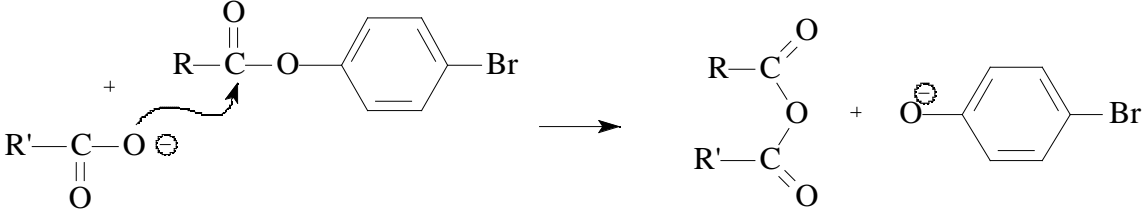
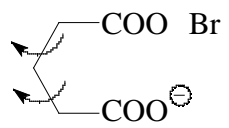
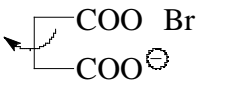
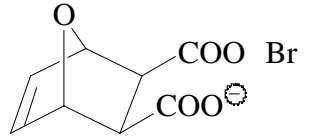


Biochemistry 341 - Problem Set V - Due Wednesday 31

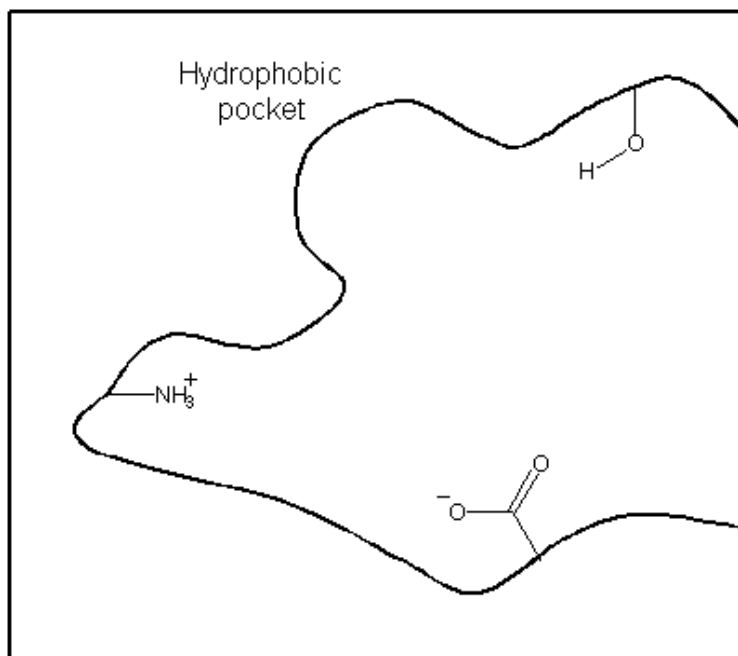
- Describe the difference between an enzyme substrate complex and the transition state in an enzyme catalyzed reaction (10 points).
- Consider the following series of reactions for the formation of anhydrides. The general mechanism is shown in the top box (20 points):

	
Reactants ¹	Relative Rate Constant
$\text{CH}_3\text{COO Br} + \text{CH}_3\text{COO}^-$	1.0
	$\sim 1 \times 10^3$
	$\sim 2 \times 10^5$
	$\sim 5 \times 10^7$

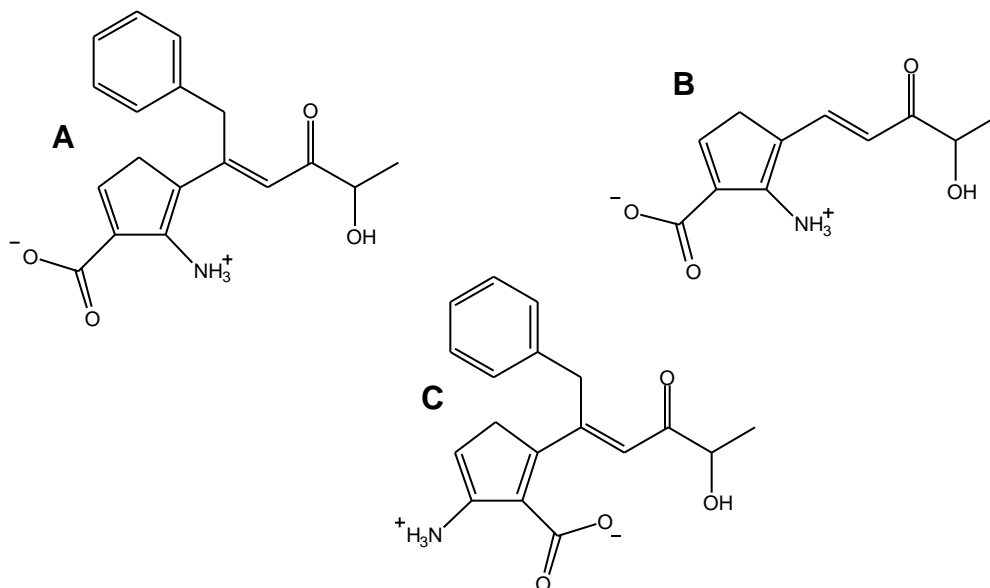
¹ designates the phenyl ring. Curved arrows indicate rotational freedom. Adapted from T. C. Bruice *Ann. Rev. Biochem.* 45:343 (1976).

- Write the products that you expect for each of the four reactions.
- What principle of catalysis that is used by enzymes is illustrated by this series of compounds? Explain why each successive reaction proceeds faster. You need to think of the different thermodynamic contributions to the binding energy (S, H, solvation, etc., etc.).

3. Consider the active site of an isomerase ($R\text{-CO-CHOH-R} \rightleftharpoons R\text{-CHOH-CO-R}$, 30 points):

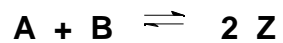


Say that you have made 3 synthetic substrates for this enzyme, shown below:



- Which substrate will react faster? Why? Justify your answer by dissecting the contributions to the total binding energy of the different substrates.
- Write a detailed reaction mechanism for the isomerisation of the best substrate.

4. Consider the reversible reaction with elementary steps (20 points):



- i. Write the rate equation for the forward reaction.
- ii. What is the reaction order for each reactant? What is the overall reaction order?
- iii. Write the rate equation for the back reaction.
- iv. What is the reaction order for each reactant? What is the overall reaction order?