Organic Reactions

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Reaction Mechanism

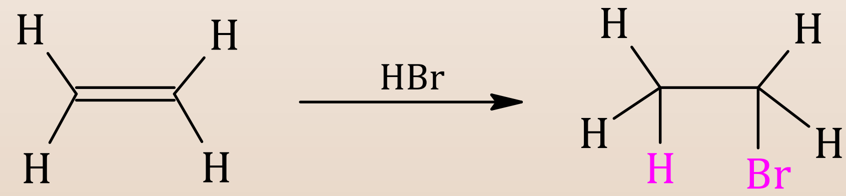
Reaction mechanisms are how reactions take place at a molecular level. Here we study:

- What bonds are broken and made as reaction progress.
- Learn to draw curved arrows to show transfer of electrons and form/break bonds.
- We also learn to determine if a reaction can take place.

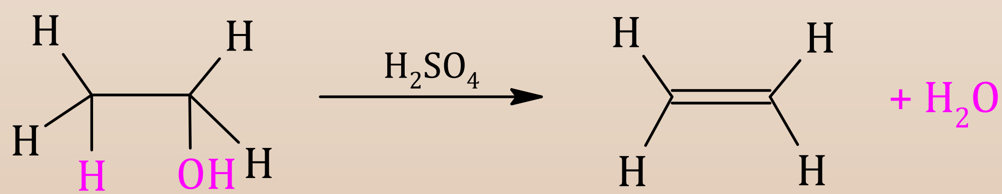
Types of Reactions

In general chemistry we learn about types of reactions such as single displacement, synthesis etc. or neutralization, precipitation etc. We can use those classifications here also, but organic chemistry has some more classifications as shown below.

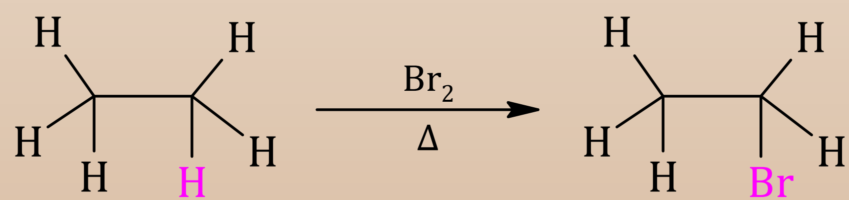
- Addition: Atoms are added to an unsaturated system.



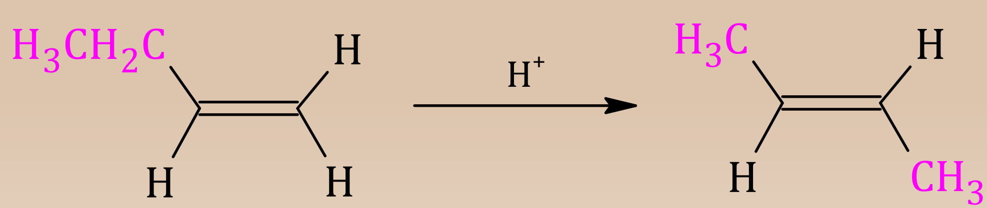
- Elimination: Atoms are removed to give unsaturation.



- Substitution: One atom is replaced by another.



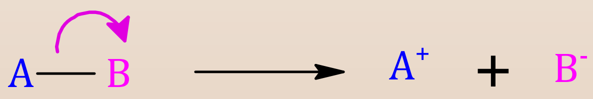
- Rearrangement: Atoms rearrange to give a different carbon molecule, a type of constitutional isomer.



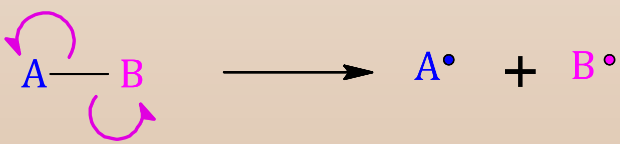
Steps in Reaction Mechanism

Bond formation or breakage can be symmetrical or unsymmetrical/asymmetric.

- **Unsymmetrical or Heterolytic fission -** gives two species of opposite charges. Use full headed arrow to show transfer of two electrons.
- **Symmetrical or Homolytic fission -** gives two species of same charge. Use half headed arrow to show transfer of one electron.



Unsymmetrical- Bond breaks with one atom taking both the electrons in the bond, creating a cation and an anion.



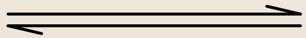
Symmetrical- Bond breaks with equal distribution of electrons, with each atom getting one electron, creating radicals. Radicals are electrically neutral.

Unsymmetrical- Electron rich anion forms a bond by giving electrons to electron poor cation.

Symmetrical- Each radical contributes one electron to bond formation.

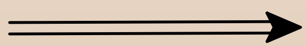
Arrows in Organic Chemistry

Synthesis

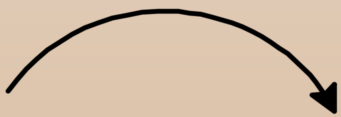


Equilibrium

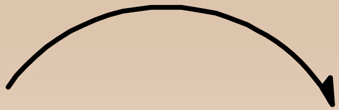
Resonance



Retrosynthesis (going backward)



Transfer of two electrons



Transfer of one electron

Kinetics of Chemical Reactions

Kinetics explain the mechanisms in chemistry.

Order of reaction tells us how many reactants and in what quantity they might be affecting the rate of reaction. After experimentation, the rate law equation tells us about the order of reaction.

The rate law is determined experimentally to see which reactants affect the rate of reaction when their concentration is changed.

- 0 order is when rate of reaction is unaffected by change in concentration of the reactants.
- 1st order is when rate of reaction doubles when one of the reactants is doubled.
- 2nd order is when rate of reaction quadruples when either two of the reactants are doubled or when one of the reactant concentration is doubled.

Order of reaction help to understand how the reactions work: which reactants are involved in the transition state, which helps to understand in order the bonds break and form.

Kinetics

Consider the following rate equations for the reaction above.

$$A + B \longrightarrow C + D$$

Speed/rate of the reaction is monitored by keeping concentration of one reactant constant and changing the other to see the effect. Some examples of rate laws possible are given below.

Rate = k [A]	This indicates that rate of reaction 1st order with respect to A, meaning that rate of reaction is dependent only on concentration of A. When [A] is doubled rate of reaction is doubled. The reaction is zero order with respect to [B] which indicates that changing [B] does not change the rate of reaction
Rate = k $[A]^2$	This indicates that rate of reaction 2nd order with respect to A, meaning that rate of reaction is dependent only on concentration of A. When [A] is doubled rate of reaction is quadrupled.
Rate = [A] [B]	This indicates that rate of reaction 1st order with respect to A and 1st order with respect to B. Rate of reaction is dependent on concentrations of A and B. When [A] or [B] is doubled, rate of reaction is doubled. When both [A] and [B] are doubled, rate quadruples.

Transition State and Collision Theory

From **transition state theory** of kinetics, we know that:

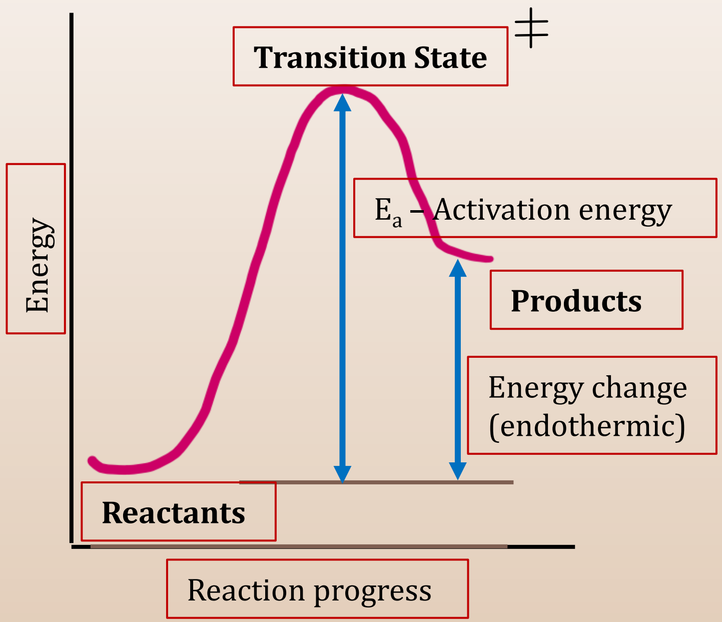
- Activation energy is the minimum energy required to get the reactants to the transition state.
- Order of reaction tells us about the molecularity of the reaction which tells what species are involved in the transition state. For a first order reaction, there is only one species (molecule) in the transition state. For a second order reaction, there are two species (two molecules) in the transition state.
- The number of transition states tell us how many steps a reactions has.

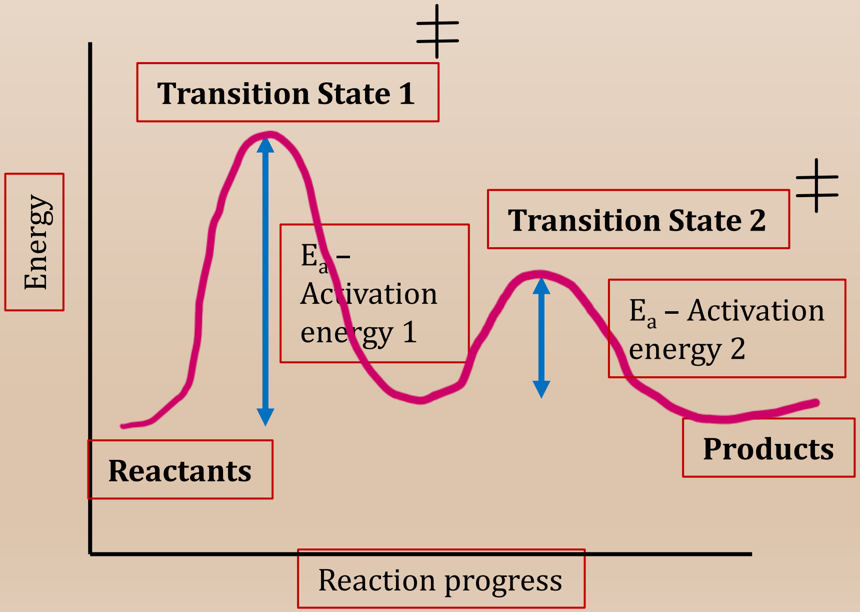
From **collision theory** we learn the following:

- More collisions of molecules leads to more product. Number of collisions can be increased by increasing the temperature of the reaction.
- Collisions should be in the correct orientation of molecules to allow for bond formation. 3D shapes (conformation, stereochemistry) of molecules help us to determine their orientation in the reaction.

Transition State Theory

- The graph on the right gives us the following information:
  - There is one transition state.
  - The reaction is endothermic.



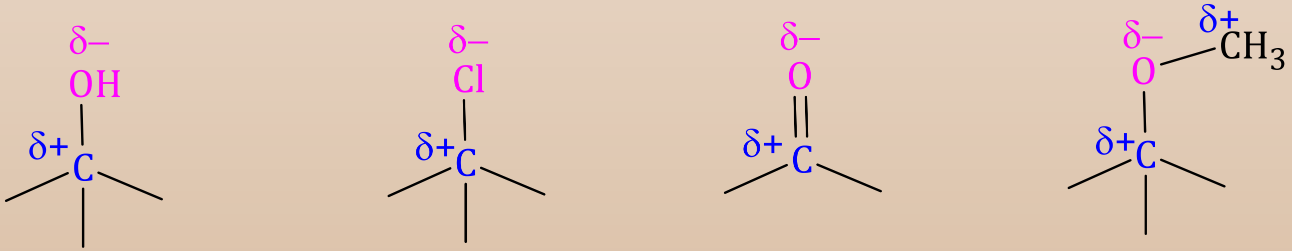


- The graph on the left gives us the following information:
  - There are two transition states.
  - The reaction is endothermic.

Polar Reactions

Reactions occur at polar bonds, where there is a charge distribution due to electronegativity. These bonds are more susceptible to breaking due to higher energy.

- The more electronegative element will have a partial negative charge and be the Lewis base. As shown below, O, Cl fall in this category.
- The atom bonded to the electronegative atom will have a partially positive charge and will be the Lewis acid.
- Elements such as O, F, N, Cl are more electronegative than carbon.



Polarized Reaction

The Lewis acid	The Lewis base
• positive center • electron poor • the electrophile	• negative center • electron rich • the nucleophile

Full headed arrow showing a pair of electrons moving from B^- to A^+

Electrophile
Electron poor

Nucleophile
Electron rich

New bond formed

Carbon Intermediates

There are four carbon intermediates in organic chemistry. All are formed in specific conditions and react also in specific way.

Carbocation: **C^+** Carbon is positive. It is formed from heterolytic fission. It can be considered a Lewis acid.

Carbanion: **C^-** Carbon is negative. This is usually formed by bonding with a metal. It can be considered a Lewis base.

Carbon radical: **C•** Carbon has a single electron. It is electrically neutral. It does not undergo the normal acid/base or Nu^-/E^+ reactions.

Carbene: **C:** Carbon has a pair of electrons. It is electrically neutral.

Carbon Intermediate	Charge on Carbon	Formed From	Reactivity
Carbocation: **C^+**	Positive	Heterolytic fission	It can be considered a Lewis acid.
Carbonanion: **C^-**	Negative	Bonding with a metal	It can be considered a Lewis base.
Carbon radical: **C•**	Neutral	Homolytic fission	Needs specific conditions for reactions
Carbene: **C:**	Neutral	Reaction with a metal	Needs specific conditions for reactions

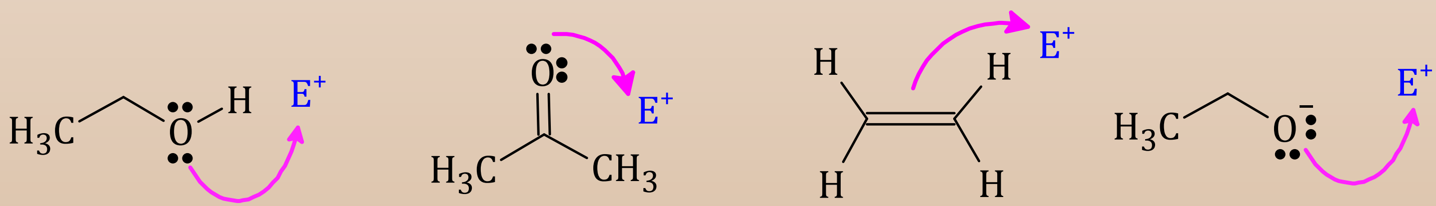
Arrows in Reaction Mechanism

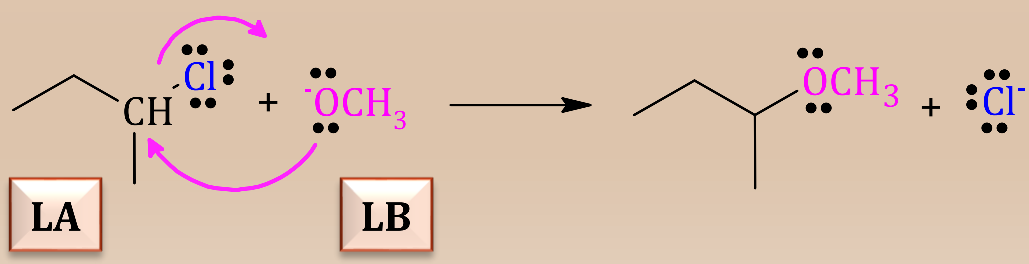
Curved arrows in chemistry helps us to keep a track of movement of electrons from higher density to lower density.

Rules for writing curved arrows:

- Start from electron rich species – the nucleophile (Nu^-) or Lewis base – LB.
- Bring the arrow to electron poor species – the electrophile (E^+) or Lewis acid – LA.
- The atoms where the arrow starts and ends are the atoms that form a bond or break.

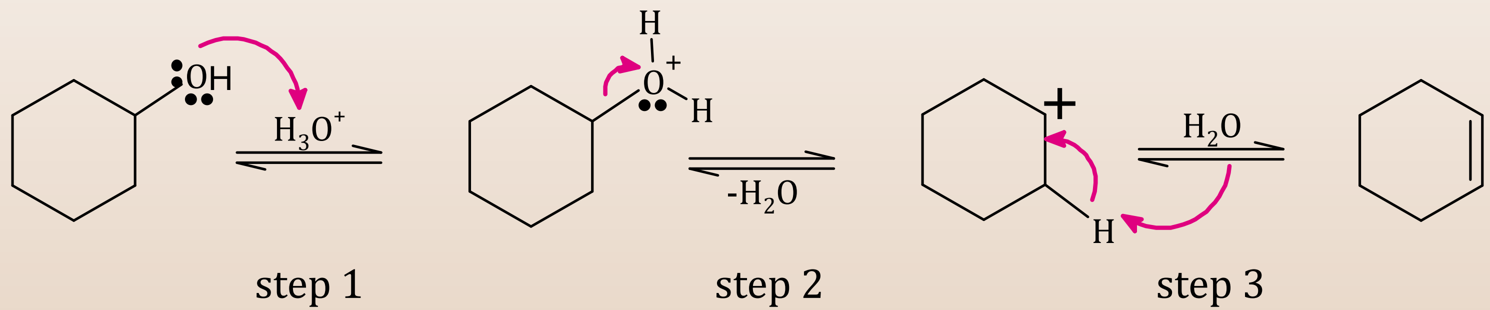
Below are some examples of arrows going from LB to LA (E^+).





Example of Arrows in Organic Reaction - 1

Here is a simple arrow writing in organic chemistry.



Step 1 – Acid base reaction. The LB, OH picks up a proton from acid, H_3O^+.

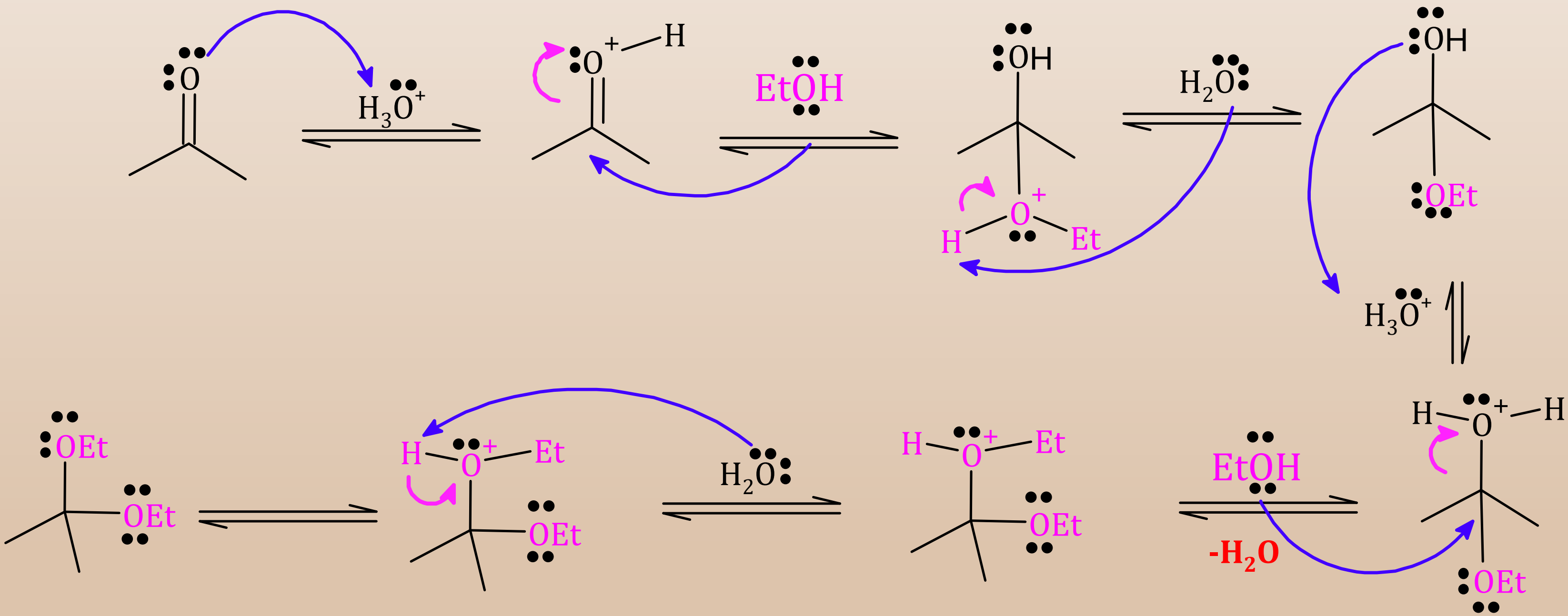
Step 2 – The H_2O leaves from taking the electrons with it, breaking the C-O bond and creating a carbocation.

Step 3 – H_2O, LB, then picks up a proton which leaves its electron on the bond that has the carbocation.

The organic molecule is neutral again in the end.

Example of Arrows in Organic Reaction - 2

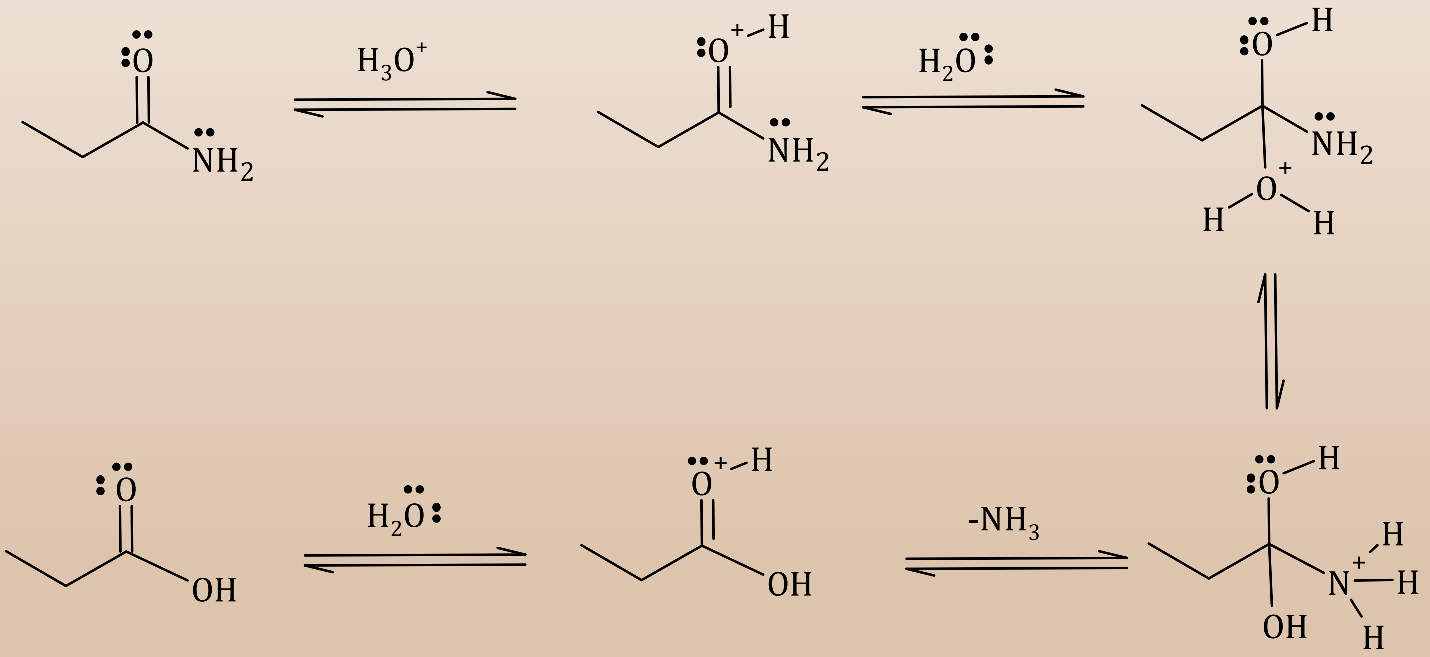
Here is a reaction of a ketone with alcohol in acidic conditions. In steps where there are two arrows, the blue is first and the second arrow is the pink one. In all these steps, just look at what atom is reacting with which one and what bonds are forming and breaking.



Solved Problem: Drawing Arrows

Draw all the arrows in the reaction mechanism below.

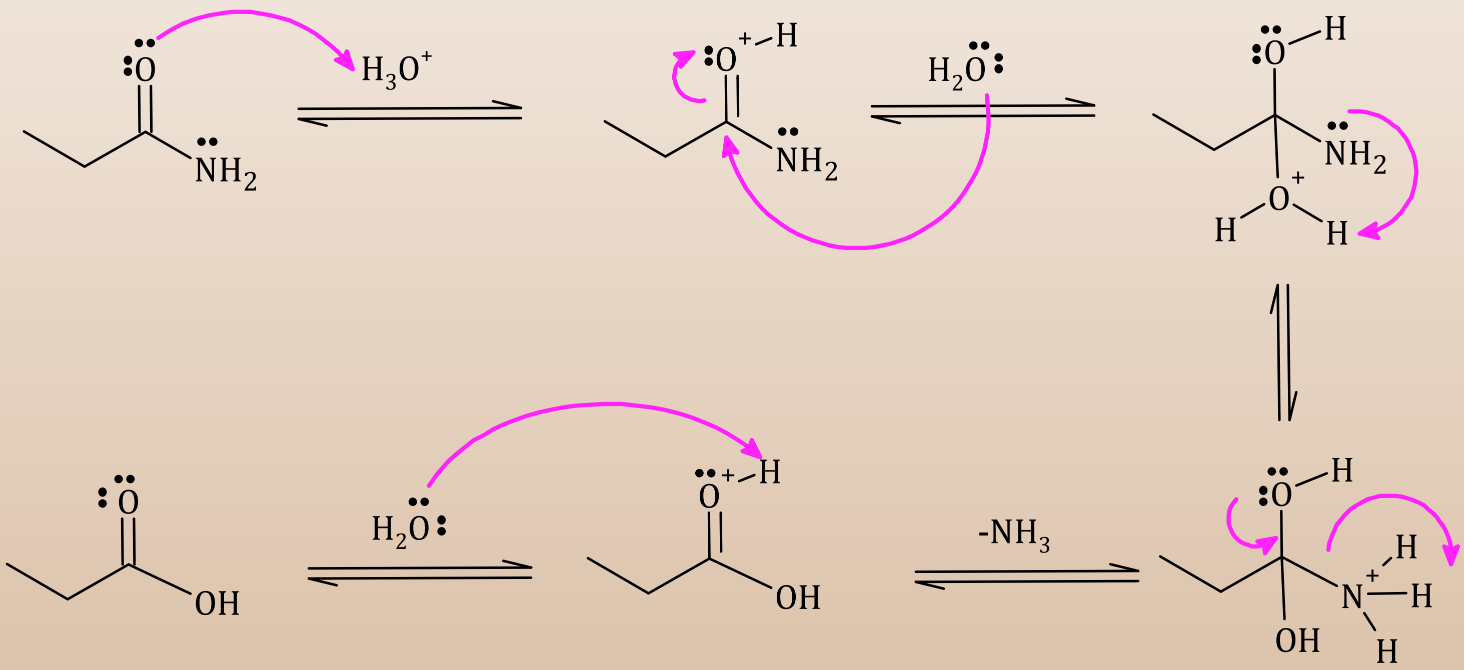
Hint: Look at the reactant and product for each step and see any new bond formed or proton transfers and draw the arrow from electron rich species to electron poor species.



Solved Problem: Drawing Arrows

Draw all the arrows in the reaction mechanism below.

Answer:



Key Words/Concepts

- Reaction Types
  - Addition
  - Elimination
  - Substitution
  - Rearrangement
- Polarity of bond
- Electrophile
- Nucleophile
- Heterolytic cleavage
- Homolytic cleavage
- Reaction mechanisms
- Order of reaction
- Transition states
- Activation energy
- Drawing arrows