

Intermolecular Forces

- IMF are in solids and liquids NOT gases (molecules are well separated)

London Dispersion

- Aka induced dipole- induced dipole forces
- Instantaneous dipole
- Induces dipole in its neighbour
- Pure substances
- Primary IMF between nonpolar molecules
- Strength increases with atomic number and size of the molecule
- Transient dipole
- Sometimes LD can be stronger the DD

Dipole Dipole Forces

- Polar molecule
- Permanent dipole
- Bond dipoles and asymmetric shape

Hydrogen Bonding Forces

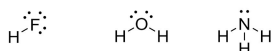
- Strongest covalent bond

Ion Dipole

- Involves aqueous ions
- H NOF
- Increases reaction strength
- Very strong in solids but are weaker and unfavourable in water due to solvation

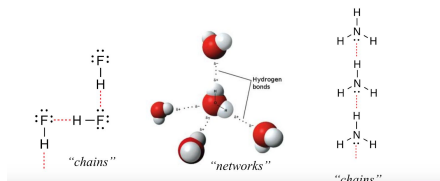
- Phase change causes only IMF bonds to be broken
- Comparing molecules with similar number of electrons, dipole forces are more significant than dispersion forces.

12-1 Hydrogen bonding



	HF	H ₂ O	NH ₃
# of δ ⁺ H atoms	1	2	3
# of lone pairs on δ ⁻ atom	3	2	1
average # of H-bonds per molecule in bulk sample (2 x "limiting reactant")	2	4	2
Boiling point (°C)	19	100	-33

	HF	H ₂ O	NH ₃
average # of H-bonds per molecule in bulk sample (2 x "limiting reactant")	2	4	2



Physical Property	Effect of increasing IMF
Melting point (mp)	increases
Boiling point (bp)	increases
Standard enthalpy of vaporization ($\Delta_{\text{vap}}H^\circ$)	increases
Vapour pressure	decreases
Viscosity	increases

Vaporization (or evaporation)

- molecules at the surface of a liquid have enough energy to overcome intermolecular forces of attraction and escape to the gas phase
- Vaporization occurs more readily with:
 - Increased temperature
 - Increased surface area
 - Decreased IMF strength

Vapour Pressure (closed system)⁹

- Vapour pressure is the equilibrium partial pressure of the vapour in the space above a liquid.
- Happens till rate of e= rate of condensation
- $A(l) \rightleftharpoons A(g) \quad K = P_{A(g)}$
- Standard BP is $P_{\text{vap}}=1\text{bar}$

Sweating

- Fast moving molecules at the surface are held less tightly rather than the interior
- Endothermic

Below BP- evaporate on the surface, Above- fully spontaneous

Triple Point: all three states are in equilibrium, transient state

Supercritical Fluid: substance has so much energy that it can't form IMF bonds, thermal energy breaks it but pressure keeps it together. A temperature and pressure beyond which liquid and gas are indistinguishable.

- Surface tension of liquid approaches zero
- Interface between l and g disappears

Liquid Water has a negative slope.

Organic Chemistry

Alkyne: linear (180)

Octet rule

- more important than formal charge considerations in determining the best Lewis structure
- Trumps formal charge

Hybridization

- Minimize energy of the molecule by maximizing orbital overlap in a bond
- Number of standard atomic orbitals = number of hybrid orbitals
- Promotion: e in orbital gets excited and promoted
- Rearrange and merge orbitals: sp^3 closer to P as there are more P orbitals in the hybridization
- Orbital energy is conserved
- AVERAGE ENERGY OF ELECTRONS in hybrid orbitals are higher
- Slightly higher potential energy
- Positive and positive phase add to each other
- Negative and positive subtract each other.. More negative

SP3

- Tetrahedral
- Saturated
- Four electrons
- Each sp^3 has one electron
- 25 s character, 75 p character

SP2

- Trigonal planar- maximizes distance more than tetrahedral
- Only 3 orbitals are hybridized and 1 P is not hybridized
- Left over exist above and below hybridized orbitals
- Unhybridized P has higher energy than hybridized
- 120

SP

- 180 bond angle
- Alkynes, linear
- Orbital lobes point along a straight line

Carbocation

- sp^2 -
- Less e
- Empty p orbital

Carboanion

- sp^3
- Has even more e than a neutral molecule

Sigma Bond

- Orbital overlap end on
- Hard to break
- Strong bond
- 180 rotation
- Sigma bonds are harder to break
- Head on overlap
- Free rotation

Pi Bond

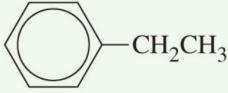
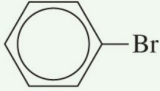
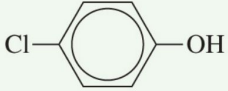
- Easy to break
- Overlap side on
- Double bonds
- More reactive
- Pi bonds in Alkenes make it reactive

Nomenclature/ Functional Groups

Recognize and name a variety of functional groups:

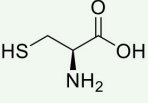
- Alkane, Alkene, Alkyne, Alkyl halides, Aromatic 0
- Alcohol, Ether, Amine, Thiol 1
- Ketone, Aldehyde 2
- Carboxylic acid, Ester, Amide 3

- Arranged in order of oxygen states
- As you go down more oxidized and for nomenclature priority, function increases

Class	Structural Formula ^a	Example
Amide	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$
Arene	$\text{Ar}-\text{H}^{\text{d}}$	
Aryl halide	$\text{Ar}-\text{X}^{\text{b}}$	
Phenol	$\text{Ar}-\text{OH}$	

Class	General Structural Formula ^a	Example
Aldehyde	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	$\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$
Ketone	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	$\text{CH}_3\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}\text{CH}_2\text{CH}_2\text{CH}_3$
Carboxylic acid	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
Ester	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$	$\text{CH}_3\text{CH}_2\text{CH}_2\overset{\text{O}}{\parallel}{\text{C}}-\text{OCH}_3$
Carboxylic acid anhydride	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$	$\text{H}_3\text{C}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$

6.2 p. 1214

Class	General Structural Formula ^a	Example
Alkane	$\text{R}-\text{H}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Alkene	$\text{C}=\text{C}$	$\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$
Alkyne	$-\text{C}\equiv\text{C}-$	$\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Alcohol	$\text{R}-\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
Alkyl halide	$\text{R}-\text{X}^{\text{b}}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
Ether	$\text{R}-\text{O}-\text{R}$	$\text{CH}_3-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3$
Amine	$\text{R}-\text{NH}_2$	$\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$
Thiol	$\text{R}-\text{SH}$	

Sn1 Mechanism

- Intermediate is a tertiary 3 carbocation
- Must bind with a 90 degree orientation

Conformations

- Atom arrangement can be changed by rotation about single bonds (σ bonds), without breaking any bonds.
- Alkane (sigma- 180 rotation- same molecule)

Configuration

- (permanent geometries) resulting from spatial arrangement of bonds.
- Changing atom arrangement requires breaking the π bond.
- "Restricted rotation"
- Different molecules

Z

- Lower melting point
- Higher priority groups are on the same side of the double bond

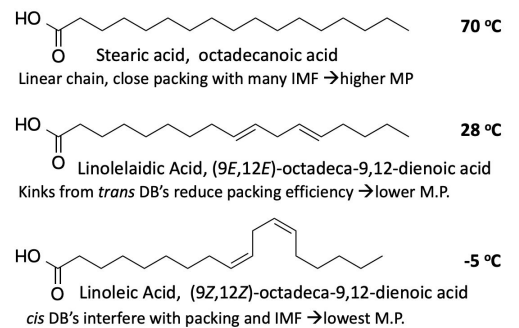
E

- Higher melting point
- Higher priority group are on the opposite sides of the double bond

Primary, Secondary, Tertiary

- We will see 1°, 2°, and 3° designations applied to saturated alkyl halides, carbocations, and alcohols.

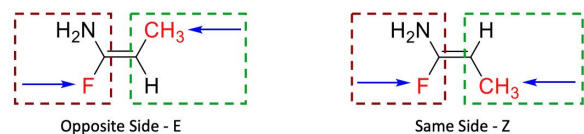
Designation	Alkyl halide	Carbocation	Alcohol
Primary (1°)			
Secondary (2°)			
Tertiary (3°)			



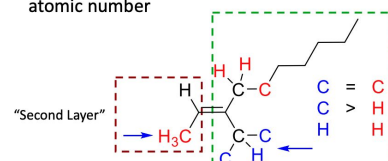
Cis/Trans- only disubstitute alkenes

Cahn- Ingold Prelog (CIP)

- Rule 1- use atomic number to define priority for each pair of atoms bound to each carbon in the C=C bond



atomic number



- Rule 2- equal priorities- compare them in order of decreasing atomic number

IF THERE ARE IDENTICAL GROUPS ON A SIDE- its neither

Rules:

- Name the longest carbon chain
- Cyclo- circles
- Assign E or Z for some alkenes
- Suffix depends on highest priority group

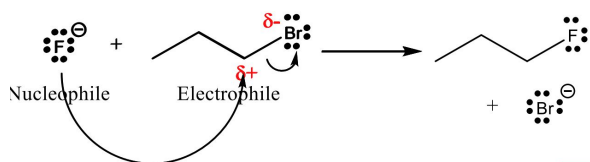
Nucleophilic substitution

Nucleophile:

- (nucleus loving) = electron donor = Lewis base
- hydroxide, amines, halides, alkenes, etc
- High electron density
- provides a source of electron density. It often contains a lone pair of electrons or electron density in a pi bond.
- has two pair of electrons that it will use bond- loves the nucleus- looking for something with a positive charge- DOES NOT HAVE TO BE CHARGED but needs a lone pair of electrons

Electrophile:

- (electron loving) = electron acceptor = Lewis acid (positive)
- Examples: alkyl halides, proton, carbonyl, etc.
- Low electron density
- look at delta positive stuff such as carbon
- a lack of electron density. It is often a carbon atom bonded to an electronegative atom (called the leaving group).



- Curvy arrows: where bonds are broken and made, drawn with the end of the arrow at the nucleophile and the head of the arrow pointing at the electrophile.
- Bonds: hybridized orbitals where electrons live
- E go in to an area that can one day be defined as a bond
- arrow pointing from an area of high electron density to an area of low electron density

SN1

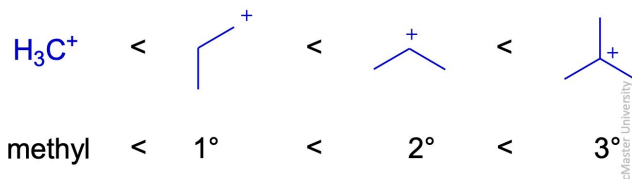
- nucleophilic substitution with one species in the rate limiting step
- RDS: UNIMOLECULAR
- only dependent on one concentration
- High E_a for the first step
- 3(tertiary) electrophile (most stable, most reactive)
- more stable carbocation intermediate, more steric hindrance to nucleophilic attack

- involves a carbocation intermediate: most stable = 3o , least stable = methyl.
- First Step: Loss of a Leaving Group (fast)
- Second Step: nucleophilic attack (slow)

SN2

- nucleophilic substitution with two species in the rate limiting step
- Bimolecular reaction, sufficient energy
- Ea: is higher in Sn2 vs Sn1
- ONE STEP
- First step that has to happen: nucleophile and electrophile have to be close in space
- 1(primary) electrophile = SN2
- less stable carbocation intermediate, less steric hindrance to nucleophilic attack
- does not involve a carbocation
- intermediate. Bond forming and bond breaking occur at the same time.

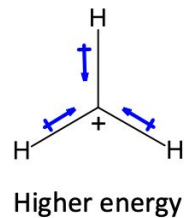
Stability increases with number of alkyl substituents:



Carbocation Stability

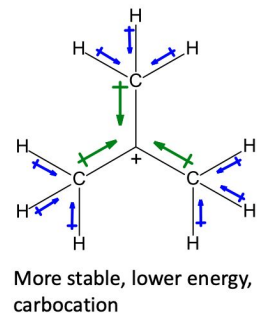
Electronic:

- Alkyl substituents are electron donating compared with H.
- Donating electrons to a carbocation center stabilizes it.

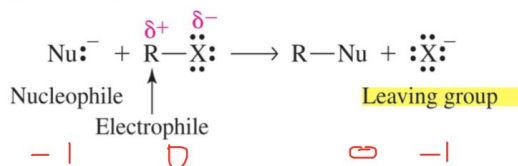


Steric:

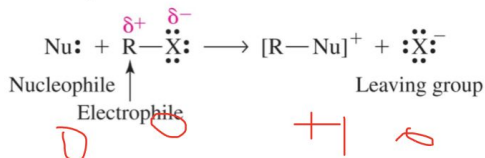
Carbocations with three substituents benefit from the larger C-C+-C angle of 120° (sp²) compared to ~109.5° found in tetrahedral alkanes (sp³).



Charged nucleophiles:



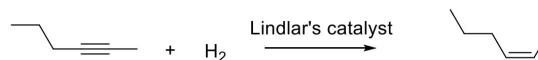
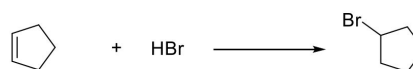
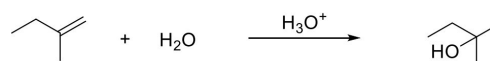
Neutral nucleophiles:



Reactions

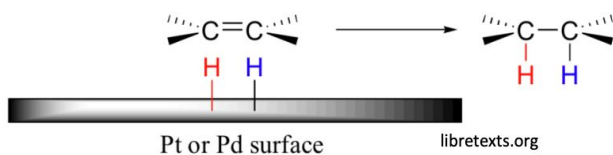
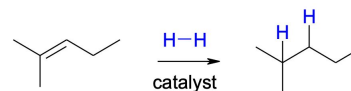
Addition reaction:

- a molecule adds across a multiple bond of another molecule.
- Catalyst:
 - H₃O⁺ (H₂O)
 - Lindlar's Catalyst (H₂)
 - No Catalyst (halogens, HBr)

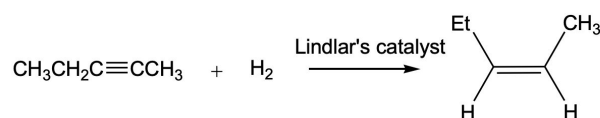
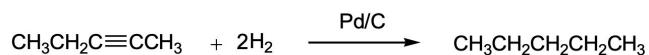


Hydrogenation (Reduction) of Alkenes

- The catalyst is typically a group 10 metal (Pd, Pt or Ni).
- SYN addition (H atoms add to same face of alkene)
- Similarly for alkynes:
- Lindlar's catalyst is deactivated (poisoned).
- Syn addition results in only the Z-isomer (cis-isomer).

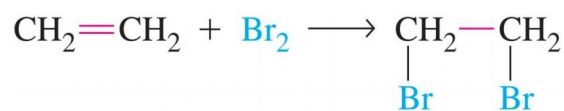


- Similarly for alkynes:



Halogenation of Alkenes

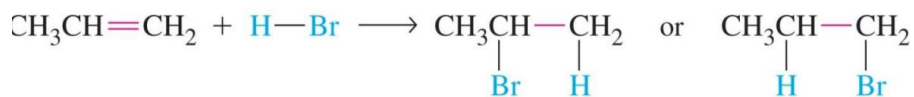
- Bromination adds one Br to each alkene carbon C.
- The result is a dibromoalkane.



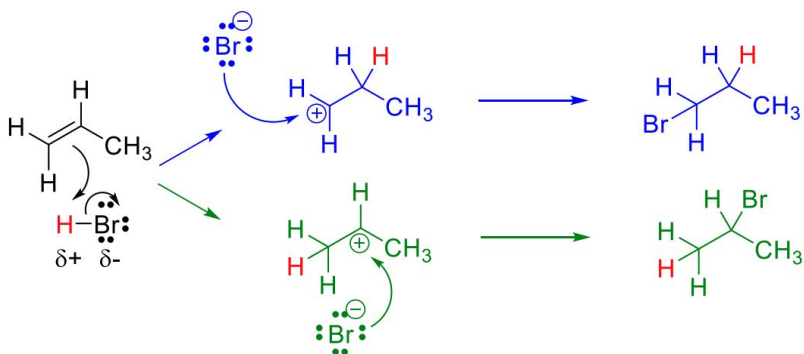
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Hydrohalogenation of Alkenes

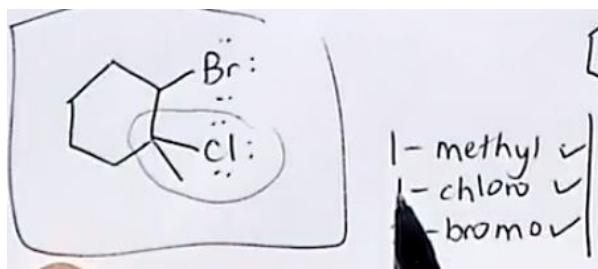
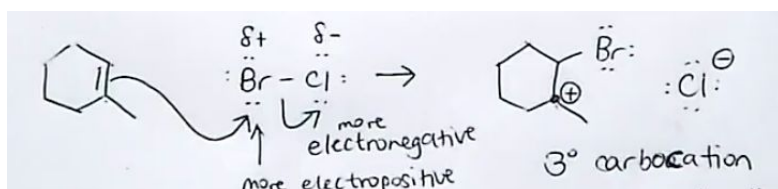
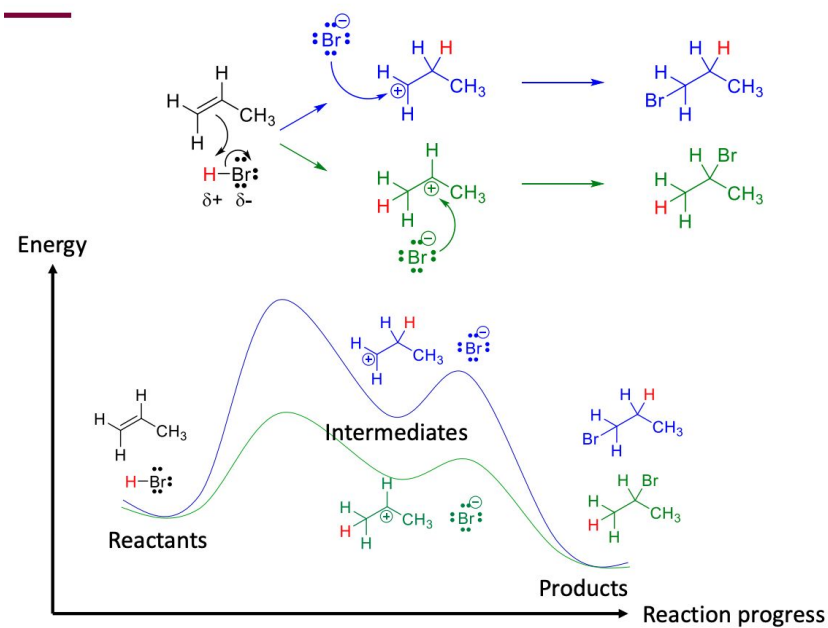
- When HX adds to the double bond of an alkene:
- The H atom adds to the carbon atom with the smallest number of alkyl groups.
- The X atom adds to the carbon atom with the largest number of alkyl groups.
- This is called "Markovnikov's Rule".
- Lowest path of resistance



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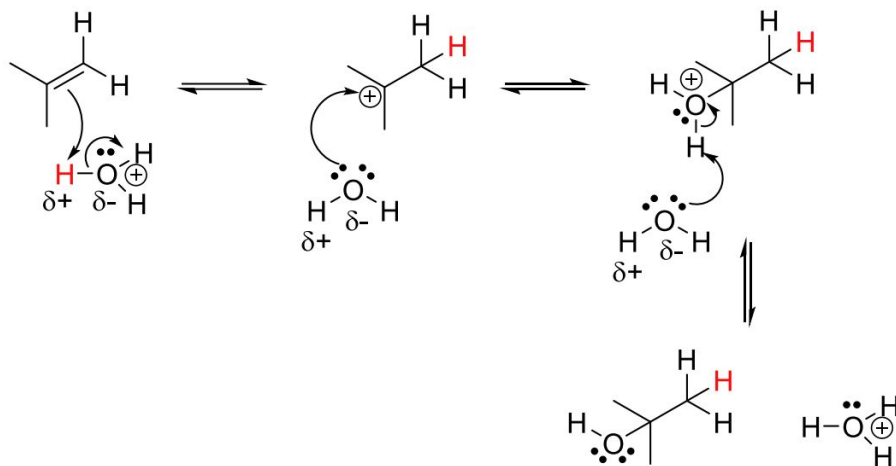
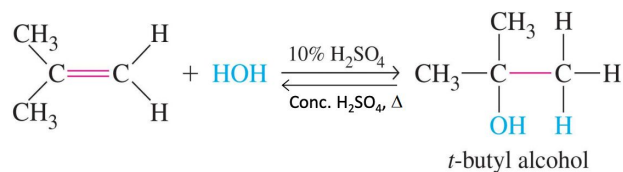


Δ-5 Hydrohalogenation of Alkenes



Hydration of Alkenes

- Addition (the forward reaction) is favoured in dilute acid H₂SO₄ (10%) is used as its conjugate base (HSO₄⁻) won't add to the cation. HCl would lead to mixture of hydration and addition products.
- Alkene to alcohol DILUTE acid
- Still follows markovnikovs rule
- ELIMINATION (the reverse reaction) is favoured in concentrated H₂SO₄ , with heat.

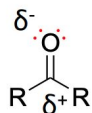


Alkenes & alkynes:

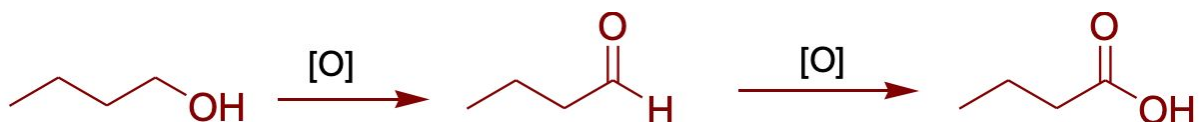
- Alkenes (or alkynes) have one σ -bond and one (or two) π bond(s) between two carbon atoms.
- The π -bond acts as a nucleophile.
- Alkenes undergo addition reactions: a molecule (H₂, X₂, HX, H₂O, another alkene) adds across a multiple bond.
- The mechanism of addition involves a carbocation intermediate: most stable = 3^o, least stable = methyl.
- Markovnikov's Rule: the carbon that is already bonded to more hydrogen atoms gets the hydrogen (or less electronegative atom).

The Carbonyl Group: Ketones and Aldehydes

AX_3 trigonal planar geometry
 sp^2 -hybridized at C



Primary alcohol \rightarrow aldehyde \rightarrow carboxylic acid



Secondary alcohol \rightarrow ketone



Tertiary alcohol \rightarrow no reaction a C-C bond would have to break in order for oxidation to occur

- Only at 1 for carboxylic acid

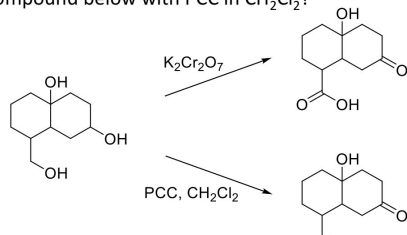
Oxidation of Alcohols

- Recall: oxidation \Rightarrow gain an oxygen OR lose two hydrogens.
- Oxidizing agents
- commonly metals in high oxidation states (transfer of 2 to 4 electrons) e.g., MnO_4^- , $Cr_2O_7^{2-}$ ($KMnO_4$, $K_2Cr_2O_7$)
- Usually done in acid or base to facilitate electron transfer
- Pyridinium chlorochromate (PCC in CH_2Cl_2)
 - Specific for oxidizing 1 $^\circ$ alcohols to aldehydes
 - Will also oxidize secondary alcohol to ketone (does one oxidation step only)

Worked Example

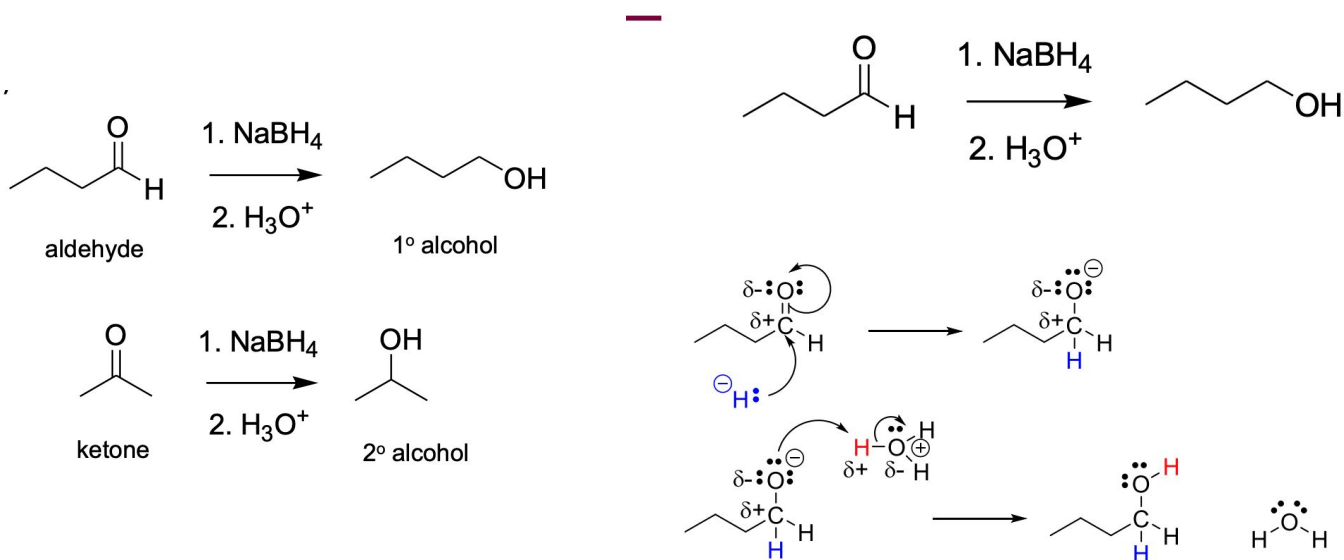
What is the expected product upon oxidation of the organic compound below with $K_2Cr_2O_7$?

What is the expected product upon oxidation of the organic compound below with PCC in CH_2Cl_2 ?



Reduction of aldehydes and ketones:

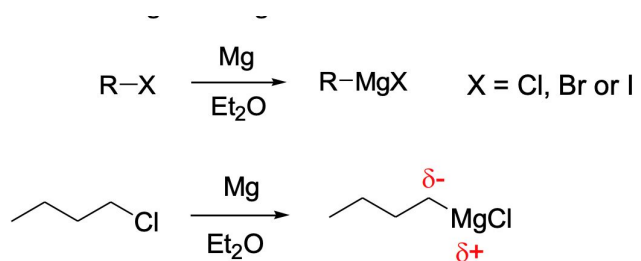
- Overall reaction: addition of "H₂" (note) to C=O.
- Step 1: reaction with hydride (H⁻) at C(δ⁺).
- Step 2: reaction with proton (H⁺) at O(δ⁻).
- Note: "H₂" = H⁻ & H⁺
- NaBH₄ is a source of H⁻ (hydride) and H₃O⁺ is the source of H⁺ (proton). (only for making aldehydes and ketones)



Grignard Reagent

- Counts as an addition reaction

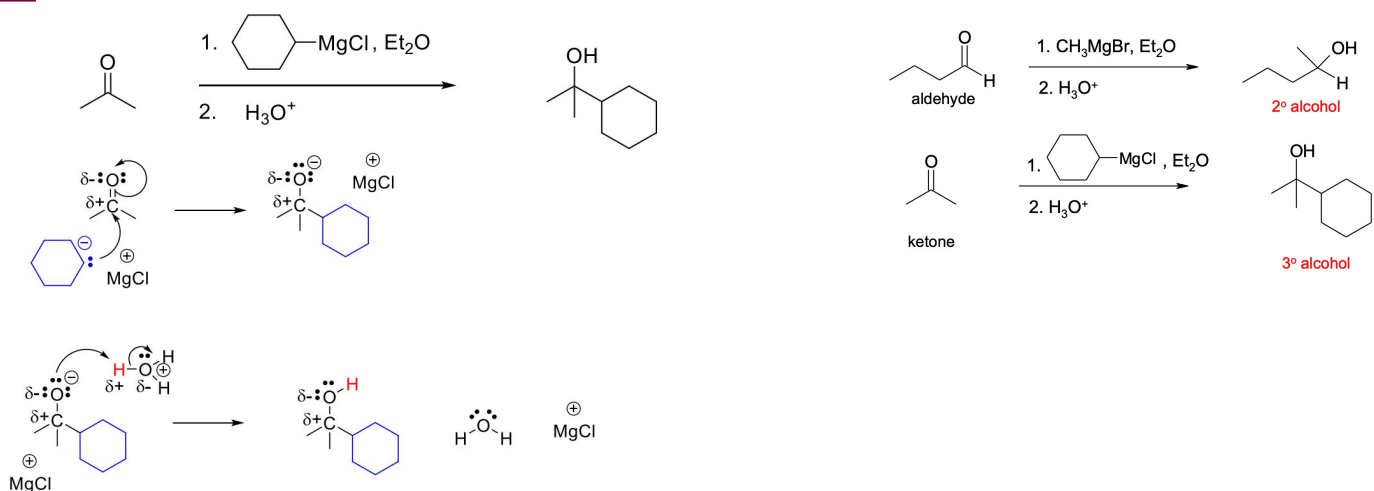
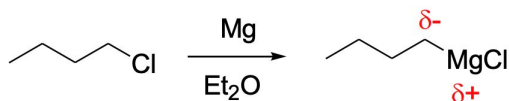
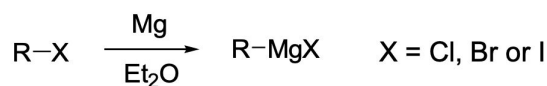
Formation of a Grignard reagent:



Magnesium is very electropositive:

→ Carbon in Grignard reagent gains partial negative charge

→ **This carbon now acts as nucleophile**



- The carbanion of a Grignard reagent acts as a Lewis base (can be viewed as carbon with a lone pair of electrons and a formal negative charge).
- The carbonyl carbon atom is electron poor and acts as a Lewis acid.
- The σ bond formation between Grignard & carbonyl carbon causes the π bond between carbon and oxygen to break; the π electrons end up as a lone pair, and negative charge, on O.
- Addition of acid produces a neutral functional group (alcohol, or carboxylic acid if you started from CO_2).

Aldehydes & Ketones – Key Concepts

- Oxidation of primary or secondary alcohols yields aldehydes or ketones, respectively.
- Oxidation of a tertiary alcohol yields no reaction.
- Oxidation of a primary alcohol with KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ yields a carboxylic acid; oxidation of a primary alcohol with **PCC yields an aldehyde**.
- **Oxidation of primary or secondary alcohols yields aldehydes or ketones, respectively.**

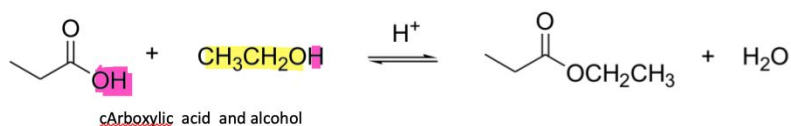
- **Reduction of aldehydes or ketones yields primary or secondary alcohols, respectively.**
- The mechanism of C=O reduction involves H⁻ and H⁺ rather than H₂ for alkenes.
- **Reaction of aldehydes or ketones with Grignard reagents yields secondary or tertiary alcohols.**
- The mechanism of Grignard + C=O is similar to reduction.

Carboxylic Acids & Derivatives

- Carboxylic acid derivatives involve a carbonyl group, with an electronegative atom or group bonded to the central C.

Preparation of Esters

- Fischer Esterification
- Acid catalyst, heat
- Condensation reaction
- Keep anhydrous (remove water)

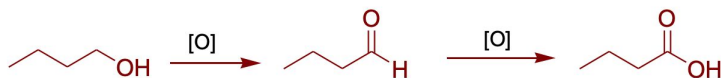


Hydrolysis of Esters

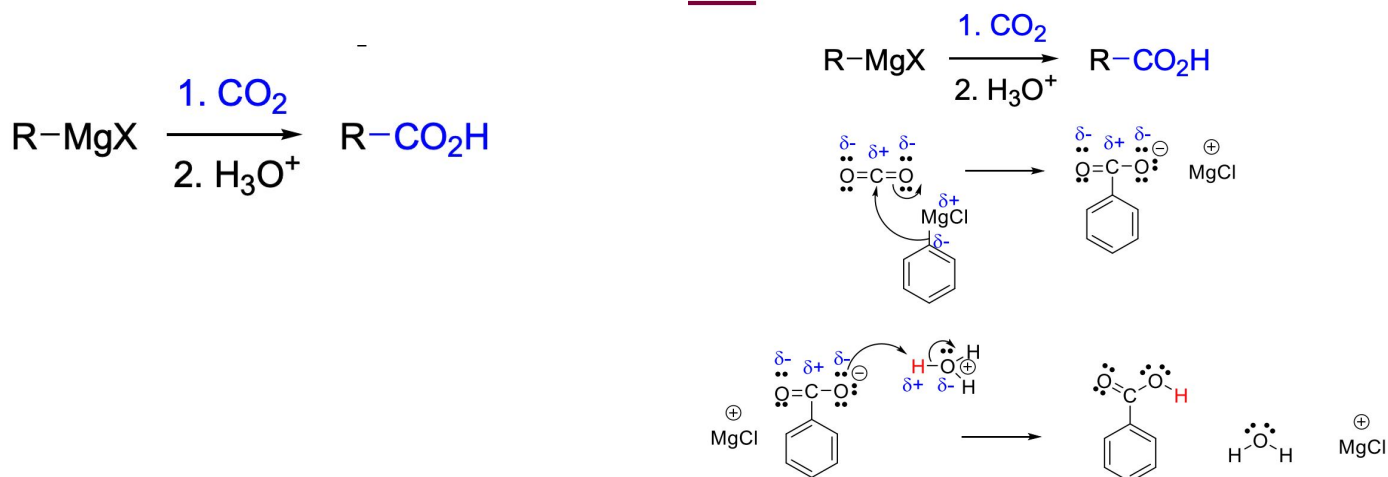
- Produce more product by removing water, le chatelier principle
- Reverse of previous reaction
- Also requires acid catalyst
- Use excess water, heat

Synthesis of carboxylic acids

- Oxidation of 1° alcohol or aldehyde



- Addition of Grignard to CO₂, with acid work-up



Carboxylic Acids – Key Concepts

- Carboxylic acids and derivatives have a carbonyl group with an electronegative substituent on C.
 - Carboxylic acids react with alcohols to form esters + water.
 - The reaction is reversible and requires an acid catalyst & heat in both directions.
 - Grignard reagents react with CO₂ & acid work-up to give carboxylic acids. The mechanism is similar to the reaction of a Grignard reagent with an aldehyde or ketone.
-
- In alkenes the unhybridized p-orbitals form a π -bond and force the substituents attached to the alkene C atoms to become eclipsed.
 - sp²-hybridized orbitals are lower in energy than sp³-hybridized orbitals.
 - For a carbon atom the angle between sp²-hybrid orbitals is greater than the angle between sp³-hybrid orbitals.
 - For a given atom, sp-hybrid orbitals are separated by a 180° angle.

A 0.125 M aqueous solution of a weak acid (HA), volume = 25.0 mL, was titrated with a 0.100 M NaOH solution. HA and NaOH react in a 1:1 mole ratio. The pH at the equivalence point was 11.13. What is the pK_a of HA?

- Find K_b of A-
- Then convert

In unimolecular decomposition reactions, molecules start breaking apart when they gain energy equivalent to the activation energy of decomposition.

C) Activation energies influence reaction rates.

D) Activation energies can be measured by comparing reaction rates at different temperatures.

E) According to collision theory, the activation energy corresponds to the minimum amount of kinetic energy molecules need to react during collisions.

Decomposition of compound A follows second-order kinetics. The following values for [A] were observed during its decomposition. 2018

The transition state of the rate-limiting step must NOT always be the highest energy point in the reaction progress diagram

reaction intermediate is both formed and consumed during the reaction.

C) A transition state species has partially formed and/or partially broken bonds.

D) In reaction intermediates, bonds are in the process of being formed or broken.

E) Transition state species have higher potential energies than adjacent reaction intermediates.

2017

the reaction $A + B \rightarrow C$, the absorbance (Abs) of C was monitored as a function of time. The starting concentrations of both A and B were 0.15 M. For $[C] = 0.10$ M, Abs = 1.42. What was the reaction rate?

- $0.10\text{M}/1.42 \text{ abs} = x\text{M}/0.228\text{abs}$ (this is @ 120s)
- Solve for x, u get 0.016M
- Do the same for 90s, u get 0.012M
- Then u just do $\Delta[\text{conc}]/\Delta t$ to find the rate
- Rate = $(0.016-0.012)/(120-90)$
- This gives $1.333333333 \times 10^{-4}$, or just 1.3×10^{-4} , which is A
- This works bc this is zero order, so no fancy natural log needed
 - U can find this out by finding the slope of absorbance, which is k, and you'll see that u dont need to do $\ln[A]$ or $1/[A]$, just standard $[A]$

2019

- Gives K_a

The initial pH of the weak acid solution, provided its concentration is known

(iii) the pH at the equivalence point, provided the concentration of the conjugate base is known

(iv) the pH at the half-equivalence point (2015)

hybridization

Carbon is not the only atom that undergoes hybridization. B) The ideal angle between sp^3 -hybridized orbitals is 109.5° . C) Mixing three atomic orbitals always results in the formation of three hybrid orbitals. D) In carbon, electrons in an sp^2 -hybridized orbital are higher in energy than those in an sp -hybridized orbital (2015)

The transition state has the same potential energy forward and backwards

A 0.125 M aqueous solution of a weak acid (HA), volume = 25.0 mL, was titrated with a 0.100 M NaOH solution. HA and NaOH react in a 1:1 mole ratio. The pH at the equivalence point was 11.13. What is the pKa of HA?

② ANSWER A

$$\text{mols of HA} = (0.125\text{M})(0.025\text{L}) = 3.125 \times 10^{-3} \text{ mols}$$

$$\text{So mols of A}^- = 3.125 \times 10^{-3} \text{ at equiv pt.}$$

$$\text{mols of OH}^- = 3.125 \times 10^{-3} \text{ mols} = (0.100\text{M})(V)$$

$$V = 31.25 \text{ mL}$$

$$\text{So Total volume} = 56.25 \text{ mL at equiv pt.}$$

$$= 0.05625 \text{ L}$$

$$[\text{A}^-] = \frac{3.125 \times 10^{-3}}{0.05625 \text{ L}} = 0.0556 \text{ M}$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-(14-11.13)} = 10^{-2.87} = 1.35 \times 10^{-3} \text{ M}$$

$$\frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = K_b = \frac{[\text{OH}^-]^2}{[\text{A}^-] - [\text{OH}^-]} = \frac{(1.35 \times 10^{-3})^2}{(0.0556 - 1.35 \times 10^{-3})} = 3.36 \times 10^{-5} \text{ * } K_b \text{ for A}^-$$

$$\text{So } K_a \text{ of HA is } \frac{10^{-14}}{K_b} = 2.98 \times 10^{-10}$$

$$\text{pKa} = -\log K_a = 9.52$$

- Since its a 1 to 1 ratio, find total volume
- Use mol of HA as A-
- Find conc of A-
- Find Oh- Conc by using EP PH
- Solve for Kb---- pka

In order to prepare a buffer of pH 4.60, you start with 500.0 mL of 0.100 M benzoic acid (C6H5COOH) and add NaOH(s). What mass (in g) of NaOH is required? Assume there is no volume change upon NaOH(s) addition.

$$\text{④ } K_a = 6.3 \times 10^{-5}$$

$$\text{pKa} = -\log K_a = 4.20$$

$$\text{pH} = \text{pKa} + \log \frac{\text{A}^-}{\text{HA}}$$

$$4.60 = 4.20 + \log \frac{\text{A}^-}{\text{HA}}$$

$$\log \frac{\text{A}^-}{\text{HA}} = 0.4 \rightarrow \frac{\text{A}^-}{\text{HA}} = 10^{0.4} = 2.51$$

ANSWER D

You know that:

$$\text{A}^- + \text{HA} = (0.5\text{L})(0.1\text{M}) = 0.05 \text{ mols total}$$

$$\text{A}^- + \text{HA} = 0.05$$

$$\text{A}^- = 0.05 - \text{HA}$$

$$\frac{\text{A}^-}{\text{HA}} = \frac{0.05 - \text{HA}}{\text{HA}} = 2.51$$

$$0.05 - \text{HA} = 2.51 \text{ HA}$$

$$0.05 = 3.51 \text{ HA}$$

$$0.0142 \text{ mols} = \text{HA in buffer}$$

$$\text{Therefore } 0.05 - 0.0142 = 0.0358 \text{ mols OH}^- \text{ added}$$

$$0.0358 \text{ mols} \times \frac{40\text{g NaOH}}{\text{mol}} = 1.43\text{g}$$

The oxidation of ethanol to acetic acid in presence of excess oxygen is found to be pseudo-first order in ethanol. Use the data the table below to estimate the rate constant for this reaction.

$$\text{⑤ } 1^{\text{st}} \text{ order so } \text{rate} = k[\text{EtOH}]$$

$$\text{from data: } \text{rate} = \frac{\Delta[\text{EtOH}]}{\Delta t} = \frac{0.001 \text{ M}}{360 \text{ sec}} = 2.78 \times 10^{-6} \text{ M/s}$$

$$\text{rate} = k[\text{EtOH}]$$

$$2.78 \times 10^{-6} \frac{\text{M}}{\text{s}} = k[0.02] \text{ * use [EtOH]}$$

$$k = 1.39 \times 10^{-4} \text{ s}^{-1} \quad \text{ANSWER E}$$

in

A student adds 3.34 mL of HCl to 225 mL of a neutral protein solution, causing it to precipitate. The student then separately titrates 100.0 mL of the same HCl solution to its equivalence point with 11.3 mL of 0.01023 M NaOH. What is the isoelectric point of the protein? (Assume that the protein does not affect the pH.)

2) Isoelectric pt is the pH when protein precipitates.
 from NaOH titration: mols OH^- added = $(0.01023\text{M})(0.0113\text{L}) = 1.156 \times 10^{-4}$ mols
 at equiv. point
 Therefore $[\text{HCl}] = \frac{1.156 \times 10^{-4} \text{ mols}}{(0.100 \text{ L sample})} = 1.156 \times 10^{-3} \text{ M}$
 if 3.34 mL of HCl added to protein, $[\text{H}^+] = \frac{(1.156 \times 10^{-3} \text{ M})(0.00334 \text{ L})}{(0.225 \text{ L} + 0.00334 \text{ L})} = 1.69 \times 10^{-6}$
 ANSWER E $\text{pH} = -\log[\text{H}^+] = 4.77$

Calculate the pH of the resulting solution when 100.0 mL of a 0.100 M ammonia (NH_3) solution is titrated to the equivalence point with 0.0500 M HCl(aq).

$$\text{mols } \text{A}^- = (0.100\text{M})(0.100\text{L}) = 0.01 \text{ mols} = \text{mols HA at equiv. pt.}$$

$$\text{mols } \text{H}^+ \text{ needed} = 0.01 \text{ mols} = (0.05\text{M})(V)$$

$$V = 0.200 \text{ L}$$

$$\therefore \text{Total volume} = 0.300 \text{ L at equiv pt.}$$

$$[\text{HA}] = \frac{0.01 \text{ mols}}{0.3 \text{ L}} = 0.033 \text{ M}$$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_a = \frac{x^2}{[\text{HA}]} \quad 5.56 \times 10^{-10} = \frac{x^2}{0.033} \Rightarrow x = 4.30 \times 10^{-6}$$

$$= [\text{H}^+]$$

$$\text{pH} = 5.37$$

ANSWER A

Catalysts lower activation energies, thereby increasing reaction rates.

B) A reaction intermediate will exist at a local minima in a reaction profile diagram.

C) The hydrogenation of cyclohexene in the presence of Pt(s) is an example of heterogeneous catalysis.

D) An exothermic reaction with one elementary step will have a higher activation

energy for the reverse versus forward reaction. (NOT POTENTIAL)

E) There can be more than one transition state during a reaction.

An enzymatic reaction has a rate, v_0 , of $2.2 \times 10^{-4} \text{ M s}^{-1}$ when $[S] = 10^{-2} \text{ M}$ and $K_M = 10^{-5} \text{ M}$. What would the reaction rate be if $[S]$ were changed to 10^{-5} M ?

$$v = \frac{V_{\max}[S]}{K_M + [S]}$$
$$2.2 \times 10^{-4} \frac{\text{M}}{\text{s}} = \frac{V_{\max}(10^{-2})}{(10^{-5}) + (10^{-2})} \quad V_{\max} = 2.202 \times 10^{-4}$$
$$v_0 \text{ rate} = \frac{(2.202 \times 10^{-4})(10^{-5})}{(10^{-5}) + (10^{-5})} = 1.01 \times 10^{-4} \text{ M/s}$$

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ANSWER D

An isolated orbital is pictured below. The lone pair electrons of the nitrogen atom in pyridine occupy this type of orbital, but the lone pairs in water do not. This type of orbital occurs somewhere in cyclohexene. What type of orbital is it? sp^2

Bond strength is not a linear increase

- Increasing steric crowding around the electrophilic carbon will tend to favour an SN_1 over SN_2 mechanism.
- B) SN_2 reactions become nine times faster when $[\text{nucleophile}]$ and $[\text{electrophile}]$ both increase by a factor of three.
- C) SN_2 reactions consist one step involving two molecules.
- D) SN_2 reactions proceed with inversion of configuration at the electrophilic carbon atom.
- E) SN_2 reactions may involve charged or neutral nucleophiles.

A researcher wishes to continuously monitor the brain function of a patient for several hours using a PET scan with radiolabelled 18F-fluorodeoxyglucose (18FDG). After an initial injection of 2.0 pg per kg of body weight, 18FDG is injected continuously to maintain a steady state concentration of 2.0 pg/kg. Assume a 50 kg patient, and that 18FDG is lost only by radioactive decay. At what rate (in pg/h) must 18FDG be injected?

Data: $t_{1/2}$ (

18FDG) = 110 min

pg = picogram = 10^{-12} g

Must be injected at the same rate it is consumed

$$t_{1/2} = \frac{0.693}{k} = 1.83 \text{ hrs.}$$

$$k = 0.379 \text{ hr}^{-1}$$

$$2.0 \frac{\text{pg}}{\text{kg}} \times 50 \text{ kg} = 100 \text{ pg}$$

ANSWER C

$$\begin{aligned} \text{rate} &= k [18\text{FDG}] \\ &= (0.379 \text{ hr}^{-1})(100 \text{ pg}) \\ &= 37.9 \frac{\text{pg}}{\text{hr}} \end{aligned}$$