Organic Chemistry Summary Notes

Characteristics of Organic Compounds

1. Covalent bonds
2. Linear (higher m.p. and b.p. because of bigger surface area), branched (lower m.p. and b.p. because of smaller surface area), ring
3. Saturated (single bonds only) / Unsaturated (double/triple bonds)
4. Functional group
    - Meth (1C), Eth (2C), Prop (3C), But (4C), Pent (5C), etc.
5. Homologous series
    - Related compounds sharing the same functional group; addition of methylene (-CH_2) each time
6. Isomerism
    - Structural
        i. -ol ↔ ether
        ii. -al ↔ -one
        iii. -oic ↔ ester
        } Different connected structures
    - Stereo-isomerism: geometrical
        i. C=C
        ii. Ring
7. a) Structural formula
    b) Expanded formula
    c) Condensed formula
    d) Line structure
8. –Ane
    - C_nH_{2n+2}, σ bond

    --Ene
    - CnH_{2n}, σ + π bonds

    --yne
    - C_nH_{2n-2}, σ + π + π bonds

    --Aromatic
    - Benzene/benzene derivatives
    - Delocalized electrons add to stability, thus unreactive

Nomenclature

1. Find longest chain (functional group)
2. Identify substituents
3. Number the parent chain
4. List substituents in alphabetical order and give their locant, (lowest possible number)
5. Name the parent chain – usually only one suffix (max of 2 suffix)

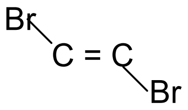
(Refer to sheet “Naming Organic Compounds” for further nomenclature)

Alkanes

- σ bonded
- Tetrahedral (Bond angle: 109.5 degrees)
- Stable due to strong C-C, C-H bonds
- Non-polar (does not dissolve in water, only non-polar solvents)
- Low mp/bp because of weak IMFAs (only LDF)
- Mp/bp goes up as molecular mass increases → LDF increases
- Combustion
  - Complete, Excess O_2 → $CO_2 + H_2O$ } + Heat
  - Incomplete, Limited O_2 → $C + CO + H_2O$ } (used as fuels)
- Substitution Reactions
  - $CH_4 + Br_2 \xrightarrow{UV} CH_3Br + HBr$

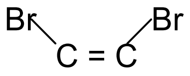
Alkene

- σ + π bonds
- Trigonal Planar (Bond angle: 120 degrees)
- Non-polar
- LDF (3 bonds → Unstable → Addition Reactions)
- Halogenation
  - **Test for unsaturated bonds** (Alkenes)
  - $CH_2 = CH_2 + Br_2$ → $CH_2Br - CH_2Br$
    Red/Org. Colourless
- Hydrogenation: C=C + H_2 → C-C (makes margarine, heterogenous catalysis); Ni/200 C
- Hydration: C=C + HOH → C-C-OH (Markovnikov's Rule: Hydrogen goes to the carbon already attached to the most hydrogens), dilute sulphuric acid required
- Hydrogen Halide: C=C + HX → H-C-C-X (Markovnikov's Rule)
- Oxidizing Agent (**Test for Unsaturated bonds** → diol)
  - $KMnO_4/H^+$ Purple → Colourless
  - $K_2Cr_2O_7/H^+$ Orange → green
  - C=C + [O] + H-OH → OH–C–C –OH
- Polymerisation (Ms. Pall: Can't make out the section! Sowwy ☹)
- Cis/Trans – In alkenes, the orientation of substituents matter, since they are fixed in position.



Trans

More Stable, higher mp/bp



Cis

Less Stable,lower mp/bp

(due to steric hinderance), more polar

Organic Reaction Mechanisms

Definition: Reaction Mechanisms

During any reaction, bonds are broken and made. As bonds are attractive forces between positive and negative bits of particles, making and breaking bonds means moving electrons around. A **mechanism** is a description of a successful collision (an effective collision) between the reactants and the electron rearrangement that happens as reactants are changed into products.

1) Homolytic Substitution

(A free radical photochemical chain reaction)

A common example is the reaction between methane and chlorine in the presence of UV light.

{E = hf, for a quantum of UV light, f = 1 x $10^{15}s^{-1}$; E = 6.6 x 10^{-19} J. For 1 mole of quantum E = 6.6 x 10^{-19} J (N_A/mol) = 400 kJ/mol}

To break a Cl – Cl bond (Bond dissociation energy = 242 kJ/mol)

To break a C – C bond (bond dissociation energy = 348 kJ/mol)

Evidence for Mechanism

- Reaction takes place in sunlight, not darkness
- Small amounts of C_2H_6 detected
- If $Pb(CH_3)_4$ added (this dissociates → CH_3), reaction takes place in the dark as well.

Stage 1 – Initiation: The Production of Free Radicals

A chlorine molecule absorbs UV radiation, breaking the bond in the molecule *homolytically* producing two free radicals.

Because the reaction is started by light it is a *photochemical* reaction.

$Cl – Cl \rightarrow 2Cl\bullet$ (Very low Ea of 25 kJ/mol)

Stage 2 – Propagation

The reaction between a free radical and a molecule to make another free radical. There are many possible steps:

(1) $Cl\bullet + CH_4 \rightarrow \bullet CH_3 + HCl$ (2) $Cl\bullet + CH_4 \rightarrow CH_3Cl + H\bullet$

Reaction #1 is more likely, since the making of H – Cl is highly exothermic (431 kJ/mol) compared to the making of a C – Cl bond (350 kJ/mol) Because each step makes another reactive free radical, the reaction is a *chain reaction*.

Step 3 – Termination

The reaction between two free radicals makes an unreactive molecule. Three possible reactions:

(1) $2Cl\bullet \rightarrow Cl_2$ (2) $2\bullet CH_3 \rightarrow C_2H_6$ (3) $Cl\bullet + \bullet CH_3 \rightarrow CH_3Cl$

Because any two free radicals can meet, this type of reaction always produces a mixture of products.

NOTE:
1) Reaction between toluene, Benzene – CH3 + X2 → Same Mechanism
2) Rate of reaction F2 > Cl2 > Br2 > I2 (Slow and reversible) due to H-X bond releases more energy in H – F than H – I.

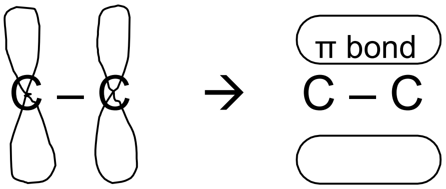
2) Electrophilic Addition

Addition to Alkenes is referred to as: Heterolytic Electrophilic Addition

The bonding between two doubly bonded carbon atom is stronger than the single bond in alkanes.

C – C	C = C
(348 kJ/mol, longer bond)	(612 kJ/mol, shorter bond)

This makes the alkenes more thermally stable than alkanes. Since the strength of the double bond is not twice that of a single bond, thus the double bond is a different kind of bond.



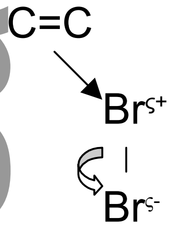
p-p overlap
Perpendicular to bond axis = π bond

Two regions of negative charge are a reactive site for electrophilic attack. The π-electron clouds make alkenes to be more reactive than alkanes.
(The π-electron cloud may even induce dipole in nearby particles)

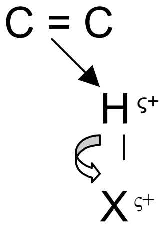
Evidence for Mechanism
1. a) Br_2 + inert solvent → Br – C – C – Br
   b) Br_2 + polar solvent → Br – C – C – OH
2. Br_2 + M^+Cl^- → Br – C – C – Cl

Mechanism: $H_2C=CH_2 + X_2$

- Rate law: Rate = k[alkene][X2] (bimolecular)



Induced dipole

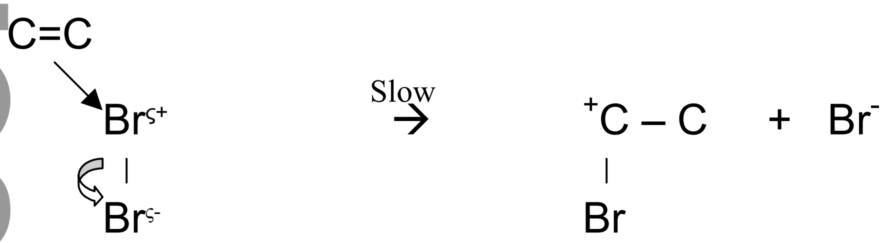


Permanent dipole

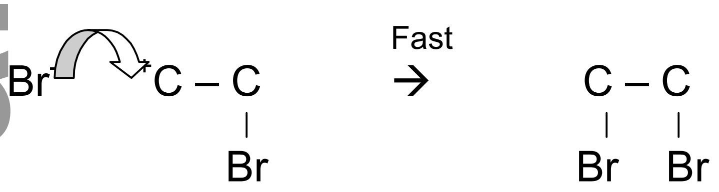
π-electrons becoming σ electrons as they bond to a new atom to the carbon skeleton.

First Step

To attack π-electrons of the alkene on an electrophile Rep^n (What does that stand for?) between π-electron of the double bond and the X-X bond, inducing a dipole in the $X^{\varsigma+} – X^{\varsigma-}$. Further approach, allows X – X to undergo heterolytic fission, and the formation of a weak complex between the two ends of the $^{\varsigma+}Br – Br^{\varsigma-}$ molecule and the π-electrons of the C=C bond.



The carbocation rapidly reacts with the nucleophilic Br^- from the backside to the bond that was made in the heterolysis.



NOTE

1. When a substance such as HX adds onto an alkene, the H- always adds onto the C-atom with the most H's already attached to it. → Markovnikov's Rule, due to the delocalisation of the charge on C+ (C+3 > C+2 > C+1)
2. Hydration of alkenes C=C + $^{\varsigma+}H – ^{\varsigma-}OSO_2OH$ → C – C – OH
3. Test for alkenes (1) Br2, (2) Oxidizing agent like OH – C – C – OH