Chem 1B Objective 6:
Describe reaction mechanisms and relate mechanism to rate law and reaction energy diagram.

Key Ideas:
A reaction mechanism helps us understand how a reaction occurs. (E.g., drug companies try to figure out drug mechanism.)
Important in developing drugs and medical treatments.

Reaction mechanism is the sequence of elementary steps (sequence in which bonds break and form).
The slowest step determines the reaction rate (rate determining step).

A catalyst changes the reaction mechanism.

Objective: Determine the Reaction Mechanism

The **Rate Law** Tells You About The **Reaction Mechanism**
A Reaction Mechanism Is The Sequence of ***Elemental Steps***,
i.e., the Order In Which Bonds Break and Form

Sum of elemental steps = overall reaction.

Overall reaction:

home --> Chem 1B lecture

Mechanism (elemental steps):

home → car	(1)	1 minute
car → parking lot	(2)	16 minutes
parking lot → office	(3)	2 minutes
office → Chem 1B lecture	(4)	1 minute

Which step is the ***slowest*** step?
The slowest step is the ***rate determining step***.

Reaction mechanism animation:
http://www.sasked.gov.sk.ca/branches/elearning/tsl/resources/subject_area/science/chem_30_resources/lesson_3/default.shtml

Mechanism is important to understand how a reaction works.
See mechanism of how a drug works and drug design.

Objective: Determine the Reaction Mechanism

The **Order of the Reaction** (from the Rate Law) Tells Us the **Number of Reactant Particles** in the ***Rate Determining Step*** in the Reaction Mechanism

Rate Determining Step = Slowest Step

Objective: Determine the Reaction Mechanism

The Order of the Reaction (from the Rate Law) Tells Us the Number of Reactant Particles in the *Rate Determining Step* in the Reaction Mechanism

E.g., A + B ---> Products rate = $k [A]^1 [B]^2$

Reaction is 1st order in A and 2nd order in B

Overall Order = 3

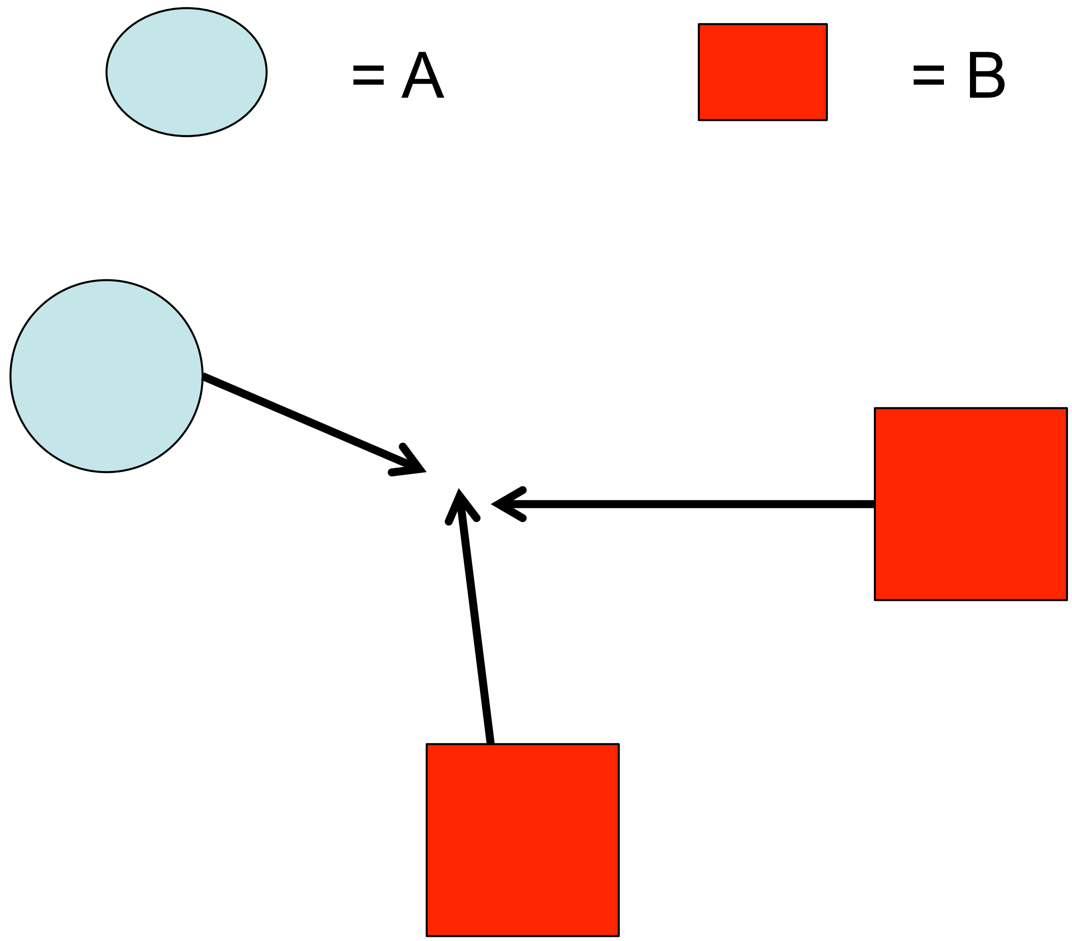
In **Rate Determining Step** of Reaction Mechanism:

1 A and 2 B are involved

Elemental step: 1 A + 2 B --->

A + B ---> Products

rate = k $[A]^1 [B]^2$



In **slow** step: 1 A reacts with 2 B to form intermediate

What is highest *possible* overall reaction order?

a. 1 b. 2 c. 3 d. 4 e. 5

http://www.eoht.info/page/Billiard+ball+model

Rate Law --> **Order of the Reaction** ---> **Number of Reactant Particles** in the ***Rate Determining Step***

Chang, "Gen Chem: Essential Concepts", 6th ed., p. 503, # 14.47

The rate law for the reaction

$2\ NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g)$ rate = k [NO][Cl_2].

What is the **overall** order of this reaction?

(i) 0
(ii) 1
(iii) 2

Rate Law --> **<u>Order of the Reaction</u>** ---> **<u>Number of Reactant Particles</u>** in the ***<u>Rate Determining Step</u>***

Chang, "Gen Chem: Essential Concepts", 6th ed., p. 503, # 14.47

The rate law for the reaction

$$2\ NO\ (g) + Cl_2\ (g) \rightarrow 2\ NOCl\ (g) \qquad rate = k\ [NO][Cl_2].$$

The following reaction mechanism has been proposed:

$NO\ (g) + Cl_2\ (g) \rightarrow NOCl_2\ (g)$ (1)

$NOCl_2\ (g) + NO\ (g) \rightarrow 2\ NOCl\ (g)$ (2)

If this mechanism if correct, what does it imply about the **relative** rates of these two steps? In other words, <u>which step is the **slow** step</u>?

rate of elemental step 1 = $k\ [NO]\ [Cl_2]$ Does this fit rate law?

rate of elemental step 2 = $k\ [NOCl_2]\ [NO]$ Does this fit rate law?

<u>Note</u>: reaction order for elemental step is based on coefficients in balanced equation.

Practice Problem: Studies show that CFC's destroy the ozone layer. Another way that ozone in the upper atmosphere is destroyed is by high flying aircraft that produce NO:

O_3 (g) + NO (g) ----> NO_2 (g) + O_2 (g).

rate law: rate = 33 [O_3 (g)][NO (g)]

Four possible mechanisms for this reaction are shown below. Which mechanism best fits the data? Give reasons.

(i) O_3 ---> O_2 + O
O + NO ---> NO_2

(ii) O_3 + NO ----> NO_3 + O
NO_3 + O ----> NO_2 + O_2

(iii) NO ---> N + O
O + O_3 + NO ----> 2 O_2
O_2 + N ----> NO_2

(iv) O_3 + NO ----> NO_2 + O_2

Practice Problem: ***Lab 3: Iodine Clock Reaction***

$IO_3^- + 3\ HSO_3^- \text{-->} I^- + 3\ SO_4^{2-} + 3\ H^+$ rate = k $[IO_3^-][HSO_3^-]$

Which mechanism fits this reaction?

Mechanism A:

$IO_3^- \text{--->} IO^- + O_2$

$IO^- + HSO_3^- \text{--->} I^- + SO_4^{2-} + H^+$

$O_2 + HSO_3^- \text{--->} O + SO_4^{2-} + H^+$

$O + HSO_3^- \text{--->} SO_4^{2-} + H^+$

Mechanism B:

$IO_3^- + HSO_3^- \text{--->} IO_2^- + HSO_4^-$

$IO_2^- + HSO_3^- \text{--->} IO^- + HSO_4^-$

$IO^- + HSO_3^- \text{--->} I^- + HSO_4^-$

Mechanism C:

$IO_3^- + HSO_3^- \text{--->} I^- + O_2 + SO_4^- + H^+$

$O_2 + 2HSO_3^- \text{--->} 2\ SO_4^{2-} + 2\ H^+$

<u>Objective</u>: How does a catalyst work?

A Catalyst:

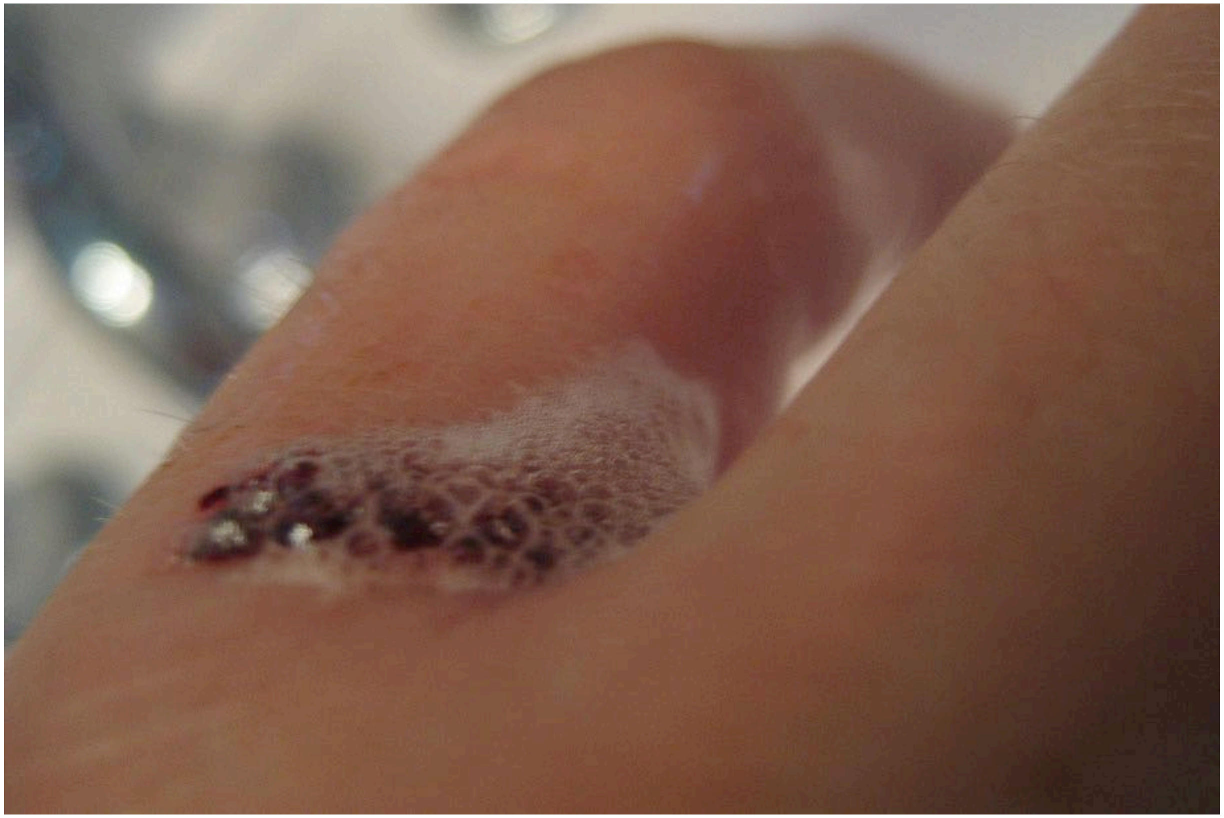
- Increases the Reaction Rate (**Inhibitor** <u>de</u>creases reaction rate)
- Lowers E_a of a reaction
- Is Involved In A Reaction Mechanism (mechanism changes when a catalyst is involved)
- Is Regenerated at the end of a reaction (need only a small amount and can be used again)
- Is Not involved in the Overall Reaction (you don' t show a catalyst as a reactant or product)

Catalysts are found in:

- our body (enzymes)
- cars (catalytic converter)
- many industrial processes, e.g., plastics, ammonia, …

Scientists and Engineers: a LOT of $$ in Catalysts!!

Hydrogen Peroxide, H_2O_2, is a disinfectant.
What happens when H_2O_2 is applied to a cut?



http://indianapublicmedia.org/amomentofscience/first-aid-bubbles/

H_2O_2 is toxic! Blood contains an enzyme (**peroxidase**) that catalyzes the decomposition of H_2O_2.

Other substances, e.g., I^-, also catalyze this reaction.

http://antoine.frostburg.edu/chem/senese/101/kinetics/faq/mechanism-h2o2-iodide.shtml

Overall reaction: $2\ H_2O_2 \text{ --> } 2\ H_2O + O_2$

Without a catalyst: rate = k $[H_2O_2]^2$

Mechanism: $2\ H_2O_2 \text{ --> } 2\ H_2O + 2\ O$

$2\ O \text{ --> } O_2$

With I^- catalyst: rate = k $[H_2O_2]\ [I^-]$

Mechanism: $H_2O_2 + I^- \text{ --> } H_2O + IO^-$

$H_2O_2 + IO^- \text{ --> } H_2O + I^- + O_2$

http://www.sparknotes.com/chemistry/kinetics/ratelaws/section2.rhtml

A Catalyst Changes the Reaction Mechanism.

Compare with and w/o catalyst. See Chang, p. 494, 14.103.

Old Foamey demo http://www.kentchemistry.com/KentsDemos.htm

A Catalyst Lowers E_a

$2\ H_2O_2 \dashrightarrow 2\ H_2O + O_2$

E_a = 72 kJ for uncatalyzed H_2O_2 decomposition
E_a = 28 kJ for catalyzed H_2O_2 decomposition (catalase in liver)

Compare rate constants for catalyzed vs. uncatalyzed reaction:
Use Arrhenius eq:

$$k = A\, e^{-Ea/RT}$$

$$\frac{k_{cat}}{k_{uncat}} = 3 \times 10^7$$

Catalyst speeds up this reaction by a factor of 30 million!

Without enzymes, e.g., peptidase, it would take ***300 years*** to digest a steak in our stomach!

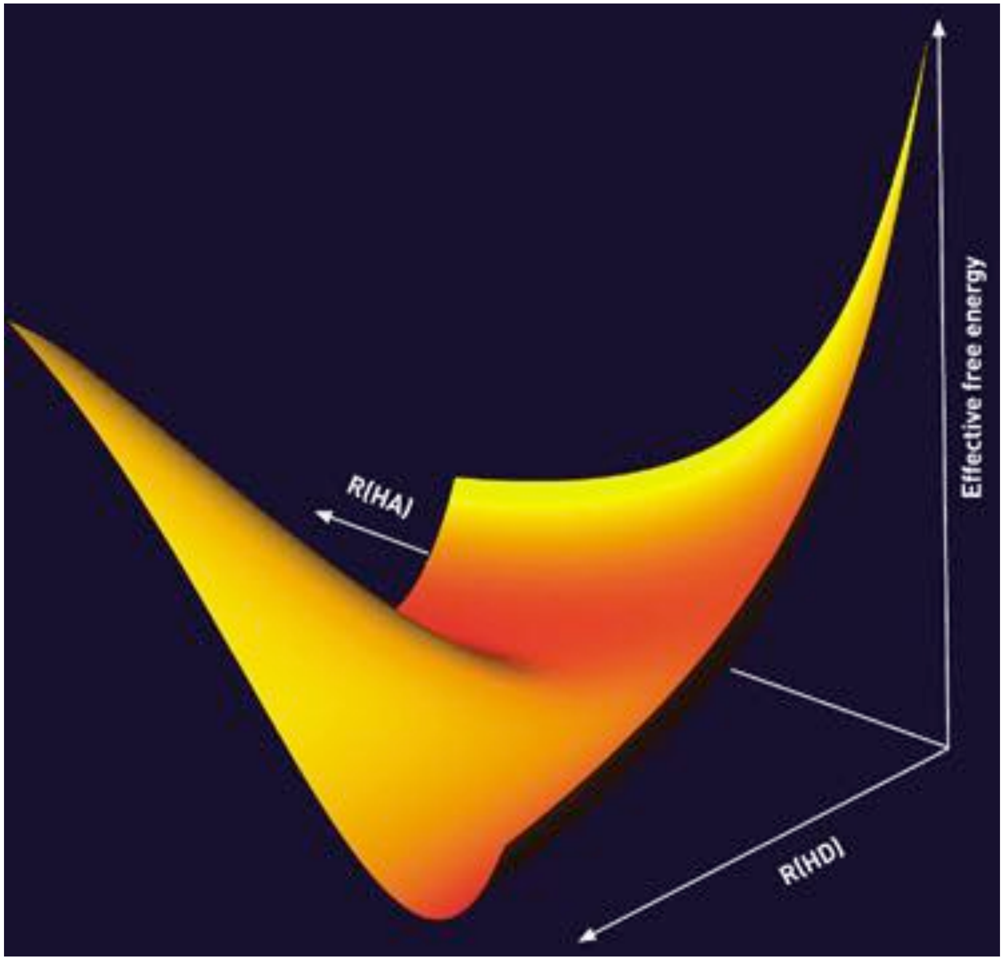
http://courses.chem.psu.edu/Chem112/Summer/Lecture%2520Notes/2_KINETICS_3.pdf

http://www.deliciousfood4u.com/tag/steak/

Some Enzymes Increase Rate By 10^{20} Fold (CEN, 2/23/04, p. 35)

Enzymes generally catalyze reactions by stabilizing transition states (activated complexes), enabling reactants to convert easily to products.

Proposals: electrostatics, quantum mechanical tunneling, coupled protein motions, low-barrier hydrogen bonds, and near-attack conformations have a role.



Free energy surface for the hydride-transfer reaction catalyzed by dihydrofolate reductase as a function of hydride-to-acceptor and hydride-to-donor distances--R(HA) and R(HD), respectively. The reaction proceeds from one side of the troughlike surface to the other by clambering over the saddle point (the transition state)--or tunneling through it.

What Causes A Hangover?

http://health.howstuffworks.com/hangover.htm

See Chang, p. 494, 14.106.

http://www.care2.com/greenliving/7-tips-to-cure-the-holiday-hangover.html

C_2H_5OH	→	CH_3CHO	→	CH_3COOH
Ethanol		acetaldehyde		acetic acid
	alcohol dehydrogenase		aldehyde dehydrogenase	

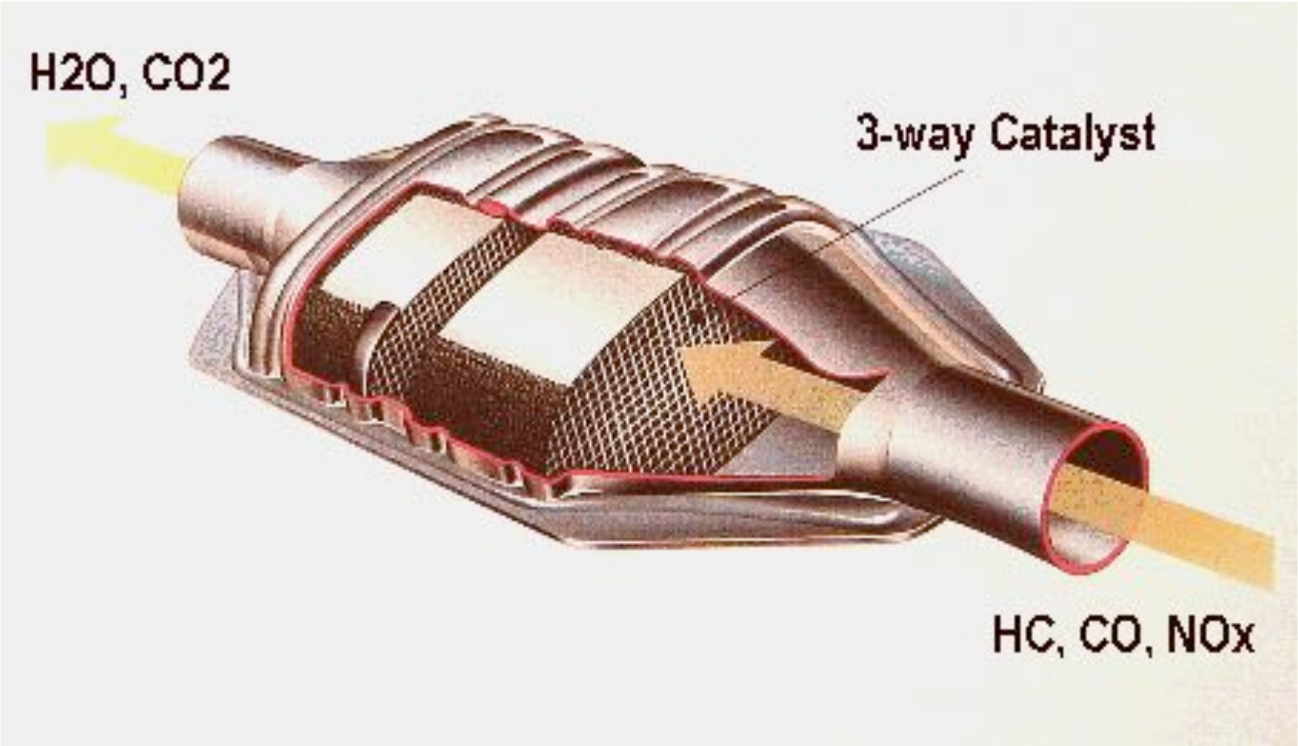
What type of reaction occurs?

CEN, 9/20/21, Newscripts, "Putting the D in drinking"
https://cen.acs.org/food/Drinking-science-Deuterated-ethanol-biochemical/99/i34

Deuterated ethanol causes alcohol dehydrogenase to work ***4.5X SLOWER*** than it does on normal ethanol but ***NO*** rate change on aldehyde dehydrogenase.

"Fun" effects of ethanol come from GABA neurotransmitter. *Sentia* is a non-alcoholic product that uses botanical extracts that modulate GABA.

How Does The Catalytic Converter In A Car Work?
http://auto.howstuffworks.com/catalytic-converter2.htm



http://dev.nsta.org/evwebs/3368/History/History.htm

http://cen.acs.org/articles/90/i21/Ever-Cleaner-Auto-Exhaust.html

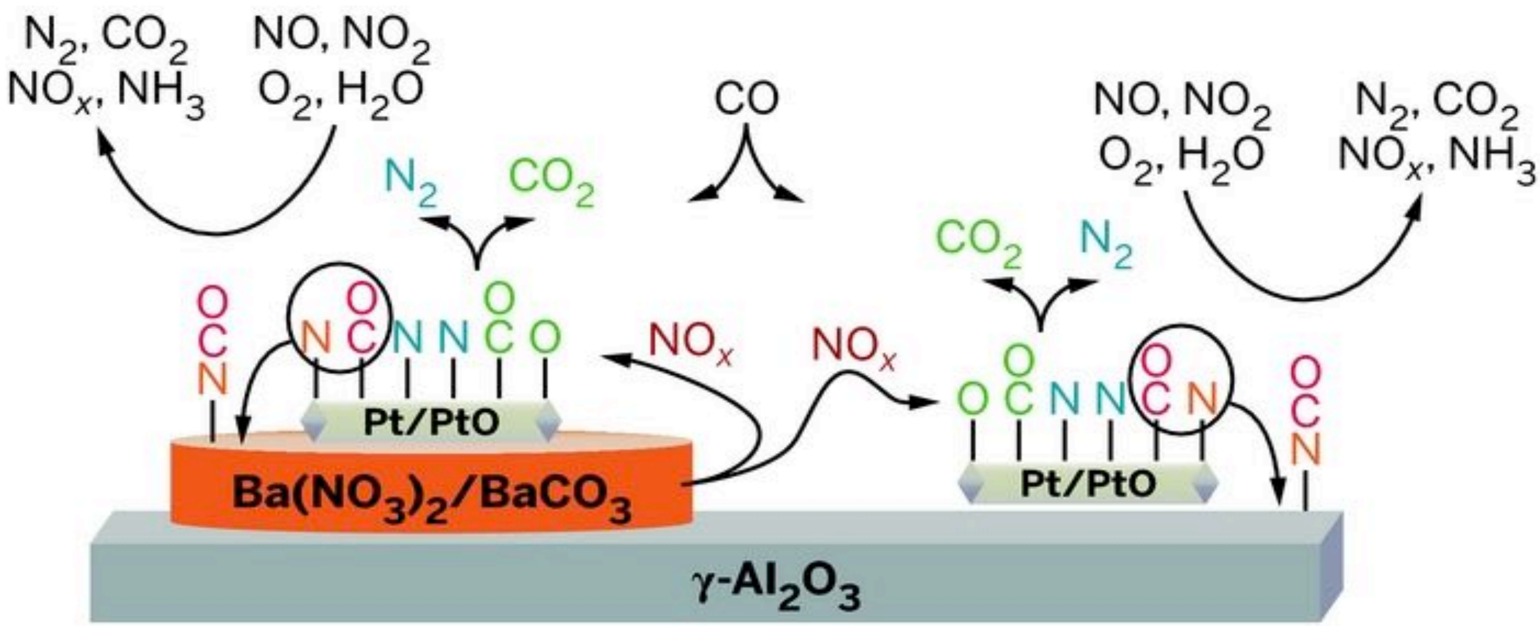
5/21/13, CEN, p. 10 “Ever-Cleaner Auto Exhaust”

Hydrocarbon (HC) emission limits”
1970s: 1.5 g/mile
Current: 0.01 g/mile

Porous ceramic bricks (monoliths) coated with precious metals and other materials lie at the heart of catalytic converter technology.

Hydrocarbons ---> $CO_2 + H_2O$

NO_x -- NH_3 --> $N_2 + H_2O$
Ammonia from urea



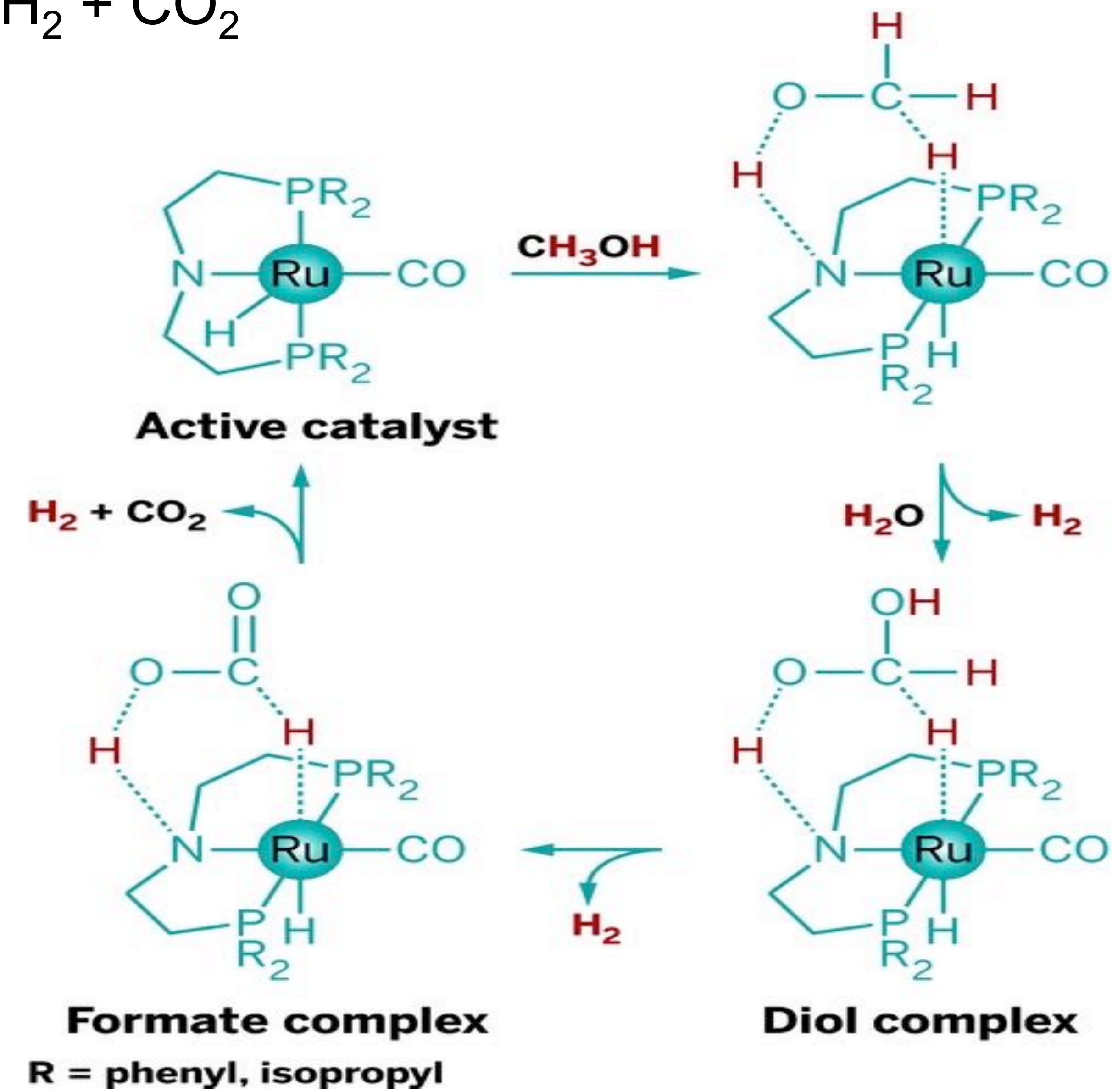
Is H_2 the Fuel of the 21st Century?

$CH_3OH + H_2O \dashrightarrow 3\ H_2 + CO_2$

HYDROGEN GENERATOR

Organo-ruthenium catalyst liberates three molecules of hydrogen from methanol at relatively low temperatures.

(CEN, 3/4/13, p.9, http://cen.acs.org/articles/91/i9/Cool-Way-Make-Hydrogen-Methanol.html)



I just want to say one word to you. Just one word. Plastics.

Plastics

Two types: condensation and addition

Radical reaction mechanism. See Chang, p. 494, 14.105.

http://www.cem.msu.edu/~reusch/VirtualText/polymers.htm

Symbol	Acronym	Full name and uses
1	PET	Polyethylene terephthalate - Fizzy drink bottles and frozen ready meal packages.
2	HDPE	High-density polyethylene - Milk and washing-up liquid bottles
3	PVC	Polyvinyl chloride - Food trays, cling film, bottles for squash, mineral water and shampoo.
4	LDPE	Low density polyethylene - Carrier bags and bin liners.
5	PP	Polypropylene - Margarine tubs, microwave-able meal trays.
6	PS	Polystyrene - Yoghurt pots, foam meat or fish trays, hamburger boxes and egg cartons, vending cups, plastic cutlery, protective packaging for electronic goods and toys.
7	Other	Any other plastics that do not fall into any of the above categories. For example melamine, often used in plastic plates and cups.

Is carbonic acid stable?

Carbonic Acid decomposition:

$$H_2CO_3\ (g) \dashrightarrow H_2O + CO_2\ (g)$$

E_a = 44 kcal/mole at 300 K
Half-life = 180,000 years

Much faster decomposition mediated by 1 or 2 water molecules.

Researchers suggest looking for carbonic acid in deep space.
(http://pubs.acs.org/isubscribe/journals/cen/78/i10/html/7810scic.html, CEN, March 6, 2000, p. 39)