Review/Polycyclic aliphatic compounds

Steroid:



When naming the compounds above, it is necessary to describe the location of the two methyl groups even if they are located on the same substituent because all of these are dimethylcyclopropanes (i.e. from left to right: **1,1**-dimethyl-, **1,2-cis-**dimethyl-, **1,2-trans**-dimethyl- cylcopropane).



Enantiomers (non-superimposable mirror images)

Reactions of alkanes

1) Combustion:

R-H + O₂ $\xrightarrow{\Delta=heat}$ CO₂ + H₂O

R = any alkyl group

General formula for combustion reactions:

$$C_nH_{2n+2} + (\frac{3n}{2} + \frac{1}{2})O_2$$
 (n+1) H₂O + n CO₂

e.g. propane

$$\overbrace{CH_3CH_2CH_3}^{\Delta} \qquad \overbrace{5O_2}^{5O_2} \qquad \xrightarrow{\Delta} \qquad 3CO_2 + 4H_2O$$

2) Halogenation of alkanes

			hv			
R-H	+	X_2	\rightarrow	R-X	+	HX

R = any alkyl group, R-X = alkyl halide / haloalkane (X= Cl, Br, F); F_2 is the most reactive and I_2 fails to react.

 $h = Planck's constant 6.6 \times 10^{-34} joules-sec$

v = frequency of light

E = hv, are the symbols we use to describe light energy

In this course, we will be focused on chlorination and bromination.

Substitution reaction (via radicals) – Substitute H with X



e.g. Chlorination of methane

Mechanism of reaction:

- Step by step description (proposal) of a reaction process (hypothetical and difficult to "prove")

Two kinds of mechanism

1. **Homolytic** (radical): One electron goes to each atom once the bond in broken. e.g. Free radical halogenation of alkanes



The red half arrows above describe the movement of one electron, full arrows describe movement of lone pairs.

2. **Heterolytic** (polar reaction): The electron pair goes to one of the atoms once the bond is broken. e.g. Addition reactions of alkenes; elimination reactions



Homolytic reactions are less common than heterolytic reactions - Initiated by heat (Δ) or by light (h υ)

Mechanism of halogenation of CH₄:

Propagation is the main step within the process. The termination step is the combination of radicals and is quite rare during the progress of the reaction, yet any one of the three listed can occur to terminate the reaction.

Note: The above mechanism also applies to other halogens (F, Cl, Br; not I)

Example: Ethane (analogous)

$$H_3C - CH_3 \xrightarrow{Cl_2} CH_3 - CH_2 - CI + HCI$$

Example: Bromination of cyclohexane

Step 1



Example: Methylcyclohexane



Other Examples:



The reaction can utilize either heat (Δ) or light (hv)

Different types of hydrogen can be pulled from a methylcyclohexane in a radical halogenation reaction to give various products. However, one main product is obtained. This is explained in terms of the stability of the radical formed during the reaction process.

Stability of radicals:

- Stability increases with alkyl substitution
- Alkyl groups are polarizable and donate electrons to electron deficient sites better than hydrogens (this is called **inductive effect** and occurs through sigma bonds)



Or it can be summarized from least to most stable radicals:

·CH ₃	<	[·] CH ₂ R	<	[·] CHR ₂	<	·CR ₃
methyl		primary (1°)		secondary (2°)		tertiary (3°)
radical		radical		radical		radical
(least stab	ole)					(most stable)

More Examples

A. 1,1,3-trimethylcyclopentane bromination



1,1,3-trimethylcyclopentane

B. 2,2,4-trimethylpentane chlorination



2,2,4-trimethylpentane