Kinetics: From Clock Reactions to Challenges in Catalysis

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August 16, 2011

Summer Chemistry Workshop

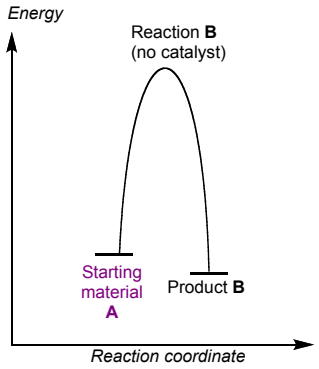
Outline

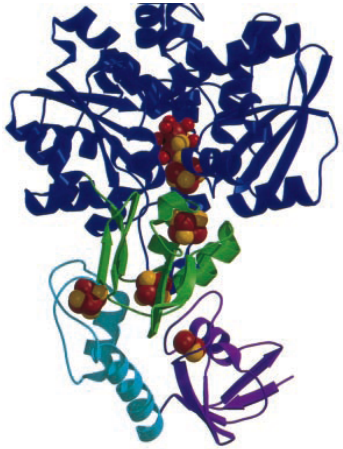
- Kinetics: Applications

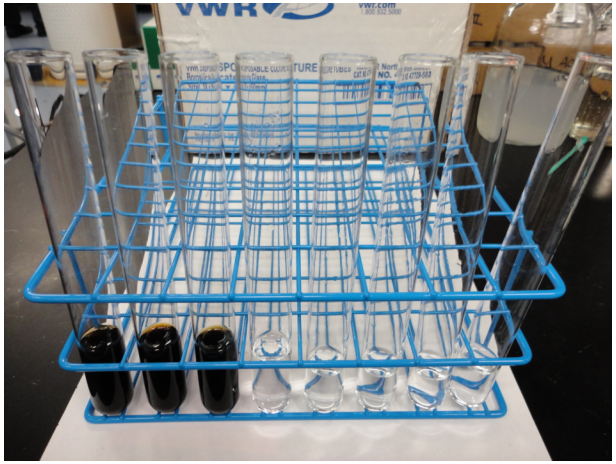
- Kinetics and Catalysis

- Clock reactions

- Oscillating reactions







(Some) Areas of Current Interest

Kinetics -- applications in a wide variety of fields:

Atmospheric chemistry (reactions of various gases or pollutants in the atmosphere):
Depletion of O_3 layer by chlorofluorocarbons (CFC)

Biology: Reaction mechanisms of enzymes / Inhibitors / Selectivity / Regulation / Signaling

Materials: Polymerization / Plastics with different physical properties

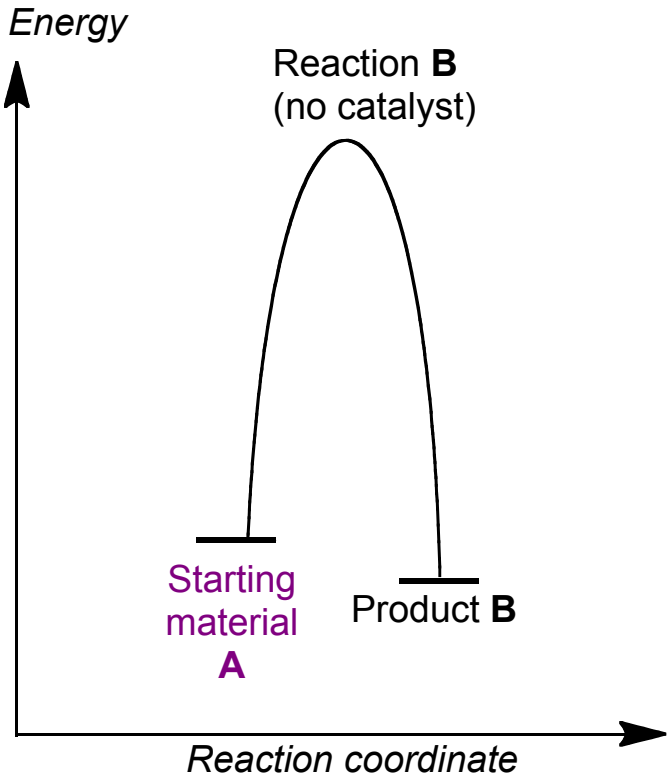
Electron transfer: in proteins that are part of the cellular respiratory chain, corrosion of metallic surfaces

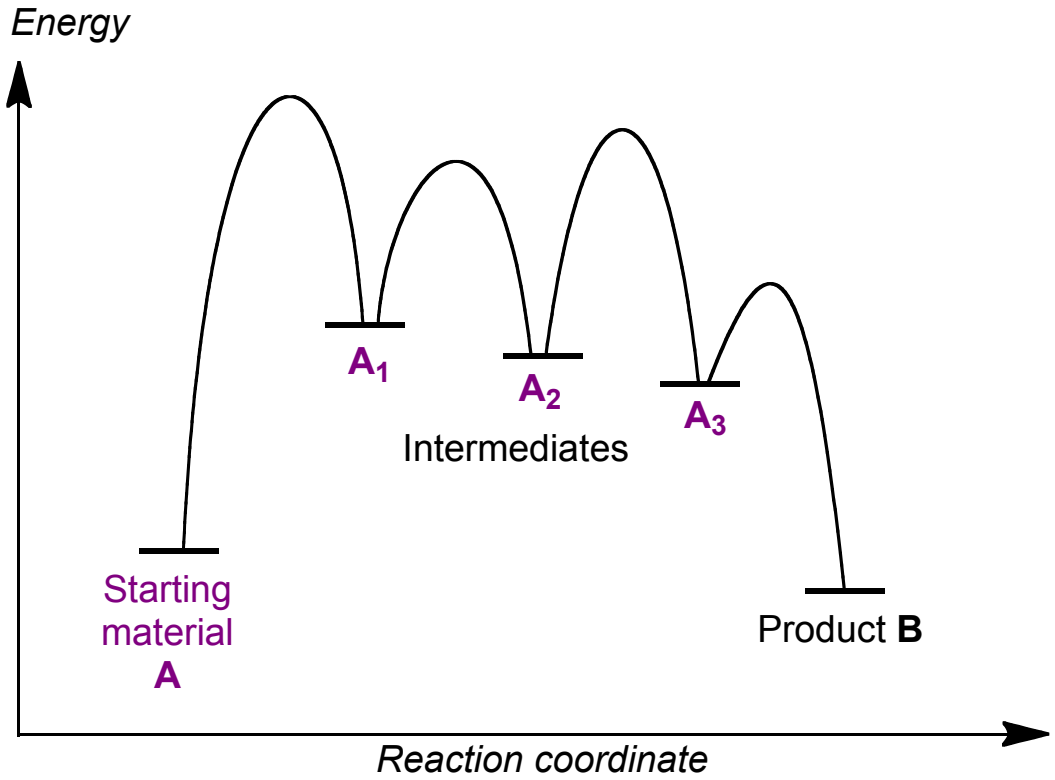
Conversion of fuels: fuels from solar energy, alternative liquid fuels

Nuclear chemistry

Catalysis

Reaction Mechanisms: Levels of Complexity

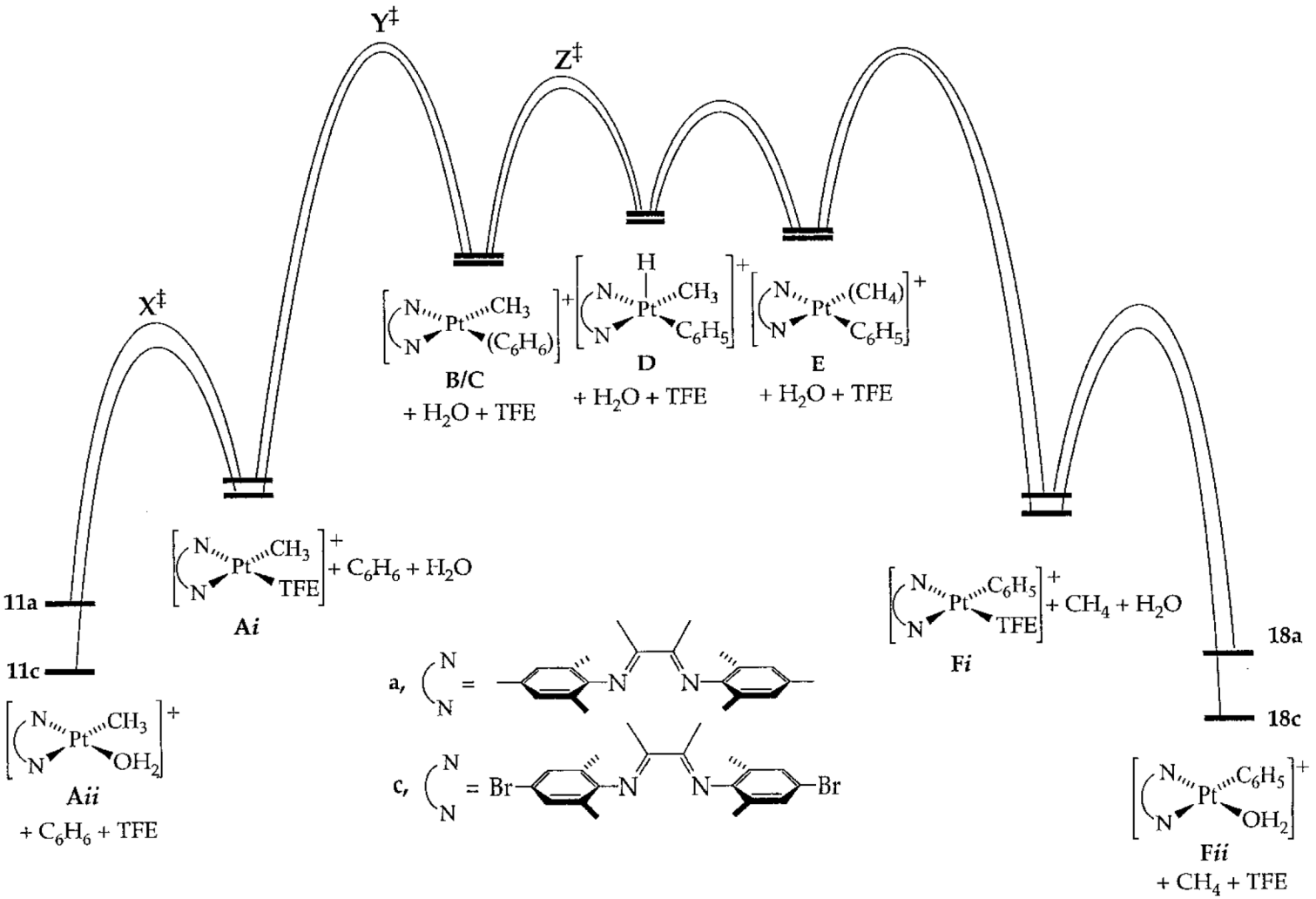




A ⟶ **B**

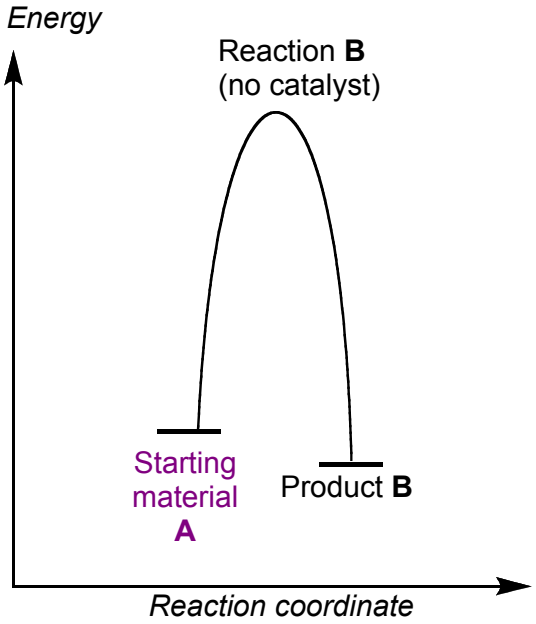
$$\ln k = -\frac{E_a}{RT} + \ln A$$

Reaction Mechanisms: Example from Current Literature



Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378-1399.

Catalysis: Lowering of Activation Barriers



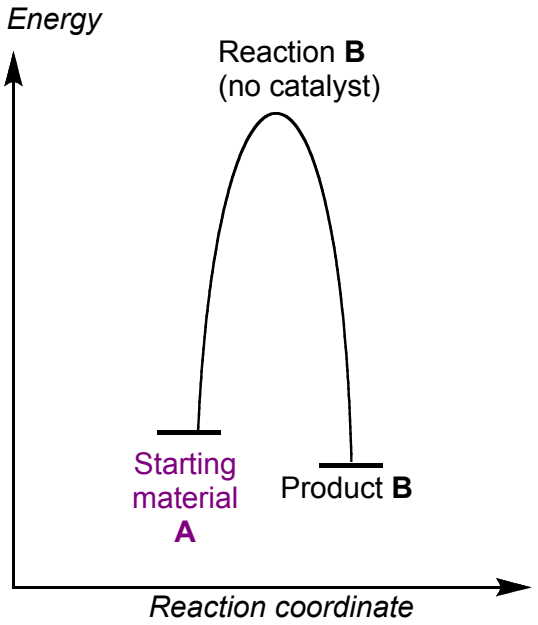
no catalyst

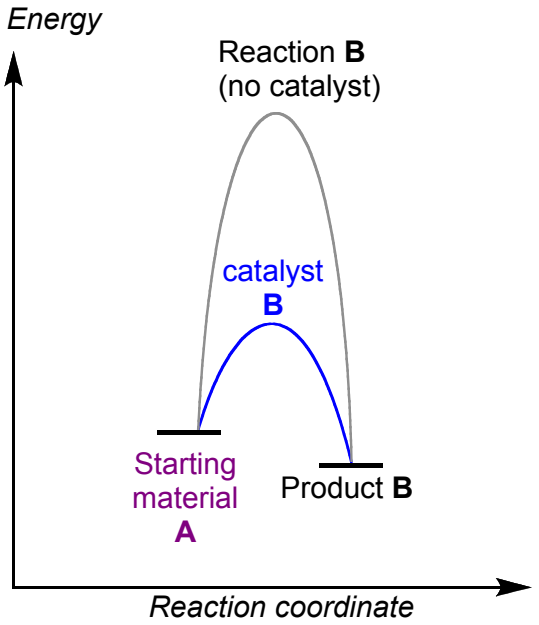
A → B

catalyst
B

A → B

Catalysis: Lowering of Activation Barriers





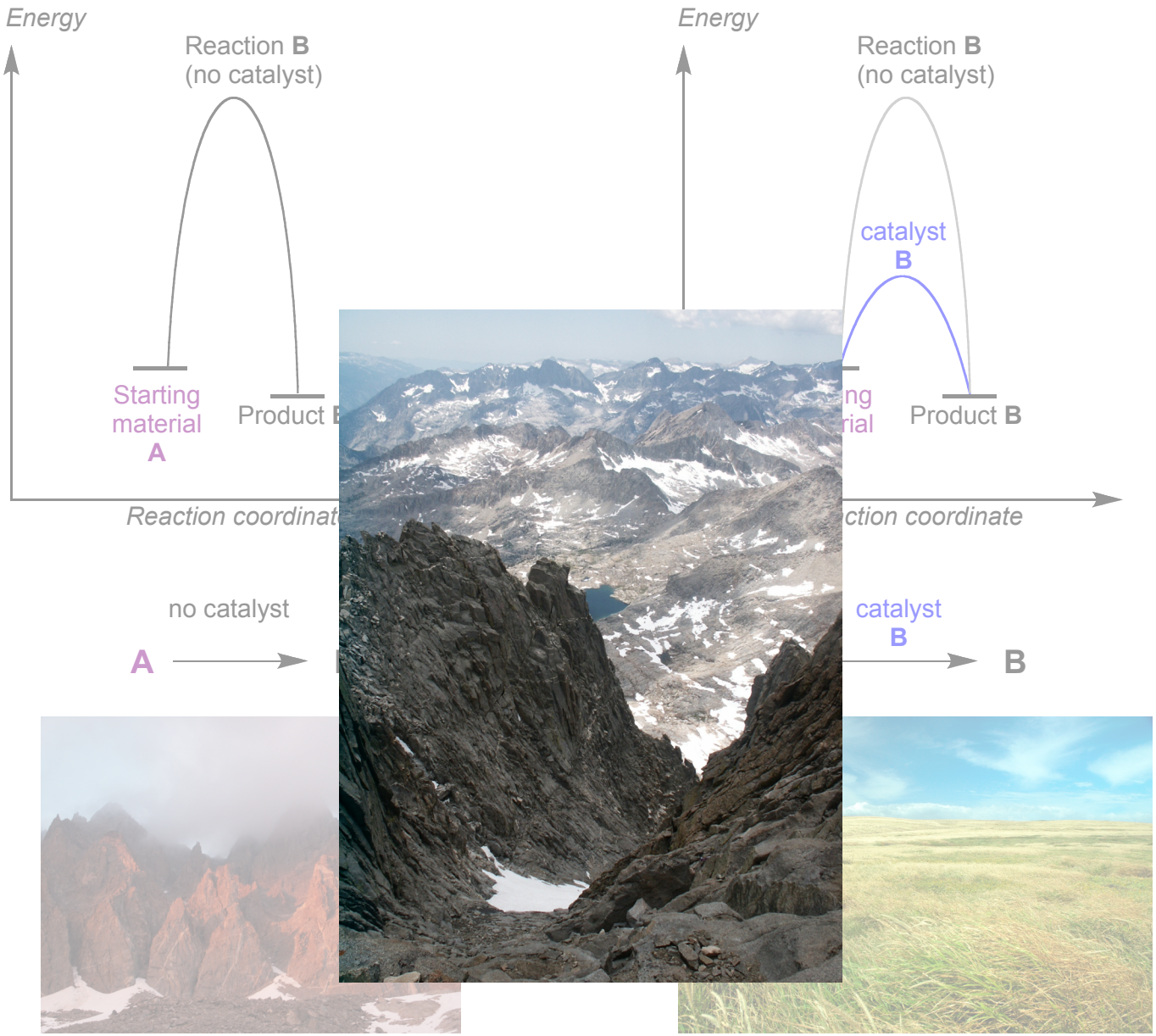
no catalyst

A ⟶ **B**

catalyst **B**

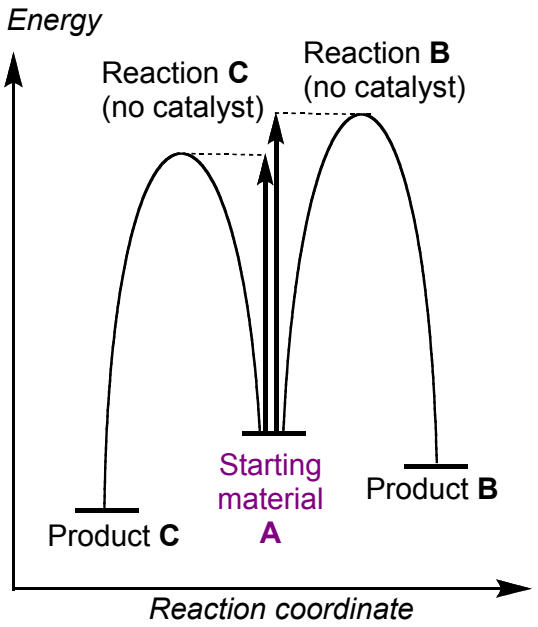
A ⟶ **B**

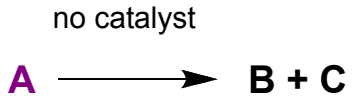
Catalysis: Lowering of Activation Barriers



Possible Chemical Scenarios

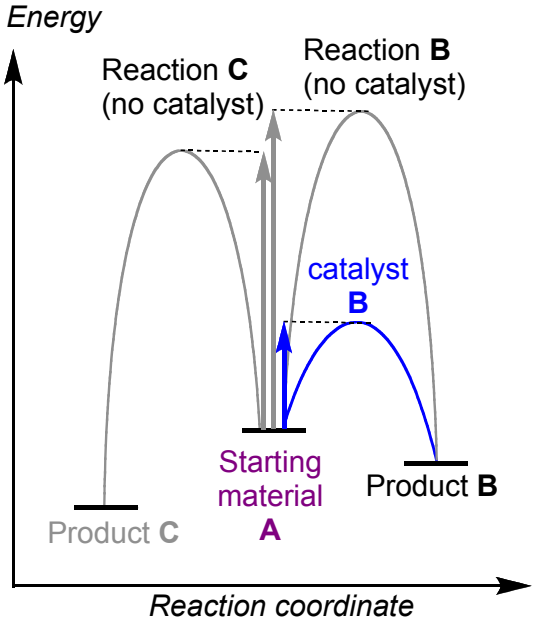
No Catalyst Present

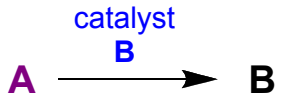




- Separation required
- Energy expensive
- Low yield

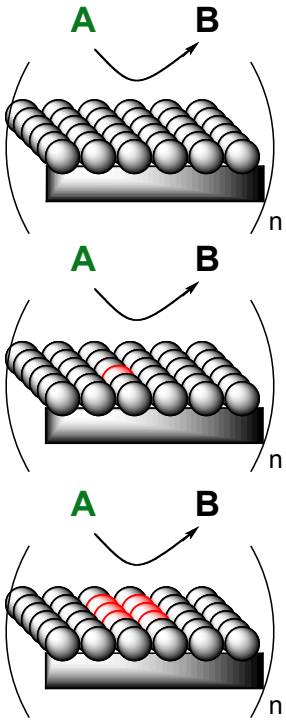
Catalyst B Present





- One product => No separation
- Energy economical
- 100 % yield in desired product
- No detrimental byproducts

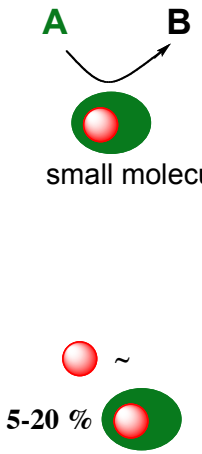
(Some) Types of Catalysts



Surface / Heterogeneous Catalysts:

***Disadvantages**
- **Ill defined**
- **Difficult to study**
- **Difficult to improve rationally**

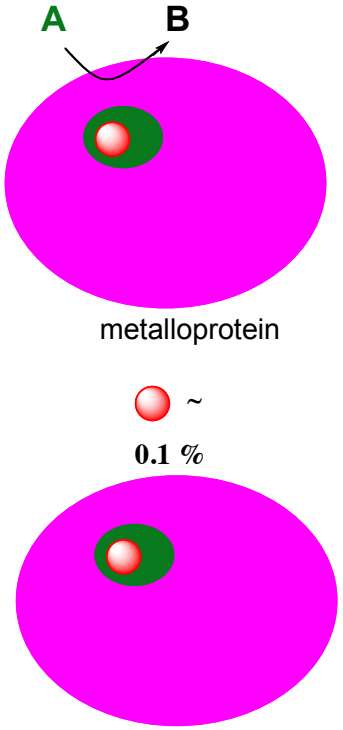
***Advantages**
- **Easy to separate**
- **Robust**
- **Reusable**



Small Molecule / Homogeneous Catalysts:

***Disadvantages**
- **Often unstable**
- **Difficult to separate**
- **Often not reusable**

***Advantages**
- **Often well-defined**
- **Easier to study and rationally improve**



Metalloproteins:

***Disadvantages**
- **Unstable**
- **Often require partners**
- **Often expensive**

***Advantages**
- **Evolved to get the job done (under the right conditions)**

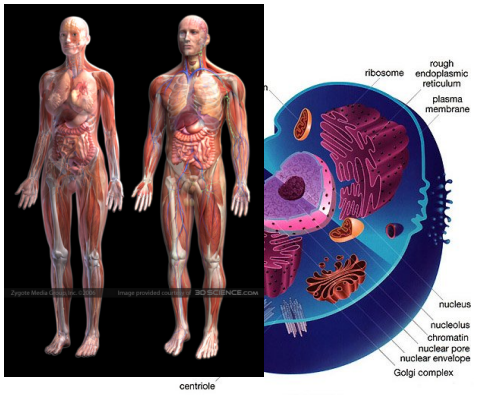
Catalysis -- Applications

Construction Materials

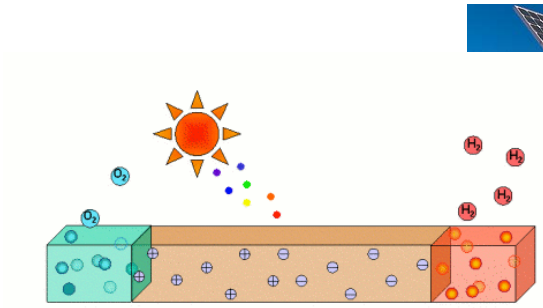
Packaging Materials

Fertilizers

Pharmaceuticals

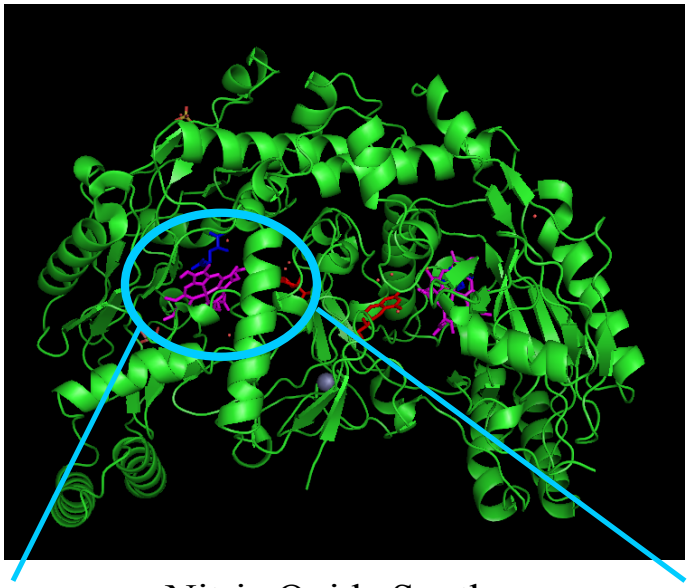


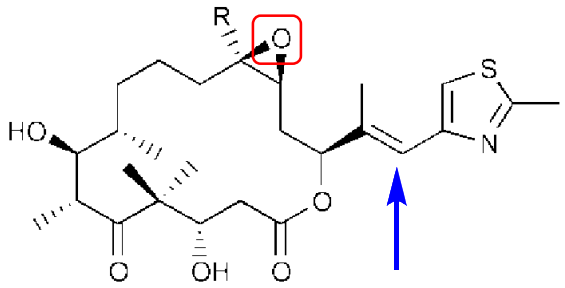
Biochemical Processes



Energy Storage and Conversion

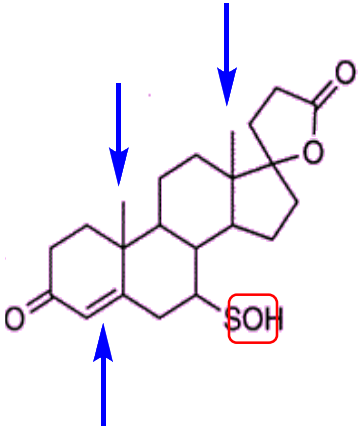
Complex Catalysts in Natural Product Biosynthesis

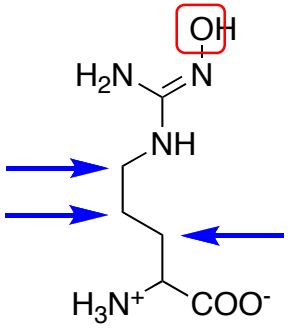


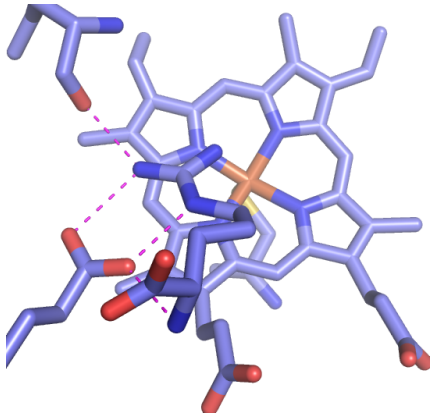


Anticancer drug synthesis by microorganisms

Nitric Oxide Synthase
(Molecular Weight > 100 KDa)







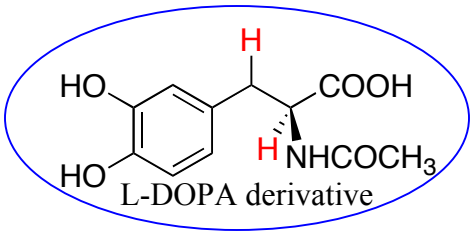
Hormone biosynthesis

Intermediate in NO biosynthesis

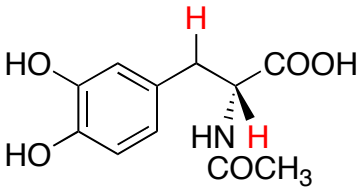
Tainer, J. A. *et al*. *Science* **1998**, *279*, 2121.

L-DOPA

- Essential biological role in the synthesis of certain neurotransmitters
- Treatment for:
  - Parkinson's disease
  - Dopamine responsive distonia
- Nobel Prize awarded for the general applications in synthesis



L-DOPA derivative



L-DOPA: Catalytic Synthesis

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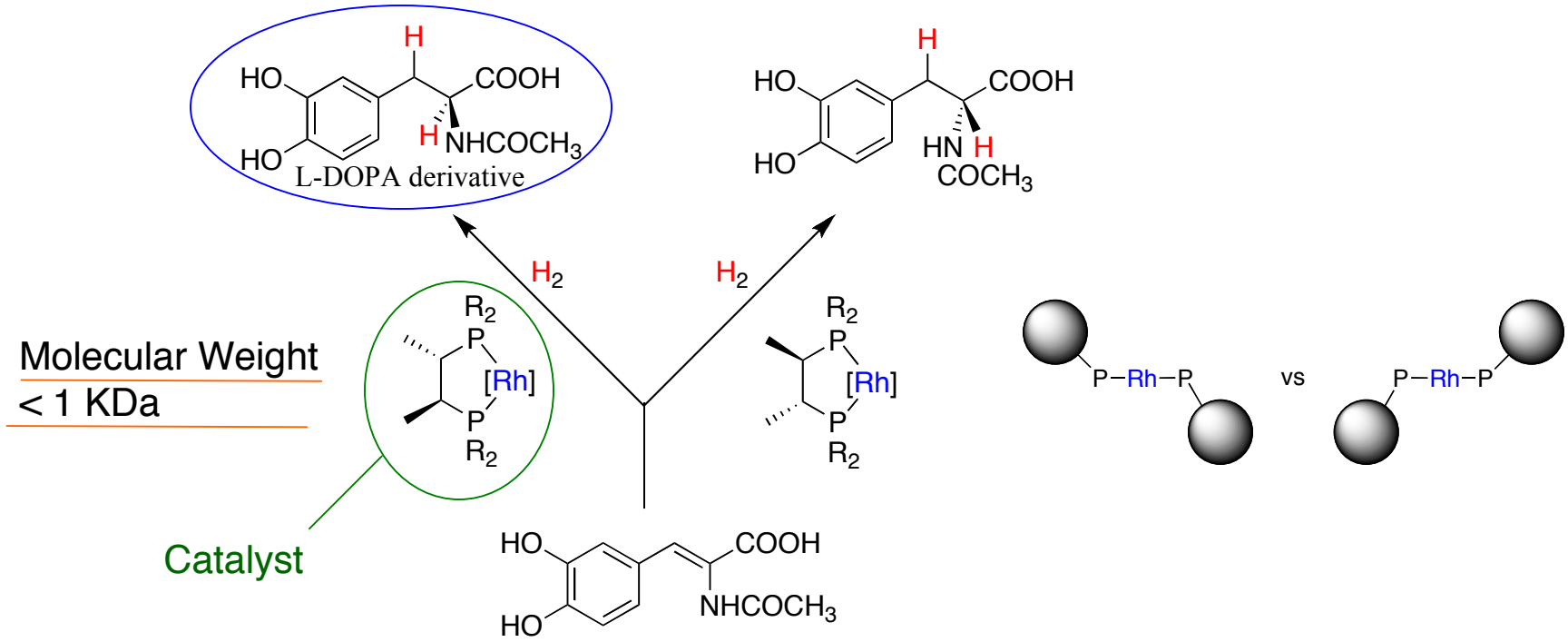

Halpern, J. *Science* **1982**, *217*, 401

L-DOPA: Catalytic Synthesis

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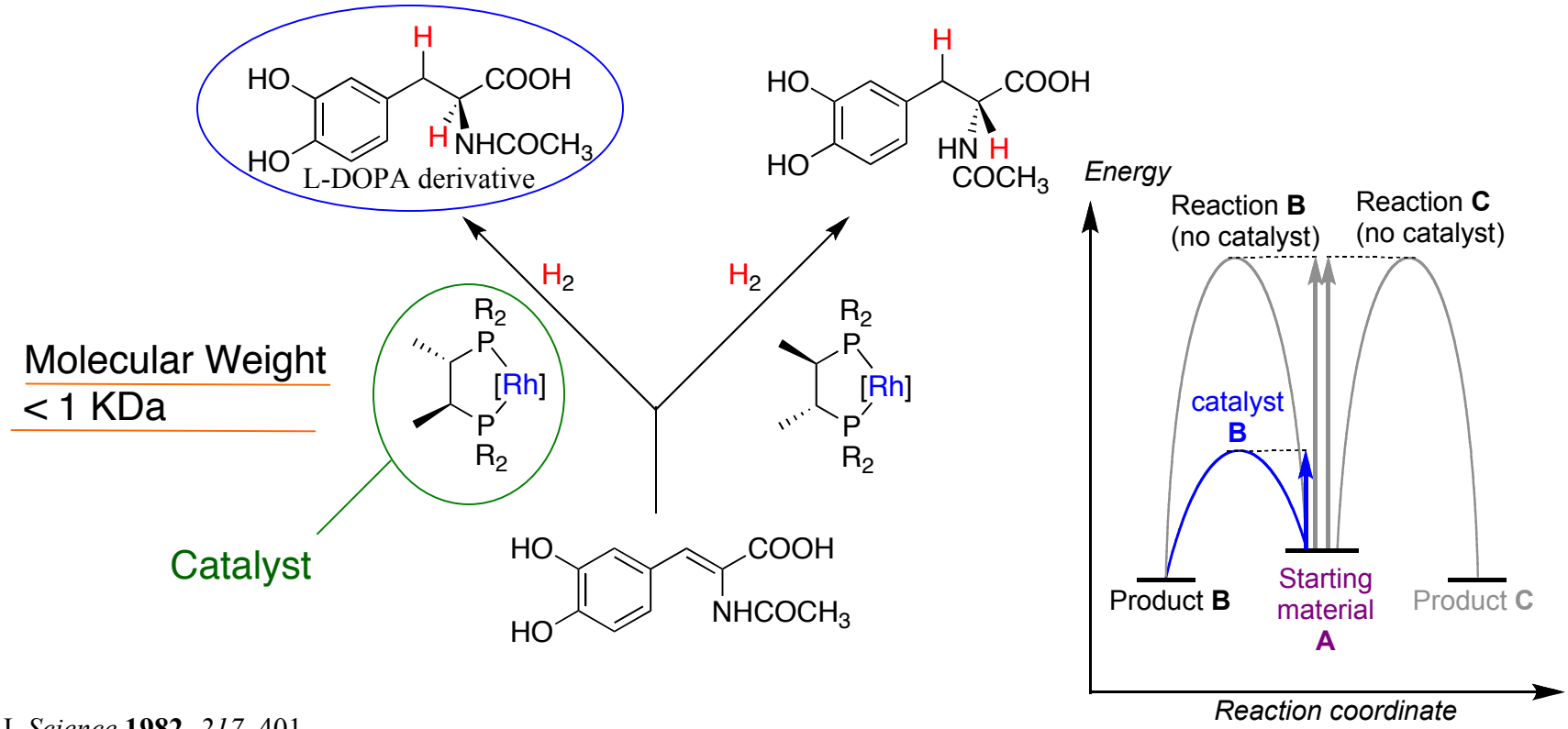
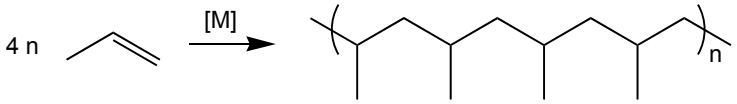
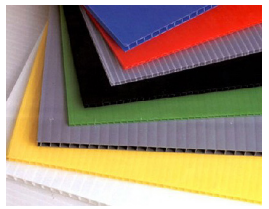


Halpern, J. *Science* **1982**, *217*, 401

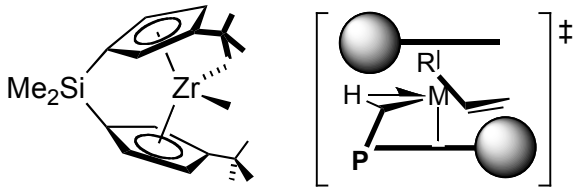
Synthesis of Plastics

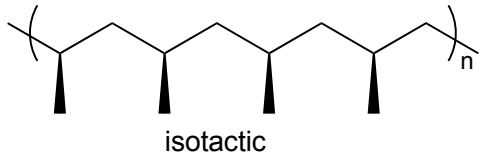


45.1 million tons (2007)

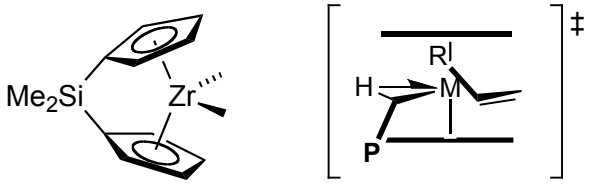


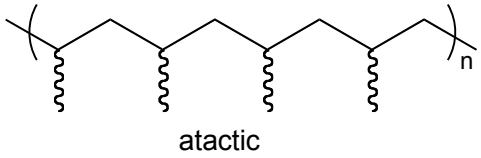
Catalyst:





Melting point: 161 °C





Melting point: close to room temperature

Molecular Weight
< 1 KDa

Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223-1253.

Reaction Under Study: Method of Detection

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$

Method of detection is required for kinetics measurements (UV-Vis, IR, NMR spectroscopy, etc -- we'll visit some of the facilities tomorrow).

Detection of of I_3^- as a complex with starch - visually detected color change.

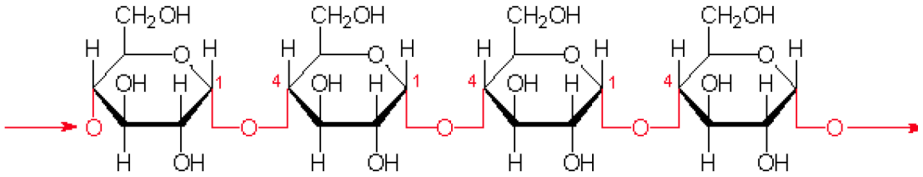


Figure 1. alpha-1,4- acetal linkages in amylose

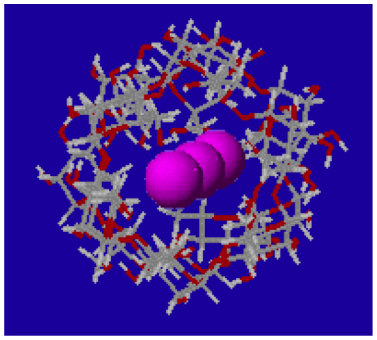
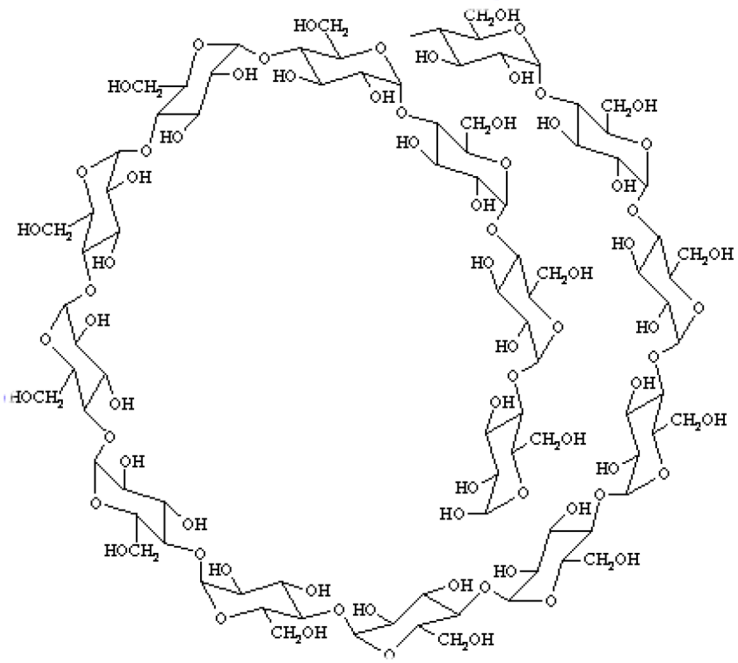


Figure 3. Starch/iodine



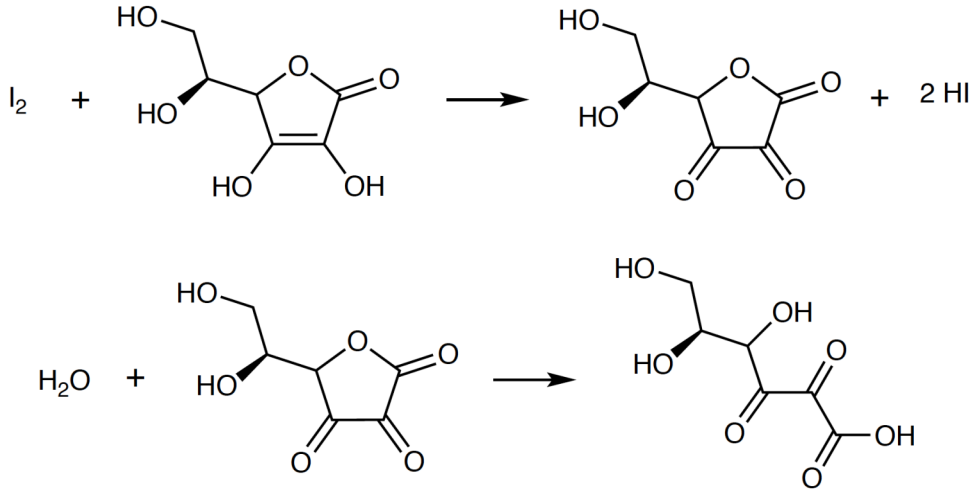
Clock reactions with sharp color changes allows for easier detection of end-points in kinetic runs.

Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Clock Reaction: Consumption of a Known Amount of Product

In the present case, Vitamin C reacts with the product, I_2, delaying the appearance of the color of the I_3^-/starch complex.

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$



The clock reaction allows for initial rate determination. If a solution containing 0.001 M of Vitamin C takes 20 s to change color, then the initial rate is calculated as:

$$R = -\frac{\Delta[H_2O_2]}{\Delta t} = \frac{\Delta[Vit\,C]}{\Delta t} = \frac{0.0010M}{20s} = 5.0\,x10^{-5}\,M/s$$

Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Reaction Order by Initial Rates Method

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$

$$R = -\frac{\Delta[H_2O_2]}{\Delta t} = k[H_2O_2]^a[I^-]^b[H^+]^c \ldots$$

$$R_1 = -\frac{\Delta[H_2O_2]}{\Delta t} = k[H_2O_2]_1^{\ a}[I^-]_1^{\ b}[H^+]_1^{\ c} \ldots$$

$$R_2 = -\frac{\Delta[H_2O_2]}{\Delta t} = k[H_2O_2]_2^{\ a}[I^-]_1^{\ b}[H^+]_1^{\ c} \ldots$$

$$\frac{R_1}{R_2} = \frac{k[H_2O_2]_1^a[I^-]_1^b[H^+]_1^c}{k[H_2O_2]_2^a[I^-]_1^b[H^+]_1^c} = \frac{[H_2O_2]_1^a}{[H_2O_2]_2^a} = \left[\frac{[H_2O_2]_1}{[H_2O_2]_2}\right]^a$$

$$\ln\left[\frac{R_1}{R_2}\right] = a \ln\left[\frac{[H_2O_2]_1}{[H_2O_2]_2}\right]$$

Plotting of ln(R) vs ln[H_2O_2] will will give a straight line with slope *a*.

Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Reaction Order by Initial Rates Method

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$

$$R = -\frac{\Delta[H_2O_2]}{\Delta t} = k[H_2O_2]^a[I^-]^b[H^+]^c \ldots$$

$$\ln\left[\frac{R_1}{R_2}\right] = a \ln\left[\frac{[H_2O_2]_1}{[H_2O_2]_2}\right]$$

This equation states mathematically that doubling the concentration of H_2O_2 will:

(a) have no effect on a process which is zero order with respect to H_2O_2 (a=0)
(b) double the rate of a process which is first order with respect to H_2O_2 (a=1)

OR

(c) quadruple the rate of a process which is second order with respect to H_2O_2 (a=2)

Experimentally:

$$\frac{d[I_3^-]}{dt} = k_1^0[H_2O_2][I^-] + k_1[H_2O_2][I^-][H^+]$$

Two competing mechanisms… Dependence on acid concentration not discussed today.

Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Effect of Temperature on Initial Rates: Determination of E_a

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$

$$R = -\frac{\Delta[H_2O_2]}{\Delta t} = k[H_2O_2]^a[I^-]^b[H^+]^c \ldots$$

$$\mathbf{\ln k = -\frac{E_a}{RT} + \ln A}$$

If other parameters are kept constant, initial rates can be substituted for rate constants in the Arrhenius equation.

$$\ln\left[\frac{R_1}{R_2}\right] = \frac{-E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Plotting of ln(R) vs 1/T will will give a straight line with slope -E_a/R.

Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Vitamin C Clock Reaction Initial Rates: Teacher Guide

Preparing Reagents:

Material	Instructions to make 1 L of each solution
0.25 M H_2O_2	Start with 3 % H_2O_2 (can be purchased at a drugstore). This solution is approximately 1 M. Dilute by 4 (e.g. mix 250 ml of this solution and 750 ml of deionized water) to achieve the desired concentration.
0.25 M NaI	Sodium iodide has a molecular mass of 149.89 g/mol. To prepare a 0.25 M NaI solution, dissolve 37.5 g in 1 L of deionized water.
0.05 M Vitamin C	Vitamin C, also known as L-ascorbic acid, has a molecular mass of 176.12 g/mol. To prepare a 0.05 M vitamin C solution, dissolve 8.8 g in 1 L of deionized water.
1 M acetic acid with starch	Acetic acid (glacial) has a molar mass of 60.05 g/mol and a density of 1.05 g/cm^3. To make the desired solution, combine 57 ml of acetic acid with 142.8 ml of starch (can be bought in a can from a drugstore) and 800 ml of water.

Of these solutions, you will need the following amount per set of experiments:

- 25.5 ml of 0.25 M H_2O_2
- 25.5 ml of 0.25 M NaI
- 5.5 ml of 0.05 M Vitamin C
- 5.5 ml of 1 M acetic acid with starch

Other materials (per set of experiments):

- deionized water (15 ml)
- 2 1 ml syringes
- 3 5 ml syringes
- 11 large test tubes or vials (each tube or vial should have a volume of at least 15 ml for adequate mixing)
- a stopwatch

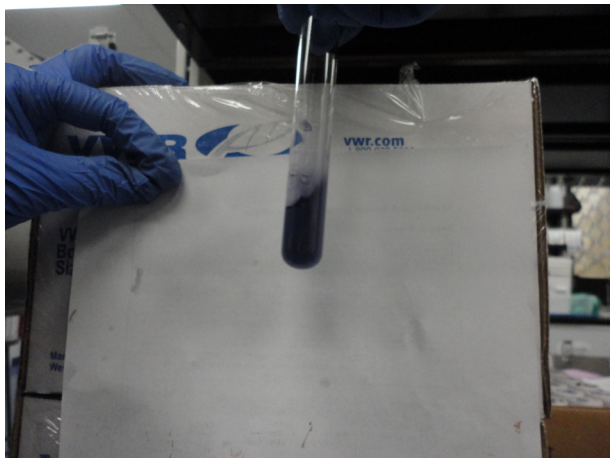
References

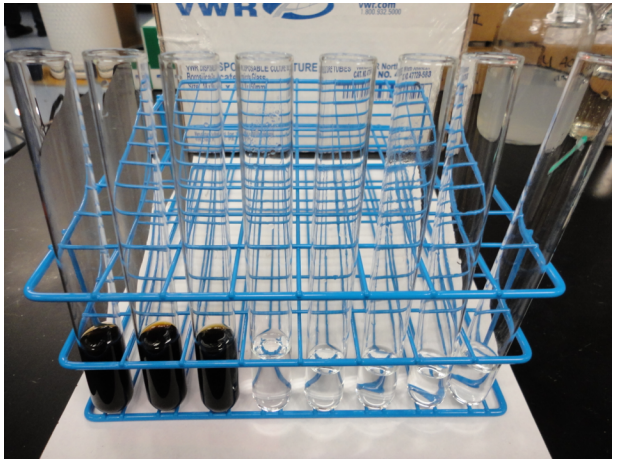
1. Wright, Stephen W. *J. Chem. Ed.* **2002**, *79*(1), 41-43.
2. Vitz, E. *J. Chem. Ed.* **2007**, *84*(7), 1156-1157.

Today's Experiment

Trial	Vitamin C (ml)	Acetic Acid (ml)	Iodide (ml)	H_2O (ml)	H_2O_2 (ml)	Time (sec)
1	0.5	0.5	3	0	3	
2	0.5	0.5	2.5	0.5	3	
3	0.5	0.5	2	1	3	
4	0.5	0.5	1.5	1.5	3	
5	0.5	0.5	1	2	3	
6	0.5	0.5	0.5	2.5	3	
7	0.5	0.5	3	0.5	2.5	
8	0.5	0.5	3	1	2	
9	0.5	0.5	3	1.5	1.5	
10	0.5	0.5	3	2	1	
11	0.5	0.5	3	2.5	0.5	

Vary only one parameter (concentration) per experiment.
Determine time required for color change (I_2/starch complex formation, corresponding to complete Vitamin C consumption)
Plotting of ln(1/t) vs ln[H_2O_2] or ln[I^-] will will give a straight line with slope corresponding to the order in reagent.





Reaction Order from Integrated Rate Expressions

$$\mathbf{A \rightarrow P}$$

Zero Order Reaction	First Order Reaction	Second Order Reaction
$r = -\frac{d[A]}{dt} = k$	$r = -\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k \cdot [A]^2$
$[A] = -kt + [A]_0$	$\ln \frac{[A]}{[A]_0} = -kt$	$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$
Plotting [A] vs t will give a straight line with slope -k.	Plotting ln[A] against time will give a straight line with slope -k.	A plot of 1/[A] vs t produces a straight line with slope k and intercept $1/[A]_o$.

Clock Reaction Experiment: From Initial Rates to Integrated Rate Expressions

Trial	Vitamin C (ml)	Acetic Acid (ml)	Iodide (ml)	H_2O (ml)	H_2O_2 (ml)	Time (sec)
1	3	0.5	3	0	1.5	
2	2.5	0.5	3	0.5	1.5	
3	2	0.5	3	1	1.5	
4	1.5	0.5	3	1.5	1.5	
5	1	0.5	3	2	1.5	
6	0.5	0.5	3	2.5	1.5	

Pseudo-first order in I^-.
Vary the concentration of Vitamin C.
Remaining concentration of H_2O_2 at color change can be calculated.
Time at color change is measured.
Use integrated rate law plots to determine order in H_2O_2 and the rate constant.

Best fit will give the order in H_2O_2 and the rate constant.

Oscillating Reaction

Solution A: 4.0 M H_2O_2 (all solutions must be at room temp for the demo to work!)
Solution B: 0.2 M KIO_3, 0.077 M H_2SO_4
Solution C: 0.15 M malonic acid, 0.020M $MnSO_4$, starch

$$5\ H_2O_2(aq) + 2\ IO_3^-(aq) + 2\ H^+(aq) \longrightarrow I_2(aq) + 5\ O_2(g) + 6\ H_2O(l)$$

$$5\ H_2O_2(aq) + I_2(aq) \longrightarrow 2\ IO_3^-(aq) + 2\ H^+(aq) + 4\ H_2O(l)$$

Overall: $$2\ H_2O_2(aq) \longrightarrow O_2(g) + 2\ H_2O(l)$$

More partial reactions (the first can go by two mechanisms):

$$IO_3^- + 2\ H_2O_2 + H^+ \longrightarrow HOI + 2\ O_2 + 2\ H_2O$$

$$HOI + CH_2(CO_2H)_2 \longrightarrow ICH(CO_2H)_2 + H_2O$$

Shakhashiri, B. Z. *Chemical Demonstrations: A Handbook for Teachers of Chemistry*; University of Wisconsin: Madison, 1983; Vol 2, 248.

Oscillating Reaction

More partial reactions (the first can go by two mechanisms):

$$IO_3^- + 2\,H_2O_2 + H^+ \longrightarrow HOI + 2\,O_2 + 2\,H_2O$$

$$HOI + CH_2(CO_2H)_2 \longrightarrow ICH(CO_2H)_2 + H_2O$$

First step:

High I^- concentration, slow non-radical mechanism:

$$IO_3^- + I^- + 2\,H^+ \longrightarrow HIO_2 + HOI$$

$$HIO_2 + I^- + H^+ \longrightarrow 2\,HOI$$

$$HOI + H_2O_2 \longrightarrow I^- + O_2 + H^+ + H_2O$$

Low I^- concentration, fast radical mechanism (autocatalytic):

$$IO_3^- + HIO_2 + H^+ \longrightarrow 2\,IO_2^{\bullet} + H_2O$$

$$IO_2^{\bullet} + Mn^{2+} + H_2O \longrightarrow HIO_2 + Mn(OH)^{2+}$$

$$Mn(OH)^{2+} + H_2O_2 \longrightarrow Mn^{2+} + H_2O + HOO^{\bullet}$$

$$2\,HOO^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$2\,HIO_2 \longrightarrow IO_3^- + HOI + H^+$$

Second step:

Fast: $$I^- + HOI + H^+ \longrightarrow I_2 + H_2O$$

$$I_2 + CH_2(CO_2H)_2 \longrightarrow ICH(CO_2H)_2 + H^+ + I^-$$