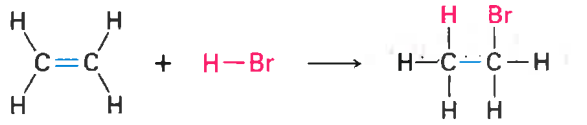
Chapter 6: Introduction to Mechanisms

Addition reactions – two molecules combine

★ formation of single bonds from double bonds



Ethylene (an alkene) + **Bromoethane (an alkyl halide)**

2 reactants → 1 product

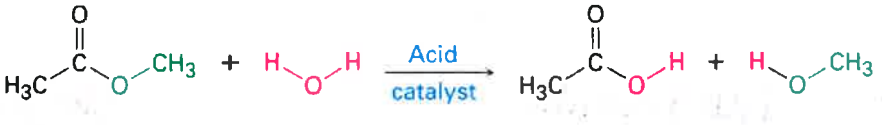
Elimination reactions – one molecule splits into two

★ Formation of double bonds!

Ethanol (an alcohol) → **Ethylene (an alkene)** + **H_2O**

one reactant → 2 products

Substitution – parts from two molecules exchange

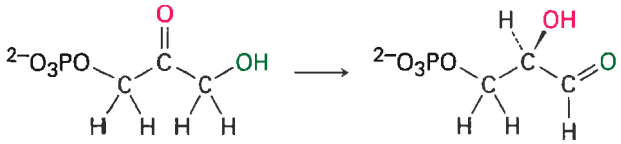


Methyl acetate (an ester) + **Acetic acid (a carboxylic acid)** + **Methanol (an alcohol)**

2 reactants → 2 products

Rearrangement reactions – a molecule undergoes changes in the way its atoms are connected

★ Stays within one molecule, does not react with a 2nd molecule



Dihydroxyacetone phosphate → **Glyceraldehyde 3-phosphate**

one reactant → one isomeric product

page 150 in 9th edition textbook

Classify the following reactions...

$CH_3Br + KOH \rightarrow CH_3OH + KBR$ Substitution

$CH_3CH_2BR \rightarrow H_2C{=}CH_2 + HBr$ elimination

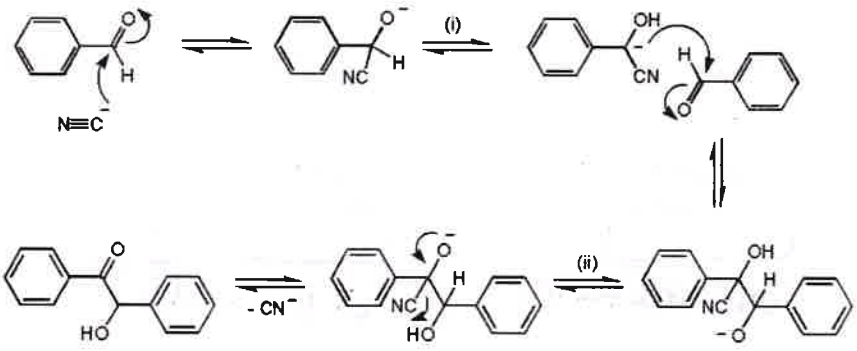
$H_2C{=}CH_2 + H_2 \rightarrow CH_3CH_3$ addition

Steps in Mechanisms

- We classify the types of steps in a sequence
- A step involves either the formation or breaking of a covalent bond
- Steps can occur in individually or in combination with other steps
- When several steps occur at the same time they are said to be ***concerted***

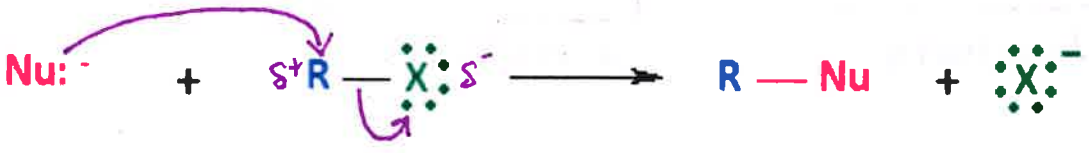
nucleophile = nucleus loving

electrophile = electron loving



Rules for Using Curved Arrows

1. The arrow goes from the nucleophilic reaction site to the electrophilic reaction site.



Nucleophile

Electrophile

Leaving group

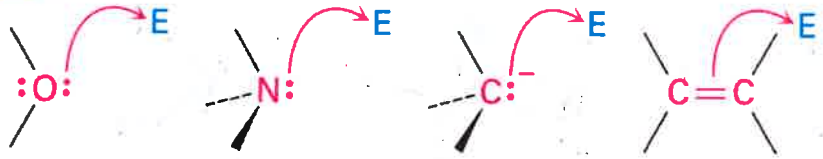
2. The nucleophilic site can be neutral or negatively charged

3. The electrophilic site can be neutral or positively charged

4. The octet rule must be followed

1. The arrow goes from the nucleophilic reaction site to the electrophilic reaction site

Nucleophile Examples:



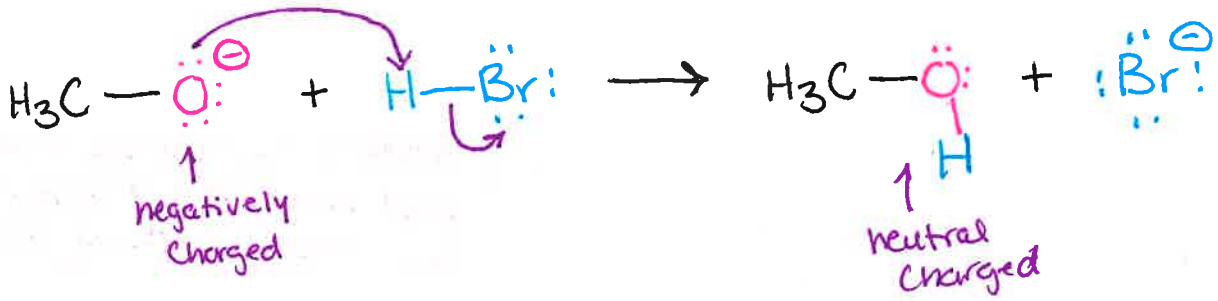
* Electrons typically flow from one of these nucleophiles

Electrophile Examples

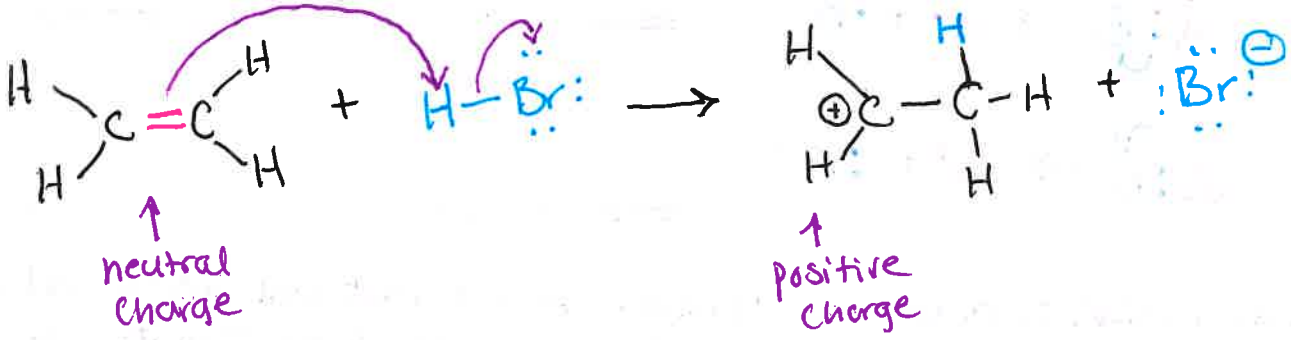
* Electrons usually flow to one of these electrophiles

2. Nucleophile can be either negatively charged or neutral

Negatively charged example:

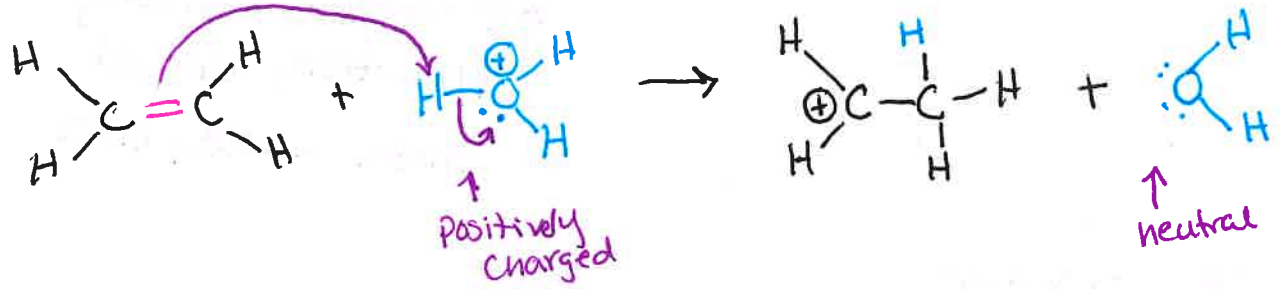


Neutral example:

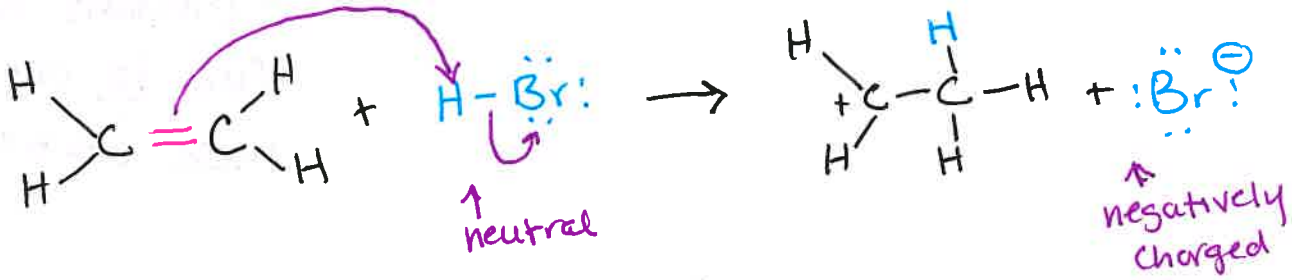


3. Electrophile can be either positively charged or neutral

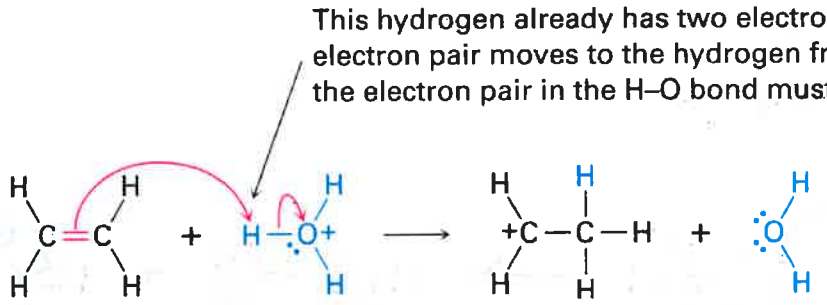
Positively charge example:



Neutral Example



4. The octet rule must be followed



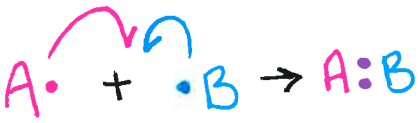
Processes that involve symmetrical bond breaking and bond making are called Radical Reactions

Symmetrical vs. Unsymmetrical Bond Breaking

Symmetrical bond-breaking (radical):
one bonding electron stays with each product.

Unsymmetrical bond-breaking (polar):
two bonding electrons stay with one product.

*a free radical is a neutral chemical species that contains an odd number of electrons and therefore has a single unpaired electron in one of its orbitals



Symmetrical bond-making (radical):
one bonding electron is donated by each reactant.

Unsymmetrical bond-making (polar):
two bonding electrons are donated by one reactant.

Generalized Polar Reactions

An **electrophile**, an electron poor species, combines with a **nucleophile**,

an electron rich species

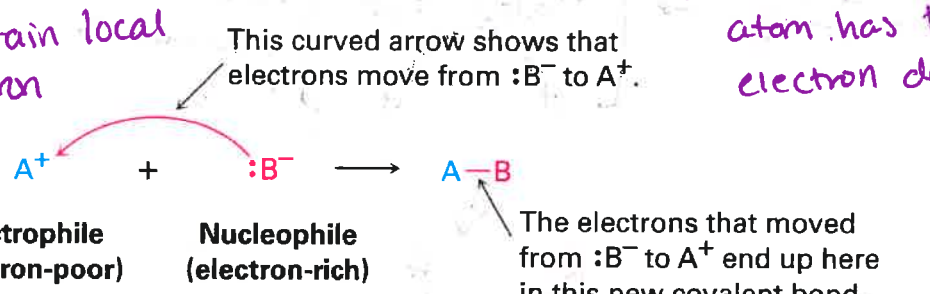
An electrophile is a Lewis acid and n nucleophile is a Lewis base

The combination is indicate with a curved arrow from nucleophile to electrophile

How Polar Reactions occur

1) Molecules can contain local unsymmetrical electron distributions due to differences in electronegativities

3) The more electronegative atom has the greater electron density



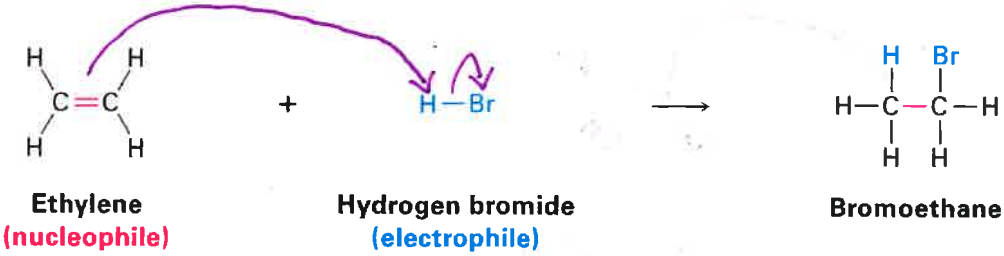
2) This causes a partial negative charge on an atom and a compensating partial positive charge on an adjacent atom

Mechanism of HBr to Ethylene

Bromide adds to the positive center of the **carbocation**, which is an electrophile, forming a C-Br σ bond

The result is that ethylene and HBr combine to form bromoethane

All polar reactions occur by combination of an electron-rich site of a nucleophile and an electron-deficient site of an electrophile



HBr adds to the π part of C-C double bond. HBr electrophile is attacked by π electrons of ethylene (nucleophile) to form a carbocation intermediate and bromide ion

The π bond is electron-rich, allowing it to function as a nucleophile

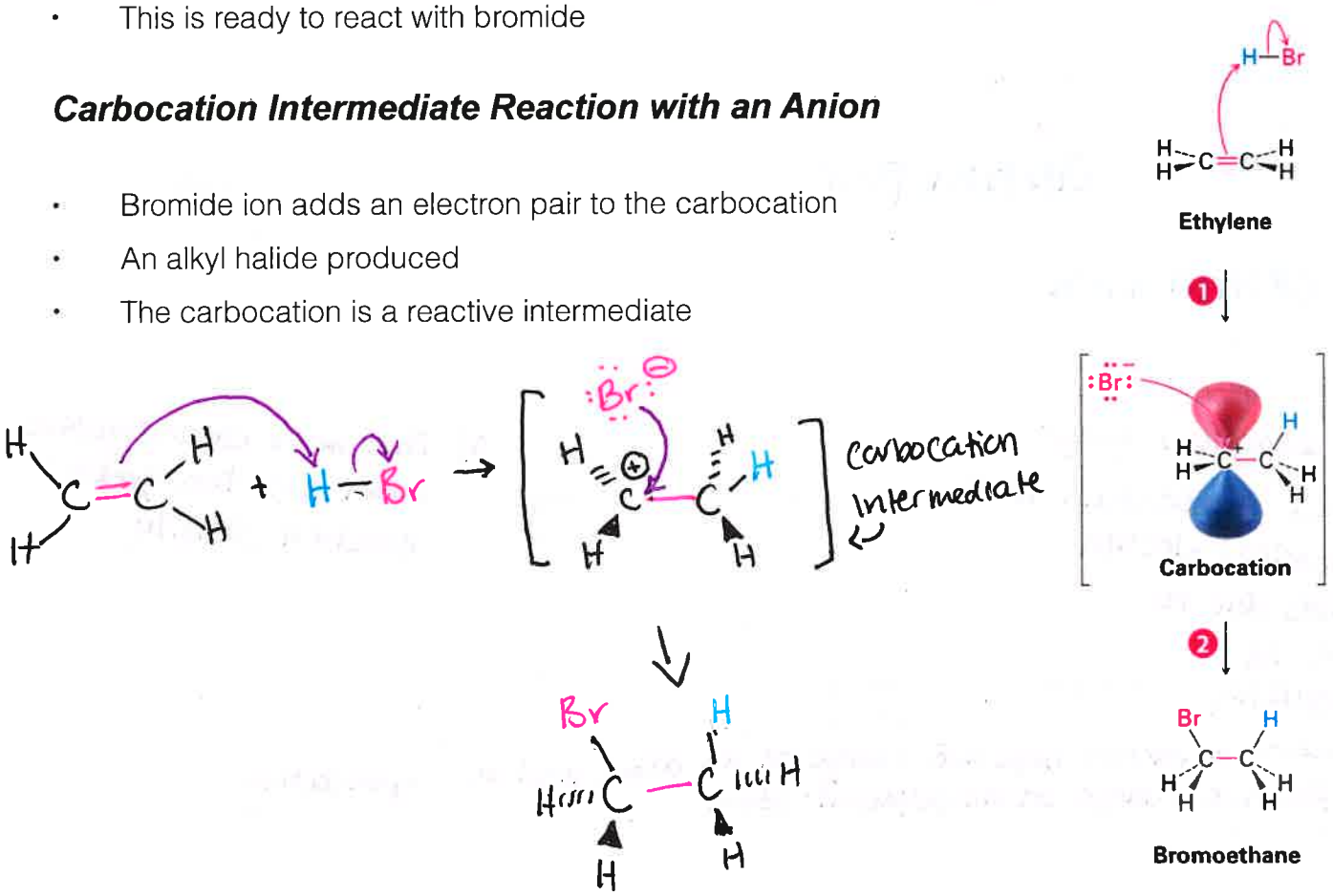
H-Br is electron deficient at the H since Br is much more electronegative, making HBr an electrophile

Formation of a Carbocation Intermediate

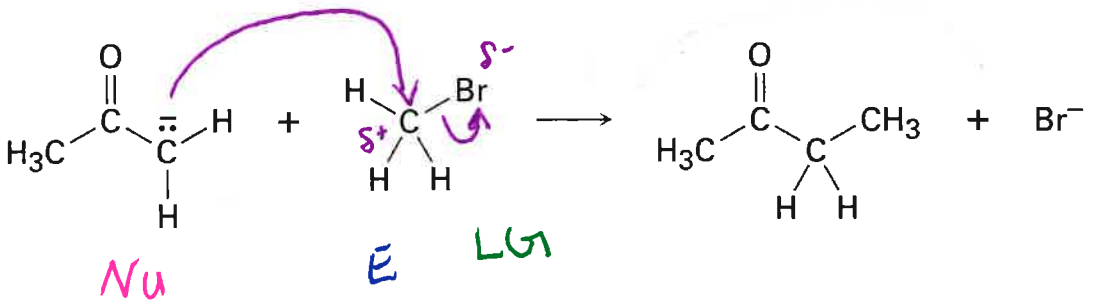
- HBr, a Lewis acid, adds to the π bond
- This produces an intermediate with a positive charge on carbon - a carbocation
- This is ready to react with bromide

Carbocation Intermediate Reaction with an Anion

- Bromide ion adds an electron pair to the carbocation
- An alkyl halide produced
- The carbocation is a reactive intermediate



Mechanism Practice



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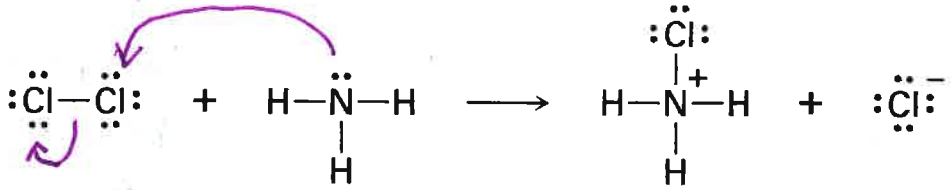

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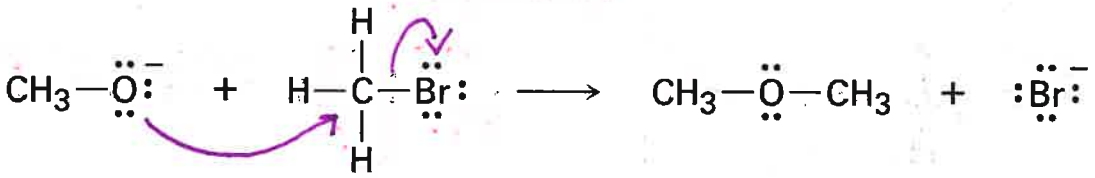

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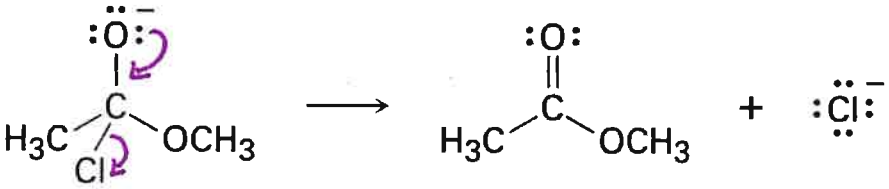


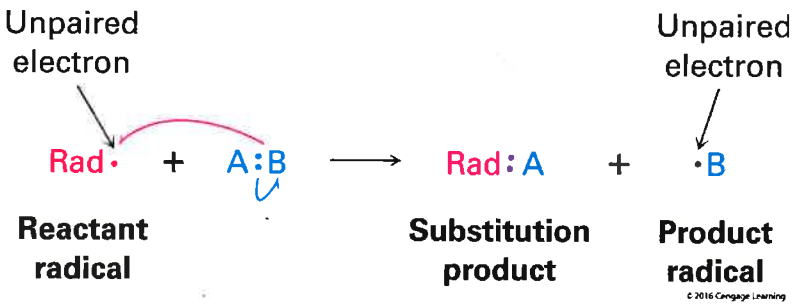
Radical Reactions

Not as common as polar reactions but are still important in industrial processes and biological pathways

Radicals are highly reactive - contains an atom with an odd number of electrons in its valence shell

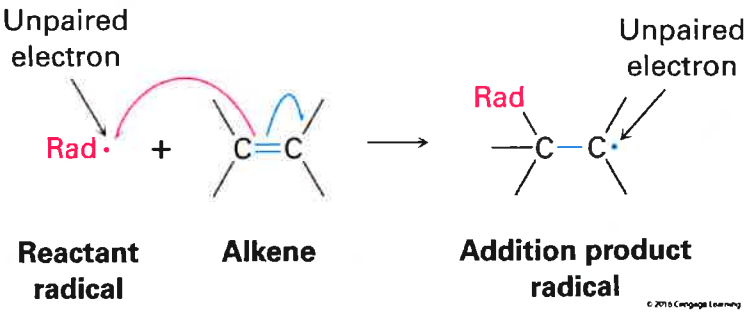
↳ usually 7 electrons

Radical Substitution Reaction:



Radicals may abstract an atom and one bonding electron from another reactant, leaving behind a new radical - ***radical substitution reaction***

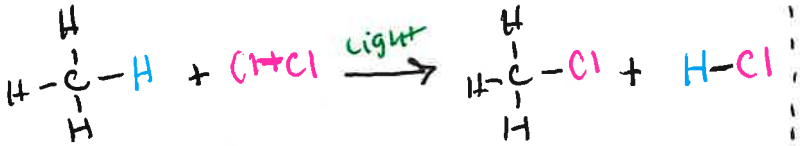
Alternatively to substitution: a reactant radical might add to a double bond, taking one electron from the double bond and yielding a new radical.



Radical Addition Reaction

Many radical reactions require 3 steps: ***initiation***, ***propagation*** and ***termination***

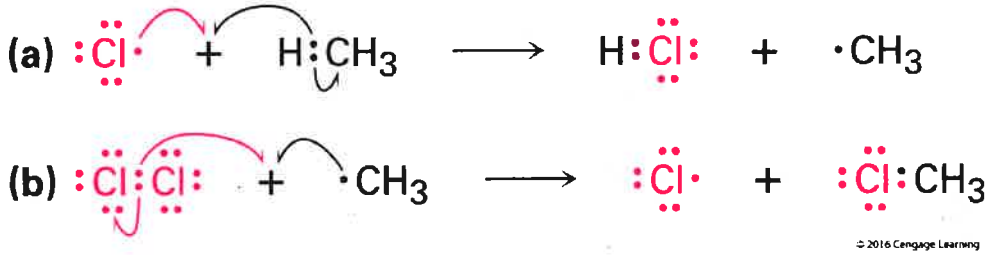
Example of an industrially useful radical Rxn is the chlorination of methane to yield chloromethane:



Initiation:

Initiation - ultraviolet light begins the reaction but breaking the relatively weak Cl-Cl bond creating a few reactive chlorine radicals

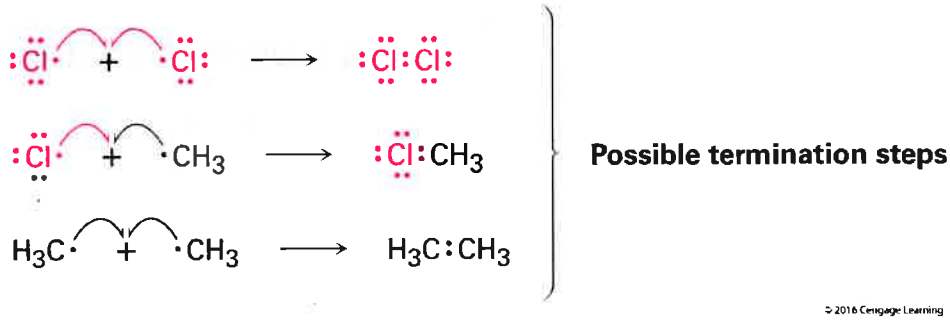
Propagation:



Propagation - reactive chlorine radical collides with a methane molecule in propagation, abstracting a hydrogen atom to create HCl and a methyl radical, the methyl radical reacts further with Cl_2 in a second propagation step creating chloromethane and a new chlorine radical which cycles back and repeats the first propagation step

Once the sequence has been initiated it becomes a self-sustaining cycle repeating over and over, becoming a chain reaction

Termination:



Termination - occasionally 2 radicals may collide and combine to form a stable product, when this happens the reaction is broken and the chain stops

Useful Practice Problems: 6-12, 17-19, 27-31, 33-35, 38-41, 45-48