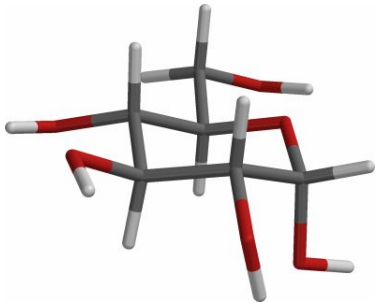
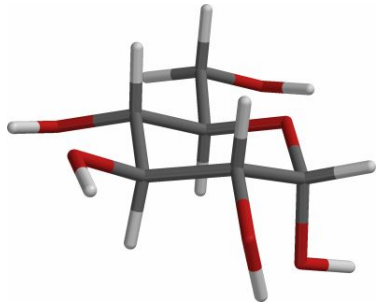




Chem 109 C

Fall 2014

Armen Zakarian
Office: Chemistry Bldn 2217

http://web.chem.ucsb.edu/~zakariangroup/courses.html

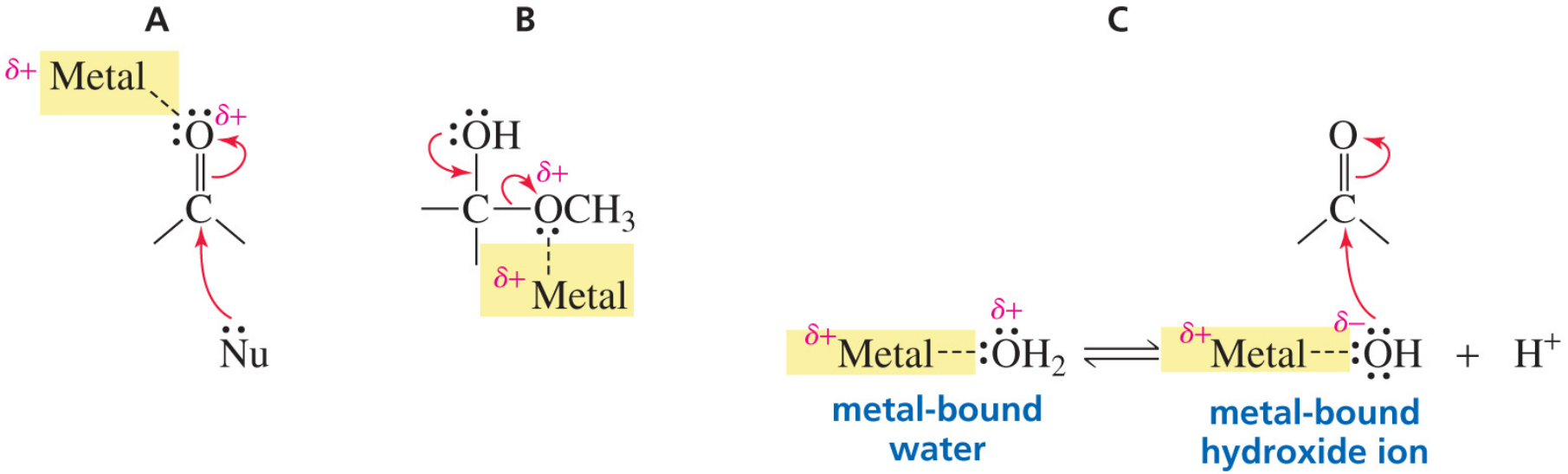
METAL-ION CATALYSIS

suggested additional exercise:

fill in the blanks throughout these slides

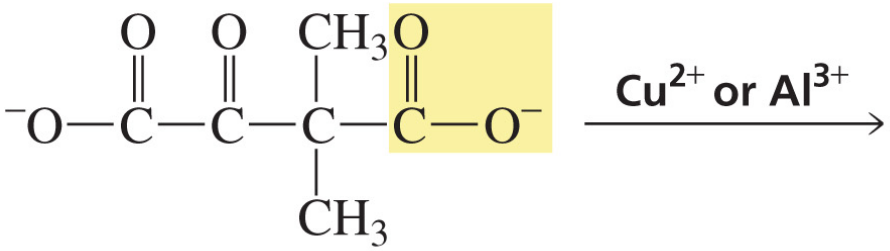
METAL-ION CATALYSIS

catalysis through coordination of the metal ions to substrate



METAL-ION CATALYSIS

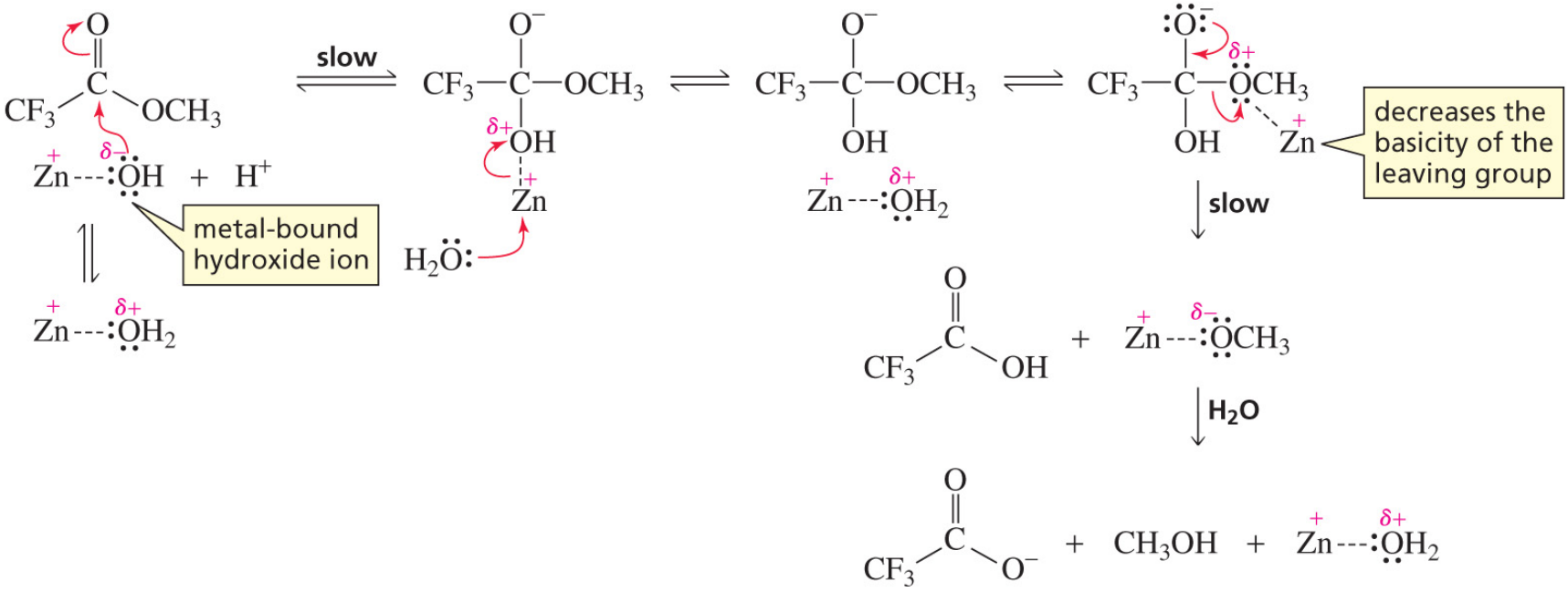
examples: decarboxylation



dimethyloxaloacetate

METAL-ION CATALYSIS

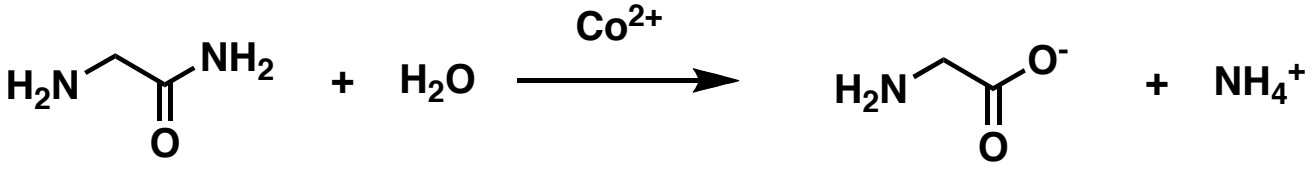
examples: hydrolysis



examples: hydrolysis

PROBLEM 8

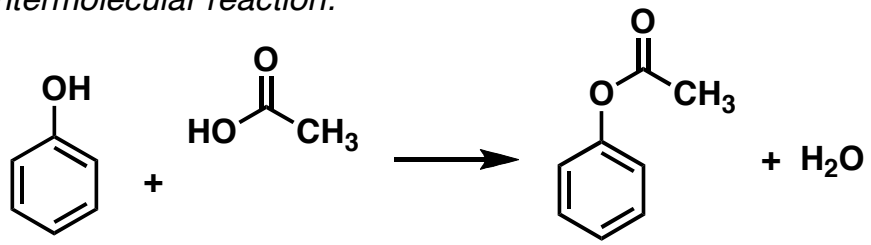
The hydrolysis of glycinamide is catalyzed by Co^{2+}, Propose a mechanism for this reaction



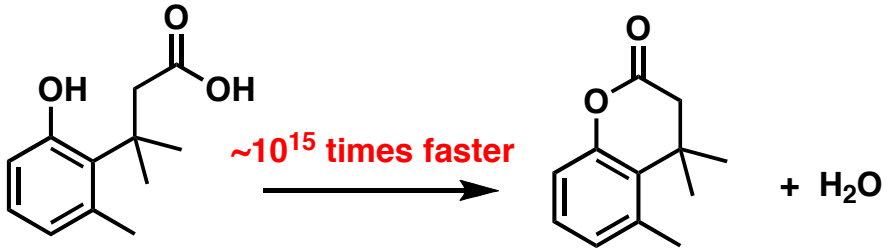
INTRAMOLECULAR CATALYSIS

intramolecular and intermolecular reactions -
why are intramolecular reactions faster?

intermolecular reaction:



intramolecular reaction:



"intramolecular catalysis", "neighboring group participation", "anchimeric assistance" are interchangeable terms

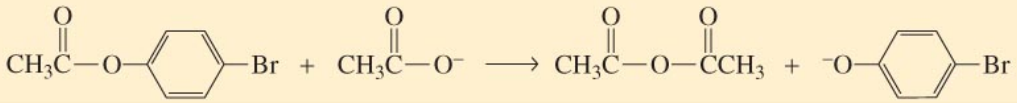
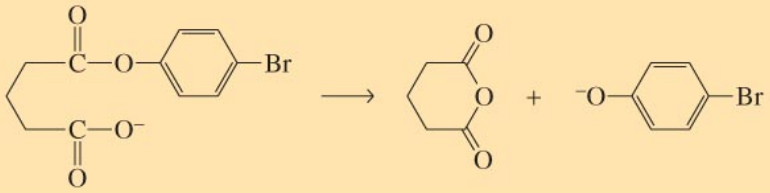
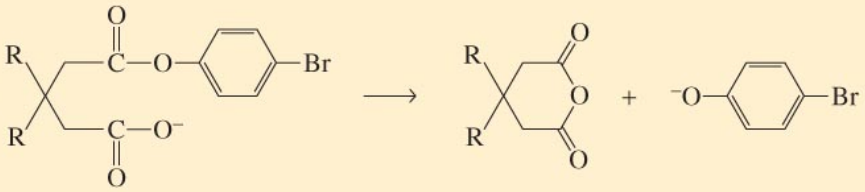
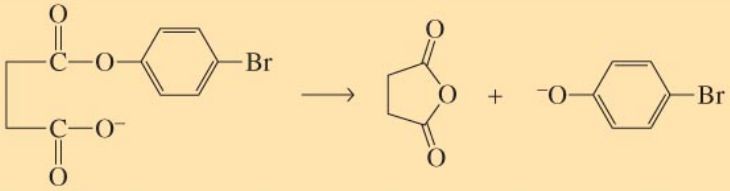
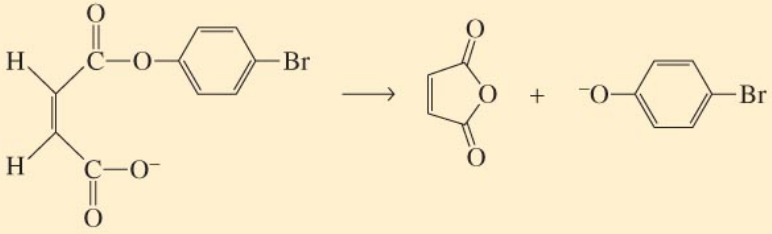
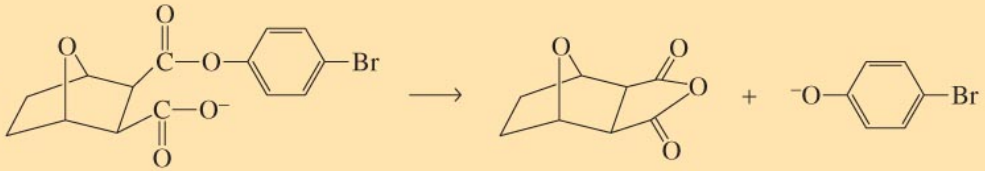
INTRAMOLECULAR REACTIONS

$$\text{reaction rate} = \text{number of collisions per unit time} \times \text{fraction with sufficient energy} \times \text{fraction with proper orientation}$$

$$\text{relative rate} = \frac{k_{\text{intramol}}}{k_{\text{intermol}}} = \frac{\text{first order } k}{\text{second order } k} = \frac{s^{-1}}{s^{-1}\,M^{-1}} = M$$

effective molarity

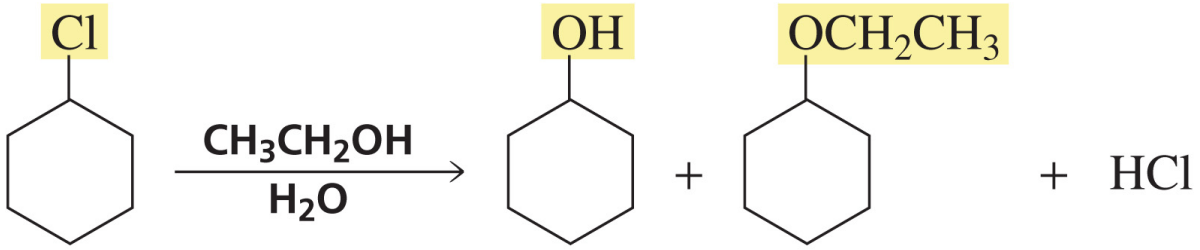
Table 24.2 Relative Rates of an Intermolecular Reaction and Five Intramolecular Reactions

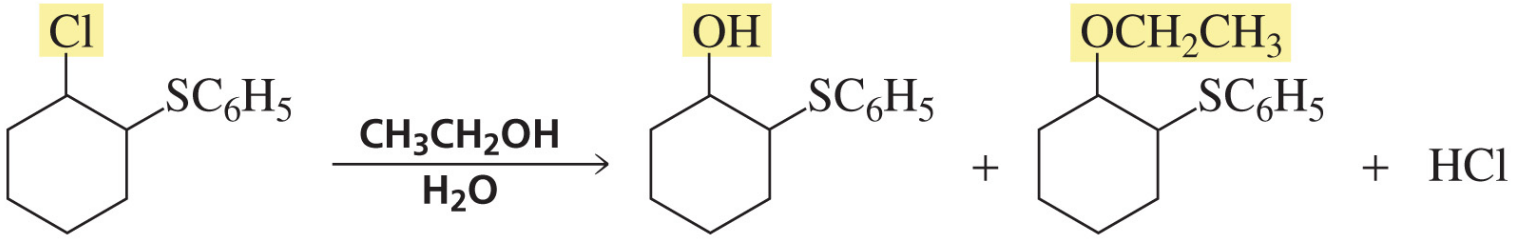
Reaction	Relative rate
A 	1.0
B 	1×10^3 M
C 	2.3×10^4 M R = CH_3 1.3×10^6 M R = $(CH_3)_2CH$
D 	2.2×10^5 M
E 	1×10^7 M
F 	5×10^7 M

INTRAMOLECULAR CATALYSIS

catalyst is a part of the reacting molecule

intramolecular nucleophilic catalysis:



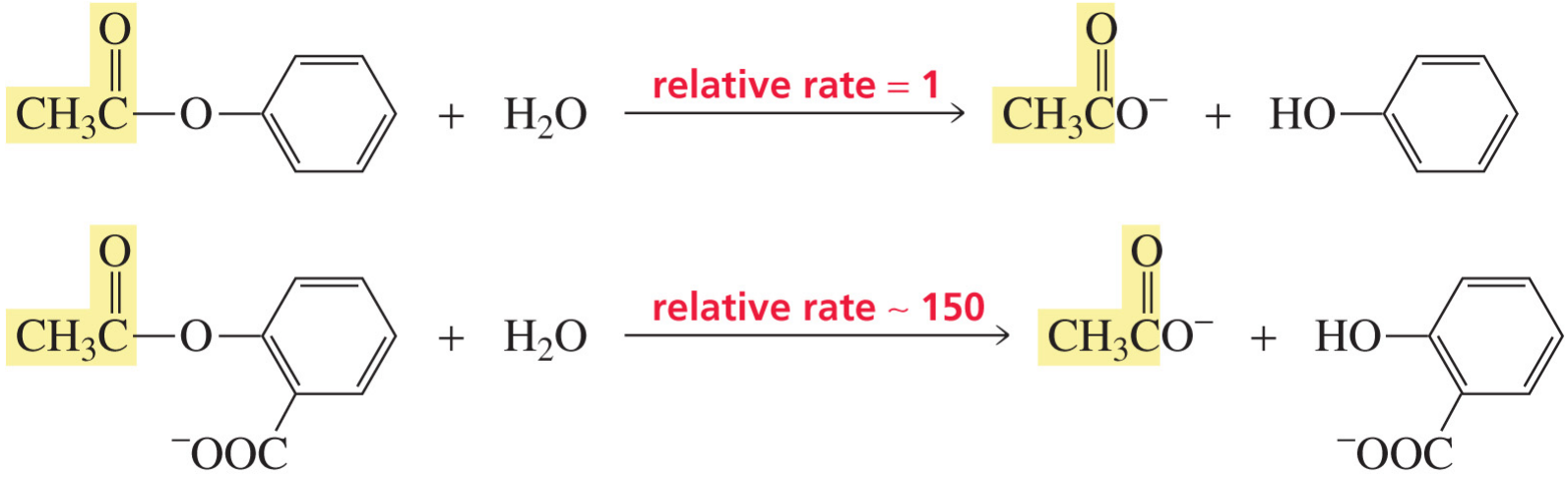


- ***why is this 70,000 times faster?***
- ***what type of catalysis is this?***

INTRAMOLECULAR CATALYSIS

catalyst is a part of the reacting molecule

intramolecular general base catalysis



INTRAMOLECULAR CATALYSIS

catalyst is a part of the reacting molecule.

intramolecular metal catalysis