Introduction to Reaction mechanisms

Definition

- A reaction mechanism is the step by step sequence of elementary reactions by which overall chemical change occurs.
- It is also a detailed description of the process leading from the reactants to the products of a reaction, including a characterization as complete as possible of the composition, structure, energy and other properties of reaction intermediates, products, and transition states.

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Definitions…

- A unimolecular reaction is a reaction where there is a single reactant molecular entity that is involved in the microscopic chemical event constituting an elementary reaction.
- A bimolecular reaction is where there are two reactant molecular entities that is involved in the microscopic chemical event constituting an elementary reaction.

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Reaction Intermediate

- A Reaction Intermediate is often also defined as "A molecule that is created and destroyed during a particular reaction pathway”.
- A stepwise reaction is a chemical reaction with at least one reaction intermediate and involving at least two consecutive elementary reactions.

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Nucleophile

- A nucleophile (nucleus loving species, i.e. negtively charged): this is a species which is rich in electrons, and serves as an electron source.
- In general nucleophiles have lone pairs of electrons, can have a negative charge, or the source of electrons is the pie bond.

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Electrophile

- Electrophile (electron loving species i.e. positively charged): this is a species which is electron deficient and serves as an electron sink.
- In general, electrophiles have a vacant orbital which can accept electrons, or have a polarised bond which can give off a leaving group.

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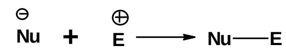
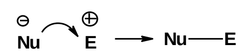
Flow of electrons

- The flow of electrons originates from the nucleophile to the electrophile e.g.



- Better still, the use of curly arrow



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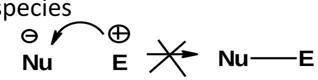
Curly Arrow

- Curly arrow (as the name implies) an arrow showing migration of electrons from a nucleophile (an electron-rich species, often negatively-charged) to an electrophile (an electron-deficient species, often positively-charged).
- Note: When a bond is broken, electrons leave where the bond was and this is represented by a curved arrow pointing away from the bond (nucleophile) and ending the arrow pointing towards the electrophilic species



wrong direction

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Advantages of using curly arrows

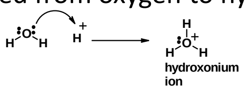
- First it permits us to keep track of valence shell electrons during a chemical reaction and thus serves as a method for electronic bookkeeping.
- Second it shows how *changes in bonding result from changes in electron* distribution.
- Third it can show likely mechanisms for chemical reactions in terms of the breaking and making of chemical bonds.

Curly arrows summary

- Keep two things in mind when drawing curved arrows: The tail of the arrow needs to be in the right place, and the head of the arrow needs to be in the right place.
- Don't forget that electrons occupy orbitals. Other than radicals, the electrons in the orbitals are either bonding pairs or lone pairs. This means that the tail of the curved arrow must be at a lone pair or a bonding pair. (A radical may have the tail of the curved half arrow originating at the unpaired electron.)
- The head of the curved arrow indicates where a lone pair is going or where a bond will form.

Curly Arrow: An example

- As mentioned earlier, the curved arrow depicts movement of an electron pair *from the tail of the arrow to the head of the arrow.*
- For example, in the reaction of a proton with water to produce the hydroxonium ion, a new bond is formed from oxygen to hydrogen.



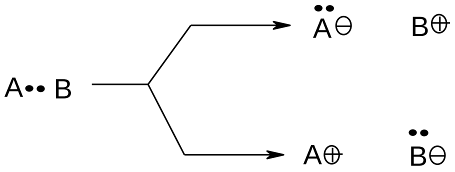
- The electrons in that bond start out as a lone pair on oxygen and are donated to and shared with the proton.

Heterolytic bond cleavage

- Heterolysis (or Heterolytic bond cleavage) is a process where the electron pair that comprised a bond moves to one of the atoms that was formerly joined by a bond.
- The bond breaks, forming a negatively charged species (an anion with octet configuration) and a positively charged species (a cation with sextet configuration).
- The anion is the species that retains the electrons from the bond while the cation is stripped of the electrons from the bond.

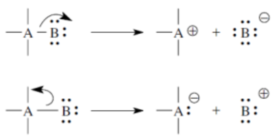
Heterolytic bond cleavage

- Heterolytic fission is unsymmetrical wherein one of the fragments takes both the electrons of the shared pair, leaving none on the other. This results into two charged particles as:



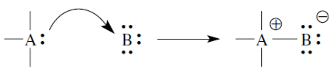
Heterolytic bond cleavage

- The movement of electrons during heterolytic cleavage follows the direction of bond polarity. In a polar covalent bond the shared pair is displaced toward the more electronegative element.
- Upon cleavage the pair of bonded electrons are transferred completely to the more electronegative element, which becomes negatively charged, and the more electropositive element loses the bonded electron pair and becomes positively charged.



Heterolytic bond formation

- The formation of a bond between two atoms can proceed by one of the atoms donating an electron pair and the other atom accepting the electron pair.
- The charge must be conserved and the loss and gain in electrons by the donor and acceptor, respectively, must be accompanied by a corresponding change in formal charge.

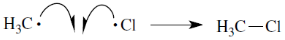


HOMOLYTIC Bond Cleavage

- If a bond is particularly weak and/or non polar, bond cleavage can occur by a non polar or homolytic process.
- One electron of the shared pair goes with each of the two bonded atoms. Bond breaking then is the movement of single electrons rather than electron pairs and is indicated in curved-arrow notation as “half-headed” arrows.
- Homolytic cleavage of a bond does not result in the formation of charge but does result in the formation of unpaired electron intermediates called free radicals.

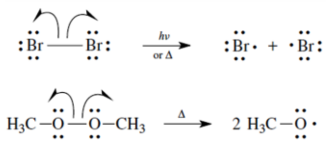
Homolytic bond formation

- Homolytic bond formation can occur when two free-radical species contact each other. Each has an available unpaired electron, and if these two electrons are shared, a new bond will result.
- This is simply the reverse of the homolytic cleavage.



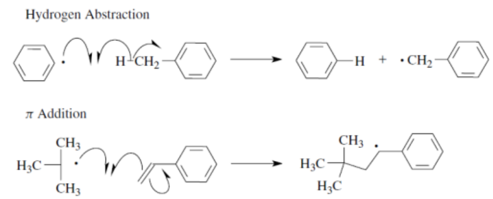
HOMOLYTIC BOND Cleavage

- Free radicals normally have seven electrons in the valence shell and as a consequence are very reactive intermediates.



Homolytic bond formation

- Homolytic bond formation can also occur by the reaction of a free radical with a bonded pair of electrons.

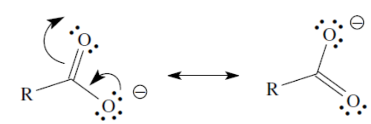


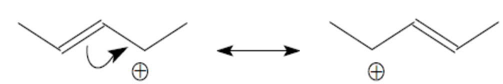
Homolytic bond formation: π-addition

- Addition to π bonds is a second very common reaction of free radicals. Interaction of the free radical with the π-electron pair causes one of the π electrons to pair up with the unpaired electron of the free radical to produce a new bond to one of the π-bonded atoms.
- The remaining π electron is now unpaired and thus forms a new free-radical species. The process is often very favorable since the new σ bond (70–90 kcal/mol) formed in the addition process is normally much stronger than the π bond (60 kcal/mol) which is broken in the reaction.

RESONANCE STRUCTURES

- Curly-arrow notation is also a very useful device with which to generate resonance structures.





Rules to follow for drawing contributing resonance structures:

1. Structures should be valid Lewis structures.
2. The positions of the atoms in different Lewis structures do not change.
3. The number of electron pairs stays the same in each structure.
4. Not all structures contribute equally to the resonance hybrid. The most stable structures contribute the most.

Substitution Reaction

- A substitution reaction is a reaction, elementary or stepwise, in which one atom or group in a molecular entity is replaced by another atom or group.
- It is a reaction in which one atom or group in a molecular entity is replaced by another atom or group contained in an "attacking" nucleophile (which is a molecular entity that brings a pair of electrons) attacks an electrophile.

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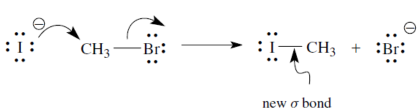
DEPICTION OF MECHANISM

- The mechanism of a reaction is the stepwise process by which reactants are converted to products, and generally each step involves bond making and/or bond breaking that can readily be depicted by curved-arrow notation.
- a nucleophile donates electrons to the electrophile, in this case a carbon with a leaving group attached, to produce a new *σ bond.* As the new σ bond is formed, the bond to the leaving group breaks and the substitution of one group for another is completed.



Summary of Mechanisms:

- Write a balanced equation for the reaction showing the correct Lewis structures for reactants and products.
- The use of curved arrows for electron movement is guided by bond polarities, electron donor– acceptor properties and electronegativities.
- Evaluate intermediates for stability and valence.