining

Physical Properties of Alkanes

- Solubility
 - Alkanes are not soluble in water
 - They are soluble in each other
- Reactions of Alkanes
 - The most important chemical property of alkanes is their inertness
 - They are quite unreactive toward any of the normal ionic reaction conditions.

Reactions of alkanes:

alkane + $H_2SO_4 \rightarrow$ no reaction (NR)

alkane + $NaOH \rightarrow$ NR

alkane + $Na \rightarrow$ NR

alkane + $KMnO_4 \rightarrow$ NR

alkane + $H_2Ni \rightarrow$ NR

alkane + $Br_2 \rightarrow$ NR

alkane + $H_2O \rightarrow$ NR

(Alkanes are typically non-reactive. They don't react with acids, bases, active metals, oxidizing agents, reducing agents, halogens, etc.)

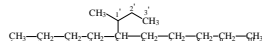
Lower Membered Alkanes trivial (common) names

Condensed

- METHANE CH_4
- ETHANE CH_3CH_3
- PROPANE $CH_3CH_2CH_3$

IUPAC System

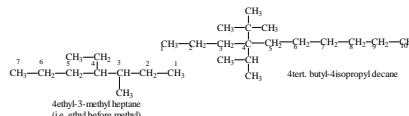
- Branched-chain substituent groups are given appropriate names by a simple extension of the system used for branched chain hydrocarbon. The longest chain of the substituting is numbered starting with the carbon attached directly to the parent hydrocarbon chain. Parentheses are used to separate the numbering of the substituent and the main hydrocarbon chain.



5-(1-methyl propyl)-decane

IUPAC System

- When there are two or more different substituent present, the question arises as to what order they should be cited in naming the compound. Two systems are commonly used which cite the alkyl substituent
 - in order of increasing complexity
 - in alphabetical order (Chemical Abstract)

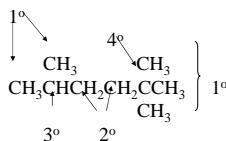


4-ethyl-3-methyl heptane
(i.e. ethyl before methyl)

4-tert-butyl-4-isopropyldecane

“classes of carbons”

- primary carbon** (1°) – a carbon bonded to one carbon
- secondary carbon** (2°) – a carbon bonded to two carbons
- tertiary carbon** (3°) – a carbon bonded to three carbons
- quaternary carbon** (4°) – a carbon bonded to four carbons

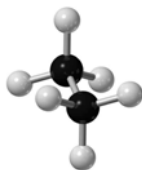


Conformers of Alkanes

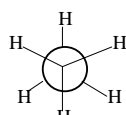
- Structures resulting from the free rotation of a C-C single bond
- May differ in energy. The lowest-energy conformer is most prevalent.
- Molecules constantly rotate through all the possible conformations.

Ethane Conformers

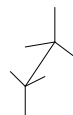
- Staggered conformer has lowest energy.
- Dihedral angle = 60 degrees



model



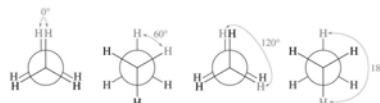
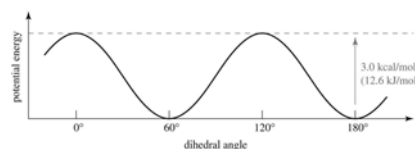
Newman projection



sawhorse

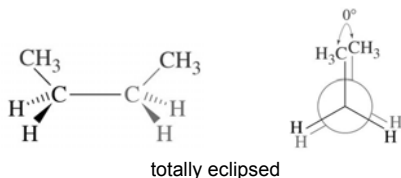
Conformational Analysis

- Torsional strain: resistance to rotation.
- For ethane, only 3.0 kcal/mol



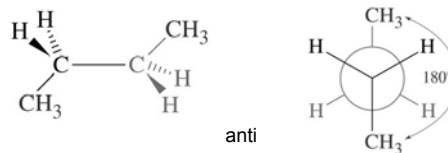
Butane Conformers C2-C3

- Highest energy has methyl groups eclipsed.
- Steric hindrance
- Dihedral angle = 0 degrees



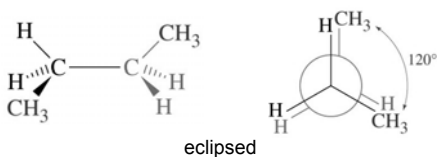
Butane Conformers (2)

- Lowest energy has methyl groups anti.
- Dihedral angle = 180 degrees



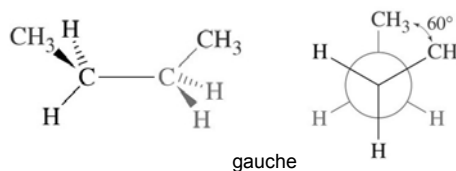
Butane Conformers (3)

- Methyl groups eclipsed with hydrogens
- Higher energy than staggered conformer
- Dihedral angle = 120 degrees

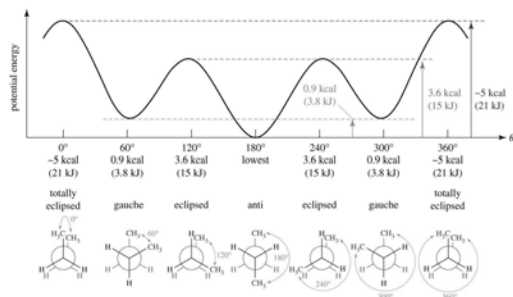


Butane Conformers (4)

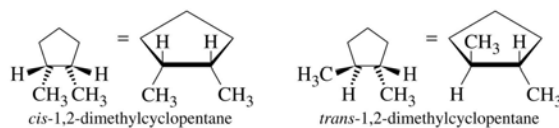
- Gauche, staggered conformer
- Methyls closer than in anti conformer
- Dihedral angle = 60 degrees



Conformational Analysis



Cis-Trans Isomerism



- Cis: like groups on same side of ring
- Trans: like groups on opposite sides of ring

Cycloalkanes

- Rings of carbon atoms (CH_2 groups)
- Formula: C_nH_{2n}
- Nonpolar, insoluble in water
- Compact shape
- Melting and boiling points similar to branched alkanes with same number of carbons

Cycloalkane Stability

- 5- and 6-membered rings most stable
- Bond angle closest to 109.5°
- Angle (Baeyer) strain
- Measured by heats of combustion per $-\text{CH}_2-$

Heats of combustion/ CH_2

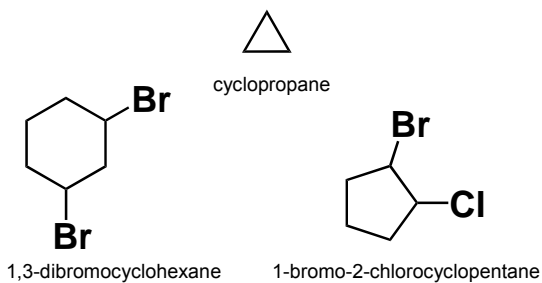
Cyclane (CH_2) _n	n	$\Delta\text{H}/n$ (kJ)	
n-alkane		658.6	free of angle strain
cyclopropane	3	697.0	
cyclobutane	4	686.0	
cyclopentane	5	664.0	
cyclohexane	6	658.7	free of angle strain!!! Why?
cycloheptane	7	662.4	
cyclooctane	8	663.8	
cyclopentadecane	15	659.0	

Cyclohexane

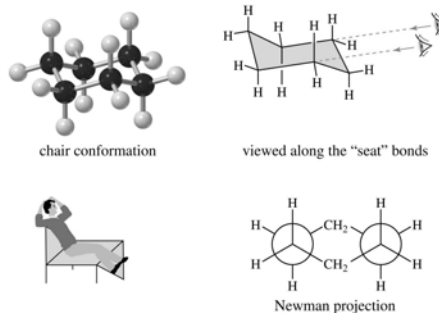
- Combustion data shows it's unstrained.
- Angles would be 120° , if planar.
- The chair conformer has 109.5° bond angles and all hydrogens are staggered.
- No angle strain and no torsional strain.

Nomenclature of cycloalkanes

Cycloalkanes are named by adding the prefix **cyclo** to the name of the corresponding *n*-alkane.



Chair Conformer

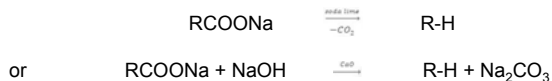


General Methods of Preparation of Alkanes

(i) Decarboxylation :

(a) Decarboxylation means removal of CO_2 from molecules having -COOH gp.

(b) Saturated monocarboxylic acid salt of sodium/potassium on dry distillation with soda lime gives alkane.



(c) The alkane formed always contains one carbon atom less than the original acid.

(d) The yield is good in case of lower members but poor for higher members.

(e) Soda lime is prepared by soaking quick lime CaO in caustic soda solution and then drying the products. It is generally written as $\text{NaOH} + \text{CaO}$. Its reaction is milder than caustic soda. Otherwise the reaction will occur violently. Also CaO used along with NaOH keeps it dry (NaOH is hygroscopic) to aid fusion.

(f) The decarboxylation of sodium formate yields H_2 .



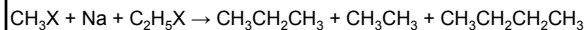
(ii) Wurtz reaction:

(a) A solution of alkyl halide in ether on heating with sodium gives alkane.

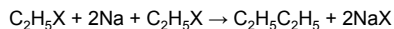
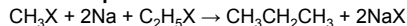


(b) An alkyl halide on Wurtz reaction leads to the formation of symmetrical alkane having an even number of carbon atoms.

(c) Two different alkyl halides, on Wurtz reaction give all possible alkanes.

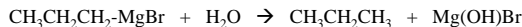
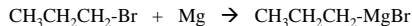
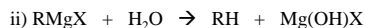


The different steps are:

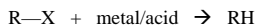


2. Reduction of an alkyl halide

a) hydrolysis of a Grignard reagent (two steps)

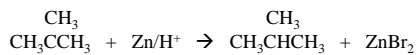
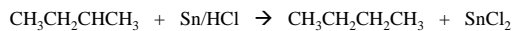


b) with an active metal and an acid

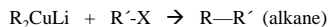


active metals = Sn, Zn, Fe, etc.

acid = HCl, etc. (H^+)



3. Corey-House synthesis

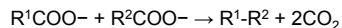


($\text{R}'\text{-X}$ should be 1° or methyl)

This synthesis is important because it affords a synthesis of a larger alkane from two smaller alkyl halides.

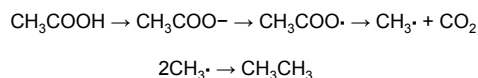
Kolbe electrolysis or Kolbe reaction

The Kolbe reaction is formally a **decarboxylative dimerisation** and proceeds by a radical reaction mechanism. Generally, the reaction can be observed as:



If R^1 , R^2 are different, then alkanes $R^1\text{-R}^1$ and $R^2\text{-R}^2$ are also formed.

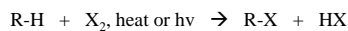
As an example, electrolysis of acetic acid yields ethane and carbon dioxide:



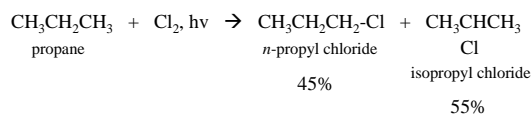
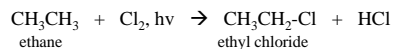
Alkane, reactions:

- Halogenation
- Combustion (oxidation)
- Pyrolysis (cracking)

1. Halogenation



- heat or light required for reaction.
- X_2 : $\text{Cl}_2 > \text{Br}_2 \neq \text{I}_2$
- yields **mixtures** ☹
- H: $3^\circ > 2^\circ > 1^\circ > \text{CH}_4$
- bromine is more selective



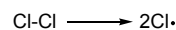
gives a mixture of both the possible alkyl halides! ☹

The mechanism?

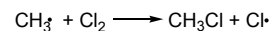
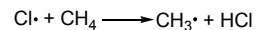
- $\text{Cl}-\text{Cl} \xrightarrow[\Delta]{h\nu} 2\text{Cl}\cdot$
 - $\text{Cl}\cdot + \text{H}-\text{CH}_3 \rightarrow \text{CH}_3\cdot + \text{HCl}$
 - $\text{H}_3\text{C}\cdot + \text{Cl}-\text{Cl} \rightarrow \text{CH}_3\text{Cl} + \text{Cl}\cdot$
- 2, 3, 2, 3, 2 etc.

Chain Reaction

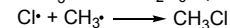
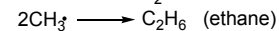
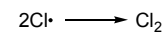
Chain initiation:



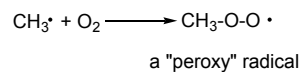
Chain propagation:



Chain termination:

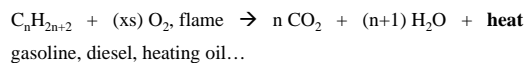


Inhibitors

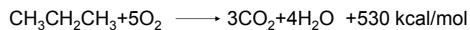
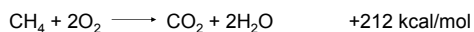


A compound which slows down or stops a reaction, even when present in small quantities, is called an inhibitor.

2. Combustion



Oxidation of hydrocarbons is the basis for their uses as energy sources for heat and power



Pyrolysis (cracking)

alkane, 400-600°C → smaller alkanes + alkenes + H₂

Used to increase the yield of gasoline from petroleum. Higher boiling fractions are "cracked" into lower boiling fractions that are added to the raw gasoline. The alkenes can be separated and used in to make plastics.

Cyclopropane

