(17) **Today**

6.1 How Enzymes Work

6.2 Kinetics

**Next Class** (18)

6.2 Kinetics

6.3 Enzyme Kinetics

(19) **Second Class from Today**

6.3 Enzyme Kinetics

**Third Class from Today** (20)

Chap 7: Carbohydrates

**Monday office hours rescheduled to 1:10 to 2:10 from now on.**

Please rework* on a separate piece of paper test 1 and hand in on Friday March 21

*On a piece of paper separate from your test, for each question that your did not receive full credit provide a more complete answer.

I do not need your test back, please just hand in the reworked answers.

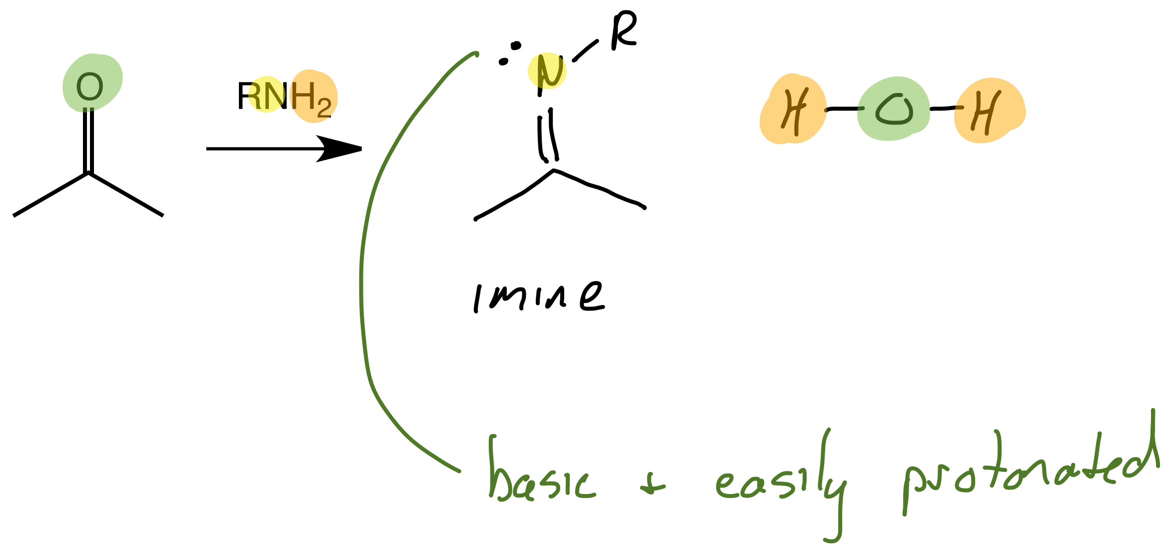
Acid-Base Catalysis - using acid and bases to increase electrophilicity or nucleophilicity
using acids and bases to decrease the gap between reactants and transition states

Metals Cations and Electrostatic Effects - Metals cations can stabilize developing negative charges

$Fe^{2+}$, $Co^{2+}$, $Zn^{2+}$

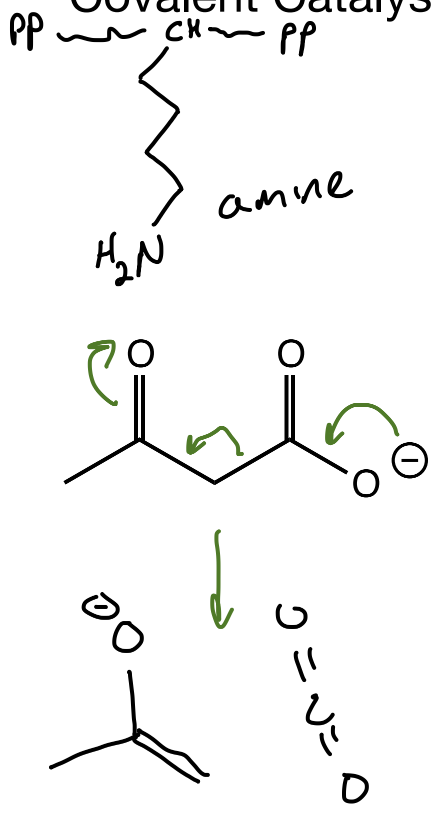
Metals Cations and their ability to to Polarize Bonds - Metal cations can polarize bond and, for example, make water more acidic

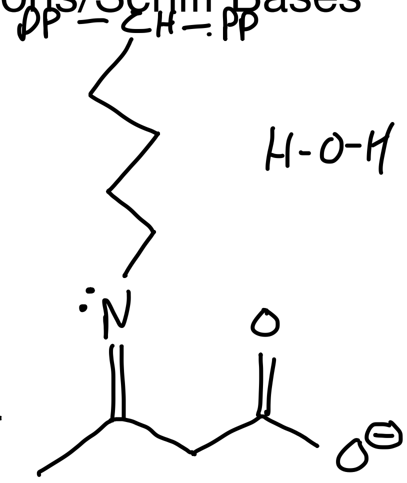
Covalent Catalysis - catalysis can covalently bond to the substrate, speed up one step and then be released

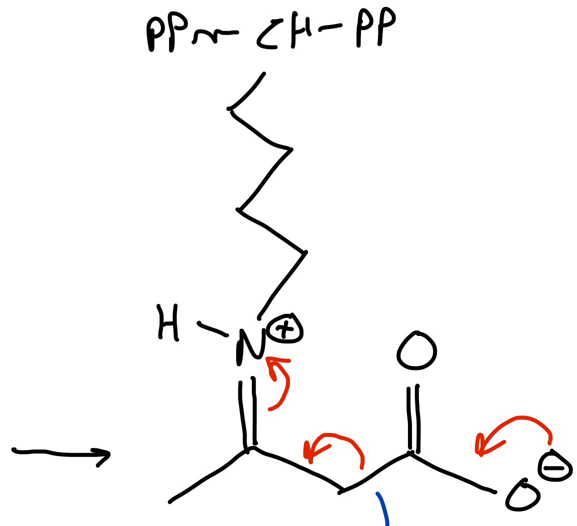

O
RNH2
N
R
imine
H
O
H
basic + easily protonated

# Covalent Catalysis: Iminium ions/Schiff Bases





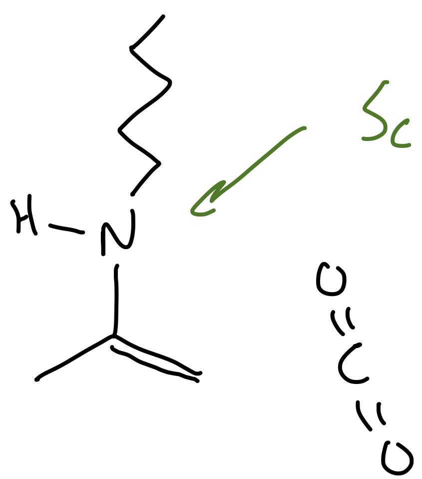




imines are more basic than carboxylates

iminium ion is more attractive to the e⁻'s

it's easier to break this bond because the e⁻'s are attracted to the N⊕



Schiff bases are easily converted back to C=O

Rate Laws, the mathematical expressions that describe the rate of a reaction, have to be determined experimentally.

Rate laws help us understand the mechanism of a reaction

$S_N1$ vs $S_N2$ different rate Law different mechanisms

The are determined by measuring the

Initial Rates, the rate at the beginning of the reaction, $v_0$, is measured at various concentrations to determine the "order" of the reaction

Integrated Rate laws

Concentrations are measured over time, and compared to a rate law that has been integrated

This is a mechanism, a one step mechanism where A is converted P



$$A \xrightarrow{k_1} P$$

rate is the change in … concentration of the reactants or product with respect to time

we like to express rates as a positive number

As time goes by [A] is decreasing, whereas [P] is increasing

$$rate = -\frac{d[A]}{dt} = \frac{d[P]}{dt}$$

is an instantaneous rate

Since the conc. of A is decreasing, $[A]_t - [A]_0$ is $< 0$

so a "–" is added to make the rate positive

0 "naught" for starting time

# Kinetics: First Order Rate Laws



If it's a 1-step mechanism with 1 reactant the rate depends just on the conc. of that reactant

$$A \xrightarrow{k_1} P$$

$$\text{rate} = -\frac{d[A]}{dt} = k_1[A]^1$$

← this 1 is why the reaction is "first order"

this is the rate constant must be determined experimentally

reactions that are first order w/r/t a given reactant have rates that increase proportionally with that reactant

# Kinetics: Integrated First Order Rate Law



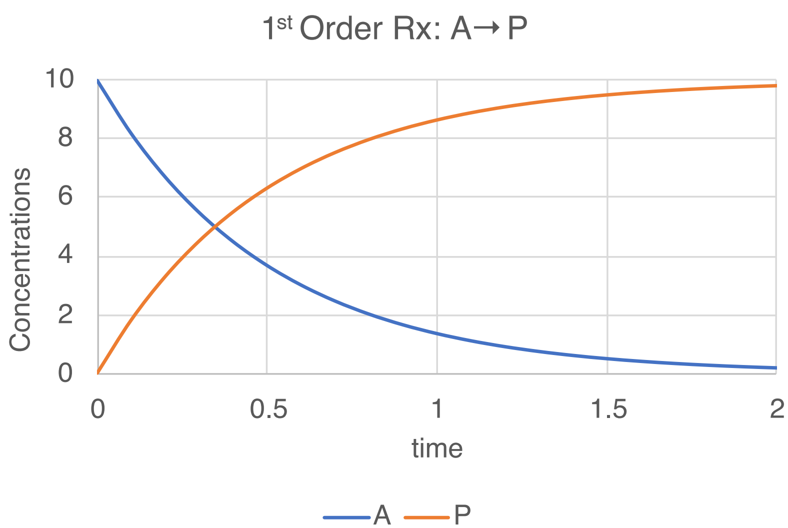
$$\text{rate} = -\frac{d[A]}{dt} = k_1[A]$$

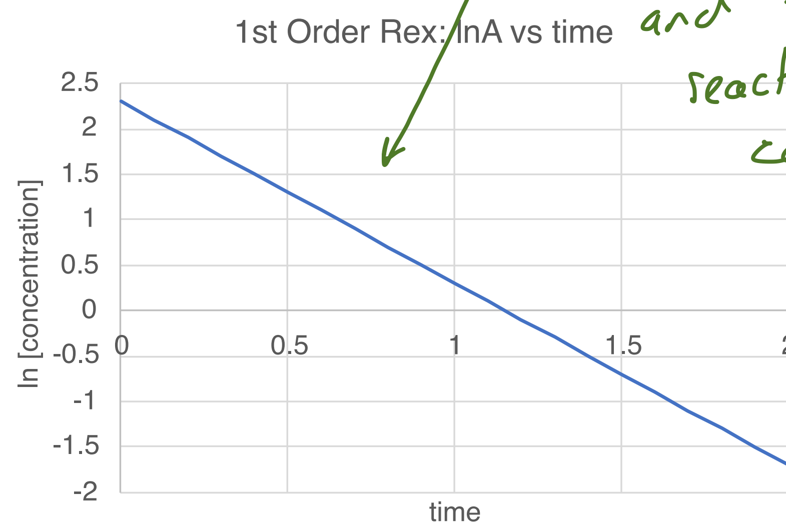
$$\int_0^t \frac{d[A]}{[A]} = -k_1\int_0^t dt$$

$$[A]_t = [A]_0 e^{-kt}$$

$$\ln[A]_t = \ln[A]_0 - kt$$

rxns that are 1st order have linear relationship between time and the ln of reactant concentration

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# Kinetics: Second Order Rate Laws

6.2.1

doubling conc. of A doubles the chance of a successful collision thus doubles the rate... 1st order w/r/t A

$$A + B \xrightarrow{k_1} P$$

$$\text{rate} = k_1[A][B]$$

this reaction is 2nd order overall...

order w/r/t [A] is 1 w/r/t [B] is 1

$1 + 1 = 2$

pseudo first order

Increase conc of B so much that [B] is essentially constant

$$\text{rate} = k_1[A][B]^*$$

$$\text{rate} = k_1[B]^*[A]$$

$$\text{rate} = k_1^*[A]$$

doubling this also doubles this

so the rate quadruples

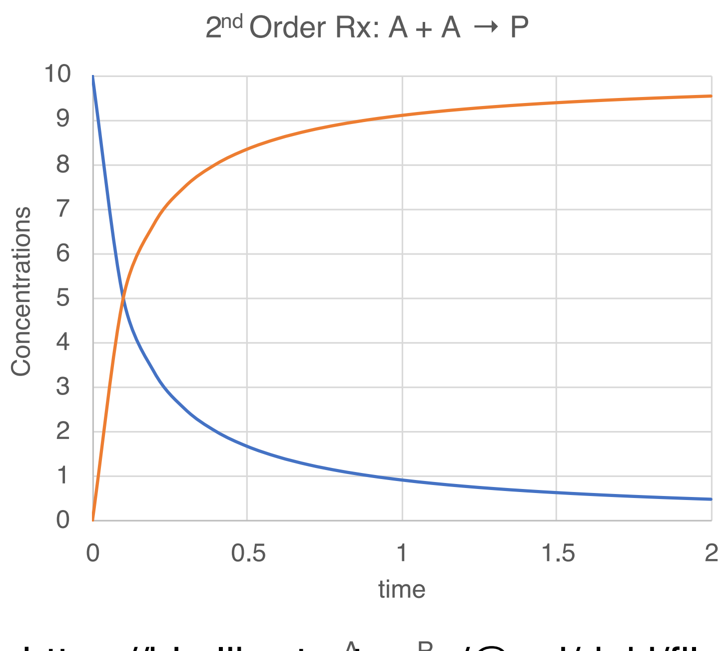
$$A + A \xrightarrow{k_1} P$$

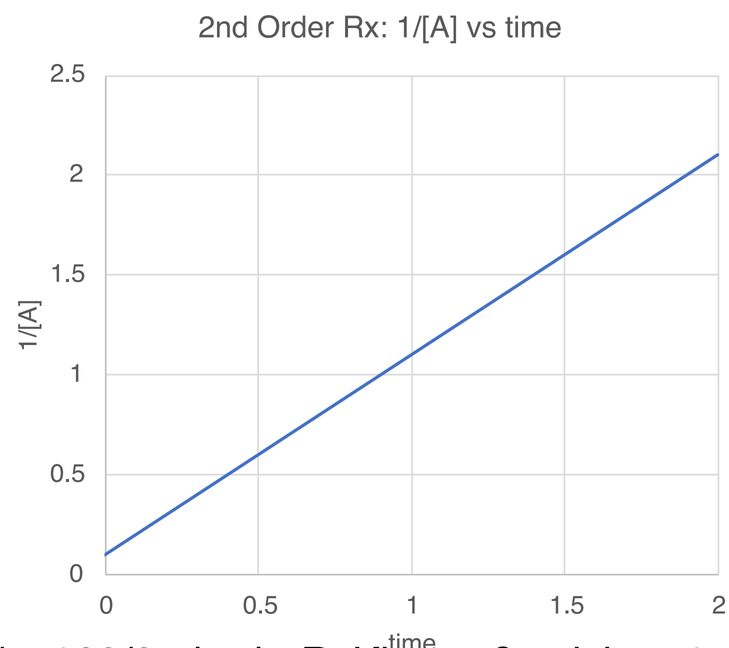
$$-\frac{d[A]}{dt} = k_1[A]^2$$

2nd order w/r/t [A]

integrate

$$\frac{1}{[A]} = \frac{1}{[A]_0} + k_1 t$$

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plot $\frac{1}{[A]}$ as y

t as x

straight line? yes... 2nd order